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Passerine Exposure to Metal Contaminants from Oilsands Mining in the Athabasca Region of Northeastern Alberta, Canada

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by

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Abstract

I characterized passerine exposure to metals from waste-materials associated with oilsands mining. I measured metal concentrations in whole blood of tree swallows (*Tachycineta bicolor*), Tennessee warblers (*Oreothlypis peregrina*), and chipping sparrows (*Spizella passerina*). Additionally, I measured metal concentrations in kidney, liver, and stomach contents of nestling tree swallows, and monitored tree swallow nest success and nestling growth. I identified insects fed to nestlings to understand the influence of diet on metal accumulation in tissues, and collected insects to assess metal levels in available prey. I found high variability in metal concentrations in blood correlated with small blood sample volume, and suggest that blood may not be suitable for monitoring metal contamination in small birds. I found no evidence that metals were elevated in tissues of passerines near oilsands operations. Nest success and nestling growth were influenced by local environmental conditions and not affected by proximity to mining operations.

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Chapter One: Introduction

Metals are increasingly a concern in the environment because in areas of contamination, high levels of these elements may be transported from air, water, and soil into plants and the animal food chain (Singh and Prasad 2011). In trace amounts, many elements such as iron, copper, and zinc are essential nutrients for both plants and animals (Hamilton and Hoffman 2003). Other elements, such as cadmium and lead, are not essential and can be toxic (Scheuhammer 1987; Nagajyoti et al. 2010). Metal contamination affects the species composition of plants, insects, birds, and small mammals, because some species are less tolerant of contamination and are displaced by more tolerant species (Heliovaara and Vaisanen 1991; Eeva and Lehikoinen 1996; Ruohomaki et al. 1996; Kiikkilä 2003; Koptsik et al. 2003; Mukhacheva et al. 2010). Some metals can increase susceptibility to disease, or cause neurological damage and behavioural changes (Scheuhammer 1987; Perez-Lopez et al. 2008). Metals also affect the reproductive function of organisms (Blottner et al. 1999; Castellanos et al. 2010; Wirth and Mijal 2010; Marettova et al. 2012). Metals can bioaccumulate, raising concerns about predator-prey transfer within ecosystems (Chapman et al. 1996; Strady et al. 2011; Jelaska et al. 2014).

The toxicity of metals is dependent on the specific element, whether it is present alone or in a mixture with other elements, its concentration and route of exposure, the age of an individual, and other factors that influence absorption and accumulation in organisms (Fairbrother et al. 2007). Each metal can exhibit unique toxicological properties (Tchounwou et al. 2012). For example, exposure to nickel can result in respiratory irritation and allergic skin reactions in humans (Schaumloffel 2012). Ingestion of vanadium can result in weight loss, and liver and kidney malfunction (Rattner et al. 2006). Strontium is naturally abundant in the Earth's crust and in ocean water, and ingestion at high doses can lead to bone disease (Cohen-Solal 2002). Cadmium accumulates in the kidney and can result in kidney disease (Scheuhammer 1987). It has also been shown to deposit in bone (Kasuya 2000), and reduce egg production in birds (Marettova et al. 2012). Lead is a metabolic poison affecting reproductive, vascular, and neurological systems in organisms (Needleman 2004; Patrick 2006).

The harmful effects of metals occur when non-essential metals replace essential metals in proteins and enzymes, and bind to the physiological sites that control metabolic and signaling pathways in cells, thereby disrupting normal cell and enzymatic functions (Kasprzak 2002). For example, as an essential element, zinc is found in proteins and enzymes, stabilizes DNA, and is essential for normal growth and reproduction (Eisler 2000a), and bone development (Yamaguchi 2010). The replacement of zinc by non-essential metals such as cadmium or lead can cause damage to cell membranes and DNA leading to disease and abnormal growth (Liu et al. 2008). However, high levels of zinc can interfere with calcium and iron metabolism (Eisler 2000a), disrupt fetal development in mammals (Sandstead and Au 2007), and affect skeletal formation in birds (Kaji et al. 1988) and mammals (Yamaguchi 2010).

Metal interactions can result in some metals enhancing (synergistic) or reducing (antagonistic) the harmful effects of other metals. For example, metal mixtures containing copper and cadmium can enhance the uptake and absorption of other metals (Chu and Chow 2002). The presence of selenium can reduce the toxic effects of mercury (Yu 2001), arsenic (Patrick 2003; Sah et al. 2013), and cadmium (Marettova et al. 2012). Diets that are high in calcium can decrease the accumulation of lead in bone (Scheuhammer 1996), and calcium can also lower the gastrointestinal absorption of cadmium (Scheuhammer 1987). As well, organisms have evolved mechanisms to deal with exposure to toxic elements (Fossi et al. 1995), and proteins are produced that bind to metals and render them non-toxic (Scheuhammer 1987; Andrews et al. 1996; Haq et al. 2003; Domenech et al. 2006).

Birds are considered good indicators of environmental contamination and ecosystem health (Koskimies 1989; Gregory and van Strien 2010; Smits and Fernie 2013) because they respond quickly to changes in their environment, and as such are sensitive indicators of habitat quality. The effects of environmental contamination on birds can be studied by examining exposure levels and comparing to natural reference conditions (Carere et al. 2010). Contaminant exposure in birds has been extensively studied (e.g. Grasman et al. 1998; Gamberg et al. 2005; Burger and Gochfeld 2009; Custer et al. 2010; Berglund and Nyholm 2011), and is implicated in the decline of some arctic species of seabirds, in which concentrations of metals and trace elements were high relative to other seabirds (Wayland et al. 2001; Stout et al. 2002; Wilson et al. 2003). The levels of metals have been measured in great tits (*Parus major*) (Janssens et al. 2001), and environmental exposure to a metal mixture containing lead, cadmium, arsenic, mercury, copper, zinc, and selenium was linked to poor hatching success and higher incidence of nest desertion (Janssens et al. 2003). Pied flycatchers (*Ficedula hypoleuca*) experienced high mortality and growth abnormalities in an environment in which they were exposed to a mixture of copper, zinc, nickel, and lead (Eeva and Lehikoinen 1996). Exposure to copper, zinc, nickel, and lead in the environment also resulted in lower survival of adult female pied flycatchers compared to males (Eeva et al. 2009), and lower population density in six species of ground foraging and foliage gleaning songbirds (Eeva et al. 2002). Differences exist in the ability of birds to metabolize and eliminate toxic elements, and bird species with more specialized diets are less likely to tolerate exposure to non-essential metals than species that consume a broader diet and that have developed an evolutionary tolerance through exposure to a wider range of elements in the environment (Fossi et al. 1995).

Tree swallows (*Tachycineta bicolor*) have been used to monitor ecosystems exposed to environmental contaminants (Smits and Fernie 2013), and are likely representative of other insectivorous avian species. Tree swallows are useful model organisms because they readily breed in nest boxes, allowing for adequate sample sizes, predator control, and standardization of methods (Jones 2003). Individuals are readily captured and can be uniquely marked, greatly facilitating research and experimental field manipulations. Tree swallows are also semi-colonial, and birds will nest in close proximity to each other allowing relatively high densities of breeding birds within a nesting area (McCarty 2001/2002). Birds nesting in a common area should be exposed to the same contaminants, reducing the variability in exposure and making it possible to collect an appropriate sample size to study the effects from contaminant exposure.

There has been little research regarding avian exposure to metal contaminants from oilsands mining in northeastern Alberta. Metals occur naturally in the environment in this region, and are found in the geological formations that are exploited for the development of the oil resources (Conly et al. 2007). The excavation and crushing of materials for the raw bitumen, and the disposal of waste materials, potentially exposes the environment to metal contamination. Surface mining of the oilsands has been ongoing north of Fort McMurray, Alberta, since 1967 (Gosselin et al. 2010) and production has grown substantially over the last decade. Development of the oilsands is expected to continue expanding in the coming years (CAPP 2014).

Waste materials in tailings process-water and in air emissions from mine upgraders can release metals into the environment and contaminate surface waters (Barton and Wallace 1979; Kelly et al. 2010; Puttaswamy and Liber 2012). Higher concentrations of vanadium, chromium, nickel, arsenic, strontium, cobalt, molybdenum, iron, and selenium have been measured in lichen (*Hypogymnia physodes*) within 50 km of oilsands operations compared to farther distances (Edgerton et al. 2012). Organic and inorganic compounds measured in snow and in atmospheric bulk samplers were attributed to oilsands emissions (Kelly et al. 2009; Kelly et al. 2010; Bari et al. 2014). However, information on the toxic effects of potential environmental contamination from the oilsands is unclear. Wetlands that have formed in response to oilsands effluent contain contaminants that affect fish health and will not support fathead minnow (*Pimephales promelas*) and brook stickleback (*Culaea inconstans*) (Bendell-Young 2000). These same wetlands support low-diversity, benthic communities dominated by Chironomidae, as well as aquatic plants such as cattail (*Typha latifolia*) (Bendell-Young 2000). Therefore, direct contact with process-affected water poses health risks to higher trophic-level organisms that may use these wetlands for breeding habitat. However, studies that have examined health effects in birds near oilsands operations have not been able to demonstrate a direct cause and effect relationship between the oilsands and measured physiological effects (Gentes et al. 2006; Gentes et al. 2007a; Harms et al. 2010). The reasons for this may be due to the naturally occurring levels of metals and organics that occur in the regional geology. Natural erosion processes expose bitumen deposits along the banks of the Athabasca River that contribute polycyclic aromatic compounds (PACs) and metals into the sediments of the river system. There were no measurable increases in concentrations of PACs in downstream sediments due to rapid growth of the oilsands over the past 25 years (Hall et al. 2012), and some metals in downstream sediments have decreased (Wiklund et al. 2012). The levels of hydrocarbon emissions from oilsands upgraders are modest compared to major petrochemical facilities, although levels are significantly elevated above natural conditions

(Simpson et al. 2010). The Athabasca River and its tributaries demonstrate naturally high values for some elements (Hebben 2009).

The purpose of my study was to determine if birds are being exposed to metals from oilsands mining operations, and if there are effects on nest success and nestling growth. Most avian studies emphasize ingestion as the primary route of exposure because other routes such as inhalation and absorption through skin are uncommon (McCarty 2001/2002). I hypothesized that birds would be exposed to metals from their food and predicted that exposure would result in higher metal concentrations in blood and other tissues compared to concentrations in individuals at reference locations that represent natural environmental conditions. To test this hypothesis, I used tree swallows as the model organism to study metals in food items provided to nestlings by adult birds, and metal levels in tissues. I predicted that metal concentrations in the stomach contents of tree swallows would be correlated with their tissue-metal concentrations. I used tree swallows, Tennessee warblers (*Oreothlypis peregrina*), and chipping sparrows (*Spizella passerine*) to examine the variability of metal exposure among passerine species as determined by sampling whole blood. I expected blood metal concentrations to be higher in tree swallows that have more specialized insectivorous feeding habits. I measured tree swallow nest success and nestling growth to determine the possible effects of metal exposure. My research provides information on metal levels in passerines that, in conjunction with similar data from other groups of vertebrates such as small mammals, can guide assessments of wildlife health in the oilsands region.

The main chapters of my thesis are written as manuscripts for publication in scientific journals. The three manuscripts (Chapters 2, 3, and 4) encompass the different aspects of metal exposure and the measured ecological endpoints of passerines over four years of study.

Chapter 2 describes the levels of essential and non-essential metal and metalloid elements measured in whole blood from live sampling tree swallows, Tennessee warblers, and chipping sparrows. This chapter discusses the variability associated with blood metal levels and potential reasons for the variability. Chapter 3 investigates metal exposure from food and the levels of metals in the tissues of nestling tree swallows. I determined correlations between diet and tissue metal accumulations. I also collected insects using Malaise traps and measured the metal levels of those taxa that I identified in the nestling diet. Chapter 4 compares reproductive success and the growth of nestling tree swallows near operations and at reference sites, and presents in more detail the diet of the nestlings, including grit and calcareous items collected by adults while foraging on the ground. This chapter also describes the relationship between local weather and diet on reproductive and growth endpoints. Chapter 5 is a discussion that highlights the major findings of my research and the implications regarding metal exposure to passerines nesting near oilsands mine operations.

Chapter Two: Metal Concentrations in Blood of Three Species of Birds in the Athabasca Oilsands Region of Alberta

2.1 Introduction

There is little information regarding avian exposure to heavy metals from oilsands mining in northeastern Alberta. The shallow nature of the Athabasca oilsands reserves in some areas of the region is amenable to mining technology, and major rivers and their tributaries have naturally exposed the bitumen deposits to the environment (Gosselin et al. 2010). Mining and other human activities have further exposed the environment to the raw bitumen, and the by-products of bitumen recovery. The heavy metals in tailings process-water, and in air emissions from mine upgraders may include a long list (Timoney and Lee 2009; Kelly et al. 2010; Bari et al. 2014), and metals have been identified in the surrounding vegetation (Edgerton et al. 2012). Nickel and vanadium in particular, are found in appreciable concentrations within the raw oilsands material, or bitumen (Research Council of Alberta 1953; Har 1981). Nickel is a concern due to the potential for respiratory irritation and allergic skin reactions in humans (Schaumloffel 2012), and more serious toxic effects resulting from altered protein function (Forgacs et al. 2012). Less is known about vanadium toxicity, although ingestion may result in weight loss, and liver and kidney malfunction (Rattner et al. 2006).

Raw bitumen is upgraded into a lower viscosity synthetic crude oil, which can be pipelined to refineries several hundreds of kilometers away in central Alberta to create lighter petroleum products such as gasoline and diesel fuel. Two upgraders have been responsible for the majority of bitumen upgrading from mining, and are considered the centre of oilsands operations. Gas emissions released from the upgraders are dispersed over long distances (Simpson et al. 2010). Few data are available to determine the distance within which metal deposition occurs, although deposition is expected to decrease with increasing distance from an emission source. Metal deposition occurred in moss (*Pleurozium schreberi*) at least 28 km from a metal smelter in northern Sweden, with deposition decreasing significantly beyond 18 km (Berglund and Nyholm 2011). Concentrations of vanadium, chromium, nickel, arsenic, strontium, cobalt, molybdenum, iron, and selenium measured in lichen (*Hypogymnia physodes*) was highest within 50 km from the centre of oilsands operations (Edgerton et al. 2012).

Published peer-reviewed studies in the Athabasca oilsands region have not examined the potential effects of metal contaminants from mining activities on birds. Birds are frequently used as bioindicators of metal exposure (Eens et al. 1999; Dauwe et al. 2004; Custer et al. 2009; Brumbaugh et al. 2010; Bryan et al. 2012). Birds inhabiting areas near oilsands operations may be exposed to heavy metals via contact with tailings pond process-water, and from airborne particulate deposition. The measurement of metals in the whole blood of birds has been used as a non-lethal method to assess effects from industrial sources (e.g. Golden et al. 2003; Tsipouraa et al. 2008; Geens et al. 2010; Alvarez et al. 2013). Blood is regarded as suitable for monitoring metal exposure as blood metal concentrations will reflect short-term exposure, including while on the breeding grounds (Furness 1993; Burger and Gochfeld 1997).

The objective of my study was to investigate the levels of heavy metals, including essential metals and other metalloid elements, in three passerine species inhabiting areas near oilsands mining operations. I hypothesized that passerines near oilsands operations are exposed to metal contaminants in the environment. I measured the element burden in whole blood in tree swallows (*Tachycineta bicolor*), Tennessee warblers (*Oreothlypis peregrina*) and chipping sparrows (*Spizella passerina*). Studies on tree swallows have been occurring near oilsands operations since 1997 (Smits et al. 2000; Gentes et al. 2006; Gentes et al. 2007a; Harms et al.

2010). Tennessee warblers and chipping sparrows are locally abundant. If oilsands operations are exposing passerines to metal contaminants, then I predicted the whole blood of passerines would reflect higher metal levels compared to passerines in unexposed reference locations that closely resemble natural environmental conditions.

Passerines comprise a diverse group of insect- and seed-eating bird species, and tree swallows, Tennessee warblers, and chipping sparrows represent different foraging guilds. Heavy metals may enter the food chain, and birds that forage on seeds are unlikely to experience the same exposure to metal contaminants as are species foraging on invertebrates that originate from terrestrial or aquatic habitats. Metal uptake by plants is regulated by physiological mechanisms that will reduce metal accumulation in reproductive organs such as seeds and fruits (Ernst et al. 1992; Bagatto et al. 1993; Ernst et al. 2000). Metal concentrations vary in invertebrates of the same or different species (Hendrickx et al. 2004; Bel'skii and Belskaya 2013), and exposure may depend on the proportions and taxa of insects that are consumed. Therefore, bird species that exhibit different foraging behaviours and diet may experience differences in metal exposure.

Tree swallows are aerial insectivores and consume brachyceran, nematoceran and cyclorrhaphan Diptera, as well as Trichoptera, Ephemeroptera, Odonata and Hemiptera (McCarty and Winkler 1999a; Smits et al. 2000). During the breeding season, Tennessee warblers consume primarily lepidopteran larvae (Holmes 1998), but also adult and larval Coleoptera and Hymenoptera (Rimmer and McFarland 2012). Tennessee warblers are also important predators of spruce budworm (Lepidoptera *Choristoneura fumiferana* (Clemens)) (Venier 2009). Chipping sparrows consume seeds from grasses and forbs (Pulliam 1986). When insects are available, chipping sparrows also consume adult Coleoptera, Orthoptera and

Lepidoptera that are gleaned from vegetation (Allaire and Fisher 1975). These insects may also be fed to nestlings as a source of protein.

Runoff from spring snowmelt and rain events may lead to increased metal concentrations in surface water and sediments (Kelly et al. 2010). Insectivorous birds are upper trophic-level consumers which makes them vulnerable to food web accumulation of contaminants (Maul et al. 2006). Therefore, I expected metal concentrations to be highest in tree swallows that forage on insects that originate from aquatic habitats. I expected metal concentrations to be lowest in chipping sparrows due to their consumption of seeds and terrestrial insects.

Individual variability in metal exposure may also occur due to age and body mass (Berglund et al. 2011; Burger and Gochfeld 1997, 2000), habitat use, or interactions between biological factors such as bird health and physical ability to cope with environmental stress (Peakall and Burger 2003; Rainio et al. 2012). I therefore examined the variability of metal concentrations among sites, the three species, and their age classes. The levels of metal and metalloid elements in the blood of the birds are compared with those obtained from published studies conducted on birds inhabiting areas near metal smelters in northern Europe, and metal contaminated sites across Canada and the United States. There are no reference concentrations for metals in the blood of Tennessee warblers or chipping sparrows, and metal levels for these species are presented here for the first time.

2.2 Methods

2.2.1 Study Sites

My study was conducted in 2011 and 2012 with populations of tree swallows using nest boxes, and wild populations of Tennessee warblers and chipping sparrows near Fort McMurray, Alberta. I collected blood samples at twelve sites at various distances from active oilsands mine and upgrader operations (Figure 2.1). Sample locations were chosen based on habitat and access considerations. Each site was near water with adjacent upland deciduous and coniferous mixed forest, and supported open areas for nest boxes or dense vegetation for other nesting species. Tree swallow nest boxes had been placed at four sites (Sites 1, 2, 3, and 4) for previous studies conducted near oilsands operations and were used in my study. These four sites were within about 5 km of active mining, and thus assumed to be exposed to aerial particulate emissions from the upgraders. In 2011, Tennessee warblers and chipping sparrows were sampled at six sites. Three of these sites were within 5 km of oilsands operations (Sites 2, 3, and 5), overlapping with two of the tree swallow sites. The three other sites (Sites 6, 7, and 8) were about 20 km to the north and east of Fort Mackay, and were potentially exposed to emissions from the upgraders. The prevailing winds in the region are to the north and northeast, and the sites further to the north were used to describe the differential distribution of metals in birds.

In 2012, four additional sites were sampled. Tree swallow nest boxes were installed and birds captured at two sites (Sites 9 and 10) about 60 km and 65 km south from the centre of oilsands operations and the upgraders. Tennessee warblers and chipping sparrows were captured at two sites approximately 35 km (Site 11) and 65 km (Site 12) south. I expected samples collected south of the upgraders at distances of 35 km and greater to represent reference conditions due to the direction of the prevailing winds. Therefore, reference sites were considered to be unexposed to upgrader emissions and oilsands waste-materials. Sites were grouped into three categories based on distance for analysis: reference (9, 10, 11, 12), potentially exposed (6, 7, 8), and near operations (within about 5 km; 1, 2, 3, 4, 5).

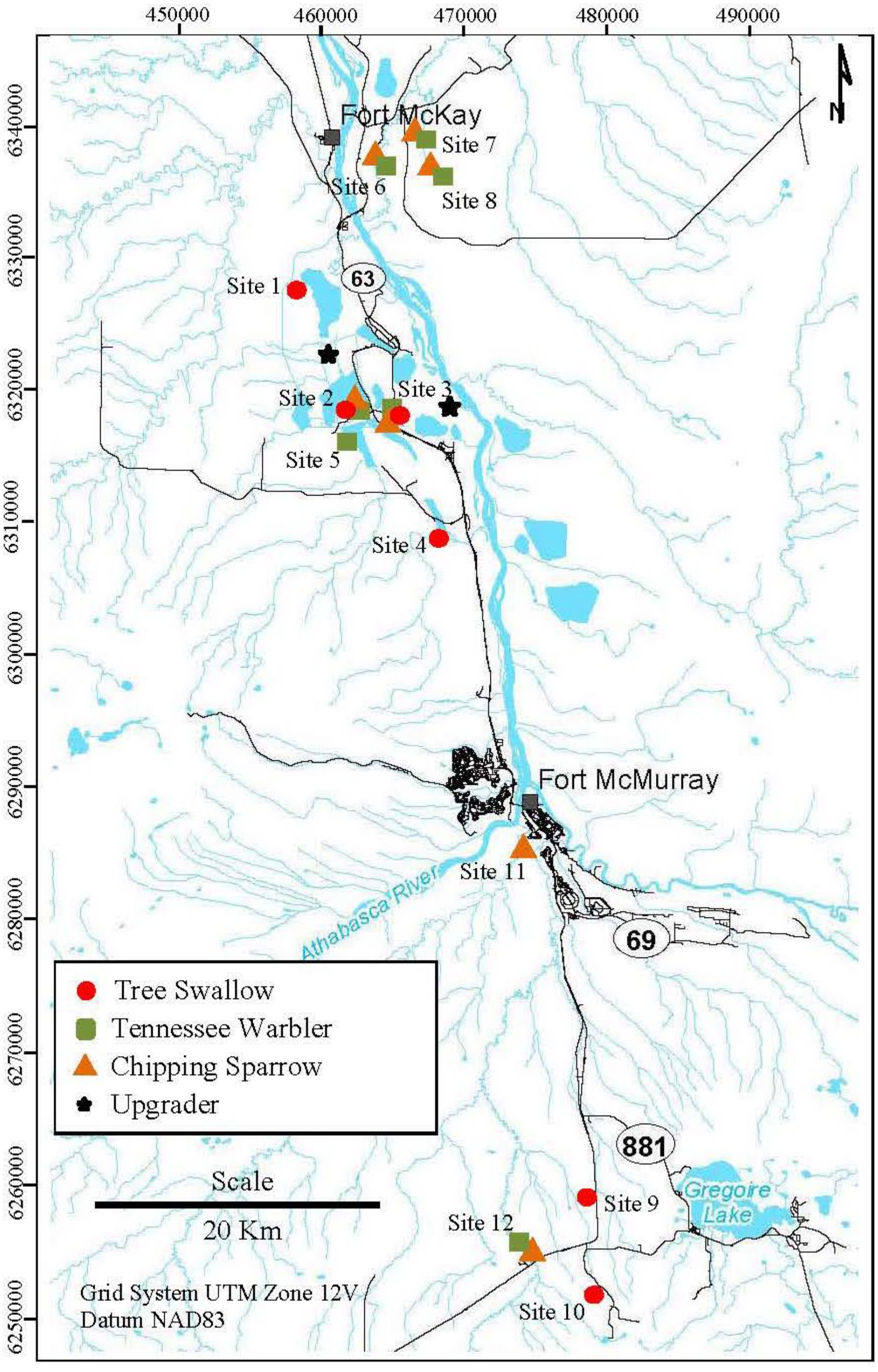


Figure 2.1 Study sites where tree swallow, Tennessee warbler and chipping sparrow samples were obtained; near oilsands mining operations (1, 2, 3, 4, 5), potentially exposed sites north of Fort McMurray (6, 7, 8), and reference sites (9, 10, 11, 12) to the south.

2.2.2 Bird Capture

I monitored tree swallow nest boxes daily or every second day from the initiation of nest building beginning about May 20th, and during egg laying through hatching, and the age of nestlings was thus known. Blood samples were collected from nestling tree swallows at the age of 14 days, within a few days of fledging. Adult tree swallows were captured and sampled opportunistically while they occupied the nest box during incubation and feeding of nestlings.

Tennessee warblers and chipping sparrows were captured passively using mist-nets beginning June 10th through mid- to late July when hatch-year birds began to fledge and disperse from the breeding grounds. At each site, eight to 13 mist-nets were set up and monitored constantly from sunrise to 6 hours after sunrise once every 10 days through the breeding season. Adult cloacal protuberance and brood patches were used to indicate territorial nesting birds. Fledgling birds were identified and sampled if they still had juvenile plumage that was characteristic of birds coming from the local sampling area as defined by net placement (DeSante et al. 2010).

2.2.3 Blood Sampling and Analysis

I collected blood in ammonium-heparinized Micro-Hematocrit capillary tubes (Fisher Scientific, Pittsburgh, PA) after puncturing the brachial vein with a 27-gauge needle. Average blood sample volume varied by species from 70 µL to 100 µL, and lower volumes were generally collected from Tennessee warblers due to their smaller body size. Sample volumes less than 25 µL were excluded from the analyses as greater variability in metal concentrations for the duplicate samples was observed at volumes of 20 µL and smaller, indicating possible instability of analytical methods at low blood volumes.

Up to 200 μL of blood was collected from 15 adult tree swallows, and these samples were divided in two in the field for duplicate laboratory analysis. Duplicate samples were collected by using multiple capillary tubes during blood sampling; blood from the first capillary tube was transferred to a microcentrifuge tube, while blood from the second capillary tube was transferred to a separate microcentrifuge tube. Microcentrifuge tubes were labelled such that the laboratory was unaware of the duplicate samples.

Whole blood samples were stored at 4ºC until shipped on ice to the Prairie Diagnostic Services (PDS) laboratory at the Western College of Veterinary Medicine in Saskatoon, Saskatchewan. The methods and blood sampling protocols used in this study were approved by the Animal Care Committee at the University of Calgary (LESACC protocol number BI11R-27), in compliance with standards set by the Canadian Council on Animal Care.

Precautions were taken to avoid contamination during blood sample collection. Disinfecting alcohol was used to clean the area around the brachial vein. However, the evaporation of the alcohol caused the vein to recede, reducing the ability to collect an adequate volume of blood. Therefore, distilled water was used instead. Control samples were prepared to test for possible metal contamination from the distilled water and from the capillary tubes. Control samples were also prepared to test for metal contamination from dust and bird handling in the field by swabbing bird feathers with sterile cotton-tipped swabs, including wings and body, as well as equipment, and hands. To test for consistency in laboratory analyses at small sample volumes, control standards for nickel and strontium were also prepared, different from the standards used for instrument calibration by the PDS laboratory. Double-distilled water was spiked with strontium chloride hexahydrate ($SrCl_2 6H_2O$) and nickel(II) chloride hexahydrate ($NiCl_2 6H_2O$). Five 50 μL spiked replicates were prepared containing 25 ppb nickel and 50 ppb strontium to represent low concentrations of these metals, and a second set of five 50 μL samples were prepared containing 500 ppb nickel and 1500 ppb strontium to represent high concentrations. Thus, the control samples included distilled water (1), double-distilled water (5), two standards of 25 ppb Nickel / 50 ppb Strontium (5) and 500 ppb Nickel / 1500 ppb Strontium (5), double-distilled water from four capillary tubes (5), swabs of wing and body feathers of blood sampled birds (7), and swabs of miscellaneous equipment for bird capture and handling (4).

Laboratory analysis of blood and control samples involved wet digestion with HNO_3 in a pressurized Microwave-Accelerated Reaction System (MARS) following the instructions by the manufacturer (CEM Corporation). In order of increasing atomic number, and from non-essential to essential, the metal and metalloid elements vanadium, chromium, nickel, arsenic, strontium, molybdenum, iron, cobalt, copper, zinc, and selenium were quantified using an Inductively Coupled Plasma-Mass-Spectrometer (ICP-MS, Thermo Jarrell-Ash Corporation, Franklin, MA, USA). Whole blood samples were diluted to a standard volume of 500 μL and back-calculations based on sample weight were used to determine element concentrations. Stock standards used by PDS were purchased from SCP Science or VWR International, and standard reference materials were purchased from the National Institute of Standards and Technology. Instrument detection limits (IDLs) based on a standard volume of 500 μL for this study were: vanadium (10 ppt), chromium (10 ppt), nickel (17 ppt), arsenic (80 ppt), strontium (3 ppt), molybdenum (10 ppt), iron (0.90 ppt), cobalt (1.35 ppt), copper (36 ppt), zinc (0.36 ppb), and selenium (172 ppt) (PDS Laboratory).

2.2.4 Data Analyses

Statistical analyses were conducted using SAS software 9.3 (SAS 2008. SAS/STAT® 9.3 User's Guide. SAS Institute Inc.). Element concentrations were analyzed with generalized linear models (GENMOD procedure in SAS). The GENMOD procedure was used to accommodate the difference in variance observed in element concentrations among locations. As the data were not normally distributed, I used a Gamma distribution with a log-link function for modelling each element. Year differences were significant, and as changes were made to the distribution of sampling sites, I analyzed each year separately. Log-transformed element concentrations in blood were tested including species, age class (adult, hatch-year), location relative to operations, Julian date of blood collection, and interaction terms as fixed effects in the model. Given that several sites were used to define a location, a site within a location was tested as a nested effect (i.e. site (location)) in each model to determine if variability among sites contributed significantly to the results. The influence of the blood volume, measured by the PDS laboratory as blood wet-weight (ww), on each element was also tested. I present data as arithmetic means and standard deviations. The level of statistical significance for the Chi-square (χ^2) test in the GENMOD procedure was $p < 0.05$.

The blood sample duplicates from the adult tree swallows were used to provide a measure of reproducibility of the data. The relative percent difference (RPD) in the duplicate samples was calculated according to the following formula:

$$\text{RPD} = \frac{|x_1 - x_2|}{\bar{x}} * 100$$

Where x_1 and x_2 are the observed blood metal concentrations, and $\bar{x}$ is the mean of the observed concentrations.

The statistical approach that was used takes into account the unequal variance observed among locations. The lack of normally distributed data precluded standard tests of equal variance to understand the extent of dispersion or variability in element concentrations among species and locations. To examine the variability, the Coefficient of Variation (CV) for each logged element concentration was calculated for each year, location, and species. An F-test was performed on the CVs for each element to compare the variance between the locations near and far from operations. Given that no reference sites south of Fort McMurray were sampled in 2011 to compare against values for near operations, the 2011 values for potentially exposed sites were used instead and were considered far from operations.

2.3 Results

High variability was observed in the blood metal concentrations of the three passerine species in 2011, and additional sampling was conducted at distances farther south of oilsands operations in 2012 to ensure sampling in reference conditions. High variability was also observed in 2012. A total of 321 blood samples were collected over the two years (Table 2.1).

Table 2.1 Number of birds sampled of each species and age class in 2011 and 2012

	2011		2012		
	Adult	Hatch-Year	Adult	Hatch-Year	Total
Tree Swallow	12	13	23	38	86
Tennessee Warbler	48	30	47	29	154
Chipping Sparrow	40	14	27	0	81

Laboratory analyses of control samples demonstrated good repeatability for 8 of the 11 elements. Low variability in control samples was observed in the measured concentrations of vanadium, chromium, nickel (Figure 2.2), arsenic, molybdenum, iron, zinc, and selenium. High variability in control samples was observed in the measured concentrations of strontium (Figure 2.2) and copper, and the capillary tubes introduced cobalt contamination. Because the reliability in the laboratory analyses of strontium, cobalt, and copper was poor, these elements were excluded from further statistical analyses.

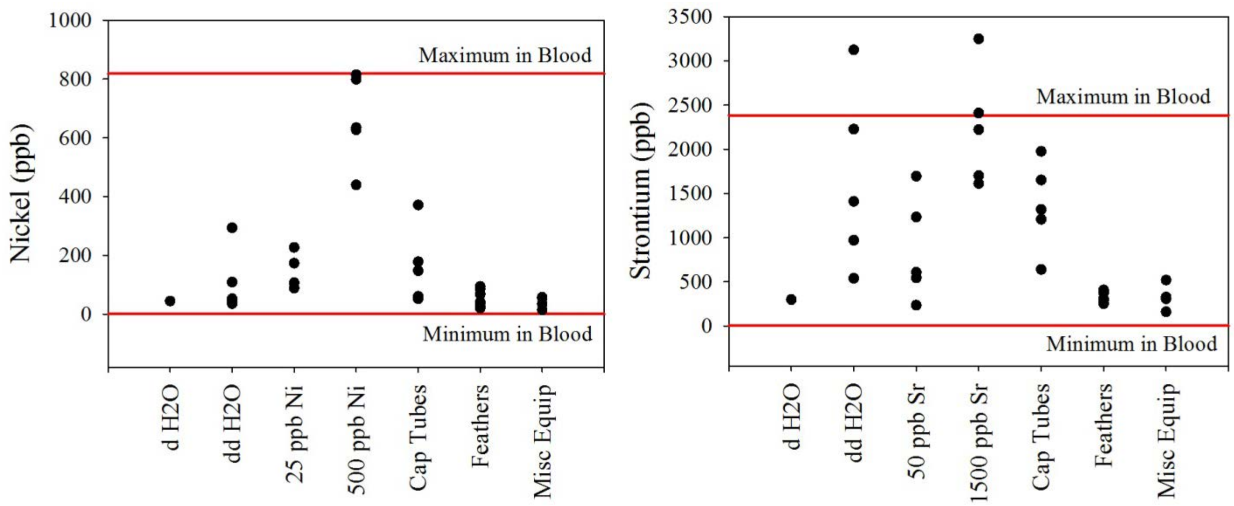


Figure 2.2 Nickel (ppb) and strontium (ppb) concentrations in control samples and the minimum and maximum concentrations observed in the blood of passerines

Overall, laboratory analyses of blood samples demonstrated poor repeatability. For the 15 duplicate blood samples from tree swallows in 2012, median RPD for vanadium, chromium, nickel, arsenic, and molybdenum was between 25% and 60%, suggesting that the duplicate samples varied greatly for these elements (Figure 2.3). Closer RPDs between 5% and 16% were obtained for iron, zinc, and selenium.

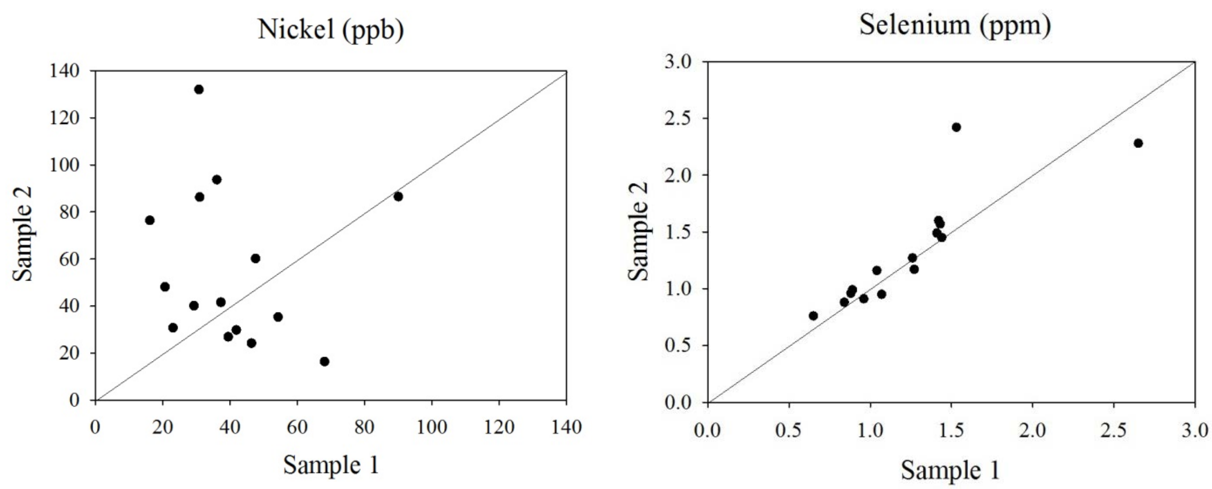


Figure 2.3 Median RPD of nickel was 40% and selenium was 9% in 15 duplicate blood samples from adult tree swallows

Log-transformed blood mass was a significant model predictor of concentration for seven elements (Table 2.2 and Table 2.3). In each case, the amount of blood sampled was negatively related to the element concentration, indicating that smaller blood sample volumes had higher element concentrations (Figure 2.4). The partial regression coefficients, representing the slope of the line for the effect of log blood mass on each element, while holding the effects of year, species, age, and location constant are also provided in Figure 2.4.

Table 2.2 Generalized linear model Chi-square (χ^2) statistic and level of significance (*p*) of non-essential metal concentrations (log-transformed values) in the blood of three passerines

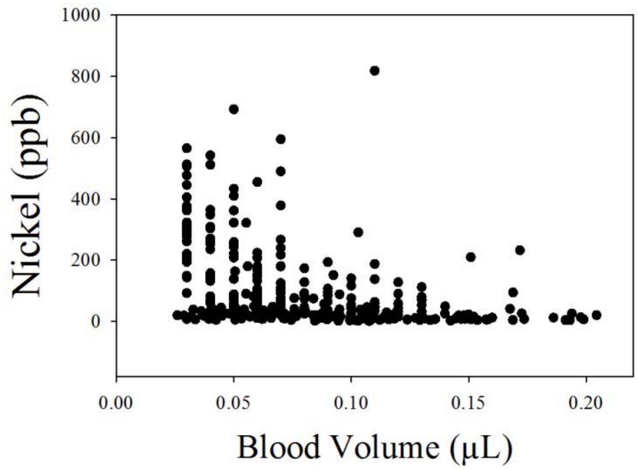
Model Predictors	Vanadium	Chromium	Nickel	Arsenic
Year	88.99 (<0.01)	369.91 (<0.01)	58.46 (<0.01)	0.00 (0.97)
Location	3.33 (0.19)	2.99 (0.22)	3.54 (0.17)	0.34 (0.84)
Species	7.95 (0.02)	16.05 (<0.01)	0.50 (0.78)	13.34 (<0.01)
Site(Location)	8.13 (0.52)	4.33 (0.89)	3.84 (0.92)	15.70 (0.07)
Age Class	0.22 (0.64)	0.03 (0.86)	0.37 (0.54)	1.64 (0.20)
Age Class*Distance	2.11 (0.35)	1.54 (0.46)	1.23 (0.54)	3.22 (0.20)
Julian Date	0.06 (0.80)	0.04 (0.84)	0.12 (0.73)	4.48 (0.03)
Julian Date*Distance	2.79 (0.25)	3.36 (0.19)	4.13 (0.13)	0.02 (0.99)
Log Blood (ww)	6.87 (0.01)	25.32 (<0.01)	16.57 (<0.01)	11.25(<0.01)
Log Blood (ww)*Distance	0.42 (0.8090)	3.74 (0.15)	2.79 (0.25)	4.93(0.09)

Notes: ww=wet-weight; Site(Location) tested for nested effects of a site within a location
Shaded cells denote significant effects

Table 2.3 Generalized linear model Chi-square (χ^2) statistic and level of significance (*p*) of essential metal concentrations (log-transformed values) in the blood of three passerines

Model Predictors	Molybdenum	Iron	Zinc	Selenium
Year	224.23 (<0.01)	5.94 (0.01)	30.34 (<0.01)	4.20 (0.04)
Location	9.37 (0.01)	1.74 (0.42)	12.75 (<0.01)	2.05 (0.36)
Species	1.57 (0.46)	2.27 (0.32)	0.24 (0.89)	17.72 (<0.01)
Site(Location)	3.49 (0.94)	5.10 (0.83)	28.61 (<0.01)	25.83 (<0.01)
Age Class	2.22 (0.14)	15.05 (<0.01)	2.62 (0.11)	59.58 (<0.01)
Age Class*Distance	2.01 (0.37)	1.94 (0.38)	15.73 (<0.01)	14.48 (<0.01)
Julian Date	3.03 (0.08)	3.92 (0.04)	1.95 (0.16)	2.66 (0.10)
Julian Date*Distance	13.52 (<0.01)	3.45 (0.18)	16.68 (<0.01)	0.24 (0.88)
Log Blood (ww)	12.11 (<0.01)	15.87 (<0.01)	27.41 (<0.01)	1.82 (0.18)
Log Blood (ww)*Distance	2.16 (0.34)	7.56 (0.02)[1]	1.83 (0.40)	5.75 (0.06)

[1]No effect of log-transformed blood mass on the log-transformed iron concentration was found near operations
Notes: ww=wet-weight; Site(Location) tested for nested effects of a site within a location
Shaded cells denote significant effects



Element	Partial Reg Coeff (SE)	Lower CI	Upper CI
V	-0.16 (0.06)	-0.28	-0.04
Cr	-0.17 (0.03)	-0.24	-0.10
Ni	-0.22 (0.05)	-0.32	-0.11
As	-0.13 (0.04)	-0.20	-0.05
Mo	-0.08 (0.02)	-0.12	-0.03
Fe	-0.03 (0.01)	-0.04	-0.02
Zn	-0.28 (0.05)	-0.38	-0.17
Se	-0.02 (0.02)	-0.05	0.01

Figure 2.4 Relationship between blood volume and nickel concentration in the blood of passerines. Also provided are the partial regression coefficients and confidence limits of log blood mass on the logged concentrations of vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), molybdenum (Mo), iron (Fe), zinc (Zn), and selenium (Se)

Julian date of blood collection was a significant model predictor for arsenic and iron (Table 2.2 and Table 2.3). Arsenic concentrations increased in passerines over time, and the increase was not significantly different for reference, near operations, and potentially exposed locations (Figure 2.5). Iron decreased over time in passerines from reference locations. The effect of Julian date on molybdenum and zinc was significantly different for the three locations, and molybdenum decreased over time in reference locations and near operations (Figure 2.5). Zinc decreased over time near operations.

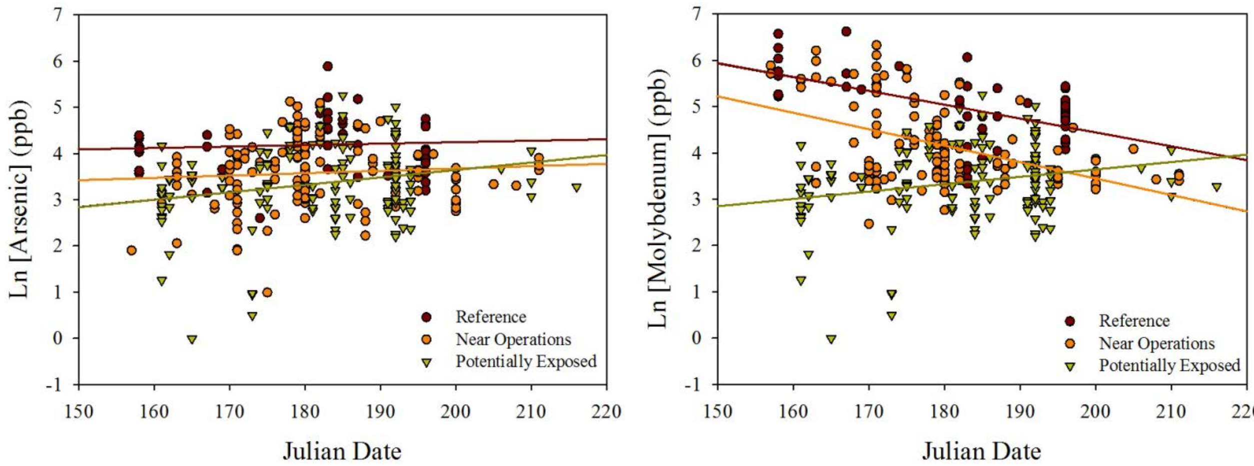


Figure 2.5 Relationship between Julian sample date and log arsenic and log molybdenum concentrations in the blood of passerines at reference, near operations, and potentially exposed sites

A significant year effect was found for seven elements in passerine blood (Table 2.2 and Table 2.3). Element concentrations were higher in 2012 compared to 2011. Even though blood-sample collection methods were unchanged between years, the amount of blood collected in 2012 was significantly lower compared to 2011 (χ^2 =22.17, p<0.0001) for tree swallows and Tennessee warblers. Significant differences occurred in the amount of blood collected from each of the three species (χ^2 =16.40, p=0.0003), due to bird size and the corresponding size of the brachial vein. The brachial vein of Tennessee warblers would close quickly after puncturing making it difficult to obtain a blood sample, and therefore the smallest blood volumes were from Tennessee warblers in both years (Figure 2.6).

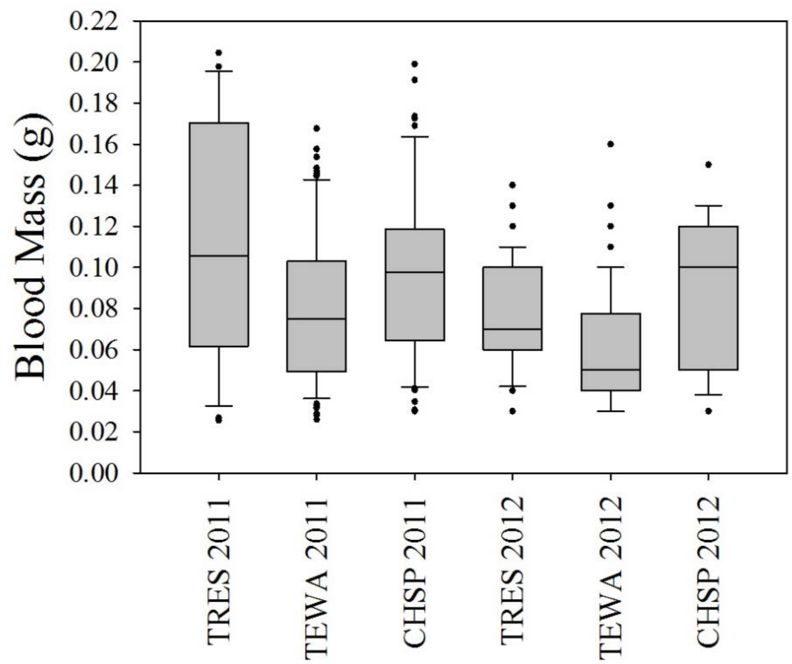


Figure 2.6 Median and interquartile range of blood mass collected from tree swallows (TRES), Tennessee warblers (TEWA), and chipping sparrows (CHSP) in 2011 and 2012

Changes in sample collection locations occurred between 2011 and 2012, and each year was tested separately to determine the effects of location and age class on each species in each year (Table 2.4). Generalized linear model Chi-square (χ^2) statistics and significance levels are presented Appendix A. Element concentrations in blood were not significantly elevated near oilsands operations. Overall, when there was a significant effect of location, the lowest metal concentrations were (5/6 cases) found in passerines closest to the oilsands operations. In 2011, selenium concentrations for Tennessee warblers were highest near operations. Element concentrations for each age class in each year and location are presented in Appendix B.

Age-related differences were found for all elements and occurred more frequently for tree swallows. Vanadium and molybdenum were highest in adult tree swallows. No age-related differences were found for vanadium and molybdenum in Tennessee warblers and chipping sparrows. The levels of nickel and zinc were generally highest in hatch-year birds for all three species. Levels of arsenic, iron, and selenium were highest in adults overall. Chromium showed no pattern between age classes.

Table 2.4 Significant model predictors (√) when including age class, location, and interaction between age class and location as fixed effects, and site within a location as a nested effect, for element concentrations in the blood of passerines in 2011 and 2012

		Tree Swallow		Tennessee Warbler		Chipping Sparrow	
Element	Model Predictors	2011[1]	2012	2011	2012	2011	2012[2]
V	Location				√		
	Site(Location)					√	
	Ageclass	√	√				
Cr	Ageclass			√		√	
	Ageclass*Location			√			
Ni	Location				√		
	Ageclass	√	√	√		√	
	Ageclass*Location			√			
As	Site(Location)		√				
	Ageclass	√	√	√		√	
Mo	Ageclass		√				
Fe	Ageclass	√	√			√	
Zn	Location			√			
	Site(Location)					√	
	Ageclass	√	√	√	√		
Se	Location		√	√			√
	Site(Location)		√				
	Ageclass	√	√	√	√	√	
	Ageclass*Location		√				

[1] In 2011, tree swallows were sampled only near operations
[2] One hatch-year chipping sparrow was captured and sampled in 2012, therefore age class was not included in the model

The three passerines exhibited differences in habitat use and the samples sites were within habitats that increased capture probability for each species. Within reference and potentially exposed locations, tree swallows did not occur at the same sites as Tennessee warblers and chipping sparrows. Therefore, statistical differences among species were determined by comparing samples collected only near oilsands operations, as the three passerines overlapped in space in this location. Significant differences in metal concentration occurred among the three species (Table 2.5).

Table 2.5 Generalized linear model Chi-square (χ^2) statistic and level of significance (*p*) of effect of species on element concentrations in blood near operations in 2011 and 2012; birds near operations were analyzed to determine species differences, as all three species closely overlapped in space in this location

Element	χ^2 (*p*)
Vanadium	20.64 (<0.01)
Chromium	20.90 (<0.01)
Nickel	10.50 (<0.01)
Arsenic	11.05 (<0.01)
Molybdenum	0.82 (0.66)
Iron	10.69 (<0.01)
Zinc	4.28 (0.12)
Selenium	8.21 (0.02)

Chromium and nickel were highest in chipping sparrows and lowest in Tennessee warblers. Vanadium and iron were highest in Tennessee warblers, and not different for tree swallows and chipping sparrows. Arsenic was not different for tree swallows and Tennessee warblers, and was lowest in chipping sparrows. Selenium was highest in tree swallows, and not different for Tennessee warblers and chipping sparrows. No species differences were found for molybdenum and zinc. Element concentrations in the blood of each species averaged across all locations in 2011 and 2012 are provided in Table 2.6.

Table 2.6 Mean and standard deviation (minimum and maximum) element concentrations in the blood of tree swallows, Tennessee warblers, and chipping sparrows; data were combined for all locations and age classes in 2011 and 2012. For full results used in statistical analyses, see Appendix B

Element	Tree Swallow (n=86)	Tennessee Warbler (n=154)	Chipping Sparrow (n=81)
V (ppb)	229.4 ± 205.4 (1.95 – 986.4)	321.8 ± 340.1 (0.33 – 1815)	151.4 ± 172.6 (0.35 – 626.1)
Cr (ppb)	112.4 ± 151.0 (5.25 – 1338)	104.2 ± 127.0 (2.1 – 710.6)	92.6 ± 165.2 (4.15 – 825.8)
Ni (ppb)	89.1 ± 89.7 (4.25 – 489.8)	113.3 ± 137.4 (2.48 – 594.6)	80.6 ± 156.4 (0.73 – 818)
As (ppb)	69.1 ± 51.4 (6.69 – 359.4)	47.5 ± 31.9 (0.99 – 192.3)	26.2 ± 20.7 (2.69 – 106)
Mo (ppm)	0.14 ± 0.14 (0.02 – 0.71)	0.08 ± 0.07 (0.00 – 0.35)	0.10 ± 0.13 (0.01 – 0.75)
Fe (ppm)	424.4 ± 136.7 (163.5 – 772.6)	444.9 ± 109.8 (87.3 – 925.8)	444.4 ± 95.8 (201.3 – 671.2)
Zn (ppm)	10.9 ± 20.2 (2.65 – 145.1)	10.5 ± 19.8 (1.0 – 195.2)	14.3 ± 50.2 (2.61 – 400)
Se (ppm)	1.14 ± 0.74 (0.08 – 4.04)	0.60 ± 0.39 (0.04 – 2.22)	0.48 ± 0.39 (0.03 – 2.38)

High variability in the blood metal concentrations was evident across all three locations (Figure 2.7). The ability to find consistent patterns of element concentrations in passerine blood may have been compromised by low sample sizes for some species and age classes, and locations, or the variability may reflect patchy distribution of element exposure in the environment.

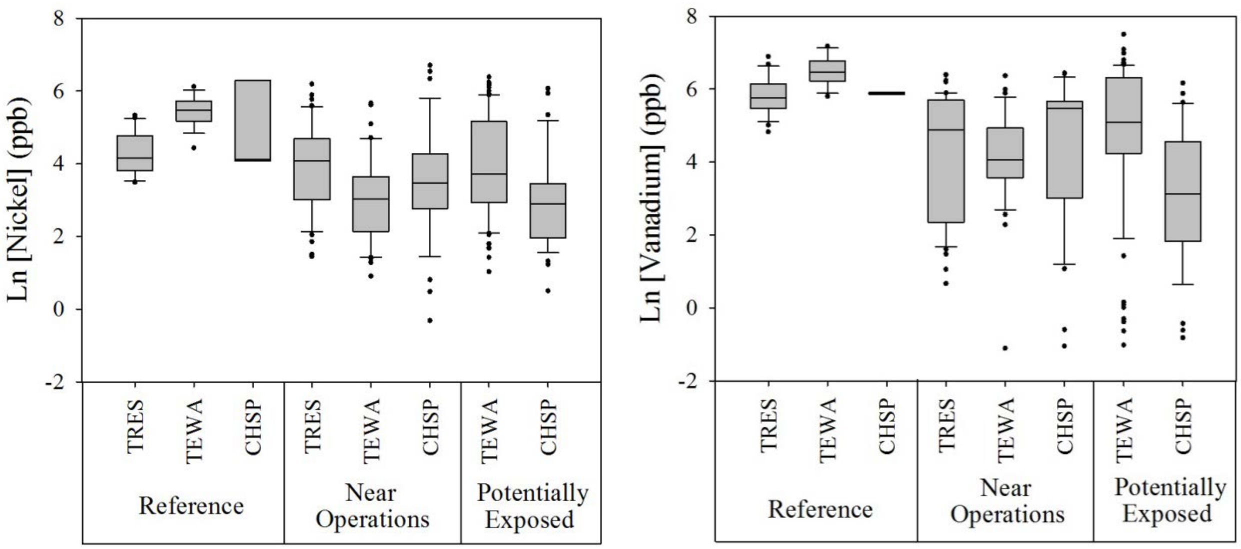


Figure 2.7 Median and interquartile range of log nickel and log vanadium concentrations for tree swallows (TRES), Tennessee warblers (TEWA), and chipping sparrows (CHSP) in each location, 2011 and 2012

I examined the pattern of variability by calculating the CV of the element concentrations near and far from oilsands operations to determine if variability was highest near oilsands mining from patchy distribution of elements in the environment. The CV was calculated for each element in each species and in each year, from which a mean and standard deviation were derived (Figure 2.8). The mean CV for each element was not different between locations based on paired two-sample t-tests ($p > 0.06$ for all comparisons). The F-test for equal variance indicated significantly higher variation near operations for arsenic (df=4, F=0.1565, p=0.0293).

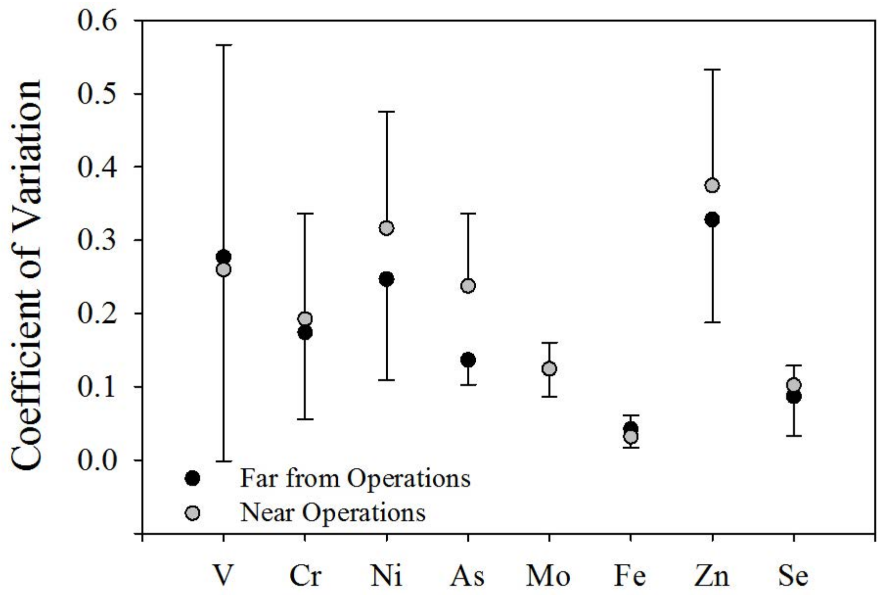


Figure 2.8 The mean and standard deviation of the Coefficient of Variation for logged concentrations of vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), molybdenum (Mo), iron (Fe), zinc (Zn), and selenium (Se) near and far from operations

2.4 Discussion

Blood levels of vanadium, chromium, nickel, arsenic, molybdenum, iron, and zinc in the three passerines were not elevated near oilsands operations. Only selenium in Tennessee warblers was significantly higher near operations compared to reference sites in 2011. Differences in blood metal concentrations were found among the three bird species, although differences were not as expected based on foraging behaviour, and were not consistent among species or age classes. If metal deposition was occurring from oilsands operations, metal concentrations would be expected to increase in surface water and sediments as a result of overland runoff (Davidson and Gunn 2012), and subsequently metals would accumulate in the larvae of aquatic insects (Hare 1992). Therefore, I expected element concentrations, and in particular the non-essential heavy metals, to be highest in tree swallows that forage on aquatic insects, and lowest in chipping sparrows that forage on terrestrial insects and seeds. However, this was not observed. Blood concentrations of metals varied greatly. The high variation could be related to a number of factors apart from ingestion of different amounts of these metals through food or preening, including variation in environmental conditions, sampling methods and blood sample volumes, laboratory handling and instrument analysis, or contamination of samples from syringes and laboratory-related materials. Field sampling methods did not change through the study, and I took precautions to ensure that the sampling area where the birds were handled and the area around the punctured vein were clean to prevent contamination from skin or feathers.

Element concentrations were generally higher in 2012. The reasons for the increase are not known. Annual variations in blood metal concentrations have been observed in previous studies on birds (Burger and Gochfeld 1997; Adair 2002), including tree swallows (Adair 2002), but the reasons for the variation were not discussed. Environmental conditions in my study area were influenced by the extensive regional forest fire that permeated the area with ash and smoke in 2011. Forest fires produce ash that contains vanadium, chromium, nickel, arsenic, molybdenum, zinc, and selenium (Pitman 2006). Iron and zinc are particularly abundant in some types of wood ash (Aronsson and Ekelund 2004). Subsequent mobilization of elements into the food chain may have contributed to the increased element concentrations in 2012. However, the lack of a consistent increase in iron and zinc in any of the three species suggests that the forest fire in 2011 was not a large contributor to the increases in element concentrations in 2012. The influence of potential changes in aerial emissions from oilsands operations is not known.

The observed variation in element concentrations may also be due to unequal exposure and patchy distribution of elements in the environment. The CV for element concentrations in blood was high for most of the elements tested. Although variability for some elements appeared higher near the oilsands operations compared to reference, this difference in variability was significant only for arsenic. The results indicate that some birds experienced increased arsenic exposure near oilsands mining. High CV was also reported in metal concentrations in the blood of shorebirds from metal-polluted wetlands, indicating either naturally high species variability or potential contamination during sampling (van Eeden and Schoonbee 1996).

Blood element concentrations were different for the three species. Vanadium and iron were highest in Tennessee warblers, while chromium and nickel were highest in chipping sparrows. Selenium was highest in tree swallows. Zinc was similar in tree swallows and Tennessee warblers, and there were no species differences for molybdenum and zinc. All three species arrive in the study area in mid- to late May and establish breeding territories, and would thus be exposed to similar environmental conditions once on the breeding grounds. The differences among the three species may be due to differences in diet and body size. If metals are transferred from the soil and aquatic environment into invertebrates, insectivorous birds may accumulate more metals than those species that feed on seeds or vegetation (Hunter and Johnson 1982; Gochfeld and Burger 1987a; Eens et al. 1999; Deng et al. 2007) because of the protective mechanisms in plants (Ernst et al. 1992; Bagatto et al. 1993; Ernst et al. 2000). Based on diet, chipping sparrows might be exposed to lower levels of the non-essential elements in particular. However, this was not observed in blood levels. Metabolic rates of small passerines vary inversely with body mass (Teal 1969), and with foraging behaviour (Holmes et al. 1979; Nudds and Bryant 2000). In my study, tree swallows were the heaviest (23 ± 2.2 SD g), followed by chipping sparrows (12 ± 0.9 SD g), and Tennessee warblers (9 ± 0.8 SD g). Tree swallows forage on the wing, while Tennessee warblers and chipping sparrows forage by gleaning insects from vegetation or collect food on the ground. Patterns in element accumulation were not consistent with variation in either body mass or foraging behaviour.

Although I found age-related differences in metal levels, they were not consistent among the three species. Many factors can affect element accumulation in birds (Gochfeld and Burger 1987b). Exposure time on the breeding grounds may influence accumulated element levels in adult birds. Nestlings may show higher levels of essential elements due to demands during growth (Berglund et al. 2011). In my study, nickel and zinc were highest in hatch-year birds, while arsenic, iron and selenium were highest in adult birds. Vanadium, chromium and molybdenum exhibited no consistent pattern with age class. These differences may be attributed to differences in diet or differences in metal uptake by insects. The uptake of metals can vary among insects, as well as among similar insect species within the same site (Kramaz 1999a and b; Rabitsch 1997). Adult and young birds may eat different foods, different proportions of the same foods, or metabolize foods differently (Burger and Gochfeld 1997). Age-related differences were found more frequently in tree swallows. Nestling tree swallows were sampled while still occupying nest boxes and being fed by adults, while Tennessee warbler and chipping sparrow hatch-year birds were sampled shortly after fledging. The extent to which the hatch-year birds remained dependent on the adults for food may account for some of these differences, as fledgling birds may forage on a more varied than when in the nest.

Comparing the results from my study with those in the published literature (Appendix C) was complicated because results were reported in different units (dry or wet-weight, µg/dl, ng/mL, µg/g), mean calculations were presented as either arithmetic, geometric, or median values, and the results were complicated by different age distributions and environmental conditions. As well, most experimental studies on metal exposure evaluate acute effects associated with high doses, and few chronic exposure studies are available for comparison.

I could not find published literature on the normal range of vanadium levels in the blood of passerines. However, blood levels of vanadium in 2012 exceeded the levels found in long-tailed ducks (*Clangula hyemalis*) and common eiders (*Somateria mollissima*) in the Beaufort Sea (Franson et al. 2004), but in 2011 the vanadium levels were similar to, or lower than those reported. Vanadium levels in the blood of unexposed domestic chickens (*Gallus gallus*) were provided by the PDS laboratory (B. Blakley pers. comm.), and were 62.5 ± 37.7 ppb (n=6; 6.6-204 ppb). In my study, vanadium levels in 2011 were well within this range for all three species. In 2012, vanadium levels exceeded the normal range for chickens, particularly in reference samples for Tennessee warblers which were assumed to be relatively unaffected by oilsands activities.

My study measured total chromium, rather than specific chromium oxidation states, in the whole blood of birds. The values for total chromium were lower than those reported in blood for tree swallows and other passerines in an urbanized natural area near a landfill (Tsipouraa et al. 2008). As with vanadium, chromium exhibited year differences, and the levels of chromium in 2011 were lower compared to values reported in blood for gull species from urban and freshwater marsh habitats (Burger and Gochfeld 1997), while in 2012 my values were higher.

The blood nickel levels were similar to or lower than those reported for tree swallows and other passerines from sites on remediated land formerly occupied by a metal smelter (Adair 2002). Nickel levels were generally similar to those found for great tits (*Parus major*) both near (Dauwe et al. 2005) and far (Geens et al. 2010) from an active heavy metal smelter, although levels did occasionally exceed those reported, particularly for Tennessee warblers and chipping sparrows in 2012. Levels were also similar to those reported for mallards (*Anas platyrhynchos*) in urban wetlands and in ponds far from urban areas (Binkowski and Meissner 2013). Nickel levels were far below those reported for shorebird species inhabiting a metal-polluted wetland (van Eeden and Schoonbee 1996), and lower than reference levels in coots (*Fulica cristata*) (van Eeden 2003).

The arsenic levels that I found were lower than the reference levels for pied flycatchers (*Ficedula hypoleuca*) (Berglund and Nyholm 2011), and lower than in herring gulls (*Larus argentatus*) inhabiting urban and industrialized areas (Burger and Gochfeld 1997). Blood arsenic concentrations were also far lower than the levels for great tits near an active heavy metal smelter (Dauwe et al. 2005). However, arsenic levels were higher than those reported in blood of passerines, including tree swallows near a landfill (Tsipouraa et al. 2008), and were higher than in Franklin's gulls (*Larus pipixcan*) inhabiting a clean water marsh (Burger and Gochfeld 1997). The arsenic levels in my study were within the range of normal values (0 to 0.18 µg/g dry weight) determined from an oral dosing study of adult Zebra finches (*Taeniopygia guttata*) (Albert 2006), suggesting that the levels are not harmful to birds.

The normal molybdenum level in the whole blood of passerines has not been previously reported. In my study, molybdenum did not exhibit species differences or a consistent pattern in age class distribution, and levels did not differ among locations. Daily fluctuations in molybdenum have been suggested, with levels decreasing over the day (Rosenthal et al. 2005).

Homeostatic mechanisms regulate the absorption, storage and excretion of the essential elements iron, zinc, and selenium (Liu et al. 2008). Iron was highest in Tennessee warblers in my study. The blood iron levels were similar or slightly higher than reference levels of nestling black-crowned night herons (*Nycticorax nycticorax*) (Golden et al. 2003). Iron levels were also similar to those reported for mallards from urban wetlands (Binkowski and Meissner 2013) and to those reported for arctic waterfowl from a relatively undisturbed nesting area (Franson et al. 2004).

Zinc exhibits daily fluctuations and levels are highest in the morning, decreasing through the day (Hetland and Brubakk 1973; Rosenthal et al. 2005), and variability in blood levels can be attributed to the time of sampling (Yokoyama et al. 2000). Although I did not control for time of day, blood samples were generally collected in the morning and completed by noon. Timing coincided with bird activity and capture protocols, which were normally early morning. In my study, zinc was highest in hatch-year birds and blood levels were not different for the three bird species. Generally, the levels were similar to published reference levels (Geens et al. 2010; Berglund and Nyholm 2011). Zinc levels occasionally exceeded those measured in other passerines (Adair 2002; Dauwe et al. 2005; Brumbaugh et al. 2010). Published literature could not be found on the levels of zinc in the whole blood of passerines that would reflect toxicological concern.

There are large differences in selenium blood levels in human populations from different geographic regions due to the natural availability of selenium in the environment (ATSDR 2003). Adult passerines in my study appeared to have selenium levels in blood that were higher than the normal range for birds, but below levels causing harm (Ohlendorf and Heinz 2011). The blood selenium levels varied by age class, and were similar to those found for water birds (Golden et al. 2003; Alvarez et al. 2013) and lower than levels that appeared not harmful for marine birds (Wayland et al. 2008) and gulls (Conover and Vest 2009).

The reasons for the high variability in my study are not known. Blood sampling occurred over one month during the breeding season, and changes in food resources over this time or annually potentially contributed. Alternatively, the metal levels in whole blood may be inherently more variable than in other tissues. Under uniform laboratory sampling conditions, the moisture content of blood remains fairly consistent, but under field conditions the moisture content of blood can vary substantially potentially affecting metal concentrations (Ohlendorf and Heinz 2011). Water balance may also affect haematocrit levels, the proportion of blood volume that is composed of red blood cells. A positive relationship between hot daytime temperatures and average haematocrit values was reported in nestling tree swallows (Ardia 2013). Some metals such as vanadium and chromium accumulate in red blood cells, while other metals bind to proteins in the red blood cell membrane (Valko et al. 2005). Variation in red blood cell volume may have a dramatic effect on metal concentrations.

Variability in blood metals may also be attributed to metal metabolism, absorption rates and bioavailability from food (Luoma and Rainbow 2005). Some metals are more readily absorbed from food than others (Reinfelder and Fisher 1994). If an organism is exposed to an environment containing excess quantities of metals, the mechanisms used to minimize potential toxicity include reduced uptake, enhanced excretion, or sequestration of the metals to render them non-toxic (Baker 1981). Interactions among metals are complex, affecting metal absorption, metabolism, excretion, and the homeostatic mechanisms that regulate these processes (reviewed in Brzoska and Moniuszka-Jakaniuk 2001). For example, lead and cadmium were readily taken up by rice roots when present alone, but when presented together the uptake of both declined by up to 40% (Srivastava et al. 2014).

The duplicate samples taken from adult tree swallows exhibited large relative percent differences for vanadium, chromium, nickel, arsenic, and molybdenum. Repeatability was better for iron, zinc, and selenium. Essential elements are normally present at higher concentrations of parts per million, compared to the lower parts per billion observed for most non-essential elements. This improves the ability to measure concentrations of essential elements in blood. The mass of the blood samples had a significant effect on the element concentration measurements, with the smaller blood samples tending to have higher levels of the elements. If the concentration in the sample is approaching the detection limit, the smaller blood samples may limit the ability to measure the metal level and would result in substantial variation (B. Blakley pers. comm.). The variation may vary with the metal and how close the actual concentration is to the detection limit. However, the minimum observed concentrations were well above the established IDLs for my study, and variation was likely from other unknown causes (B. Blakley pers. comm.). For example, laboratory handling and weighing may be more difficult and introduce measurement variation and variability in the results for small blood samples. The blood element concentrations were calculated on a per weight basis. Variation in weight measurements may be more pronounced in small samples, increasing the potential error and variability compared to larger samples. When larger volumes of blood (3 to 5 mL) were used in other studies, less variability was reported (Burger and Gochfeld 1997; Golden et al. 2003). These large blood volumes can only be obtained during live sampling of large birds such as waterfowl.

A combination of the factors discussed above likely contributed to the high variability in blood levels of heavy metals. More study is needed to understand the relationship between blood volume and metal concentrations, and interactions of metals in blood to determine if non-lethal methods such as blood collection to analyze for metals is appropriate to study industrial effects on small birds. In areas where metal contamination has been demonstrated to be biologically significant, patterns of exposure may be more evident in blood. The results from my study suggest that exposure to low metal contaminant levels may not be easily demonstrated through blood sampling.

The oilsands mine operations do not appear to be exposing passerines to metal levels above those that occur naturally. However, from the results of the blood sampling, I was not able to conclude that there is no biological risk to birds. Some metals will potentially bioaccumulate in the food chain and could be expected to have adverse effects on bird health and reproduction. Measuring metal levels in other tissues and in the diet, and evaluating effects on reproductive endpoints would provide further evidence as to whether metal exposure from oilsands mining is low.

Chapter Three: Relationships Between Metal Concentrations in Nestling Tree Swallows and Their Food in the Alberta Oilsands

3.1 Introduction

The release of heavy metals into the environment is increasingly a concern in the Athabasca oilsands region north of Fort McMurray, Alberta (Timoney and Lee 2009; Kelly et al. 2010; Schindler 2010). Surface mining of the oilsands has been occurring since 1967, and bitumen production from mining is expected to increase from 0.9 million barrels per day (bpd) in 2010 to about 1.6 million bpd by 2020 (ERCB 2011). A complex mixture of contaminants is derived from bitumen extraction and upgrading. Nickel and vanadium are found in appreciable concentrations within the raw oilsands material (Research Council of Alberta 1953; Har 1981), and are present, along with other metals, in the by-products from bitumen production (Jervis et al. 1982; Holloway et al. 2005; Puttaswamy and Liber 2012). Nickel, cadmium, lead, zinc, and other metals were measured in particulates in snow and were attributed to oilsands upgrader emissions (Kelly et al. 2010).

Metal contamination in soil and surface water affects the species composition of plant, insect, bird, and small mammal taxa, because those species less tolerant of contamination are displaced by more tolerant species, thus altering the abundance and diversity of species (Heliovaara and Vaisanen 1991; Eeva and Lehikoinen 1996; Ruohomaki et al. 1996; Kiikkilä 2003; Koptsik et al. 2003; Mukhacheva et al. 2010). However, there are no published peer-reviewed studies that have examined the health effects of metals on wildlife in the oilsands region. Birds are often used to monitor the environment for metal contamination from industrial activities (Swiergosz et al. 1998; Eens et al. 1999; Bel'skii et al. 2005; Eeva et al. 2009; Berglund et al. 2010), and insectivorous birds in particular are useful for studying effects from metal exposure because the accumulation of metals can occur through the diet (Hunter and Johnson 1982; Gochfeld and Burger 1987a; Eens et al. 1999).

Tree swallows (*Tachycineta bicolor*) have been used as an indicator of environmental exposure to contaminants in the oilsands region (Smits and Fernie 2013). Tree swallows are an ideal model organism because they readily use nest boxes, allowing for appropriate sample sizes and standardization of methods (Jones 2003). Tree swallows are semi-colonial, and birds will nest in close proximity to each other, allowing relatively high densities of birds within a small area (McCarty 2001/2002). Birds nesting in a common area are assumed to be exposed to the same contaminants, reducing the variability in dietary metal concentrations and making it possible to study the potential effects from metal exposure.

The objective of my study was to investigate the levels of metals and other metalloid elements in nestling tree swallows inhabiting areas near oilsands operations. I hypothesized that exposure to metals was from the diet, because contaminant exposure through foraging has been most frequently documented (McCarty 2001/2002), compared to exposure from inhalation or absorption. I measured the element burden in bird tissues and in the food items provided to the nestlings by adults, as determined from stomach contents. I predicted that I would find higher levels of metals in the tissues of nestlings near oilsands mining operations compared to those birds in reference locations that would reflect natural environmental conditions. If the nestlings were being exposed to metal contaminants from food, then I also predicted that metal levels in tissues would be correlated to the metal levels in the diet.

The insectivorous diet of tree swallows is well understood, and these birds forage primarily on invertebrates with aquatic larval stages (Mengelkoch et al. 2004). Tree swallows will consume brachyceran, nematoceran and cyclorrhaphan Diptera, as well as Trichoptera, Ephemeroptera, Odonata, and Hemiptera (McCarty and Winkler 1999a; Smits et al. 2000). Tree swallows will forage within a few hundred metres of their nest through the breeding season (Quinney and Ankney 1985; McCarty and Winkler 1999a; McCarty 2002; Mengelkoch et al. 2004). Therefore, any measured metal accumulations in nestlings can be attributed to local exposure from foods brought to them by adults (Echols et al. 2004). I collected invertebrate samples near nest locations to measure metal concentrations in dietary items to understand the variability in metal exposure in the tree swallow diet.

3.2 Methods

3.2.1 Study Sites

My study was conducted in 2012 and 2013 with populations of tree swallows using nest boxes near Fort McMurray. I sampled tree swallow nestlings at six sites; Sites 1, 2, and 3 were within 5 km of active oilsands mine operations and were exposed to aerial emissions and potentially to contaminants in water (Figure 3.1). The reference sites (Sites 4, 5, and 6) were located 60 to 65 km south of the active mining area. The prevailing winds in the region are to the north and northeast. Therefore, reference sites were considered to be unexposed to upgrader emissions. Each site supported 20 to 30 nest boxes, and was near an open water wetland or pond. Near operations, Site 1 was located on a pond built in 1993 to support tailings research, and contained fine tailings that have settled to the bottom and a cap of natural surface water. Site 2 was a reclaimed area and on the edge of a wetland that formed following reclamation in 2003. Site 3 was also reclaimed and was planted with white spruce (*Picea glauca*), jack pine (*Pinus banksiana*), and Siberian larch (*Larix sibiricain*) in 1983. This site was an overburden dump from mine development and now supports a mature upland forest and wetland habitat. The reference Site 4 was located on the edge an old borrow pit that provided gravel fill for road construction, and has naturally revegetated and filled with water. Site 5 was adjacent to a beaver pond and natural drainage system. Site 6 was on a grass-sedge wetland on the edge of Maqua Lake.

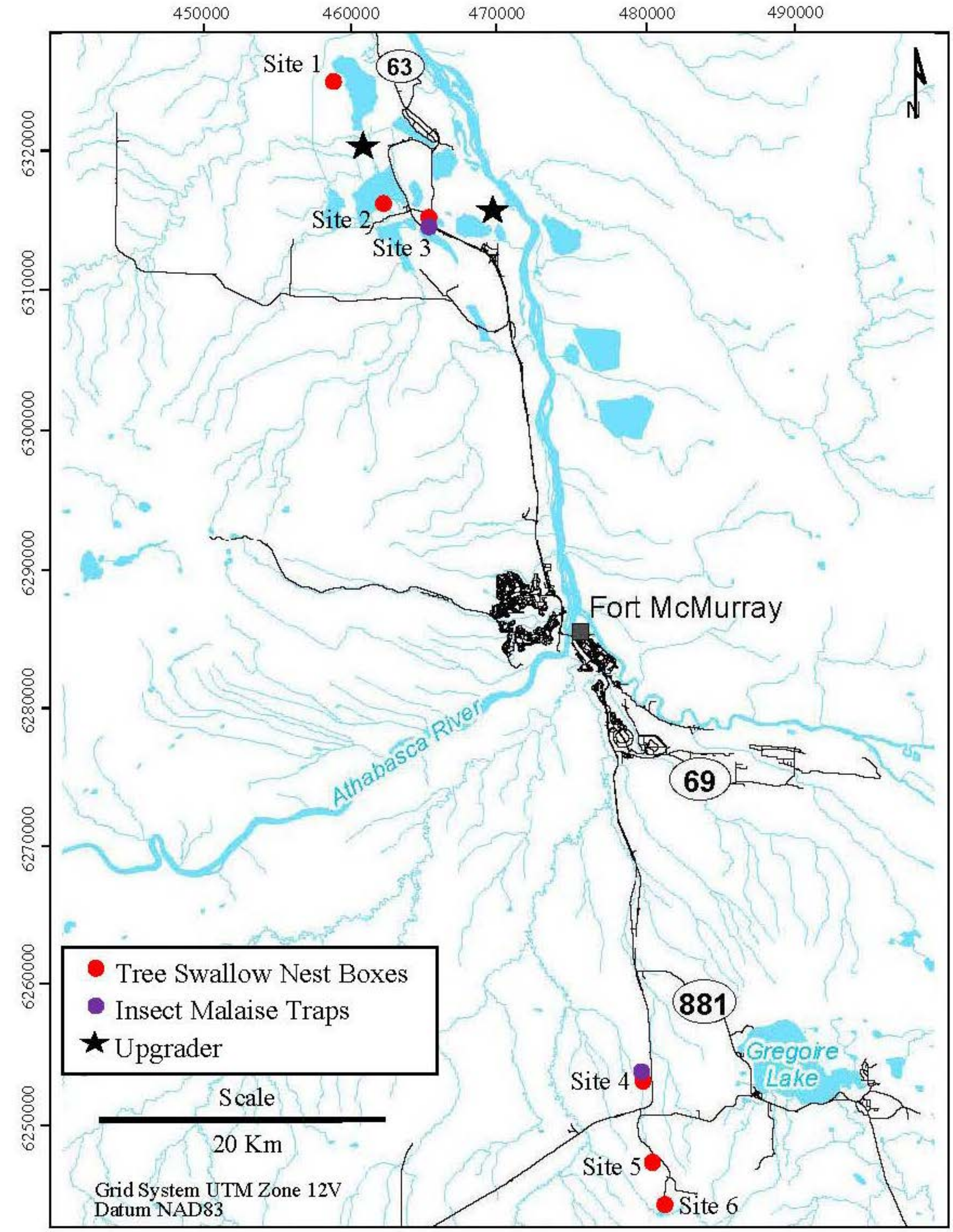


Figure 3.1 Study sites where tree swallow and invertebrate samples were obtained near oilsands mining operations north of Fort McMurray, and reference sites to the south.

3.2.2 Tissue Sampling

I monitored tree swallow nest boxes regularly from the initiation of nest building beginning about 20 May in both 2012 and 2013. Nest boxes were inspected daily or every second day during egg laying to determine the date of clutch completion. Nest boxes were left undisturbed during incubation until hatching, and then checked daily until all nestlings hatched. At the age of 14 days, one to three nestlings were randomly collected from each nest box. Three nestlings were occasionally collected from nests of larger brood sizes (six or more nestlings) to improve sample sizes. Nestlings were anesthetized with isoflurane, and then euthanized by cervical dislocation. Once nestlings were euthanized, the liver and kidney were removed and immediately frozen in liquid nitrogen. The stomach was removed and kept on ice until transferred to a freezer at the end of each day. The protocols used in this study were approved by the Animal Care Committee at the University of Calgary (LESACC protocol number BI11R-27), in compliance with standards set by the Canadian Council on Animal Care.

Liver and kidney samples were shipped on dry-ice to the Prairie Diagnostic Services (PDS) laboratory at the Western College of Veterinary Medicine in Saskatoon, Saskatchewan, for metal analysis. The stomach contents were removed for identification of the food items to the lowest taxonomic level possible, and the percent volume of each taxon was visually estimated. Following identification, the contents of each stomach sample were oven dried at 40°C for 48 to 72 hours. The dried samples were then shipped to the PDS laboratory for metal analysis.

3.2.3 Invertebrate Sampling

A Malaise trap was used to collect flying insects at Site 3 near mine operations and at the reference Site 4. The traps were installed near the nest boxes and in close proximity to open water and tall shrubs that provided cover for insects. Insects would fly into the central tent wall and were funneled upwards and into a wide-mouth plastic sample bottle containing 70% ethanol. Insects were collected over three weeks, in one sample bottle per week providing three samples per location, beginning 15 June, when nestlings started hatching, until fledging. The insects from each sample bottle were sorted and those insects that were identified in the nestling diet were removed. Insect samples were oven dried at 40°C for 48 to 72 hours, and the dried samples were shipped to the PDS laboratory for metal analysis.

3.2.4 Laboratory Analyses

Laboratory analysis of liver, kidney, stomach contents, and invertebrate samples involved digestion with HNO_3 in a pressurized Microwave-Accelerated Reaction System (MARS) following the instructions by the manufacturer (CEM Corporation). In order of increasing atomic number, and from non-essential to essential, the 13 metal and metalloid elements measured were vanadium, chromium, nickel, arsenic, strontium, molybdenum, cadmium, lead, iron, cobalt, copper, zinc, and selenium. Elements were quantified using an Inductively Coupled Plasma-Mass-Spectrometer (ICP-MS, Thermo Jarrell-Ash Corporation, Franklin, MA, USA). The metal concentrations are expressed on a per wet or dry weight basis. Stock standards used by PDS were purchased from SCP Science or VWR International, and standard reference materials were purchased from the National Institute of Standards and Technology. Instrument detection limits (IDLs) for this study were: vanadium (10 ppt), chromium (10 ppt), nickel (17 ppt), arsenic (80 ppt), strontium (3 ppt), molybdenum (10 ppt), cadmium (6 ppt), lead (2.6 ppt), iron (0.9 ppt), cobalt (1.35 ppt), copper (36 ppt), zinc (0.36 ppb), and selenium (172 ppt) (PDS Laboratory personal communication).

3.2.5 Data Analyses

I used SAS software 9.3 (SAS, 2008. SAS/STAT® 9.3 User's Guide. SAS Institute Inc.) to conduct the statistical analyses. The measured element concentrations in tissues, stomach contents, and insect samples were log-transformed to achieve a normal distribution. Element concentrations were analyzed with generalized linear models with a log link function (GENMOD procedure in SAS). I used the GENMOD procedure to accommodate for the difference in variance in element concentrations among locations. For tissues and stomach contents, each model contained year, location, and the interaction between year and location as fixed effects. Given that three sites were used to define each location, variability among sites was accounted for by including a site within a location as a nested effect (site (location)) within each model. A Spearman Rank correlation was used to test correlations in metal levels among the liver, kidney, and stomach contents. Insect samples were tested with location as a fixed affect, and I included sample mass in the model to account for variability associated with the amount in each sample. I present data as arithmetic means and standard deviations. The level of statistical significance was $p < 0.05$ for all statistical tests.

Tissue element data in swallows and other birds are available for a number of locations across the United States (Franson et al. 1995; Custer et al., 2001, 2005, 2006, 2009, 2013; Rattner et al. 2006) and from a study in Europe (Llacuna et al. 1995) and these help put data from the oilsands region into context. To compare the liver and kidney data with literature values where results were expressed in dry weights, a conversion ratio (wet-weight:dry-weight) for liver (0.25) and kidney (0.20) was used based on an approximate mean value for percent moisture content for liver (75%) and kidney (80%) determined from various studies (Scanlon 1982; Franson et al. 1995; van Eeden and Schoonbee 1996; van Eeden 2003). Thus, 1 μg/g wet-weight (ww) equals approximately 4 μg/g dry-weight (dw) for liver and 5 μg/g (dw) for kidney. For conversion of units, 1 μg/g equals 1 mg/kg, which also equals 1 ppm. Similarly, 1 μg/kg equals 1 ng/g, which equals 1 ppb, and 1 ppm is equivalent to 1000 ppb.

3.3 Results

A total of 98 nestling tree swallows were sampled at reference locations and near operations in 2012 and 2013 (Table 3.1). Of the 28 nestlings that were collected near operations in 2013, six were collected following several days of heavy rain and cool weather. The stomach contents in these six nestlings contained minimal food, suggesting they had not been fed recently. Two of these stomachs were completely empty and were not included in the analysis, while the other four contained various amounts of grass, likely nest material, and undigested food items of adequate amounts to include in the analyses.

Table 3.1 Number of tree swallow nestlings sampled in 2012 and 2013

	2012	2013
Reference	16	31
Near Operations	23	28
Total	39	59

The nestling diet as determined from the stomach contents varied by location, and in each year (Table 3.2). Overall, in the samples that I analyzed, it appeared that a greater proportion of Coleoptera was consumed in 2012 compared to 2013. The nestlings at the reference location appeared to consume a greater proportion of Ephemeroptera, while the nestlings near operations appeared to consume more Odonata (suborder Zygoptera). The consumption of Ephemeroptera and Diptera appeared to increase in birds near operations in 2013 compared to 2012.

Table 3.2 Percent by volume and minimum and maximum percent of invertebrates consumed by 14-day old tree swallow nestlings in 2012 and 2013

	Reference (%)		Near Operations (%)		
Taxa	2012	2013	2012	2013	Larval Habitat
Coleoptera	28 (5-75)	10 (0-30)	37 (0-75)	14 (5-65)	Terrestrial
Ephemeroptera	25 (0-90)	46 (0-100)	0	10 (0-85)	Aquatic
Diptera	27 (0-85)	25 (0-95)	9 (0-25)	31 (0-85)	Terrestrial/Aquatic
Tipulidae	0	<1 (0-15)	0	4 (0-40)	Aquatic
Odonata	<1 (0-10)	2 (0-50)	30 (0-80)	9 (0-80)	Aquatic
Hymenoptera	3 (0-25)	4 (0-35)	6 (0-30)	6 (0-40)	Terrestrial
Lepidoptera	<1 (0-3)	1 (0-10)	5 (0-90)	1 (0-10)	Terrestrial
Trichoptera	1 (0-10)	3 (0-65)	0	2 (0-30)	Aquatic
Hemiptera	<1 (0-5)	1 (0-10)	<1 (0-5)	1 (0-10)	Terrestrial
Neuroptera	0	0	0	<1 (0-5)	Terrestrial
Other	2 (0-20)	<1 (0-5)	1 (0-15)	<1 (0-1)	
Unknown	13 (0-35)	8 (0-55)	13 (0-60)	16 (0-50)	

I found no significant location differences in element concentrations in liver tissue between the reference location and near operations for 11 of the 13 elements (Figures 3.2 to 3.8, at the end of this chapter). In 2012, chromium was significantly lower in liver at the reference location ($\chi^2 = 4.35$, $p = 0.0370$). There was no significant difference for chromium in 2013. In 2012, lead was significantly higher at the reference location ($\chi^2 = 7.00$, $p = 0.0082$), but no significant difference was found in 2013. Year differences occurred in liver for vanadium, arsenic, and cadmium, with levels significantly higher in 2013 than 2012 (vanadium, $\chi^2 = 43.29$, $p < 0.0001$; arsenic, $\chi^2 = 3.86$, $p = 0.0494$; cadmium, $\chi^2 = 9.23$, $p = 0.0024$) at reference locations and near operations.

I found no significant location differences for 12 of the 13 elements in kidney. In 2012, selenium was significantly higher in kidney at the reference location than near operations

(χ^2 = 14.34, p = 0.0002) (Figures 3.2 to 3.8). Year differences were found for vanadium, chromium, and zinc, with levels significantly higher in 2013 compared to 2012 (vanadium, χ^2 = 35.96, p < 0.0001; chromium, χ^2 = 8.37, p = 0.0038; zinc, χ^2 = 5.02, p = 0.0250) at reference locations and near operations. Across locations, metal concentrations in liver and kidney were positively correlated for vanadium, arsenic, and iron in 2013, and for cadmium, cobalt, and selenium in both years (Table 3.3).

I found no significant location differences in the stomach contents for 11 of the 13 elements. Stomach contents from reference locations were significantly higher in copper and selenium compared to near operations (copper, χ^2 = 5.48, p = 0.0192; selenium, χ^2 = 4.74, p = 0.0294) (Figures 3.2 to 3.8). Significant year differences were found for chromium and arsenic in the stomach contents, and were higher in 2013 compared to 2012 at reference locations and near operations (chromium, χ^2 = 5.02, p = 0.0251; arsenic, χ^2 = 4.88, p = 0.0272). The metal concentrations in the stomach contents were positively correlated with levels in the liver for arsenic and cadmium in 2012, for molybdenum, iron, and cobalt in 2013, and for selenium in both years (Table 3.3). Element concentrations in the stomach contents and kidney were positively correlated for cadmium in 2012, for chromium, lead, and iron in 2013, and for cobalt and selenium in both years. Molybdenum and copper were negatively correlated between stomach contents and kidney in 2013. The levels of nickel, strontium, and zinc in the stomach contents were not correlated with kidney or liver. Vanadium was correlated only between liver and kidney. Element concentrations (mean ± SD, range) in liver, kidney, and stomach contents for 2012 and 2013 are provided in Appendix D.

Table 3.3 Spearman Rank correlation coefficients (r) and *p* values for relationships of element concentrations between liver and kidney and stomach contents of 14 day-old tree swallow nestlings in 2012 and 2013. Bold font indicates a statistically significant correlation (*p* < 0.05)

	2012			2013		
	Liver-Kidney	Liver-Stomach	Kidney-Stomach	Liver-Kidney	Liver-Stomach	Kidney-Stomach
V	0.25 (0.16)	-0.10 (0.57)	0.11 (0.52)	**0.44 (<0.01)**	0.15 (0.31)	0.08 (0.56)
Cr	-0.13 (0.46)	-0.01 (0.94)	-0.09 (0.60)	0.16 (0.30)	0.08 (0.60)	**0.31 (0.03)**
Ni	0.06 (0.73)	-0.14 (0.40)	0.13 (0.44)	0.20 (0.20)	0.08 (0.59)	0.03 (0.86)
As	0.35 (0.05)	**0.41 (0.02)**	0.14 (0.43)	**0.57 (<0.01)**	0.26 (0.08)	0.21 (0.13)
Sr	0.25 (0.16)	-0.18 (0.29)	-0.06 (0.73)	0.27 (0.07)	-0.10 (0.48)	-0.24 (0.10)
Mo	0.06 (0.74)	-0.06 (0.70)	-0.12 (0.50)	-0.28 (0.07)	**0.29 (0.04)**	**-0.30 (0.04)**
Cd	**0.76 (<0.01)**	**0.62 (<0.01)**	**0.71 (<0.01)**	**0.33 (0.02)**	0.15 (0.31)	0.23 (0.11)
Pb	0.08 (0.70)	0.28 (0.14)	0.19 (0.28)	-0.05 (0.76)	-0.12 (0.40)	**0.31 (0.03)**
Fe	0.07 (0.71)	-0.08 (0.62)	-0.05 (0.76)	**0.45 (<0.01)**	**0.40 (<0.01)**	**0.32 (0.03)**
Co	**0.50 (<0.01)**	0.30 (0.07)	**0.47 (<0.01)**	**0.64 (<0.01)**	**0.42 (<0.01)**	**0.35 (0.01)**
Cu	0.28 (0.12)	-0.13 (0.45)	-0.08 (0.64)	0.11 (0.49)	0.01 (0.96)	**-0.31 (0.03)**
Zn	-0.28 (0.11)	-0.17 (0.30)	-0.04 (0.83)	-0.07 (0.66)	-0.18 (0.22)	-0.15 (0.29)
Se	**0.71 (<0.01)**	**0.56 (<0.01)**	**0.56 (<0.01)**	**0.80 (<0.01)**	**0.38 (<0.01)**	**0.30 (0.03)**

I sorted invertebrates collected from Malaise traps based on the nestling diet, and selected nine taxonomic groups for metal analyses: Coleoptera (beetles), Odonata (Zygoptera (damselflies)), five from the Order Diptera (Muscomorpha (flies), Syrphidae (hoverflies), Tipulidae (crane flies), Tabanidae (horse flies), and Culicidae (mosquitoes)), Lepidoptera (moths), and Hymenoptera (Ichneumonidae (parasitic wasps)). Ephemeroptera were not captured in the traps and therefore could not be tested. Element concentrations in insect taxa are provided in Appendix E.

Significant differences occurred in element concentrations between the reference site and near operations for each invertebrate taxa (Figures 3.9 to 3.12). When there was a significant location difference in element concentrations, it was most often (27 of 33 cases) highest at the reference site (Table 3.4). Low samples sizes (n=3 for reference; n=3 for near operations) and high variability likely influenced the ability to detect significant differences for some elements. No significant differences were found for chromium between the reference location and near operations.

Coleoptera at the reference site had significantly higher levels of strontium and cadmium compared to near operations. For the five taxa belonging to the Order Diptera (Culicidae, Muscomorpha, Syrphidae, Tabanidae, and Tipulidae) the concentrations of vanadium, nickel, arsenic, molybdenum, cadmium, cobalt, copper, zinc, and selenium, were significantly higher at the reference site than near operations in 14 of 17 cases. Iron was significantly higher near operations in three of nine cases. Vanadium levels in Tabanidae were also significantly higher near operations, while vanadium levels in Culicidae and Tipulidae were significantly higher at the reference site. Where significant location differences occurred for Ichneumonidae, Lepidoptera, and Zygoptera, higher levels of elements were found at the reference site. Ephemeroptera were not captured in the Malaise traps and element levels were not tested, however, four stomach samples from the reference site contained greater than 90% of this taxon. These four samples had higher than average levels of vanadium, iron, copper, and selenium, and lower than average levels of strontium and zinc. All remaining elements were similar to the average element concentrations measured in other taxa.

Table 3.4 Generalized linear model Chi-square (χ^2) statistic and level of significance (*p*) of element concentrations (log-transformed values) for significant location differences of each invertebrate taxon. Grey highlights indicate highest near operations, whereas all others are highest at the reference site

Element	COLE	CULI	ICHN	MOTH	MUSC	SYRP	TABA	TIPU	ZYGO
V	NS	**5.12 (0.02)**	NS	NS	NS	NS	**6.89 (0.01)**	**5.05 (0.02)**	NS
Cr	NS	NS	NS	NS	NS	NS	NS	NS	NS
Ni	NS	NS	NS	NS	NS	**4.21 (0.0402)**	NS	NS	NS
As	NS	NS	**16.56 (<0.01)**	NS	NS	NS	NS	**11.04 (<0.01)**	NS
Sr	**7.23 (<0.01)**	NS	NS	NS	NS	NS	NS	NS	NS
Mo	NS	NS	**13.01 (<0.01)**	NS	NS	NS	NS	**20.06 (<0.01)**	**5.32 (0.02)**
Cd	**12.53 (<0.01)**	NS	**4.24 (0.04)**	**10.29 (<0.01)**	**13.25 (<0.01)**	NS	**5.28 (0.02)**	**10.49 (<0.01)**	**5.28 (0.02)**
Pb	NS	NS	NS	**4.57 (0.03)**	NS	NS	NS	NS	NS
Fe	NS	NS	NS	**6.20 (0.01)**	**8.71 (<0.01)**	NS	**5.84 (0.02)**	NS	NS
Co	NS	NS	NS	NS	**22.25 (<0.01)**	**7.31 (<0.01)**	NS	NS	NS
Cu	NS	NS	NS	**6.79 (<0.01)**	NS	**3.97 (0.04)**	NS	**10.58 (<0.01)**	**6.05 (0.01)**
Zn	NS	NS	NS	**4.25 (0.04)**	NS	NS	NS	**6.28 (0.01)**	NS
Se	NS	NS	**15.62 (<0.01)**	**8.75 (<0.01)**	NS	**10.76 (<0.01)**	NS	NS	**5.50 (0.02)**

Notes: Coleoptera (COLE), Culicidae (CULI), Ichneumonidae (ICHN), Lepidoptera (MOTH), Muscomorpha (MUSC), Syrphidae (SYRP), Tabanidae (TABA), Tipulidae (TIPU), and Zygoptera (ZYGO); Vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), cadmium (Cd), lead (Pb), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn), and selenium (Se); NS is not significant

3.4 Discussion

I predicted that I would find higher levels of metals in nestlings near oilsands mining operations. However, significant location differences in element concentrations were not found for most elements in liver, kidney, or the stomach contents. In 2012, chromium was highest in liver near operations, while lead in liver was highest at reference locations. In 2012, selenium in kidney was highest at reference locations. The stomach contents were highest for copper and selenium at reference locations in both years. No location differences in tissues were found for vanadium, nickel, arsenic, strontium, molybdenum, cadmium, iron, cobalt, and zinc.

Significant year differences were found, and the levels of elements in tissues were higher in 2013 than 2012 for vanadium, arsenic, and cadmium in liver, for vanadium, chromium, and zinc in kidney, and for chromium and arsenic in the stomach contents. The reasons for the observed differences are not known. Environmental conditions in 2013 were much wetter than in 2012, and spring rains resulted in major regional flooding, and nest box abandonment occurred across my study area. High rainfall and overland runoff increased the concentrations of some metals in the sediments of Guanabara Bay, Brazil (Fonseca et al. 2013). Increased surface runoff potentially affected metal uptake in nestling food and tissues. The influence of potential changes in aerial emissions from oilsands operations is not known, and emissions can vary annually (NPRI 2014).

Element concentrations were positively correlated among the three tissues for cadmium, iron, cobalt, and selenium. Positive correlations also occurred between stomach contents and liver or kidney for chromium, arsenic, and lead, providing support for the hypothesis that exposure to metals is via food. Studies comparing metal levels between food and liver or kidney have found low correlations due to variability of metals in food (Adair 2002; Dauwe et al. 2005;

Custer et al. 2009). I found no correlations in the levels of nickel, strontium, and zinc in the three tissues, and negative correlations for molybdenum and copper.

The diet of nestling tree swallows in my study based on stomach contents, varied by location, and similar results have been reported previously (Beck et al. 2013). Although the types of invertebrate taxa consumed were similar to other studies, I found that the proportion of each type of invertebrate in the diet was different. Coleoptera was consumed in higher quantities than previously reported (Kraus 1989; Johnson and Lombardo 2000; Custer et al. 2005; Beck et al. 2013). Overall, the proportion of Coleoptera in the diet was higher in 2012 compared to 2013, while the proportions of Ephemeroptera and Diptera were highest in 2013. Even though I found location differences in the diet, and metal concentrations were correlated between food and tissues, I found no influence of location on the metal concentrations in the stomach contents, kidney, and liver. However, the annual differences in the diet may have contributed to the higher levels of metals measured in 2013 compared to 2012. Across both years, element concentrations in the stomach contents were generally consistent with or lower than concentrations reportedly at normal levels in the diet of tree swallows at Agassiz National Wildlife Refuge in northwestern Minnesota (geometric means) for strontium (19.9 μg/g dw), molybdenum (1.13 μg/g dw), cadmium (0.37 μg/g dw), iron (581 μg/g dw), copper (25.5 μg/g dw), zinc (214 μg/g dw), and selenium (1.12 μg/g dw) (Custer et al. 2006).

For invertebrate taxa collected from Malaise traps, no significant location differences occurred in element concentrations for over 70% of the cases tested. Where significant location differences occurred, element concentrations were highest at the reference location in most instances. In six cases, elements were higher near operations: vanadium in Tabanidae, lead in Lepidoptera, iron in Lepidoptera, Muscomorpha, and Tabanidae, and copper in Lepidoptera.

Ephemeroptera were not captured in the Malaise traps and were consumed in the highest proportion at the reference location. Malaise traps sample insects within 1 m of the ground, and may not adequately capture Ephemeroptera (Didham et al. 2012). Stomach samples that contained mostly Ephemeroptera had higher than average levels of vanadium, iron, copper, and selenium, potentially influencing the levels of these elements measured in reference nestlings.

The concentration of elements in the invertebrate taxa exhibited high variability. Metal concentrations in the same invertebrate species can vary based on the element properties, as well as invertebrate size, age, sex, and developmental stage (Hare et al. 1989; Hare 1992; Hare and Campbell 1992). Metals measured in the gut contents of invertebrates can represent up to 65% of the metals measured in the invertebrate body (Chapman 1985; Hall et al. 1988; Gower and Darlington 1990). For example, the metal variability I found in Culicidae may be from some individuals consuming a blood meal prior to being captured. However, where exposure to metals is high from environmental contamination, the levels measured in insects do reflect the relative exposure levels (Dauwe et al. 2004; Bel'skii and Belskaya 2013).

Elements emitted from oilsands operations that are of environmental concern include vanadium, chromium, nickel, arsenic, strontium, molybdenum, cadmium, and lead (Bari et al. 2014). Most experimental studies consider acute exposure levels rather than chronic exposure over long periods.

Limited data are available on vanadium toxicity in birds, making interpretations of my data difficult. Toxicity can result in weight loss, liver necrosis, renal congestion, and intestinal lesions (Rattner et al. 2006). Vanadium levels in Canada geese (*Branta canadensis*) found dead at a fly ash pond in Delaware, United States, were 57 µg/g (dw) in liver and 226 µg/g (dw) in kidney, while concentrations in liver and kidney of unexposed mallards (*Anas platyrhynchos*) and geese were below 1.4 µg/g (dw) (Rattner et al. 2006). These results suggest that the range of vanadium levels measured in liver (approx. dw equivalent 0.1-0.9 ppm), and in kidney (approx. dw equivalent 0.1-1.6 ppm) in my study were from birds unexposed to high levels of vanadium. Rattner et al. (2006) also exposed mallards to vanadium provided as sodium metavanadate and found that dietary exposure of 250 ppm over 4 weeks resulted in modest accumulation of vanadium in liver and kidney (<5 µg/g dw) and mild intestinal hemorrhage. This dose was over 20 times higher than the maximum vanadium concentration that I measured in stomach contents or invertebrate taxa.

Chromium occurs in different ionic states. Trivalent chromium is an essential element required for normal glucose metabolism, while hexavalent chromium is a carcinogen (Valko et al. 2005). I measured total chromium in bird tissues and invertebrates. Tissue levels greater than 4 µg/g (dw) total chromium is evidence of exposure to chromium contamination (Eisler 2000b). The levels of total chromium that I measured in tree swallow tissues were well below this value (liver approx. dw equivalent 0.9-1.3 ppm; kidney approx. dw equivalent 1.3-1.5 ppm). Adverse effects have been documented at exposure to 10 ppm of hexavalent chromium in the diet of sensitive wildlife species (Eisler 2000b). Insect taxa in my study reached 2 ppm total chromium, while nestling stomach contents contained a maximum of 7 ppm total chromium. Nestling tree swallows in my study were not exposed to elevated chromium based on tissue element measurements for other insectivorous passerines in a non-polluted environment; rock bunting (*Emberiza cia*) 0.42 µg/g (dw) in liver and 3.70 µg/g (dw) in kidney, blackbird (*Turdus merula*) 0.70 µg/g (dw) in liver and 2.29 µg/g (dw) in kidney, and great tit (*Parus major*) 0.82 µg/g (dw) in liver and 3.06 µg/g (dw) in kidney (Llacuna et al. 1995).

The toxic effects of nickel are related to changes in calcium metabolism, and nickel can alter intracellular calcium levels (Valko et al. 2005). Nickel can also substitute for zinc by replacing zinc at binding sites in some enzymes, thereby altering protein function (Forgacs et al. 2012). In humans, lung irritation, diseases of the respiratory tract, and allergic skin reactions are the concern in occupational exposure studies (Schaumloffel 2012). Birds in unpolluted environments generally have nickel concentrations in tissues ranging from about 0.1 to 5 µg/g (dw), and in polluted environments from about 0.5 to 80 µg/g (dw) (Outridge and Scheuhammer 1993). The nickel levels that I measured in liver (approx. dw equivalent 0.05-0.16 ppm) and kidney (approx. dw equivalent 0.27-0.30 ppm) tissues were near the lowest levels reported for those birds in unpolluted environments.

Arsenic binds to sulfhydryl proteins, and in particular keratin resulting in deposits in skin, hair, nails, and feathers, the effects of which are moderated by the presence of selenium (reviewed in Patrick 2003). The levels of total arsenic that represented normal values in an experimental study of nestling zebra finches ranged in liver from 0.05 to 0.31 µg/g (dw) and in kidney from 0.05 to 0.2 µg/g (dw) (Albert 2006). The levels of arsenic that I measured in liver (approx. dw equivalent 0.07-0.20 ppm) of nestling tree swallows were well within the normal range for zebra finches. Kidney arsenic levels (approx. dw equivalent 0.18 ppm) in nestlings near oilsands operations were within the reported normal range, while levels in kidney measured at reference locations (approx. dw equivalent 0.39 ppm) were above this range.

Strontium is naturally abundant in the environment and is absorbed primarily through the gastrointestinal tract, and at high doses will replace calcium in bone, potentially leading to bone disease (Cohen-Solal 2002). Few interpretive data for strontium in avian tissues are available. Strontium measured in liver of nestling tree swallows at Agassiz National Wildlife Refuge in northwestern Minnesota was reportedly at normal levels and ranged from 0.13-0.27 μg/g (dw; geometric mean concentrations) (Custer et al. 2006). Strontium in the liver of cavity nesting birds from Summit County, Colorado was also reportedly at normal levels with a geometric mean of 0.21 (0.14-0.30 (95% CI)) μg/g (dw) (Custer et al. 2009). Mean strontium levels in nestling tree swallow liver (approx. dw equivalent 0.32-0.53 ppm) in my study were above the reported values, with similar levels measured near operations and at reference locations. The results suggest that strontium was not elevated due to oilsands activity and likely reflected natural geological levels in the environment. I could not find comparative information for normal levels of strontium in avian kidney. The kidney is primarily responsible for the elimination of strontium, and when kidney function is compromised there is an increased risk of strontium accumulation (Cohen-Solal 2002).

Molybdenum is an essential trace element required for optimal activity of molybdenum-containing enzymes, and deficiency in organisms may be fatal (Mendel 2013). Molybdenum has a role in maintaining normal copper absorption, minimizing copper over exposure, and may also be important in iron metabolism (Deur et al. 1981). High dietary copper prevents the accumulation of molybdenum (Eisler 2000c). Molybdenum is not easily absorbed from food, and birds are able to tolerate relatively high levels of molybdenum in their diet (Eisler 2000c). Adverse effects have been reported on growth at dietary concentrations of 200 to 300 mg/kg, on reproduction at 500 mg/kg, and on survival at 6000 mg/kg (Eisler 2000c). These levels are far higher than molybdenum levels measured in stomach contents (maximum 3.69 ppm dw) and invertebrate taxa (maximum in Culicidae 2.95 ppm dw) in my study. Molybdenum measured in nestling tree swallow liver that were reported to reflect normal levels were between 2.00-2.62 μg/g (dw) (geometric mean) (Custer et al. 2006), and 1.47 (1.13-1.91 (95% CI)) μg/g (dw) (geometric mean) (Custer et al. 2009). I measured molybdenum levels in liver to be 2.8-3.2 ppm (approx. dw equivalent), and values were similar both near oilsands operations and at reference locations. Concentrations of molybdenum representing normal levels found in kidneys of seaducks at Misty Fjords National Monument in Southeast Alaska ranged from 2.4-8.0 ppm (dw) (Franson et al. 1995). The values I measured in kidney (approx. dw equivalent 2.7-3.0 ppm) in my study are well within the reported normal range.

Cadmium accumulates in the liver and kidney, with the highest levels often found in the kidney potentially leading to renal tubular damage (Jarup et al. 1998; Patrick 2003). In my study, cadmium levels were correlated in liver and kidney. Cadmium interacts with zinc (Brzoska and Moniuszka-Jakoniuk 2001) and with selenium (Patrick 2003), and both elements may reduce cadmium absorption and accumulation. Cadmium toxicity generally occurs due to the substitution and reduced absorption of other essential elements, such as calcium, zinc, and iron (Wayland and Scheuhammer 2011). The approximate normal levels for cadmium in terrestrial birds ranges from 0.1-9.3 μg/g (ww) in liver and 0.02-57.2 μg/g (ww) in kidney (Wayland and Scheuhammer 2011). The maximum cadmium levels measured in my study were at the lowest ends of these ranges in liver (0.1 ppm) and kidney (0.1 ppm) of nestling tree swallows.

Lead is a metabolic poison affecting reproductive, vascular, and neurological systems by interfering with enzymes through binding to sulfhydryl groups found on enzymes, mimicking calcium, iron, and zinc in biological processes such as the production of hemoglobin, and interfering with the release of neurotransmitters that are important for cell signaling (Needleman 2004; Patrick 2006). Birds with no history of high lead exposure have liver and kidney lead concentrations of less than 2 mg/kg (ww) (Franson and Pain 2011). Nestling tree swallows in my study had mean lead levels in liver and kidney of less than 0.05 ppm (0.05 mg/kg or 50 ppb), suggesting that these birds experienced minimal lead exposure.

Cobalt is chemically similar to nickel, iron, and zinc, and can compete for molecular binding sites of these elements resulting in vitamin and iron deficiencies (reviewed in Paustenbach et al. 2013). Cobalt has rarely been measured in tree swallow tissues (Custer et al. 2005, 2009), and the variability in normal levels for birds has not been described. Cobalt measured in liver (approx. dw equivalent 0.03-0.06 ppm) in my study was above levels reported to be near normal (0.02 µg/g dw) for tree swallows (Custer et al. 2009). In my study, cobalt levels in kidney were 0.06-0.09 ppm (approx. dw equivalent). Cobalt measured in liver (0.28-1.26 ppm dw) and kidney (0.25-1.29 ppm dw) for adult female great tits (*Parus major*) nesting near an active heavy-metal smelter in Belgium (Dauwe et al. 2005) was up to five times higher than measured in my study. The reported levels indicate that cobalt measured in nestling tree swallows in my study could be attributed to natural geological conditions.

The essential elements iron, copper, and zinc are tightly regulated in metabolic processes (Gaetke and Chow 2003; Valko et al. 2005; Shander et al. 2012). Toxicity from these elements is expected to be rare unless birds are exposed to high doses. Levels of iron, copper, and zinc in nestling tree swallow liver and kidney were not different between reference locations and near operations. Copper exposure as determined from stomach contents was highest for reference locations. The levels of these three essential elements were higher than normal levels reported in other studies of tree swallows from across the United States (Custer et al. 2001, 2005, 2006, 2009, 2013), and well below levels causing harm to birds in experimental studies of acute toxicity where birds were fed high doses of zinc (Gasaway and Buss 1972), iron (Olsen et al. 2006), and copper and zinc (Mondal et al. 2010).

Selenium is also an essential element with a narrow range of beneficial dietary concentrations compared to other essential elements (Ohlendorf and Heinz 2011). Selenium toxicity is rare, and selenium may have a protective effect against cadmium, mercury, and arsenic exposure via the antioxidant activity of selenoproteins that prevent cellular oxidative damage (Zwolak and Zaporowska 2012). Ohlendorf and Heinz (2011) summarized the levels of selenium tissue and diet concentrations of birds. Liver concentrations of less than 10 mg/kg (dw) and kidney concentrations between 2.2 and 5.2 mg/kg (dw) are indicative of normal levels. Selenium less than 3 mg/kg in the diet of birds typically represents normal exposure. In my study, selenium measured in nestling tree swallow liver, stomach contents, and insect taxa were similar or lower than these normal levels, while kidney selenium levels were higher.

Elevated concentrations of vanadium and nickel are the best indicators of exposure to the products of oilsands operations, as these elements tend to be found in association with bitumen and bitumen production (Zhao et al. 2000, 2002). Aeshnidae (dragonfly) nymphs exposed to oilsands petroleum coke treatments and waste-water, accumulated low levels of vanadium (1.6 mg/L; approx. 400 ppb dw) and higher levels of nickel (17 mg/L; approx. 4000 ppb dw) relative to natural water exposure, and chironomid larvae showed higher but variable metal concentrations (Baker et al. 2012). Near Sudbury, Ontario, reference concentrations of nickel in gypsy moth larvae (*Lymantria dispar*) ranged from 0.4-7.2 µg/g (dw) (Bagatto and Shorthouse 1996). Nickel measured in galls induced by the chalcid wasp (*Hemadas nubilipennis*) collected from an uncontaminated site in Newfoundland was 3.4 µg/g (dw) (Bagatto and Shorthouse 1991). In my study, levels of vanadium and nickel were highest in reference samples of Culicidae (758 ppb dw vanadium; 3291 ppb dw nickel) and Tipulidae (725 ppb dw vanadium; 527 ppb dw nickel). Also, the levels of nickel were highest in reference samples of the terrestrial

Coleoptera and Ichneumonoidea, and were lower than the levels reported in dragonfly nymphs (Baker et al. 2012), and within the ranges reported from the uncontaminated sites in Ontario and Newfoundland (Bagatto and Shorthouse 1991, 1996). These results indicate that invertebrates in my study were likely exposed to levels of elements that were naturally present rather than contaminants from oilsands operations.

I found a relationship between the element concentrations in the stomach contents of nestling tree swallows and the levels in liver and kidney, and the composition of invertebrates in the nestling tree swallow diet varied by location and by year. Thus, it is important to consider the metal variability in food when interpreting element concentrations in bird tissues. Tree swallows foraged extensively on terrestrial insects, possibly limiting their exposure to aquatic trace elements. In my study, the concentrations of individual elements measured in nestling tree swallows and their food were not at levels of toxicological concern. The oilsands mine operations do not appear to be exposing tree swallows to metal levels above those that occur from natural exposure attributed to the local geology.

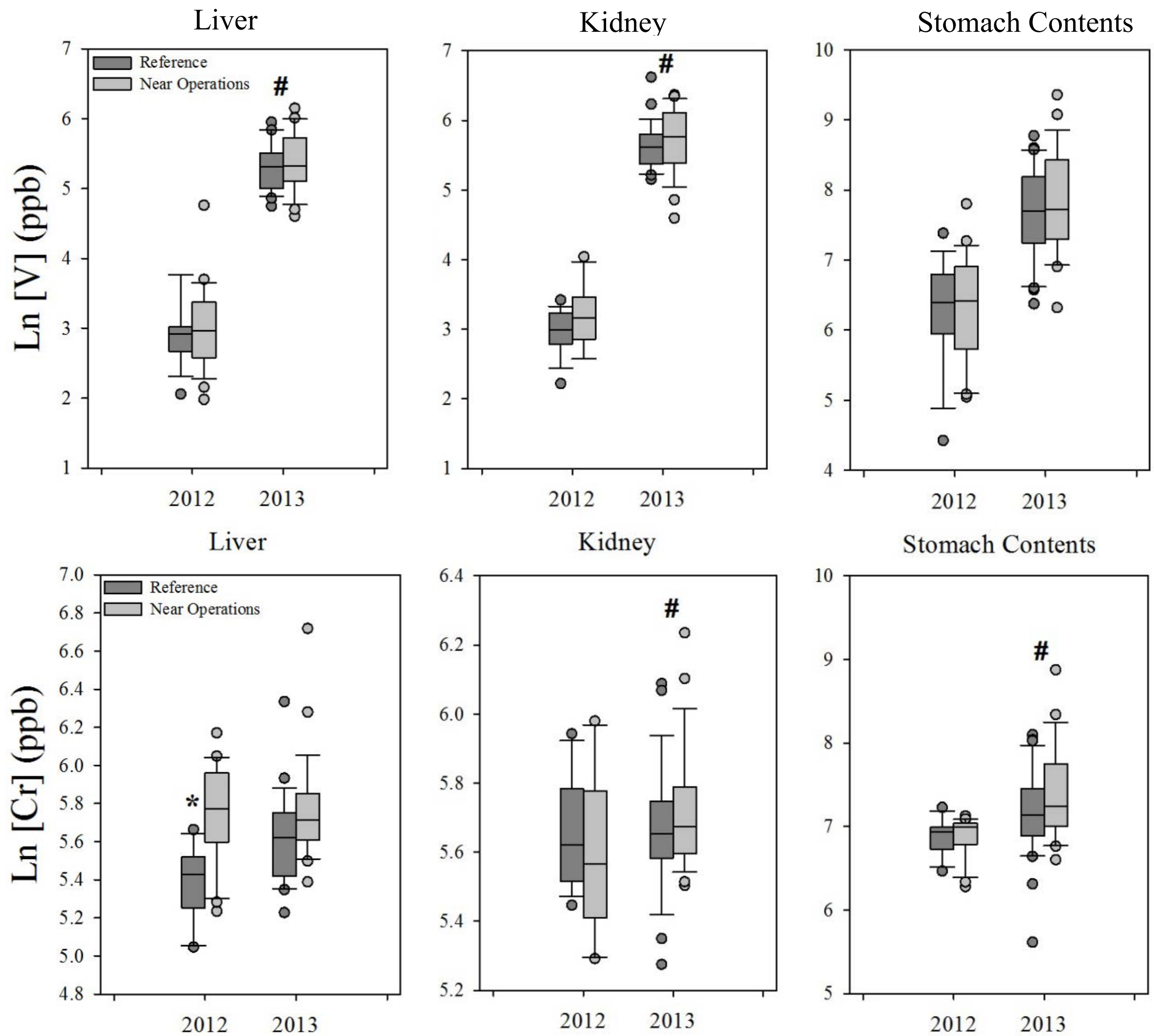


Figure 3.2 Median and interquartile range of logged vanadium (V) and chromium (Cr) concentrations in liver, kidney, and stomach contents of 14-day old tree swallow nestlings in 2012 and 2013. Significant location differences (*p* < 0.05) are indicated by the * above the bars, and significant year differences are indicated by the #

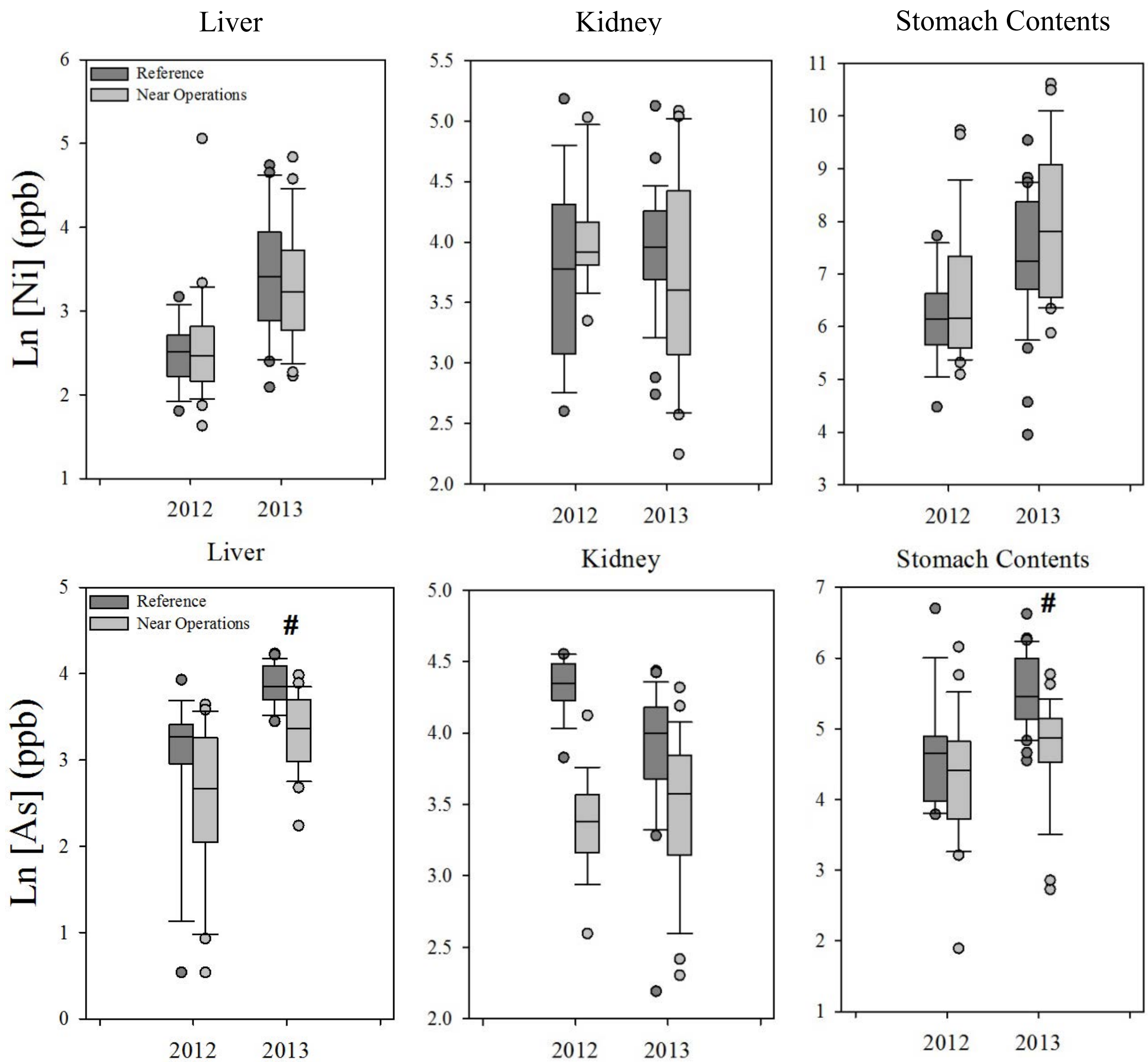


Figure 3.3 Median and interquartile range of logged nickel (Ni) and arsenic (As) concentrations in liver, kidney, and stomach contents of 14-day old tree swallow nestlings in 2012 and 2013. Significant year differences (*p* < 0.05) are indicated by the #

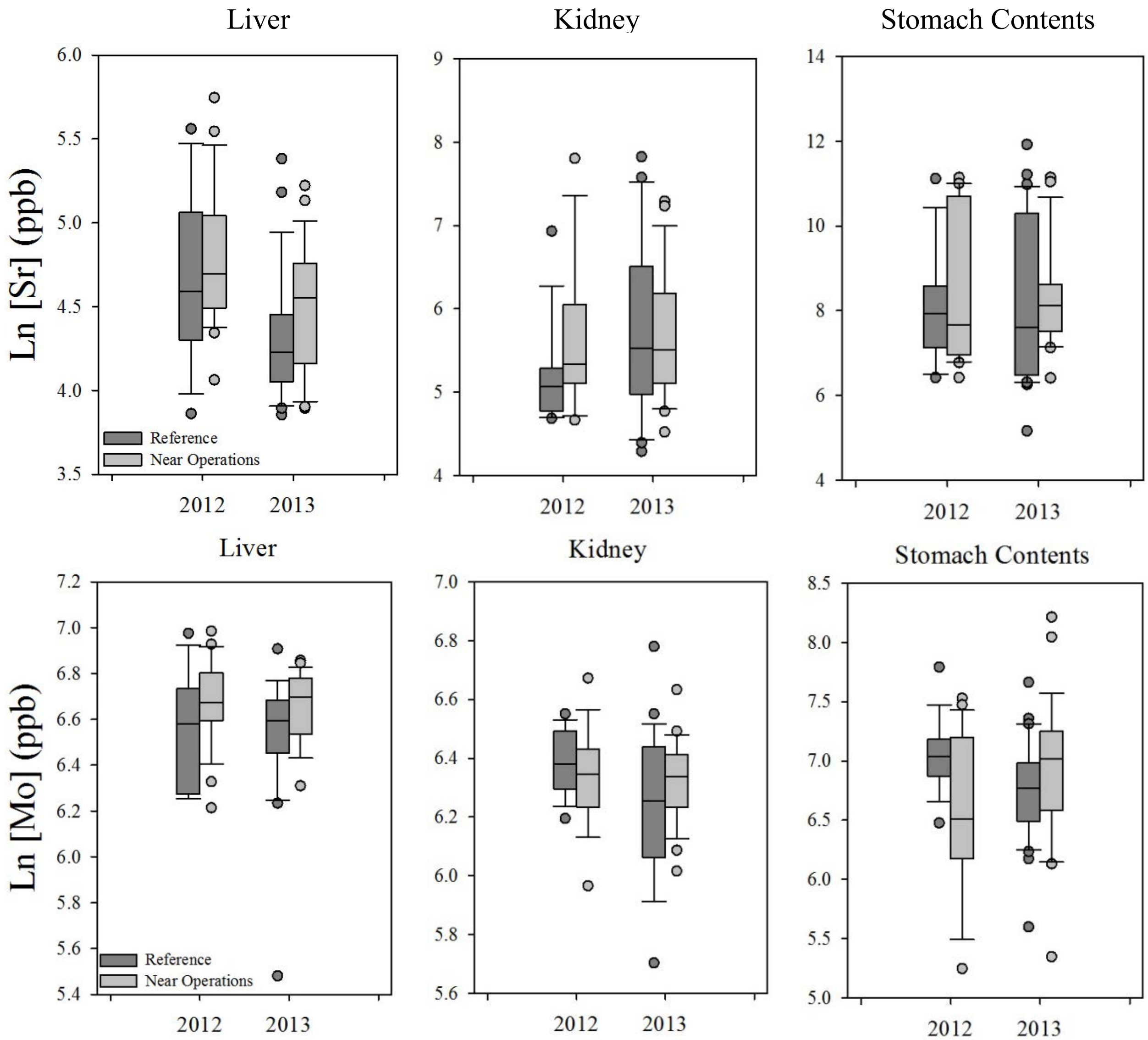


Figure 3.4 Median and interquartile range of logged strontium (Sr) and molybdenum (Mo) concentrations in liver, kidney, and stomach contents of 14-day old tree swallow nestlings in 2012 and 2013

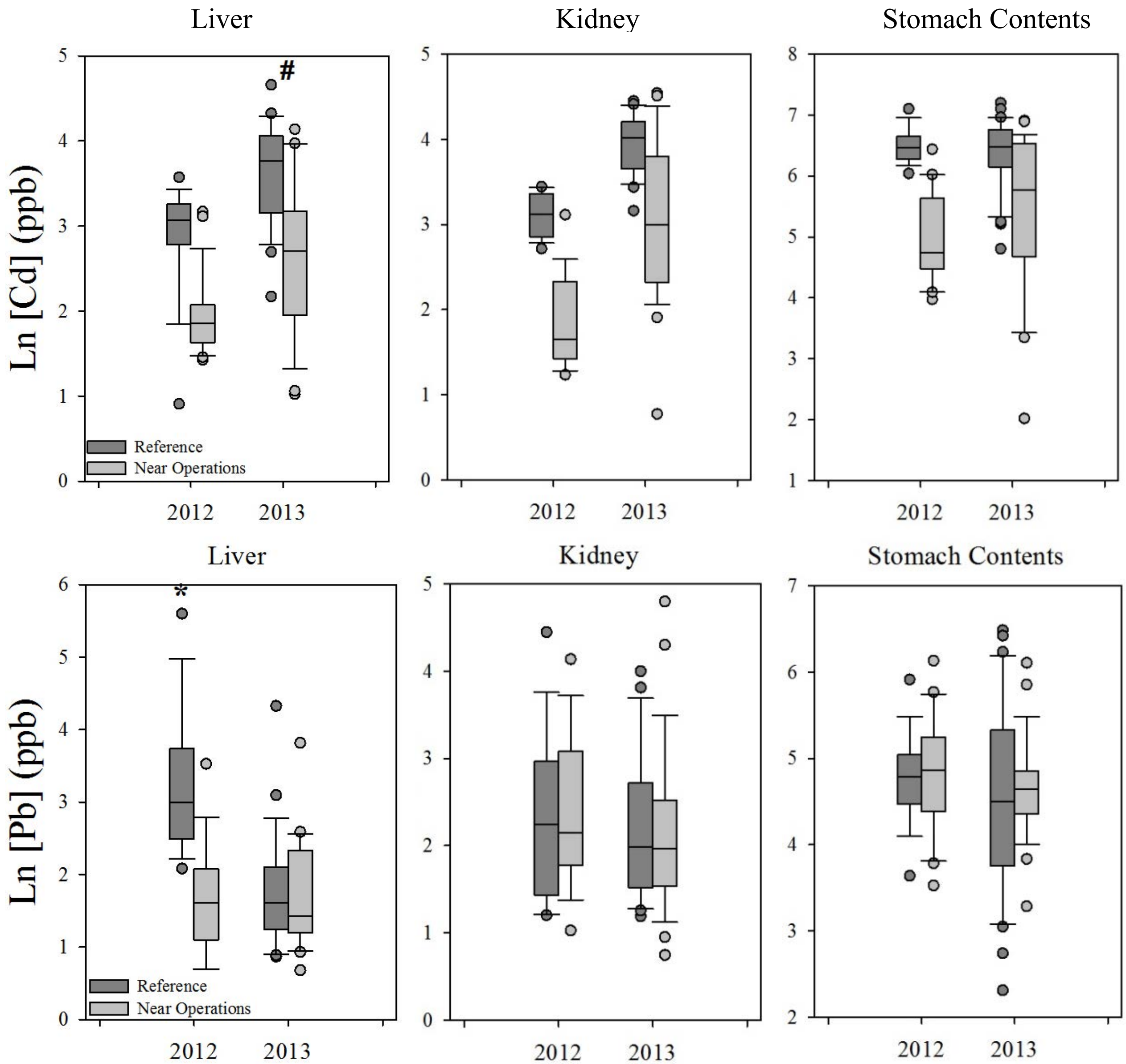


Figure 3.5 Median and interquartile range of logged cadmium (Cd) and lead (Pb) concentrations in liver, kidney, and stomach contents of 14-day old tree swallow nestlings in 2012 and 2013. Significant location differences (*p* < 0.05) are indicated by the * above the bars, and significant year differences are indicated by the #

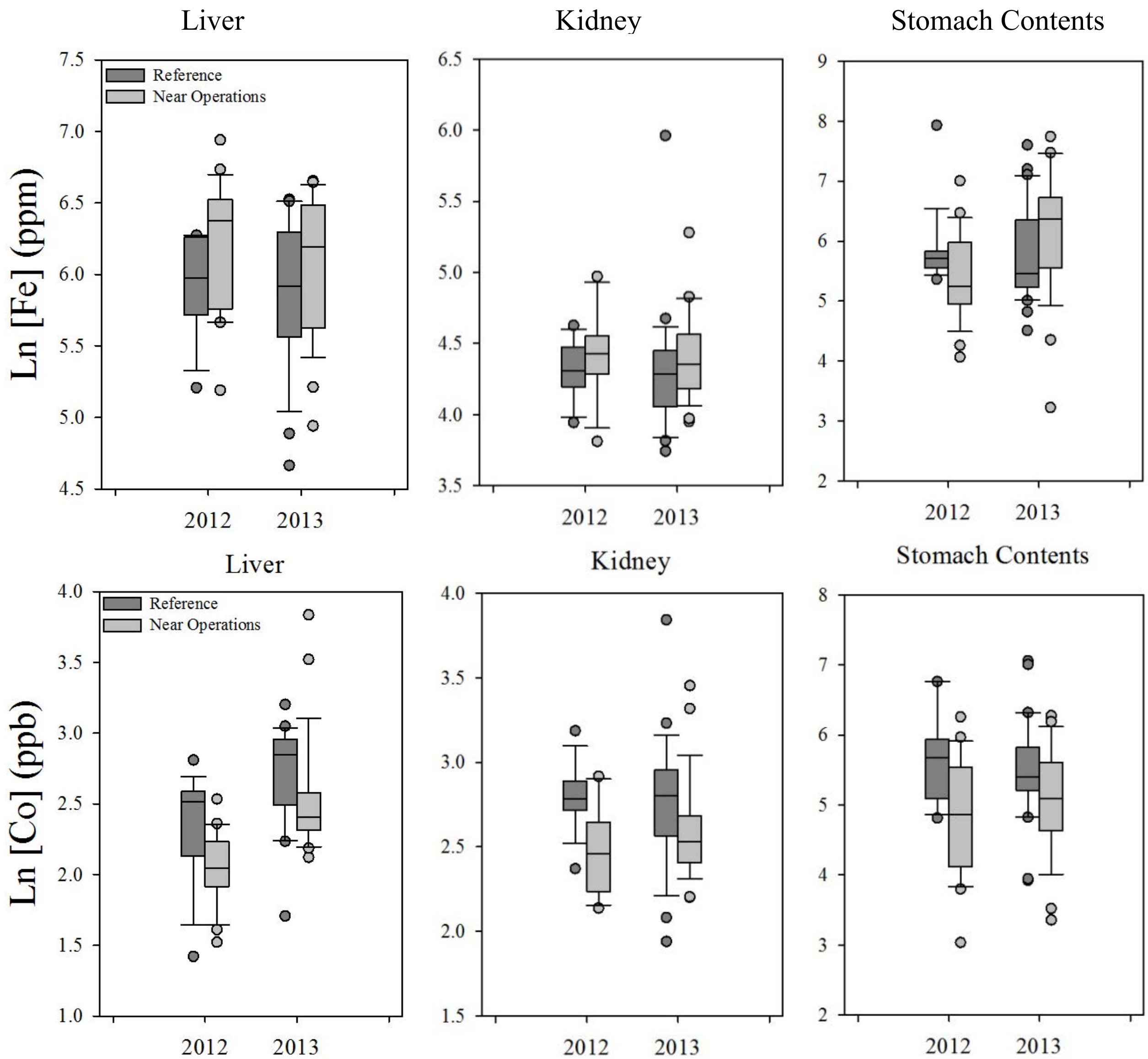


Figure 3.6 Median and interquartile range of logged iron (Fe) and cobalt (Co) concentrations in liver, kidney, and stomach contents of 14-day old tree swallow nestlings in 2012 and 2013

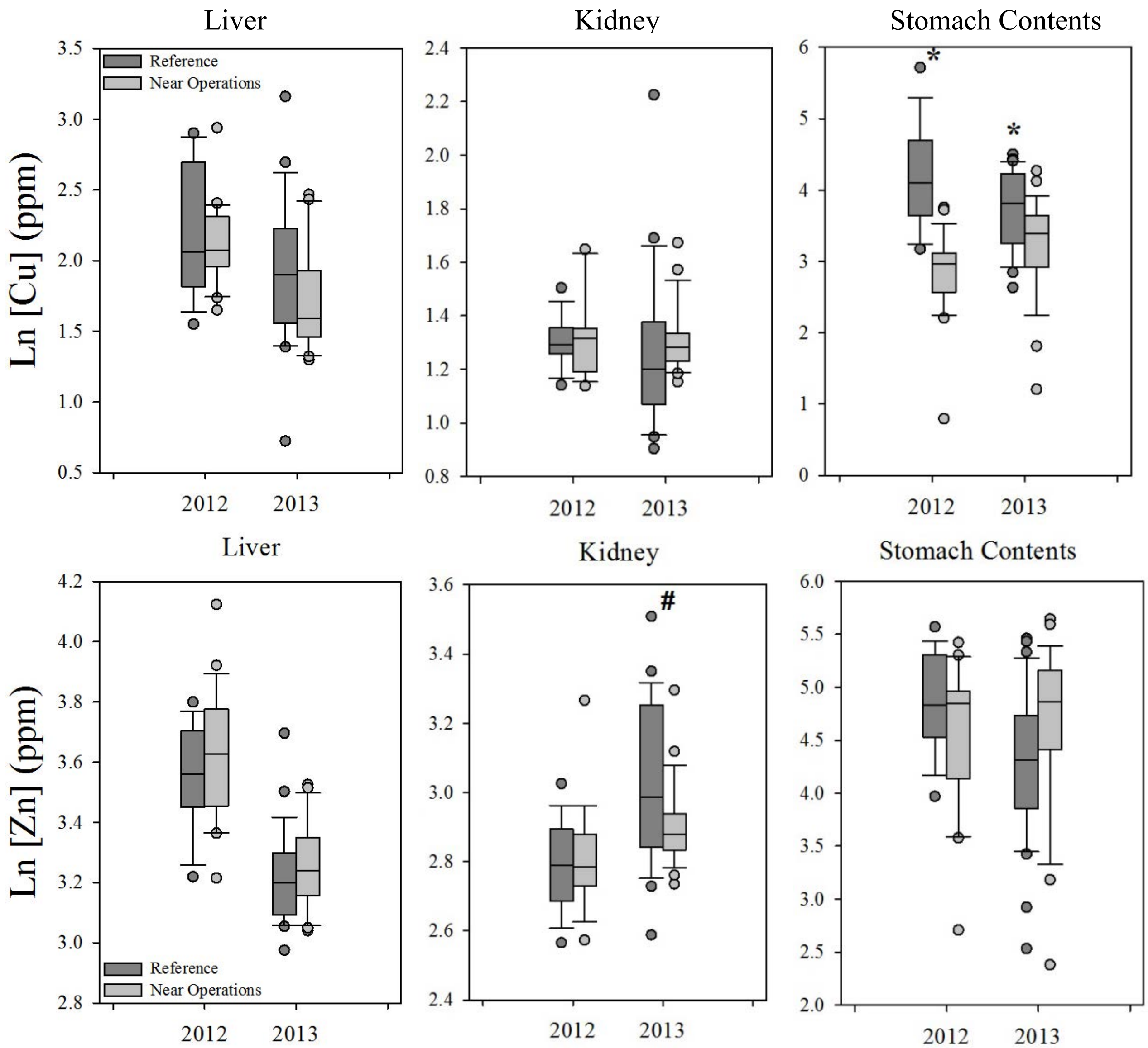


Figure 3.7 Median and interquartile range of logged copper (Cu) and zinc (Zn) concentrations in liver, kidney, and stomach contents of 14-day old tree swallow nestlings in 2012 and 2013. Significant location differences (*p* < 0.05) are indicated by the * above the bars, and significant year differences are indicated by the #

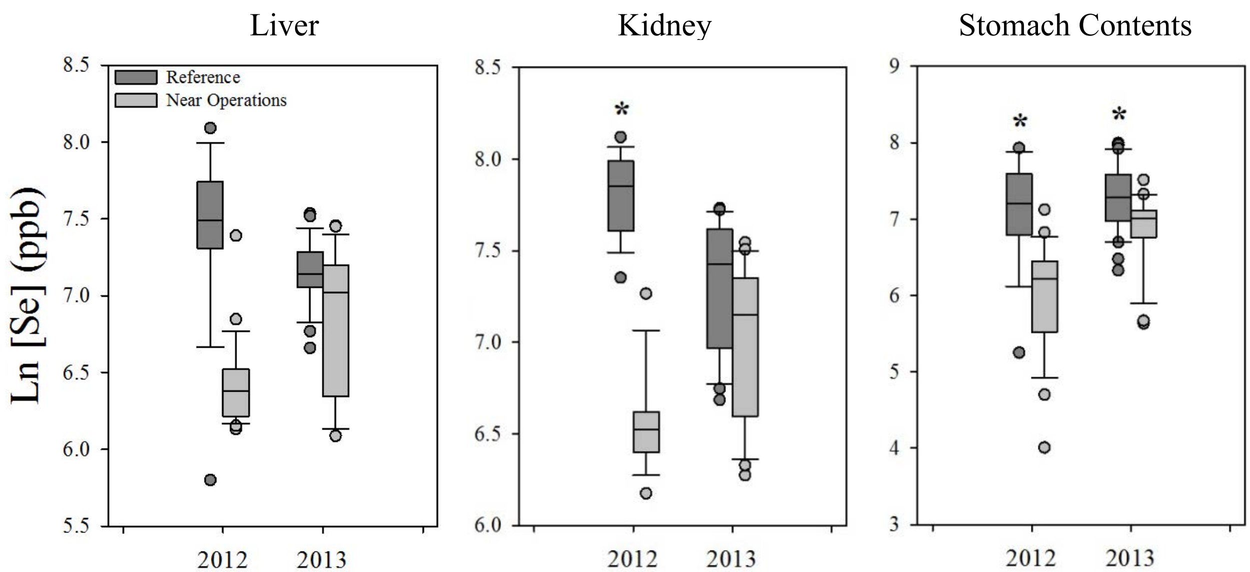


Figure 3.8 Median and interquartile range of logged selenium (Se) concentrations in liver, kidney, and stomach contents of 14-day old tree swallow nestlings in 2012 and 2013. Significant location differences ($p < 0.05$) are indicated by the * above the bars

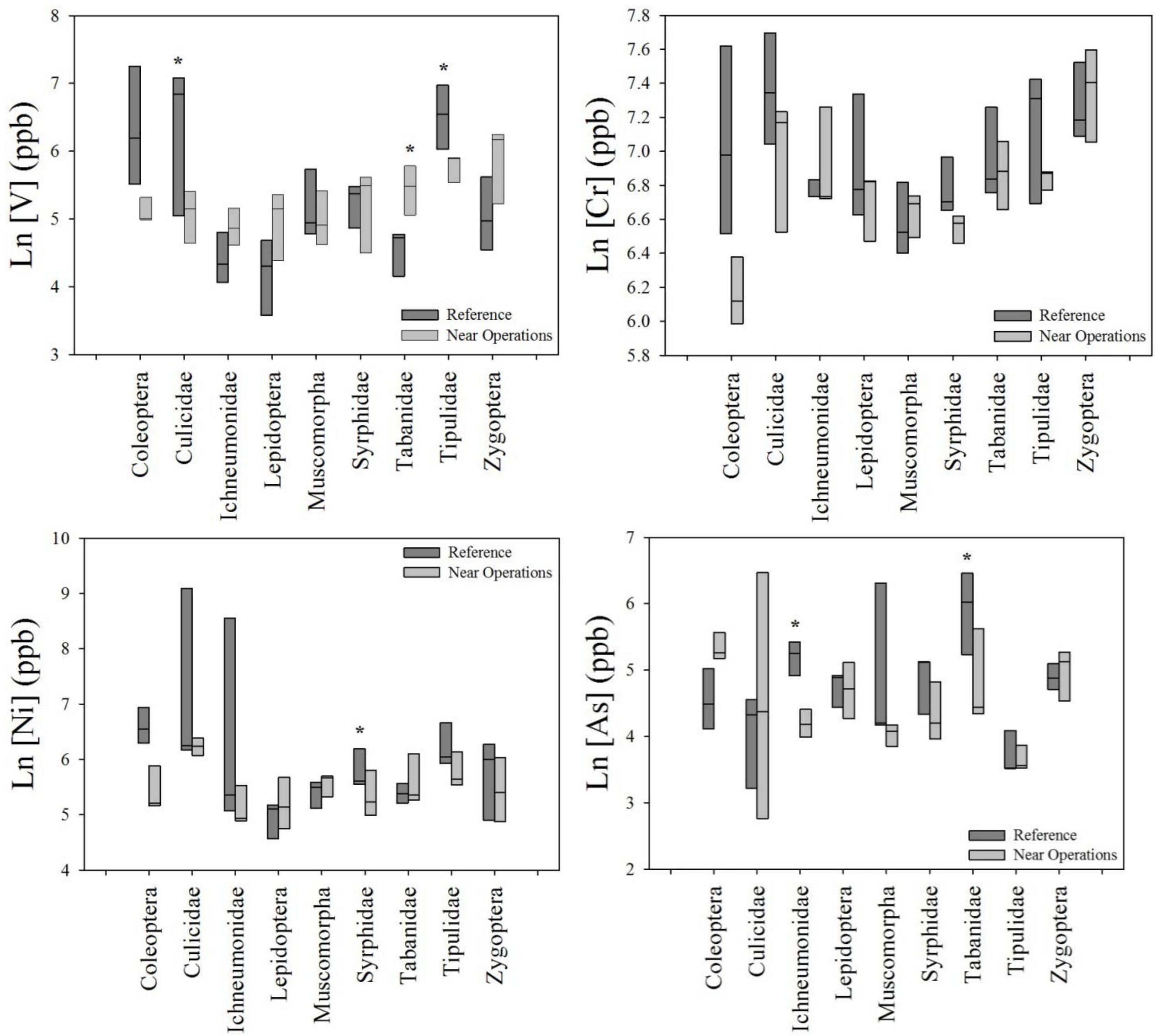


Figure 3.9 Median and range (n=3 reference; n=3 near operations) of log vanadium (V), chromium (Cr), nickel (Ni), and arsenic (As) concentrations in invertebrates collected from Malaise traps in 2013. Significant within-taxon differences (*p* < 0.05) are indicated by the * above the bars

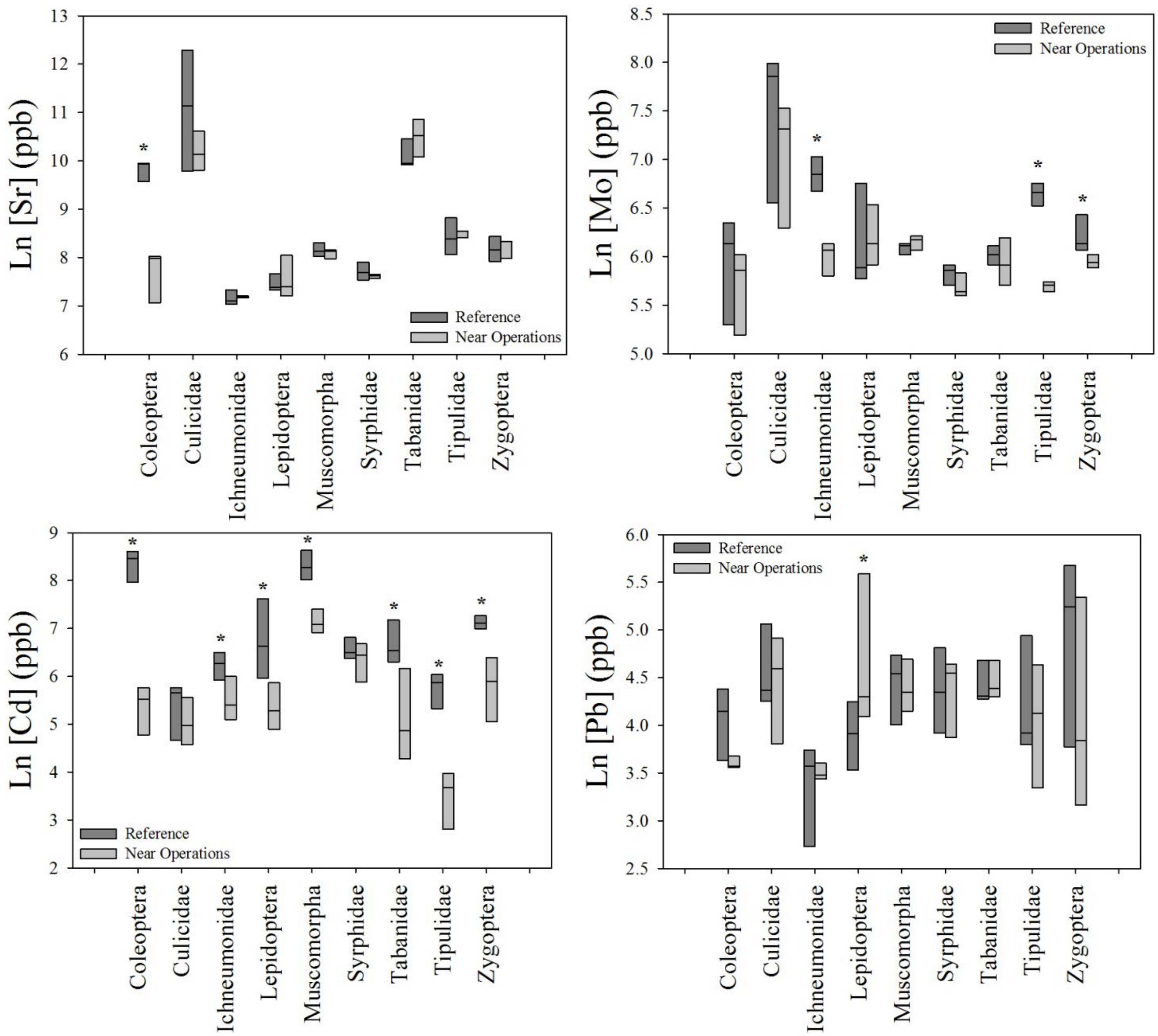


Figure 3.10 Median and range (n=3 reference; n=3 near operations) of log strontium (Sr), molybdenum (Mo), cadmium (Cd), and lead (Pb) concentrations in invertebrates collected from Malaise traps in 2013. Significant within-taxon differences (*p* < 0.05) are indicated by the * above the bars

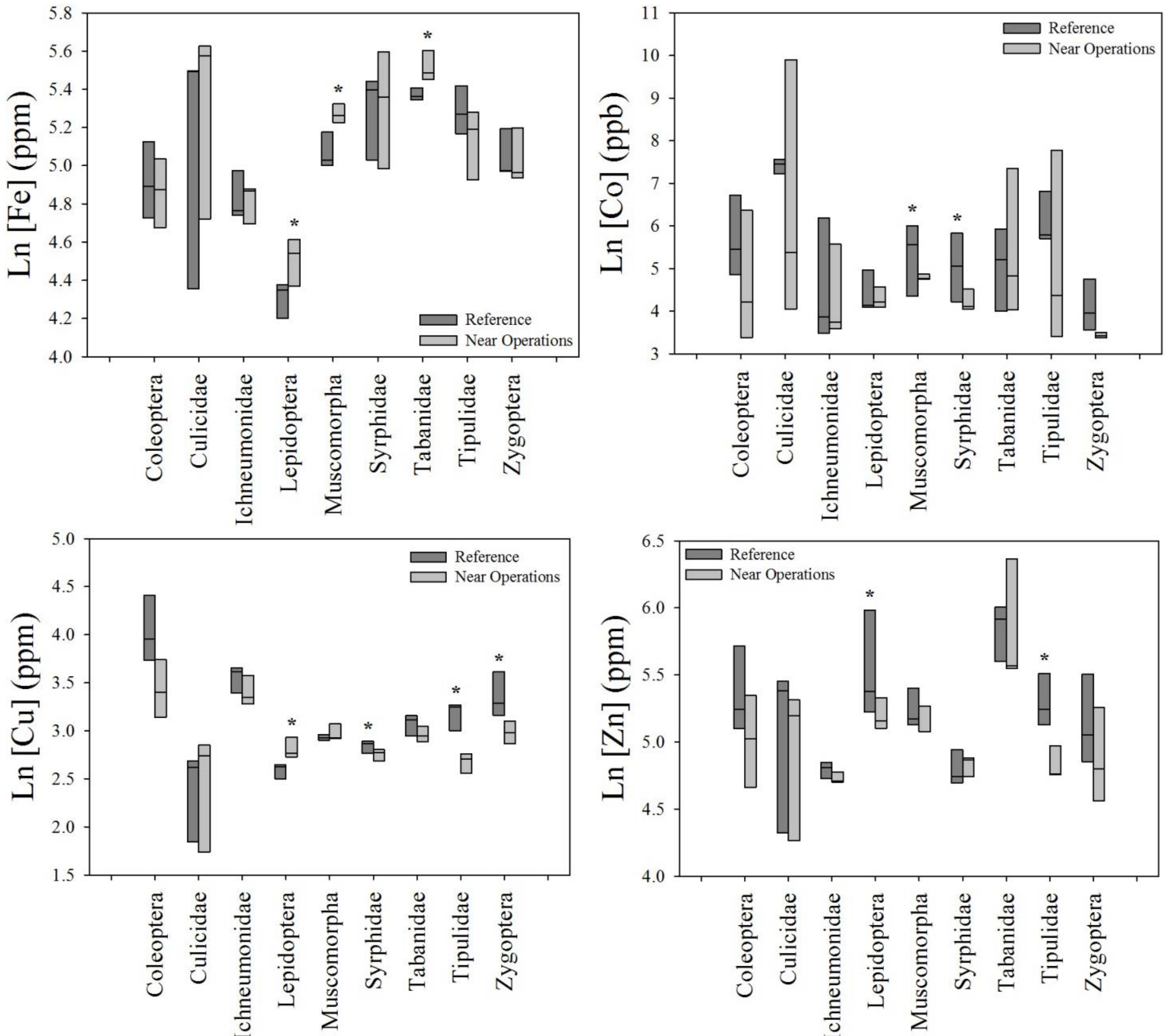


Figure 3.11 Median and range (n=3 reference; n=3 near operations) of log iron (Fe), cobalt (Co), copper (Cu), and zinc (Zn) concentrations in invertebrates collected from Malaise traps in 2013. Significant within-taxon differences (*p* < 0.05) are indicated by the * above the bars

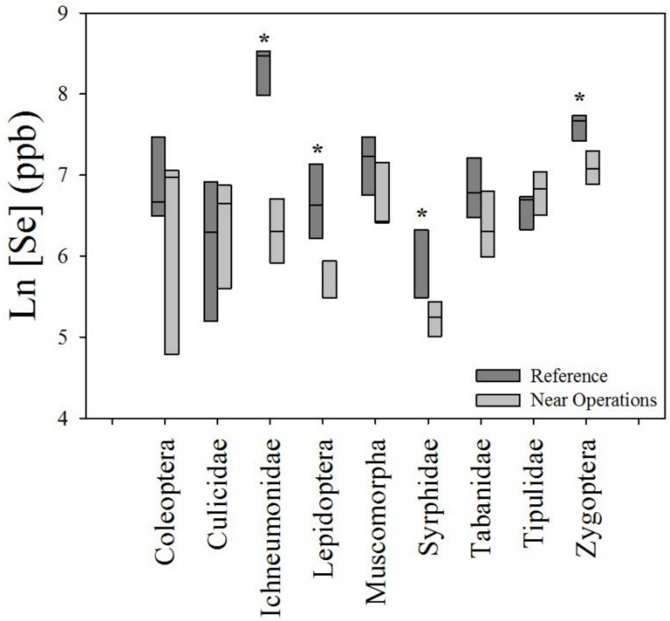


Figure 3.12 Median and range (n=3 reference; n=3 near operations) of log selenium (Se) concentrations in invertebrates collected from Malaise traps in 2013. Significant within-taxon differences (*p* < 0.05) are indicated by the * above the bars

Chapter Four: Effects of Oilsands Mining Operations on Tree Swallow Nest Success and Nestling Growth

4.1 Introduction

Tree swallows (*Tachycineta bicolor*) are wide spread across North America (Winkler et al. 2014) and are easily attracted to areas by nest boxes (Hussell 2012). This makes tree swallows popular choices for field studies of ecology (Hussell and Quinney 1987; Dunn and Hannon 1992; McCarty and Winkler 1999a; Mengelkoch et al. 2004) and toxicology (Kraus 1989; McCarty 2001/2002; Echols et al. 2004; Custer 2011). Studies have attempted to correlate reproductive endpoints such as clutch size, hatching success, survival to fledging, and growth, with environmental contamination from industrial development (McCarty and Secord 1999; Harris and Elliott 2000; Dods et al. 2005). Nestling growth is responsive to environmental stress, and retarded growth is a predictor in failure of nestlings to fledge (Zach and Mayoh 1982). However, sublethal and chronic effects of industrial development on birds may be expected more frequently than acute responses such as higher mortality (Scheuhammer 1987).

The oilsands in Alberta is the third-largest proven crude oil reserve in the world, of which about 800 km^2 are currently being mined (Alberta Energy 2014). Disturbance, and potential exposure to contaminants from mine waste products in airborne particulates or tailings process-water, may increase stress on birds, affect nesting habitat, and reduce food resources. Tree swallows have been used as an indicator of environmental exposure to contaminants (Smits and Fernie 2013), and physiological effects have been demonstrated in the oilsands region (Gentes et al. 2006; Gentes et al. 2007a; Harms et al. 2010). A two-year study of tree swallows in the oilsands region found that nestlings on reclaimed sites weighed less compared to the reference site, although effects were found in only one year (Gentes et al. 2006). Changes in foraging behaviour to include more distant habitats may explain some of the variation in nestling growth that was observed in tree swallows nesting near oilsands process-affected wetlands (Farwell et al. 2014).

Exposure to contaminants found in crude oil can reduce egg production, hatching success, and nestling growth in birds (Albers 2006). Decreased nestling growth and breeding success were measured in nestling great tits (*Parus major*) near a copper smelter in Finland, which emitted copper, nickel, and lead pollutants (Eeva and Lehikoinen 1996). The observed effects in these studies may alternatively be attributed to local environmental conditions rather than contaminant exposure, leading to differences in diet and the abundance of insects available as food (Wayland et al. 1998; Newsted et al. 2006; Dunn and Hannon 1992; Hussell and Quinney 1987; Quinney et al. 1986; McCarty and Winkler 1999b).

The objective of my study was to investigate reproductive and growth endpoints in tree swallows inhabiting areas near oilsands mine operations and reference sites to determine if these endpoints reflect the current level of environmental disturbance. I hypothesized that tree swallows near oilsands operations would experience higher levels of environmental stress. I predicted reduced reproductive success and nestling growth of tree swallows near oilsands operations compared to less-disturbed habitats. Nestling growth may also be influenced by the order of hatching (Clotfelter et al. 2000), and environmental conditions can affect female and male nestlings differently (Hogle and Burness 2014). I evaluated whether local weather conditions and nestling diet were confounding factors in the measured endpoints. I also documented the annual return rates and movements of adult and nestling tree swallows from banding data.

4.2 Methods

4.2.1 Study Sites

In four summers (2011 to 2014), I monitored tree swallows using nest boxes near Fort McMurray in northeastern Alberta. Over the four seasons, the number and location of nest boxes increased to include eight sites from an initial four sites in 2011. Four sites were within 5 km of active mine operations and mine upgraders, and were exposed to aerial emissions and potentially to contaminants in water originating from bitumen-processing (Figure 4.1). Four reference sites were located 55 to 65 km south of active mining. Nest boxes located at three sites (Sites 1, 2 and 4) near operations were installed seven to 14 years previously, and were deteriorating by 2011. Few tree swallows occupied these boxes. In 2012, the old nest boxes at Sites 1 and 2 were replaced and new nest boxes were installed at Site 3 near operations. Also in 2012, new nest boxes were installed at two reference sites (Sites 5 and 6), with a third reference site being added in 2013 (Site 7). In late spring 2013, nest boxes were replaced at Site 4 near operations, and new nest boxes added to include a fourth reference site (Site 8), although these sites were not studied in 2013 due to low occupancy. All eight sites were monitored in 2014.

Each of the eight sites supported 15 to 30 nest boxes, and was near a wetland or pond. Site 1 was at a pond built in 1993 to support tailings research, and contained fine tailings that have settled to the bottom with a cap of natural surface water. Site 2 was a reclaimed area on the edge of a wetland that formed naturally following reclamation in 2003. Site 3 was also reclaimed and planted with coniferous trees in 1983. This site was an overburden dump from mine development and now supports a mature upland forest and wetland habitat. Site 4 is adjacent to a reservoir. The reference Sites 5 and 8 were on the edge of old borrow pits that provided gravel fill for road construction, and have naturally revegetated and filled with water. Site 6 was adjacent to a beaver pond and natural drainage system. Site 7 was on a grass-sedge wetland on the edge of Maqua Lake.

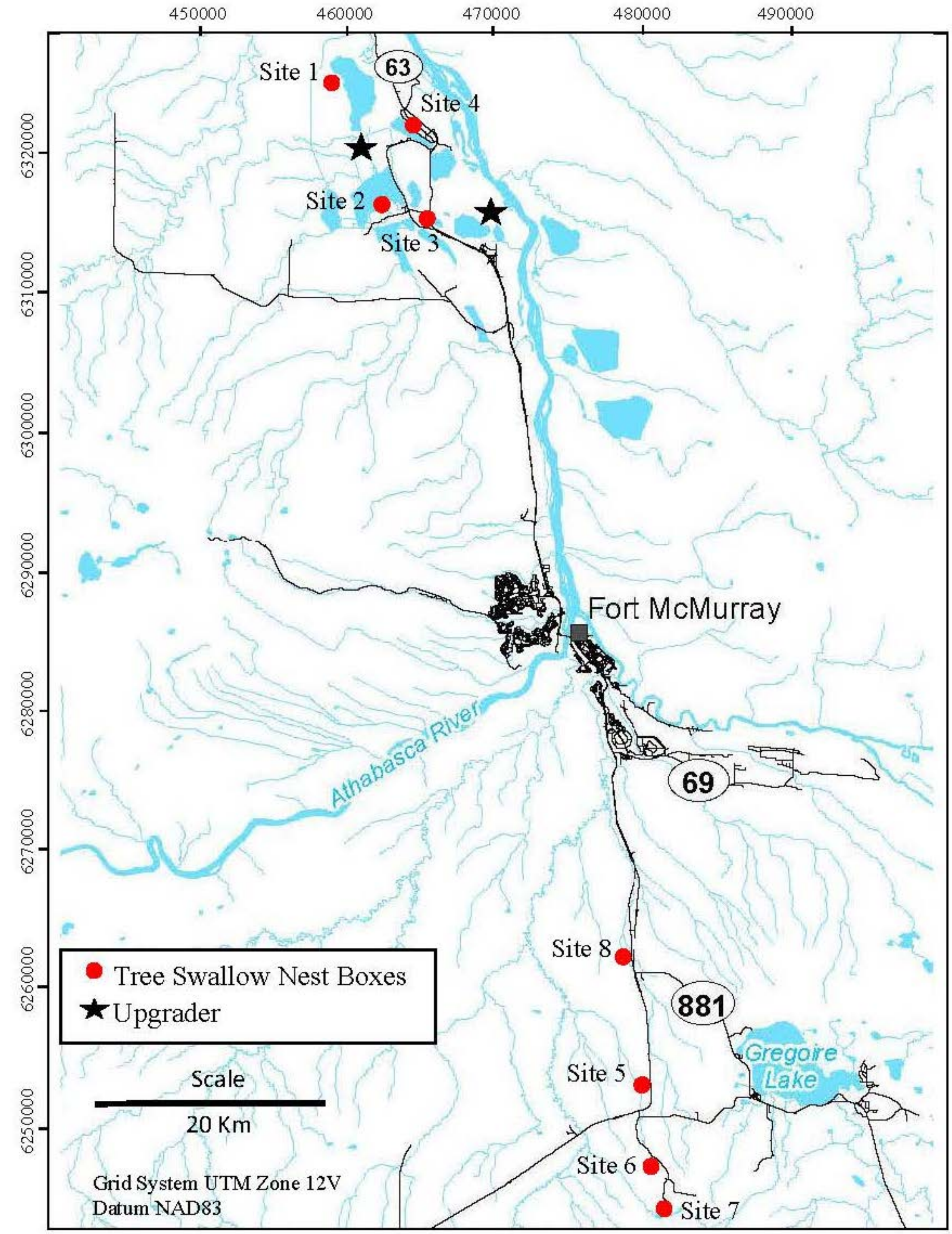


Figure 4.1 Study sites near oilsands mining operations north of Fort McMurray, and reference sites to the south for the study of tree swallow reproductive success and nestling growth

4.2.2 Nest Box Monitoring

From mid-May to July, nest boxes were visited daily or every second day during nest-building and egg-laying, and daily close to hatching to determine date of clutch initiation, clutch size, and day of hatching. The day that half or more eggs hatched was designated day zero. Hatching success was determined by the number of eggs hatched divided by the clutch size, not including nests that were destroyed or preyed upon prior to hatching.

On days 9 and 14, nestlings were weighed using a digital balance (iBALANCE^{TM}) (±0.1 g), and the unflattened wing chord measured with a wing ruler. Nestlings were marked individually on day 9 by colouring the feathers of the femoral tract behind the legs using a non-toxic marker. Nestlings were banded with individually numbered Canadian Wildlife Service bands on day 14.

Nests were not visited beyond day 14 to minimize the risk of premature fledging, as nestlings can fledge after 16 days of age (Dunn and Hannon 1992). Fledging success was determined by the number of nestlings reaching 14 days of age, minus birds found dead in the box on visits to the nest box for cleaning after at least 25 days, divided by the number of eggs hatched.

During egg-laying, incubation, and feeding of nestlings, adult females were captured opportunistically in the nest box and banded. Occasionally males were also captured and banded. Females were aged as second-year (SY) or after second-year (ASY) based on plumage characteristics (Hussell 1983; Pyle 1997). A few females could not be aged and were called after hatching year (AHY).

To examine the effects of local weather conditions on hatching and fledging success, I used Environment Canada data collected at the Fort McMurray airport weather station to determine daily precipitation (mm), and minimum and maximum temperatures (°C) during incubation and feeding of the nestlings.

4.2.3 Nestling Diet

In 2012 and 2013, I collected nestling tree swallows for contaminant studies (results reported in Chapter 3 of this thesis) and examined their stomach contents for diet composition. At 14 days of age, I sacrificed one to three nestlings that I selected randomly from each nest box. I euthanized individuals using isoflurane, followed by cervical dislocation. During the necropsy, the sex of each bird was determined by visual examination of the gonads. The protocols used in this study were approved by the Animal Care Committee at the University of Calgary (LESACC protocol number BI11R-27), in compliance with standards set by the Canadian Council on Animal Care.

From the stomach contents, I identified the food and other items being fed to the nestlings. I scanned the stomach samples under a dissecting microscope and identified the contents to the lowest possible taxonomic level (usually family or genus). The relative abundance of each taxonomic group was estimated based on the percent volume in each sample. Visual estimates of the percent volume were repeatable between different observers to within 10 percent. Even though stomach contents were partly digested, it was possible to identify each type and the quantity of food items from the heads, whole bodies, matching pairs of wings and elytra, and mandibles.

4.2.4 Statistical Analyses

I used SAS software 9.3 (SAS, 2008. SAS/STAT® 9.3 User's Guide. SAS Institute Inc.) to conduct statistical analyses. Nestling size at days 9 and 14 were compared among locations and years using a mixed model analysis of variance (PROC MIXED procedure in SAS) with nest box as a random effect. This statistical procedure accounts for the lack of independence among nestlings within the same nest box. The MIXED model also minimizes the effects of unequal sample sizes. Each model contained year, location (near operations, reference), interaction between year and location, clutch initiation date (Julian calendar), and clutch size as fixed effects. I also tested for size differences between male and female nestlings.

I tested for location and year differences in clutch size, and hatching and fledging success using a generalized linear mixed model (PROC GLIMMIX procedure in SAS) with site as a random effect. The GLIMMIX model combines the features of a generalized linear model for analyzing non-normal data, with the ability to account for non-independence of nest boxes within a site that may be affected by local weather conditions and timing of adult bird arrival. Each model contained year, location, clutch initiation date (Julian calendar), clutch size, and interaction terms as fixed effects. I also included the weather variables in each model by calculating the total precipitation, and the average minimum and maximum temperatures over the periods of egg incubation and nestling feeding for each nest. A significance level of $p < 0.05$ was chosen for all statistical tests.

4.3 Results

The weather varied among the four years and affected nesting conditions and, likely, bird behaviour. An extensive regional forest fire permeated the area with ash and smoke in 2011. The fire started in mid-May as birds were arriving on the breeding grounds, and continued burning through the nesting season. Smoke reduced the air quality in the nearby communities of Fort McMurray and Fort MacKay (WBEA 2011), and thick smoke was frequently encountered during the nest box monitoring. Of the 10 nest boxes that were occupied in 2011, five clutches were initiated late in the season (after June 7), and four boxes failed. One box successfully fledged only two nestlings from six eggs. Nest boxes were old and in poor condition, and, along with the forest fire smoke, this likely had a large impact on tree swallow occupancy and nest success in the 2011 season, so the data from 2011 were not included in the following analyses.

Daily minimum and maximum temperatures during the nestling stage were lowest on average in 2012 ($F_{min\ temp} = 96.91$, $p < 0.01$; $F_{max\ temp} = 17.24$, $p < 0.01$), while minimum temperatures in 2013 were significantly warmer during incubation ($F = 29.28$, $p < 0.01$) compared to the other years (Figures 4.2a and b). Dry conditions prevailed in 2012 and 2014, while 2013 experienced significantly higher rainfall ($F = 166.69$, $p < 0.01$) (Figure 4.3) in June that resulted in flood conditions in the local rivers. In 2013, heavy rains occurred on nine days between 5 and 15 June, during egg incubation of about 80% of occupied nest boxes.

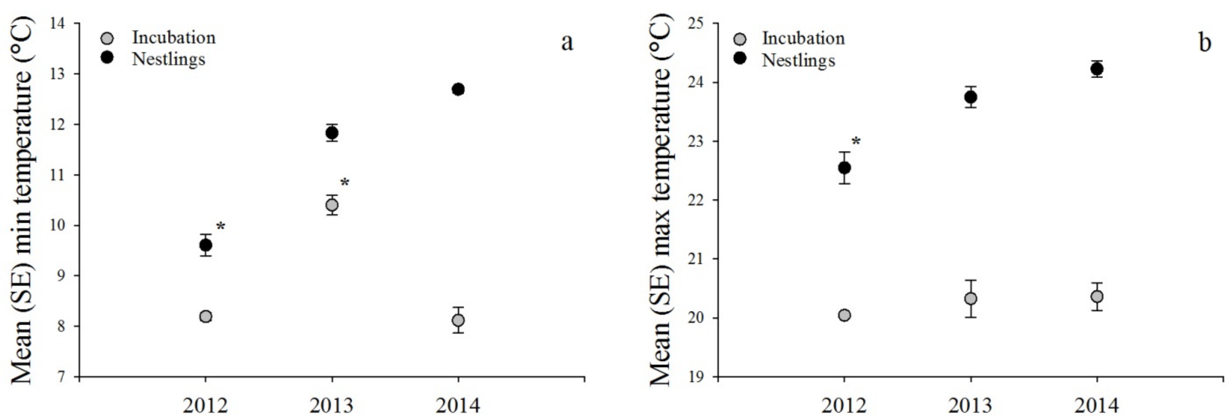


Figure 4.2 Mean (SE) a) minimum and b) maximum daily temperatures during egg incubation and nestling feeding; *denotes minimum daily temperature was higher during incubation in 2013, and minimum and maximum daily temperatures were lower during the nestling stage in 2012 (*p*<0.05 in each case)

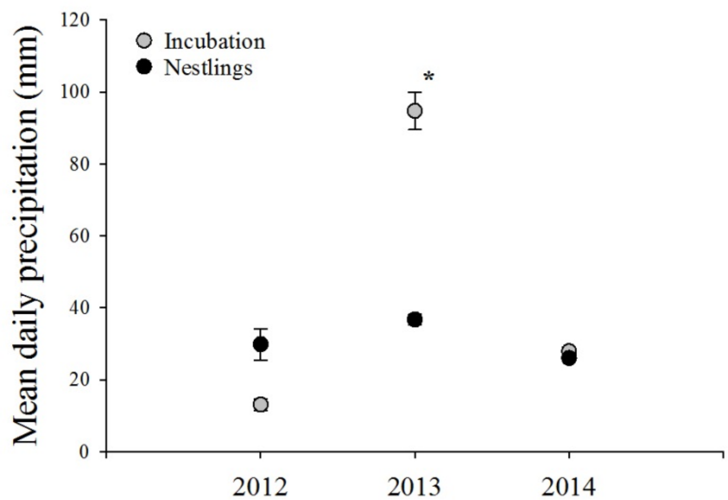


Figure 4.3 Mean (SE) daily precipitation (mm) during egg incubation and the nestling stage; *denotes a significant difference (*p*<0.05)

The number of available nest boxes increased each year, as did occupancy (Table 4.1). In my study area, tree swallows have a single brood and although late nesting occurred, double brooding was not observed. Some birds re-nested when their eggs were lost, although unbanded females were often captured in nest boxes of these late nests suggesting they were birds that were not present in the nest boxes earlier in the season. Females usually laid one egg per day, although interruptions did occur and were more frequent in 2014. Females began incubating about one day prior to the last egg being laid, and eggs were incubated for 13 to 17 days. Nest predation occurred in only one box in 2014, and was presumed to be by a mustelid. Eggs occasionally disappeared from boxes, potentially due to other birds. Over all years, five nests were destroyed by bears just prior to nestlings reaching 14 days of age.

Table 4.1 Number of occupied nest boxes and percent occupancy near operations and at reference sites in each year

	2012		2013		2014	
	Available	Occupied (%)	Available	Occupied (%)	Available	Occupied (%)
Near Operations	54	17 (31)	83	24 (29)	103	36 (35)
Reference	55	10 (18)	70	25 (36)	85	31 (36)
Total	129	27 (21)	158	49 (31)	193	67 (35)

Although there appeared to be a trend towards earlier clutch initiation near operations compared to reference sites in each year, after controlling for year and interaction effects, there was no significant difference in the timing of clutch initiation between locations (F = 0.93, p = 0.37) (Figure 4.4a). Egg-laying began significantly earlier in 2012 compared to other years (F = 3.89, p = 0.02). Clutch sizes were most frequently six or seven eggs (Figure 4.4b), with five to eight eggs occurring in over 90% of occupied nests. Mean clutch sizes were not different between locations, but were significantly higher in 2014 (F = 3.62, p = 0.03). Clutch size generally declined as the season progressed, and was significantly related to the date of clutch initiation (F = 49.70, p = 0.03).

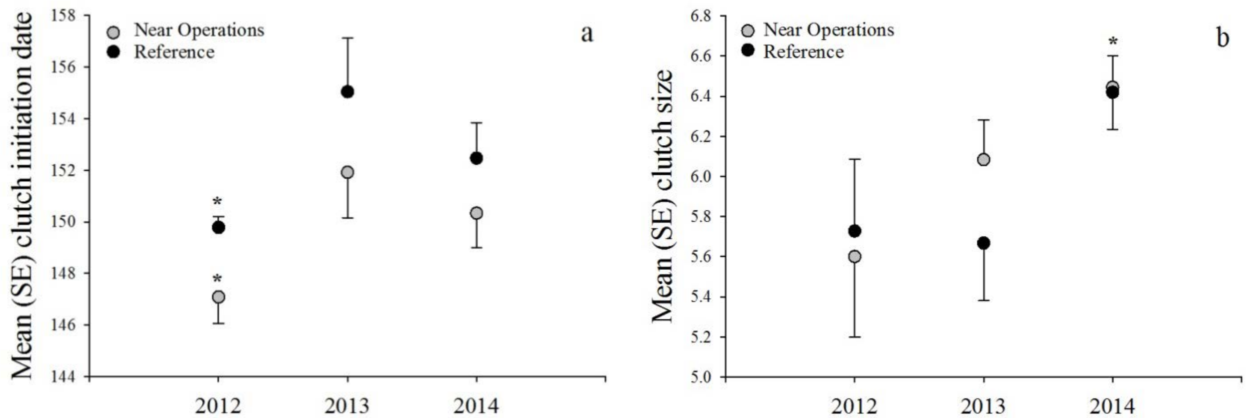


Figure 4.4 Mean (SE) a) clutch initiation date (Julian calendar) and b) clutch size near operations and at reference sites in each year; *denotes clutch initiation date at both locations was earlier in 2012, and clutch sizes at both locations were higher in 2014 (*p*<0.05)

There was no location difference in hatching success (F = 0.82, *p* = 0.37) (Figure 4.5). Over the three years, hatching success averaged from 57 to 88% near operations, and from 56 to 86% at the reference sites. Nests in 2014 tended to be most successful, although when taking into account other fixed effects such as weather conditions, this difference was not statistically significant (F = 2.47, *p* = 0.09). Hatching success was influenced primarily by precipitation (F = 5.30, *p* = 0.02), but not average daily temperature (F = 1.24, *p* = 0.27), and hatching success decreased with an increase in precipitation during egg incubation.

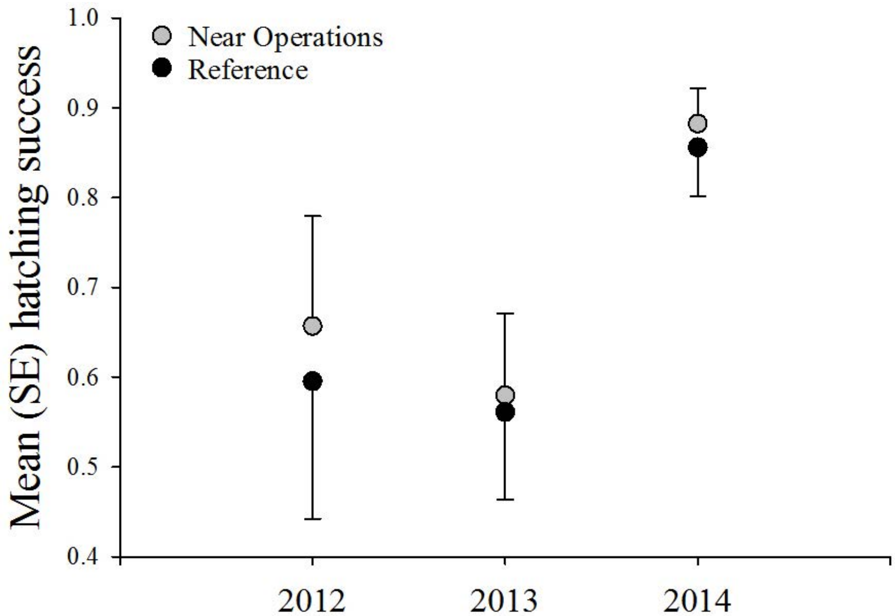


Figure 4.5 Mean (SE) hatching success near operations and at reference sites in each year

There was no significant location difference in fledging success (F = 0.19, $p = 0.67$) (Figure 4.6). Over the three years, fledging success averaged from 80 to 96% near operations, and from 95 to 100% at the reference sites. When weather and other fixed effects were taken into account, year differences were statistically significant (F = 3.34, $p = 0.04$). Fledging success was influenced primarily by precipitation, decreasing with increasing in precipitation during the nestling stage (F = 11.18, $p < 0.01$).

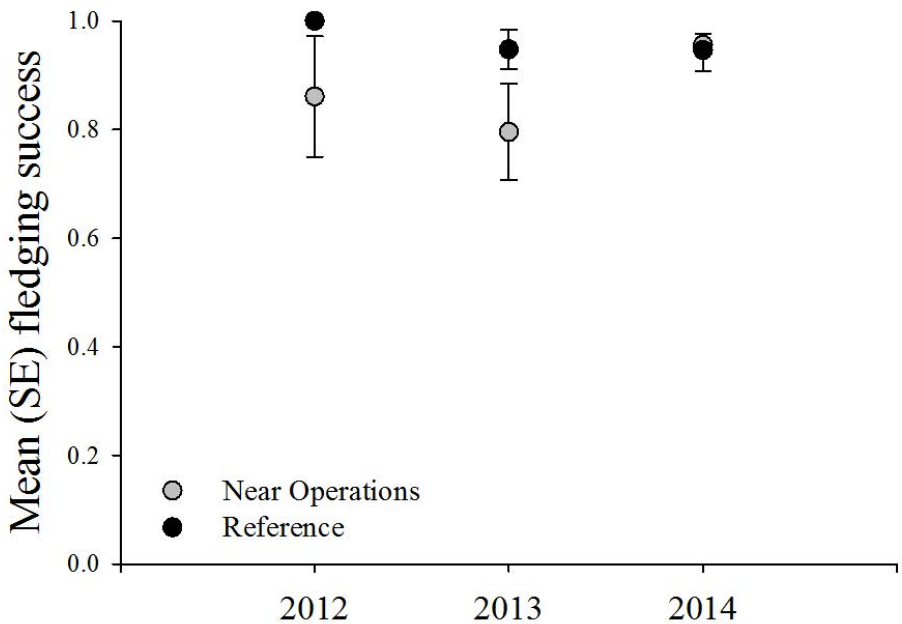


Figure 4.6 Mean (SE) fledging success near operations and at reference sites in each year

I measured body mass and wing length of nestlings at 9 and 14 days of age. Asynchronous hatching of nestlings occurred, and hatching was often completed over a 24-hour period. The differential growth among nest mates due to asynchronous hatching resulted in high variability of mass and wing length measurements (Figure 4.7). Nestlings near operations tended to weigh less on day 9 in 2013, compared to reference nestlings and nestlings in other years; however, when the effect of clutch size was taken into account, this difference was not statistically significant (F = 3.48, $p = 0.07$). By 14 days of age, nestlings at both locations in 2013 remained below the mean mass of nestlings of the same age in other years (F = 4.30, $p = 0.02$). No location or year differences in day 9 and day 14 wing measurements were observed.

I collected a total of 104 nestlings in 2012 and 2013, and subsequently the sex of each nestling was determined. The male:female sex ratio was 49:51 near operations, and 51:49 at the reference sites, indicating a near equal proportion of males and females in both locations. Male nestlings weighed more than females at day 9 (F = 5.37, $p = 0.02$), and day 14 (F = 7.28, $p < 0.01$). The wing length of males was longer at day 9 (F = 4.54, $p = 0.04$), but this difference was not significant by 14 days of age (F = 2.19, $p = 0.14$).

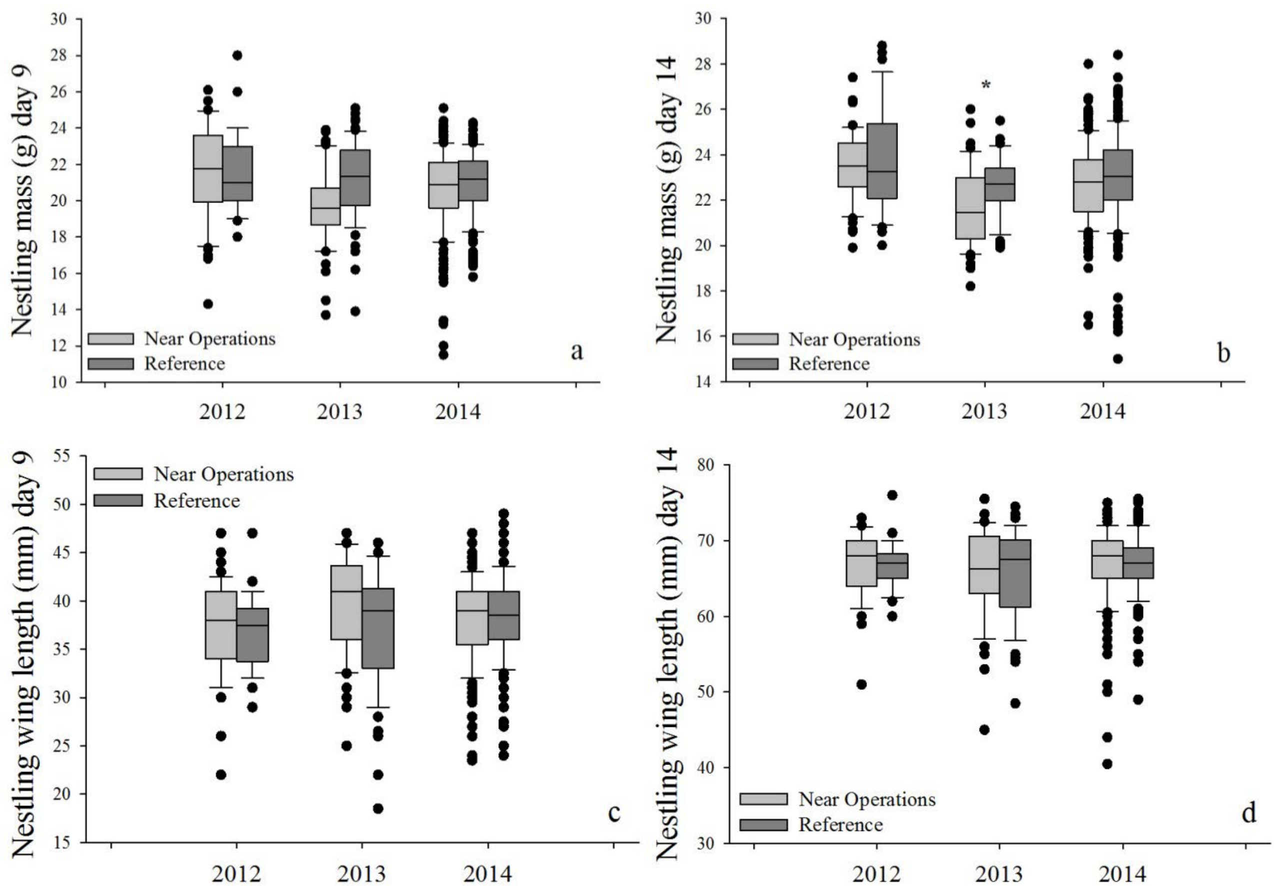


Figure 4.7 Median and interquartile range of nestling mass (g) and wing lengths (mm) of nestlings at 9 and 14 days of age. Nestling mass at 14 days of age was lower in 2013 than in other years (*p<0.05)

I banded a total of 125 adult females and 485 nestlings over the four years. Approximately 24% of females were aged SY, and this proportion was not different between locations. Approximately 12% of females could not be aged. The percent of year-to-year adult female returns varied from 10 to 30% (Table 4.2). From 2012 to 2014, six adult females returned to near operations (eight recaptures including multiple recaptures) and nine returned to reference sites (11 recaptures, including multiple recaptures). However, too few birds returned to either area, and the length of the study period was short to establish survival estimates. Of the 19 total recaptures, five females occupied the same nest box in the year following initial banding. Four females returned to a different site, and dispersal distances were up to 8 km from their original banding site. Ten females returned to the same site, but moved to a different box. One female banded near operations as an ASY in 2011, was recaptured in each of the following three years at the site of banding. Two other females banded at the reference sites, also returned in each of the following two years. The longevity record for tree swallows is 12 years (USGS 2014). Of the 123 nestlings that were banded from 2011 to 2013, none returned as breeders to the nest boxes in subsequent years.

Table 4.2 Annual returns of banded adult female tree swallows for all study sites

Year	New Bandings	Yr-Yr Recaptures	Multiple-Yr Recaptures
2011	10		
2012	20	1 (10%)	
2013	47	6 (30%)	1 (3%)
2014	48	8 (17%)	3 (4%)

As the capture-recapture effort focused on adult females, inferences cannot be made about males. A total of 30 adult males were banded in the four years. Of the 19 males banded from 2011 to 2013, two were recaptured in subsequent years, both near operations.

I determined the relative proportion of invertebrates and other items consumed in the nestling diet by examining the stomach contents of 98 nestlings at 14 days of age in 2012 and 2013 (Table 4.3). The nestling diet varied by location, and in each year. Overall, it appeared that a greater proportion of Coleoptera was consumed in 2012 compared to 2013. The nestlings at reference sites appeared to consume a greater proportion of Ephemeroptera, while the nestlings near operations appeared to consume more Odonata. The consumption of Ephemeroptera and Diptera appeared to increase in birds near operations in 2013 compared to 2012. Insect taxa with a terrestrial larval life stage comprised up to one third of the nestling tree swallow diet, and included Coleoptera, Hymenoptera, and several Dipteran families. The weather conditions in 2013 likely influenced the ability of adults to feed nestlings. Almost no food was contained in the stomachs of nestlings that were collected after the heavy rains in 2013. These nestlings were in two nest boxes near operations and appeared to have been abandoned, as the stomachs were either empty or contained grass from nest material. The composition of each taxon in the diet of the nestling tree swallows is listed in Table 4.4. Other items and plant material found in the stomach contents are listed in Table 4.5.

Table 4.3 Mean (range) percent by volume of invertebrates and other items consumed by 14-day old tree swallow nestlings near operations and from reference sites in 2012 and 2013

	Near Operations (Mean % (range))		Reference (Mean % (range))		
Stomach Contents	2012 (n=23)	2013 (n=28)	2012 (n=16)	2013 (n=31)	Larval Habitat
Coleoptera	37 (0-75)	14 (5-65)	28 (5-75)	10 (0-30)	Terrestrial
Ephemeroptera	0	10 (0-85)	25 (0-90)	46 (0-100)	Aquatic
Diptera	9 (0-25)	31 (0-85)	27 (0-85)	25 (0-95)	Terrestrial/Aquatic
Odonata	30 (0-80)	9 (0-80)	<1 (0-10)	2 (0-50)	Aquatic
Hymenoptera	6 (0-30)	6 (0-40)	3 (0-25)	4 (0-35)	Terrestrial
Lepidoptera*	5 (0-90)	1 (0-10)	<1 (0-3)	1 (0-10)	Terrestrial
Trichoptera	0	2 (0-30)	1 (0-10)	3 (0-65)	Aquatic
Tipulidae	0	4 (0-40)	0	<1 (0-15)	Aquatic
Hemiptera	<1 (0-5)	1 (0-10)	<1 (0-5)	1 (0-10)	Terrestrial/Aquatic
Homoptera	<1 (0-1)	0	<1 (0-1)	0	Terrestrial
Neuroptera	0	<1 (0-5)	0	0	Terrestrial
Psocoptera	0	0	<1 (0-1)	0	Terrestrial
Other	1 (0-15)	<1 (0-1)	2 (0-20)	<1 (0-5)	Incidental
Unknown	13 (0-60)	16 (0-50)	13 (0-35)	8 (0-55)	Unknown
Mollusc**	10 (43)	5 (18)	4 (25)	13 (42)	Aquatic
Grit**	11 (48)	7 (25)	3 (19)	9 (29)	Terrestrial
Plant**	5 (22)	8 (29)	2 (13)	6 (19)	Incidental

*Order composed of unidentified moth species

**Number (%) of stomach samples containing Mollusc shells (Class Gastropoda and Class Bivalvia), grit composed of sandstone or quartz, and plant material

Table 4.4 Composition of each taxon found in nestling tree swallow stomach contents near operations and at reference sites over the two years of sampling. Taxa within Ephemeroptera, Lepidoptera, Trichoptera, and Tipulidae were not identified below the level of Order

Order Coleoptera	**Order Diptera**	**Order Odonata**	**Order Hymenoptera**

Unidentified
Superfamily Caraboidea
Family Carabidae
Family Cerambycidae
  Genus Lepturobosca
    Chrysocoma *Sp.*
  Genus Acmaeops
    Proteus proteus
Family Scarabaeidae
Family Lyctidae
Family Lycidae
Family Scolytidae
Family Bostrichidae
	Suborder Nematocera
	  Family Tipulidae
	  Family Chironomidae
	  Family Mycetophilidae*
	  Family Culicidae
	  Family Bibionidae*
	  Family Scatopsidae*
	Suborder Brachycera
	  Family Syrphidae
	  Family Tabanidae
	  Family Dolichopodidae
	  Family Empididae
	  Family Tephritidae*
	  Family Milichiidae*
	    Genus Desmometopa
	  Family Diastatidae
	  Family Bombyliidae*
	  Superfamily Muscoidea
		Suborder Zygoptera
		  Family Coenagrionidae
			Unidentified
			Family Formicidae
			  Subfamily Myrmicinae
			Family Ichneumonidae
			Family Braconidae
			Superfamily Apoidea
			Superfamily Bethyloidea

Order Hemiptera	**Order Homoptera**	**Order Neuroptera**	**Order Psocoptera**
Unidentified Suborder Auchenorrhyncha Family Corixidae	Suborder Sternorrhyncha Superfamily Aphidoidea	Suborder Hemerobiiformia	Suborder Eupsocida

*Larvae terrestrial in origin

Table 4.5 Other food items and plant material found in nestling tree swallow stomach contents near operations and at reference sites over the two years of sampling

Other	**Plant Material**
Class Arachnida	Unidentified
Order Araneae	Unidentified peduncle
Dipteran Eggs	Family Asteraceae seed
Moth Eggs	Unidentified seed pods
Family Calliphoridae	Unidentified grass
Genus Protocalliphora (larvae)	Carex sp. Bracts
Unidentified larvae	Woody material

I frequently observed tree swallows foraging on the ground along trails and road edges, where they were possibly picking up grit, as well as shells along water edges. Grit in the stomachs consisted of sandstone and quartz, and purple stones were observed most frequently in the nestling stomachs (Figure 4.8). Stones were normally between 2 and 4 mm in diameter, and in some instances up to 6 mm. Most shells were in small pieces; however, a whole gastropod shell was 9 mm by 5 mm (Figure 4.9), and a freshwater clam shell was 6 mm by 5 mm, and another clam shell piece was 7 mm long.

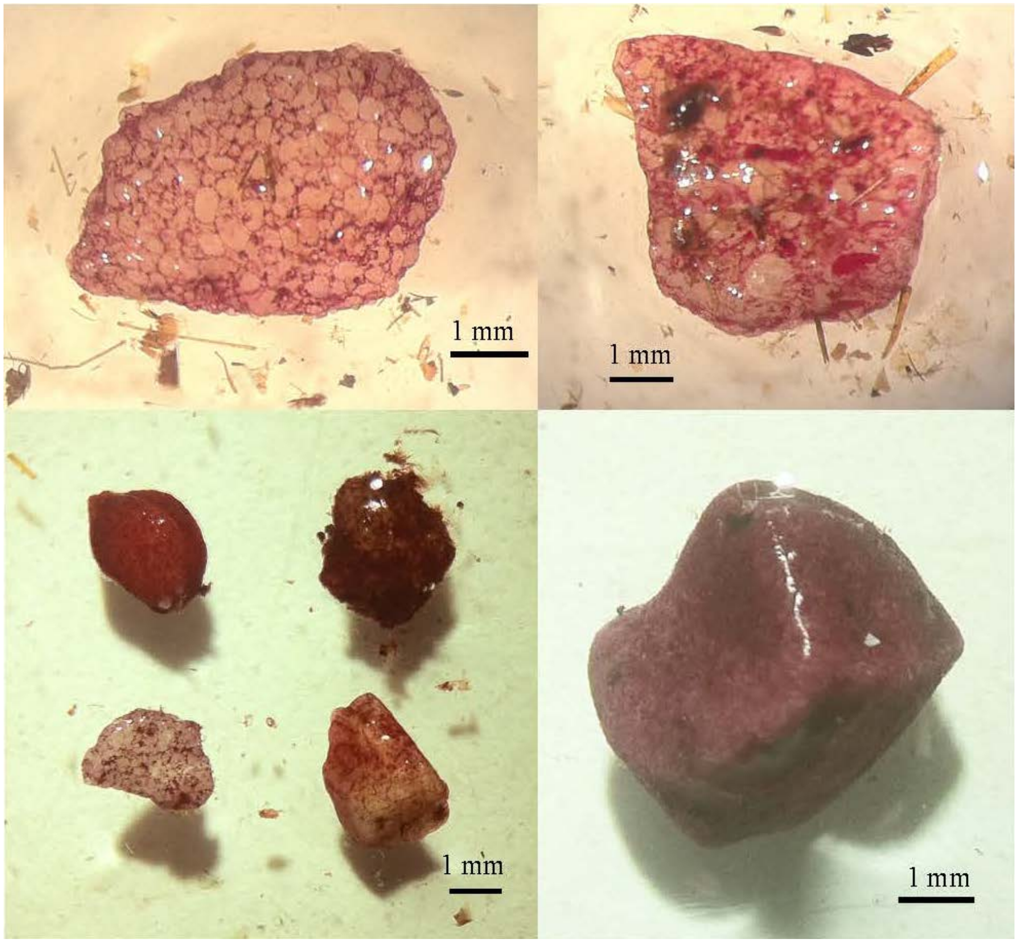


Figure 4.8 Stones found in stomachs of nestling tree swallows

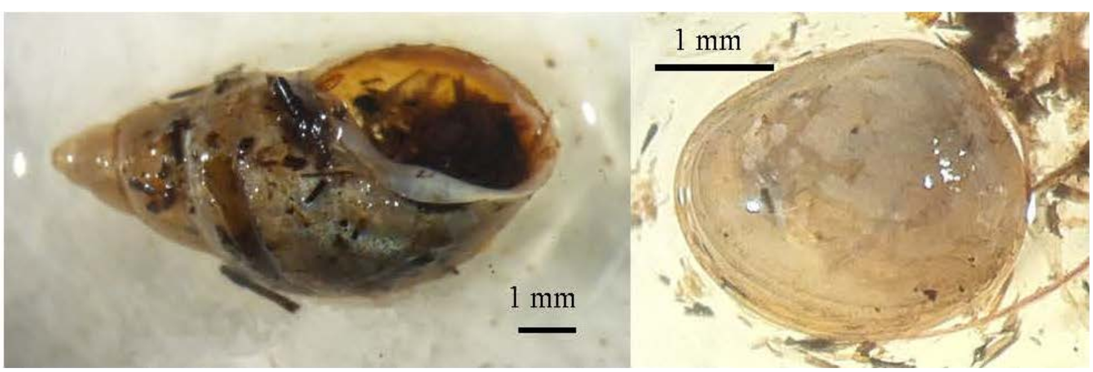


Figure 4.9 Mollusc shells found in stomachs of nestling tree swallows

4.4 Discussion

I found no evidence of a relationship between reproductive endpoints or nestling growth and proximity to oilsands mining operations. Hatching success was moderate to high, with fledging success being generally high. Hatching success of tree swallows between 72 and 94% was reported from a previous two-year study near oilsands operations (Smits et al. 2000), although weather conditions were not reported. Fledging success of nestling tree swallows was 100% across all sites near oilsands operations during a previous one-year study (Harms et al. 2010). The age of adult female tree swallows influenced reproductive performance during a four year study in Ontario that reported hatching success between 80 and 92%, and fledging success between 81 and 93% (Stutchbury and Robertson 1988).

The most common clutch size in my study was seven eggs, and was related to the date of clutch initiation. Clutch size was similar to other studies of tree swallow reproductive success in central Alberta (Dunn and Hannon 1992), and in the oilsands region (Smits et al. 2000). Previous work indicates that the relationship of clutch size to date of clutch initiation is consistent across northern North America (Winkler et al. 2002). Clutch size may be influenced by latitudinal differences in tree swallow populations, with larger clutch sizes in more northern areas related to longer day length (Rose and Lyon 2013).

Predation was not a major factor in my study. In the four years, only one box was lost to predation. However, black bears are common and the loss of five nest boxes was from bears knocking boxes off, or bending poles to the ground. Black bears appeared to be attracted to the nest boxes from curiosity and the increased vocalization of the older begging nestlings. No boxes were opened by bears to indicate predatory behaviour, and in three instances some nestlings were still alive and were able to fledge after repairs were made to the nest box or pole.

Weather conditions influenced reproductive success and nestling growth. Warm and dry weather occurred in spring and summer 2014, while the previous two years had higher rain and lower temperatures. Precipitation influenced hatching and fledging success, and probably nestling growth in 2013. Reproductive success was unrelated to location, suggesting that tree swallows in my study were influenced more by the prevailing environmental conditions than by proximity to mining. Weather conditions can influence the reproductive success of tree swallows by reducing food availability (Quinney et al. 1986; Hussell and Quinney 1987; Dunn and Hannon 1992; McCarty and Winkler 1999b). Wet weather was implicated in dramatically higher nestling mortality reported in a previous study near oilsands mining operations (Gentes et al. 2006).

Even though nest boxes were located near water, I found the consumption of insects with an aquatic larval stage averaged as low as 40%, and some individual nestlings consumed less than 30% of insects with an aquatic origin. Tree swallows in some colonies near water in Tennessee foraged extensively on terrestrial insects (Beck et al. 2013), and about 37% of the tree swallow diet was terrestrial insects in birds nesting along the Woonasquatucket River in Rhode Island (Custer et al. 2005). Tree swallow adults are more selective when higher quality food items are available, but will not reject lower quality food items (Quinney and Ankney 1985). The variability in the nestling diet has implications for dietary quality, nestling growth, and contaminant exposure.

The reduced nestling mass in 2013 may have been due to short-term fluctuations in food availability and thermoregulation costs due to the wet weather. Differences in growth were related to sex, and male nestlings were significantly larger than females. When exposed to poor environmental conditions, female nestlings grow more slowly than male nestlings (Hogle and

Burness 2014). Growth rates are also influenced by the length of the nestling period (Zach and Mayho 1982), which is determined by food availability and adult provisioning of nestlings (Stodola et al. 2010). Studies have found that density of breeding birds, food supply, parental care, temperature, and parasite load, among other factors, played an important role in nestling growth (McCarty 2001; Ardia 2006; Gentes et al. 2007b), and unless exposure to environmental contamination is high, effects on growth from contaminant exposure may not be detected (Gerrard and St. Louis 2001; Longcore et al. 2007).

In my study, nestlings exhibited asynchronous hatching, which contributed to the variability in mass and wing length measurements. The order of hatching has been reported to affect growth rates in tree swallows (Zach 1982; Clotfelter et al. 2000; Johnson et al. 2003). Differences in nestling mass related to hatching order affect survival early in the nestling period. These differences are less pronounced as nestlings reach fledging age (Clotfelter et al. 2000). Sex-related differences in growth also disappear as nestlings age (Hogle and Burness 2014). Nestlings deprived of food in an experimental study were significantly smaller at day 9 than nestlings that received food, but nestlings were able to overcome the poor early growth with these differences no longer apparent by day 16 (Wiggins 1990). The compensatory mechanisms in nestling growth are not understood, but may be explained by the heritability of body size. The mass of younger nestlings may be a better predictor of post-fledging survival. However, nestling growth rate may not be an appropriate metric for studies of industrial effects on tree swallows unless the many factors affecting growth can be accounted for appropriately.

Other than sex-related size differences, there was no difference in nestling wing-length measurements. Primary feather growth at fledging is about two-thirds complete, and feather growth is less reliable in predictive growth models than mass, due to the high variability in wing length among broods (Zach and Mayoh 1982). Wing length is an important predictor of fledging age, and attaining a critical wing length before fledging may be necessary for survival post-fledging (Michaud and Leonard 2000). Larger nestlings are more likely to return to nest boxes in subsequent years (McCarty 2001), although my study had no returns of nestlings.

The return rate of banded fledglings and adults may be reflective of the low number of birds that I banded in each year. Between 10 and 30% of adult females returned to the nest boxes in the year following banding, and no fledglings were recaptured. Survival studies based on banding data require many years and large numbers of banded birds to detect trends (DeSante et al. 2009). Return rates of adult female tree swallows in two study areas in central Alberta were 26 and 29%, while return rates of fledglings were about 1% (Dunn and Hannon 1992). In central Saskatchewan, the mean percentage of adult females encountered from one year to the next over 16 years of monitoring was 12.8%, and for nestlings it was 0.8% (Houston and Houston 1987). The proportion of adult females that returned to my study area is within these reported values, and as more nestlings are banded, some are also expected to return.

Some adult females in my study were recaptured up to 8 km from their banding site. Females are easier to capture than males, so I was not able to determine dispersal distances of males in my study area. Sex differences in dispersal distance have been documented in tree swallows, and females disperse further than males (Winkler et al. 2004, 2005), and younger females are more likely to disperse than older females (Winkler et al. 2004).

The results from my study suggest that the breeding and foraging ecology of tree swallows was not influenced by proximity to oilsands mining operations. Local environmental conditions influenced reproductive performance and the types of food consumed by nestling tree swallows. Food resources in a region can vary spatially, and from day to day as different groups of insects emerge (McCarty 2001/2002). The abundance and quality of insects as food is worth exploring further. Order of hatching and nestling sex contributed to the variability in nestling growth. My study illustrates that a number of important factors must be considered when interpreting the effects from industrial development.

Chapter Five: Conclusions

The primary objective of my study was to determine if passerines were being exposed to, and if so, affected by, metals from oilsands mining operations. Birds are often used as indicators of environmental change (Koskimies 1989; Gregory and van Strien 2010), and some species readily adapt to share human inhabited environments and as such, share similar exposure to contaminants. Insectivorous birds are also upper trophic-level consumers which makes them vulnerable to food web accumulation of contaminants from industrial developments (Maul et al. 2006). Tree swallows are effective indicators of exposure to a variety of contaminants, and correlation between contaminants in the environment and uptake of contaminants by swallows is well documented (Kraus 1989; Custer et al. 2001; Gerrard and St. Louis 2001; Custer et al. 2003; Echols et al. 2004; Custer et al. 2005). Tree swallows meet many of the criteria for species suitable for field studies on contaminant exposure, including geographic range and habitat use, population size, our knowledge of their ecology and diet, their tolerance of human disturbance, and our ability to easily obtain samples (McCarty 2001/2002 and 2002; Jones 2003; Custer 2011; Winkler et al. 2014). I used tree swallows as the model organism for my study. I also used Tennessee warblers and chipping sparrows to examine species-level effects, as these two species represent different foraging guilds, their ecology is relatively well known (Allaire and Fisher 1975; Pulliam 1986; Holmes 1998; Venier 2009; Rimmer and McFarland 2012), and they are locally abundant.

The oilsands have received substantial media attention, raising concerns about environmental disturbance and contamination from mining activities. A number of studies have found some level of contamination in the environment, including increased levels of metals near the oilsands mines (Bendell-Young 2000; Hebben 2009; Kelly et al. 2009; Timoney and Lee

2009; Kelly et al. 2010; Simpson et al. 2010; Edgerton et al. 2012; Bari et al. 2014). However, data were not available to understand whether contaminants were at biologically relevant levels that would enter the food chain, or deposit on feathers and be consumed through preening, and cause harm to birds. Passerines inhabiting areas near oilsands operations could be exposed to metals that accumulate in their food via uptake from mine waste-products deposited in tailings pond process-water, and from airborne particulates released during the bitumen upgrading process. Nickel and vanadium are considered signature metals associated with bitumen and the raw oilsands materials (Research Council of Alberta 1953; Har 1981). I hypothesized that passerines near oilsands operations are exposed to metal contaminants in the environment. My study sought to determine whether metal exposure was correlated with food, and if exposure was affecting nestling survival and growth.

A key component of contaminant studies is to document and quantify exposure levels. The extent to which birds and other wildlife are affected by metal exposure is dependent on the elements that are i) present in the environment, and ii) at potentially toxic levels. Absorption of metals also depends on the route of exposure, and other factors that influence the ability of organisms to absorb, accumulate, and metabolize these elements (Fairbrother et al. 2007). If passerines are exposed to metals locally on the breeding grounds, exposure would be reflected in metal levels in their tissues (Furness 1993; Burger and Gochfeld 1997; Echols et al. 2004).

I measured the levels of essential and non-essential metal and metalloid elements in the whole blood of live-sampled tree swallows, Tennessee warblers, and chipping sparrows. I found no evidence that blood metal and metalloid levels were elevated near oilsands operations (Table 2.4 and Appendix B). Metals accumulate in the larvae of aquatic insects (Hare 1992), and I expected concentrations to be highest in tree swallows that forage on insects that originate from aquatic habitats. However, species' differences were not as expected based on foraging behaviour, and the levels of elements in blood were not consistent among species or age classes.

I found high variability in the element concentrations in blood, which was confounded by the volume of the blood samples having a significant effect on the measurement and variability of the element (Figure 2.4). Smaller blood samples had higher levels of each element, and the reasons for this effect are not known. Repeatability of laboratory measurements was poor for non-essential elements. A combination of factors likely contributed to the high variability. The blood matrix may be inherently more variable due to moisture content (Ohlendorf and Heinz 2011), haematocrit (packed cell) proportion of the blood (Ardia 2013), metal absorption, and metabolism (Luoma and Rainbow 2005). High blood metal levels have been measured in birds where metal contamination from industrial facilities has been demonstrated (Dauwe et al. 2005; Tsipouraa et al. 2008; Geens et al. 2010), suggesting that the concentration of metals in blood indicate exposure. More study is needed to understand the effect of moisture content, or other factors affecting field-collected blood samples, such as red blood cell status and haematrocrit, on measuring metal concentrations in whole blood. The volume of blood required to sample for metal concentrations may be too large to be obtainable from small, live passerines, and variability may increase when exposure to metals is low. My results suggest that small samples of whole blood may not be suitable for monitoring metal accumulation in birds, particularly when metal concentrations are low.

Similar to the results for the blood metal levels, I found no evidence that the metal levels in the kidney and liver of nestling tree swallows were elevated near oilsands operations (Figures 3.2 to 3.8). The concentrations of elements in nestling kidney and liver could be attributed to uptake in food exposed to the local natural geological formations (Schmidt et al. 2012).

Few studies have examined metal concentrations over multiple years, but my results found that the levels of some metals in kidney and liver were higher in 2013 compared to 2012. Annual variations were reported in the blood metal concentrations of Herring (*Larus argentatus*) and Franklin's (*Larus pipixcan*) gulls (Burger and Gochfeld 1997), and in tree swallows (Adair 2002), but possible explanations for the variation were not discussed. The reasons for the year differences in my study are not known. Annual fluctuations in aerial emissions occurred from oilsands operations. For example, at one oilsands facility, nickel increased from 1.6 tonnes in 2012 to 2.5 tonnes in 2013, while at a second facility nickel decreased from 1.3 tonnes in 2012 to 0.67 tonnes in 2013 (NPRI 2014). A similar pattern for vanadium was also reported from these facilities. The effect of changes in aerial emissions on metal accumulation in organisms remains to be studied. Alternatively, the wet weather in 2013 may have influenced the deposition of metals from surface runoff into wetlands and streams, and subsequently the metal uptake into birds. High rainfall and overland runoff increased the variability and concentrations of some metals in estuarine sediments originating from the surrounding catchment areas of Guanabara Bay in Brazil, one of the most polluted coastal environments on the Brazilian coastline (Fonseca et al. 2013).

Some element concentrations were positively correlated between liver, kidney, and stomach contents of nestling tree swallows (Table 3.3), providing evidence that metal exposure was, in large part, via food. The analysis of nestling stomach contents illustrated the importance of terrestrial insects in the diet, as well as providing useful insight into the variety of items that are fed to nestlings by adults. By examining the metal concentrations in both the nestling stomach contents and the invertebrates collected from Malaise traps, I was able to document that terrestrial insect taxa contributed to the metal concentrations in the nestling diet. Even though nest boxes were located near water, I found the consumption of insects with a terrestrial larval stage to be greater than many studies have reported (Table 4.3) (McCarty and Winkler 1991; McCarty and Winkler 1999a; Mengelkoch et al. 2004; Custer et al. 2005; Dods et al. 2005; Custer 2011). My results suggest that it is problematic to assume reliance on only one segment of available food resources, such as emergent aquatic insects, when monitoring contaminant exposure in insectivorous birds in riparian areas. Neglecting the influence of terrestrial species in the diet may bias conclusions about the route of exposure, the uptake of contaminants, and the potential for toxicological effects. Based on my results, I found no evidence that nestlings near operations are exposed to higher than expected levels of elements in terrestrial and aquatic food items. However, because of the large variation in metal concentrations in the nestlings' tissues, I suggest that future research consider the complexity of the diet and potential food resources when examining contaminant exposure in insectivorous birds.

Reduced reproductive success and nestling growth has been documented in birds in response to metal exposure (Eeva and Lehikoinen 1996). I predicted, but did not find, decreased reproductive success or compromised nestling growth of tree swallows near oilsands operations compared to reference sites. Instead, hatching and fledging success were influenced primarily by precipitation. Clutch initiation date exhibited annual variation, and appeared to occur two or three days earlier near oilsands operations than in reference sites (Figure 4.4a). Local experience in breeding pairs of tree swallows significantly affects clutch initiation date (Lombardo and Thorpe 2010). Experienced breeders possess information about the local area, and returning earlier allows them to be selective about their nest location (Winkler et al. 2004). The advantages provided to early arrivals may be important to reproductive success, as clutch size decreases with later clutch initiation date (Winkler et al. 2002), as I also found in this study. Populations of tree swallows are established near operations, using nest boxes set-up for previous studies. I placed new boxes in reference sites for this study, and as birds acquire information about these new nest boxes, perhaps clutch initiation dates will be more similar. However, if birds preferred the established nest boxes near operations, I would expect occupancy levels near operations to be higher than reference sites. Occupancy levels were similar and were low across my study area compared to long-term studies in southern Ontario (Hussell 2012). I also found that the return rates of banded adult females were similar across my study area, and philopatry does not appear to explain the earlier occupancy of nest boxes near operations.

I found no evidence that the growth of nestling tree swallows was influenced by the proximity to oilsands operations (Figure 4.7). Contaminant exposure has been shown to affect nestling growth (McCarty and Secord 1999; Harris and Elliott 2000; Dods et al. 2005). I found high variability in nestling mass and wing length, and the ability to detect effects on nestling growth was confounded by several factors. Differences in growth were related to sex, with male nestlings being significantly larger than females. Nestlings also exhibited asynchronous hatching within a nest box, and nest-mates often completed hatching over a 24-hour period. In addition, I found location and year differences in the nestling diet. Differences in nestling mass are more pronounced in younger nestlings, and become less evident closer to fledging age (Clotfelter et al. 2000; Hogle and Burness 2014; Wiggins 1990). Primary feather growth is incomplete at fledging, and wing length is a predictor of fledging age as nestlings attain a critical wing length before they fledge (Michaud and Leonard 2000). Therefore, in studies of industrial effects, the mass of younger nestlings may be a more suitable predictor of post-fledging survival than wing length. Other factors that I did not consider are the age and experience of breeding adults, and adult provisioning of nestlings. Nestling growth may not be an appropriate endpoint for studies of industrial effects on tree swallows unless the many factors affecting growth can be accounted for appropriately.

Nickel and vanadium are present in high concentrations in bitumen and are of most concern in the toxicity of aquatic invertebrates exposed to oilsands leachates and process-water (Puttaswamy and Liber 2011, 2012). The levels of these metals in invertebrate food items, stomach contents of nestlings, and in the tissues of nestlings, exhibited patterns that are likely from exposure to the regional geological formations and natural processes. Tree swallows foraged on terrestrial insects, possibly limiting their exposure to elements that accumulate in aquatic invertebrate species. The diet of nestling tree swallows was varied, and it is possible that individual birds that forage more frequently on aquatic insects may be more at risk of metal exposure. However, most passerines spend about two months of their annual life-cycle on the breeding grounds in my study area. As well, birds and other organisms have evolved mechanisms to bind and eliminate potentially toxic elements, minimizing toxic effects (Fossi et al. 1995; Andrews et al. 1996; Haq et al. 2003; Domenech et al. 2006). Therefore, based on the results of my study of metal concentrations in the tissues of tree swallows, Tennessee warblers, and chipping sparrows, I suggest that passerines are currently at low risk of toxic effects due to exposure to metal contaminants from oilsands mining operations.

Based on diet, tree swallows are likely to be representative of a range of insectivorous birds. Other swallow species, and possibly nightjars, are most likely to have metal exposure levels similar to tree swallows. Species with other foraging modes, such as warblers and sparrows, may differ in the degree of metal exposure. The foraging ecology of tree swallows is also broadly similar to insectivorous bats, and tree swallows may be a surrogate for measuring exposure of metals in bats. The metal concentrations that I measured in Diptera, Lepidoptera, and Coleoptera may be useful in understanding exposure in bats, which I suggest is low based on the results of my study.

My research is the first to investigate metal exposure in birds in the oilsands region. Over the four years of my study, I observed annual fluctuations in local weather conditions that contributed to the reproductive success of tree swallows, and possibly to the differences in nestling diet. I also found high variability in the biological variables. There are limitations to using birds as study organisms. In particular, birds are mobile and will experience a number of stressors across a broad geographic range through their life cycle. The carry-over effects in returning breeding adults are not known. Migratory species such as tree swallows, Tennessee warblers, and chipping sparrows may not be as sensitive to metal contamination in the environment compared to resident species. The diet of these three species may also be more variable and opportunistic than assumed in my study.

The results of my study may have implications on other toxicological research on tree swallows in the oilsands region. Other studies have used immunological indicators to examine potential effects in tree swallows from exposure to oilsands operations (Smits et al. 2000; Harms et al. 2010). These studies were unable to detect negative effects on immune function. Immune function in adult tree swallows may be affected by local weather (Lifjeld et al. 2002), and effort to provision nestlings (Ardia 2005). Immune function in nestlings may be influenced by the hatching asynchrony of nest-mates (Martinez-Padilla and Vinuela 2011), but immunotoxicology test methods are variable in their sensitivity and ease of application, making direct comparisons among studies difficult. Thyroid hormones measured in tree swallows (Gentes et al. 2007a), and in wood frogs (*Lithobates sylvaticus*) (Hersikorn and Smits 2011), were elevated near oilsands processing. Variation in thyroid hormones may be attributed to food consumption (Scanes and Griminger 1990).

My study did not investigate the effects of organic contaminants, and I suggest that such contaminant studies also consider the ecological factors that influence exposure and variability. My study illustrates the need for longer-term monitoring to characterize the variability associated with natural environmental conditions that may affect tree swallows. Otherwise, the effects due to natural variability may be inappropriately attributed to industrial effects.

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APPENDIX A: GENERALIZED LINEAR MODEL RESULTS OF ELEMENT CONCENTRATIONS IN PASSERINES

Table A.1 Generalized linear model Chi-square (χ^2) statistic and level of significance (*p*) of non-essential metal concentrations (log-transformed values) in each year for tree swallows (TRES), Tennessee warblers (TEWA), and chipping sparrows (CHSP)

Element	Model Predictors	TRES 2011[1]	TRES 2012	TEWA 2011	TEWA 2012	CHSP 2011	CHSP 2012[2]
V	Location	NA	0.42(0.52)	0.30(0.58)	**8.95(0.01)**	2.62(0.11)	1.11(0.57)
	Site(Location)	NA	0.68(0.95)	1.83(0.77)	0.36(0.84)	**20.22(<0.01)**	0.38(0.94)
	Ageclass	**8.11(<0.01)**	**9.06(<0.01)**	0.04(0.85)	2.07(0.15)	0.57(0.45)	NA
	Ageclass*Location	NA	0.18(0.67)	0.40(0.53)	1.69(0.19)	1.12(0.29)	NA
Cr	Location	NA	0.00(0.95)	0.57(0.45)	5.61(0.06)	0.52(0.47)	1.38(0.50)
	Site(Location)	NA	0.80(0.94)	8.24(0.08)	0.00(0.99)	5.33(0.15)	2.62(0.45)
	Ageclass	0.04(0.83)	1.77(0.18)	**5.80(0.02)**	0.82(0.37)	**7.59(0.01)**	NA
	Ageclass*Location	NA	0.98(0.32)	**4.56(0.03)**	0.14(0.71)	0.00(0.98)	NA
Ni	Location	NA	0.56(0.45)	1.83(0.18)	**6.32(0.04)**	1.29(0.26)	1.16(0.56)
	Site(Location)	NA	6.76(0.15)	4.21(0.38)	0.68(0.71)	1.64(0.65)	2.98(0.39)
	Ageclass	**3.87(0.04)**	**23.76(<0.01)**	**8.03(<0.01)**	2.27(0.13)	**3.90(0.04)**	NA
	Ageclass*Location	NA	0.02(0.88)	**7.72(<0.01)**	1.16(0.28)	1.34(0.25)	NA
As	Location	NA	3.58(0.06)	2.22(0.14)	0.22(0.89)	0.52(0.47)	4.77(0.09)
	Site(Location)	NA	**13.70(<0.01)**	1.10(0.89)	3.94(0.14)	4.16(0.24)	6.96(0.07)
	Ageclass	**32.07(<0.01)**	**31.91(<0.01)**	**14.07(<0.01)**	0.31(0.58)	**10.47(<0.01)**	NA
	Ageclass*Location	NA	1.30(0.25)	1.24(0.27)	0.02(0.89)	3.03(0.08)	NA

Notes: Vanadium (V), chromium (Cr), nickel (Ni), and arsenic (As); **bold** indicates a significant effect, $p<0.05$.
[1] In 2011, tree swallows were sampled only near operations
[2] One hatch-year chipping sparrow was captured and sampled in 2012, therefore age class was not included in the model

Table A.2 Generalized linear model Chi-square (χ^2) statistic and level of significance (*p*) of essential metal concentrations (log-transformed values) in each year for tree swallows (TRES), Tennessee warblers (TEWA), and chipping sparrows (CHSP)

Mo	Location	NA	0.00(0.99)	1.93(0.16)	2.59(0.27)	1.19(0.27)	3.36(0.19)
	Site(Location)	NA	1.98(0.74)	3.50(0.48)	4.47(0.11)	0.07(0.99)	3.31(0.35)
	Ageclass	1.47(0.23)	**32.99(<0.01)**	2.14(0.14)	0.23(0.63)	2.05(0.15)	NA
	Ageclass*Location	NA	0.23(0.63)	1.44(0.23)	3.36(0.07)	0.41(0.52)	NA
Fe	Location	NA	0.42(0.52)	0.07(0.79)	2.22(0.33)	2.18(0.14)	0.06(0.97)
	Site(Location)	NA	2.68(0.61)	3.91(0.42)	1.07(0.59)	5.45(0.14)	0.97(0.81)
	Ageclass	**25.44(<0.01)**	**40.35(<0.01)**	0.01(0.91)	0.61(0.43)	**6.43(0.01)**	NA
	Ageclass*Location	NA	3.69(0.05)	0.07(0.78)	0.17(0.68)	0.42(0.52)	NA
Zn	Location	NA	0.66(0.42)	**5.29(0.02)**	1.65(0.44)	0.97(0.33)	1.18(0.55)
	Site(Location)	NA	1.61(0.81)	6.33(0.18)	0.17(0.92)	**11.42(<0.01)**	1.66(0.65)
	Ageclass	**13.60(<0.01)**	**24.81(<0.01)**	**14.97(<0.01)**	**3.94(0.04)**	0.87(0.35)	NA
	Ageclass*Location	NA	0.20(0.65)	0.24(0.63)	0.02(0.89)	0.11(0.74)	NA
Se	Location	NA	**4.06(0.04)**	**8.50(<0.01)**	5.69(0.06)	3.10(0.08)	**7.90(0.02)**
	Site(Location)	NA	**9.99(0.04)**	3.33(0.50)	5.63(0.06)	6.34(0.09)	5.56(0.13)
	Ageclass	**46.45(<0.01)**	**4.52(0.03)**	**59.27(<0.01)**	**12.47(<0.01)**	**29.62(<0.01)**	NA
	Ageclass*Location	NA	**7.02(<0.01)**	1.79(0.18)	1.24(0.27)	0.00(0.96)	NA

Notes: Molybdenum (Mo), iron (Fe), zinc (Zn), and selenium (Se); **bold** indicates a significant effect, $p<0.05$

[1] In 2011, tree swallows were sampled only near operations

[2] One hatch-year chipping sparrow was captured and sampled in 2012, therefore age class was not included in the model

APPENDIX B: BLOOD ELEMENT CONCENTRATIONS IN PASSERINES

Table B.1 Blood element concentrations (wet-weight) (mean ± SD) for adult and hatch-year tree swallows in 2011 and 2012

Element	Near Operations 2011		Reference 2012		Near Operations 2012	
	Adult (n = 12)	Hatch-Year (n = 13)	Adult (n = 10)	Hatch-Year (n = 16)	Adult (n = 13)	Hatch-Year (n = 22)
V (ppb)	12.24 ± 6.21	10.26 ± 8.94	487.00 ± 187.84	308.21 ± 203.86	335.05 ± 151.74	230.69 ± 114.47
Cr (ppb)	9.64 ± 3.51	10.77 ± 8.64	127.82 ± 36.22	142.32 ± 68.38	113.30 ± 18.24	194.75 ± 259.28
Ni (ppb)	16.29 ± 8.97	78.17 ± 125.01	48.20 ± 16.32	107.84 ± 58.06	58.55 ± 23.85	155.96 ± 114.55
As (ppb)	67.39 ± 21.85	39.38 ± 12.91	55.36 ± 20.67	126.72 ± 73.10	28.95 ± 12.66	73.86 ± 44.90
Sr (ppb)	91.94 ± 68.97	225.05 ± 155.23	192.36 ± 165.85	205.64 ± 116.95	167.46 ± 173.15	478.25 ± 579.93
Mo (ppm)	0.03 ± 0.01	0.04 ± 0.01	0.34 ± 0.17	0.12 ± 0.10	0.29 ± 0.12	0.10 ± 0.06
Fe (ppm)	419.73 ± 48.62	315.01 ± 59.63	608.25 ± 63.25	329.91 ± 98.49	563.78 ± 78.40	394.39 ± 130.10
Co (ppb)	12.10 ± 13.30	13.67 ± 7.47	5.07 ± 1.74	5.54 ± 2.99	5.71 ± 3.75	7.21 ± 10.17
Cu (ppm)	0.34 ± 0.11	0.43 ± 0.23	0.51 ± 0.09	0.84 ± 0.46	0.61 ± 0.20	1.03 ± 0.42
Zn (ppm)	4.27 ± 0.83	27.64 ± 48.73	5.35 ± 1.05	11.37 ± 7.97	5.94 ± 3.97	9.71 ± 3.69
Se (ppm)	1.58 ± 0.55	0.57 ± 0.23	1.68 ± 0.54	1.94 ± 0.79	0.94 ± 0.25	0.54 ± 0.35

Note: Vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

Table B.2 Blood element concentrations (wet-weight) (mean ± SD) for adult and hatch-year Tennessee warblers in 2011

Element	Potentially Exposed 2011		Near Operations 2011	
	Adult (n = 26)	Hatch-Year (n = 18)	Adult (n = 22)	Hatch-Year (n = 12)
V (ppb)	59.29 ± 38.38	54.04 ± 53.94	52.17 ± 39.77	56.03 ± 31.19
Cr (ppb)	10.01 ± 4.51	9.17 ± 4.11	11.76 ± 6.92	7.01 ± 2.68
Ni (ppb)	22.71 ± 16.59	24.25 ± 22.67	46.16 ± 67.38	11.24 ± 8.37
As (ppb)	40.64 ± 16.25	30.17 ± 23.48	55.65 ± 22.75	27.03 ± 8.28
Sr (ppb)	83.38 ± 47.35	191.88 ± 121.34	126.18 ± 74.68	172.11 ± 165.83
Mo (ppm)	0.03 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
Fe (ppm)	436.70 ± 137.93	426.73 ± 92.23	431.16 ± 84.81	409.68 ± 54.64
Co (ppb)	8.74 ± 13.09	7.11 ± 4.91	18.43 ± 32.43	3.58 ± 2.09
Cu (ppm)	0.33 ± 0.11	0.32 ± 0.11	0.36 ± 0.14	0.28 ± 0.06
Zn (ppm)	20.24 ± 27.52	5.60 ± 2.35	17.12 ± 41.45	3.86 ± 0.45
Se (ppm)	0.68 ± 0.26	0.19 ± 0.09	0.80 ± 0.40	0.28 ± 0.11

Note: Vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

Table B.3 Blood element concentrations (wet-weight) (mean ± SD) for adult and hatch-year Tennessee warblers in 2012

Element	Reference 2012		Potentially Exposed 2012		Near Operations 2012
	Adult (n = 6)	Hatch-Year (n = 12)	Adult (n = 33)	Hatch-Year (n = 17)	Adult (n = 8)
V (ppb)	706.78 ± 320.82	710.70 ± 272.62	442.26 ± 308.55	625.62 ± 343.71	267.78 ± 163.33
Cr (ppb)	231.65 ± 122.43	235.10 ± 57.37	190.47 ± 132.97	211.22 ± 139.38	126.35 ± 52.39
Ni (ppb)	231.63 ± 123.53	251.36 ± 85.39	182.22 ± 179.62	234.14 ± 111.74	81.16 ± 85.41
As (ppb)	49.90 ± 25.51	64.14 ± 27.65	55.96 ± 42.42	51.94 ± 44.42	63.75 ± 64.56
Sr (ppb)	1087.13 ± 288.36	1061.31 ± 514.83	722.74 ± 762.82	1011.88 ± 636.78	252.86 ± 470.09
Mo (ppm)	0.11 ± 0.07	0.14 ± 0.04	0.13 ± 0.06	0.12 ± 0.08	0.19 ± 0.10
Fe (ppm)	469.13 ± 123.89	453.79 ± 99.96	468.45 ± 132.17	428.89 ± 104.20	507.80 ± 72.10
Co (ppb)	13.64 ± 5.94	15.43 ± 3.72	10.68 ± 8.72	13.53 ± 6.52	8.14 ± 5.76
Cu (ppm)	1.89 ± 0.85	1.81 ± 0.69	1.30 ± 1.26	1.73 ± 0.94	0.55 ± 0.79
Zn (ppm)	7.00 ± 3.00	9.70 ± 2.90	6.77 ± 4.57	8.39 ± 4.24	5.33 ± 2.11
Se (ppm)	0.88 ± 0.39	0.55 ± 0.20	0.83 ± 0.40	0.41 ± 0.29	0.59 ± 0.49

Note: Vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

Table B.4 Blood element concentrations (wet-weight) (mean ± SD) for adult chipping sparrows in 2011

Element	Potentially Exposed 2011		Near Operations 2011	
	Adult (n = 23)	Hatch-Year (n = 10)	Adult (n = 17)	Hatch-Year (n = 4)
V (ppb)	32.68 ± 35.24	24.51 ± 29.48	39.25 ± 32.86	4.97 ± 7.82
Cr (ppb)	9.19 ± 5.38	38.26 ± 61.27	16.17 ± 23.04	147.63 ± 267.22
Ni (ppb)	19.87 ± 21.03	55.09 ± 80.12	27.89 ± 37.49	221.41 ± 398.19
As (ppb)	22.82 ± 16.75	15.91 ± 5.13	28.34 ± 18.99	13.24 ± 2.98
Sr (ppb)	84.48 ± 109.94	112.13 ± 52.38	79.68 ± 63.32	62.38 ± 28.11
Mo (ppm)	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.04 ± 0.01
Fe (ppm)	423.26 ± 93.53	346.99 ± 74.59	427.77 ± 61.29	354.03 ± 46.22
Co (ppb)	19.62 ± 58.05	5.75 ± 3.38	6.43 ± 2.65	16.59 ± 15.90
Cu (ppm)	0.36 ± 0.17	0.38 ± 0.17	0.38 ± 0.15	0.34 ± 0.06
Zn (ppm)	16.24 ± 46.34	7.19 ± 5.59	30.77 ± 95.54	4.28 ±0.65
Se (ppm)	0.41 ± 0.41	0.15 ± 0.11	0.55 ± 0.49	0.17 ± 0.07

Note: Vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

Table B.5 Blood element concentrations (wet-weight) (mean ± SD) for adult chipping sparrows in 2012

Element	Reference 2012 Adult (n = 3)	Potentially Exposed 2012 Adult (n = 7)	Near Operations 2012 Adult (n = 17)
V (ppb)	360.63 ± 9.07	300.54 ± 89.47	357.22 ± 144.21
Cr (ppb)	331.10 ± 319.01	230.84 ± 268.86	189.85 ± 168.68
Ni (ppb)	220.93 ± 278.32	141.24 ± 182.59	142.91 ± 198.57
As (ppb)	36.90 ± 25.04	37.06 ± 13.06	31.34 ± 32.58
Sr (ppb)	94.03 ± 43.44	101.03 ± 81.88	209.22 ± 338.91
Mo (ppm)	0.42 ± 0.30	0.22 ± 0.10	0.21 ± 0.13
Fe (ppm)	521.13 ± 143.21	516.90 ± 44.95	524.78 ± 63.63
Co (ppb)	11.39 ± 6.87	6.33 ± 6.06	8.18 ± 6.25
Cu (ppm)	0.69 ± 0.15	0.48 ± 0.22	0.61 ± 0.54
Zn (ppm)	6.34 ± 2.11	5.13 ± 2.27	7.04 ± 6.26
Se (ppm)	0.90 ± 0.32	0.65 ± 0.11	0.63 ± 0.26

Note: Vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

APPENDIX C: BLOOD ELEMENT CONCENTRATIONS IN PUBLISHED LITERATURE

Table C.1 Published blood element concentrations in birds

Element	Units	Data	Concentration[1]	Species	Source	Approximated Conversion[2]
V	µg/g dw	mean ± SE (range)	0.24 ± 0.025 (0.11-0.64)	Long-tailed Duck (*Clangula hyemalis*)	Franson et al. 2004	60 ppb ww
V	µg/g dw	mean ± SE (range)	0.31 ± 0.020 (0.19-0.53)	Common Eider (*Somateria mollissima*)	Franson et al. 2004	78 ppb ww
Cr	ppb ww	mean ± SE	518 ± 104	Red-winged Blackbird (*Agelaius phoeniceus*)	Tsipouraa et al. 2008	518 ppb ww
Cr	ppb ww	mean ± SE	505 ± 78.6	Marsh Wren (*Cistothorus palustris*)	Tsipouraa et al. 2008	505 ppb ww
Cr	ppb ww	mean ± SE	1030 ± 212	Tree Swallow (*Tachycineta bicolor*)	Tsipouraa et al. 2008	1030 ppb ww
Cr	µg/dl dw	mean ± SE	27.4 ± 2.4	Franklin's Gull (*Larus pipixcan*)	Burger & Gochfeld 1997	64 ppb ww
Cr	µg/dl dw	mean ± SE	35.3 ± 1.2	Herring Gull (*Larus argentatus*)	Burger & Gochfeld 1997	83 ppb ww
Ni	ppm ww	mean (95% CI)	0.32 (0.24-0.44)	European Starling (*Sturnus vulgaris*)	Adair 2002	320 ppb ww
Ni	ppm ww	mean (95% CI)	0.23 (0.017-0.31)	Bluebird (*Sialia currucoides*)	Adair 2002	230 ppb ww
Ni	ppm ww	mean (95% CI)	0.37 (0.28-0.50)	Tree Swallow (*Tachycineta bicolor*)	Adair 2002	370 ppb ww
Ni	ppm ww	mean (95% CI)	0.79 (0.30-2.04)	Chickadee (*Parus atricapillus*)	Adair 2002	790 ppb ww
Ni	ppm dw	median (range)	0.13 (0.03-0.39)	Great Tits (*Parus major*)	Dauwe et al. 2005	33 ppb ww
Ni	µg/g ww	mean ± SE	0.18 ± 0.03	Great Tits (*Parus major*)	Geens et al. 2010	180 ppb ww
Ni	µg/g ww	interquartile range	0-0.25	Mallard (*Anas platyrhynchos*)	Binkowski & Meissner 2013	250 ppb ww
Ni	µg/g dw	mean ± SD (range)	20.9 ± 12.5 (7.4-42.9)	Redknobbed Coot (*Fulica cristata*)	van Eeden & Schoonbee 1996	5225 ppb ww
Ni	µg/g dw	mean ± SD (range)	18.4 ± 14.1 (6.6-62.7)	Sacred Ibis (*Threskiornis aethiopicus*)	van Eeden & Schoonbee 1996	4600 ppb ww
Ni	µg/g dw	mean ± SD (range)	21.0 ± 22.0 (3.7-51.4)	Reed Cormorant (*Phalacrocorax africanus*)	van Eeden & Schoonbee 1996	5250 ppb ww
Ni	µg/g dw	mean ± SD (range)	11.4 ± 7.0 (5.7-33.3)	Redknobbed Coot (*Fulica cristata*)	van Eeden 2003	2850 ppb ww
Ni	µg/g dw	mean ± SD (range)	8.6 ± 5.3 (3.2-25.9)	Redknobbed Coot (*Fulica cristata*)	van Eeden 2003	2150 ppb ww
As	µg/g dw	mean ± SE (range)	0.055 ± 0.048 (0-0.18)	Zebra finches (*Taeniopygia guttata*)	Albert 2006	13.8 ppb ww

Element	Units	Data	Concentration[1]	Species	Source	Approximated Conversion[2]
As	ppb ww	mean ± SE	4.64 ± 1.98	Red-winged Blackbird (*Agelaius phoeniceus*)	Tsipouraa et al. 2008	4.6 ppb ww
As	ppb ww	mean ± SE	3.73 ± 2.61	Marsh Wren (*Cistothorus palustris*)	Tsipouraa et al. 2008	3.7 ppb ww
As	ppb ww	mean ± SE	0.95 ± 0.85	Tree Swallow (*Tachycineta bicolor*)	Tsipouraa et al. 2008	0.9 ppb ww
As	µg/dl dw	mean ± SE	1.8 ± 0.4	Franklin's Gull (*Larus pipixcan*)	Burger & Gochfeld 1997	4.2 ppb ww
As	µg/dl dw	mean ± SE	55.6 ± 7.7	Herring Gull (*Larus argentatus*)	Burger & Gochfeld 1997	131 ppb ww
As	µg/g ww	mean ± SD	0.11 ± 0.13	Pied Flycatchers (*Ficedula hypoleuca*)	Berglund & Nyholm 2011	111 ppb ww
As	µg/g ww	mean ± SD	0.33 ± 0.18	Pied Flycatchers (*Ficedula hypoleuca*)	Berglund & Nyholm 2011	333 ppb ww
As	ppm dw	median (range)	2.22 (0.14-17.6)	Great Tits (*Parus major*)	Dauwe et al. 2005	555 ppb ww
Mo	-	-	-	-	None Available	-
Fe	µg/g ww	geometric mean (range)	412.5 (243-590)	Black-crowned Night Herons (*Nycticorax nycticorax*)	Golden et al. 2003	413 ppm ww
Fe	µg/g ww	interquartile range	250-400	Mallard (*Anas platyrhynchos*)	Binkowski & Meissner 2013	400 ppm ww
Fe	µg/g ww	interquartile range	50-175	Mallard (*Anas platyrhynchos*)	Binkowski & Meissner 2013	175 ppm ww
Fe	µg/g dw	mean ± SE (range)	2086 ± 21.1 (1960-2250)	Long-tailed Duck (*Clangula hyemalis*)	Franson et al. 2004	522 ppm ww
Fe	µg/g dw	mean ± SE (range)	2061 ± 12.5 (1950-2160)	Common Eider (*Somateria mollissima*)	Franson et al. 2004	515 ppm ww
Fe	µg/g dw	mean ± SE (range)	2010 ± 18.6 (1820-2200)	Long-tailed Duck (*Clangula hyemalis*)	Franson et al. 2004	503 ppm ww
Fe	µg/g dw	mean ± SE (range)	2051 ± 14.9 (1900-2200)	Common Eider (*Somateria mollissima*)	Franson et al. 2004	513 ppm ww
Zn	ppm ww	mean (95% CI)	8.42 (7.35 -9.65)	European Starling (*Sturnus vulgaris*)	Adair 2002	8.4 ppm ww
Zn	ppm ww	mean (95% CI)	5.98 (5.24 -6.83)	Bluebird (*Sialia currucoides*)	Adair 2002	6.0 ppm ww
Zn	ppm ww	mean (95% CI)	6.51 (8.53 -7.27)	Tree Swallow (*Tachycineta bicolor*)	Adair 2002	6.5 ppm ww
Zn	ppm ww	mean (95% CI)	8.52 (5.47 -13.27)	Chickadee (*Parus atricapillus*)	Adair 2002	8.5 ppm ww
Zn	ppm dw	median (range)	21.6 (18.3-34.6)	Great Tits (*Parus major*)	Dauwe et al. 2005	5.4 ppm ww
Zn	µg/g dw	mean	26.4	American Tree Sparrow (*Spizella Arborea*)	Brumbaugh et al. 2010	6.6 ppm ww

Element	Units	Data	Concentration[1]	Species	Source	Approximated Conversion[2]
Zn	µg/g dw	mean	21.6	Common Redpoll (*Carduelis flammea*)	Brumbaugh et al. 2010	5.4 ppm ww
Zn	µg/g dw	mean ± SD	27.7 ± 10.8	Savannah Sparrow (*Passerculus sandwichensis*)	Brumbaugh et al. 2010	6.9 ppm ww
Zn	µg/g ww	mean ± SE	7.9 ± 0.7	Great Tits (*Parus major*)	Geens et al. 2010	7.9 ppm ww
Zn	µg/g ww	mean ± SD	9.1 ± 4.5	Pied Flycatchers (*Ficedula hypoleuca*)	Berglund & Nyholm 2011	9.1 ppm ww
Zn	µg/g ww	mean ± SD	8.1 ± 2.2	Pied Flycatchers (*Ficedula hypoleuca*)	Berglund & Nyholm 2011	8.1 ppm ww
Se	µg/g ww	geometric mean (range)	0.499 (0.335-0.814)	Black-crowned Night Herons (*Nycticorax nycticorax*)	Golden et al. 2003	0.5 ppm ww
Se	ng/mL	geometric mean (range)	521 (455-587)	Cattle Egret (*Bubulcus ibis*)	Alvarez et al. 2013	0.5 ppm ww
Se	ng/mL	geometric mean (range)	463 (296-873)	Purple Heron (*Ardea purpurea*)	Alvarez et al. 2013	0.5 ppm ww
Se	ng/mL	geometric mean (range)	506 (443-656)	Glossy Ibis (*Plegadis falcinellus*)	Alvarez et al. 2013	0.5 ppm ww
Se	ng/mL	geometric mean (range)	415 (323-550)	Coot (*Fulica atra*)	Alvarez et al. 2013	0.4 ppm ww
Se	ng/mL	geometric mean (range)	465 (335-646)	Shoveler (*Anas clypeata*)	Alvarez et al. 2013	0.5 ppm ww
Se	ng/mL	geometric mean (range)	262 (108-634)	Mallard (*Anas platyrhinchos*)	Alvarez et al. 2013	0.3 ppm ww
Se	µg/g ww	geometric mean (95% CI)	4.6 (4.0-5.3)	King Eiders (*Somateria spectabilis*)	Wayland et al. 2008	4.6 ppm ww
Se	µg/g dw	mean ± SE	25.1 ± 7.9	California gulls (*Larus californicus*)	Conover & Vest 2009	6.3 ppm ww

[1]Maximum values reported

[2]Converted for comparison with this study and based on an approximate 75% moisture content in bird blood (van Eeden & Schoonbee 1996; van Eeden 2003)

APPENDIX D: ELEMENT CONCENTRATIONS IN NESTLING TREE SWALLOW LIVER, KIDNEY, AND STOMACH CONTENTS

Table D.1 Liver element concentrations (wet-weight) (mean ± SD, range) for 14-day old tree swallow nestlings in 2012 and 2013

Element	Reference 2012 (n = 15)	Near Operations 2012 (n = 23)	Reference 2013 (n = 25)	Near Operations 2013 (n = 27)
V (ppb)	19.90 ± 10.11 (7.82-43.20)	24.13 ± 21.89 (7.24-116.7)	213.2 ± 72.99 (115.4-383.7)	236.4 ± 97.89 (99.9-469.1)
Cr (ppb)	220.00 ± 42.35 (155.4-287.9)	321.93 ± 78.88 (187.5-478.4)	279.8 ± 77.03 (186.3-563.9)	331.8 ± 116.45 (218.8-827.3)
Ni (ppb)	12.83 ± 4.85 (6.09-23.8)	19.45 ± 30.61 (5.1-157.5)	39.6 ± 30.23 (8.1-114.5)	35.6 ± 29.50 (9.3-126.2)
As (ppb)	23.41 ± 12.62 (1.71-50.9)	16.33 ± 11.18 (1.71-38.2)	49.4 ± 11.06 (31.4-69.0)	30.1 ± 11.57 (9.4-53.7)
Sr (ppb)	123.69 ± 66.76 (47.5-259.9)	131.52 ± 60.22 (58.1-313)	80.2 ± 39.77 (47.2-217.4)	96.6 ± 37.53 (49.1-185.2)
Mo (ppm)	0.71 ± 0.18 (0.52-1.07)	0.81 ± 0.14 (0.50-1.08)	0.70 ± 0.15 (0.24-1.00)	0.78 ± 0.11 (0.55-0.95)
Cd (ppb)	21.01 ± 7.90 (2.48-35.6)	7.81 ± 5.03 (4.16-23.8)	43.31 ± 22.86 (8.78-105.60)	19.6 ± 16.82 (2.8-62.7)
Pb (ppb)	44.6 ± 67.63 (8-270)	6.93 ± 7.90 (2-34)	9.12 ± 14.56 (2.38-75.60)	7.21 ± 8.39 (1.97-45.4)
Fe (ppm)	396.80 ± 119.52 (182.5-530.6)	526.3 ± 219.08 (179.4-1033)	391.21 ± 173.80 (106.10-681.80)	478.8 ± 196.21 (139.8-775.6)
Co (ppb)	11.22 ± 3.31 (4.14-16.6)	8.00 ± 1.96 (4.58-12.6)	15.9 ± 4.63 (5.5-24.6)	13.7 ± 8.19 (8.3-46.3)
Cu (ppm)	9.53 ± 4.59 (4.71-18.20)	8.57 ± 2.79 (5.20-18.90)	7.51 ± 4.49 (2.06-23.60)	5.87 ± 2.33 (3.66-11.80)
Zn (ppm)	35.60 ± 6.03 (25-44.7)	38.56 ± 8.58 (24.9-61.8)	25.22 ± 4.39 (19.6-40.3)	26.3 ± 3.94 (20.9-34.0)
Se (ppm)	1.87 ± 0.70 (0.33-3.26)	0.64 ± 0.24 (0.46-1.62)	1.30 ± 0.26 (0.78-1.87)	1.01 ± 0.43 (0.44-1.73)

Note: vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), cadmium (Cd), lead (Pb), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

Table D.2 Kidney element concentrations (wet-weight) (mean ± SD, range) for 14-day old tree swallow nestlings in 2012 and 2013

Element	Reference 2012 (n = 16)	Near Operations 2012 (n = 20)	Reference 2013 (n = 25)	Near Operations 2013 (n = 28)
V (ppb)	20.24 ± 5.77 (9.19-30.50)	26.88 ± 12.38 (13.1-56.8)	292.24 ± 119.85 (172.60-749.3)	329.61 ± 136.88 (99-582.1)
Cr (ppb)	289.3 ± 48.1 (231.8-381.0)	273.64 ± 61.87 (198.6-395.3)	293.64 ± 55.51 (195.4-440.5)	307.29 ± 60.31 (245.5-510)
Ni (ppb)	54.7 ± 41.7 (13.5-178.1)	60.79 ± 33.63 (28.50-152.9)	58.10 ± 30.38 (15.50-168.2)	55.92 ± 47.66 (9.46-161.50)
As (ppb)	77.1 ± 13.3 (46-95)	30.68 ± 10.63 (13.4-61.8)	53.31 ± 18.34 (8.95-84.40)	35.18 ± 16.16 (10.0-75.1)
Sr (ppb)	227.5 ± 226.9 (108.5-1024)	478.31 ± 635.76 (106.2-2449)	533.85 ± 652.96 (73-2500)	403.03 ± 372.90 (92.1-1468)
Mo (ppm)	0.59 ± 0.06 (0.49-0.70)	0.57 ± 0.09 (0.39-0.79)	0.53 ± 0.13 (0.30-0.88)	0.56 ± 0.08 (0.41-0.76)
Cd (ppb)	23.1 ± 5.50 (15.1-31.3)	7.14 ± 4.78 (3.44-22.5)	53.76 ± 18.05 (23.60-85.50)	29.53 ± 26.22 (2.17-93.90)
Pb (ppb)	16.6 ± 20.4 (3.33-85.2)	15.11 ± 14.97 (2.79-62.50)	13.83 ± 14.06 (3.29-54.50)	15.60 ± 25.12 (2.11-121)
Fe (ppm)	76.3 ± 14.9 (51.6-102.1)	87.63 ± 25.77 (45.2-144.2)	83.75 ± 65.77 (42.2-388.3)	86.49 ± 30.92 (52.0-196.3)
Co (ppb)	16.8 ± 3.2 (10.7-24.2)	11.91 ± 3.01 (8.47-18.5)	17.05 ± 7.54 (6.96-46.60)	14.05 ± 5.13 (9.04-31.60)
Cu (ppm)	3.69 ± 0.34 (3.13-4.50)	3.79 ± 0.56 (3.12-5.20)	3.71 ± 1.40 (2.47-9.26)	3.73 ± 0.49 (3.17-5.33)
Zn (ppm)	16.49 ± 2.04 (13-20.6)	16.79 ± 2.81 (13.10-26.20)	21.22 ± 5.02 (13.30-33.40)	18.29 ± 2.31 (15.40-27.00)
Se (ppm)	2.50 ± 0.51 (1.56-3.36)	0.72 ± 0.23 (0.48-1.43)	1.58 ± 0.50 (0.80-2.28)	1.19 ± 0.44 (0.53-1.89)

Note: vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), cadmium (Cd), lead (Pb), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

Table D.3 Stomach content element concentrations (dry-weight) (mean ± SD, range) for 14-day old tree swallow nestlings in 2012 and 2013

Element	Reference 2012 (n = 16)	Near Operations 2012 (n = 23)	Reference 2013 (n = 31)	Near Operations 2013 (n = 26)
V (ppb)	647.39 ± 395.55 (83.4-1608)	731.20 ± 540.26 (155.30-2449.00)	2533.55 ± 1617.57 (586.90-6459.00)	3261.96 ± 2658.46 (554.50-11600.00)
Cr (ppb)	996.73 ± 201.33 (642.3-1377)	995.87 ± 209.39 (532.70-1243.00)	1423.17 ± 711.41 (273.80-3293)	1962.36 ± 1408.36 (735.20-7154.00)
Ni (ppb)	667.76 ± 608.24 (87.9-2264)	2034.27 ± 4504.03 (163.20-16900.00)	2848.66 ± 2916.00 (51.90-13900)	6996.82 ± 10515.80 (358-40700)
As (ppb)	148.63 ± 197.00 (44.2-814.7)	105.45 ± 104.05 (6.63-472.90)	282.24 ± 152.80 (94.80-755.70)	133.29 ± 71.30 (15.30-321.10)
Sr (ppb)	8324 ± 16803 (615-67300)	19586 ± 24782 (615-69000)	17457 ± 31249 (175-150500)	9946 ± 18009 (610-69100)
Mo (ppm)	1.19 ± 0.40 (0.65-2.42)	0.86 ± 0.50 (0.19-1.86)	0.95 ± 0.40 (0.27-2.13)	1.21 ± 0.75 (0.21-3.69)
Cd (ppb)	680.36 ± 200.36 (419.90-1211.00)	190.06 ± 149.95 (53.00-625.20)	666.13 ± 291.39 (122.10-1339.00)	394.54 ± 306.99 (7.55-1000)
Pb (ppb)	131.44 ± 75.71 (38.00-370.00)	149.74 ± 99.99 (34.00-460.00)	160.12 ± 175.61 (10.10-654.90)	125.00 ± 89.64 (26.70-448.80)
Fe (ppm)	451.01 ± 624.41 (213.90-2786.00)	286.17 ± 233.19 (58.40-1101.00)	461.31 ± 443.86 (90.90-2003.00)	702.25 ± 576.87 (25.20-2304)
Co (ppb)	336.81 ± 226.89 (123.00-867-50)	176.54 ± 128.77 (20.80-522.10)	305.38 ± 252.75 (50.50-1165.00)	205.90 ± 140.02 (28.70-531.70)
Cu (ppm)	82.03 ± 71.90 (23.90-303.70)	19.24 ± 9.23 (2.21-42.80)	47.03 ± 22.20 (13.90-90.10)	30.08 ± 15.42 (3.34-71.50)
Zn (ppm)	139.24 ± 61.07 (53.00-262.30)	115.26 ± 56.10 (15.00-226.50)	90.63 ± 57.89 (12.60-235.00)	128.93 ± 71.01 (10.80-282.20)
Se (ppm)	1.45 ± 0.73 (0.19-2.78)	0.49 ± 0.28 (0.06-1.24)	1.61 ± 0.66 (0.56-2.97)	1.03 ± 0.38 (0.28-1.83)

Note: vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), cadmium (Cd), lead (Pb), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

APPENDIX E: ELEMENT CONCENTRATIONS IN INVERTEBRATE TAXA

Table E.1 Element concentrations (dry-weight) (mean ± SD, range) for Coleoptera, Culicidae, and Icnheumonoidea in 2013

	Order Coleoptera		Family Culicidae		Superfamily Ichneumonoidea	
Element	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)
V (ppb)	715.5 ± 613.5 (247.6-1410)	166.40 ± 32.50 (146.40-203.90)	757.90 ± 536.74 (155.4-1185)	166.10 ± 59.88 (103.40-222.70)	85.10 ± 32.30 (58.40-121.00)	134.10 ± 36.78 (100.20-173.20)
Cr (ppb)	1262.2 ± 701 (676.6-2039)	479.70 ± 98.16 (397.30-588.30)	1629.67 ± 531 (1143-2196)	1121.50 ± 383.64 (681.50-1386)	869.07 ± 50.87 (839.40-927.80)	1031.93 ± 340.44 (830.70-1425.00)
Ni (ppb)	758.1 ± 252.2 (539.5-1034)	238.87 ± 104.67 (173.70-359.60)	3290.57 ± 4836.3 (478-8875)	511.47 ± 79.02 (433.60-591.60)	1849.93 ± 2882.31 (159.30-5178.00)	174.73 ± 67.24 (133.00-252.30)
As (ppb)	100.3 ± 46.6 (60.9-151.7)	210.50 ± 45.23 (176.80-261.90)	65.2 ± 36.06 (25.00-94.70)	246.77 ± 346.35 (15.80-645.00)	184.93 ± 45.03 (137.10-226.50)	67.13 ± 14.14 (54.00-82.10)
Sr (ppb)	18700 ± 3639 (14500-20900)	2387 ± 1058 (1166-3044)	101033 ± 103054 (17800-216300)	28033 ± 11545 (18100-40700)	1290.00 ± 211.29 (1132.00-1530.00)	1320.67 ± 24.03 (1296.00-1344.00)
Mo (ppm)	0.41 ± 0.19 (0.20-0.57)	0.31 ± 0.12 (0.18-0.41)	2.08 ± 1.21 (0.70-2.95)	1.30 ± 0.68 (0.54-1.86)	0.95 ± 0.17 (0.79-1.13)	0.41 ± 0.07 (0.33-0.46)
Cd (ppb)	4347 ± 1313 (2893-5447)	228.57 ± 101.87 (118.10-318.80)	237.73 ± 114.83 (106.40-319.20)	167.20 ± 84.54 (96.90-261.00)	523.33 ± 146.62 (374.10-667.20)	263.10 ± 124.71 (163.60-403.00)
Pb (ppb)	60.43 ± 21.25 (37.90-80.10)	36.70 ± 2.43 (35.10-39.50)	102.43 ± 48.32 (70.30-158.00)	93.50 ± 46.00 (45.00-136.50)	30.93 ± 13.90 (15.30-41.90)	33.43 ± 2.91 (31.10-36.70)
Fe (ppm)	137.93 ± 27.93 (122.80-168.00)	130.70 ± 23.10 (107.40-153.60)	188.03 ± 95.29 (78.00-243.60)	217.87 ± 91.93 (112.00-277.50)	125.40 ± 16.86 (114.30-144.80)	123.53 ± 12.35 (109.30-131.40)
Co (ppb)	394.87 ± 374.87 (128.3-823.50)	225.10 ± 306.65 (29.30-578.50)	1662.00 ± 274.32 (1364-1904)	6724.6 ± 11410.5 (57.3-19900.0)	187.23 ± 254.87 (32.50-481.40)	113.40 ± 128.90 (35.90-262.20)
Cu (ppm)	58.87 ± 21.06 (41.80-82.40)	31.77 ± 9.67 (23.10-42.20)	11.57 ± 4.58 (6.32-14.70)	12.82 ± 6.26 (5.67-17.30)	35.17 ± 4.79 (29.70-38.60)	30.30 ± 4.86 (26.60-35.80)
Zn (ppm)	218.83 ± 74.01 (163.90-303.0)	156 ± 52.47 (105.7-210.4)	175.67 ± 87.37 (75.20-233.90)	151.60 ± 70.69 (71.00-203.10)	121.00 ± 7.20 (113.20-127.40)	113.13 ± 4.83 (110.10-118.70)
Se (ppm)	1.07 ± 0.60 (0.66-1.76)	0.78 ± 0.58 (0.12-1.16)	0.58 ± 0.42 (0.18-1.01)	0.67 ± 0.36 (0.27-0.97)	4.25 ± 1.15 (2.93-5.04)	0.58 ± 0.23 (0.37-0.82)

Note: vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), cadmium (Cd), lead (Pb), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

Table E.2 Element concentrations (dry-weight) (mean ± SD, range) for Lepidoptera, Muscomorpha, and Syrphidae in 2013

	Order Lepidoptera		Infraorder Muscomorpha		Family Syrphidae	
Element	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)
V (ppb)	72.37 ± 36.02 (35.70-107.70)	154.40 ± 67.34 (80.10-211.40)	189.27 ± 103.44 (119.40-308.10)	153.87 ± 63.56 (101.30-224.50)	194.73 ± 57.87 (129.50-239.90)	202.87 ± 99.28 (89.80-275.80)
Cr (ppb)	1055.53 ± 420.33 (755.80-1536.00)	827.70 ± 157.29 (646.10-920.80)	733.03 ± 162.81 (602.30-915.40)	769.67 ± 97.48 (659.40-844.40)	883.90 ± 154.64 (775.60-1061.00)	701.73 ± 57.51 (637.70-749.00)
Ni (ppb)	145.87 ± 43.60 (96.00-176.80)	192.27 ± 90.02 (115.40-291.30)	225.90 ± 53.04 (166.30-267.90)	264.40 ± 50.95 (205.70-297.10)	340.30 ± 129.46 (257.60-489.50)	221.90 ± 98.01 (146.20-332.60)
As (ppb)	117.63 ± 28.94 (84.30-136.30)	116.40 ± 47.75 (71.40-166.50)	228.03 ± 280.82 (64.90-552.30)	56.83 ± 9.21 (46.80-64.90)	137.13 ± 52.77 (76.20-168.10)	81.13 ± 38.31 (52.30-124.60)
Sr (ppb)	1752.67 ± 327.62 (1524-2128)	2034.67 ± 959.45 (1343.00-3130.00)	3506.33 ± 499.77 (3065-4049)	3257.67 ± 307.53 (2905.00-3470.00)	2259.00 ± 427.61 (1867.00-2715.00)	2025.67 ± 82.13 (1941.00-2105.00)
Mo (ppm)	0.51 ± 0.30 (0.32-0.86)	0.51 ± 0.17 (0.37-0.69)	0.44 ± 0.03 (0.41-0.46)	0.47 ± 0.04 (0.43-0.50)	0.34 ± 0.04 (0.30-0.37)	0.30 ± 0.04 (0.27-0.34)
Cd (ppb)	1058.20 ± 863.91 (387.30-2033.00)	227.10 ± 112.73 (133.40-352.20)	4190.00 ± 1290.49 (3048.00-5590.00)	1279.67 ± 330.34 (1002.00-1645.00)	720.67 ± 166.25 (587.80-907.10)	595.13 ± 220.98 (358.00-795.30)
Pb (ppb)	51.37 ± 17.83 (34.20-69.80)	133.93 ± 116.48 (59.90-268.20)	87.57 ± 29.94 (55.00-113.90)	83.27 ± 23.43 (63.40-109.10)	83.63 ± 36.81 (50.40-123.20)	82.10 ± 29.96 (47.90-103.70)
Fe (ppm)	74.53 ± 6.88 (66.70-79.60)	91.17 ± 11.18 (78.90-100.80)	159.53 ± 15.21 (148.60-176.90)	194.43 ± 9.82 (185.60-205.00)	201.60 ± 42.41 (153.00-231.10)	209.40 ± 61.65 (146.30-269.50)
Co (ppb)	88.23 ± 46.77 (59.60-142.20)	74.37 ± 19.30 (59.60-96.20)	247.00 ± 164.39 (77.70-406.00)	120.53 ± 8.05 (115.30-129.80)	188.03 ± 137.79 (68.00-338.50)	69.87 ± 18.55 (57.50-91.20)
Cu (ppm)	13.37 ± 1.02 (12.20-14.10)	16.67 ± 1.87 (15.30-18.80)	18.73 ± 0.55 (18.20-19.30)	19.57 ± 1.76 (18.50-21.60)	17.17 ± 1.12 (15.90-18.00)	15.73 ± 0.93 (14.70-16.50)
Zn (ppm)	266.23 ± 113.99 (185.90-396.70)	181.67 ± 22.24 (164.20-206.70)	188.73 ± 28.80 (168.50-221.70)	171.57 ± 19.52 (160.10-194.10)	121.30 ± 16.52 (109.10-140.10)	125.30 ± 9.41 (114.50-131.70)
Se (ppm)	0.84 ± 0.39 (0.50-1.26)	0.29 ± 0.08 (0.24-0.38)	1.33 ± 0.45 (0.86-1.75)	0.84 ± 0.38 (0.61-1.28)	0.35 ± 0.18 (0.24-0.56)	0.19 ± 0.04 (0.15-0.23)

Note: vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), cadmium (Cd), lead (Pb), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)

Table E.3 Element concentrations (dry-weight) (mean ± SD, range) for Tabanidae, Tipulidae, and Zygoptera in 2013

	Family Tabanidae		Family Tipulidae		Suborder Zygoptera	
Element	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)	Reference 2013 (n = 3)	Near Operations 2013 (n = 3)
V (ppb)	98.30 ± 30.10 (63.70-118.40)	240.87 ± 84.15 (156.70-325.00)	725.17 ± 327.24 (414.80-1067.00)	327.23 ± 63.91 (253.50-366.70)	171.17 ± 93.77 (94.20-275.60)	394.07 ± 181.49 (185.70-517.60)
Cr (ppb)	1069.67 ± 305.46 (859.10-1420.00)	971.93 ± 191.34 (778.40-1161.00)	1325.80 ± 458.44 (806.40-1674.00)	935.63 ± 55.59 (871.70-972.60)	1456.00 ± 349.09 (1197.00-1853.00)	1596.33 ± 416.55 (1158.00-1987.00)
Ni (ppb)	220.20 ± 39.68 (182.90-261.90)	283.23 ± 140.26 (192.70-444.80)	527.07 ± 224.23 (374.40-784.50)	333.23 ± 113.07 (254.50-462.80)	355.30 ± 201.62 (134.30-529.20)	256.10 ± 145.30 (131.50-415.70)
As (ppb)	413.30 ± 224.90 (187.80-637.60)	146.40 ± 113.35 (77.00-277.20)	42.37 ± 15.01 (33.60-59.70)	38.93 ± 7.54 (33.90-47.60)	135.43 ± 26.83 (111.10-164.20)	151.77 ± 52.66 (92.80-194.10)
Sr (ppb)	25233 ± 8116 (20300-34600)	37633 ± 14061 (23900-52000)	4778.67 ± 1838.06 (3170-6782)	4935.67 ± 369.52 (4510-5174)	3612.67 ± 932.49 (2744-4598)	3323.67 ± 695.79 (2911-4127)
Mo (ppm)	0.41 ± 0.04 (0.37-0.45)	0.39 ± 0.10 (0.30-0.49)	0.77 ± 0.09 (0.68-0.86)	0.30 ± 0.02 (0.28-0.31)	0.50 ± 0.10 (0.43-0.62)	0.38 ± 0.03 (0.36-0.41)
Cd (ppb)	847.57 ± 405.53 (543.50-1308.00)	225.13 ± 217.40 (72.20-474.00)	326.57 ± 109.58 (205.60-419.20)	36.33 ± 18.53 (16.50-53.20)	1248.33 ± 171.24 (1087.00-1428.00)	372.83 ± 220.30 (157.30-597.60)
Pb (ppb)	84.90 ± 20.22 (72.00-108.20)	87.33 ± 17.88 (73.80-107.60)	78.27 ± 53.37 (44.60-139.80)	64.53 ± 37.35 (28.40-103.00)	175.13 ± 124.93 (43.60-292.20)	92.93 ± 100.99 (23.60-208.80)
Fe (ppm)	215.17 ± 7.20 (209.30-223.20)	248.33 ± 20.03 (233.00-271.00)	198.40 ± 25.40 (175.30-225.60)	171.13 ± 29.90 (138.00-196.10)	156.30 ± 20.62 (144.00-180.10)	154.33 ± 22.84 (139.20-180.60)
Co (ppb)	204.43 ± 161.66 (54.50-375.70)	575.10 ± 840.65 (56.10-1545.00)	512.53 ± 347.81 (297.30-913.80)	831.27 ± 1345.79 (30.00-2385.00)	67.63 ± 42.90 (34.90-116.20)	30.80 ± 1.87 (29.10-32.80)
Cu (ppm)	21.67 ± 2.36 (19.00-23.50)	19.30 ± 1.57 (17.90-21.00)	24.03 ± 3.42 (20.10-26.30)	14.57 ± 1.50 (12.90-15.80)	29.20 ± 7.11 (23.60-37.20)	19.83 ± 2.30 (17.60-22.20)
Zn (ppm)	348.87 ± 70.15 (270.40-405.50)	367.00 ± 186.04 (257.40-581.80)	201.60 ± 40.79 (168.60-247.20)	125.80 ± 15.76 (116.50-144.00)	176.77 ± 61.80 (127.80-246.20)	136.43 ± 50.03 (95.50-192.20)
Se (ppm)	0.96 ± 0.36 (0.65-1.36)	0.62 ± 0.26 (0.40-0.90)	0.74 ± 0.15 (0.56-0.84)	0.91 ± 0.24 (0.67-1.14)	2.04 ± 0.32 (1.68-2.29)	1.21 ± 0.25 (0.98-1.48)

Note: vanadium (V), chromium (Cr), nickel (Ni), arsenic (As), strontium (Sr), molybdenum (Mo), cadmium (Cd), lead (Pb), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn) and selenium (Se)