BIOMONITORING AND ASSESSMENT OF AIRBORNE FLUORIDE FROM FERTILIZER PRODUCTION

By

Yihan Zhao

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Land Reclamation and Remediation

Department of Renewable Resources

University of Alberta

© Yihan Zhao, 2017

ABSTRACT

Phosphogypsum (PG) is an acidic by-product created during phosphate fertilizer production (Rutherford et al 1994). In open or operational PG stacks, airborne fluorides are emitted from phosphogypsum process water pond surface evaporation or particulate fluoride that can be transported as fluoride containing dust. This two year research project aimed to improve the understanding of effects of airborne fluoride on plants. Various plant species were sampled in the vicinity of the Agrium Redwater PG stack since 2008 throughout the growing season. In 2015 and 2016, a biomonitoring system was developed to standardize greenhouse cultivation, field exposure and plant harvest. *Lolium perenne* L. (perennial rye grass) was selected as a bioindicator and exposed in different locations surrounding the emission source. Biomass was harvested for fluoride analysis.

Distance from the source had the greatest influence on internal fluoride accumulation of perennial rye grass, followed by exposure time, then wind direction. Internal fluoride concentrations in perennial rye grass decreased exponentially with distance from the source, with a sharp drop within 500 m. Although age had no significant impact on internal fluoride accumulation of perennial rye grass, with longer exposure there were greater differences among three ages of plants. Wind direction may have considerable impacts on internal fluoride concentrations in perennial rye grass, with effect becoming weaker with the increasing distance from the source. From long term monitoring, the monthly pattern of total fluoride in forage was consistent year by year, peaking in fall. Concentration of soluble fluorides in PG ponds, air temperature and precipitation may contribute to total fluoride variation in forage over time. The latter two may have significant impacts on external fluoride accumulations. On average 32.3 % of total fluoride can be washed off plans biomass, approximation amount of external fluoride, and indicating that most fluoride in forage was internal.

Biomonitoring can be a cost effective approach for detecting long term environmental impacts of airborne pollution and this research can be applied as a standardized biomonitoring method for airborne fluoride with plant species for Alberta which can be used in various reclamation and management scenarios.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere gratitude to my supervisor Dr M Anne Naeth, who gave me an opportunity to pursue my dream. I am extremely grateful for her constant support, encouragement and guidance during my study. I am truly appreciative for everything I learnt and get inspired from you, your vision, your passion, your confidence, your leadership and your professionalism. You are a role model and hero for me, and I feel so lucky and honoured to be a Naethian. It made Canada a second home for me, and made my master study an extraordinary and pleasant journey.

I thank Dr Connie Nichol, my supervisory committee member and industry contact. Thank you for your time, support, advice, insight, patience and invaluable feedback to this research project. It has been such a pleasure to work with you!

Special thanks to Sarah Wilkinson for your advice with the experimental design, field guidance and help in technical writing. I thank Michal Guzowski for everything you helped me with and your input for my time in the Land Reclamation International Graduate School (LRIGS) that made it such a wonderful experience. I thank Stacy Campbell-Court for all your help, kindness and lending a hand in my greenhouse experiment. I thank Leanne McKinnon for your administrative support. I thank all my graduate student helpers, Jaime Aguilar Rojas, Jasmine Lamarre and Martin Robinson. I thank the undergraduate research assistants Adam Iverson, Ashley Kocsis, Marissa Gutstch and Rachel Whitehouse who helped me for long hours in the field. I thank all other my past and present fellow graduate students in the Naethian family, Alison Murata, Autumn Watkinson, Caitlin Low, Jenna Abourizk, Laurie Frerichs, Valerie Miller, Stephanie Ibsen and Sarah Ficko.

Thank you to the China Scholarship Council (CSC) and the Land Reclamation International Graduate School (LRIGS) through the NSERC CREATE program and Agrium Inc. for providing scholarship and research funding.

To my family, I thank my parents for unconditional love and support for everything. To Dr Xianli Wang, thank you for your endless help and encouragement during difficult times. You have always shown me the important qualifications of a good scientist. To my boyfriend, Chang, thank you for being by my side and continuously inspiring me to overcome challenges.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. BACKGROUND

1. FLUORIDE EMISSION FROM FERTILIZER PRODUCTION

1.1. Phosphogypsum Production

Phosphogypsum (PG) is an acidic by-product of phosphate fertilizer production (Rutherford et al 1994). For every tonne of phosphoric acid there will be 5 tonnes of PG produced (Thorne 1990). Thus, large quantities of PG are produced annually in at least 80 countries (FIPR 2006). Approximately 15 % of world PG production is recycled as construction materials, agricultural fertilizers or soil stabilization amendments; most are put into large stockpiles exposed to weathering (Tayibi et al 2009). Canada has PG stacks in Alberta, British Columbia, Ontario, Quebec and New Brunswick (Thorne 1990). The largest and only active stack is at Agrium Redwater Fertilizer Operations in Alberta (Nichol 2007), with approximately 47 million tonnes of PG, occupying 275 hectares (Agrium Incorporated 2014).

During production of phosphoric acid for phosphate fertilizer, PG is formed when phosphate rock (fluorapatite) is mixed and digested by sulphuric acid (H_2SO_4) by the following simplified reaction: $Ca_{10}(PO_4)_6F_2CaCO_3 + 11H_2SO_4 = 11CaSO_4.nH_2O + 6H_3PO_4 + 2HF + CO_2 + H_2O$, and $SiO_2 + 4HF = SiF_4 + 2H_2O$ (Weinstein and Davidson 2004).This is the most common method, called the wet process. End products are mostly phosphoric acid (H_3PO_4) and gypsum ($CaSO_4.nH_2O$), with the latter slurries being pumped and stockpiled in large piles, known as PG stacks, containing gypsum (> 90 %), fluorides, residual acids, sulphate ions, trace metals and organic matter (Rutherford et al 1995, Tayibi et al 2009). PG is considered acidic (pH < 3) due to the residual acids. Typically, PG has a large proportion of medium (0.250 to 0.045 mm) and fine (< 0.045 mm) diameter size particles (Rutherford et al 1994). Process water ponds are usually accompanied by growing stacks and are created on top of them, serving as a reservoir for storing and providing process water under dry and wet weather conditions (Weinstein and Davidson 2004).

1.2. Fluoride Emissions

In Canada, anthropogenic airborne fluoride emissions are monitored by the Environment Canada National Pollutant Release Inventory program. Approximately 3,226 tonnes of hydrogen fluoride are released annually (Environment Canada 2014). Phosphate fertilizer production accounts for 48 % of annual industrial releases, twice that of the second highest source (Environment Canada 1993). Main industry sources of airborne fluoride are the phosphate fertilizer industry; aluminium smelting; petroleum refining; glass, fiberglass, brick, tile, pottery, cement, iron and steel manufacturing; and coal combustion (Weinstein and Davidson 2004).

The phosphate fertilizer industry is one of the biggest sources of PG, resulting in fluoride emissions during storage (Weinstein and Davison 2004). Phosphogypsum management is challenging as it requires large areas for storage and causes fluoride emissions to the atmosphere, water and soil. In open or operational stacks, airborne fluorides can be emitted to the air through PG process pond water surface evaporation and particulate fluoride from transportation of fluoride containing dust in PG storage area (Rutherford et al 1994). The fluoride gases are primarily hydrogen fluoride (HF) from the PG pond water and very low concentrations of silicon tetrafluoride (SiF_4) from drier surfaces (Rutherford et al 1994, LaCosse et al 1999). In process ponds water, soluble fluoride concentrations commonly range from 4 to 14 g/L (Weinstein and Davidson 2004). However, it is difficult to provide accurate evaporation rates due to variations in pond water composition and temperature. A representative study estimated that there is approximately 0.10 kg of fluoride coming from operational process ponds per hectare per day (Wissa 2002).

2. FLUORIDE MOVEMENT, DEPOSITION, UPTAKE AND FATE

2.1. Fluoride Movement And Dispersal

Gases and particles of fluoride can be carried by wind, easily removing or depositing fluoride on rough structures (Rutherford et al 1994). Wind can lead to strong fluctuations in fluoride concentrations at ground level even if emission rates are relatively constant from the source (Franzaring et al 2007). The higher the wind speed, the further the emissions can be carried away (Weinstein and Davison 2004). Wind driven fluoride is able to reach the adjacent environment of the PG stack, and thus wind can enlarge the impacted zone with less soluble and more mobile forms of fluoride.

Biomonitoring has been conducted to assess spatial movements of airborne fluoride, with results indicating distance from the emission source significantly influences fluoride dispersion. For example, a study on the movement of hydrogen fluoride shows that fluoride concentrations steeply decrease with increasing distance from the emission source (Rodriguez et al 2012). A model was developed by Real et al (2003) to delineate the fluoride dispersal in the vicinity of a fluoride pollution generating factory, and they found that the highest fluoride content was close to the factory and that no severe emissions occurred further than 2 km from the source.

2.2. Fluoride Deposition

The plant canopy or its leaves can slow the winds that are carrying fluoride gases or particles, and produce a still air layer surrounding the canopy and leaves (Weinstein and Davison 2004). This provides opportunities for fluoride gas and particle deposition on leaf surfaces, which may stay or be lost over time. There are two types of deposition, dry and wet. Dry deposition occurs when fluoride lands on a surface or is taken up through stomata via gas exchange. Different surfaces (leaf, soil, lake) have different adsorption capacities. Usually, wet surfaces can absorb more fluoride than dry surfaces; thus wet leaves after a rain have a higher capacity for uptake than dry leaves. However, rainfall can reduce fluoride wet deposition. Wet deposition occurs when the fluoride is removed from the deposition process by rain, snow and mist. When hydrogen fluoride is emitted into the air, it will dissolve and form hydrofluoric acid in atmospheric water; then it will be removed by wet deposition from the air (ATSDR 2003) which will then eventually reduce fluorides.

2.3. Fluoride Uptake Pathways

Studies on fluoride uptake by plants are extensive and the process is well understood. Weinstein and Davison (2004) found two main pathways by which fluorides enter plants. The first is through biological membranes via gas exchange. When fluoride gas is transported via hydrogen fluoride non-ionic diffusion (HF) and lands on leaves; it diffuses through the leaf boundary layer, then through stomata into the space between guard cells. The second pathway is from soil and water via the root system through passive diffusion, including nutrient uptake and dissociated fluoride ion (F^-) exchange. Hydrogen fluoride is a neutral molecule that can penetrate cell membranes faster than the dissociated fluoride ion (F^-), thus intracellular intake of hydrogen fluoride is more pronounced (Baunthiyal and Ranghar 2014).

After fluoride penetrates the cell walls of vascular plant leaves, it is transported rapidly and moves towards the higher concentration gradients of transpiration streams (Weinstein and Davison 2004). Fluoride accumulates at the few mm near the leaf tip and margins where evaporation is greatest (Kamaluddin and Zwiazek 2003) and has hundreds of times more fluoride than other parts of plants (Weinstein and Davison 2004). After fluoride accumulates in plants, there is little or no further translocation from leaf to leaf and to other organs or plant parts, such as stems and roots (Ledbetter et al 1960). However, there is still controversy around whether movement wihtin the plant occurs or not (Keller 1974).

Fluoride uptake occurs through stomatal pores then goes into solution and accumulates in plants; it is time consuming, taking hours or days, depending on rate of water movement and leaf area (Weinstein and Davison 2004). The pollution pattern of fluoride shows significant changes over weeks and days of time (Blakemore 1978, Davison et al 1979), although plants do not normally respond to short term (minutes) exposure (Weinstein and Davison 2004).

Age of plants affects fluoride uptake and accumulation, although few published studies investigated age effects. Generally, plant sensitivity decreases with age (Weinstein and Davison 2004). Some researchers found higher fluoride concentrations in young plants, while others found higher concentrations in older plants. For example, Junior et al (2008) found no significant difference in leaves of different ages in *Bidens pilosa* L (blackjack), *Ipomoea cairica* (L) Sweet (Cairo morning glory) and *Calopogonium mucunoides* Desv (Calopo) at distances of 5.4 and 10.5 km from the source of the fluoride emission. However, with the same species of *Calopogonium mucunoides* at a closer distance from the source of 2.9 km, significantly higher concentrations of fluorides were detected in younger leaves. Another study found that fluoride in older needles of *Pinus radiata* L (radiata pine) was significantly greater than that in younger needles (Rodriguez et al 2012). Similarly, Atasoy et al (2016) found fluoride concentrations in leaves and stems increased with aging.

2.4. Physiological And Biochemical Response To Fluoride

Fluoride interferes with almost all physiological and biochemical processes in plants, including enzyme activities in the plant cells, photosynthesis, gas exchange and mitochondrial respiration (Weinstein and Davison 2004, Baunthiyal and Ranghar 2014). Fluoride inhibits many enzyme activities (Mendoza-Schulz et al 2009), specifically by binding functional amino acid groups in the active centre of the enzyme (Barbier et al 2010). The signaling pathways that are engaged in plant cell proliferation and apoptosis (cell death) are interrupted by the inhibition of protein synthesis and secretion (Baunthiyal and Ranghar 2014). The increased oxidative stress results in degradation of plant cellular membranes and reduction of mitochondrial activity. The mechanisms of respiration inhibition and stimulation that are caused by fluoride is strongly associated with the inhibition of enzymes of respiration and with an uncoupling of phosphorylation. Many plant respiratory enzymes are very sensitive to the fluorides, such as succinate, malate and NADH dehydrogenases.

The mechanism by which fluoride affects photosynthesis is well studied. It is mainly because fluoride reduces chlorophyll synthesis, degrades chloroplasts and inhibits Hills reaction (Yamauchi et al 1983). Fluoride influences adenotriphosphate synthase, ribulose bisphosphate carboxylase oxygenase and sucrose synthase in chloroplasts (Baunthiyal and Sharma 2014). Fluoride affects the photosynthetic electron transport chain. Photosystem-I (PS-I) electron transport rate increases as fluoride inhibits photosystem-II (PS-II) electron transport, a possible mechanism for fluoride toxicity (Ballantyne 1991). Accumulation during early plant growth reduces Chl-a, Chl-b and total chlorophyll during photosynthesis (Baunthiyal and Sharma 2014).

Fluoride's ultra-structural and structural damaging of tissues and cells is due to its accumulation in leaves, which could affect stomatal conductance and gas exchange of plants (Robinson et al 1998, Alves et al 2008). For fluoride induced visible damage, metabolic and physiological effects could be explained by the interaction with calcium (Ca^{2+}) in the guard cells (Abdallah et al 2006). Since fluoride has a high ability to react with free calcium (Ca^{2+}) and forms calcium fluoride (CaF_2) as the main compound, the decreased calcium is likely to detract from stomatal control, therefore triggering closure of the stomata (Peiter et al 2005).

Mechanisms of respiration inhibition and stimulation caused by fluoride are strongly associated with inhibition of enzymes of respiration and uncoupling of phosphorylation (Weinstein and Davison 2004). Inhibition depends on age of plant tissue since the pathway may shift from glycolysis to pentose phosphate (Gibbs and Beevers 1955) and some glycolytic enzymes could be more sensitive to fluoride with plant aging (Weinstein and Davison 2004).

2.5. Fate Of Fluoride

Eventually, after leaves die from high airborne fluoride concentrations, fluoride will be transferred to soil where it is strongly adsorbed (Weinstein and Davison 2004). An estimated 1 $\mu g/m^3$ of airborne fluoride may cause 0.63 to 2.52 kg fluoride deposition in soils per ha per year; however, leaching is slow. In natural or undisturbed soils, deposited fluoride may sequester in the upper cm of soil under the surface (Loganathan et al 2001); when soil is disturbed, as with plowing, fluoride may be sequestered at 30 to 50 cm depth (Weinstein and Davison 2004).

Fluoride can remain in soils for years. Omueti and Jones (1977) found fluoride added to soil between 1904 and 1924 remained after 67 years, with a mean loss rate of 2.5 mg/kg/year. At a site 700 m from an eight year old fertilizer factory, where airborne fluoride concentrated at 4 to 5 $\mu g/m^3$, increase in fluoride of the soil humus layer was approximately 1,600 mg/kg (Sidhu 1979).

3. FLUORIDE ENVIRONMENTAL EFFECTS AND STANDARD

3.1. Airborne Fluoride Effects

There are two main environmental effects of airborne fluorides. The primary effect is damage in plants by fluoride accumulation (Weinstein and Davison 2004). Acute fluoride injury occurs if fluoride inactivation and translocation cannot be as rapid as absorption in a short time under high atmospheric concentrations, thus causing leaf lesions (McCormac 2012). Chronic injury happens when plants uptake, translocate and accumulate fluorides slowly, resulting in cell death. This is because fluoride in plants can be accumulated with time and cause severe damage; typically, the first symptoms are marginal and interveinal chlorosis (acute or chronic) when fluoride accumulation exceeds a threshold for the species (Weinstein and Davison 2004).

The second effect is severe damage to herbivores (livestock, wildlife) from fluoride in forages (Weinstein and Davison 2004). Ingestion of all fluoride forms accumulated or deposited on leaves outer surfaces can have toxic effects on herbivores, such as fluorosis (Wissa 2002, Weinstein and Davison 2004). Signs of fluorosis generally occur in teeth, bones and soft tissues or organs, referred to dental, skeletal and non-skeletal fluorosis, respectively (Choubisa 2012).

3.2. Ambient Fluoride Standard

Unlike sulphur and nitrogen, fluoride is not an essential element for plants and it is one to three fold more toxic to plants than other common pollutants, such as ozone (O_3) and sulfur dioxide (SO_2) (Weinstein 1977). To protect wildlife and livestock, reference concentrations for ambient fluoride and in forage materials are developed. Canadian ambient air quality regulatory values are 1.1 $\mu g/m^3$ for a 24 hour average, 0.5 $\mu g/m^3$ for a 7 day average (CCME 1999). Alberta maximum fluoride values are 0.49 $\mu g/m^3$ for an hour average; and 35 μg/g for forage materials (dry weight) for the growing season, 60 μg/g for two consecutive months and 80 μg/g for any single 30 day period (Alberta Environment 2016).

4. FLUORIDE MONITORING

4.1. Analytical Instruments Limitation

Monitoring airborne fluoride is usually with physical and chemical instruments. The National Institute of Occupational Safety and Health (NOISH) developed standard air monitoring methods for hydrogen fluoride that follow analytical techniques based on active or pump and tube sampling. Method 7902 uses extraction and analysis, testing airborne hydrogen fluoride by collecting it on cellulose ester membrane filters with sodium carbonate treated cellulose pads (NIOSH 1994a). Method 7903 uses silica sorbent tubes with glass fibre filters for collection before desorbing with a bicarbonate / carbonate buffer solution and ion chromatography analysis. Method 7906 uses extraction and analysis to collect hydrogen fluoride on cellulose ester membrane filters with cellulose pads treated with sodium carbonate (NIOSH 1994b).

The biggest limitations of analytical devices for monitoring hydrogen fluoride are technical and financial (Franzaring et al 2007). Although there are methods for determining airborne fluoride, they are expensive, lack sensitivity, are labour intensive and require power supplies. The current commonly used devices such as laser detection, are feasible for detecting the gas hydrogen fluoride on a single site but may be limited by distance, from 5 to 120 m (Senscient 2016). Automated measurement of continuous airborne fluoride is not commercially available (Junior et al 2008). Information from fluoride measurement is not usually sufficient to predict ecological effects (Weinstein and Davison 2004). Due to these limitations of monitoring airborne fluoride, researchers suggested using bioindicators to monitor and investigate the effect of fluoride.

4.2. Fluoride Biomonitoring

Biomonitoring is more cost effective than analytical instruments involving surveys, and is suitable for long term impact monitoring of fluoride emissions in plants (Weinstein et al 1990). It may be effective to monitor fluoride accumulation of plants and detect potential environmental impacts in areas adjacent the emission source. This may help increase public and consumer trust in industrial operations known to emit fluoride to the atmosphere (Franzaring et al 2007).

A standardised biomonitoring method was developed in the 1960s, and used to monitor fluoride in 1974 (VDI 2003). In 1978 this method was considered a guideline by the Association of Germany Engineers, the Verein Deutscher Ingenieure (VDI), and further developed (VDI 2003). The principle of the standardized grass culture is based on exposing plants in the field and measuring accumulated pollutants or contaminants in the biomass produced during exposure. The procedures include greenhouse cultivation, field exposure and plant harvest which are highly standardized. Therefore, accumulation of pollutant concentrations in plants are only affected by air pollution present, climate conditions during exposure and plant growth (biomass production) of receptor plants. This standardized grass culture biomonitoring system has been used for decades in many countries, such as Tunisia, German, Spain, Brazil and Argentina.

Generally, plants, animals and other groups of organisms can be used as bioindicators for monitoring fluorides, but plants are usually the first option since they are easily widespread and common enough to provide a long term pattern of fluoride effects (Weinstein and Davison 2004). A bioindicator plant is a species that could provide a characteristic and predictable response in a region or habitat under different environmental and climate conditions (Gibert 1968, Mellanby 2000). Best bioindicators for detecting airborne pollutants are plants most susceptible, sensitive or tolerant to fluoride (Arndt 2001).

Studies found many plant species are suitable bioindicators for monitoring fluorides. For example, *Pinus sylvestris* L (Scots pine) was used in Finland (Rozhkov and Mikhailova 1993). Mezghani et al (2005) used five tree species, *Olea europaea* L (olive tree)*, Amygdalis communis* L (almond tree), *Ficus carica* L. (fig tree), *Prunus harmonica* L. (apricot tree) and *Rosa agrestis* Savi (rose bush) for airborne fluoride monitoring near a phosphate fertilizer plant in Tunisia by analyzing fluoride contents in leaves. Two native mosses, *Hypnum cupressiforme* Hedw (hypnum moss) and *Scleropodium purum* (Hedw) Limpr. (neat feather moss) were used to monitor fluoride concentrations near an aluminium smelter in Spain (Real et al 2003). It is challenging to select the best bioindicators since they can be very regionally dependent; meaning some plant species may be less sensitive to fluoride at one region than at another region, resulting from different climate and soil conditions. For example, this is the case with *Eucalyptus globulus* Labill (Tasmanian blue gum) which can be used as an effective bioindicator (Doley 1986).

Herbaceous vegetation has successfully been applied in many source oriented air quality biomonitoring projects world wide. They include mostly fast growing plant species, with easy to control factors such as age of plants. Gladiolus species and other members of the *Liliaceae* (lily) family such as *Tulipa gesnecriana* L (tulip) and *Narcissus tazeta* L (narcissus) are well studied and have been used as sensitive bioindicators for monitoring fluoride over decades (Laurie et al 1949, Hendrix and Hall 1958, Hitchcock et al 1962). Tolerant bioindicators are also well studied, such as members of the *Diapeniaceae, Leguminosae, Malvaceae, Melastomataceae, Rubiaceae, Theaceae* and *Ulmaceae* families (Weinstein and Davison 2004).

5. KNOWLEDGE GAPS AND RESEARCH OBJECTIVES

Many studies have used plants in situ, although this approach does not provide any information about sensitivity or repeatability of measurements, a basic requirement in assessing the optimal experimental procedure with plants. It is difficult to determine pollution induced accumulation in plants due to many disturbance factors. For example, plants in situ may not be at the same age of development with the same growing conditions, such as soil, fertilizer and water supply, and thus cannot reflect the changes to a certain exposure time accurately. Therefore, it is necessary to develop a standardized protocol for plant species for exposure, sampling and analysis.

No standardized guidelines have been developed for Canada for biomonitoring air pollution by plant species. Verein Deutscher Ingenieure (VDI) can be practically referred as a guideline and applied in Canada. However, most studies that used VDI do not consider the influence of distance from the emission source, exposure duration and age on fluoride accumulation of plants as there are only a few records available regarding these aspects. The VDI method could be adjusted accordingly in this study to close these gaps and have a better understand of fluoride environmental effects.

The main objective of the research is to investigate historical fluoride accumulation patterns of emissions from a phosphate fertilizer production plant and PG stacks on nearby vegetation; to assess effectiveness of perennial rye grass as a bioindicator reflecting the environmental impacts of airborne fluoride; and to fill the research gaps and have a better understanding of the influence of wind, exposure duration, distance from emission source and age on fluoride accumulation in plants to quantify bioavailability of airborne fluoride. This allows for evaluation of ecological risks and provides information on the air emission patterns around the fertilizer production facility and for developing a biomonitoring protocol for airborne fluoride with plant species for Alberta.

II. HISTORICAL FLUORIDE BIOMONITORING

1. INTRODUCTION

Phosphogypsum (PG) is an acidic by-product created during phosphate fertilizer production (Rutherford et al 1994). During phosphate fertilizer production phosphoric acid (H_3PO_4) and gypsum ($CaSO_4.nH_2O$) are generated as end products, with the latter slurries being pumped and stockpiled in large piles, known as PG stacks (Rutherford et al 1995). These stacks are usually associated with cooling, surge and storage ponds which serve as reservoirs for storing and providing process water under dry and wet weather conditions (Weinstein and Davidson 2004). In open or operational PG stacks, fluoride gases are emitted into the air as a function of process water pond surface evaporation and particulate fluoride transportation (Rutherford et al 1994). Generally, both gasses and particles of fluoride can be carried by wind, which is a very efficient way to remove or deposit fluoride on rough structures.

There are two main environmental effects of airborne fluorides. The primary effect is the damage to plants by fluoride accumulation, and typically the first symptom is marginal and interveinal chlorosis (acute or chronic) when fluoride accumulation exceeds a threshold for the species (Weinstein and Davison 2004). The second effect is toxicity to herbivores (livestock and wildlife) known as fluorosis, due to ingestion of fluoride contained in forage crops (Wissa 2002, Weinstein and Davison 2004). The signs of fluorosis generally occur in teeth, bones and soft tissues or organs (Choubisa 2012).

2. RESEARCH OBJECTIVES

The general objective of this research is to increase the knowledge and understanding of effects of airborne fluoride on vegetation in the vicinity of Agrium Redwater Operations. The research focused on historical long term fluoride accumulation patterns in nearby vegetation. Specific objectives were as follows.

- Determine what factors influence fluoride accumulation in selected plant species over time.
- Determine whether fluoride concentrations in selected plant species changes over time.
- Determine relationships between internal and external fluoride in forage.
- Determine whether selected plant species will respond differently to factors that affect fluoride accumulation spatially and temporally.

3. MATERIALS AND METHODS

3.1. Research Site Description

The fluoride source for this research was emitted from the large PG stack at Agrium Redwater Fertilizer Operations, located approximately 48 km northeast of Edmonton Alberta (53°50'56"N and 113°5'26"W). The fertilizer plant occupies 372 ha along the North Saskatchewan River including cooling ponds, surge ponds and six storage ponds (Figure 2.1). The plant is the sole source of phosphate fertilizer production in Canada. Until mid 2013 the phosphate rock was sourced from Agrium's phosphate mine near Kapuskasing Ontario; since 2013 the source has been changed to Morocco. The PG stack at Redwater has operated for approximately 48 years (since 1969), accumulating approximately 47 million tonnes of PG, stored in 275 ha area.

3.2. Vegetation Sampling

To monitor potential environmental impacts of fluoride on vegetation in areas adjacent the Redwater facility, a fluoride monitoring program has been conducted annually for several years. The program consists of biweekly forage sampling and annual vegetation surveys which were conducted by Agrium personnel and/or consultants in the growing season. It was done since 2005 using methods of the Montana Department of Environmental Quality (Rule 17.8.230).

Since Agrium sampled forage from representative areas that may potentially serve as pasture, most sampling occurred east of the plant across the North Saskatoon River. Sample locations changed over the years, at different directions 1,245 m to 3,629 m from the PG stack. Distance refers to distance between a sample location and the closest PG stack boundary. Sample locations changed mainly due to accessibility (construction) and land use. Historical forage sample locations are shown in Figure 2.2 and vegetation sample locations in Figure 2.3.

Sampling of forage species typically was in early June or May to late October with a minimum 12 day interval each year. Start date was determined by weather and forage growth. The vegetation survey was usually in August. In each sample location, W, X or Z shaped patterns were used for sampling, traversing the full plot area. A zig-zag pattern was used for road allowances. At regularly spaced distances, at 3 cm above ground surface, samples were collected by cutting with scissors to procure at least 25 clippings per site. Composite clippings (100 to 150 g) were placed in large ziploc bags, kept in coolers in the field, then stored in a laboratory refrigerator at 4 ± 2 ºC before delivering to a commercial laboratory for analysis.

3.3. Fluoride Analyses

Total fluoride includes internal fluoride and any fluoride on the external part of the plant; total fluoride results result from analyzing unwashed samples. Internal fluoride refers to samples that have been washed, so fluoride that is contained in particles and accumulates on plant surfaces can be removed. Washing does not remove internal fluoride deposited in plant cells.

The wash solution (0.05 % liquinox and 0.05 % tetrasodium ethylenediamine tetraacetate) and wash process were standardized at Agrium's laboratory (Agrium Fertilizer Laboratory Services 2010, Agrium Fertilizer Laboratory Services 2012). A 200 ml wash solution was prepared in a 500 ml polyethylene bottle and vegetation samples were washed with gentle agitation pouring water from the polyethylene bottle for 30 seconds. A sieve over the sink was used to collect samples and drain the wash solution before transferring the samples to a clean 1,000 ml beaker filled with 700 ml deionized water. Samples were rinsed for 10 seconds, then collected by sieve and drained. The rinsing and draining procedure was repeated two more times with clean 1,000 ml beakers until no soap bubbles were present.

Washed and unwashed samples were delivered to Maxxam Analytics in Edmonton and all samples were oven dried and finely ground in preparation for analysis. Fluoride analysis was conducted using sodium hydroxide fusion (Sager 1987) or instrumental neutron activation analysis (Knight et al 1977) before 2015, after which samples were analysed by ion selective electrode (Meyerhoff and Opdycke 1986). All forage fluoride analytical values refer to total fluoride, and all vegetation fluoride monitoring results refers to internal fluoride.

3.4. Data Collection And Processing

Meteorological data, including wind speed, wind direction, temperature and precipitation from 2008 to 2016 were collected from two stations. Continuous data, such as outdoor air temperature (ºC), wind speed (km/h) and wind direction (degrees) were obtained from the Fort Air Partnership Ambient Air Monitoring Station (CASA 2016). The station is located at the main gate of Agrium Redwater Fertilizer Operations, less than 5 km to the furthest sample location. Precipitation data (mm) were obtained from Radway station via Alberta Agriculture Agroclimatic Information Service website before the Redwater Industrial station had data available in 2016 (AARD 2016). Radway station is approximately 30 km northeast of the Redwater site.

Fluoride laboratory and Redwater PG pond soluble fluoride data were procured from Agrium Inc. Forage fluoride data were from 2008 to 2016 and internal fluoride from 2008 to 2012.

Vegetation fluoride data (internal fluoride) from 2008 to 2012 was organized after procurement from Agrium. For the purpose of satisfying the minimum sample size requirement of statistical tests, vegetation sampling sites were merged into four main locations based on wind direction (downwind, upwind) and distance (D1, D2). The locations include Downwind-D1, Downwind-D2, Upwind-D1 and Upwind-D2. Downwind locations refer to the area south and east of the PG stack, and upwind locations refer to the area north and west of the PG stack. Distances within 1,650 m of the stack were D1, and further distances were D2.

Sampled species differed over the months and years of sample collection. Forage was a mix of common grass in the area, including *Leymus innovatus* (Beal) Pilg (hairy wild rye), *Bromus inermis* Leyss (smooth brome) and *Phalaris arundinacea* L (reed canary grass). Crop species were *Hordeum vulgare* L (barley), *Triticum aestivum* L (wheat) and *Brassica napus* L (canola). Tree species were mainly *Populus tremuloides* Michx (trembling aspen), *Populus balsamifera* L (balsam poplar), *Populus deltoides* L (cottonwood), *Acer negundo* L (Manitoba maple), *Picea glauca* Moench Voss (white spruce); shrub species were *Caragana arborescens* Lam. (caragana), *Rosa acicularis* Lindl (wild rose), *Prunus virginiana* L (chokecherry) and *Amelanchier alnifolia* Nutt (saskatoon). To ensure enough sample size of species at each location for analyses, all species were categorized into three main groups, tree, shrub and grass. However, there were no data for grass species in 2008 at location Upwind-D1.

3.5. Statistical Analyses

Statistical analyses were conducted with R (R Core Team 2015). Assumption of normality was tested with the Shapiro-Wilk test, and qual variances with Bartlett's test. Natural logarithm transformation was performed to achieve normality and equal variances assumptions. A three way analysis of variance (ANOVA) was performed for testing main factor effects (distance, year, month). Since data were unbalanced (unequal replication), least square means were calculated (lsmeans package in R). Multiple least square means comparisons and multiplicity adjustment were done by Tukey's Honest Significant Difference test. Significance was accepted at $p < 0.05$.

Pearson product moment correlation coefficient is a parametric analysis, measuring statistical linear dependence between mean total fluoride concentrations and various meteorological variables over months and years, between mean total fluoride concentrations and distance, between mean external fluoride concentrations and distance, and between external fluoride concentrations and meteorological variables. Normality and equal variance assumptions were checked before performing the analysis. The correlation coefficient (r) is a measure of the dependence between two variables, ranging between +1 and −1, inclusive; where 1 is total positive linear correlation, 0 is no linear correlation, −1 is total negative linear correlation. A $p < 0.05$ indicates significant correlation between parameters; otherwise there is no significant correlation found for those variables.

Multiple linear regression is a common method for conducting linear regression analysis. Other than correlation analysis and ANOVA, this method helps to explain the relationship between fluoride concentrations and various meteorological variables. Normality and equal variance assumptions were checked before conducting multiple linear regression. The stepwise variable selection method was used in the model building to decide which of the variables were relevant and should therefore be kept in the model, by comparing the index of Akaike's Information Criterion (AIC) among the models. To calculate how much variation of each relevant variable (temperature, precipitation, source fluoride) was accounted for, the partial sum-of-squares with their total were calculated.

k-means cluster analysis is a prototype based partitioning method to partition observations into groups and assign each observation to the cluster with the nearest mean. The optimal numbers of clusters can be achieved by partitioning around medoids based on the optimum average silhouette width (fpc package in R) to minimum the within cluster sum of squares. This test was performed to partition plant species sampled in different years into groups based on their performance for internal fluoride accumulation.

4. RESULTS

4.1. Meteorological Parameters

Mean 2008 to 2016 temperature for the vegetation sampling months was 16.5 ^{o}C in June, 18.2 ^{o}C in July, 17.7 ^{o}C in August, 12.7 ^{o}C in September and 7.0 ^{o}C in October. Mean precipitation was 2.2 mm in June, 2.7 mm in July, 1.2 mm in August, 0.8 mm in September and 0.6 mm in October. Wind direction and wind speed were relatively constant over all of the sampling months. Mean wind speed was slightly higher in October (12.3 km/h) than in June (11.8 km/h), July (10.9 km/h), August (10.2 km/h) and September (11.5 km/h).

Mean annual wind direction, wind speed, temperature and precipitation for the growing season from 2008 to 2016 are shown in Table 2.1. Prevailing winds changed slightly over the years, blowing from west (W), northwest-west (WNW) in 2008 to 2013 and north-west (NW) in 2014 to

2016 from early June to late October. Wind speed did not change much from year to year and tended to be lower in recent years. Mean growing season temperature took an upward trend from 2008 to 2015, increasing to 17.2 °C in 2015, and decreasing to 14.9 °C in 2016. Some years had less precipitation (2008, 2009, 2015) than others (2011, 2016).

4.2. Forage Fluoride Accumulation

4.2.1. Fluoride monthly pattern

Fluoride monthly concentrations in forage were consistent from year to year. It was low in early summer (June, July), then peaked in fall, mostly from August to early October (Figure 2.4). Total fluoride concentrations generally trended upward throughout the growing season (2012, 2013, 2014, 2015), with a marked decrease in late fall after the peaks (2008, 2009, 2010, 2011, 2016).

Fluoride concentrations varied temporally and spatially among sampling dates within month. For example, in September 2011 mean fluoride concentration was 138.3 µg/g in forage sampled September 6, about half that of September 19 samples (65.8 µg/g). Sample locations from 2008 to 2016 were 1,241 to 3,629 m from the PG stack boundary. Distance from the stack was significantly negatively correlated with total fluoride concentrations ($p < 0.001$, $r = -0.647$), decreasing with increasing distance from the stack. From 2008 to 2016, total fluoride concentrations differed by 57.8 µg/g between nearest and furthest distances from the PG stack.

Mean 2008 to 2016 concentrations of total fluoride in June and July were below regulatory values (Table 2.2). August 2015 and 2016 concentrations were slightly above regulatory values, and that of other years were below. September and October means exceeded regulatory values in 2011, 2013, 2014 and 2016. June to July mean values were lower than regulatory. Mean July and August concentrations were mostly below regulatory, except for 2015 and 2016. August to September and September to October exceeded regulatory values in 2011, 2013, 2014, 2015 and 2016. Seasonal concentrations for 2009 and 2010 were below regulatory, 2008 and 2012 slightly higher, and that of other years higher, varying from 54.5 to 86.8 µg/g (2008 to 2016).

4.2.2. Fluoride yearly pattern

Mean fluoride concentrations in forage fluctuated year to year (Figure 2.5). Mean growing season fluoride concentrations peaked in 2011, rose gradually and then reached a second peak in 2016. Lowest mean fluoride concentration occurred in 2010. It was 36.6 µg/g in 2008, similar in 2009, then decreased to 25.7 µg/g in 2010. The 58.9 µg/g in 2011 was significantly higher than in any of the previous years, after which concentration increased to 86.8 µg/g in 2016.

Total fluoride concentrations trended higher in recent (2013 to 2016) than previous years (2008 to 2012) (Figure 2.6). Differences between mean values and frequency values were observed. The x-intercept of the major peak of 2016 was 52.8 μg/g, slightly lower than that of 2015 (54.9 μg/g), indicating that highest values occurred in 2015 instead of 2016 when comparing the frequency distribution of fluoride concentrations. Although the mean value of 2008 was higher than 2012 and followed by 2009, the x-intercept of the major peak in 2009 (12.9 μg/g) was slightly higher than that in 2012 (12.8 μg/g) and 2008 (11.3 μg/g).

4.2.3. Factors affecting fluoride variation over time

Monthly fluoride concentrations in forage were significantly correlated with temperature, precipitation (mean and accumulated) and soluble fluorides in PG ponds (Figure 2.7). A significant interaction between temperature and precipitation was detected. Wind speed did not show any strong relationship with total fluoride over the months. This may be because mean wind speed varied by 0.71 km/h (6.4 %) on average from June to October from 2008 to 2016. Soluble fluoride in the PG pond showed a similar trend over months (Figure 2.8.A) while temperature and precipitation showed an opposite trend (Figure 2.8.B, 2.8.C).

Mean temperature, precipitation, temperature and precipitation interaction and soluble fluorides in PG ponds were regressed. The partial sum of squares with their total of each independent variable was calculated to determine how much is accounted for (how important) by each factor. Influence of soluble fluoride monthly means in PG ponds on total fluoride monthly variation was greatest, followed by mean temperature and mean precipitation. Approximately 23.4 % total fluoride concentration variation can be explained by PG ponds fluoride concentrations, 15.4 % by temperature, 13.8 % by precipitation (residuals = 46.9 %).

Correlation analyses between total fluoride annual mean and series means of variables on a nine year scale indicated that year to year fluoride variation over 2008 to 2016 was strongly associated with soluble fluoride in PG ponds (Figure 2.9). The positive correlation indicated that total fluoride annual variation in forage may have the same trend with changes of soluble fluoride in PG ponds (Figure 2.10).

4.2.4. Differentiating internal and total fluorides

Unwashed plant samples include internal and external fluorides. External fluoride is particulate fluoride that may deposit on plant leaf surfaces. Internal fluoride refers to soluble and bioavailable fluoride in plants. The difference between total and internal fluoride in forage from

June to October (2008 to 2012) provides an approximate relationship between internal and external fluoride. On average 32.3 % of fluoride can be washed off by water and considered an approximation of external fluoride. This indicated the highest proportion of fluoride in forage was internal, which may be coming from gaseous fluoride uptake and particle fluoride deposition.

Correlation analyses investigated whether there was a relationship between external fluoride accumulation and meteorological variables, and source fluoride. Although fluoride transportation and deposition are complex and may have numerous influences, temperature, precipitation, wind speed and soluble fluoride in the PG pond were focused on. Series temperature and precipitation (mean and accumulate) were strongly negatively correlated with external fluoride concentrations (Figure 2.11). Wind speed and soluble fluoride in PG ponds had no significant effects. Significant interactions occurred between temperature and precipitation, and between temperature and wind speed.

Thus temperature and precipitation may have affected external fluoride over time. External fluoride concentrations might be higher under cool and dry weather and less under warm and humid weather. The highest external fluoride was in the fall (September or October) when weather became cooler and drier, at approximately 22.8 µg/g. Lowest external fluoride occurred in summer (June or July) at approximately 3.69 µg/g. This trend was consistent from 2008 to 2012. External fluoride on plant surfaces may be lower in summer when frequent heavy rains removed it from plant surfaces.

There was a strong negative correlation between distance from the stack and external fluoride concentrations ($p = 0.022$, $r = -0.810$). There was more particle phase fluoride than internal fluoride in forage close to the PG stack, and it decreased with distance. The nearest sample location over 2008 to 2012 was approximately 1,300 m from the emission source with 22.4 µg/g external fluoride relative to the furthest site (3,600 m) where external fluoride was 4.25 µg/g.

4.2.5. Fluoride accumulation in non forage species

Mean fluoride differed in groups of species (grass, shrub, tree) at four locations (Downwind-D1, Downwind-D2, Upwind-D1, Upwind-D2). Mean internal fluoride concentrations of species were highest in Downwind-D1, followed by Upwind-D1, Dowinwind-D2 and Upwind-D2.

Strong species impacts on fluoride accumulation were detected at four locations ($p < 0.001$). Mean fluoride differences were significant among grass, shrub and tree species at two upwind locations ($p < 0.05$), while differences were not obvious between tree and shrub species at downwind locations (Figure 2.12). Shrub species had highest internal fluoride, averaging 23.1 to

208.2 μg/g at four locations for 2008 to 2012. Tree species was mostly lower than shrub species, from 12.3 to 142.0 μg/g. Grass species were lowest, from 5.3 to 45.3 μg/g.

Grass, shrub and tree species had consistent internal fluoride year to year variation patterns at four locations (Figure 2.13); similar to forage (Figure 2.5) which showed notably higher fluoride in 2011. Tree and shrub species showed higher year to year fluctuations than grass at four locations over the years. Mean fluctuations were approximately 51.7 % for tree, 38.9 % for shrub and 24.3 % for grass species at four locations. Mean fluctuation was most notable in tree (55.5 %) and shrub (49.7 %) species at four locations relative to grass species (25.2 %) Thus fluoride uptake of woody species in the vicinity of the PG stack may be more prone to volatile than grass species.

Cluster analysis indicated plant species in the vicinity of the PG stack from 2008 to 2012 partitioned into two groups (Figure 2.14). Generally, tree and grass species partitioned as one group, while shrub species partitioned as a second group. Internal fluoride accumulation in tree species in 2011 was similar to the shrub group and shrub species in 2010 was similar to the grass and tree group. Internal fluoride in plants was generally low in 2010 and high in 2011.

5. DISCUSSION

5.1. Fluoride Variation Factor

Total fluoride in forage over time was strongly affected by fluoride source, air temperature and precipitation. The latter two meteorological factors had a strong connection with external fluoride variation. Relatively cooler and drier weather may promote total fluoride accumulation in vegetation over time.

Low temperature may cause closure of stomatal pores, and thus slow gas exchange and fluoride dry deposition in foliage. Therefore, more external fluoride may remain on the leaf surface in particle phase in fall than in summer.

Effects of precipitation are complex and conflictive based on other publications. Heavy rain can wash off external fluoride and thus less fluoride may remain on plant leaves. The negative correlation of precipitation with total and external fluoride in our study is similar to that of De Temmerman and Baeten (1988) who found precipitation could reduce fluoride concentrations in grass cultures by 50 %. However, a wet surface can absorb more fluoride than a dry surface which means wet leaves after a rain have a higher capacity for fluoride uptake than dry leaves

(Weinstein and Davison 2004) and may increase particulate fluoride deposition rate. There are many records showing that precipitation can promote dry deposition. For example, Less et al (1975) found artificial rain increased fluoride concentrations in plants two fold. Based on our results, high precipitation was assumed to reduce fluoride on plant surfaces.

Generally, when soluble fluoride increased in PG ponds, total fluoride concentrations increased in forage. This could explain the increasing trend of fluoride in recent years (2013 to 2016) relative to previous years (2008 to 2012). Increasing PG pond fluorides might be attributed to the source of phosphate rock used. Soluble fluoride concentrations in the PG ponds strongly vary with source rock (Rutherford et al 1995). At Agrium Redwater, the source of phosphate rock was changed over the years. The phosphate rock is likely a mix from various sources, but mainly sourced from Kapuskasing (Ontario Canada) before 2013 and from Morocco (Africa) after that (Agrium Incorporated 2014). Approximately 0.15 % fluoride ion was found in the PG composition using Morocco phosphate rock during fertilizer production (Sebbahi et al 1997) which was expected to cause higher fluoride in PG and process pond water. This might explain why seasonal mean total fluorides in forage grass increased notably since 2013 (Figure 2.5).

The change of sample locations may have resulted in different seasonal mean fluoride concentrations between early (2008 to 2012) and recent years (2013 to 2016). Total fluoride concentrations were relatively low in forage far away from the emission source. Some forage samples were harvested at far distances from the PG stack (> 3,000 m) before 2013. However, most forage samples were harvested less than 2,000 m after 2013. When these data (from far distance) were taken into account for calculation, it may lower the mean seasonal values of previous years (2008 to 2012) relative to that of recent years (after 2013).

5.2. External Fluoride

Gaseous and particulate forms of fluoride may have different toxicity, and thus it is important to understand the relationship between gaseous fluoride and particulate fluoride. Numerous studies assumed that the difference between total and internal fluoride of each sample is external particulate fluoride. Other than calculating the difference between total fluoride and internal fluoride, analyzing fluoride content in washing water can assist in detecting external fluoride. Franzaring et al (2007) achieved 100 % total recovery of fluoride by analyzing washed and unwashed samples, and accounted for washing water, water volume and grass mass washed. This method could determine if all fluoride has been considered in comparing washed and unwashed grass samples. Unfortunately, previous washing water data were not available.

The wash off percentage can only be a rough estimation as other co-deposited elements (calcium, sulfur, aluminum) also contributed to uptake pathways and some fluoride adsorbate on plant leaves may have been included as a part of internal fluoride.

External fluoride concentrations were determined by calculating the difference between total and internal fluoride to investigate how much fluoride can remain on plant surfaces in particulate form. Historically there were 51 samples with higher internal than total fluoride out of 411 samples (2008 to 2012). Agrium (Agrium Incorporated 2011) indicated samples could not have been mislabeled or switched since each had a unique identification. The reason for such a phenomenon is unknown, thus these data were removed as outliers.

On average 32.3 % total fluoride can be washed off. At Agrium Fort Saskatchewan, external fluoride of grass species grown on topsoil covering PG was unfortunately not calculable since both total and internal fluoride concentrations were very low (< 5 μg/g). Trees planted on closed PG ponds had wide variations; for example there was approximately 38.5 % total fluoride in *Populus balsamifera* considered external fluoride, 46 % in *Salix viminalis* L (basket willow) and 70.3 % in *Salix dasyclados* Wimm (holme willow). In other studies, approximately 22 % total fluoride can be removed by washing *Lolium multiflorum* cv. Lema (Italian rye grass) (Franzaring et al 2007), 24 % from *Eucalyptus rostrata* Schlecht. (gum tree), 39 % from *Populus hybridus* L (hybrid poplar) and 51 % from *Pinus radiata* D (radiata pine) (Rodriguez et al 2012). Thus species might accumulate external fluoride differently. The wash off percentage and amount of external fluoride might be determined by species characteristics, such as epicuticular waxes, geometry and roughness of the surfaces.

5.3. Different Response Of Species

Responses to internal fluoride accumulation in species of the same group (grass, shrub, tree) varied. Unlike other woody species, *Caragana arborescens* Lam (caragana) and *Populus tremuloides* were extreme accumulators. *Caragana arborescens*, a common shrub near the Redwater facility, had a seasonal internal fluoride mean of 173.2 μg/g, more than three times that of *Amelanchier alnifolia* Nutt. (saskatoon), four times *Prunus virginiana* L (chokecherry) and five times *Rosa acicularis* Lindl (wild rose) over 2008 to 2012. *Populus tremuloides* accumulated two to ten times more internal fluoride (seasonal mean) than the other four tree species.

Based on the historical heath survey records, different levels of chlorosis were observed on *Populus tremuloides* leaves (2008 to 2012) and marginal chlorosis and sporadic necrosis were observed at 5 km south-east from the emission source. Different levels of chlorosis were found on *Caragana arborescens* leaves, from marginal to entire, at 2.5 km southeast of the source over 2008 to 2012. However, the chlorosis was unlikely caused by fluoride kilometres away from the emission source. There might be other sources that can result in chlorosis on these plants, such as the use of herbicide.

Compared to grass species, fluoride accumulation in woody species had significant changes of internal fluoride over the years (Figure 2.13). This may due to characteristics, such as height, leaf area, leaf shape and sensitivity to fluoride. As tree species are generally taller than shrub and grass species, airborne fluoride transportation and deposition process on trees might be less affected by blocking of buildings or taller plants.

6. CONCLUSIONS

Monthly pattern of total fluoride in forage was consistent among years. Peak total fluoride concentrations in forage occurred late August to early October with low values in early summer (June, July). Mean seasonal fluoride concentrations in forage during the growing season were relatively high in 2011 and after 2013 over a nine year period. Month to month total fluoride changes in forage can be mainly attributed to soluble fluorides in PG ponds, followed by temperature and precipitation.

On average 32.3 % of total fluoride can be washed off plant tissue, thus most fluoride in forage was internal. Temperature, precipitation and distance had a strong negative correlation with external fluoride concentrations. Highest amounts of external fluoride were in fall (September or October) when weather was cooler and drier; lowest external fluoride occurred in summer (June or July). Particle phase fluoride was greater than internal fluoride in forage close to the PG stack and it decreased with distance.

Different groups of species responded differently to internal fluoride accumulation. Mean internal fluoride concentrations in plant species were highest downwind and close to the PG stack and lowest upwind and far away from the PG stack. Shrub species had highest internal fluoride, following by tree and grass species. Plant species near the PG stack partitioned into shrub species as one group, tree and grass species as a second group.

Table 2.1. Mean wind direction, wind speed, air temperature and precipitation from June 1 to October 31 2008 to 2016.

Year	Wind Direction	Wind Speed (km/h)	Temperature (°C)	Precipitation (mm)	
	Main	Mean	Mean	Mean	Accumulated
2008	W	12.5	13.2	1.3	169.1
2009	WNW	12.7	14.8	1.0	144
2010	W	10.6	14.1	1.5	204.8
2011	WNW	11.4	14.4	1.9	262.2
2012	WNW	11.9	14.6	1.8	240.1
2013	WNW	10.9	14.4	1.7	247.3
2014	NW	10.9	15.2	1.6	221.6
2015	NW	10.6	17.2	1.2	168.0
2016	NW	10.6	14.9	1.9	224.3

Table 2.2. Mean total fluoride in forage from 2008 to 2016.

	One Month Mean Regulatory < 80 µg/g					Seasonal Mean Regulatory < 35 µg/g
Year	June	July	August	September	October	June to October
2008	7.3	18.3	35.6	61.1	66.8	36.6
2009	10.4	29.5	28.1	54.6	40.0	32.1
2010	9.4	17.9	35.3	37.5	23.3	25.7
2011	16.0	28.8	70.9	102	77.3	59.0
2012	10.1	19.9	35.1	53.9	64.9	36.8
2013	12.9	30.0	52.2	98.2	90.3	54.5
2014	16.7	38.9	64.6	97.1	98.1	58.7
2015	37.0	57.6	90.3	77.2	71.4	64.0
2016	40.5	49.3	81.0	147.0	105.1	86.8

Two Consecutive Months Mean Regulatory < 60 µg/g				
Year	June and July	July and August	August and September	September and October
2008	10.1	31.3	45.8	63.9
2009	19.9	28.7	38.7	47.3
2010	13.7	28.4	36.1	33.8
2011	22.4	49.9	86.5	89.7
2012	15	27.5	44.5	59.4
2013	23.9	39	74.5	94.4
2014	29.5	48.6	80.9	97.6
2015	45.3	73.9	83.7	74.3
2016	46.4	68.4	107.4	133

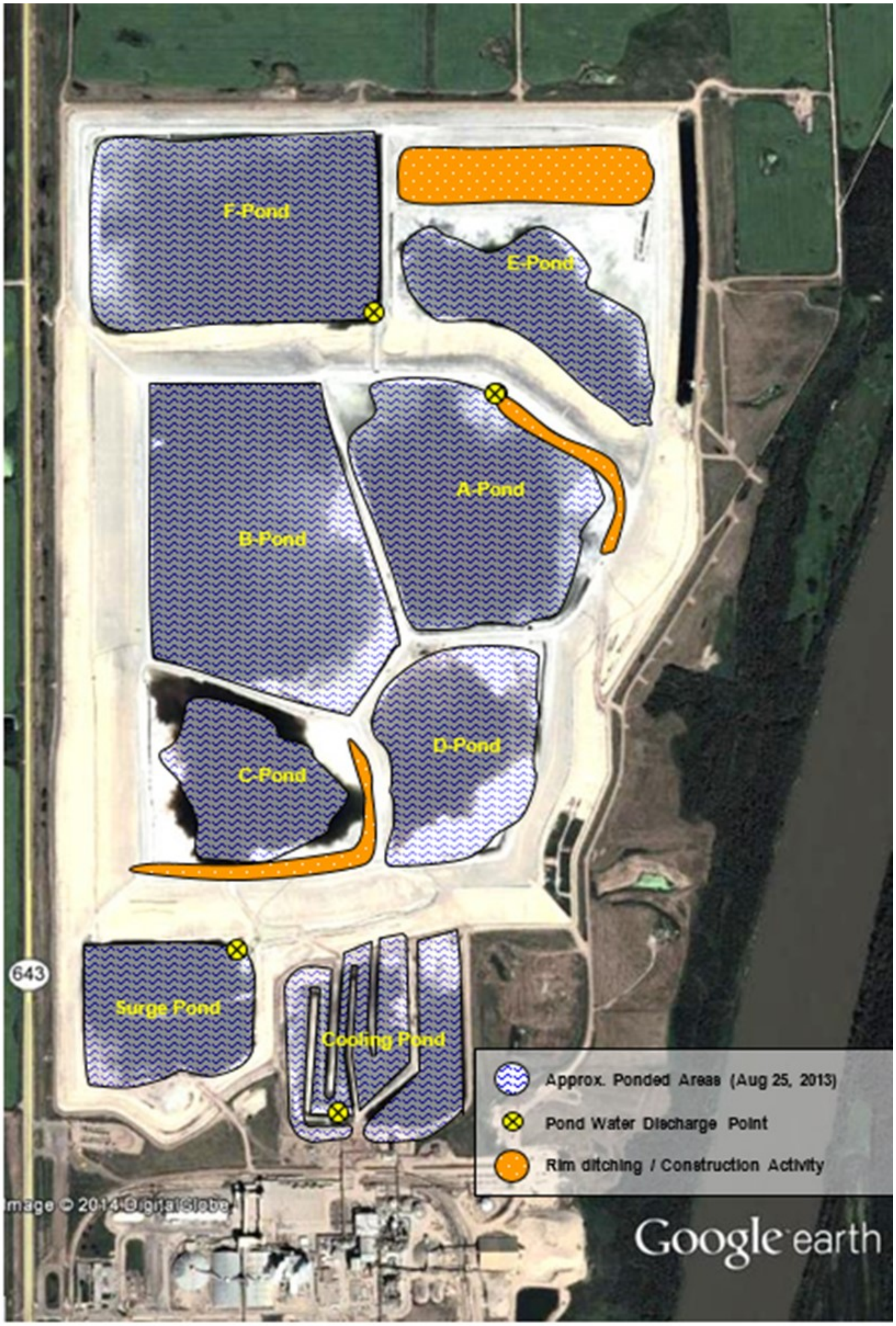

Figure 2.1. Map of active process ponds on the phosphogypsum stack at the Agrium Redwater Operation Facility.

Figure 2.2. Map of Agrium forage sample locations from 2008 to 2016.

Figure 2.3. Map of Agrium vegetation sample locations from 2008 to 2016.

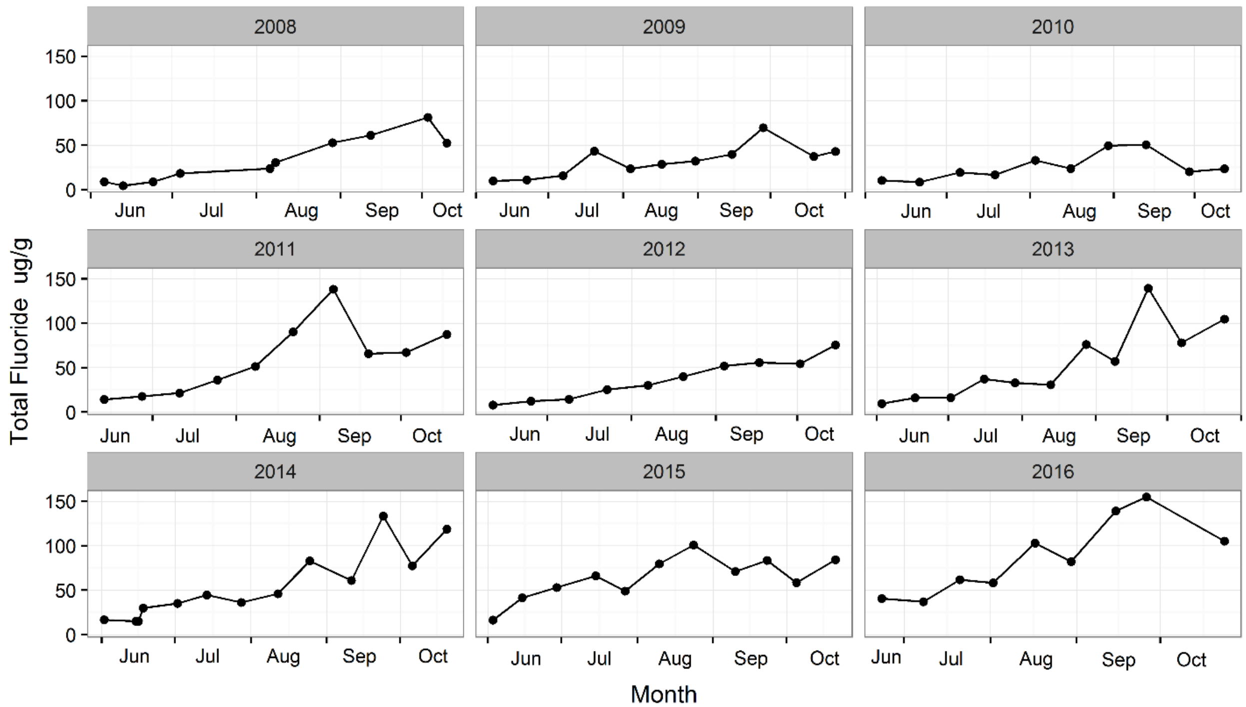

Figure 2.4. Monthly pattern of mean fluoride concentrations in forage from 2008 to 2016.

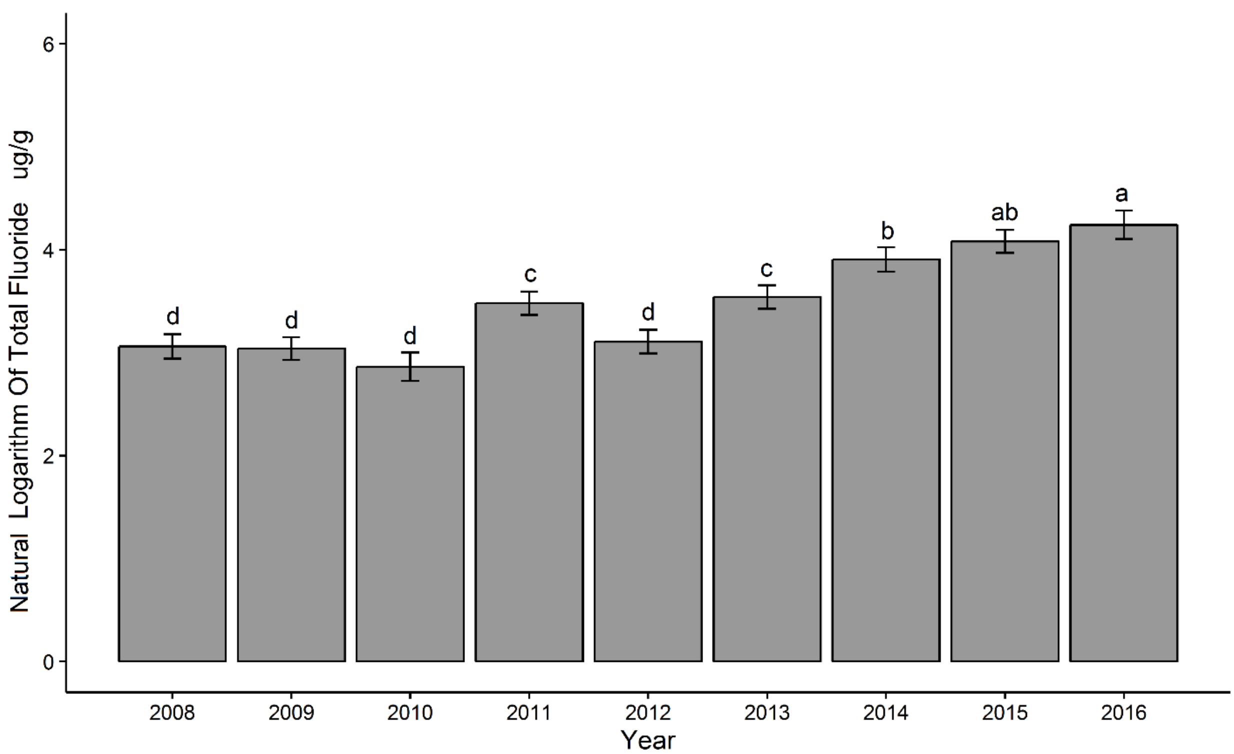

Figure 2.5. Mean total fluoride concentrations over years. Different letters indicate significant differences among years.

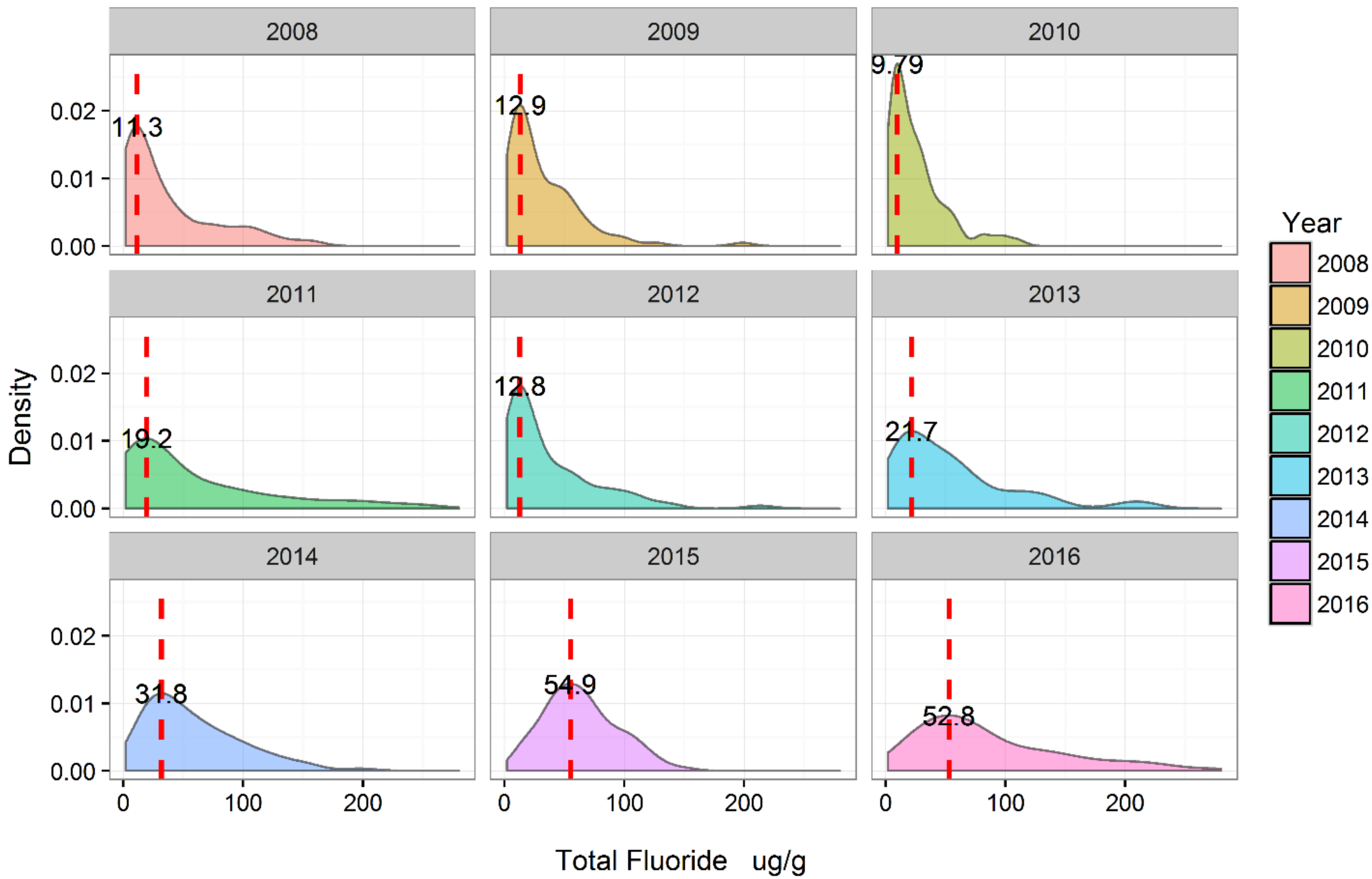

Figure 2.6. Probability density (frequency) of seasonal mean fluoride concentrations from 2008 to 2016 growing seasons. Density curves display fluoride concentration distribution. The area under the curve in a range of fluoride values indicates the proportion of values in that range. Density of the total area equals one. Red dashed lines refer to major peak of concentrations.

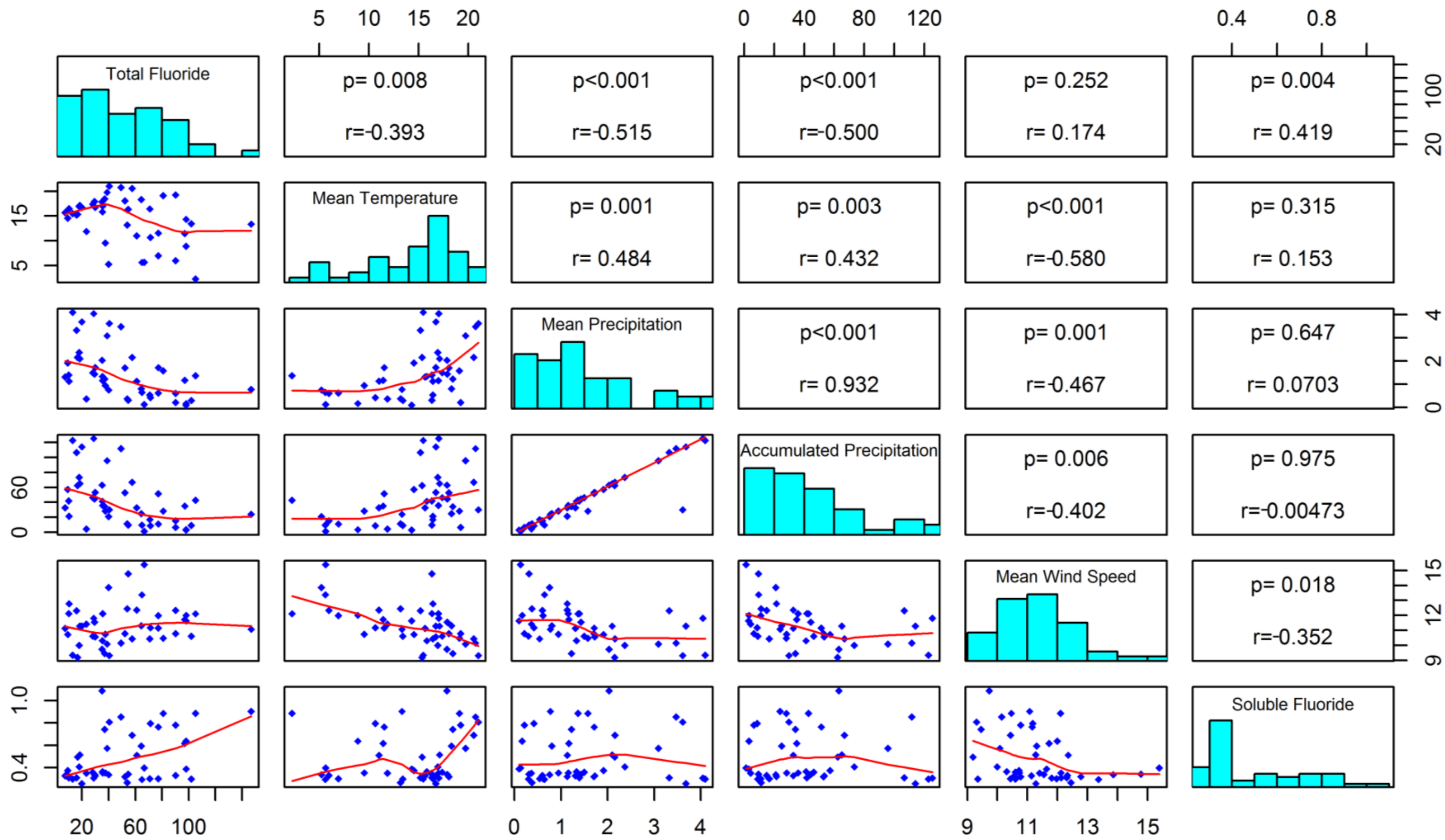

Figure 2.7. Correlogram of monthly total fluoride and mean temperature, mean precipitation, accumulated precipitation, mean wind speed and soluble fluoride in PG ponds.

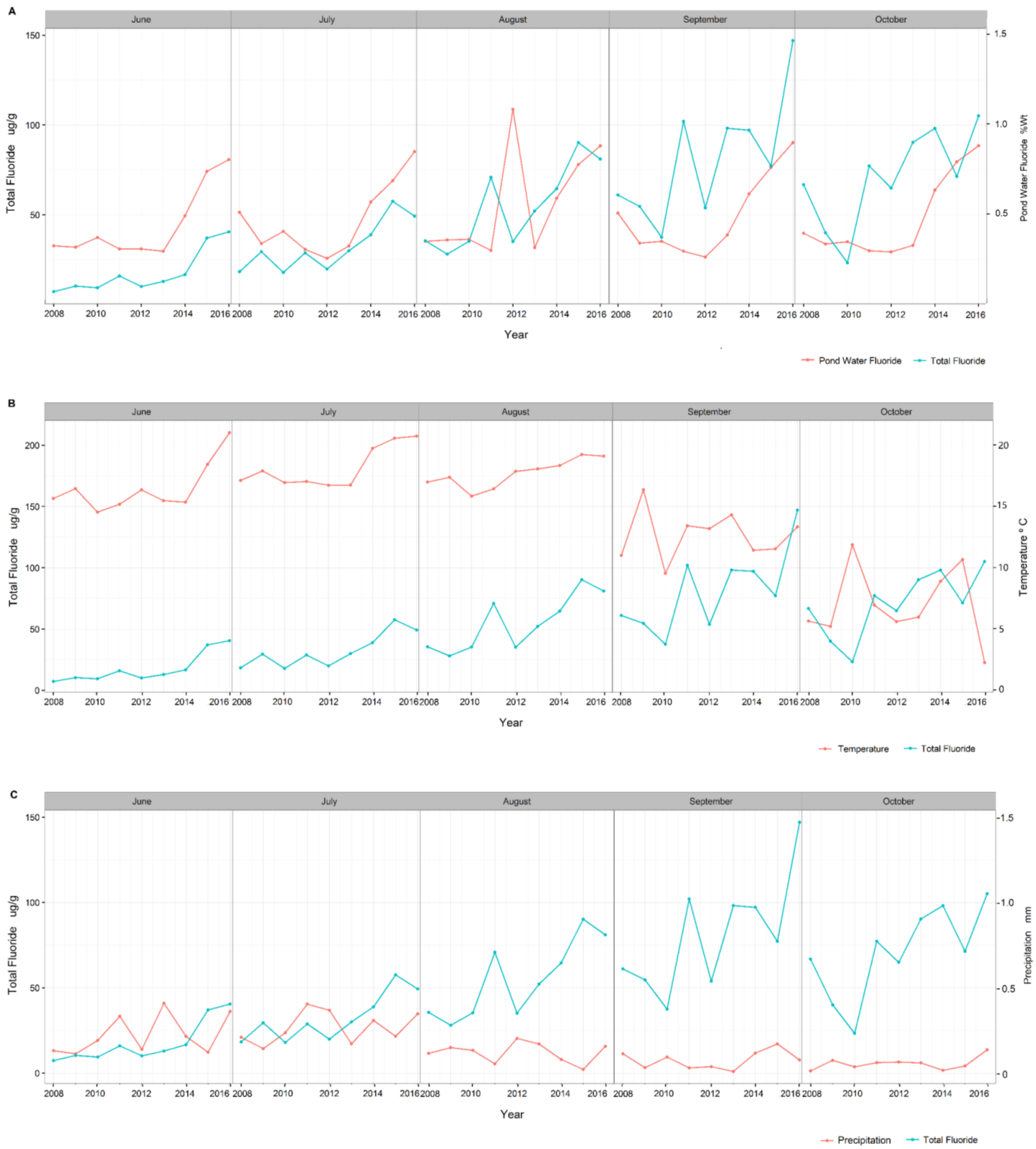

Figure 2.8. Month to month variation of total fluoride concentrations in forage with change of soluble fluoride in phosphogypsum ponds (A), temperature (B) and precipitation (C).

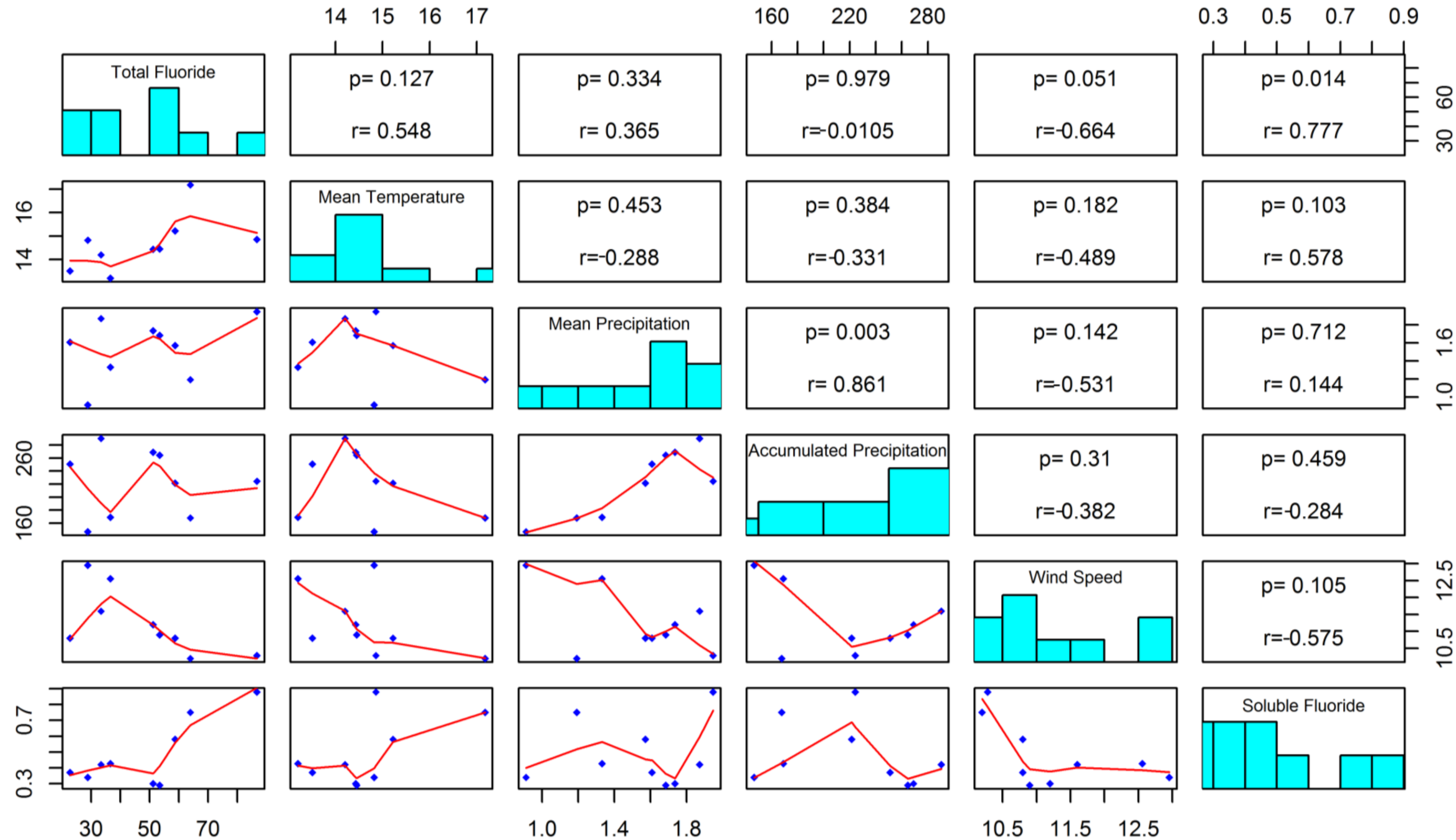

Figure 2.9. Correlogram of yearly mean total fluoride and mean temperature, precipitation, accumulated precipitation, wind speed and soluble fluoride in PG ponds.

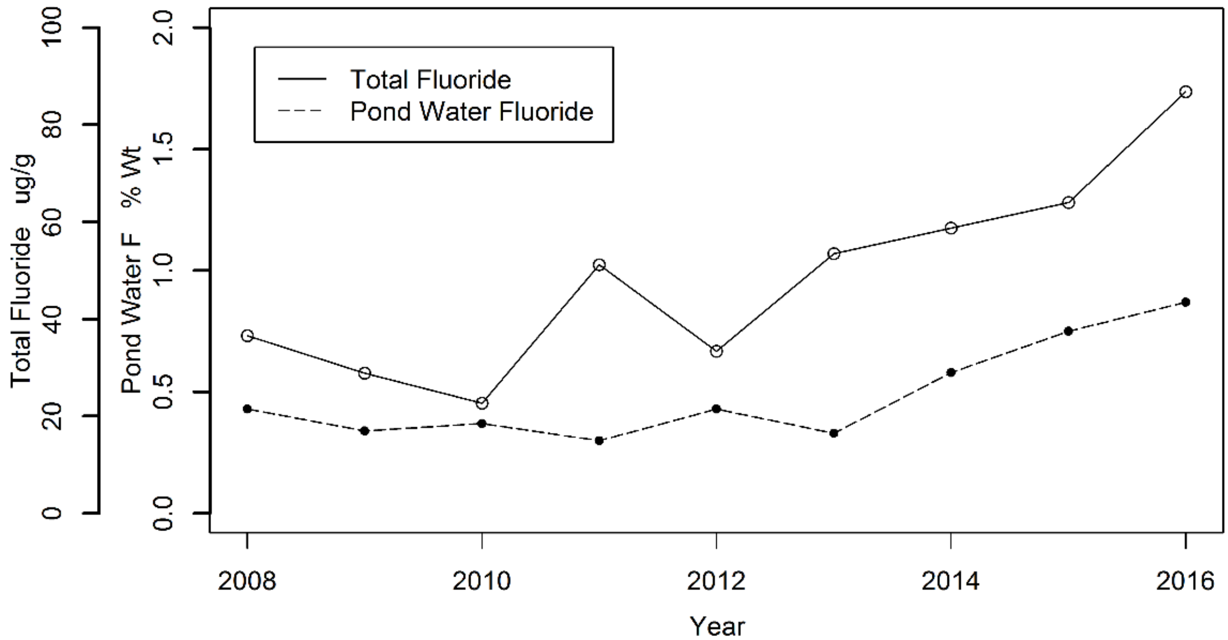

Figure 2.10. Year to year variation of total fluoride in forage and soluble fluoride in PG ponds.

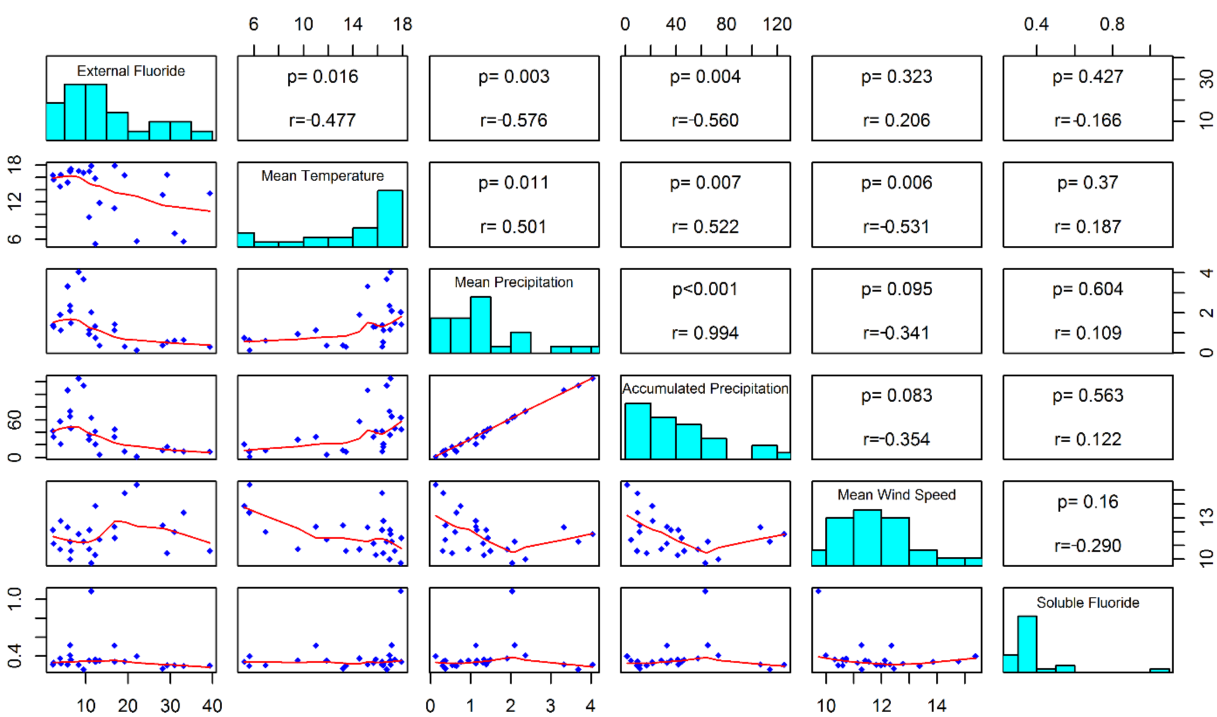

Figure 2.11. Correlogram of mean monthly external fluoride and mean temperature, precipitation, accumulated precipitation, wind speed and soluble fluoride in PG ponds.

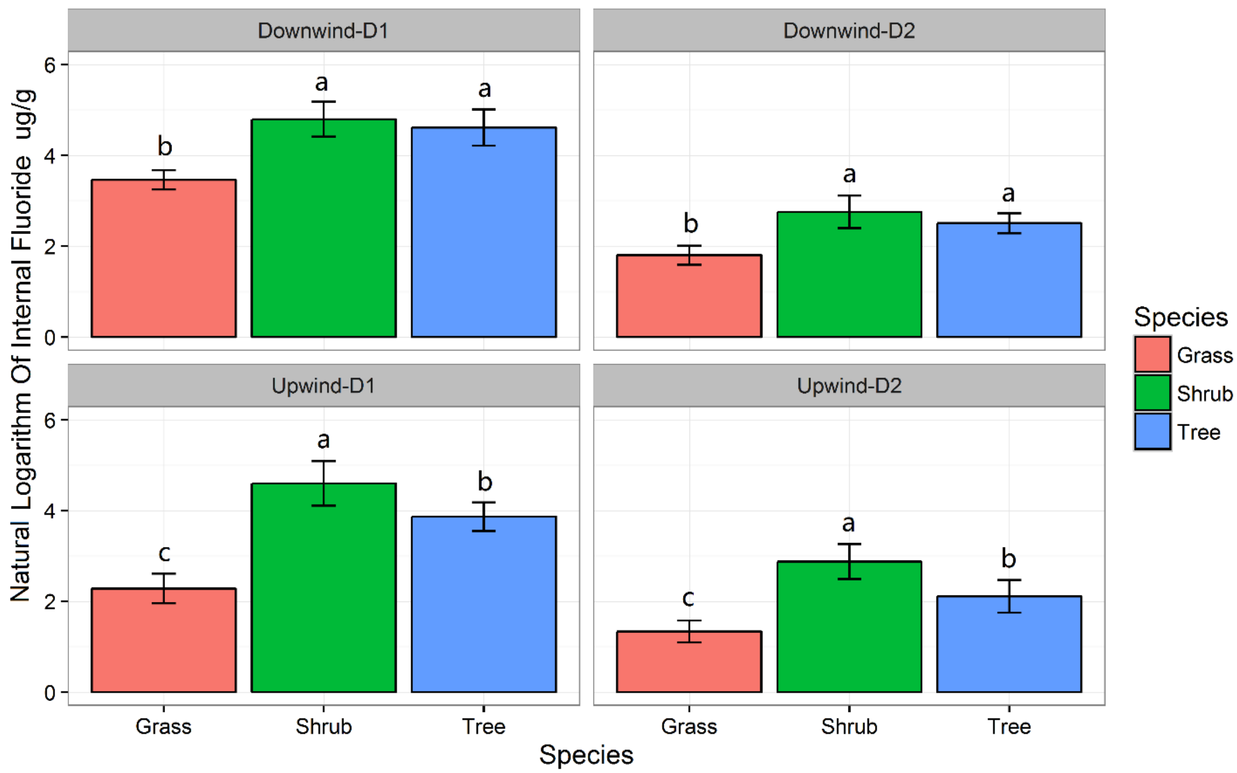

Figure 2.12. Internal fluoride in grass, shrub and tree species at four sample locations (four exposure periods pooled). Error bars are standard error. Different letters indicate significant differences within a location.

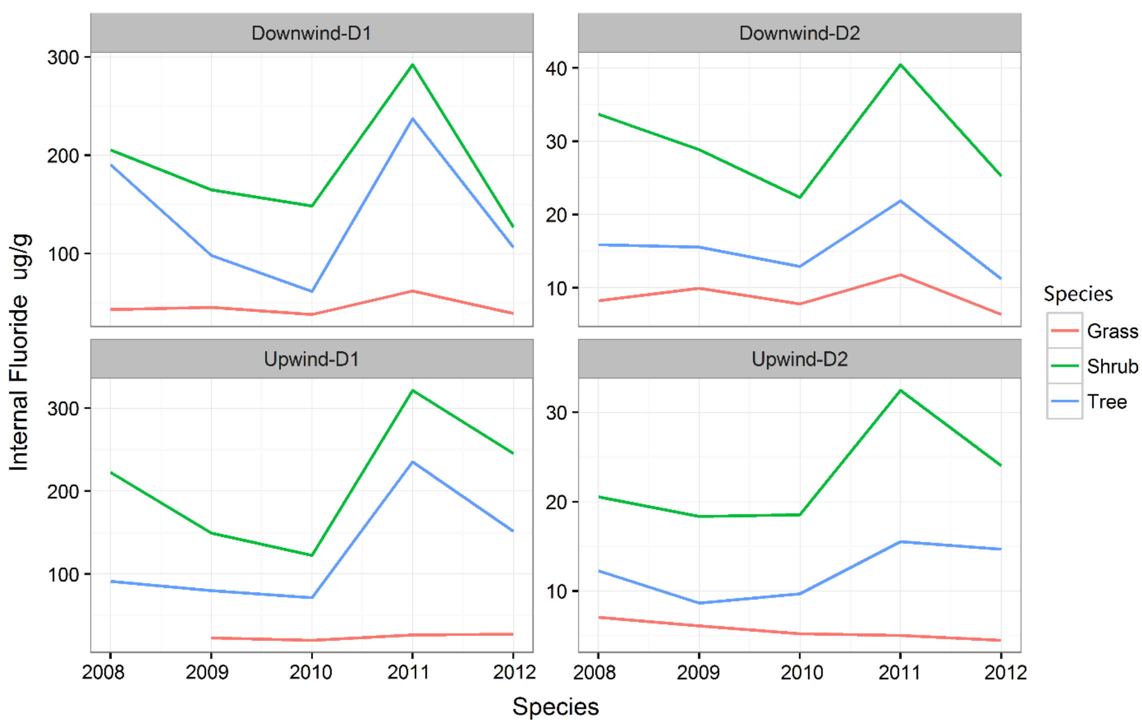

Figure 2.13. Annual variation of internal fluoride in grass, shrub and tree species at four locations.

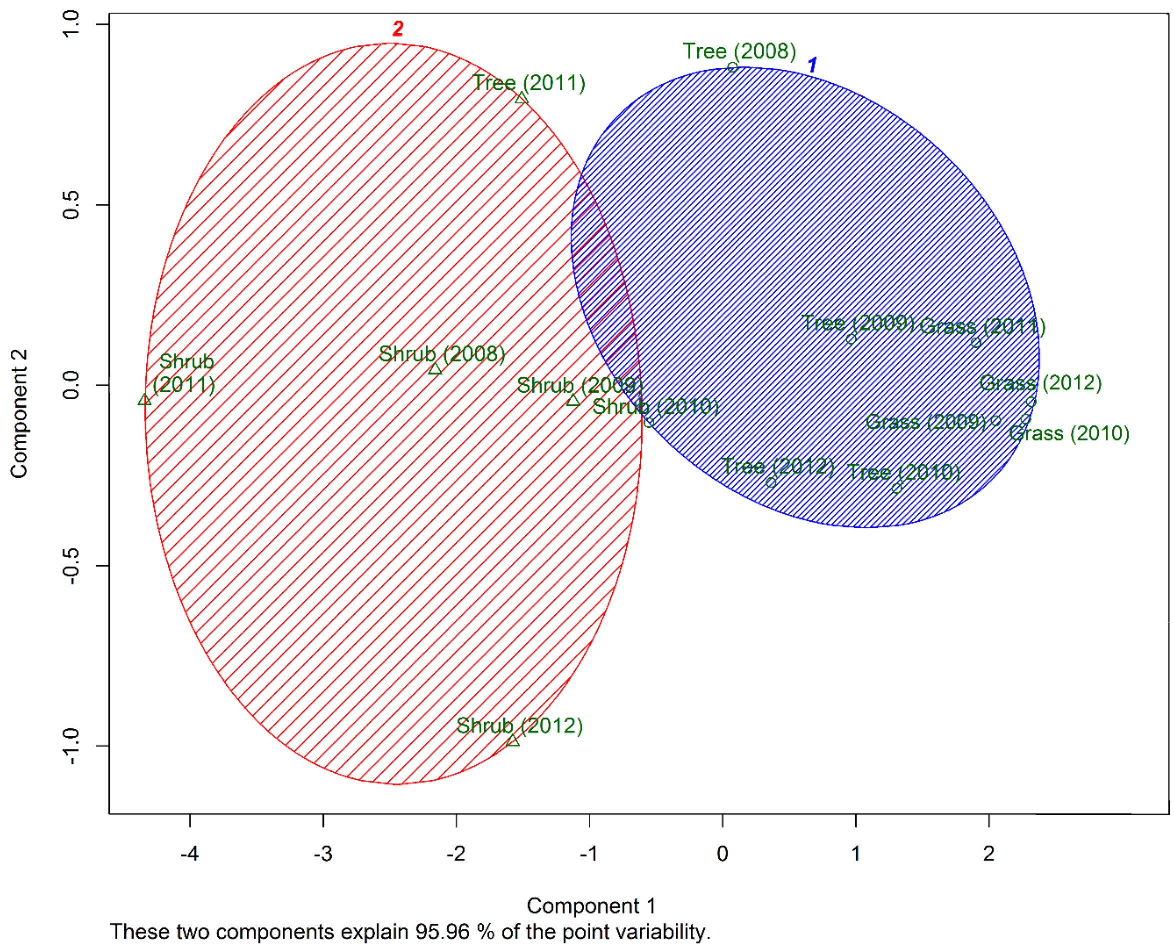

Figure 2.14. Bivariate clustering plot of plant species in the vicinity of the Agrium PG stack over 2008 to 2012. All observations are represented by points, using principal components scaling. An ellipse is drawn around each cluster.

III. STANDARDIZED FLUORIDE BIOMONITORING

1. INTRODUCTION

Airborne fluoride emission is an environmental concern from fertilizer production and phosphogypsum (PG) storage (Rutherford et al 1994). PG is an acidic by-product created during phosphoric acid production and consists mainly of solid gypsum, fluorides, residual acids, sulphate ions, trace metals and organic matter (Rutherford et al 1995, Tayibi et al 2009). For every one tonne of phosphoric acid produced, there will be 5 tonnes of PG (Thorne 1990). Only 15 % of world PG is recycled as construction materials, agricultural fertilizers or soil stabilization amendments; most are in large stockpiles exposed to weathering (Tayibi et al 2009).

In active PG stacks, fluoride can be transported through movement of particulate dust and process water pond surface evaporation (Weinstein and Davison 2004). It is challenging to estimate fluoride vapour pressure based on evaporation rate due to variations in pond water composition and air temperature. The ground level fluoride dispersion pattern and concentration gradient depend on environmental and topographical factors.

Winds can lead to fluctuations in fluoride concentrations at ground level even if emissions are relatively constant (Franzaring et al 2007). Generally, gas and particle fluoride can be carried by wind, and it is very efficient to remove or deposit fluoride on rough structures. The higher the wind speed, the further the emissions can be carried away (Weinstein and Davison 2004). Wind driven fluoride can reach into the adjacent environment of the PG stack, and thus winds can enlarge the contamination zone with less soluble and more liberated mobile forms of fluoride.

Distance from the emission source significantly influences fluoride dispersion. Studies on movement of hydrogen fluoride shows that fluoride concentrations steeply decrease with increasing distance from the emitter (Rodriguez et al 2012). For example, a model developed by Real et al (2003) to delineate fluoride dispersal in the vicinity of a fluoride pollution generating factory found highest fluoride concentrations close to the factory and no severe pollution further than 2 kilometres around the source. In general, the pattern of fluoride effects on vegetation is typically non-linear (Mezghani et al 2005).

The decrease in fluoride with distance from source occurred because of wind turbulence and type of deposition, dry or wet (Weinstein and Davison 2004). Dry deposition occurs when fluoride lands on a surface or is taken up by vegetation through the stomata via gas exchange. Different surfaces (leaf, soil, lake, etc.) have different absorption capacities. A wet surface can absorb more fluoride than a dry surface which means wet leaves after rain have a higher capacity for fluoride uptake than dry leaves. Rainfall events could reduce fluoride emissions by wet deposition, which occurs when fluoride is taken away from the deposition process by rain, snow and mist. When hydrogen fluoride is emitted into the air, it will dissolve and form hydrofluoric acid in atmospheric water, which will then be removed by wet deposition from the air (ATSDR 2003), eventually reducing the fluorides.

The airborne fluoride uptake process, through stomatal pores, to transport and accumulate in plants, is time consuming, taking hours or days, depending on rate of water movement and leaf area (Weinstein and Davison 2004). Pollution patterns of fluoride content significantly change over weeks and days (Blakemore 1978, Davison et al 1979), but plants do not respond to short term (minutes) exposure (Weinstein and Davison 2004). When fluoride penetrates cell walls of vascular plant leaves, it interferes with almost all physiological and biochemical processes, including enzyme activities in plant cells, photosynthesis, gas exchange and mitochondrial respiration (Weinstein and Davison 2004, Baunthiyal and Ranghar 2014). Fluoride inhibits enzyme activities (Mendoza-Schulz et al 2009) by binding functional amino acid groups in the active centre of the enzyme (Barbier et al 2010), and reduces chlorophyll synthesis, degrades chloroplasts and inhibits Hills reaction (Yamauchi et al 1983). Fluoride accumulation in leaves could affect stomatal conductance and gas exchange (Robinson et al 1998, Alves et al 2008).

Age of plants may affect fluoride accumulation although there are few published studies on this. Plant sensitivity generally decreases with age (Weinstein and Davison 2004). Fluoride concentration in plants near PG stacks can accumulate with time and can cause severe damage when concentrations reach critical levels for species. If thresholds are exceeded marginal and interveinal chlorosis can be the first symptoms. If fluoride containing forage is ingested by animals, it may cause fluorosis and raise health concerns to humans (Klumpp 1997, Vike 1999, Galan 2002). Respiration inhibition and stimulation caused by fluoride is strongly associated with inhibition of enzymes of respiration and uncoupling of phosphorylation (Baunthiyal and Ranghar 2014).

2. RESEARCH OBJECTIVES

The general objective of this research is to implement a biomonitoring method for Agrium Redwater Operations and to increase the knowledge and understanding of the effects of hydrogen fluoride on vegetation. Specific objectives were as follows.

- Determine plant bioaccumulation of airborne fluoride as related to air emission patterns around a fertilizer production facility.
- Determine effect of fertilizer production on surrounding vegetation, and when and at what concentration internal fluoride appears in the vicinity of the PG stack.
- Develop a biomonitoring method for hydrogen fluoride with a plant species for Alberta.

3. MATERIALS AND METHODS

3.1. Research Site Description

The hydrogen fluoride source for this research was emitted from the large PG stack at Agrium Redwater Fertilizer Operations, located approximately 48 km northeast of Edmonton Alberta (53°50'56"N and 113°5'26"W). The fertilizer plant occupies 372 ha along the North Saskatchewan River including cooling ponds, surge ponds and six storage ponds (Figure 2.1). The plant is the sole source of phosphate fertilizer production in Canada. Until mid 2013 the phosphate rock was sourced from Agrium's phosphate mine near Kapuskasing Ontario; since 2013 the source has been Morocco. The PG stack at Redwater has operated for approximately 48 years, accumulating approximately 47 million tonnes of PG, stored in 275 ha area

3.2. Plant Materials

In 2015 and 2016, *Lolium perenne* L. (perennial rye grass) was used as a bioindicator for airborne fluoride. Rye grass is ideal for biomonitoring airborne fluoride as it is tolerant of high concentrations and may accumulate high tissue concentrations (VDI 1989). Rye grass is commonly grown in Alberta and has a good seed supply at a low cost. It has a short time for cultivation and cultivation conditions can be easily achieved. Rye grass has been used as a bioindicator around the world (Franzaring et al 2007, Rey-Asensio and Carballeira 2007).

In 2016, *Helianthus annuus* L (sunflower), *Koeleria macrantha* (Ledeb) Schult (June grass), *Medicago sativa* L (alfalfa) and *Zea mays* L (corn) were used to assess response to airborne fluoride of other common grass, forb and crop species relative to rye grass.

3.3. Experimental Design

In 2015, a complete randomized experiment was designed with three factors direction, distance and exposure time; with 64 (4 x 4 x 4) treatment combinations, as they were identified as potentially influencing fluoride air emissions from the PG stack. Sample locations were established in each cardinal direction (east, west, south, north) at four distances (on stack, near, medium, far) from the source, 0, 500, 1,200 and 2,000 m representing near, medium and far distances, respectively (16 sample locations). Distance refers to the distance between a sample location and the closest PG stack boundary. To determine effect of exposure time on fluoride concentration in plant tissue, plants were harvested after 28, 57, 81 and 110 days. At each sample location, there were four replicate sites. The exception was on stack locations which had one replicate site to provide emission source references. There were 52 sites (experimental units) (12 sample locations x 4 replicates + 4 sample locations x 1 replicate) in total.

Based on 2015 results, another complete randomized experiment was established in 2016 to investigate distance from the phosphogypsum stack, exposure time and age of perennial rye grass on fluoride accumulation in plant tissue, with 24 (2 x 4 x 3) treatment combinations. Sample sites were only established in the east direction from the source at two distances, near (within 500 m) and medium (about 1,200 m). The east and south directions, downwind of the stack, were identified as the locations with highest risk of fluoride pollution in 2015. The east was focused on as grazing is common in this area but not in the south. The far distance which was part of the experimental design in 2015 was not resampled in 2016 as fluoride concentrations in plant tissue were consistently very low. Plants were harvested at the same four exposure periods used in 2015. To determine effect of perennial rye grass age on fluoride accumulation, three ages of plants (20, 40, 60 days) were exposed on each site.

At each distance, five replicate sites were established; sites were evenly distributed parallel to the east side of the phosphogypsum stack to reduce within distance variability. There were 10 sample sites in total (2 distances x 5 replicates). One reference site, established on the east side of the phosphogypsum stack in 2015, was again sampled in 2016. The purpose of the reference in 2016 was to compare source fluoride concentrations between years. Sample sites in 2015 and 2016 are shown in Figure 3.1. Sample sites were not located in forest areas or immediately adjacent to them as this may impede fluoride deposition.

A sub experiment was designed to compare internal fluoride concentrations of four common grass, forb and crop species with those of perennial rye grass within exposure times. *Helianthus annuus*, *Koeleria macrantha*, *Medicago sativa* and *Zea mays* were placed and harvested on the same as the main experiment. These species were only placed at EM4 site (medium distance, fourth replicate), as plants had considerably higher fluoride concentrations here in 2015. There were four replicate pots per species within the site.

3.4. Greenhouse Cultivation And Field Placement

In 2015, perennial rye grass was grown in 20.32 cm diameter and 13.97 cm tall pots at the University of Alberta greenhouse under controlled conditions (20 ^{o}C, 16 h photoperiod). Seeding density was 5 plants per pot. The potting soil was a commercial product (Sunshine Mix, Sungro®, Agawam, MA) mixed with hydrogel (SoilMoist, JRM Chemical Inc, Cleveland, OH) at a rate of 10 g per pot to augment water holding capacity. Pots were watered to maintain approximate field capacity.

In early June 2015, after 20 days in the greenhouse, pots were placed in the field. Mean plant density per pot was 4. Mean plants height was 20 cm. Twelve pots were placed at each site, 624 pots in total at the 52 sites. Pots were carefully transported from the greenhouse and placed on pallets in a truck for transport to the field.

In 2016, perennial rye grass was grown in the greenhouse at the University of Alberta greenhouse in 25.4 cm diameter and 19 cm tall pots under controlled conditions (20 ^{o}C, 16 h photoperiod). There were three seeding dates to obtain the three ages of plants for field placement. The 60, 40 and 20 day treatments were seeded on April 18, May 8 and May 27, respectively. Seeding density was 20 seeds per pot to ensure sufficient biomass at harvest. At time of placement in the field on June 15 or 16, plant density was 16 plants per pot. Twenty-four pots were placed at each site, except 8 pots of 20 day old plants at the reference site.

On May 27 2016, alfalfa, corn, sunflower and june grass were seeded in the same greenhouse and size of pots. Seeding density was 6 seeds per pot. Sixteen pots per species were placed at site EM4 using the same methods as above. At the time of placement in the field, the density of each species was 5 plants per pot.

3.5. Plant Maintenance

A wick system was applied to each pot. Four 30 cm cotton ropes were set up in soil through draining holes in each pot before planting, performing as wicks. After field placement, plastic trays filled with water were set up under every two pots, soaking the ends of the wicks; therefore plants could self water by the wick system. Plants were watered (or trays were filled with water) once or twice a week, depending on precipitation and exposure to sunlight. Approximately 0.3 L of water per pot was used to fill the trays (water container) of the wick systems by water jugs.

A herbivory issue was identified in the first week of placing pots in the field in 2015. Initially, this problem was more serious in eastern and northern sites, where pots were placed mainly in hay lands and fields with short grasses and bushes. The organic animal repellant Plantskydd (Tree World®, St. Joesph, MO). This was not effective and very quickly herbivory became a concern at most sites even those inside Agrium's operations. Sites located on bare ground or with less vegetation in surrounding areas were less affected. The insecticide Marathon (1 % imidacloprid) (OHP Inc, Mainland, PA) was sprayed on pots and surrounding vegetation once or twice a week at a dilution of 1:300. The main pest appeared to be the two striped grasshopper (Melanoplus bivittatus), which is widespread in Canada and common throughout Alberta.

In 2016, to minimize pests and decrease shelter by surrounding plants, all pots were placed on 10 cm high wooden pallets. Seven 1 x 2 m triangular metal cages were used at 5 sites located outside the Agrium plant to mitigate potential biomass loss as deer were observed in this region in 2015. Roughly once a month, a deer and small animal repellent Bobbex (Bobbex®, Monroe, CT) was sprayed around pots to protect them from insects and small rodents. No severe insect issue occurred in 2016. Sample sites at the near distance were all located within the Agrium Redwater industrial complex which is fenced and thus were not at risk from grazing herbivores.

3.6. Plant Harvest And Tissue Analysis

Perennial rye grass was harvested after 28 (July 13), 56 ± 1 (August 10 and 11), 81 (September 3) and 110 (October 3) days in the field to determine effect of exposure time during the growing season in 2015 and 2016. At each harvest, biomass was removed from three or two randomly selected pots at each site in 2015 and 2016, respectively. Plants were carefully cut at the soil surface and placed in large plastic ziploc bags and sealed. Biomass from each site was combined in the field into one composite sample per site for analyses. At the same dates, above ground biomass from one randomly selected pot per species per replicate of sunflower, june grass, alfalfa and corn were harvested, and sealed in bags to be used for analysis separately.

Fluoride concentrations refer to internal fluoride, which means samples were washed so that fluoride bound to particles and accumulated on the surface of leaves was removed. In the laboratory, fresh weight of each sample was weighed. A standard washing solution was prepared by mixing 200 ml C10-C18 alkylbenaene sulfonate, 50 ml alcohol ethoxylate, 50 ml coconut eiethanolamide, 70 ml sodium xylene sulfonate, 50 ml EDTA and 500 ml water, and then preparing a 1:100 dilution with water. Each composite biomass sample was placed in a clean plastic bucket. The diluted washing solution was sprayed on samples for 20 seconds using a plastic spray bottle, then rinsed for 20 seconds with deionized water. Spraying and rinsing were repeated in clean buckets until no soap bubbles were present. Washing to remove external fluoride on leaves helps to target effects on internal plant parts and provides a better understanding of response of fluoride accumulation in plant tissue. Internal fluoride is less affected by environmental factors such as precipitation and vegetation disturbance.

Washed samples were submitted to a local commercial laboratory (Maxxam Analytics Inc., Edmonton Alberta), who sent them to their Ontario laboratory for analyses. Samples were oven dried and finely ground in preparation for analysis. Internal fluoride analyses were conducted by ion selective electrode (Meyerhoff and Opdycke 1986) (ISO 17025 procedure).

3.7. Meteorological Data

A meteorological station located at the main gate of Agrium Redwater Fertilizer Operations, the Fort Air Partnership Ambient Air Monitoring Station, is less than 5 km to the furthest sample site. Continuous data, such as outdoor air temperature (°C), wind speed (km/h) and wind direction (degrees) was obtained from in this station (CASA 2016). Through the Alberta Agriculture Agroclimatic Information Service website, precipitation data (mm) was obtained from Radway station in 2015 (approximately 30 km northeast of Redwater Fertilizer Operations) before Redwater Industrial station had data available in 2016 (AARD 2016).

3.8. Statistical Analyses

Statistical analyses were conducted with R (R Core Team 2015). The assumption of normality was assessed with the Shapiro-Wilk test, and the assumption of equal variances with Bartlett's test. 2015 data violated the normality assumption before and after data transformation (log, square root, box-cox). Outliers were visually noted and then checked by Local Outlier Factor (LOF), an algorithm for detecting density based outliers by comparing with replicate site values (Breunig et al 2000), and was performed by R package DMwR. Data from two sites (SN3 and WN2) were considered as outliers by the test, and values were higher than their replicate sites or sites with similar treatments. Outliers were removed from statistical analyses, after which the data achieved normality and equal variance assumptions by natural logarithm transformation.

A new factor, wind direction, was created by grouping sample site directions into two treatments, downwind and upwind locations, to detect the impacts of wind direction on fluoride accumulations. A three way analysis of variance (ANOVA) was conducted to test effects of main factors and their interactions, wind direction, exposure time and distance. Since 2015 data were from an unbalanced design (unequal sample size due to missing data), least square means were calculated to adjust the influence of other main factors (lsmeans package in R). Multiple least square means comparisons and multiplicity adjustment was done by Tukey's Honest Significant Difference test. 2016 fluoride data was from a balanced design and the contrasts were orthogonal, so Tukey's Honest Significant Difference post-hoc test was conducted after a significant three way ANOVA to test significance of main factors (exposure time, age, distance) and their interactions. Significance was accepted at $p < 0.05$. To calculate how much variation each factor accounted for, partial sum of squares with their total was calculated.

To compare the internal fluoride variation from 2015 to 2016, a two way ANOVA was conducted with two factors, year and exposure period, after checking the normality and equal variance assumptions by Shapiro-Wilk test and Bartlett's test, respectively. Data are unbalanced design due to unequal replicates. Thus, treatment effects were compared and adjusted by multiple least square means comparisons (Tukey's Honest Significant Difference test).

Fluoride accumulation in rye grass and four other plant species were compared in each exposure period. Data from 28 and 56 day exposures failed the ANOVA assumptions and failed in data transformation, including log, square root and box-cox. Thus, a non-parametric Kruskal-Wallis test with species as the factor and after which a Kruskal-Wallis multiple comparisons of treatments (agricolae package in R) were performed. Data from 81 and 110 days exposure followed normality and equal variance assumptions and a one way parametric ANOVA) was conducted, after which a multiplicity adjustment was applied (Tukey's Honest Significant Difference) on least squares means comparisons adjusted for imbalance.

Pearson correlation coefficient, a parametric analysis measuring statistical linear dependence between two variables, was performed for analyzing correlation between internal fluorides and meteorological parameters (temperature, precipitation, accumulated precipitation, wind speed) as all parameters followed normality assumption. Mean values for fluoride and meterological parameters were calculated for designated periods in 2015 and 2016 (Figure 3.2). Significance was determined at $p < 0.05$. The correlation coefficient (r) is a measure of the dependence between two variables, ranging between +1 and −1 inclusive, where 1 is total positive linear correlation, 0 is no linear correlation, and −1 is total negative linear correlation.

Since ANOVA may not be suitable for continuous variables, a non-linear least squares regression was used to delineate fluoride concentration changes with distance and exposure time with parameters (package nls in R). R^2 (coefficient determination) is a statistical term to show closeness between the observed data and the predicted values, reflecting the goodness of fit of regression models.

4. RESULTS

4.1. Influence Of Meteorological Parameters

4.1.1. Influence of temperature, precipitation and wind speed

Meteorological parameters, including mean temperature, mean precipitation, accumulated precipitation and mean wind speed over the study period are shown in Figure 3.2. Highest temperature occurred in the first 28 exposure days (mid-June to mid-July) in 2015, at 20.16 ^{o}C. Then it steadily dropped and reached 11.21 ^{o}C in early October 2015. Mean temperature in the same period in 2016 was generally higher; highest temperature was 21.1 ^{o}C (mid-July to mid-August), decreasing to13.2 ^{o}C in the last 28 days of the experiment. Mean precipitation in 2015 fluctuated from 0.3 to 2.2 mm from June to October. It accumulated to 64.8 mm during 29 to 57 days. 2016 had more rain than 2015, with highest monthly precipitation in the first 28 days (mid-June to mid-July) at approximately 2.5 mm; almost three times that of 2015 at the same time. During the last 28 days, precipitation accumulated to approximately 72.5 mm. Mean wind speeds in 2015 and 2016 were similar, 9.6 to 10.5 km/h in 2015 and 9.3 to 11.5 km/h in 2016.

Correlation analyses between mean internal fluoride and series means of meteorological variables showed impacts on rye grass internal fluoride accumulations over time (growing season 2015 and 2016) (Table 3.1). There were no significant effects of temperature, precipitation and wind speed on internal fluoride accumulations on perennial rye grass based on the series averages; different than the correlation with meteorological parameters and forage internal fluoride (chapter II). A slight negative correlation between temperature and internal fluoride (Table 3.1) might indicate that temperature may have some impacts but not strong enough. Precipitation (mean and accumulated) did not show any significant influence on internal fluoride concentrations in rye grass. The lack of plant water stress during exposure may make precipitation effects difficult to detect. Consistent with long term forage (chapter II) wind speed had no strong impacts, perhaps due to its month and year variability.

4.1.2. Influence of wind direction and distance

Prevailing wind over the study period (June to early October 2015 and 2016) was expressed by direction, frequency and speed (Figure 3.3). In 2015 wind was mainly from the north west, approximately 12.5 % of the time. Thus, upwind locations referred to north and west area, and downwind locations referred to east and south. Seasonal mean wind speed was approximately 10.2 km/h. In 2016, wind was mainly from the west to north west (approximately 12.9 % of the time) and north west (approximately 12.5 % of the time). Seasonal mean wind speed was approximately 10.4 km/h in 2016. 2016 sites were only located east of the emission source (downwind), so wind effects could not be investigated.

A significant interaction was found between wind direction and distance ($p = 0.008$) which means the effects of wind direction may not be independent of distance. At the PG stack and near distance locations (within 500 m) to the emission source, fluoride accumulations at downwind locations were significantly greater than at upwind locations (Figure 3.4). There was no statistically significant difference in mean fluoride concentrations at downwind and upwind locations at medium (1,200 m) and far (2,000 m) locations from the emission source (Figure 3.4). This indicates that the influence of wind direction was most obvious near (500 m) the source, becoming weaker with increasing distance.

Rye grass plants exposed at different cardinal directions had slightly different internal fluoride concentrations although located in given downwind (or upwind) directions (Figure 3.5). Mean fluoride concentrations in south locations were generally highest, following by east locations. There were some exceptions where east locations sometimes had slightly higher concentrations than south locations, such as at near (P2, P3, P4), medium (P2) and far (P2, P3) distances. The influence of wind on perennial rye grass in west locations (upwind) was weaker, particularly further from the source. No similar pattern was found in another upwind direction (north).

4.2. Influence Of Exposure Time

4.2.1. Variation pattern of single year

Exposure time, the duration since plants were placed on sites, significantly influenced fluoride accumulation in 2015 and 2016 ($p < 0.0001$). It explained 11 % (2015) and 17 % (2016) of overall fluoride variability. With increased exposure time, fluoride concentrations in perennial rye grass on the PG stack rose from 43 to 4,600 μg/g, while concentrations at other locations were 3.6 to 394.2 μg/g in 2015 and 2016.

The upward trend of fluoride accumulation with exposure time was consistent at 16 sample locations in 2015. Fluoride mean values were low in the first 28 days and highest following 81 days of exposure (Figure 3.6.A). Approximately 70 % of locations peaked in fluoride concentrations at 81 days after which concentrations slightly declined. Two locations followed a slightly different trend (NPG, WPG), with a continuous rise that peaked after 110 days. In 2016, fluoride concentrations in perennial rye grass increased with exposure time and peaked at 110 days at most locations (Figure 3.6.B). The longer the exposure time, the more fluoride varied in tissue among locations. In the first 28 days fluoride concentration was 5 to 200 µg/g when distances from the stack were pooled. It increased to 10 to 500 µg/g at 56 days, 17 to 730 µg/g at 81 days and 24 to 900 µg/g at 110 days.

Internal fluoride concentrations increased differently approximately every 28 days. The most rapid internal fluoride accumulation period was different in 2015 and 2016; rapid accumulations occurred in 58 to 81 days at most locations in 2015 (Figure 3.7A) and 29 to 56 days (A1) or 82 to 110 days (A2, A3) in 2016 (Figure 3.7B).

4.2.2. Year to year comparison

Most notable annual variation (2015, 2016) of internal fluoride was east of the stack (EPG). In P1 (28 days exposure), mean 2016 fluoride was 1,100 µg/g, 1.5 times that in 2015. In P2 (56 ± 1 days exposure), mean 2016 fluoride (3,300 µg/g) was over twice that in 2015 (1,400 µg/g). In P3 (81 days exposure), the mean 2,700 µg/g in 2016 was 300 µg/g higher than 2015. Highest variation was in P4 (110 days exposure), 4,600 µg/g in 2016 was four times greater than 2015).

EM1, EM2, EM3 and EM4 were replicate sites approximately 1,200 m east of the source. This location was used in 2015 and 2016, therefore data were used for comparison of year to year fluoride variation. Mean internal fluoride in 2016 was generally higher than in 2015, especially in P4 (Figure 3.8). There was no significant difference in mean fluoride in 2015 and 2016 at P1, P2 and P3, and mean values between the two years were very close in the first two periods. However, at P4, mean fluoride in 2016 was significantly higher than in 2015 ($p = 0.003$). The mean value in 2016 was 48 µg/g, more than four times higher than in 2015 (10.5 µg/g).

Similarities occurred between 2015 and 2016. Three locations had high internal fluoride concentrations for monthly, two consecutive months and seasonal means (Table 3.2). In all locations concentrations were lower than regulatory, except at EN, SN and WN which were in the east, south and west, respectively, approximately 500 m from the emission source. Monthly mean fluoride concentration at EN (P3), SN (P2, P3, P4) and WN (P3) in 2015 and EN (P1, P2, P3, P4) in 2016 were above the 80 µg/g regulatory value. Regulatory concentration for two consecutive periods (60 µg/g) was exceeded in EN (2015 and 2016), SN (2015) and WN (2015). Means at these locations exceeded maximum seasonal regulations (35 µg/g). Fluoride in tissue was lower than regulatory guidelines at medium and far distances in 2015 and 2016. Regulatory values refer to maximums for total fluoride concentrations in forage (dry weight) and we used internal fluoride concentrations which should be lower than total fluoride.

4.3. Influence Of Age

Analyses assessing age could only be done on 2016 data. Age, days in the greenhouse before exposure, affected fluoride accumulation, although differences were not statistically significant ($p = 0.257$). A1 (20 days before exposure), A2 (40 days before exposure) and A3 (60 days before exposure) mean internal fluoride in rye grass tissue were not significantly different with distance (Figure 3.9). However, different patterns of internal fluoride with exposure days were found among three age treatments at two distances (Figure 3.10). Perennial rye grass in three age treatments had similar mean tissue fluoride concentrations at each distance during the first two exposure periods (28 and 56 days), with greater differences thereafter. Between 56 to 81 days, generally with longer exposure, there were greater differences among means at both distances. Mean tissue fluoride was highest for A3 (60 day old) plants followed by A1 (20 day old), then A2 (40 day old) plants for most exposure periods.

After 28 days exposure, the internal fluoride at the medium distance location accumulated about 15.2 µg/g internal fluoride in A3 grass tissues, which was the highest in all three ages, following by 9.2 µg/g in A1 tissues, and 7.2 µg/g in A2 tissues. The same trend was also found at the near distance, mean fluoride value was 101 µg/g in A3 tissues, followed by 100.4 and 87.4 µg/g in A1 and A2 tissues respectively. After 56 days, the mean internal fluoride in the medium distance location increased to 25.2 µg/g in A3 and A1 tissues, followed by 21.4 µg/g in A2 tissues. At the near distance location, the fluoride values in three age treatments were very similar, 232, 238, and 237.2 µg/g in A1, A2, and A3 tissues, respectively. By the end of 81 days, the mean fluoride in the medium distance location in tissues of three ages had a wide variation. Fluoride level in A3 tissues accumulated rapidly during 56 to 81 days at 52.4 µg/g in A3 tissues, and 44.4 µg/g in A2 tissues, and slightly increased to 25.6 µg/g in A2 tissues. In the near distance location, the mean fluoride concentrations in A1 increased to 272.8 µg/g higher than that in A2 (216 µg/g) and A3 (203.2 µg/g). During 81 to 110 days of exposure, the mean fluoride level in A1 tissues in the medium location slightly increased to 48.6 µg/g, was the highest among three ages.

4.4. Spatial Emission Pattern

4.4.1. Influence of distance from the source

Although distance from the emission source was statistically significant in 2015 ($p < 0.001$), significance may have no statistical meaning since it was confounded by the effects of wind direction due to the interaction. Distance was an independent factor and significantly influenced fluoride concentration in rye grass in 2016 ($p < 0.0001$). It was considered the factor with most influence on internal fluoride concentrations since 65 % (2016) of overall fluoride concentration variation over the study period can be explained by distance from emission source. Relative to other factors, exposure time was 11 %, interaction between distance and wind was 2 % in 2015; exposure time was 17 % and age was 0.4 % in 2016.

Obvious variability was found in fluoride geographical distance in 2015 and 2016. Fluoride concentrations were significantly different in perennial rye grass among distances in either upwind or downwind locations in 2015 and all locations (downwind) in 2016 (Figure 3.11). 2015 overall mean fluoride concentration in rye grass on the PG stack was highest at 960 µg/g over exposure periods; approximately 14, 44 and 76 times more than that at near (500 m), medium (1,200 m) and far (2,000 m) distances. Mean values and variations at distance were generally higher in 2016 than 2015. Maximum mean fluoride concentrations during the growing season were 2,925.0 µg/g at the PG stack, 12 and 100 times greater than at the near and medium distances, which were 239.2 and 29.1 µg/g (age treatments pooled), respectively.

4.4.2. Fluoride dispersal model

Overall fluoride concentration had a steep gradient near the PG stack (Figure 3.12.). During four periods of exposure in 2015 and 2016, fluoride concentrations in rye grass decreased exponentially further away from the source, with a sharp drop within the first 500 m, after which concentrations declined slightly, with very low values further than 2,000 m.

Fluoride dispersal regression models were simulated with the 2015 data to describe and predict internal fluoride concentrations in rye grass during the growing season. Overall mean internal fluoride concentration, regardless of direction from the PG stack can be determined by imputing the value of exposure days and distance from source to the equation: internal fluoride = 13.297 x exposure days x $e^{-0.01108 \text{ x distance}}$. R^2 (coefficient determination) will show how close observed and predicted values are, reflecting the goodness of fit of the regression models. In general, the higher the R^2, the better the model fits the data. In the model based on overall data, R^2 was 0.63 which means 63 % of observed data perfectly fit with the predicted values from the model.

To achieve more accuracy for predicted fluoride concentrations in rye grass tissue at a specific distance from the source, regression models were simulated for each cardinal direction, equation: internal fluoride = 18.831 x exposure days x $e^{-0.00837 \text{ x distance}}$ for east, equation: internal fluoride = 18.252 x exposure days x $e^{-0.00838 \text{ x distance}}$ for north, equation: internal fluoride = 13.900 x exposure days x $e^{-0.00377 \text{ x distance}}$ for south and equation: internal fluoride = 1.934 x exposure days x $e^{-0.00168 \times distance}$ for west. R^2 values were 0.98, 0.87, 0.80 and 0.63 for north, south, east and west models, respectively. Observed data in the west were scattered relative to other directions where data concentrated upon regression lines.

The model represented 2015 and 2016 internal fluoride data east of the source (Figure 3.13). Approximately 0.62 of 2016 data fit the east dispersal model with R^2 over four exposure periods of 0.68 (P1), 0.45 (P2), 0.76 (P3) and 0.64 (P4). The east dispersal model can represent approximately 0.90, 0.93 and 0.83 of the model in P1, P2 and P3 and only 0.37 in P4 in 2015.

4.4.3. Fluoride zones

The maximum mean fluoride concentration in forage dry weight 80 µg/g suggested by Alberta Environment (2016) for any single 30 day periods during the growing season was applied to the fluoride dispersal models as y to estimate the mean distance threshold at each direction. The distance threshold refers to distance of maximum line border within which monthly internal fluoride concentrations in perennial rye grass might be above regulatory values (Table 3.3).

Differential of distance thresholds explained why the contamination zone is not a circle and indicates that high internal fluoride concentrations may accumulate in rye grass exposed in some directions to the source (Figure 3.14). The contamination map delineated the potential zone of high internal fluoride concentrations (> 80 µg/g) by interpolation predicted fluoride values from the regression models. No grazing activities have been observed in most of these areas. The zone of high total fluoride concentrations in perennial rye grass may be much larger than the zone of internal fluoride as total fluoride should be higher than internal fluoride.

4.5. Influence Of Plant Species

4.5.1. Comparison of perennial rye grass and forage

Forage sampled in situ near the PG stack from 2008 to 2016 throughout the growing season and experimental data were compared at distances of approximately 1,200 m east of the PG stack. The monthly pattern of fluoride was consistent among years with fluoride peak values appearing in fall. Although seasonal fluoride values in forage and perennial rye grass in 2016 were notably higher than 2015, internal fluoride in perennial rye grass increased almost double that of total fluoride in forage from 2015 to 2016. Seasonal mean internal fluoride in perennial rye grass (A1 20 days) were 16 µg/g in 2015, and increased by 45.0 % in 2016 (29.1 µg/g) (Table 3.2), whereas in forage it increased less, by 26.3 % from 64.0 to 86.8 µg/g (Table 2.2).

4.5.2. Other species

Mean fluoride concentrations in alfalfa, corn, june grass, sunflower and perennial rye grass were compared after four exposure periods in 2016 (Figure 3.15). Sunflower plants had highest fluoride concentrations after 28 days, considerably higher than perennial rye grass. Although there were no significant mean differences between june grass and perennial rye grass over four exposure periods, june grass means were mostly slightly higher than rye grass. Species differences may be due to variation in fluoride tolerance and species absorption capacity.

After 28 days of exposure (P1) internal fluoride in june grass was highest (29.75 µg/g), followed by sunflower (18 µg/g); significant differences were found between corn and sunflower (p = 0.04). After 56 days of exposure (P2), mean fluoride in sunflower was 78.5 µg/g, significantly higher (p = 0.02) than in perennial rye grass (35 µg/g). Similarly, significant differences in fluoride concentrations ($p < 0.05$) were found between sunflower and rye grass after 81 (P3) and 110 days (P4). After 81 days sunflower had the highest fluoride at 59.8 µg/g, 27.1 µg/g higher than in rye grass. The biggest difference occurred after 110 days with 120 µg/g in sunflower, three times that in perennial rye grass (40.7 µg/g).

Most rapid fluoride accumulation periods were after 82 to 110 days (Figure 3.16). Sunflower had highest concentrations after 28 days exposure, significantly different than rye grass, indicating sunflower might be more fluoride sensitive than the other four species assessed. Mean fluoride in alfalfa, corn and june grass had an upward trend over exposure periods, although sunflower had a slight drop from 57 to 82 days. Alfalfa accumulated 7.25 µg/g the first 28 days, then accumulated at the same speed for 29 to 56 days, before rising to 27.5 µg/g at about double speed, increasing most rapidly during 82 to 110 days, eventually reaching 89.3 µg/g. Similarly, internal fluoride in corn increased rapidly to reach 78.5 µg/g by 110 days. There was a rapid increase of fluoride in june grass in the first (29.8 µg/g) and last 28 days (48.75 µg/g). Sunflower mean fluoride concentrations increased to 18 µg/g by 28 days and accumulated 78.5 µg/g by 56 days before dropping to 59.8 µg/g at 81 days, then increasing to 120 µg/g by 110 days.

5. DISCUSSION

5.1. Defoliation

Defoliation by insects and other fauna resulted in severe loss of biomass in 2015. In the extremely dry and hot weather of 2015, there were reports of more grasshoppers than seen for many years all across Alberta (CBC News 2015). They intensely consumed the rye grass in pots and vegetation in the surrounding area. Defoliation resulted in a loss of approximately one replicate per two treatments during the second harvest and two replicates per treatment in the third harvest. By the last harvest, three treatments lost half their replicates and the rest lost one replicate. This affected statistical analyses, as a minimum of three replicates are required. The effective use of protective measures such as wood pallets, cages and repellent and more precipitation led to fewer defoliation issues in 2016. Only one alfalfa sample was lost in the last harvest in early October which was likely due to a small rodent that got through cage openings.

Possible approaches to protect plant biomass include physical protective measures such as pest nets or elevated exposure devices; chemical protective measures such as insecticides and animal repellents; use of high seeding rates and; delaying placement of plants in the field until they are older. These improvements are suggested for future biomonitoring studies to ensure adequate samples for laboratory and data analyses.

5.2. Loss Of Fluoride

The drop in fluoride accumulation by vegetation over time has been reported in numerous other studies. For example, fluoride concentrations in spruce needles lost 340 μg/g over 5 months (Knabe 1970), and it decreased by 70 μg/g in tomato within 3 days (Davison 1982). The mechanisms of this phenomenon are not well studied or understood. Davison (1982) suggested the cause could be defoliation (death, loss), growth dilution, guttation and translocation to roots.

Defoliation by insects in 2015 was most severe from 57 to 81 days of exposure with perennial rye grass biomass. This could have affected fluoride concentrations as half the leaf margins and tips, where high fluoride concentrations are likely contained, were lost in nearly all locations. Losing biomass from death may not be taken into account as death rate is not high enough to offset fluoride deposition and uptake when atmospheric fluoride concentrations are not low.

Growth dilution, occurs when plant dry matter increases faster than fluoride is gained. Thus dilution likely only happens when grass is growing quickly and atmospheric fluoride concentration is not much above background (Weinstein and Davison 2004). During 57 to 110 days exposure in 2015, growth of perennial rye grass leaves was slow, with change in height averaging less than 5 cm. Thus, it may not be responsible for decreased fluoride in grass.

Guttation, the exudation of drops from margins and tips of leaves of vascular plants, is particularly common in grasses (Weinstein and Davison 2004). Fluoride ions in guttation droplets were detected on maize (Takmaz-Niscancioglu 1983), although the exudation rate was low. Therefore guttation may not cause great loss of fluoride.

Translocation to the root may play a significant role in reducing fluoride in perennial rye grass. In our experiment, only above ground biomass of perennial rye grass was harvested for fluoride analyses. If a proportion of fluoride in leaves and stems was transported to roots, this phenomenon could be explained. Some researchers think small amounts of fluoride may be translocated from leaf to roots (Keller 1974). However, Doly (1986) suggested fluoride might enter the xylem at night and could be carried to all parts of leaf; this is less feasible when transporting to remote parts like roots. In one study, after fluoride accumulated in plants, translocation from leaf to leaf or leaf to roots did not occur or was small (Ledbetter et al 1960).

5.3. Age Of Plants

The differences among three ages at most distances over exposure periods in our study was contradicted in some research and supported in others. Junior et al (2008) found no significant difference in fluoride in *Bidens pilosa* L (black jack), *Ipomoea cairica* (L) Sweet (morning glory) and *Calopogonium mucunoides* Desv (calopo) with different plant ages at 5,400 and 10,500 m from the emission source. However, they found significantly higher concentrations in younger leaves of *Calopogonium mucunoides* closer (2,900 m) to the source. Rodriguez et al (2012) and Atasoy et al (2016) found fluoride concentrations in plant tissue increased with age. Our highest fluoride in the oldest perennial rye grass (A3) but lowest fluoride not in youngest rye grass (A1) is not explained. Very few studies investigated the influence of age on fluoride accumulation of plants although there is extensive evidence that could explain the mechanism of how fluoride affects physiological and biochemical processes.

5.4. Dispersal Model

To simulate the relationship between distance from emission source and fluoride concentrations, there were two main regression models from previous studies, linear and non-linear. Linear regression models are used less as few studies observed a linear relationship between fluoride in plants and distance from emission source (Rodriguez et al 2012). Non-linear exponential models are more commonly used. For example, Franzaring et al (2007) found airborne fluoride had a strong exponential relationship with distance (Fluoride = $424.7 \times e^{-0.0021 \times \text{Distance}}$), with R^2 0.41. Mezghani et al (2005) simulated exponential models to describe fluoride gradients in dry weight along distances for five tree species; R^2 was 0.92 to 0.99 due to small sample size.

Similar to previous studies, we observed an exponential decrease of fluoride concentrations in perennial rye grass along distances from the PG stack. The main improvement with our model is exposure time, an additional parameter, was added to the models since we found it had a significant impact on fluoride concentrations in perennial rye grass ($p < 0.0001$) other than distance ($p < 0.0001$) over the study period. After adding the parameter of exposure time, the residual standard error of the overall model regardless of directions decreased by 20.6 on 180 degrees of freedom and a higher R^2 was achieved, increasing from 0.59 to 0.67. Thus, both parameters are important.

The R^2 of regression models of three directions (east, north, south) were high, from 0.80 to 0.98 in 2015. The R^2 of the west dispersal model was comparatively low, at 0.63. Observed data points in the west locations were scattered and the high variability impeded model accuracy, thus affecting predicted values. This might be due to ongoing construction activities in the west adjacent area of the PG stack which were less than 2 km from west research sites since it may alter low and ground level wind turbulence which could potentially affect fluoride spatial dispersion and thus influence results. Dust from traffic induced by construction activities might be a significant issue as it may alter rate of vegetation surface deposition. In future biomonitoring experiments, research sites prone to disturbance, such as construction, should be avoided when selecting sample sites.

The overall R^2 of 0.62 in 2016 was lower than 2015 (0.80), but 0.62 is good enough to simulate the relationship between fluoride changes with distance and exposure time. One possible explanation for the lower R^2 in 2016 may be the high variability of fluoride concentrations from the emission source. Fluoride from the east PG stack location varied more in 2016 than 2015, which might strongly influence the R^2. For example, fluoride in grass tissue on the PG stack was 1,200 to 2,400 µg/g in 2015, and 1,100 to 4,600 µg/g in 2016. Variability might be caused by variations in PG stack pond soluble fluoride which increased from 0.74 to 0.87 % weight. South and north dispersal models still need evaluation by future internal fluoride monitoring results.

Fluoride dispersal models are hypothetical and observed data points fit the models relatively well at closer distances to the emission source. However, models might be unstable to fit observed data at further distances to the emission source (Figure 3.12). Further than 1,200 m from the source, predicted internal fluoride concentrations approached zero. Observed internal fluoride concentrations at 1,200 m were 21.6 µg/g on average, higher than predicted concentrations. Regression models can be improved with a larger sample size in the future. The distance threshold and zone of influence were generated based on predicted values from regression models (Table 3.3, Figure 3.14), therefore the zone with high internal fluoride concentrations should be larger in practice.

6. CONCLUSIONS

Using *Lolium perenne* L. (perennial rye grass) as a bioindicator for fluoride emissions from a fertilizer plant was successful. Distance from the emission source had the greatest influences on fluoride accumulation in perennial rye grass, following by exposure time. The influence of wind direction was obvious near (500 m) the source, weakening with distance. Age was statistically unimportant in fluoride accumulation in perennial rye grass.

Fluoride accumulation in perennial rye grass peaked after 81 days of exposure in 2015 and 110 days in 2016. Age had no significant impact on fluoride accumulation. Alfalfa, corn, june grass and sunflower responded differently to fluoride than perennial rye grass. Sunflower accumulated significantly more fluoride than perennial rye grass after 28 days.

Airborne fluoride emission patterns around the fertilizer production facility were determined. The dispersal model of the area east of the emission source was well supported by 2016 fluoride data. Fluoride concentrations in perennial rye grass showed a steep pollution gradient in the vicinity of the PG stack, decreasing exponentially further away from the source, with a sharp drop within the first 500 m.

Table 3.1. Correlation analyses between internal fluoride and meteorological parameters.

Parameters	Mean Temperature		Mean Precipitation		Accumulated Precipitation		Mean Wind Speed	
	p-value	r	p-value	r	p-value	r	p-value	r
Internal Fluoride Variation	0.061	-0.685	0.275	-0.440	0.287	-0.431	0.439	0.320

Table 3.2. Mean internal fluoride in perennial rye grass over 2015 to 2016 growing season.

		One Month				Two Consecutive Months		Seasonal	
		Regulatory < 80 μg/g				Regulatory < 60 μg/g		Regulatory < 35 μg/g	
Year	Location	P1	P2	P3	P4	P1-P2	P2-P3	P3-P4	P1-P4
2015	EN	20.4	67.6	163.5	61.8	44.0	115.6	112.6	78.3
	EM	8.3	27.0	20.5	10.5	17.6	23.8	15.5	16.0
	EF	6.5	11.1	25.5	9.0	8.8	18.3	17.3	13.0
	NN	6.1	19.5	34.3	20.0	12.8	26.9	27.1	20.0
	NM	6.1	16.3	35.3	16.0	11.2	25.8	25.6	18.6
	NF	4.1	6.4	16.0	7.5	5.3	11.2	11.8	7.4
	SN	48.0	95.0	226.7	177.7	71.5	160.8	202.2	136.8
	SM	13.5	18.8	50.3	38.8	16.1	34.5	44.5	30.3
	SF	14.8	3.7	13.5	11.5	9.2	8.6	12.5	10.9
	WN	30.7	72.7	113.0	43.0	51.7	92.8	78.0	64.8
	WM	10.8	17.3	34.0	14.0	14.0	25.6	24.0	19.3
	WF	8.5	18.8	33.7	13.3	13.6	26.2	23.5	17.9
2016	EN	96.3	235.7	230.7	394.3	166.0	233.2	312.5	239.2
	EM	10.5	23.9	40.8	41.3	17.2	32.4	41.0	29.1

Table 3.3. Summary of distance threshold in four directions of the emission source.

Equation		Distance Threshold (m)				
		P1	P2	P3	P4	R^2
East	F=18.831 × Exposure days × exp (-0.00837*Distance)	225	310	352	389	0.796
North	F=18.252 × Exposure days × exp (-0.00838*Distance)	221	306	348	385	0.977
South	F=13.900 × Exposure days × exp (-0.00377*Distance)	419	607	700	781	0.872
West	F= 1.934 × Exposure days × exp (-0.00168*Distance)	0	191	399	581	0.632

Figure 3.1. Map of study sites. 2015 sample sites are shown in white points and 2016 sites in red points.

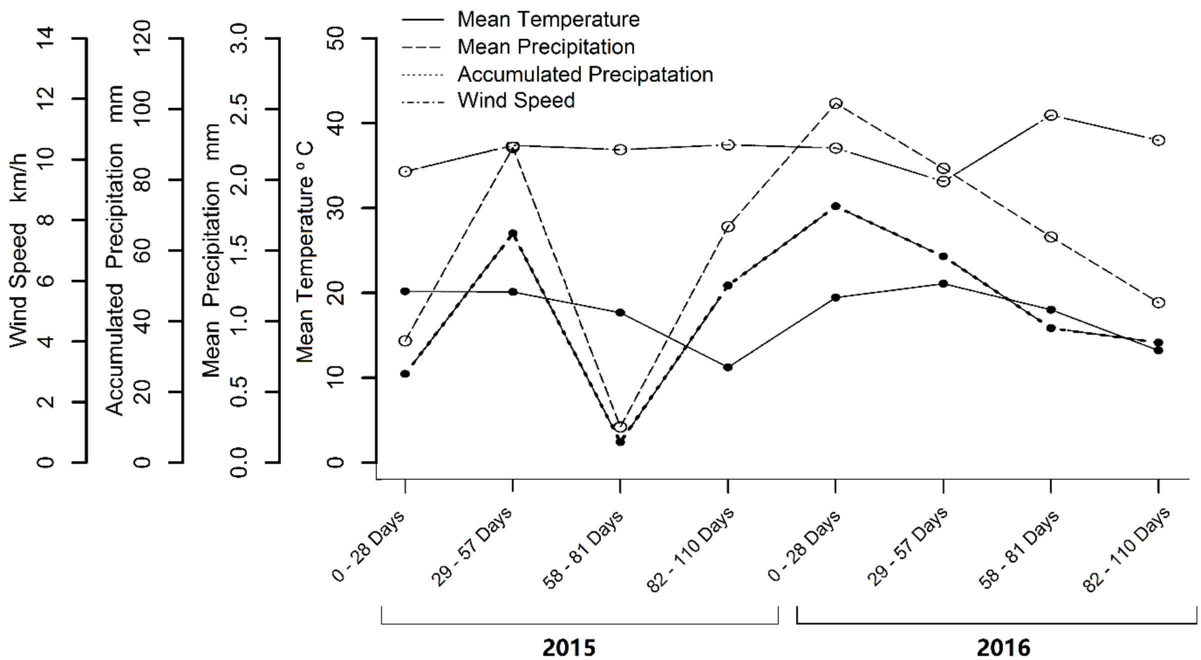

Figure 3.2. Mean temperature, mean precipitation and accumulated precipitation over study periods in 2015 and 2016.

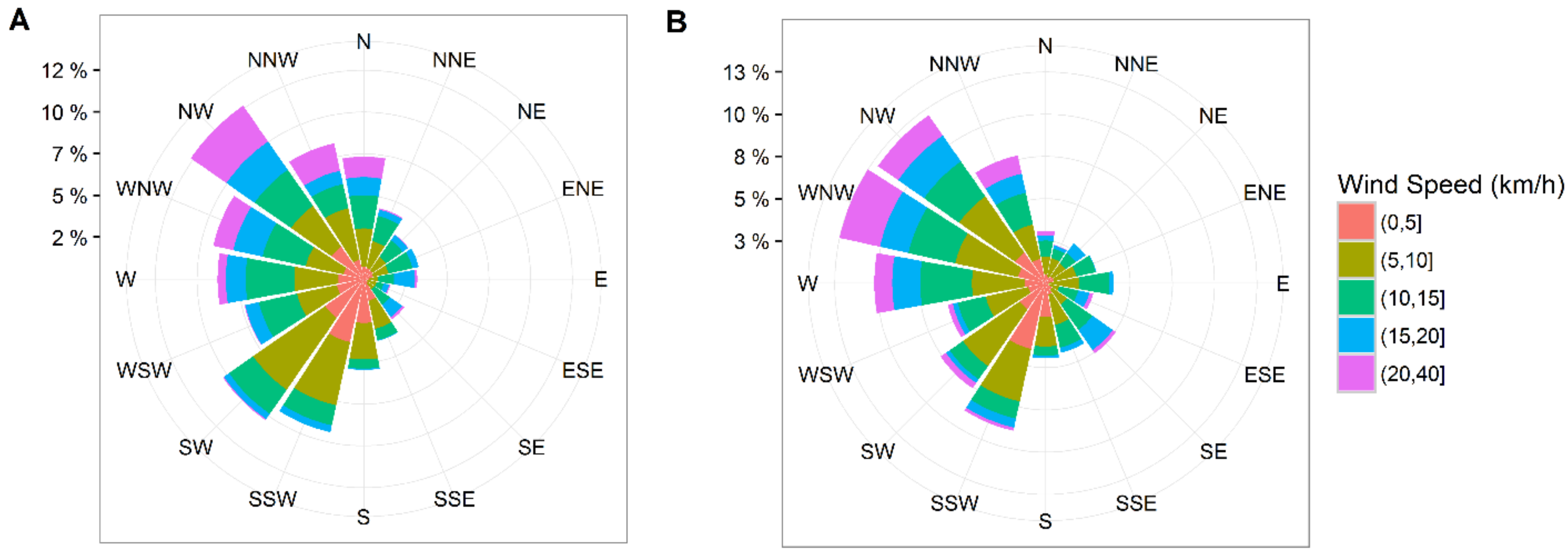

Figure 3.3. Windrose for the research area in 2015. Wind was expressed by wind direction, wind frequency and wind speed, June 15 to October 3, 2015 (A), June 15 to October 3, 2016 (B).

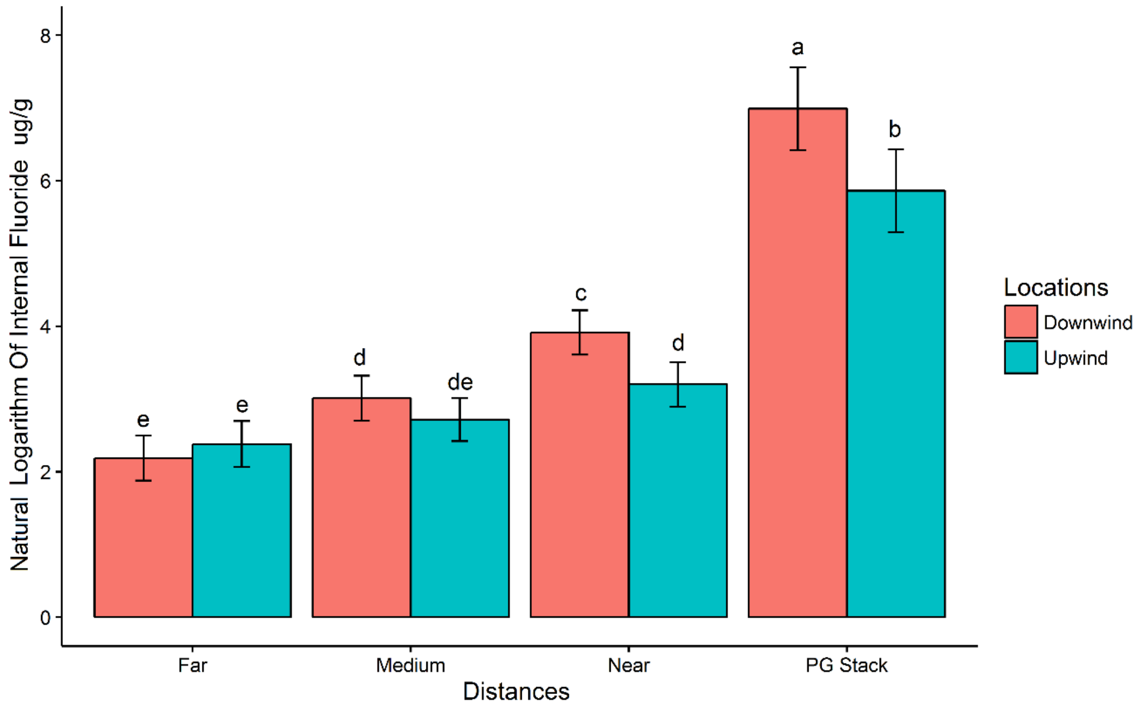

Figure 3.4. Internal fluoride in perennial rye grass exposed in upwind and downwind locations at distances. Error bars are standard error. Different letters indicate significant differences between downwind and upwind locations at four distances.

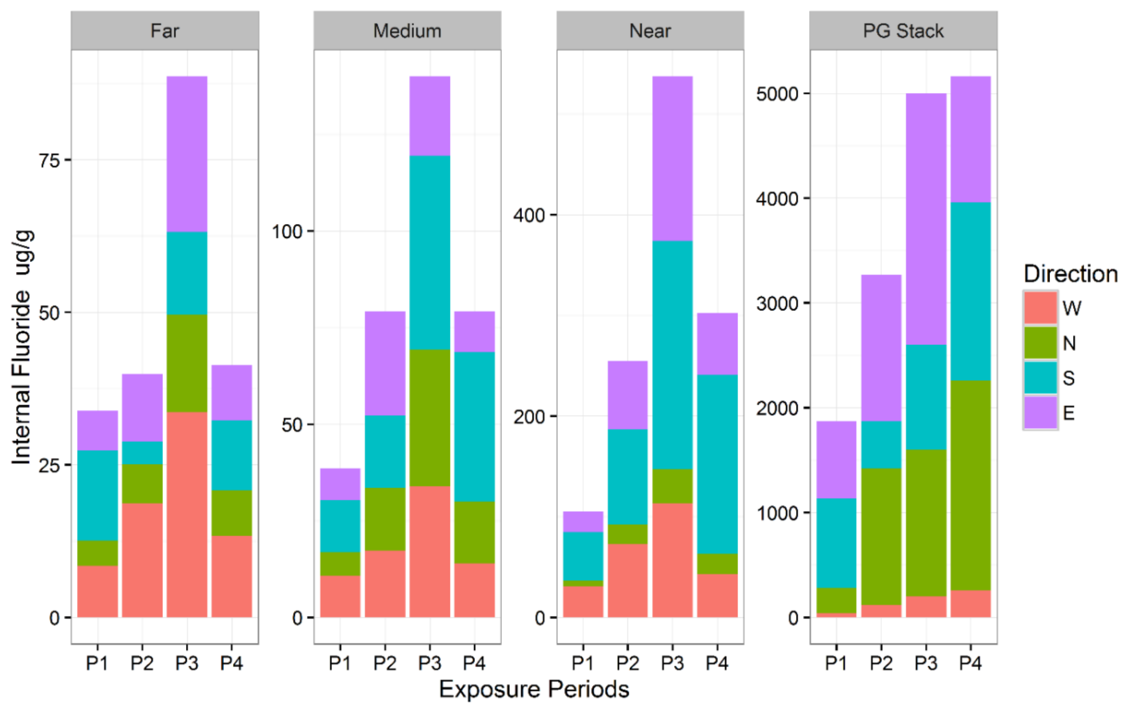

Figure 3.5. Internal fluoride in directions, distances and exposure periods. Different colours indicate the value in different directions.

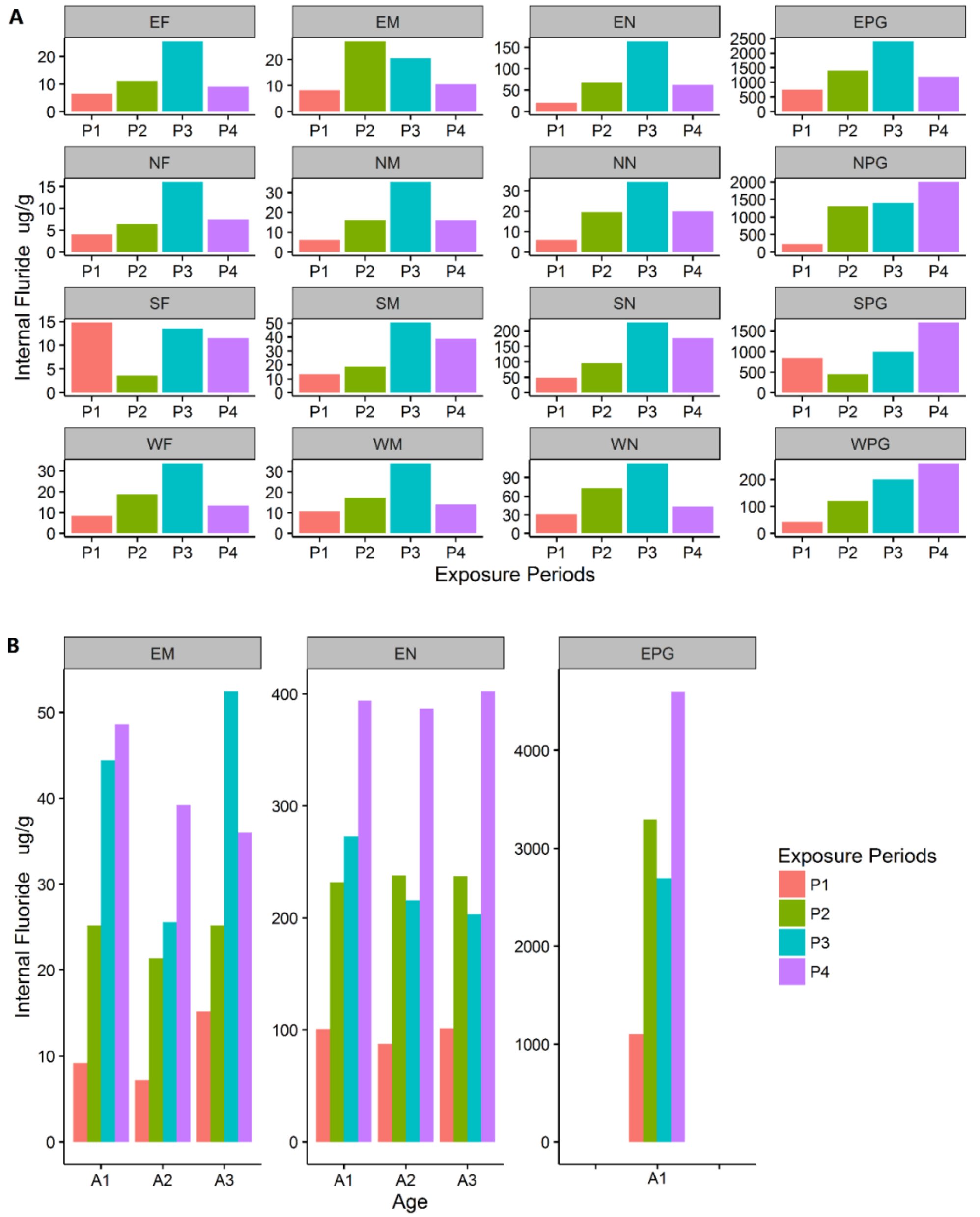

Figure 3.6. Mean internal fluoride concentrations in perennial rye grass for sample locations over four exposure periods in 2015 (A) and 2016 (B). The fluoride value is a mean of four replicates at the same location, except on the PG stack where the mean represents one value in each direction as reference values of the emission source. First letter of the location name represents the cardinal direction (N, E, S, W) and last one or two letters represents distance to the source (F = far distance, M = medium distance, N = near distance, PG = on the PG stack).

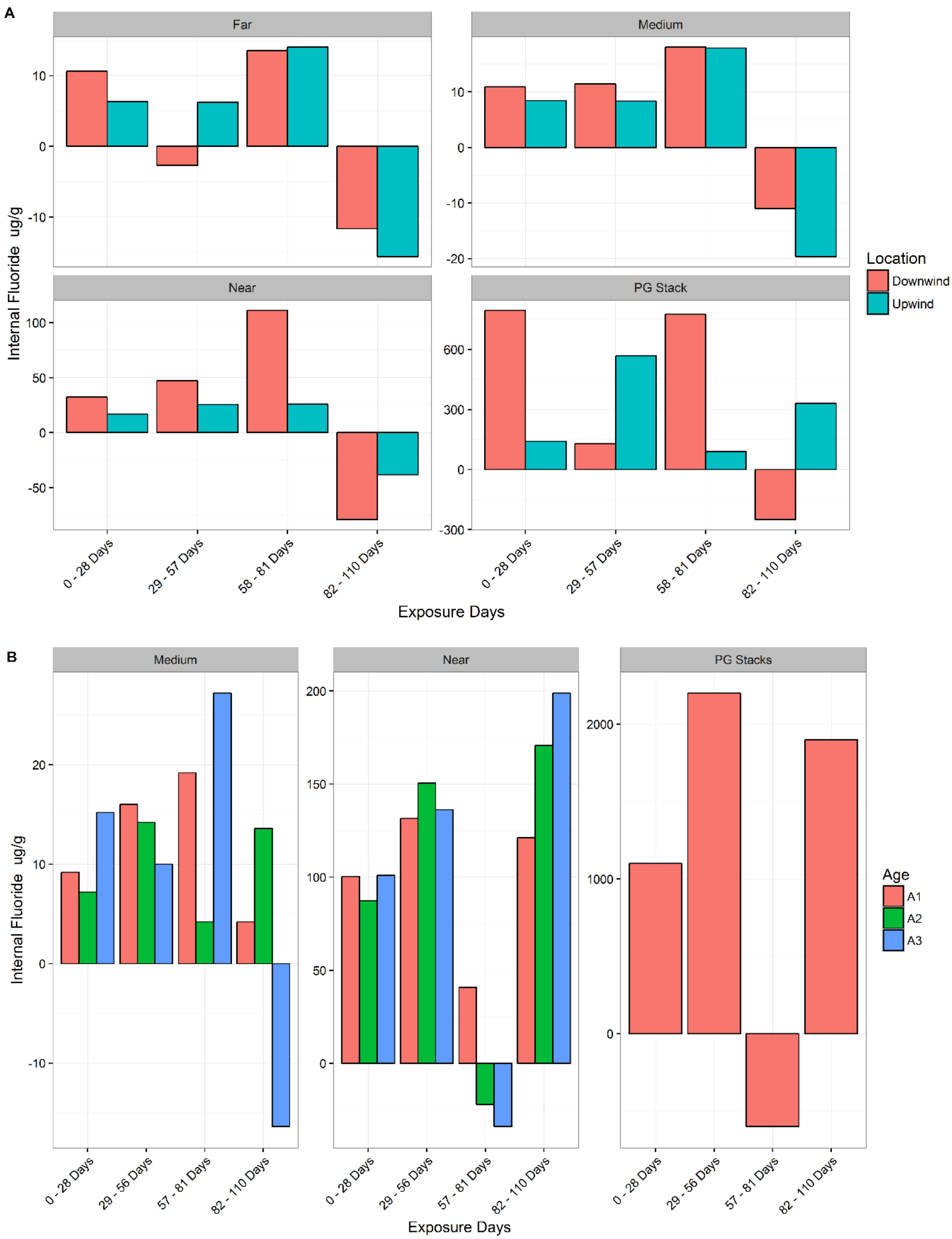

Figure 3.7. Mean variation of fluoride concentrations in tissues of different age rye grass.

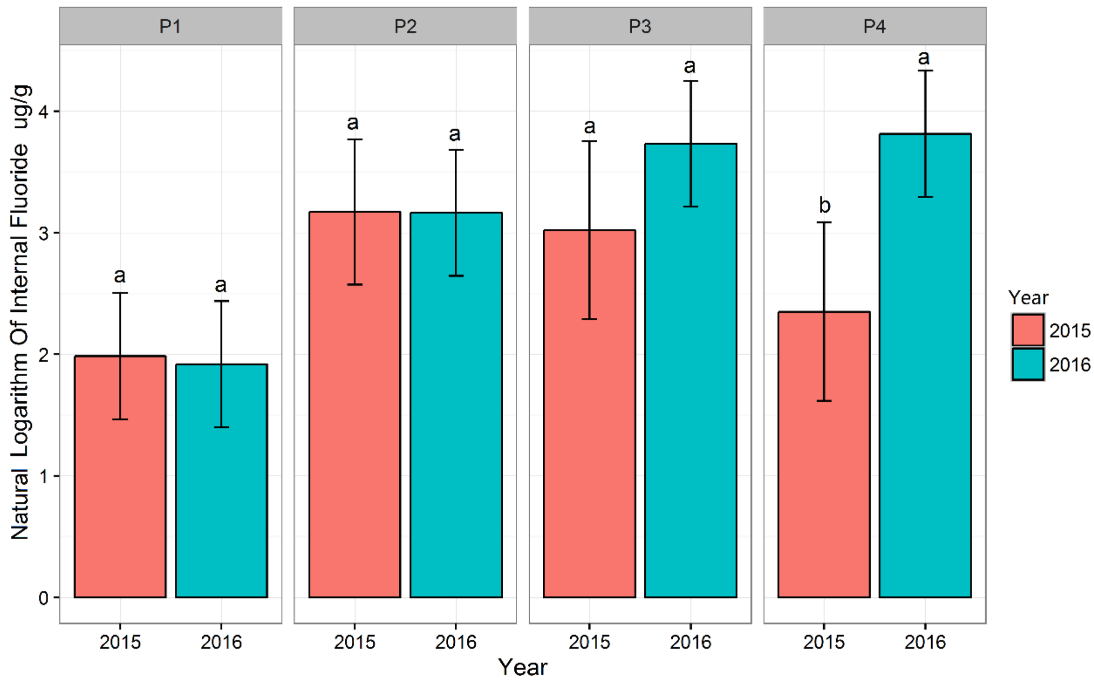

Figure 3.8. Mean internal fluoride concentrations in perennial rye grass between 2015 and 2016 over four exposure periods. Error bars are standard error. Different letters indicate significant differences in internal fluoride concentrations of 2015 and 2016.

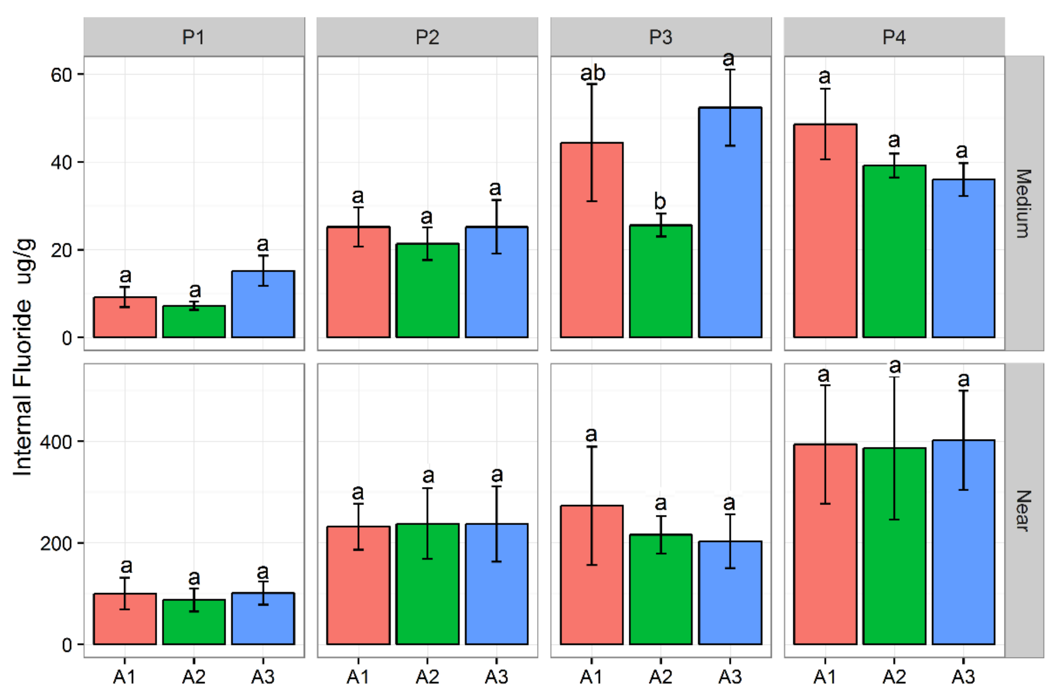

Figure 3.9. Mean fluoride concentrations in tissues of different ages of perennial rye grass. Error bars are standard error. Different letters indicate significant differences among ages.

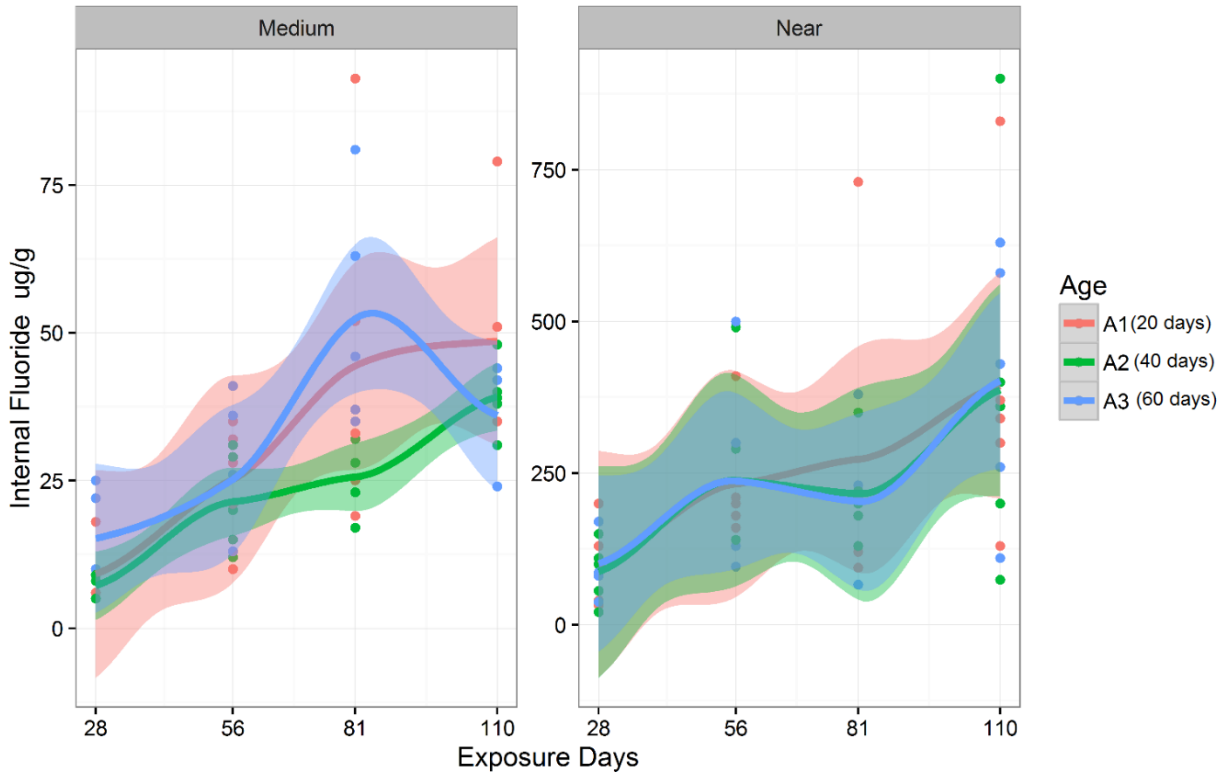

Figure 3.10. Pattern of internal fluoride accumulation of perennial rye grass with exposure days. Smooth curves were generated by LOESS method (t-based approximation). Shadows were standard deviation band on a 0.95 confidence interval.

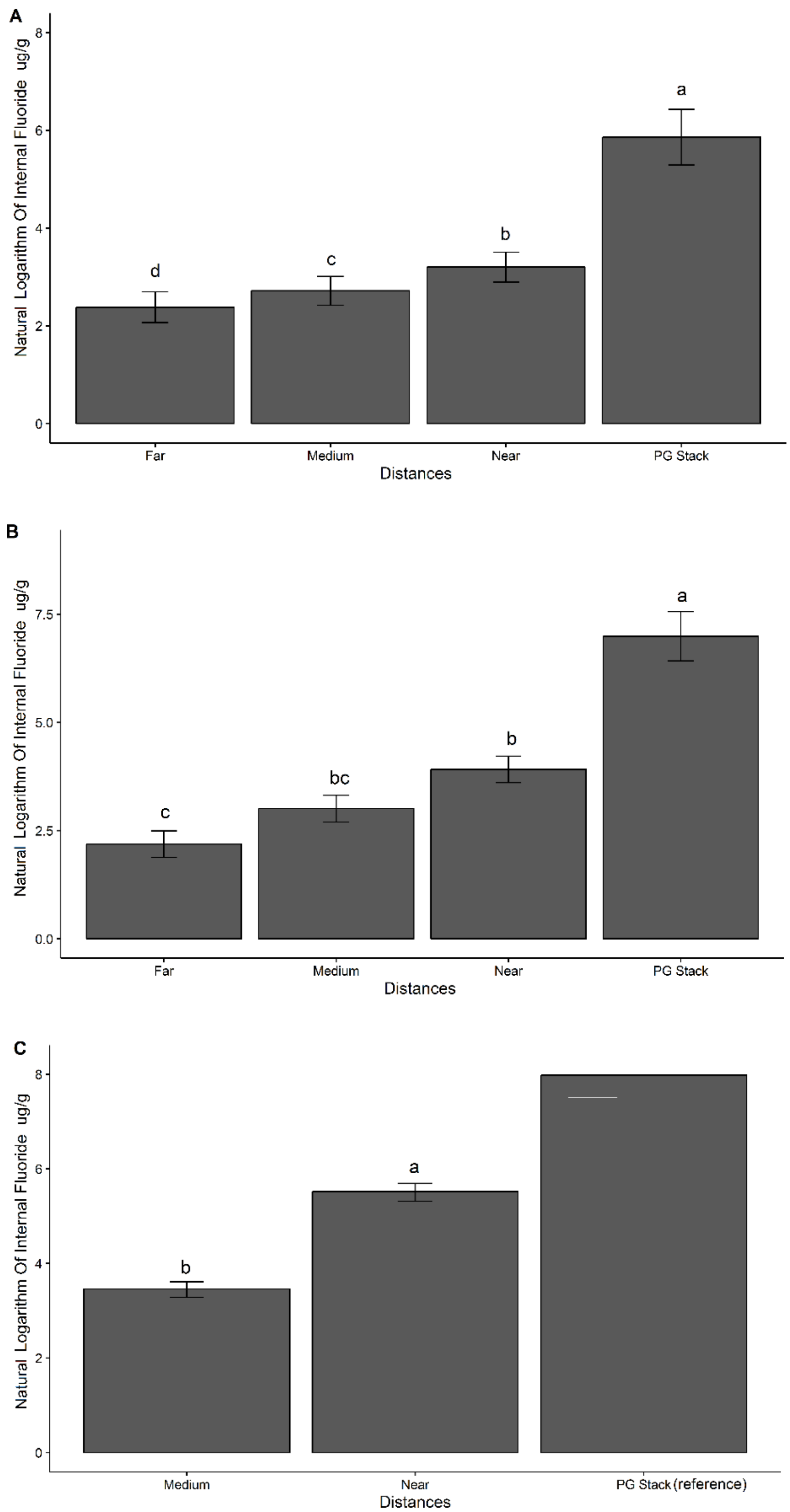

Figure 3.11. Fluoride concentrations differences at distances. 2015 upwind locations (A), 2015 downwind locations (B) and 2016 locations (C). Error bars are standard error. Different letters indicate significant differences at distances to the emission source

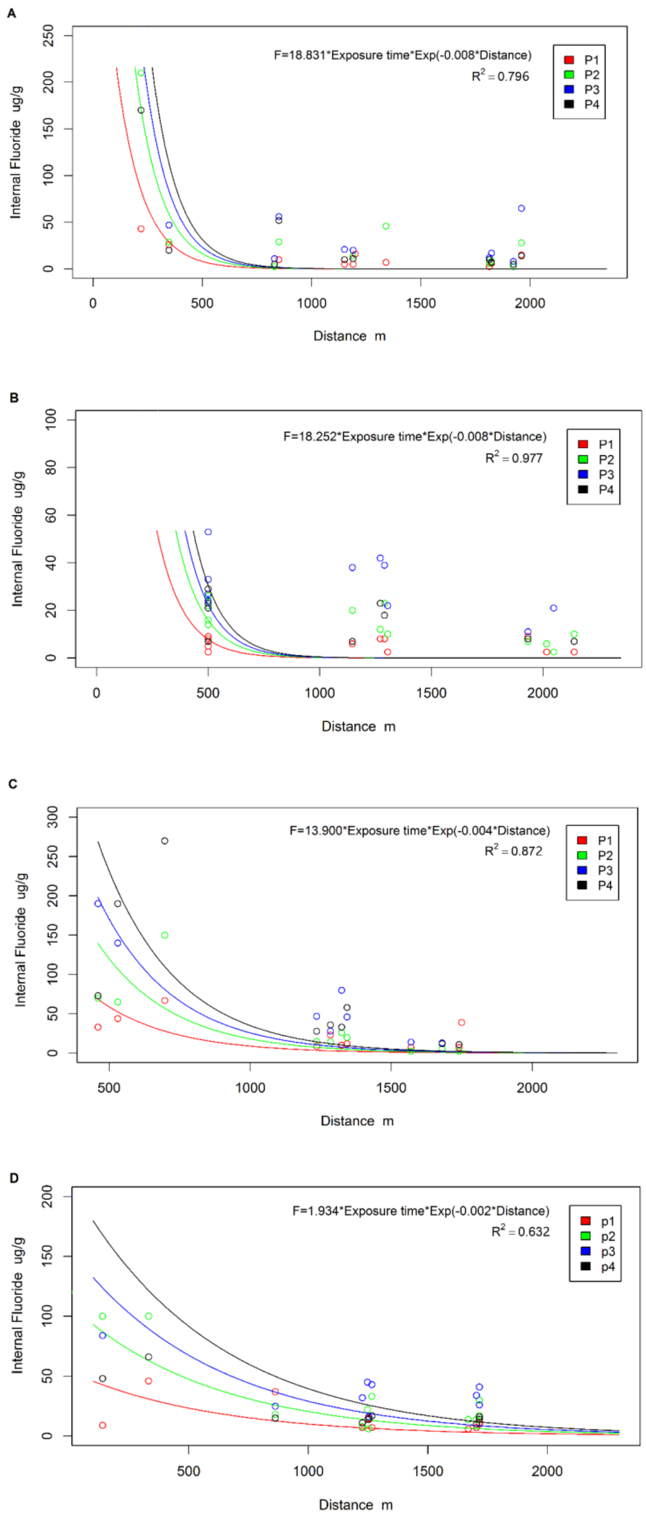

Figure 3.12. Relationship between fluoride concentrations in perennial rye grass tissue and distance from the source. Different colours indicate different exposure periods. Data east of source (A), north of source (B), south of source (C), west of source (D).

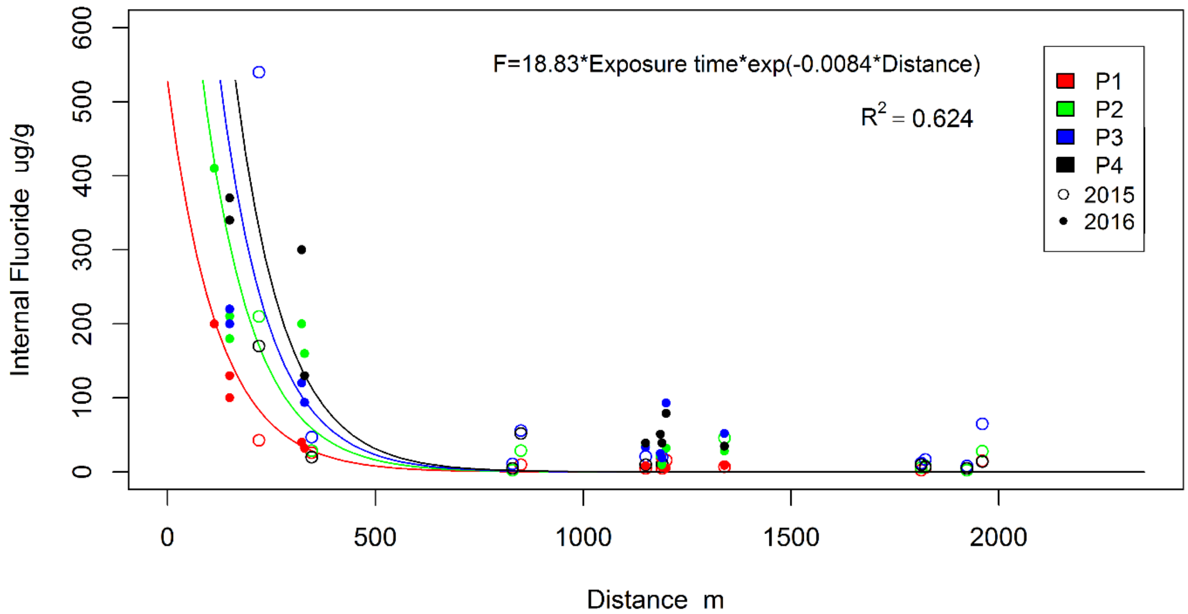

Figure 3.13. Relationship between fluoride concentrations in perennial rye grass tissues and distances from east locations in 2015 and 2016. Different symbols and colours indicate different years and exposure periods.

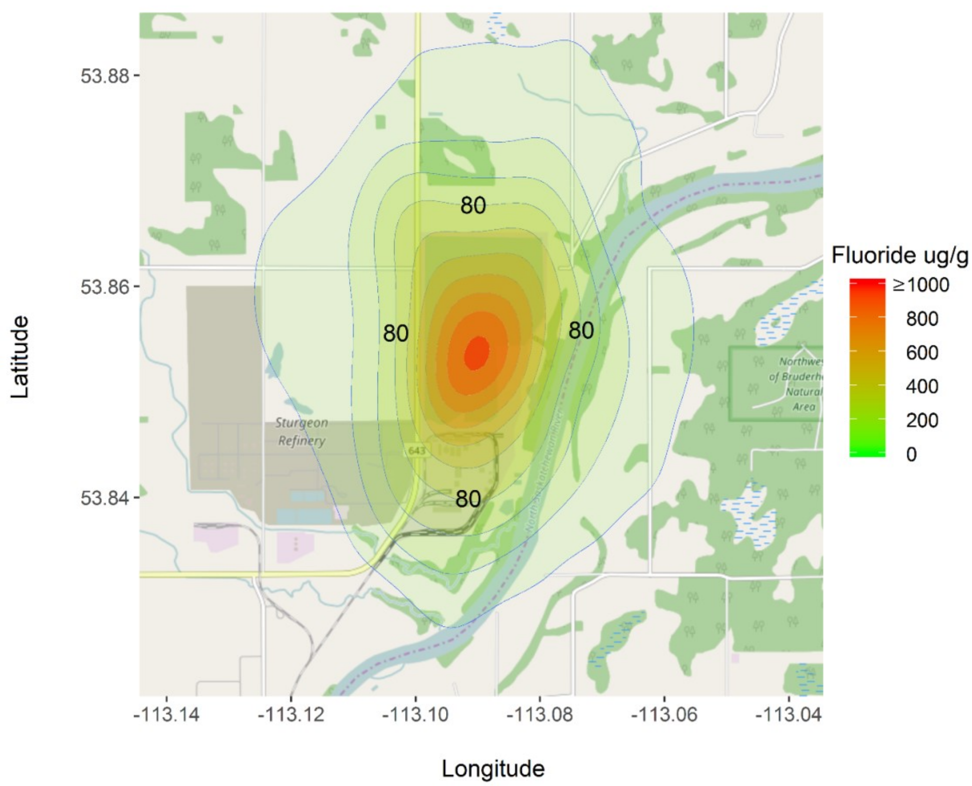

Figure 3.14. Map of internal fluoride zones for Agrium Redwater Fertilizer Operations adjacent area. Colour shows the fluoride gradient. Red for the higher values and green for lower values.

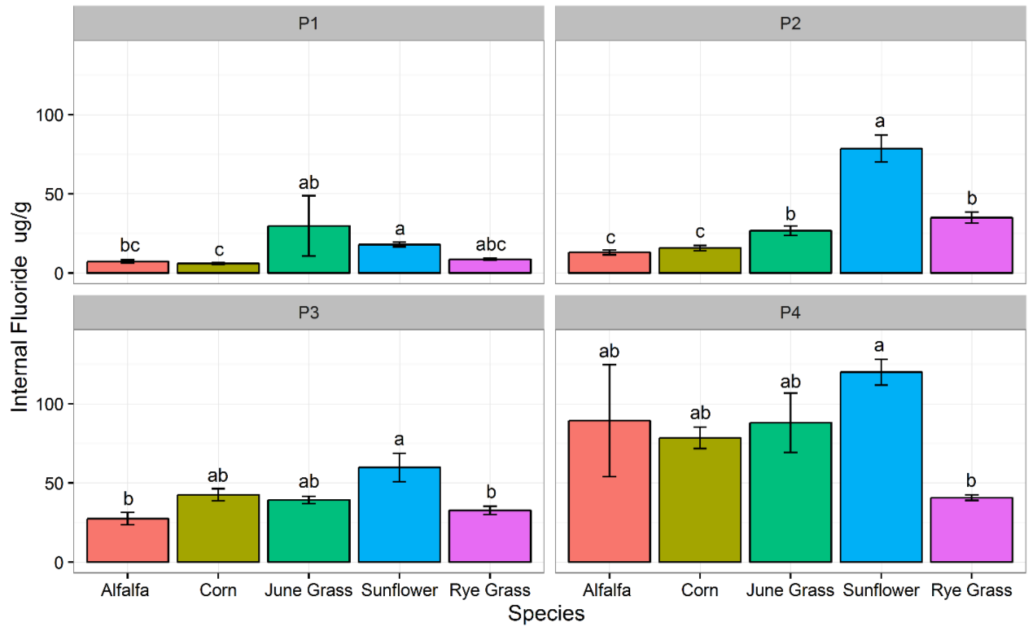

Figure 3.15. Internal fluoride in alfalfa, corn, june grass, sunflower and perennial rye grass in four exposure periods. Error bars are standard error. Different letters indicate significant differences among species.

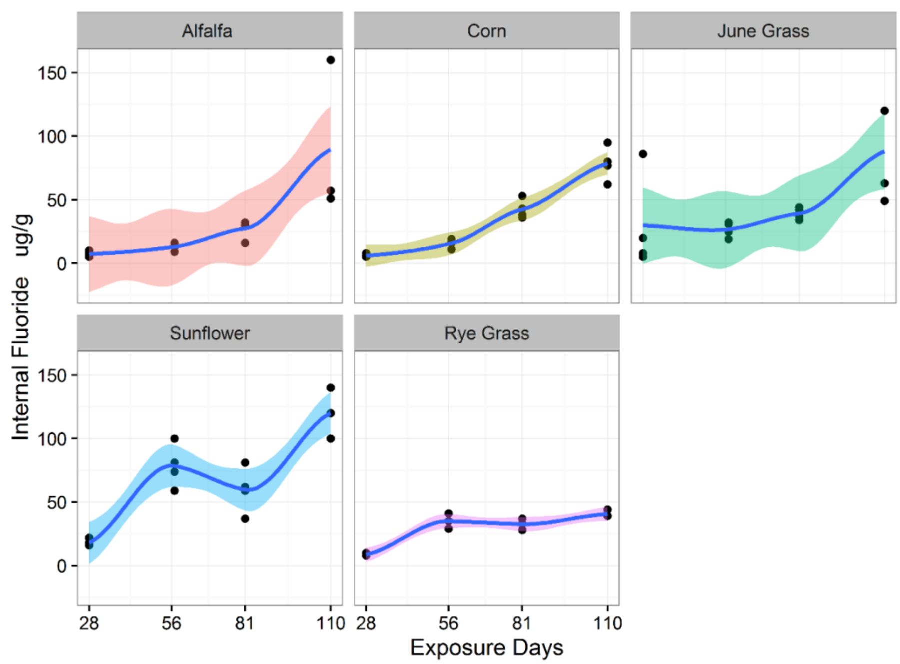

Figure 3.16. Internal fluoride accumulation in five species with exposure days. Smooth curves were generated by LOESS method (t-based approximation). Shadows were standard deviation band on a 0.95 confidence interval.

IV. SUMMARY, LIMITATIONS, APPLICATIONS AND FUTURE RESEARCH

1. RESEARCH SUMMARY

From Agrium monitoring data and meteorological data over 2008 to 2016, the monthly pattern of total fluoride in forage grass was consistent year by year. Total fluoride concentrations in forage was relatively low in early summer (June, July), peaking in fall (late August to early October). There were year to year fluctuations of the seasonal mean of total fluoride concentrations in forage. The seasonal mean was relatively low in 2010, and high in 2011 and after 2013. This fluctuation may be attributed to soluble fluoride in PG ponds. Temperature and precipitation also strongly affected monthly fluoride variations of total fluoride in forage.

Determining external fluoride accumulation is important for understanding the relationship between two forms of fluoride in forage. Temperature and precipitation had significant impacts on external fluoride accumulation in forage with highest values in fall (September or October) when weather became cooler and drier and lowest in summer (June or July). The negative correlation of external fluoride and distance indicated there may be more particle phase fluoride in forage close to the PG stack and less with distance. On average 32.3 % total fluoride can be washed off (external fluoride) indicating most fluoride in forage was internal.

From 2008 to 2012, grass, shrub and tree species responded differently to airborne fluoride at four locations. Highest internal fluoride concentrations were downwind and close to the source; lowest were upwind and farther from the source. Shrub species had highest internal fluoride, followed by tree species, then grass species. Cluster analyses suggested grass, shrub and tree species over 2008 to 2012 could be partitioned into two groups based on internal fluoride accumulation. Shrub species were partitioned as one group, tree species and grass species were partitioned as a second group.

A biomonitoring method using *Lolium perenne* L (perennial rye grass) as a bioindicator was successful. Distance from the emission source had the greatest influence on internal fluoride accumulation in perennial rye grass, followed by exposure time, then wind direction (dependent on distance). Internal fluoride concentrations in perennial rye grass showed a steep concentration gradient near the PG stack, decreasing exponentially further away from the source, with a sharp drop was within the first 500 m from the PG stack. The airborne fluoride spatial emission pattern studied by modeling fluoride dispersal showed the area east of the emission source was well supported by 2016 fluoride data.

Fluoride accumulation in perennial rye grass generally increased with exposure time. Growing season internal fluoride concentrations peaked at 81 days in 2015 and 110 days in 2016. Age showed no significant impacts on fluoride accumulation in perennial rye grass.

Wind affected fluoride accumulation of perennial rye grass depended on distance from emission source. Influence of wind direction was obvious near the emission source (500 m), becoming weaker with increasing distance.

Alfalfa, corn, june grass and sunflower accumulated internal fluoride differently than perennial rye grass. Sunflower accumulated significantly more fluoride than rye grass in 28 days.

2. APPLICATIONS

Long term biomonitoring on airborne fluoride accumulation of plants is a cost effective way to determine impacts of fluoride on plants. It can show how fluoride accumulation in plants changes over time and how different plant species respond. To improve the fluoride monitoring program around the fertilizer production facility, future monitoring is recommended for the downwind region (south and east), especially on the east side of the source. Sampling earlier than late June is not recommended; sampling should begin in July and end in late October.

The biomonitoring system, which was highly standardized in greenhouse cultivation, field exposure and plant harvest was successfully used in this research, filling some of the gaps in current knowledge. *Lolium perenne* L (perennial rye grass) showed good potential as a bioindicator for monitoring fluoride accumulations. By investigating the influence of wind, exposure duration, distance and age on fluoride accumulation of plants in the vicinity of the PG stack allowed for quantification of bioavailability of hydrogen fluoride; evaluation of ecological risks; provision of information on air emission patterns around the fertilizer production facility; and development of a biomonitoring protocol for hydrogen fluoride with plant species for Alberta which can be used in various land reclamation and management scenarios. Assessing the use of other common forage species as a biomonitoring indicator would be useful.

3. RESEARCH LIMITATIONS

A major study limitation was perennial rye grass biomass loss in the field. Defoliation by insects and other fauna caused severe loss of biomass, especially in 2015, although many approaches were applied, such as high seeding rate, physical devices and chemical sprays. Physical devices (wood pallets, metal cages) may slightly influence airborne fluoride deposition, and the potential impacts of non-fluoride containing chemical sprays (insecticides, animal repellents) on fluoride accumulation of plants are not fully understood and could not be totally controlled even when trying to not spray directly on plant surfaces. Defoliation resulted in an inadequate volume of some samples for fluoride analyses in the laboratory, and thus it may have some impacts on the mean due to missing data. The different volume of biomass collected at biomonitoring sites made it challenging to investigate the relationship of fluoride in plant tissues and plant growth. Only using one forage species for detailed assessment was a budget limitation.

4. RECOMMENDATIONS FOR FUTURE RESEARCH

Future research could further investigate whether airborne fluoride affects plant growth in the vicinity of the PG stack. In several studies, fluoride loss resulting in growth dilution indicates there could be a connection between fluoride concentrations in plant tissues and plant biomass growth. Our study was unable to reveal any relationship due to defoliation issue.

Annual external fluoride data from washed and unwashed samples and wash water could provide further information on fluoride forms in and on plants. Temperature and precipitation may strongly influence amount of external fluoride based on a 5 year scale. There might be internal factors that affect fluoride deposition, such as physiological stage of plants as we found differences in internal fluoride uptake over time among three different ages of perennial rye grass. It would be valuable to study this further by monitoring the amount of external fluoride and composition of total fluoride on different age plants in a longer time frame.

V. REFERENCES

Abdallah, FB, N Elloumi, I Mezghani, J Garrec and M Boukhris. 2006. Industrial fluoride pollution of jerbi grape leaves and the distribution of F, Ca, Mg, and P in them. Fluoride 39:43-48.

Agency for Toxic Substances and Disease Registry (ATSDR). 2003. Toxicological profile for fluorides, hydrogen fluoride and fluorines. Department of Health and Human Services. Atlanta Georgia. On line at http://www.atsdr.cdc.gov/toxprofiles/tp11.html. Assessed 26 May 2015. Accessed 25 October 2016.

Agrium Fertilizer Laboratory Services. 2010. Solution or reagent procedures section (01) working solutions – vegetation wash solution. Agrium Inc Redwater Alberta. 4 pp.

Agrium Fertilizer Laboratory Services. 2012. Sample control procedures section (04) sample preparation – washing vegetation samples. Agrium Inc Redwater Alberta. 4 pp.

Agrium Incorporated. 2011. 2010 Fluoride in vegetation monitoring report. Agrium Inc Redwater Alberta. Pp 14-15.

Agrium Incorporated. 2014. 2013 Annual air monitoring supplemental report -source flux measurements for HF and project summary. Agrium Inc Redwater Alberta. Pp 3-7.

Alberta Agriculture and Rural Development (AARD). 2016. AgroClimatic information service. Alberta agriculture and rural development. On line at http://agriculture.alberta.ca/acis/alberta-weather-data-viewer.jsp. Accessed 25 October 2016.

Alberta Environment. 2016. Alberta ambient air quality objectives and guidelines summary. On line at http://aep.alberta.ca/air/legislation/ambient-air-quality-objectives/documents/AAQO-Summary-Jun2016.pdf. Accessed September 1, 2016.

Alves, ES, B Moura and M Domingos. 2008. Structural analysis of *Tillandsia usneoides* L. exposed to air pollutants in Sao Paulo City (Brazil). Water, Air, and Soil Pollution 189:61-68.

Arndt, U. 2001. Bioindikation. In: Guderian, R. (ed.). Handbuch der umveltveranderungen und okotoxikologie 2B. Springer Verlag, Berlin Germany. Pp 293-341.

Atasoy, AD, MI Yesilnacar and AF Atasoy. 2016. Evaluation of fluoride concentration and daily intake by human from tea infusions. Harran Tarim Ve Gida Bilimleri Dergisi 20:1-6.

Ballantyne, DJ. 1991. Fluoride and photosynthetic capacity of azalea (rhododendron) cultivars. Fluoride 24:11-16.

Barbier, O, L Arreola-Mendoza and LM Del Razo. 2010. Molecular mechanisms of fluoride toxicity. Chemico-biological Interactions 188:319-333.

Baunthiyal, M and V Sharma. 2014. Response of three semi-arid plant species to fluoride;

consequences for chlorophyll florescence. International Journal of Phytoremediation 16:397-414.

Baunthiyal, M and S Ranghar. 2014. Physiological and biochemical responses of plants under fluoride stress: an overview. Fluoride 47:287-293.

Blakemore, J. 1978. Fluoride deposition to grass swards under field conditions. PhD dissertation. University of Newcastle upon Tyne. Newcastle upon Tyne United Kingdom. Cited in: Weinstein and Davison 2004.

Breunig, MM, HP Kriegel, RT Ng and J Sander. 2000. LOF: identifying density-based local outliers. Proceedings of the 2000 ACM Sigmod International Conference on Management of Data 29:93-104.

Canadian Council of Ministers of the Environment (CCME). 1999. Canadian national ambient air quality objectives: process and status. In: Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment. Winnipeg Manitoba. 6 pp.

CBC News. 2015. Grasshoppers latest plague to hit Alberta's bone-dry farms. Online at http://www.cbc.ca/news/canada/edmonton/grasshoppers-latest-plague-to-hit-alberta-s-bone-dry-farms-1.3145662. Accessed 17 November 2015.

Choubisa, SL. 2012. Status of fluorosis in animals. Proceedings of the National Academy of Sciences India Section B: Biological Sciences 82:331-339.

Clean Air Strategic Alliance (CASA). 2016. Data reports. On line at http://airdata.alberta.ca/aepContent/Reports/DataDownloadMain.aspx. Accessed 25 October 2016.

Davison, AW, J Blakemore and C Craggs. 1979. The fluoride content of forage as an environmental quality standard for the protection of livestock. Environmental Pollution 20:279-296.

Davison, AW. 1982. The effects of fluorides on plant growth and forage quality. In:Unsworth, MH and DP Ormrod (eds) Effect of gaseous air pollution in agriculture and horticultures. Butterworths. United Kingdom. Pp 267-292.

De Temmerman, L and H Baeten. 1988. The accumulation of airborne fluorides by perennial ryegrass cultures. Fluoride 21:185-192.

Doley, D. 1986. Plant-fluoride relationships. An analysis with particular reference to Australian vegetation. Inkata Press. Melbourne Australia. 128 pp.

Environment Canada. 1993. Priority substances list assessment report: inorganic fluorides. Canadian Environmental Protection Act. Environment Canada, Health Canada. Ottawa Ontario. 72 pp.

Environment Canada. 2014. National pollutant release inventory 2014 database. On line at http://www.ec.gc.ca/inrp-npri/donnees-data/index.cfm?do=common&lang=en&common _query=3&query_type=1. Accessed 15 May 2015.

Florida Institute of Phosphate Research (FIPR). 2004. Stack free: what is the future for phosphogypsum? On line at https://www.scribd.com/document/49461398/ PHOSPHOGYPSUM. Accessed 28 May 2015.

Franzaring, J, A Klumpp and A Fangmeier. 2007. Active biomonitoring of airborne fluoride near an HF producing factory using standardized grass cultures. Atmospheric Environment 41:4828-4840.

Galan, E, I Gonzalez and B Fabbri. 2002. Estimation of fluorine and chlorine emissions from Spanish structural ceramic industries. Atmospheric Environment 36:5289-5298.

Gibbs, M and H Beevers. 1955. Glucose dissimilation in the higher plant. Effect of age of tissue. Plant Physiology 30:343-347.

Gilbert, OL. 1968. Bryophytes as indicators of air pollution in the Tyne Valley. New Phytologist 67:15-30.

Hendrix, JW and HR Hall. 1958. The relationship of certain leaf characteristics and flower colour to atmospheric fluoride-sensitivity in gladiolus. American Society for Horticultural Science 72:503-510.

Hitchcock, A, P Zimmerman and R Coe. 1962. Results of ten years' work (1951-1960) on the effect of fluorides on gladiolus. Contributions from Boyce Thompson Institute 21:303-344.

Junior, AMD, MA Oliva and FA Ferreira. 2008. Dispersal pattern of airborne emissions from an aluminium smelter in ouro preto, Brazil, as expressed by foliar fluoride accumulation in eight plant species. Ecological Indicators 8:454-461.

Kamaluddin, M and JJ Zwiazek. 2003. Fluoride inhibits root water transport and affects leaf expansion and gas exchange in aspen (*Populus tremuloides*) seedlings. Physiologia Plantarum 117:368-375.

Keller, T. 1974. Translocation of fluoride in woody plants. Fluoride 7:31-35.

Klumpp, G, AKIF Modesto and M Domingos. 1997. Susceptibility of various gladiolus cultivars to fluoride pollution and their suitability for bioindication. Pesquisa Agropecuária Brasileira 32:239-247.

Knabe, W. 1970. Natural loss of fluorine from needles of norway spruce *(picea abies* karst). Staub-Reinhalt.Luft 30:29-32.

Knight, HG, AK Furr and TF Parkinson. 1977. Determination of fluorine by neutron activation analysis. Analytical Chemistry 49:1507-1510.

LaCosse, J, W Herget, R Spellicy and C Beitler. 1999. Measurement and modelling of HF emissions from phosphoric acid production facilities. Project No. 197-002. Fertilizer Institute. Washington DC, Washington. Cited in: Weinstein and Davison 2004.

Laurie, A, RF Hasek and W LaFleur. 1949. The effect of various concentrations of fluorine gas on gladiolus. Proceedings of the American Society for Horticultural Science 53:466-472.

Ledbetter, MC, R Mavrodineanu and AJ Weiss. 1960. Distribution studies of radioactive fluorine-18 and stable fluorme-19 in tomato plants. Contributions. Boyce Thompson Institute for Plant Research 20:331-348.

Less, LN, A McGregor, LHPJones, DW Cowling and EL Leafe. 1975. Fluoride uptake by gas from aluminium smelter fume. International Journal of Environmental Studies 7:153–160.

Loganathan, P, MJ Hedley, GC Wallace and A Roberts. 2001. Fluoride accumulation in pasture forages and soils following long-term applications of phosphorus fertilisers. Environmental Pollution 115:275-282.

McCormac, B. 2012. Introduction to the scientific study of atmospheric pollution. Springer Science and Business Media. New York City New York. 141.pp

Mellanby, K. 2000. Ecological indicators for the nation. National Academy Press. Washington DC Washington. 198 pp.

Mendoza-Schulz, A, C Solano-Agama, L Arreola-Mendoza, B Reyes-Márquez, O Barbier, LM Del Razo and ME Mendoza-Garrido. 2009. The effects of fluoride on cell migration, cell proliferation, and cell metabolism in GH 4 C 1 pituitary tumour cells. Toxicology Letters 190:179-186.

Meyerhoff, ME and WN Opdycke. 1986. Ion-selective electrodes. Advances In Clinical Chemistry 25: 1-47.

Mezghani, I, N Elloumi, FB Abdallah, M Chaieb and M Boukhris. 2005. Fluoride accumulation by vegetation in the vicinity of a phosphate fertilizer plant in Tunisia. Fluoride 38:69-75.

National Institute for Occupational Safety and Health (NIOSH). 1994a. NIOSH manual of sampling and analytical methods, 4th edition, method 7902, issue 2. US Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering. Cincinnati Ohio. 4 pp.

National Institute for Occupational Safety and Health (NIOSH). 1994b. NIOSH manual of sampling and analytical methods 4th edition, method 7903, issue 2. US Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering. Cincinnati Ohio. 6 pp.

Nichol, C. 2007. Reclamation of phosphogypsum stacks in Alberta, Canada. The American Society of Agronomy, Crop Science Society of America and Soil Science Society of America 2007 annual meetings. New Orleans Louisiana. 7 November 2007. On line at https://scisoc.confex.com/crops/2007am/techprogram/P30848.HTM. Accessed 29 May 2015.

Omueti, JAI and RL Jones. 1977. Fluorine content of soil from morrow plots over a period of 67 years. Soil Science Society of America Journal 41:1023-1024.

Peiter, E, FJ Maathuis, LN Mills, H Knight, J Pelloux, AM Hetherington and D Sanders. 2005. The vacuolar Ca^{2+}; activated channel TPC1 regulates germination and stomatal movement. Nature 434:404-408.

R Core team. 2015. R: a language and environment for statistical computing. R Foundation 110 for Statistical Computing. Vienna Austria. On line at http://www.R-project.org/. Accessed 2 August 2015.

Real, C, JR Aboal, JA Fernández and A Carballeira. 2003. The use of native mosses to monitor fluorine levels and associated temporal variations in the vicinity of an aluminium smelter. Atmospheric Environment 37:3091-3102.

Rey-Asensio, A. and A Carballeira. 2007. *Lolium perenne* as a biomonitor of atmospheric levels of fluoride. Environment International 33:583-588.

Robinson, MF, J Heath and TA Mansfield. 1998. Disturbances in stomatal behaviour caused by air pollutants. Journal of Experimental Botany 49:461-469.

Rodriguez, JH, ED Wannaz, ML Pignata, A Fangmeier and J Franzaring. 2012. Fluoride biomonitoring around a large aluminium smelter using foliage from different tree species. Clean Soil, Air, Water 40:1315-1319.

Rozhkov, AS and TA Mikhailova. 1993. The effects of fluorine-containing emissions on conifers. Springer Verlag. Berlin Germany. 143 pp.

Rutherford, PM, MJ Dudas and JM Arocena. 1995. Radioactivity and elemental composition of phosphgypsum produced from three phosphate rock sources. Waste Management and Research 13:407-423.

Rutherford, PM, MJ Dudas and RA Samek. 1994. Environmental impacts of phosphogypsum. The Science of the Total Environment 149:1-38.

Sager, M. 1987. Rapid determination of fluorine in solid samples. Chemical Monthly 118:25-29.

Sebbahi, TS, ML Ould-Chameikh, F Sahban, J Aride, L Benarafa and L Belkbir. 1997. Thermal behaviour of Moroccan phosphogypsum. Thermochimica Acta 12:69-75.

Senscient. 2016. Hydrogen fluoride gas laser detection overview. Online at http://www.senscient.com/hydrogen_fluoride_detection.html. Accessed 3 October 2016.

Sidhu, S. 1979. Fluoride levels in air, vegetation and soil in the vicinity of a phosphorus plant. Journal of the Air Pollution Control Association 29:1069-1072.

Takuaz-Nisancioglu, SE. 1983. Dynamics of fluoride uptake, movement and loss in higher plants. PhD dissertation. University of Newcastle upon Tyne. Cited in: Weinstein and Davison 2004.

Tayibi, H, M Choura, FA Lpez, FJ Alguacil and A Lpez-Delgado. 2009. Environmental impact and management of phosphogypsum. Journal of Environmental Management 90:2377-2386.

Thorne, WER. 1990. Reclamation of a phosphogypsum tailings pond: an examination of the relevant issues. MEDes Thesis. University of Calgary, Department of Environmental Science. Calgary Alberta. 330 pp.

Verein Deutscher Ingenieure (VDI). 1989. VDI 2310 Part 3: maximum immission values to protect vegetation- maximum Immission concentrations for hydrogen fluoride. VDI/DIN Handbuch Reinhaltung der Luft, Band 1. Berlin Germany. 48 pp.

Verein Deutscher Ingenieure (VDI). 2003. VDI 3957 Blatt 2: biological measuring techniques for the determination and evaluation of effects of air pollutants on plants (bioindication) method of standardised grass exposure. VDI/DIN Handbuch Reinhaltung der Luft, Band 1a. Berlin Germany. 28 pp.

Vike, E. 1999. Air-pollution dispersal patterns and vegetation damage in the vicinity of three minimum smelters in Norway. Science of the Total Environment 236:74-90.

Weinstein, LH. 1977. Fluoride and plant life. Journal of Occupational and Environmental Medicine 19:49-78.

Weinstein, LH, JA Laurence, RH Mandl and K Walti. 1990. Use of native and cultivated plants as bioindicators and biomonitors of pollution damage. American Society for Testing and Materials. Philadelphia 1990:117–126.

Weinstein, LH and AW Davison. 2004. Fluorides in the environment: effects on plants and animals. Oxford University Press. Oxford United Kingdom. 287 pp.

Wissa, AEZ. 2002. Phosphogypsum disposal and the environment. In: Schultz, JJ and DR Waggoner (eds). Proceedings of international workshop on current environmental issues of fertilizer production, June 7-9 1999 Prague, Czech Republic. IFDC, Muscle Shoals Alabama. Pp 195-205.

Yamauchi, M, WK Choi and Y Yamada. 1983. Fluoride Inhibition of photosynthesis in certain crop plants. Soil Science and Plant Nutrition 29:549-553.

APPENDIX

Table A1. Agrium Inc forage sampling results.

Sampling Date	Distance (m)	Total Fluoride (µg/g)	Internal Fluoride (µg/g)	External Fluoride (µg/g)	External Fluoride %
2008-06-06	2587	3.70	2.00	1.70	45.90
2008-06-06	1364	30.70	14.50	16.20	52.80
2008-06-06	1259	7.10	2.30	4.80	67.60
2008-06-06	3629	3.10	2.50	0.60	19.40
2008-06-06	1995	9.80	7.70	2.10	21.40
2008-06-06	1430	2.50	1.20	1.30	52.00
2008-06-13	2587	3.70	3.60	0.10	2.70
2008-06-13	1259	4.70	2.20	2.50	53.20
2008-06-13	3629	2.50	2.50	0.00	0.00
2008-06-13	1801	2.30	2.30	0.00	0.00
2008-06-13	1995	6.30	4.20	2.10	33.30
2008-06-24	1360	13.60	13.00	0.60	4.40
2008-06-24	3629	2.00	2.00	0.00	0.00
2008-06-24	1801	9.60	8.60	1.00	10.40
2008-06-24	1995	4.70	2.10	2.60	55.30
2008-06-24	1430	9.80	6.60	3.20	32.70
2008-07-04	2587	10.80	9.30	1.50	13.90
2008-07-04	1364	23.60	19.50	4.10	17.40
2008-07-04	1360	37.80	23.90	13.90	36.80
2008-07-04	1259	27.10	19.00	8.10	29.90
2008-07-04	3629	7.40	4.30	3.10	41.90
2008-07-04	1801	10.40	6.10	4.30	41.30
2008-07-04	1995	4.70	2.80	1.90	40.40
2008-07-04	1430	24.90	11.20	13.70	55.00
2008-08-06	2587	16.50	12.20	4.30	26.10
2008-08-06	1364	38.20	28.50	9.70	25.40
2008-08-06	1360	24.20	13.30	10.90	45.00
2008-08-06	1259	44.00	30.40	13.60	30.90
2008-08-06	3629	10.90	3.90	7.00	64.20
2008-08-06	1801	12.20	8.70	3.50	28.70
2008-08-06	1430	38.60	26.40	12.20	31.60
2008-08-08	2587	14.90	9.30	5.60	37.60
2008-08-08	1360	51.80	39.80	12.00	23.20
2008-08-08	1259	52.50	47.80	4.70	9.00
2008-08-08	3629	6.90	6.30	0.60	8.70
2008-08-08	1801	18.80	8.90	9.90	52.70
2008-08-08	1995	8.30	6.10	2.20	26.50

2008-08-08	1430	54.30	47.00	7.30	13.40
2008-08-29	2587	26.30	16.30	10.00	38.00
2008-08-29	1364	72.70	42.30	30.40	41.80
2008-08-29	1360	104.00	90.80	13.20	12.70
2008-08-29	1259	78.00	64.60	13.40	17.20
2008-08-29	3629	20.80	12.60	8.20	39.40
2008-08-29	1801	10.10	7.60	2.50	24.80
2008-08-29	1995	9.70	2.80	6.90	71.10
2008-08-29	1430	99.40	48.80	50.60	50.90
2008-09-12	2587	39.70	17.10	22.60	56.90
2008-09-12	1364	78.90	71.20	7.70	9.80
2008-09-12	1360	131.00	87.30	43.70	33.40
2008-09-12	1259	59.80	40.40	19.40	32.40
2008-09-12	3629	15.90	11.40	4.50	28.30
2008-09-12	1801	37.90	23.50	14.40	38.00
2008-09-12	1430	72.20	65.50	6.70	9.30
2008-09-12	2587	41.50	25.80	15.70	37.80
2008-09-12	1364	92.80	80.70	12.10	13.00
2008-09-12	1360	115.00	74.20	40.80	35.50
2008-09-12	1259	117.00	81.90	35.10	30.00
2008-09-12	3629	14.00	10.10	3.90	27.90
2008-09-12	1801	35.40	23.70	11.70	33.10
2008-09-12	1995	15.90	12.80	3.10	19.50
2008-09-12	1430	101.00	90.80	10.20	10.10
2008-10-03	2587	53.50	32.90	20.60	38.50
2008-10-03	1364	106.00	83.50	22.50	21.20
2008-10-03	1360	157.00	83.70	73.30	46.70
2008-10-03	1259	130.00	118.00	12.00	9.20
2008-10-03	3629	14.50	12.40	2.10	14.50
2008-10-03	1801	21.80	17.20	4.60	21.10
2008-10-03	1430	154.00	119.00	35.00	22.70
2008-10-10	2587	34.10	21.60	12.50	36.70
2008-10-10	1364	72.30	63.40	8.90	12.30
2008-10-10	1360	106.00	68.90	37.10	35.00
2008-10-10	1259	86.50	66.20	20.30	23.50
2008-10-10	3629	19.40	11.10	8.30	42.80
2008-10-10	1430	72.10	42.50	29.60	41.10
2009-06-08	2587	11.10	4.80	6.30	56.80
2009-06-08	1364	11.10	9.40	1.70	15.30
2009-06-08	1360	20.60	13.20	7.40	35.90
2009-06-08	1259	13.30	7.60	5.70	42.90
2009-06-08	3629	3.00	3.00	0.00	0.00
2009-06-08	1801	4.50	3.00	1.50	33.30

2009-06-08	1995	5.10	3.00	2.10	41.20
2009-06-08	1430	10.60	7.60	3.00	28.30
2009-06-22	2587	15.30	7.70	7.60	49.70
2009-06-22	1364	11.50	8.60	2.90	25.20
2009-06-22	1360	15.00	13.00	2.00	13.30
2009-06-22	1259	23.80	7.10	16.70	70.20
2009-06-22	3629	3.00	3.00	0.00	0.00
2009-06-22	1995	6.10	3.00	3.10	50.80
2009-06-22	1430	8.60	7.30	1.30	15.10
2009-07-07	2587	11.20	8.20	3.00	26.80
2009-07-07	1364	16.50	12.00	4.50	27.30
2009-07-07	1360	38.40	25.10	13.30	34.60
2009-07-07	1259	25.00	23.20	1.80	7.20
2009-07-07	3629	5.10	4.20	0.90	17.60
2009-07-07	1801	7.70	6.30	1.40	18.20
2009-07-07	1995	4.60	3.20	1.40	30.40
2009-07-20	2587	16.00	14.10	1.90	11.90
2009-07-20	1364	33.00	19.50	13.50	40.90
2009-07-20	1360	53.40	26.60	26.80	50.20
2009-07-20	1259	198.60	19.60	179.00	90.10
2009-07-20	3629	4.30	3.00	1.30	30.20
2009-07-20	1801	8.20	7.20	1.00	12.20
2009-07-20	1995	3.20	3.00	0.20	6.30
2009-07-20	1430	29.90	26.90	3.00	10.00
2009-08-04	1364	24.50	21.10	3.40	13.90
2009-08-04	1259	45.10	45.10	0.00	0.00
2009-08-04	3629	5.10	3.60	1.50	29.40
2009-08-04	1995	20.40	19.40	1.00	4.90
2009-08-17	2587	24.10	15.00	9.10	37.80
2009-08-17	1364	22.20	14.40	7.80	35.10
2009-08-17	1360	43.50	25.30	18.20	41.80
2009-08-17	1259	53.30	37.50	15.80	29.60
2009-08-17	3629	16.90	5.90	11.00	65.10
2009-08-17	1801	12.00	9.00	3.00	25.00
2009-08-17	1995	12.60	8.90	3.70	29.40
2009-08-17	1430	44.80	35.00	9.80	21.90
2009-08-31	2587	22.90	10.60	12.30	53.70
2009-08-31	1364	37.80	37.80	0.00	0.00
2009-08-31	1360	49.70	49.40	0.30	0.60
2009-08-31	1259	48.30	46.30	2.00	4.10
2009-08-31	3629	9.50	9.20	0.30	3.20
2009-08-31	1801	43.80	20.80	23.00	52.50
2009-08-31	1995	8.80	7.80	1.00	11.40

2009-09-15	2587	14.30	12.90	1.40	9.80
2009-09-15	1360	73.90	60.30	13.60	18.40
2009-09-15	1259	89.20	60.50	28.70	32.20
2009-09-15	3629	11.80	11.60	0.20	1.70
2009-09-15	1801	32.80	22.70	10.10	30.80
2009-09-15	1995	18.10	10.90	7.20	39.80
2009-09-15	1430	56.60	55.60	1.00	1.80
2009-09-28	2587	63.30	33.10	30.20	47.70
2009-09-28	1364	98.70	45.40	53.30	54.00
2009-09-28	1360	126.60	78.90	47.70	37.70
2009-09-28	1259	101.90	64.60	37.30	36.60
2009-09-28	3629	11.80	11.00	0.80	6.80
2009-09-28	1801	54.40	33.40	21.00	38.60
2009-09-28	1995	15.70	9.60	6.10	38.90
2009-09-28	1430	83.30	53.40	29.90	35.90
2009-10-19	2587	37.40	28.50	8.90	23.80
2009-10-19	1364	54.70	41.20	13.50	24.70
2009-10-19	1360	68.60	55.80	12.80	18.70
2009-10-19	1259	45.40	36.20	9.20	20.30
2009-10-19	3629	8.20	3.70	4.50	54.90
2009-10-19	1801	21.30	20.80	0.50	2.30
2009-10-19	1995	8.40	8.30	0.10	1.20
2009-10-19	1430	53.20	35.50	17.70	33.30
2009-10-28	2587	73.20	38.40	34.80	47.50
2009-10-28	1364	44.00	32.30	11.70	26.60
2009-10-28	1360	67.40	52.40	15.00	22.30
2009-10-28	1259	52.20	40.60	11.60	22.20
2009-10-28	3629	18.60	3.70	14.90	80.10
2009-10-28	1801	13.00	11.30	1.70	13.10
2009-10-28	1995	12.10	5.10	7.00	57.90
2009-10-28	1430	62.80	29.70	33.10	52.70
2010-06-07	2587	5.90	5.60	0.30	5.10
2010-06-07	1364	12.30	5.60	6.70	54.50
2010-06-07	1360	22.20	12.40	9.80	44.10
2010-06-07	1259	13.40	3.80	9.60	71.60
2010-06-07	1801	5.60	2.40	3.20	57.10
2010-06-07	1995	6.50	4.80	1.70	26.20
2010-06-07	1430	14.40	7.80	6.60	45.80
2010-06-21	1364	9.00	6.70	2.30	25.60
2010-06-21	1360	13.90	11.20	2.70	19.40
2010-06-21	1259	11.40	7.40	4.00	35.10
2010-06-21	3629	3.50	1.60	1.90	54.30
2010-06-21	1801	7.30	3.50	3.80	52.10

2010-06-21	1995	4.50	3.40	1.10	24.40
2010-06-21	1430	8.60	6.80	1.80	20.90
2010-07-06	2587	13.10	10.80	2.30	17.60
2010-07-06	1364	26.40	14.50	11.90	45.10
2010-07-06	1360	37.50	25.10	12.40	33.10
2010-07-06	1259	32.60	21.70	10.90	33.40
2010-07-06	1801	4.40	2.60	1.80	40.90
2010-07-06	1995	4.70	3.90	0.80	17.00
2010-07-06	1430	30.00	16.00	14.00	46.70
2010-07-19	2587	16.80	12.30	4.50	26.80
2010-07-19	1364	25.10	18.50	6.60	26.30
2010-07-19	1360	35.00	27.40	7.60	21.70
2010-07-19	1259	21.10	18.70	2.40	11.40
2010-07-19	1430	20.10	19.60	0.50	2.50
2010-08-03	2587	30.00	12.20	17.80	59.30
2010-08-03	1364	44.70	25.00	19.70	44.10
2010-08-03	1360	53.70	34.50	19.20	35.80
2010-08-03	1259	54.30	36.40	17.90	33.00
2010-08-03	3629	11.10	5.00	6.10	55.00
2010-08-03	1801	15.00	9.50	5.50	36.70
2010-08-03	1430	47.30	23.70	23.60	49.90
2010-08-16	2587	27.80	16.40	11.40	41.00
2010-08-16	1364	30.70	20.80	9.90	32.20
2010-08-16	1360	43.80	26.20	17.60	40.20
2010-08-16	1259	31.10	24.60	6.50	20.90
2010-08-16	3629	8.40	2.20	6.20	73.80
2010-08-16	1801	12.50	10.60	1.90	15.20
2010-08-16	1995	4.30	3.70	0.60	14.00
2010-08-16	1430	31.70	21.10	10.60	33.40
2010-08-30	2587	46.10	34.50	11.60	25.20
2010-08-30	1364	57.50	48.40	9.10	15.80
2010-08-30	1259	111.20	85.10	26.10	23.50
2010-08-30	3629	10.50	9.50	1.00	9.50
2010-08-30	1995	11.00	7.10	3.90	35.50
2010-08-30	1430	79.50	48.50	31.00	39.00
2010-09-13	2587	25.30	20.50	4.80	19.00
2010-09-13	1364	93.50	57.20	36.30	38.80
2010-09-13	1360	81.60	75.00	6.60	8.10
2010-09-13	1259	56.40	39.00	17.40	30.90
2010-09-13	3629	8.40	6.60	1.80	21.40
2010-09-13	1801	16.80	12.30	4.50	26.80
2010-09-13	1995	22.80	10.20	12.60	55.30
2010-09-13	1430	99.80	74.90	24.90	24.90

2010-09-29	1364	22.60	10.40	12.20	54.00
2010-09-29	1360	28.40	19.80	8.60	30.30
2010-09-29	1259	35.60	28.60	7.00	19.70
2010-09-29	3629	8.70	6.90	1.80	20.70
2010-09-29	1995	8.30	6.10	2.20	26.50
2010-10-12	2587	24.20	12.90	11.30	46.70
2010-10-12	1364	28.20	14.80	13.40	47.50
2010-10-12	1259	44.30	19.30	25.00	56.40
2010-10-12	3629	11.60	8.10	3.50	30.20
2011-06-13	2587	9.12	5.64	3.48	38.20
2011-06-13	1364	18.30	9.76	8.55	46.70
2011-06-13	1360	22.09	14.19	7.90	35.80
2011-06-13	1259	11.72	6.11	5.61	47.90
2011-06-13	3629	6.31	3.49	2.83	44.80
2011-06-13	1801	25.46	16.14	9.33	36.60
2011-06-13	1995	12.55	10.14	2.41	19.20
2011-06-13	1430	8.70	7.59	1.11	12.80
2011-06-27	2587	11.70	8.49	3.21	27.40
2011-06-27	1364	21.20	11.53	9.67	45.60
2011-06-27	1360	36.56	24.98	11.58	31.70
2011-06-27	1259	24.47	13.66	10.81	44.20
2011-06-27	3629	2.28	2.00	0.28	12.10
2011-06-27	1801	12.39	7.19	5.19	41.90
2011-06-27	1995	9.29	6.47	2.83	30.40
2011-06-27	1430	23.41	16.49	6.92	29.60
2011-07-11	2587	12.41	6.26	6.16	49.60
2011-07-11	1364	31.79	22.68	9.11	28.70
2011-07-11	1360	43.24	36.73	6.50	15.00
2011-07-11	1259	29.14	27.37	1.77	6.10
2011-07-11	3629	4.69	3.73	0.96	20.50
2011-07-11	1995	8.75	6.75	2.01	22.90
2011-07-11	1430	32.67	28.99	3.67	11.20
2011-07-25	2587	11.03	7.98	3.05	27.60
2011-07-25	1364	33.20	24.83	8.36	25.20
2011-07-25	1360	80.05	45.68	34.37	42.90
2011-07-25	1259	78.18	60.25	17.93	22.90
2011-07-25	3629	13.64	9.33	4.31	31.60
2011-07-25	1430	63.65	53.63	10.01	15.70
2011-08-08	2587	18.34	9.74	8.60	46.90
2011-08-08	1364	64.05	40.93	23.12	36.10
2011-08-08	1360	98.36	65.28	33.09	33.60
2011-08-08	1259	110.58	71.74	38.84	35.10
2011-08-08	3629	14.99	9.15	5.84	39.00

2011-08-08	1801	11.24	6.79	4.45	39.60
2011-08-08	1430	91.09	68.23	22.86	25.10
2011-08-22	2587	52.08	27.78	24.30	46.70
2011-08-22	1364	103.70	58.25	45.45	43.80
2011-08-22	1360	141.72	84.46	57.26	40.40
2011-08-22	1259	194.58	107.30	87.28	44.90
2011-08-22	3629	27.92	18.57	9.35	33.50
2011-08-22	1801	20.30	11.92	8.38	41.30
2011-08-22	1995	11.66	8.29	3.37	28.90
2011-08-22	1430	170.18	103.75	66.43	39.00
2011-09-06	2587	89.16	46.30	42.86	48.10
2011-09-06	1364	209.62	108.52	101.10	48.20
2011-09-06	1360	250.20	161.04	89.16	35.60
2011-09-06	1259	185.32	118.34	66.98	36.10
2011-09-06	3629	50.28	34.21	16.06	32.00
2011-09-06	1801	70.36	37.56	32.80	46.60
2011-09-06	1430	245.57	173.39	72.18	29.40
2011-09-19	2587	16.44	14.35	2.09	12.70
2011-09-19	1364	73.17	51.69	21.48	29.40
2011-09-19	1360	60.15	48.46	11.69	19.40
2011-09-19	1259	138.09	76.60	61.48	44.50
2011-09-19	3629	27.32	21.50	5.82	21.30
2011-09-19	1801	26.79	19.64	7.15	26.70
2011-09-19	1995	3.83	3.40	0.43	11.30
2011-09-19	1430	180.57	121.38	59.19	32.80
2011-10-03	2587	35.47	22.18	13.29	37.50
2011-10-03	1364	98.61	82.75	15.85	16.10
2011-10-03	1360	145.40	106.20	39.20	27.00
2011-10-03	1259	43.10	23.21	19.89	46.10
2011-10-03	3629	30.63	16.52	14.11	46.10
2011-10-03	1801	45.58	32.40	13.18	28.90
2011-10-03	1995	11.66	6.66	5.01	42.90
2011-10-03	1430	125.75	75.01	50.74	40.30
2011-10-18	2587	60.84	23.00	37.84	62.20
2011-10-18	1364	141.76	76.69	65.07	45.90
2011-10-18	1360	216.38	122.33	94.05	43.50
2011-10-18	1259	86.40	39.58	46.82	54.20
2011-10-18	3629	19.75	16.84	2.91	14.70
2011-10-18	1801	49.35	31.90	17.45	35.40
2011-10-18	1995	13.93	5.32	8.61	61.80
2011-10-18	1430	111.65	59.80	51.86	46.40
2012-06-11	2587	10.31	10.07	0.24	2.30
2012-06-11	1801	8.15	4.50	3.65	44.80

2012-06-11	1995	5.50	4.00	1.50	27.30
2012-06-25	2587	10.52	7.46	3.06	29.10
2012-06-25	1364	19.43	12.00	7.43	38.20
2012-06-25	1360	24.36	19.12	5.24	21.50
2012-06-25	1259	14.88	14.45	0.43	2.90
2012-06-25	3629	3.16	2.90	0.26	8.40
2012-06-25	1801	8.12	5.87	2.26	27.80
2012-06-25	1995	3.70	3.30	0.40	10.80
2012-06-25	1430	13.41	13.03	0.38	2.80
2012-07-09	1364	18.90	9.80	9.10	48.20
2012-07-09	1259	22.36	17.54	4.81	21.50
2012-07-09	1430	28.81	24.88	3.93	13.60
2012-07-23	2587	11.99	9.21	2.78	23.20
2012-07-23	1364	41.47	22.85	18.62	44.90
2012-07-23	1360	44.49	31.72	12.77	28.70
2012-07-23	1259	34.45	20.39	14.06	40.80
2012-07-23	3629	10.42	3.80	6.62	63.50
2012-07-23	1995	5.70	5.60	0.10	1.80
2012-07-23	1430	46.53	24.33	22.20	47.70
2012-08-07	2587	12.32	12.20	0.12	1.00
2012-08-07	1364	18.82	17.10	1.72	9.20
2012-08-07	1360	59.39	47.23	12.16	20.50
2012-08-07	1259	66.93	41.54	25.39	37.90
2012-08-07	3629	11.00	4.82	6.18	56.20
2012-08-07	1801	13.59	7.79	5.81	42.70
2012-08-07	1995	6.65	3.70	2.95	44.40
2012-08-07	1430	52.47	39.14	13.34	25.40
2012-08-20	2587	26.32	15.92	10.40	39.50
2012-08-20	1360	104.18	73.79	30.38	29.20
2012-08-20	1259	57.12	37.63	19.49	34.10
2012-08-20	3629	14.76	7.44	7.31	49.60
2012-08-20	1801	32.95	14.95	18.00	54.60
2012-08-20	1995	11.01	8.23	2.78	25.20
2012-08-20	1430	52.98	38.80	14.18	26.80
2012-09-04	2587	17.31	11.18	6.13	35.40
2012-09-04	1364	108.61	47.17	61.43	56.60
2012-09-04	1360	84.52	56.42	28.10	33.20
2012-09-04	1259	58.80	27.52	31.28	53.20
2012-09-04	3629	14.70	6.76	7.93	54.00
2012-09-04	1995	11.02	9.55	1.47	13.40
2012-09-04	1430	110.15	47.12	63.02	57.20
2012-09-17	2587	34.39	12.24	22.15	64.40
2012-09-17	1364	139.15	28.09	111.06	79.80

2012-09-17	1360	92.60	70.60	22.00	23.80
2012-09-17	1259	58.02	38.85	19.18	33.00
2012-09-17	3629	14.57	9.21	5.36	36.80
2012-09-17	1801	21.41	9.44	11.97	55.90
2012-09-17	1995	7.84	7.10	0.74	9.40
2012-09-17	1430	78.43	47.27	31.15	39.70
2012-10-02	2587	56.11	17.89	38.22	68.10
2012-10-02	1364	129.29	47.05	82.25	63.60
2012-10-02	1360	107.03	74.63	32.40	30.30
2012-10-02	1259	38.77	13.26	25.51	65.80
2012-10-02	3629	15.70	10.78	4.93	31.40
2012-10-02	1801	27.39	17.46	9.93	36.30
2012-10-02	1995	11.41	7.45	3.96	34.70
2012-10-02	1430	48.70	21.92	26.78	55.00
2012-10-15	2587	91.79	31.54	60.25	65.60
2012-10-15	1364	213.50	104.07	109.44	51.30
2012-10-15	1360	65.82	42.72	23.10	35.10
2012-10-15	1259	83.28	29.24	54.03	64.90
2012-10-15	3629	10.49	7.59	2.90	27.60
2012-10-15	1801	41.54	28.93	12.61	30.40
2012-10-15	1995	14.92	8.99	5.93	39.70
2012-10-15	1430	82.49	44.42	38.06	46.10
2013-06-03	2587	5.00			
2013-06-03	1364	9.00			
2013-06-03	1360	12.00			
2013-06-03	1259	10.00			
2013-06-03	1801	4.00			
2013-06-03	1995	2.00			
2013-06-03	1430	26.00			
2013-06-17	2587	11.00			
2013-06-17	1364	14.00			
2013-06-17	1360	20.00			
2013-06-17	1259	19.00			
2013-06-17	1801	29.00			
2013-06-17	1995	2.00			
2013-06-17	1430	18.00			
2013-07-02	2587	11.00			
2013-07-02	1364	14.00			
2013-07-02	1360	20.00			
2013-07-02	1259	19.00			
2013-07-02	1801	29.00			
2013-07-02	1995	2.00			
2013-07-02	1430	18.00			

2013-07-16	2587	22.00
2013-07-16	1364	36.00
2013-07-16	1360	44.00
2013-07-16	1360	52.00
2013-07-16	1259	64.00
2013-07-16	1259	64.00
2013-07-16	1801	21.00
2013-07-16	1995	5.00
2013-07-16	1430	52.00
2013-07-16	2300	14.00
2013-07-29	2587	24.00
2013-07-29	1364	42.00
2013-07-29	1360	55.00
2013-07-29	1259	50.00
2013-07-29	1801	20.00
2013-07-29	1995	5.00
2013-07-29	1430	50.00
2013-07-29	2300	17.00
2013-08-13	2587	19.00
2013-08-13	1364	41.00
2013-08-13	1360	50.00
2013-08-13	1259	36.00
2013-08-13	1801	34.00
2013-08-13	1801	19.00
2013-08-13	1995	9.00
2013-08-13	1430	53.00
2013-08-13	2300	17.00
2013-08-28	2587	38.00
2013-08-28	1364	76.00
2013-08-28	1360	109.00
2013-08-28	1259	132.00
2013-08-28	1801	74.00
2013-08-28	1995	31.00
2013-08-28	1430	118.00
2013-08-28	2300	31.00
2013-09-09	2587	50.00
2013-09-09	1364	61.00
2013-09-09	1360	102.00
2013-09-09	1259	54.00
2013-09-09	1801	56.00
2013-09-09	1995	34.00
2013-09-09	1430	67.00
2013-09-09	2300	33.00

2013-09-23	2587	121.00
2013-09-23	1364	148.00
2013-09-23	1360	219.00
2013-09-23	1259	194.00
2013-09-23	1801	99.00
2013-09-23	1995	56.00
2013-09-23	1430	212.00
2013-09-23	2300	65.00
2013-10-07	2587	74.00
2013-10-07	1364	76.00
2013-10-07	1360	105.00
2013-10-07	1259	134.00
2013-10-07	1801	84.00
2013-10-07	1995	14.00
2013-10-07	1430	82.00
2013-10-07	2300	54.00
2013-10-25	2587	111.00
2013-10-25	1364	80.00
2013-10-25	1360	208.00
2013-10-25	1259	127.00
2013-10-25	1801	45.00
2013-10-25	1995	24.00
2013-10-25	1430	137.00
2015-06-03	1732	25.00
2015-06-03	1789	15.00
2015-06-03	1426	20.00
2015-06-03	1557	14.00
2015-06-03	1398	17.00
2015-06-03	1241	13.00
2015-06-03	1266	14.00
2015-06-03	1693	14.00
2015-06-15	1732	49.00
2015-06-15	1789	36.00
2015-06-15	1426	46.00
2015-06-15	1557	40.00
2015-06-15	1398	48.00
2015-06-15	1241	51.00
2015-06-15	1266	39.00
2015-06-15	1693	23.00
2015-06-29	1732	51.00
2015-06-29	1789	44.00
2015-06-29	1426	58.00
2015-06-29	1557	41.00

2015-06-29	1398	57.00
2015-06-29	1241	53.00
2015-06-29	1266	73.00
2015-06-29	1693	48.00
2015-07-15	1732	61.00
2015-07-15	1789	60.00
2015-07-15	1426	81.00
2015-07-15	1557	70.00
2015-07-15	1398	92.00
2015-07-15	1241	63.00
2015-07-15	1266	63.00
2015-07-15	1693	39.00
2015-07-27	1732	38.00
2015-07-27	1789	41.00
2015-07-27	1426	48.00
2015-07-27	1557	44.00
2015-07-27	1398	66.00
2015-07-27	1241	62.00
2015-07-27	1266	63.00
2015-07-27	1693	30.00
2015-08-10	1732	64.00
2015-08-10	1789	92.00
2015-08-10	1426	59.00
2015-08-10	1557	92.00
2015-08-10	1398	100.00
2015-08-10	1241	85.00
2015-08-10	1266	93.00
2015-08-10	1693	53.00
2015-08-24	1732	98.00
2015-08-24	1789	73.00
2015-08-24	1426	124.00
2015-08-24	1557	117.00
2015-08-24	1398	104.00
2015-08-24	1241	103.00
2015-08-24	1266	127.00
2015-08-24	1693	60.00
2015-09-10	1732	68.00
2015-09-10	1789	77.00
2015-09-10	1426	76.00
2015-09-10	1557	67.00
2015-09-10	1398	65.00
2015-09-10	1241	110.00
2015-09-10	1266	77.00

2015-09-10	1693	28.00
2015-09-23	1732	44.00
2015-09-23	1789	110.00
2015-09-23	1426	90.00
2015-09-23	1557	100.00
2015-09-23	1398	110.00
2015-09-23	1241	84.00
2015-09-23	1266	72.00
2015-09-23	1693	57.00
2015-10-05	1732	79.00
2015-10-05	1789	31.00
2015-10-05	1426	39.00
2015-10-05	1557	44.00
2015-10-05	1398	42.00
2015-10-05	1241	73.00
2015-10-05	1266	130.00
2015-10-05	1693	29.00
2015-10-21	1732	110.00
2015-10-21	1789	82.00
2015-10-21	1426	50.00
2015-10-21	1557	110.00
2015-10-21	1398	40.00
2015-10-21	1241	64.00
2015-10-21	1266	150.00
2015-10-21	1693	69.00
2014-06-02	2370	10.00
2014-06-02	1897	16.00
2014-06-02	1775	16.00
2014-06-02	1560	18.00
2014-06-02	1312	15.00
2014-06-02	1297	27.00
2014-06-02	1333	19.00
2014-06-02	1556	12.00
2014-06-16	2370	10.00
2014-06-15	1897	15.00
2014-06-16	1775	18.00
2014-06-16	1560	20.00
2014-06-16	1312	14.00
2014-06-16	1297	18.00
2014-06-16	1333	12.00
2014-06-16	1556	14.00
2014-06-18	2370	30.00
2014-07-02	1897	44.00

2014-07-02	1775	41.00
2014-07-02	1560	44.00
2014-07-02	1312	31.00
2014-07-02	1297	35.00
2014-07-02	1333	29.00
2014-07-02	1556	23.00
2014-07-14	2370	33.00
2014-07-14	1897	57.00
2014-07-14	1775	49.00
2014-07-14	1560	61.00
2014-07-14	1312	46.00
2014-07-14	1297	48.00
2014-07-14	1333	30.00
2014-07-14	1556	33.00
2014-07-28	2370	35.00
2014-07-28	1897	40.00
2014-07-28	1775	30.00
2014-07-28	1560	62.00
2014-07-28	1312	36.00
2014-07-28	1297	33.00
2014-07-28	1333	30.00
2014-07-28	1556	24.00
2014-08-12	1897	57.00
2014-08-12	1775	38.00
2014-08-12	1560	37.00
2014-08-12	1312	39.00
2014-08-12	1297	68.00
2014-08-12	1333	29.00
2014-08-12	1556	55.00
2014-08-25	1897	97.00
2014-08-25	1775	65.00
2014-08-25	1560	76.00
2014-08-25	1312	85.00
2014-08-25	1297	84.00
2014-08-25	1333	96.00
2014-08-25	1556	78.00
2014-09-11	1897	54.00
2014-09-11	1775	40.00
2014-09-11	1560	59.00
2014-09-11	1312	52.00
2014-09-11	1297	70.00
2014-09-11	1333	95.00
2014-09-11	1556	56.00

2014-09-24	1897	99.00
2014-09-24	1775	125.00
2014-09-24	1560	127.00
2014-09-24	1312	107.00
2014-09-24	1297	129.00
2014-09-24	1333	198.00
2014-09-24	1556	149.00
2014-10-06	1897	69.00
2014-10-06	1775	81.00
2014-10-06	1560	85.00
2014-10-06	1312	68.00
2014-10-06	1297	59.00
2014-10-06	1333	82.00
2014-10-06	1556	99.00
2014-10-20	1897	155.00
2014-10-20	1775	76.00
2014-10-20	1560	120.00
2014-10-20	1312	120.00
2014-10-20	1297	100.00
2014-10-20	1333	150.00
2014-10-20	1556	110.00
2016-06-23	1732	21.00
2016-06-23	1789	87.00
2016-06-23	1426	35.00
2016-06-23	1398	59.00
2016-06-23	1266	43.00
2016-06-23	1693	41.00
2016-06-23	2242	7.00
2016-06-23	2263	31.00
2016-07-08	1732	42.00
2016-07-08	1789	52.00
2016-07-08	1426	40.00
2016-07-08	1398	63.00
2016-07-08	1266	33.00
2016-07-08	1693	27.00
2016-07-08	2242	18.00
2016-07-08	2263	21.00
2016-07-21	1732	51.00
2016-07-21	1789	70.00
2016-07-21	1426	69.00
2016-07-21	1398	110.00
2016-07-21	1266	87.00
2016-07-21	1693	31.00

2016-07-21	2242	23.00
2016-07-21	2263	52.00
2016-08-02	1732	41.00
2016-08-02	1789	65.00
2016-08-02	1426	47.00
2016-08-02	1398	66.00
2016-08-02	1266	130.00
2016-08-02	1693	64.00
2016-08-02	2242	23.00
2016-08-02	2263	29.00
2016-08-17	1732	68.00
2016-08-17	1789	140.00
2016-08-17	1426	29.00
2016-08-17	1398	190.00
2016-08-17	1266	150.00
2016-08-17	1693	71.00
2016-08-17	2242	56.00
2016-08-17	2263	120.00
2016-08-30	1732	83.00
2016-08-30	1789	100.00
2016-08-30	1426	79.00
2016-08-30	1398	120.00
2016-08-30	1266	170.00
2016-08-30	1693	54.00
2016-08-30	2242	16.00
2016-08-30	2263	34.00
2016-09-15	1732	70.00
2016-09-15	1789	200.00
2016-09-15	1426	150.00
2016-09-15	1398	210.00
2016-09-15	1266	180.00
2016-09-15	1693	100.00
2016-09-15	2242	63.00
2016-09-15	2263	140.00
2016-09-26	1732	100.00
2016-09-26	1789	220.00
2016-09-26	1426	140.00
2016-09-26	1398	280.00
2016-09-26	1266	220.00
2016-09-26	1693	87.00
2016-09-26	2242	62.00
2016-09-26	2263	130.00
2016-10-24	1732	82.00

2016-10-24	1789	120.00
2016-10-24	1426	59.00
2016-10-24	1398	240.00
2016-10-24	1266	160.00
2016-10-24	1693	80.00
2016-10-24	2242	34.00
2016-10-24	2263	66.00

Table A2. Agrium Inc vegetation sampling results.

Sampling Date	location	Distance (m)	Species	Group	Internal Fluoride (μg/g)
2008-08-13	Upwind-D2	3500	Wheat	Grass	3.10
2008-08-13	Upwind-D1	800	Balsam Poplar	Tree	22.20
2008-08-13	Downwind-D2	1700	Balsam Poplar	Tree	19.00
2008-08-13	Upwind-D1	40	Balsam Poplar	Tree	253.00
2008-08-13	Upwind-D2	3500	Balsam Poplar	Tree	3.00
2008-08-13	Upwind-D2	3000	Balsam Poplar	Tree	2.50
2008-08-13	Upwind-D1	1650	Balsam Poplar	Tree	7.30
2008-08-13	Downwind-D1	330	Saskatoon	Shrub	151.00
2008-08-13	Upwind-D2	1700	Saskatoon	Shrub	17.70
2008-08-13	Upwind-D1	40	Trembling Aspen	Tree	372.00
2008-08-13	Upwind-D1	816	Trembling Aspen	Tree	85.00
2008-08-13	Downwind-D2	1700	Trembling Aspen	Tree	13.30
2008-08-13	Upwind-D1	1650	Trembling Aspen	Tree	12.20
2008-08-13	Upwind-D2	1700	Trembling Aspen	Tree	34.30
2008-08-13	Upwind-D2	1700	Chokecherry	Shrub	19.10
2008-08-13	Upwind-D1	1650	Chokecherry	Shrub	16.40
2008-08-13	Downwind-D2	1480	Manitoba Maple	Tree	14.00
2008-08-13	Upwind-D1	800	Manitoba Maple	Tree	34.60
2008-08-13	Upwind-D1	1650	Manitoba Maple	Tree	14.70
2008-08-13	Upwind-D1	40	Caragana	Shrub	501.00
2008-08-13	Upwind-D2	1900	Manitoba Maple	Tree	13.80
2008-08-13	Upwind-D2	1900	Caragana	Shrub	33.20
2008-08-13	Downwind-D1	330	Caragana	Shrub	607.00
2008-08-13	Downwind-D2	1480	Balsam Poplar	Tree	15.70
2008-08-13	Downwind-D1	330	Trembling Aspen	Tree	614.00
2008-08-13	Upwind-D1	800	Caragana	Shrub	150.00
2008-08-13	Upwind-D2	3500	Caragana	Shrub	12.20
2008-08-13	Downwind-D2	1480	White Spruce	Tree	15.40
2008-08-13	Upwind-D1	816	White Spruce	Tree	18.70
2008-08-13	Upwind-D2	3500	White Spruce	Tree	7.70
2008-08-14	Downwind-D1	1100	Trembling Aspen	Tree	87.60
2008-08-14	Downwind-D2	5680	Chokecherry	Shrub	5.10

2008-08-14	Downwind-D1	1100	Chokecherry	Shrub	143.00
2008-08-14	Downwind-D1	1700	Chokecherry	Shrub	60.60
2008-08-14	Downwind-D2	2460	Caragana	Shrub	104.00
2008-08-14	Downwind-D2	2010	Caragana	Shrub	20.40
2008-08-14	Downwind-D1	1100	Saskatoon	Shrub	65.50
2008-08-14	Downwind-D2	5680	Saskatoon	Shrub	5.30
2008-08-14	Downwind-D2	2010	Manitoba Maple	Tree	6.40
2008-08-14	Downwind-D2	2460	Manitoba Maple	Tree	46.90
2008-08-14	Downwind-D2	2010	White Spruce	Tree	4.00
2008-08-14	Downwind-D2	2800	Balsam Poplar	Tree	13.70
2008-08-14	Downwind-D2	5680	White Spruce	Tree	1.80
2008-08-14	Downwind-D2	5680	Balsam Poplar	Tree	8.00
2008-08-14	Downwind-D2	2530	Balsam Poplar	Tree	16.30
2008-08-14	Downwind-D1	1100	Balsam Poplar	Tree	57.70
2008-08-14	Downwind-D2	5680	Trembling Aspen	Tree	4.80
2008-08-14	Downwind-D2	2530	Trembling Aspen	Tree	29.20
2008-08-14	Downwind-D2	2460	Trembling Aspen	Tree	37.30
2008-08-14	Downwind-D1	1700	Trembling Aspen	Tree	70.60
2008-08-14	Downwind-D2	2800	White Spruce	Tree	8.50
2008-08-14	Downwind-D1	1400	Balsam Poplar	Tree	123.00
2009-08-17	Upwind-D1	40	Canola	Grass	25.70
2009-08-17	Upwind-D1	40	Balsam Poplar	Tree	185.00
2009-08-17	Upwind-D1	40	Trembling Aspen	Tree	360.50
2009-08-17	Upwind-D1	40	Smooth Brome	Grass	113.20
2009-08-17	Upwind-D1	40	Caragana	Shrub	418.00
2009-08-17	Upwind-D1	40	Canola	Grass	12.70
2009-08-17	Upwind-D1	816	Barley	Grass	2.50
2009-08-17	Upwind-D1	816	Wild Rose	Shrub	60.40
2009-08-17	Upwind-D1	816	Trembling Aspen	Tree	61.30
2009-08-17	Upwind-D1	816	Barley	Grass	9.70
2009-08-17	Upwind-D1	816	White Spruce	Tree	46.90
2009-08-17	Upwind-D1	816	Smooth Brome	Grass	15.00
2009-08-17	Upwind-D1	1650	Chokecherry	Shrub	15.40
2009-08-17	Upwind-D1	1650	Canola	Grass	4.00
2009-08-17	Upwind-D1	1650	Manitoba Maple	Tree	18.90
2009-08-17	Upwind-D1	1650	Canola	Grass	4.10
2009-08-17	Upwind-D1	1650	Trembling Aspen	Tree	14.00
2009-08-17	Upwind-D1	1650	Balsam Poplar	Tree	9.40
2009-08-17	Upwind-D1	1650	Smooth Brome	Grass	12.10
2009-08-17	Upwind-D2	1700	Barley	Grass	1.70
2009-08-17	Upwind-D2	1700	Trembling Aspen	Tree	14.70
2009-08-17	Upwind-D2	1700	Barley	Grass	3.70
2009-08-17	Upwind-D2	1700	Saskatoon	Shrub	14.00

2009-08-17	Upwind-D2	1700	Chokecherry	Shrub	15.90
2009-08-17	Upwind-D2	1700	Smooth Brome	Grass	7.30
2009-08-17	Downwind-D2	1700	Trembling Aspen	Tree	20.90
2009-08-17	Downwind-D2	1700	Balsam Poplar	Tree	12.90
2009-08-17	Downwind-D2	1700	Smooth Brome	Grass	11.50
2009-08-17	Downwind-D2	1700	Canola	Grass	3.10
2009-08-17	Downwind-D2	1700	Canola	Grass	5.20
2009-08-17	Upwind-D2	3000	Wheat	Grass	1.40
2009-08-17	Upwind-D2	3000	Wheat	Grass	3.00
2009-08-17	Upwind-D2	3000	Wild Rose	Shrub	15.20
2009-08-17	Upwind-D2	3000	Balsam Poplar	Tree	4.10
2009-08-17	Upwind-D2	3000	Smooth Brome	Grass	5.90
2009-08-17	Upwind-D2	3000	White Spruce	Tree	4.40
2009-08-18	Downwind-D1	330	Smooth Brome	Grass	234.10
2009-08-18	Downwind-D1	330	Caragana	Shrub	494.20
2009-08-18	Downwind-D1	330	Trembling Aspen	Tree	211.10
2009-08-18	Upwind-D1	800	White Spruce	Tree	12.70
2009-08-18	Upwind-D1	800	Barley	Grass	31.40
2009-08-18	Upwind-D1	800	Barley	Grass	4.60
2009-08-18	Upwind-D1	800	Caragana	Shrub	103.10
2009-08-18	Upwind-D1	800	Manitoba Maple	Tree	48.10
2009-08-18	Upwind-D1	800	Balsam Poplar	Tree	42.30
2009-08-18	Upwind-D1	800	Smooth Brome	Grass	41.20
2009-08-18	Upwind-D2	3500	Smooth Brome	Grass	4.30
2009-08-18	Upwind-D2	3500	Caragana	Shrub	10.30
2009-08-18	Upwind-D2	3500	Balsam Poplar	Tree	3.70
2009-08-18	Upwind-D2	3500	Canola	Grass	6.70
2009-08-18	Upwind-D2	3500	Canola	Grass	3.00
2009-08-18	Upwind-D2	1900	Smooth Brome	Grass	9.80
2009-08-18	Upwind-D2	1900	Barley	Grass	4.00
2009-08-18	Upwind-D2	1900	Barley	Grass	1.60
2009-08-18	Upwind-D2	1900	Caragana	Shrub	36.40
2009-08-18	Upwind-D2	1900	Manitoba Maple	Tree	16.30
2009-08-18	Downwind-D1	1700	Chokecherry	Shrub	49.90
2009-08-18	Downwind-D1	1700	Smooth Brome	Grass	21.90
2009-08-18	Downwind-D1	1700	Wild Rose	Shrub	41.80
2009-08-18	Downwind-D1	1700	Trembling Aspen	Tree	48.30
2009-08-18	Downwind-D2	2800	Cottonwood	Tree	13.70
2009-08-18	Downwind-D2	2800	Wheat	Grass	5.70
2009-08-18	Downwind-D2	2800	Wheat	Grass	6.50
2009-08-18	Downwind-D2	2800	White Spruce	Tree	9.80
2009-08-18	Downwind-D2	1480	Manitoba Maple	Tree	42.00
2009-08-18	Downwind-D2	1480	Balsam Poplar	Tree	25.20

2009-08-18	Downwind-D2	1480	Smooth Brome	Grass	23.40
2009-08-18	Downwind-D2	1480	Barley	Grass	8.50
2009-08-18	Downwind-D2	1480	Barley	Grass	2.00
2009-08-18	Downwind-D2	1480	White Spruce	Tree	14.30
2009-08-18	Downwind-D2	2530	Balsam Poplar	Tree	13.60
2009-08-18	Downwind-D2	2530	Trembling Aspen	Tree	14.80
2009-08-18	Downwind-D2	2530	Smooth Brome	Grass	17.50
2009-08-18	Downwind-D1	1100	Chokecherry	Shrub	73.50
2009-08-18	Downwind-D1	1100	Barley	Grass	11.00
2009-08-18	Downwind-D1	1100	Barley	Grass	19.30
2009-08-18	Downwind-D1	1100	Balsam Poplar	Tree	81.10
2009-08-18	Downwind-D1	1100	Trembling Aspen	Tree	50.50
2009-08-18	Downwind-D1	1100	Smooth Brome	Grass	48.00
2009-08-19	Downwind-D1	1400	Wheat	Grass	37.20
2009-08-19	Downwind-D1	1400	Wheat	Grass	15.30
2009-08-19	Downwind-D1	1400	Smooth Brome	Grass	46.90
2009-08-19	Downwind-D1	1400	Balsam Poplar	Tree	99.60
2009-08-19	Downwind-D1	330	Canola	Grass	66.80
2009-08-19	Downwind-D1	330	Canola	Grass	44.60
2009-08-19	Downwind-D2	5680	Chokecherry	Shrub	6.30
2009-08-19	Downwind-D2	5680	Balsam Poplar	Tree	2.30
2009-08-19	Downwind-D2	5680	White Spruce	Tree	3.80
2009-08-19	Downwind-D2	5680	Trembling Aspen	Tree	4.50
2009-08-19	Downwind-D2	5680	Smooth Brome	Grass	3.60
2009-08-19	Downwind-D2	5680	Saskatoon	Shrub	7.10
2009-08-19	Downwind-D2	5680	Wild Rose	Shrub	5.10
2009-08-19	Downwind-D2	2460	Trembling Aspen	Tree	21.80
2009-08-19	Downwind-D2	2460	Smooth Brome	Grass	23.90
2009-08-19	Downwind-D2	2460	Caragana	Shrub	94.40
2009-08-19	Downwind-D2	2460	Manitoba Maple	Tree	30.80
2009-08-19	Downwind-D2	2010	Caragana	Shrub	31.40
2009-08-19	Downwind-D2	2010	Barley	Grass	6.30
2009-08-19	Downwind-D2	2010	Barley	Grass	2.80
2009-08-19	Downwind-D2	2010	White Spruce	Tree	9.30
2009-08-19	Downwind-D2	2010	Manitoba Maple	Tree	9.20
2009-08-19	Downwind-D2	2010	Smooth Brome	Grass	7.80
2010-08-04	Upwind-D2	3000	Balsam Poplar	Tree	5.30
2010-08-04	Upwind-D2	3000	Smooth Brome	Grass	2.20
2010-08-04	Upwind-D2	3000	Wild Rose	Shrub	3.60
2010-08-04	Upwind-D2	3000	White Spruce	Tree	1.90
2010-08-04	Upwind-D2	3000	Canola	Grass	2.90
2010-08-04	Downwind-D2	1700	Trembling Aspen	Tree	10.80
2010-08-04	Downwind-D2	1700	Balsam Poplar	Tree	12.50

2010-08-04	Downwind-D2	1700	Smooth Brome	Grass	4.60
2010-08-04	Downwind-D2	1700	Wheat	Grass	2.10
2010-08-04	Upwind-D1	40	Trembling Aspen	Tree	189.00
2010-08-04	Upwind-D1	40	Balsam Poplar	Tree	129.00
2010-08-04	Upwind-D1	40	Caragana	Shrub	276.60
2010-08-04	Upwind-D1	40	Smooth Brome	Grass	94.80
2010-08-04	Upwind-D1	40	Wheat	Grass	21.90
2010-08-04	Upwind-D1	816	Trembling Aspen	Tree	45.10
2010-08-04	Upwind-D1	816	Canola	Grass	3.20
2010-08-04	Upwind-D1	816	Smooth Brome	Grass	14.00
2010-08-04	Upwind-D1	816	Wild Rose	Shrub	33.50
2010-08-04	Upwind-D1	816	White Spruce	Tree	6.30
2010-08-04	Upwind-D2	1500	Caragana	Shrub	47.00
2010-08-04	Upwind-D2	1500	Trembling Aspen	Tree	10.70
2010-08-04	Upwind-D2	1500	Balsam Poplar	Tree	10.00
2010-08-04	Upwind-D2	1500	Smooth Brome	Grass	8.20
2010-08-04	Upwind-D2	1700	Trembling Aspen	Tree	19.40
2010-08-04	Upwind-D2	1700	Saskatoon	Shrub	12.70
2010-08-04	Upwind-D2	1700	Barley	Grass	2.40
2010-08-04	Upwind-D2	1700	Smooth Brome	Grass	5.20
2010-08-04	Upwind-D2	1700	Chokecherry	Shrub	9.90
2010-08-04	Upwind-D2	3500	Balsam Poplar	Tree	3.20
2010-08-04	Upwind-D2	3500	Smooth Brome	Grass	2.90
2010-08-04	Upwind-D2	3500	Caragana	Shrub	6.10
2010-08-04	Upwind-D2	3500	Barley	Grass	3.30
2010-08-04	Upwind-D1	800	Smooth Brome	Grass	34.20
2010-08-04	Upwind-D1	800	White Spruce	Tree	10.10
2010-08-04	Upwind-D1	800	Cottonwood	Tree	49.30
2010-08-04	Upwind-D1	800	Canola	Grass	8.50
2010-08-04	Upwind-D1	800	Caragana	Shrub	56.80
2010-08-04	Downwind-D2	1480	Balsam Poplar	Tree	12.30
2010-08-04	Downwind-D2	1480	Canola	Grass	4.40
2010-08-04	Downwind-D2	1480	Smooth Brome	Grass	16.10
2010-08-04	Downwind-D2	1480	Manitoba Maple	Tree	28.80
2010-08-04	Downwind-D2	1480	White Spruce	Tree	16.10
2010-08-04	Downwind-D2	2800	Cottonwood	Tree	14.30
2010-08-04	Downwind-D2	2800	White Spruce	Tree	11.40
2010-08-04	Downwind-D2	2800	Canola	Grass	4.00
2010-08-05	Downwind-D1	330	Smooth Brome	Grass	131.90
2010-08-05	Downwind-D1	330	Wheat	Grass	58.60
2010-08-05	Downwind-D1	330	Caragana	Shrub	449.90
2010-08-05	Downwind-D1	330	Saskatoon	Shrub	130.20
2010-08-05	Downwind-D2	2530	Trembling Aspen	Tree	12.60

2010-08-05	Downwind-D2	2530	Balsam Poplar	Tree	9.90
2010-08-05	Downwind-D2	2530	Smooth Brome	Grass	9.10
2010-08-05	Downwind-D1	1100	Trembling Aspen	Tree	60.90
2010-08-05	Downwind-D1	1100	Balsam Poplar	Tree	51.10
2010-08-05	Downwind-D1	1100	Chokecherry	Shrub	65.70
2010-08-05	Downwind-D1	1100	Smooth Brome	Grass	34.80
2010-08-05	Downwind-D1	1700	Trembling Aspen	Tree	70.20
2010-08-05	Downwind-D1	1700	Smooth Brome	Grass	15.80
2010-08-05	Downwind-D1	1700	Chokecherry	Shrub	50.20
2010-08-05	Downwind-D1	1700	Wild Rose	Shrub	46.00
2010-08-05	Downwind-D1	1400	Balsam Poplar	Tree	64.20
2010-08-05	Downwind-D1	1400	Smooth Brome	Grass	29.10
2010-08-05	Downwind-D1	1400	Barley	Grass	26.40
2010-08-05	Downwind-D2	2460	Trembling Aspen	Tree	26.90
2010-08-05	Downwind-D2	2460	Smooth Brome	Grass	20.10
2010-08-05	Downwind-D2	2460	Caragana	Shrub	84.10
2010-08-05	Downwind-D2	2010	Smooth Brome	Grass	2.10
2010-08-05	Downwind-D2	2010	Caragana	Shrub	10.10
2010-08-05	Downwind-D2	2010	Manitoba Maple	Tree	8.70
2010-08-05	Downwind-D2	2010	White Spruce	Tree	4.20
2010-08-05	Downwind-D2	5680	Trembling Aspen	Tree	6.90
2010-08-05	Downwind-D2	5680	Balsam Poplar	Tree	4.90
2010-08-05	Downwind-D2	5680	Chokecherry	Shrub	5.60
2010-08-05	Downwind-D2	5680	Wild Rose	Shrub	6.60
2010-08-05	Downwind-D2	5680	Saskatoon	Shrub	5.20
2010-08-05	Downwind-D2	5680	White Spruce	Tree	13.30
2010-08-05	Upwind-D2	1900	Smooth Brome	Grass	12.60
2010-08-05	Upwind-D2	1900	Canola	Grass	4.80
2010-08-05	Upwind-D2	1900	Caragana	Shrub	32.00
2010-08-05	Upwind-D2	1900	Manitoba Maple	Tree	17.40
2010-08-16	Downwind-D1	1400	Barley	Grass	3.90
2010-08-17	Downwind-D2	1700	Wheat	Grass	1.00
2010-08-17	Upwind-D1	40	Wheat	Grass	1.00
2010-08-17	Upwind-D2	1700	Barley	Grass	1.40
2010-08-25	Upwind-D2	3500	Barley	Grass	1.50
2010-08-25	Downwind-D1	330	Wheat	Grass	2.20
2010-09-08	Upwind-D1	816	Canola	Grass	1.00
2010-09-08	Upwind-D2	1500	Canola	Grass	1.60
2010-09-08	Downwind-D2	2010	Canola	Grass	1.00
2010-09-13	Upwind-D2	3000	Canola	Grass	1.00
2010-09-13	Upwind-D1	800	Canola	Grass	1.30
2010-09-13	Downwind-D2	1480	Canola	Grass	1.10
2010-09-23	Downwind-D2	2800	Canola	Grass	1.00

2010-09-23	Upwind-D2	1900	Canola	Grass	1.00
2011-08-15	Upwind-D2	3000	Balsam Poplar	Tree	8.80
2011-08-15	Upwind-D2	3000	Smooth Brome	Grass	2.30
2011-08-15	Upwind-D2	3000	Wild Rose	Shrub	12.20
2011-08-15	Upwind-D2	3000	White Spruce	Tree	4.30
2011-08-15	Upwind-D2	3000	Canola	Grass	3.20
2011-08-15	Downwind-D2	1700	Trembling Aspen	Tree	25.90
2011-08-15	Downwind-D2	1700	Balsam Poplar	Tree	17.00
2011-08-15	Downwind-D2	1700	Smooth Brome	Grass	4.50
2011-08-15	Downwind-D2	1700	Barley	Grass	2.40
2011-08-15	Upwind-D1	40	Trembling Aspen	Tree	628.10
2011-08-15	Upwind-D1	40	Balsam Poplar	Tree	705.50
2011-08-15	Upwind-D1	40	Caragana	Shrub	849.30
2011-08-15	Upwind-D1	40	Smooth Brome	Grass	102.80
2011-08-15	Upwind-D1	40	Canola	Grass	29.80
2011-08-15	Downwind-D1	330	Caragana	Shrub	823.20
2011-08-15	Downwind-D1	330	Trembling Aspen	Tree	506.60
2011-08-15	Downwind-D1	330	Saskatoon	Shrub	317.10
2011-08-15	Downwind-D1	330	Smooth Brome	Grass	135.30
2011-08-15	Downwind-D1	330	Canola	Grass	81.10
2011-08-15	Upwind-D1	800	Smooth Brome	Grass	29.80
2011-08-15	Upwind-D1	800	Cottonwood	Tree	62.70
2011-08-15	Upwind-D1	800	White Spruce	Tree	15.80
2011-08-15	Upwind-D1	800	Manitoba Maple	Tree	81.70
2011-08-15	Upwind-D1	800	Caragana	Shrub	82.30
2011-08-15	Upwind-D2	1900	Manitoba Maple	Tree	6.70
2011-08-15	Upwind-D2	1900	Caragana	Shrub	31.00
2011-08-15	Upwind-D2	1900	Smooth Brome	Grass	14.20
2011-08-15	Downwind-D2	1480	White Spruce	Tree	12.20
2011-08-15	Downwind-D2	1480	Balsam Poplar	Tree	26.50
2011-08-15	Downwind-D2	1480	Manitoba Maple	Tree	28.80
2011-08-15	Downwind-D2	1480	Smooth Brome	Grass	31.50
2011-08-15	Downwind-D2	2800	Manitoba Maple	Tree	14.60
2011-08-15	Downwind-D2	2800	Caragana	Shrub	28.20
2011-08-15	Downwind-D2	2800	Balsam Poplar	Tree	29.00
2011-08-15	Downwind-D2	2800	Smooth Brome	Grass	14.50
2011-08-15	Downwind-D2	2800	Wheat	Grass	5.50
2011-08-15	Upwind-D1	816	Wild Rose	Shrub	32.40
2011-08-15	Upwind-D1	816	White Spruce	Tree	26.50
2011-08-15	Upwind-D1	816	Trembling Aspen	Tree	125.60
2011-08-15	Upwind-D1	816	Smooth Brome	Grass	16.10
2011-08-15	Upwind-D1	816	Wheat	Grass	4.90
2011-08-16	Upwind-D2	1500	Trembling Aspen	Tree	34.80

2011-08-16	Upwind-D2	1500	Caragana	Shrub	102.00
2011-08-16	Upwind-D2	1500	Balsam Poplar	Tree	21.10
2011-08-16	Upwind-D2	1500	Smooth Brome	Grass	9.70
2011-08-16	Upwind-D2	1500	Wheat	Grass	1.40
2011-08-16	Upwind-D2	1700	Saskatoon	Shrub	18.70
2011-08-16	Upwind-D2	1700	Trembling Aspen	Tree	31.40
2011-08-16	Upwind-D2	1700	Chokecherry	Shrub	22.50
2011-08-16	Upwind-D2	1700	Smooth Brome	Grass	12.50
2011-08-16	Upwind-D2	1700	Canola	Grass	2.90
2011-08-16	Upwind-D2	3500	Balsam Poplar	Tree	1.60
2011-08-16	Upwind-D2	3500	Caragana	Shrub	8.30
2011-08-16	Upwind-D2	3500	Smooth Brome	Grass	2.40
2011-08-16	Upwind-D2	3500	Barley	Grass	2.90
2011-08-16	Downwind-D2	2530	Wild Rose	Shrub	42.30
2011-08-16	Downwind-D2	2530	Balsam Poplar	Tree	33.50
2011-08-16	Downwind-D2	2530	Trembling Aspen	Tree	32.20
2011-08-16	Downwind-D2	2530	Smooth Brome	Grass	29.60
2011-08-16	Downwind-D1	1100	Trembling Aspen	Tree	119.90
2011-08-16	Downwind-D1	1100	Chokecherry	Shrub	181.50
2011-08-16	Downwind-D1	1100	Saskatoon	Shrub	138.80
2011-08-16	Downwind-D1	1100	Balsam Poplar	Tree	196.90
2011-08-16	Downwind-D1	1100	Smooth Brome	Grass	91.50
2011-08-16	Downwind-D1	1700	Trembling Aspen	Tree	157.60
2011-08-16	Downwind-D1	1700	Chokecherry	Shrub	145.60
2011-08-16	Downwind-D1	1700	Wild Rose	Shrub	147.40
2011-08-16	Downwind-D1	1700	Smooth Brome	Grass	21.30
2011-08-16	Downwind-D1	1400	Balsam Poplar	Tree	204.70
2011-08-16	Downwind-D1	1400	Smooth Brome	Grass	20.10
2011-08-16	Downwind-D1	1400	Canola	Grass	39.90
2011-08-16	Downwind-D1	1400	Canola	Grass	1.00
2011-08-16	Downwind-D2	2460	Saskatoon	Shrub	67.90
2011-08-16	Downwind-D2	2460	Trembling Aspen	Tree	44.00
2011-08-16	Downwind-D2	2460	Manitoba Maple	Tree	46.10
2011-08-16	Downwind-D2	2460	Caragana	Shrub	139.00
2011-08-16	Downwind-D2	2460	Smooth Brome	Grass	38.80
2011-08-16	Downwind-D2	2010	Caragana	Shrub	21.60
2011-08-16	Downwind-D2	2010	White Spruce	Tree	8.50
2011-08-16	Downwind-D2	2010	Manitoba Maple	Tree	9.50
2011-08-16	Downwind-D2	2010	Smooth Brome	Grass	2.80
2011-08-16	Downwind-D2	2010	Wheat	Grass	2.60
2011-08-16	Downwind-D2	2460	Trembling Aspen	Tree	9.20
2011-08-16	Downwind-D2	2460	Saskatoon	Shrub	6.20
2011-08-16	Downwind-D2	2460	Wild Rose	Shrub	10.00

2011-08-16	Downwind-D2	2460	Chokecherry	Shrub	8.60
2011-08-16	Downwind-D2	2460	Balsam Poplar	Tree	7.90
2011-08-16	Downwind-D2	2460	White Spruce	Tree	5.20
2011-08-16	Downwind-D2	5680	Smooth Brome	Grass	8.10
2011-08-29	Downwind-D2	2800	Wheat	Grass	1.40
2011-08-29	Downwind-D2	2010	Wheat	Grass	1.20
2011-08-31	Upwind-D2	3500	Barley	Grass	1.80
2011-09-06	Downwind-D2	1700	Barley	Grass	1.80
2011-09-13	Upwind-D1	816	Wheat	Grass	1.30
2011-09-13	Upwind-D2	1500	Wheat	Grass	1.40
2011-09-15	Downwind-D1	330	Canola	Grass	1.10
2011-09-20	Upwind-D2	3000	Canola	Grass	1.00
2011-09-26	Upwind-D1	40	Canola	Grass	1.60
2011-09-26	Upwind-D2	1700	Canola	Grass	1.20
2012-08-01	Upwind-D2	3000	Balsam Poplar	Tree	6.70
2012-08-01	Upwind-D2	3000	Smooth Brome	Grass	5.30
2012-08-01	Upwind-D2	3000	White Spruce	Tree	5.60
2012-08-01	Upwind-D2	3000	Wheat	Grass	1.60
2012-08-01	Downwind-D2	1700	Balsam Poplar	Tree	6.10
2012-08-01	Downwind-D2	1700	Trembling Aspen	Tree	8.00
2012-08-01	Downwind-D2	1700	Canola	Grass	2.00
2012-08-01	Downwind-D2	1700	Smooth Brome	Grass	4.10
2012-08-01	Upwind-D1	40	Trembling Aspen	Tree	334.70
2012-08-01	Upwind-D1	40	Balsam Poplar	Tree	555.70
2012-08-01	Upwind-D1	40	Smooth Brome	Grass	141.50
2012-08-01	Upwind-D1	40	Wheat	Grass	48.40
2012-08-01	Upwind-D1	40	Caragana	Shrub	627.90
2012-08-01	Upwind-D1	816	Trembling Aspen	Tree	105.70
2012-08-01	Upwind-D1	816	Wild Rose	Shrub	71.80
2012-08-01	Upwind-D1	816	White Spruce	Tree	10.30
2012-08-01	Upwind-D1	816	Canola	Grass	17.90
2012-08-01	Upwind-D1	816	Canola	Grass	1.60
2012-08-01	Upwind-D1	816	Smooth Brome	Grass	22.30
2012-08-01	Upwind-D2	1500	Caragana	Shrub	55.70
2012-08-01	Upwind-D2	1500	Balsam Poplar	Tree	24.50
2012-08-01	Upwind-D2	1500	Canola	Grass	5.20
2012-08-01	Upwind-D2	1500	Canola	Grass	0.90
2012-08-01	Upwind-D2	1500	Smooth Brome	Grass	6.70
2012-08-01	Upwind-D2	1700	Saskatoon	Shrub	11.90
2012-08-01	Upwind-D2	1700	Chokecherry	Shrub	21.70
2012-08-01	Upwind-D2	1700	Trembling Aspen	Tree	39.60
2012-08-01	Upwind-D2	1700	Canola	Grass	7.10
2012-08-01	Upwind-D2	1700	Smooth Brome	Grass	9.50

2012-08-01	Upwind-D2	3500	Canola	Grass	5.30
2012-08-01	Upwind-D2	3500	Canola	Grass	0.90
2012-08-01	Upwind-D2	3500	Smooth Brome	Grass	2.50
2012-08-01	Upwind-D2	3500	Balsam Poplar	Tree	1.60
2012-08-01	Upwind-D2	3500	Caragana	Shrub	11.30
2012-08-01	Downwind-D1	330	Smooth Brome	Grass	153.50
2012-08-01	Downwind-D1	330	Wheat	Grass	73.40
2012-08-01	Downwind-D1	330	Trembling Aspen	Tree	316.00
2012-08-01	Downwind-D1	330	Caragana	Shrub	383.60
2012-08-01	Downwind-D1	330	Saskatoon	Shrub	193.90
2012-08-01	Upwind-D1	800	Manitoba Maple	Tree	23.80
2012-08-01	Upwind-D1	800	Smooth Brome	Grass	8.40
2012-08-01	Upwind-D1	800	Wheat	Grass	4.20
2012-08-01	Upwind-D1	800	White Spruce	Tree	5.60
2012-08-01	Upwind-D1	800	Caragana	Shrub	36.20
2012-08-01	Upwind-D1	800	Cottonwood	Tree	24.50
2012-08-02	Downwind-D2	1480	Smooth Brome	Grass	13.40
2012-08-02	Downwind-D2	1480	Wheat	Grass	3.50
2012-08-02	Downwind-D2	1480	Manitoba Maple	Tree	13.50
2012-08-02	Downwind-D2	1480	Balsam Poplar	Tree	11.80
2012-08-02	Downwind-D2	1480	White Spruce	Tree	10.90
2012-08-02	Downwind-D2	2550	Smooth Brome	Grass	8.60
2012-08-02	Downwind-D2	2550	Canola	Grass	5.70
2012-08-02	Downwind-D2	2550	Canola	Grass	0.90
2012-08-02	Downwind-D2	2550	Caragana	Shrub	23.60
2012-08-02	Downwind-D2	2550	Manitoba Maple	Tree	9.30
2012-08-02	Downwind-D2	2550	Balsam Poplar	Tree	16.20
2012-08-02	Upwind-D2	1900	Smooth Brome	Grass	3.90
2012-08-02	Upwind-D2	1900	Wheat	Grass	1.40
2012-08-02	Upwind-D2	1900	Manitoba Maple	Tree	10.00
2012-08-02	Upwind-D2	1900	Caragana	Shrub	19.50
2012-08-02	Downwind-D2	2530	Smooth Brome	Grass	11.10
2012-08-02	Downwind-D2	2530	Wild Rose	Shrub	26.30
2012-08-02	Downwind-D2	2530	Balsam Poplar	Tree	17.00
2012-08-02	Downwind-D2	2530	Trembling Aspen	Tree	15.40
2012-08-02	Downwind-D1	1100	Chokecherry	Shrub	33.60
2012-08-02	Downwind-D1	1100	Trembling Aspen	Tree	42.10
2012-08-02	Downwind-D1	1100	Balsam Poplar	Tree	51.30
2012-08-02	Downwind-D1	1100	Saskatoon	Shrub	52.00
2012-08-02	Downwind-D1	1100	Smooth Brome	Grass	41.60
2012-08-02	Downwind-D1	1700	Smooth Brome	Grass	7.00
2012-08-02	Downwind-D1	1700	Wild Rose	Shrub	57.30
2012-08-02	Downwind-D1	1700	Trembling Aspen	Tree	60.50

2012-08-02	Downwind-D1	1700	Chokecherry	Shrub	39.60
2012-08-02	Downwind-D1	1400	Wheat	Grass	12.80
2012-08-02	Downwind-D1	1400	Balsam Poplar	Tree	62.00
2012-08-02	Downwind-D1	1400	Smooth Brome	Grass	13.70
2012-08-02	Downwind-D2	2010	Smooth Brome	Grass	3.90
2012-08-02	Downwind-D2	2010	Manitoba Maple	Tree	11.10
2012-08-02	Downwind-D2	2010	Caragana	Shrub	10.40
2012-08-02	Downwind-D2	2010	White Spruce	Tree	2.60
2012-08-02	Downwind-D2	5680	Chokecherry	Shrub	3.80
2012-08-02	Downwind-D2	5680	Smooth Brome	Grass	1.20
2012-08-02	Downwind-D2	5680	Wild Rose	Shrub	3.40
2012-08-02	Downwind-D2	5680	Trembling Aspen	Tree	6.30
2012-08-02	Downwind-D2	5680	Balsam Poplar	Tree	4.90
2012-08-02	Downwind-D2	5680	White Spruce	Tree	3.40
2012-08-02	Downwind-D2	5680	Saskatoon	Shrub	3.60
2012-08-13	Upwind-D2	3000	Wheat	Grass	0.90
2012-08-15	Upwind-D1	40	Wheat	Grass	1.40
2012-08-15	Downwind-D1	330	Wheat	Grass	2.00
2012-08-15	Upwind-D1	800	Wheat	Grass	1.10
2012-08-15	Upwind-D2	1900	Wheat	Grass	1.10
2012-08-15	Downwind-D1	1400	Wheat	Grass	1.20
2012-08-20	Downwind-D2	1480	Wheat	Grass	0.90
2012-08-21	Downwind-D2	2460	Smooth Brome	Grass	12.80
2012-08-21	Downwind-D2	2460	Trembling Aspen	Tree	24.40
2012-08-21	Downwind-D2	2460	Manitoba Maple	Tree	18.60
2012-08-21	Downwind-D2	2460	Caragana	Shrub	94.90
2012-08-21	Downwind-D2	2460	Saskatoon	Shrub	35.90
2012-08-29	Downwind-D2	1700	Canola	Grass	0.80
2012-08-29	Upwind-D2	1700	Canola	Grass	1.20

Table A3. Biomonitoring results of perennial rye grass.

Year	Exposure Period	Site	Distance (m)	Distance Range	Species	Age	Internal Fluoride (µg/g)
2015	P1	EF1	1960	Far	Perennial Rye Grass	20	15
2015	P2	EF1	1960	Far	Perennial Rye Grass	20	28
2015	P3	EF1	1960	Far	Perennial Rye Grass	20	65
2015	P4	EF1	1960	Far	Perennial Rye Grass	20	14
2015	P1	EF2	1813	Far	Perennial Rye Grass	20	2.5
2015	P2	EF2	1813	Far	Perennial Rye Grass	20	6
2015	P3	EF2	1813	Far	Perennial Rye Grass	20	12
2015	P4	EF2	1813	Far	Perennial Rye Grass	20	10
2015	P1	EF3	1823	Far	Perennial Rye Grass	20	6

2015	P2	EF3	1823	Far	Perennial Rye Grass	20	8
2015	P3	EF3	1823	Far	Perennial Rye Grass	20	17
2015	P4	EF3	1823	Far	Perennial Rye Grass	20	7
2015	P1	EF4	1923	Far	Perennial Rye Grass	20	2.5
2015	P2	EF4	1923	Far	Perennial Rye Grass	20	2.5
2015	P3	EF4	1923	Far	Perennial Rye Grass	20	8
2015	P4	EF4	1923	Far	Perennial Rye Grass	20	5
2015	P1	EM1	1340	Medium	Perennial Rye Grass	20	7
2015	P2	EM1	1340	Medium	Perennial Rye Grass	20	46
2015	P1	EM2	1190	Medium	Perennial Rye Grass	20	5
2015	P2	EM2	1190	Medium	Perennial Rye Grass	20	14
2015	P3	EM2	1190	Medium	Perennial Rye Grass	20	20
2015	P4	EM2	1190	Medium	Perennial Rye Grass	20	11
2015	P1	EM3	1200	Medium	Perennial Rye Grass	20	16
2015	P1	EM4	1150	Medium	Perennial Rye Grass	20	5
2015	P2	EM4	1150	Medium	Perennial Rye Grass	20	21
2015	P3	EM4	1150	Medium	Perennial Rye Grass	20	21
2015	P4	EM4	1150	Medium	Perennial Rye Grass	20	10
2015	P1	EN1	220	Near	Perennial Rye Grass	20	43
2015	P2	EN1	220	Near	Perennial Rye Grass	20	210
2015	P3	EN1	220	Near	Perennial Rye Grass	20	540
2015	P4	EN1	220	Near	Perennial Rye Grass	20	170
2015	P1	EN2	850	Near	Perennial Rye Grass	20	10
2015	P2	EN2	850	Near	Perennial Rye Grass	20	29
2015	P3	EN2	850	Near	Perennial Rye Grass	20	56
2015	P4	EN2	850	Near	Perennial Rye Grass	20	52
2015	P1	EN3	830	Near	Perennial Rye Grass	20	2.5
2015	P2	EN3	830	Near	Perennial Rye Grass	20	2.5
2015	P3	EN3	830	Near	Perennial Rye Grass	20	11
2015	P4	EN3	830	Near	Perennial Rye Grass	20	5
2015	P1	EN4	347	Near	Perennial Rye Grass	20	26
2015	P2	EN4	347	Near	Perennial Rye Grass	20	29
2015	P3	EN4	347	Near	Perennial Rye Grass	20	47
2015	P4	EN4	347	Near	Perennial Rye Grass	20	20
2015	P1	NF1	2048	Far	Perennial Rye Grass	20	2.5
2015	P2	NF1	2048	Far	Perennial Rye Grass	20	2.5
2015	P3	NF1	2048	Far	Perennial Rye Grass	20	21
2015	P1	NF2	2017	Far	Perennial Rye Grass	20	2.5
2015	P2	NF2	2017	Far	Perennial Rye Grass	20	6
2015	P1	NF3	1933	Far	Perennial Rye Grass	20	9
2015	P2	NF3	1933	Far	Perennial Rye Grass	20	7
2015	P3	NF3	1933	Far	Perennial Rye Grass	20	11
2015	P4	NF3	1933	Far	Perennial Rye Grass	20	8

2015	P1	NF4	2140	Far	Perennial Rye Grass	20	2.5
2015	P2	NF4	2140	Far	Perennial Rye Grass	20	10
2015	P4	NF4	2140	Far	Perennial Rye Grass	20	7
2015	P1	NM1	1304	Medium	Perennial Rye Grass	20	2.5
2015	P2	NM1	1304	Medium	Perennial Rye Grass	20	10
2015	P3	NM1	1304	Medium	Perennial Rye Grass	20	22
2015	P1	NM2	1271	Medium	Perennial Rye Grass	20	8
2015	P2	NM2	1271	Medium	Perennial Rye Grass	20	12
2015	P3	NM2	1271	Medium	Perennial Rye Grass	20	42
2015	P4	NM2	1271	Medium	Perennial Rye Grass	20	23
2015	P1	NM3	1290	Medium	Perennial Rye Grass	20	8
2015	P2	NM3	1290	Medium	Perennial Rye Grass	20	23
2015	P3	NM3	1290	Medium	Perennial Rye Grass	20	39
2015	P4	NM3	1290	Medium	Perennial Rye Grass	20	18
2015	P1	NM4	1146	Medium	Perennial Rye Grass	20	6
2015	P2	NM4	1146	Medium	Perennial Rye Grass	20	20
2015	P3	NM4	1146	Medium	Perennial Rye Grass	20	38
2015	P4	NM4	1146	Medium	Perennial Rye Grass	20	7
2015	P1	NN1	500	Near	Perennial Rye Grass	20	8
2015	P2	NN1	500	Near	Perennial Rye Grass	20	26
2015	P3	NN1	500	Near	Perennial Rye Grass	20	33
2015	P4	NN1	500	Near	Perennial Rye Grass	20	21
2015	P1	NN2	500	Near	Perennial Rye Grass	20	9
2015	P2	NN2	500	Near	Perennial Rye Grass	20	14
2015	P3	NN2	500	Near	Perennial Rye Grass	20	24
2015	P4	NN2	500	Near	Perennial Rye Grass	20	29
2015	P1	NN3	500	Near	Perennial Rye Grass	20	5
2015	P2	NN3	500	Near	Perennial Rye Grass	20	22
2015	P3	NN3	500	Near	Perennial Rye Grass	20	53
2015	P4	NN3	500	Near	Perennial Rye Grass	20	23
2015	P1	NN4	500	Near	Perennial Rye Grass	20	2.5
2015	P2	NN4	500	Near	Perennial Rye Grass	20	16
2015	P3	NN4	500	Near	Perennial Rye Grass	20	27
2015	P4	NN4	500	Near	Perennial Rye Grass	20	7
2015	P1	EPG	0	PG Stack	Perennial Rye Grass	20	740
2015	P2	EPG	0	PG Stack	Perennial Rye Grass	20	1400
2015	P3	EPG	0	PG Stack	Perennial Rye Grass	20	2400
2015	P4	EPG	0	PG Stack	Perennial Rye Grass	20	1200
2015	P1	NPG	0	PG Stack	Perennial Rye Grass	20	240
2015	P2	NPG	0	PG Stack	Perennial Rye Grass	20	1300
2015	P3	NPG	0	PG Stack	Perennial Rye Grass	20	1400
2015	P4	NPG	0	PG Stack	Perennial Rye Grass	20	2000
2015	P1	SPG	0	PG Stack	Perennial Rye Grass	20	850

2015	P2	SPG	0	PG Stack	Perennial Rye Grass	20	450
2015	P3	SPG	0	PG Stack	Perennial Rye Grass	20	1000
2015	P4	SPG	0	PG Stack	Perennial Rye Grass	20	1700
2015	P1	WPG	0	PG Stack	Perennial Rye Grass	20	43
2015	P2	WPG	0	PG Stack	Perennial Rye Grass	20	120
2015	P3	WPG	0	PG Stack	Perennial Rye Grass	20	200
2015	P4	WPG	0	PG Stack	Perennial Rye Grass	20	260
2015	P1	SF1	1570	Far	Perennial Rye Grass	20	7
2015	P2	SF1	1570	Far	Perennial Rye Grass	20	2.5
2015	P3	SF1	1570	Far	Perennial Rye Grass	20	14
2015	P1	SF2	1749	Far	Perennial Rye Grass	20	39
2015	P1	SF3	1740	Far	Perennial Rye Grass	20	7
2015	P2	SF3	1740	Far	Perennial Rye Grass	20	2.5
2015	P4	SF3	1740	Far	Perennial Rye Grass	20	11
2015	P1	SF4	1680	Far	Perennial Rye Grass	20	6
2015	P2	SF4	1680	Far	Perennial Rye Grass	20	6
2015	P3	SF4	1680	Far	Perennial Rye Grass	20	13
2015	P4	SF4	1680	Far	Perennial Rye Grass	20	12
2015	P1	SM1	1235	Medium	Perennial Rye Grass	20	9
2015	P2	SM1	1235	Medium	Perennial Rye Grass	20	15
2015	P3	SM1	1235	Medium	Perennial Rye Grass	20	47
2015	P4	SM1	1235	Medium	Perennial Rye Grass	20	28
2015	P1	SM2	1324	Medium	Perennial Rye Grass	20	10
2015	P2	SM2	1324	Medium	Perennial Rye Grass	20	26
2015	P3	SM2	1324	Medium	Perennial Rye Grass	20	80
2015	P4	SM2	1324	Medium	Perennial Rye Grass	20	33
2015	P1	SM3	1343	Medium	Perennial Rye Grass	20	12
2015	P2	SM3	1343	Medium	Perennial Rye Grass	20	20
2015	P3	SM3	1343	Medium	Perennial Rye Grass	20	46
2015	P4	SM3	1343	Medium	Perennial Rye Grass	20	58
2015	P1	SM4	1284	Medium	Perennial Rye Grass	20	23
2015	P2	SM4	1284	Medium	Perennial Rye Grass	20	14
2015	P3	SM4	1284	Medium	Perennial Rye Grass	20	28
2015	P4	SM4	1284	Medium	Perennial Rye Grass	20	36
2015	P1	SN1	460	Near	Perennial Rye Grass	20	33
2015	P2	SN1	460	Near	Perennial Rye Grass	20	70
2015	P3	SN1	460	Near	Perennial Rye Grass	20	190
2015	P4	SN1	460	Near	Perennial Rye Grass	20	73
2015	P1	SN2	530	Near	Perennial Rye Grass	20	44
2015	P2	SN2	530	Near	Perennial Rye Grass	20	65
2015	P3	SN2	530	Near	Perennial Rye Grass	20	140
2015	P4	SN2	530	Near	Perennial Rye Grass	20	190
2015	P1	SN4	697	Near	Perennial Rye Grass	20	67

2015	P2	SN4	697	Near	Perennial Rye Grass	20	150
2015	P3	SN4	697	Near	Perennial Rye Grass	20	350
2015	P4	SN4	697	Near	Perennial Rye Grass	20	270
2015	P1	WF1	1703	Far	Perennial Rye Grass	20	7
2015	P2	WF1	1703	Far	Perennial Rye Grass	20	14
2015	P3	WF1	1703	Far	Perennial Rye Grass	20	34
2015	P4	WF1	1703	Far	Perennial Rye Grass	20	10
2015	P1	WF2	1715	Far	Perennial Rye Grass	20	10
2015	P2	WF2	1715	Far	Perennial Rye Grass	20	30
2015	P3	WF2	1715	Far	Perennial Rye Grass	20	41
2015	P4	WF2	1715	Far	Perennial Rye Grass	20	16
2015	P1	WF3	1715	Far	Perennial Rye Grass	20	11
2015	P2	WF3	1715	Far	Perennial Rye Grass	20	17
2015	P3	WF3	1715	Far	Perennial Rye Grass	20	26
2015	P4	WF3	1715	Far	Perennial Rye Grass	20	14
2015	P1	WF4	1669	Far	Perennial Rye Grass	20	6
2015	P2	WF4	1669	Far	Perennial Rye Grass	20	14
2015	P1	WM1	1226	Medium	Perennial Rye Grass	20	7
2015	P2	WM1	1226	Medium	Perennial Rye Grass	20	8
2015	P3	WM1	1226	Medium	Perennial Rye Grass	20	32
2015	P4	WM1	1226	Medium	Perennial Rye Grass	20	11
2015	P1	WM2	1253	Medium	Perennial Rye Grass	20	15
2015	P2	WM2	1253	Medium	Perennial Rye Grass	20	6
2015	P3	WM2	1253	Medium	Perennial Rye Grass	20	16
2015	P4	WM2	1253	Medium	Perennial Rye Grass	20	14
2015	P1	WM3	1247	Medium	Perennial Rye Grass	20	14
2015	P2	WM3	1247	Medium	Perennial Rye Grass	20	22
2015	P3	WM3	1247	Medium	Perennial Rye Grass	20	45
2015	P1	WM4	1266	Medium	Perennial Rye Grass	20	7
2015	P2	WM4	1266	Medium	Perennial Rye Grass	20	33
2015	P3	WM4	1266	Medium	Perennial Rye Grass	20	43
2015	P4	WM4	1266	Medium	Perennial Rye Grass	20	17
2015	P1	WN1	862	Near	Perennial Rye Grass	20	37
2015	P2	WN1	862	Near	Perennial Rye Grass	20	18
2015	P3	WN1	862	Near	Perennial Rye Grass	20	25
2015	P4	WN1	862	Near	Perennial Rye Grass	20	15
2015	P1	WN3	332	Near	Perennial Rye Grass	20	46
2015	P2	WN3	332	Near	Perennial Rye Grass	20	100
2015	P3	WN3	332	Near	Perennial Rye Grass	20	230
2015	P4	WN3	332	Near	Perennial Rye Grass	20	66
2015	P1	WN4	140	Near	Perennial Rye Grass	20	9
2015	P2	WN4	140	Near	Perennial Rye Grass	20	100
2015	P3	WN4	140	Near	Perennial Rye Grass	20	84

2015	P4	WN4	140	Near	Perennial Rye Grass	20	48
2016	P1	EM1	1340	Medium	Perennial Rye Grass	20	9
2016	P2	EM1	1340	Medium	Perennial Rye Grass	20	28
2016	P3	EM1	1340	Medium	Perennial Rye Grass	20	52
2016	P4	EM1	1340	Medium	Perennial Rye Grass	20	35
2016	P1	EM2	1190	Medium	Perennial Rye Grass	20	6
2016	P2	EM2	1190	Medium	Perennial Rye Grass	20	10
2016	P3	EM2	1190	Medium	Perennial Rye Grass	20	19
2016	P4	EM2	1190	Medium	Perennial Rye Grass	20	39
2016	P1	EM3	1200	Medium	Perennial Rye Grass	20	5
2016	P2	EM3	1200	Medium	Perennial Rye Grass	20	32
2016	P3	EM3	1200	Medium	Perennial Rye Grass	20	93
2016	P4	EM3	1200	Medium	Perennial Rye Grass	20	79
2016	P1	EM4	1150	Medium	Perennial Rye Grass	20	8
2016	P2	EM4	1150	Medium	Perennial Rye Grass	20	35
2016	P3	EM4	1150	Medium	Perennial Rye Grass	20	33
2016	P4	EM4	1150	Medium	Perennial Rye Grass	20	39
2016	P1	EM5	1186	Medium	Perennial Rye Grass	20	18
2016	P2	EM5	1186	Medium	Perennial Rye Grass	20	21
2016	P3	EM5	1186	Medium	Perennial Rye Grass	20	25
2016	P4	EM5	1186	Medium	Perennial Rye Grass	20	51
2016	P1	EN5	323	Near	Perennial Rye Grass	20	40
2016	P2	EN5	323	Near	Perennial Rye Grass	20	200
2016	P3	EN5	323	Near	Perennial Rye Grass	20	120
2016	P4	EN5	323	Near	Perennial Rye Grass	20	300
2016	P1	EN6	150	Near	Perennial Rye Grass	20	100
2016	P2	EN6	150	Near	Perennial Rye Grass	20	180
2016	P3	EN6	150	Near	Perennial Rye Grass	20	200
2016	P4	EN6	150	Near	Perennial Rye Grass	20	340
2016	P1	EN7	113	Near	Perennial Rye Grass	20	200
2016	P2	EN7	113	Near	Perennial Rye Grass	20	410
2016	P3	EN7	113	Near	Perennial Rye Grass	20	730
2016	P4	EN7	113	Near	Perennial Rye Grass	20	830
2016	P1	EN8	150	Near	Perennial Rye Grass	20	130
2016	P2	EN8	150	Near	Perennial Rye Grass	20	210
2016	P3	EN8	150	Near	Perennial Rye Grass	20	220
2016	P4	EN8	150	Near	Perennial Rye Grass	20	370
2016	P1	EN9	330	Near	Perennial Rye Grass	20	32
2016	P2	EN9	330	Near	Perennial Rye Grass	20	160
2016	P3	EN9	330	Near	Perennial Rye Grass	20	94
2016	P4	EN9	330	Near	Perennial Rye Grass	20	130
2016	P1	EPG	0	PG Stack	Perennial Rye Grass	20	1100
2016	P2	EPG	0	PG Stack	Perennial Rye Grass	20	3300

2016	P3	EPG	0	PG Stack	Perennial Rye Grass	20	2700
2016	P4	EPG	0	PG Stack	Perennial Rye Grass	20	4600
2016	P1	EM1	1340	Medium	Perennial Rye Grass	40	9
2016	P2	EM1	1340	Medium	Perennial Rye Grass	40	12
2016	P3	EM1	1340	Medium	Perennial Rye Grass	40	23
2016	P4	EM1	1340	Medium	Perennial Rye Grass	40	38
2016	P1	EM2	1190	Medium	Perennial Rye Grass	40	5
2016	P2	EM2	1190	Medium	Perennial Rye Grass	40	15
2016	P3	EM2	1190	Medium	Perennial Rye Grass	40	17
2016	P4	EM2	1190	Medium	Perennial Rye Grass	40	40
2016	P1	EM3	1200	Medium	Perennial Rye Grass	40	5
2016	P2	EM3	1200	Medium	Perennial Rye Grass	40	20
2016	P3	EM3	1200	Medium	Perennial Rye Grass	40	32
2016	P4	EM3	1200	Medium	Perennial Rye Grass	40	48
2016	P1	EM4	1150	Medium	Perennial Rye Grass	40	8
2016	P2	EM4	1150	Medium	Perennial Rye Grass	40	29
2016	P3	EM4	1150	Medium	Perennial Rye Grass	40	28
2016	P4	EM4	1150	Medium	Perennial Rye Grass	40	39
2016	P1	EM5	1186	Medium	Perennial Rye Grass	40	9
2016	P2	EM5	1186	Medium	Perennial Rye Grass	40	31
2016	P3	EM5	1186	Medium	Perennial Rye Grass	40	28
2016	P4	EM5	1186	Medium	Perennial Rye Grass	40	31
2016	P1	EN5	323	Near	Perennial Rye Grass	40	150
2016	P2	EN5	323	Near	Perennial Rye Grass	40	140
2016	P3	EN5	323	Near	Perennial Rye Grass	40	180
2016	P4	EN5	323	Near	Perennial Rye Grass	40	360
2016	P1	EN6	150	Near	Perennial Rye Grass	40	110
2016	P2	EN6	150	Near	Perennial Rye Grass	40	290
2016	P3	EN6	150	Near	Perennial Rye Grass	40	200
2016	P4	EN6	150	Near	Perennial Rye Grass	40	400
2016	P1	EN7	113	Near	Perennial Rye Grass	40	100
2016	P2	EN7	113	Near	Perennial Rye Grass	40	490
2016	P3	EN7	113	Near	Perennial Rye Grass	40	350
2016	P4	EN7	113	Near	Perennial Rye Grass	40	900
2016	P1	EN8	150	Near	Perennial Rye Grass	40	56
2016	P2	EN8	150	Near	Perennial Rye Grass	40	130
2016	P3	EN8	150	Near	Perennial Rye Grass	40	220
2016	P4	EN8	150	Near	Perennial Rye Grass	40	200
2016	P1	EN9	330	Near	Perennial Rye Grass	40	21
2016	P2	EN9	330	Near	Perennial Rye Grass	40	140
2016	P3	EN9	330	Near	Perennial Rye Grass	40	130
2016	P4	EN9	330	Near	Perennial Rye Grass	40	74
2016	P1	EM1	1340	Medium	Perennial Rye Grass	60	10

2016	P2	EM1	1340	Medium	Perennial Rye Grass	60	10
2016	P3	EM1	1340	Medium	Perennial Rye Grass	60	63
2016	P4	EM1	1340	Medium	Perennial Rye Grass	60	31
2016	P1	EM2	1190	Medium	Perennial Rye Grass	60	9
2016	P2	EM2	1190	Medium	Perennial Rye Grass	60	13
2016	P3	EM2	1190	Medium	Perennial Rye Grass	60	35
2016	P4	EM2	1190	Medium	Perennial Rye Grass	60	24
2016	P1	EM3	1200	Medium	Perennial Rye Grass	60	25
2016	P2	EM3	1200	Medium	Perennial Rye Grass	60	26
2016	P3	EM3	1200	Medium	Perennial Rye Grass	60	81
2016	P4	EM3	1200	Medium	Perennial Rye Grass	60	39
2016	P1	EM4	1150	Medium	Perennial Rye Grass	60	10
2016	P2	EM4	1150	Medium	Perennial Rye Grass	60	41
2016	P3	EM4	1150	Medium	Perennial Rye Grass	60	37
2016	P4	EM4	1150	Medium	Perennial Rye Grass	60	44
2016	P1	EM5	1186	Medium	Perennial Rye Grass	60	22
2016	P2	EM5	1186	Medium	Perennial Rye Grass	60	36
2016	P3	EM5	1186	Medium	Perennial Rye Grass	60	46
2016	P4	EM5	1186	Medium	Perennial Rye Grass	60	42
2016	P1	EN5	323	Near	Perennial Rye Grass	60	81
2016	P2	EN5	323	Near	Perennial Rye Grass	60	160
2016	P3	EN5	323	Near	Perennial Rye Grass	60	210
2016	P4	EN5	323	Near	Perennial Rye Grass	60	430
2016	P1	EN6	150	Near	Perennial Rye Grass	60	130
2016	P2	EN6	150	Near	Perennial Rye Grass	60	300
2016	P3	EN6	150	Near	Perennial Rye Grass	60	380
2016	P4	EN6	150	Near	Perennial Rye Grass	60	580
2016	P1	EN7	113	Near	Perennial Rye Grass	60	170
2016	P2	EN7	113	Near	Perennial Rye Grass	60	500
2016	P3	EN7	113	Near	Perennial Rye Grass	60	230
2016	P4	EN7	113	Near	Perennial Rye Grass	60	630
2016	P1	EN8	150	Near	Perennial Rye Grass	60	86
2016	P2	EN8	150	Near	Perennial Rye Grass	60	130
2016	P3	EN8	150	Near	Perennial Rye Grass	60	130
2016	P4	EN8	150	Near	Perennial Rye Grass	60	260
2016	P1	EN9	330	Near	Perennial Rye Grass	60	38
2016	P2	EN9	330	Near	Perennial Rye Grass	60	96
2016	P3	EN9	330	Near	Perennial Rye Grass	60	66
2016	P4	EN9	330	Near	Perennial Rye Grass	60	110
2016	P1	EM4	1150	Medium	Sunflower	20	22
2016	P1	EM4	1150	Medium	Sunflower	20	18
2016	P1	EM4	1150	Medium	Sunflower	20	16
2016	P1	EM4	1150	Medium	Sunflower	20	16

2016	P1	EM4	1150	Medium	June Grass	20	86
2016	P1	EM4	1150	Medium	June Grass	20	20
2016	P1	EM4	1150	Medium	June Grass	20	8
2016	P1	EM4	1150	Medium	June Grass	20	5
2016	P1	EM4	1150	Medium	Corn	20	6
2016	P1	EM4	1150	Medium	Corn	20	8
2016	P1	EM4	1150	Medium	Corn	20	5
2016	P1	EM4	1150	Medium	Corn	20	5
2016	P1	EM4	1150	Medium	Alfalfa	20	5
2016	P1	EM4	1150	Medium	Alfalfa	20	10
2016	P1	EM4	1150	Medium	Alfalfa	20	6
2016	P1	EM4	1150	Medium	Alfalfa	20	8
2016	P2	EM4	1150	Medium	Sunflower	20	100
2016	P2	EM4	1150	Medium	Sunflower	20	59
2016	P2	EM4	1150	Medium	Sunflower	20	74
2016	P2	EM4	1150	Medium	Sunflower	20	81
2016	P2	EM4	1150	Medium	June Grass	20	25
2016	P2	EM4	1150	Medium	June Grass	20	31
2016	P2	EM4	1150	Medium	June Grass	20	19
2016	P2	EM4	1150	Medium	June Grass	20	32
2016	P2	EM4	1150	Medium	Corn	20	17
2016	P2	EM4	1150	Medium	Corn	20	16
2016	P2	EM4	1150	Medium	Corn	20	19
2016	P2	EM4	1150	Medium	Corn	20	11
2016	P2	EM4	1150	Medium	Alfalfa	20	13
2016	P2	EM4	1150	Medium	Alfalfa	20	16
2016	P2	EM4	1150	Medium	Alfalfa	20	14
2016	P2	EM4	1150	Medium	Alfalfa	20	9
2016	P3	EM4	1150	Medium	Sunflower	20	59
2016	P3	EM4	1150	Medium	Sunflower	20	62
2016	P3	EM4	1150	Medium	Sunflower	20	81
2016	P3	EM4	1150	Medium	Sunflower	20	37
2016	P3	EM4	1150	Medium	June Grass	20	34
2016	P3	EM4	1150	Medium	June Grass	20	44
2016	P3	EM4	1150	Medium	June Grass	20	37
2016	P3	EM4	1150	Medium	June Grass	20	42
2016	P3	EM4	1150	Medium	Corn	20	53
2016	P3	EM4	1150	Medium	Corn	20	38
2016	P3	EM4	1150	Medium	Corn	20	43
2016	P3	EM4	1150	Medium	Corn	20	36
2016	P3	EM4	1150	Medium	Alfalfa	20	16
2016	P3	EM4	1150	Medium	Alfalfa	20	32
2016	P3	EM4	1150	Medium	Alfalfa	20	32

2016	P3	EM4	1150	Medium	Alfalfa	20	30
2016	P4	EM4	1150	Medium	Sunflower	20	120
2016	P4	EM4	1150	Medium	Sunflower	20	100
2016	P4	EM4	1150	Medium	Sunflower	20	140
2016	P4	EM4	1150	Medium	Sunflower	20	120
2016	P4	EM4	1150	Medium	June Grass	20	120
2016	P4	EM4	1150	Medium	June Grass	20	49
2016	P4	EM4	1150	Medium	June Grass	20	63
2016	P4	EM4	1150	Medium	June Grass	20	120
2016	P4	EM4	1150	Medium	Corn	20	77
2016	P4	EM4	1150	Medium	Corn	20	95
2016	P4	EM4	1150	Medium	Corn	20	80
2016	P4	EM4	1150	Medium	Corn	20	62
2016	P4	EM4	1150	Medium	Alfalfa	20	57
2016	P4	EM4	1150	Medium	Alfalfa	20	51
2016	P4	EM4	1150	Medium	Alfalfa	20	160

Table A4. Monthly mean soluble fluoride in phosphogypsum pond at Agrium Redwater.

Year	Month	Mean Soluble Fluoride (% Wt)
2008	June	0.33
2008	July	0.51
2008	August	0.35
2008	September	0.51
2008	October	0.40
2009	June	0.32
2009	July	0.34
2009	August	0.36
2009	September	0.34
2009	October	0.34
2010	June	0.37
2010	July	0.41
2010	August	0.36
2010	September	0.35
2010	October	0.35
2011	June	0.31
2011	July	0.31
2011	August	0.30
2011	September	0.30
2011	October	0.30
2012	June	0.31
2012	July	0.26
2012	August	1.09
2012	September	0.27

2012	October	0.29
2013	June	0.30
2013	July	0.33
2013	August	0.32
2013	September	0.39
2013	October	0.33
2014	June	0.50
2014	July	0.57
2014	August	0.59
2014	September	0.62
2014	October	0.64
2015	June	0.74
2015	July	0.69
2015	August	0.78
2015	September	0.76
2015	October	0.80
2016	June	0.81
2016	July	0.85
2016	August	0.88
2016	September	0.90
2016	October	0.89