ACCUMULATION AND DEPOSITION OF AIRBORNE FLUORIDE ON VEGETATION OVER NINE YEARS OF BIOMONITORING

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ABSTRACT: This biomonitoring study investigated hydrogen fluoride accumulation in forage, shrub and tree species over nine years in the vicinity of a phosphate fertilizer plant (< 6 km). Plant samples were collected at four locations during the growing season at various distances (1.6–6 km) from the plant. Results show that woody species may accumulate more total fluoride than forage species. The concentration of fluoride at the source (ponded process water on phosphogypsum stacks), air temperature and precipitation may contribute to total fluoride variation in forage over time. Peak fluoride accumulated in forage species in fall with lowest values in early summer. Washing reduced approximately 32.3 % total fluoride (approximate amount of external fluoride), indicating that most fluorides in forages were internal via stomatal uptake of hydrogen fluorides.

Key words: Internal fluoride; external fluoride; biomonitoring; temporal pattern.

INTRODUCTION

During phosphate fertilizer production, phosphoric acid (H_3PO_4) and gypsum ($CaSO_4.2H_2O$) are generated as co-products,[1] with the latter commonly referred to as phosphogypsum (PG) and stored in large piles, known as PG stacks.[2] These stacks are usually designed to serve as reservoirs for process water before it is recirculated back into the plant.[3] In open or operational PG stacks, fluoride gases are emitted into the air through evaporation from the ponded surface of process water.[1] Generally, both gases and particulate fluorides can be carried by winds from the source into the atmosphere[1].

There are two main environmental effects of airborne fluorides (predominantly hydrogen fluorides). The primary effect is 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.[3] The second effect is toxicity to herbivores (livestock and wildlife) known as fluorosis, due to ingestion of fluoride contained in forage crops.[3,4] The signs of fluorosis generally occur in teeth, bones and soft tissues or organs.[5]

Financial and technical limitations are the biggest challenge to analytical devices for monitoring airborne fluoride as they are expensive, lack sensitivity, are labour intensive, require power supplies and make it hard to distinguish between gaseous and particulate fluorides.[3,6] Information from such device measurement is usually insufficient to investigate ecological effects since automated measurement of continuous airborne fluoride is not commercially available.[3,7] Thus biomonitoring has been suggested.

Biomonitoring of air pollution with plants is an efficient tool for monitoring long term environmental impact and detecting health risks to animals and humans in areas

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adjacent to the emission source.[8,9] Plants are more important bioindicators for monitoring fluorides than other groups of organisms due to their abundance.[3] Using forages[6,10,11] and woody species (shrubs, trees) [8,12-14] *in situ* fluoride monitoring is easy to carry out, as the plants have been affected by fluorides during a relatively long period of time. This approach may help to increase public and consumer trust in industrial operations known to emit fluorides to the atmosphere.[6]

This nine year biomonitoring study focused on historical vegetation fluoride accumulation patterns and effects of gaseous and particulate fluoride in vegetation in the vicinity of a phosphate fertilizer plant. This study determined what factors influenced fluoride accumulation in selected plant species over time. Although fluoride transportation and deposition are complex and may have numerous influences, we focused on temperature, precipitation, wind speed and soluble fluoride in the PG pond water. Relationships between internal and external fluoride in forage were also investigated.

MATERIALS AND METHODS

Study Site:

The fluoride source was emitted from a phosphate fertilizer plant, located near Redwater, Alberta, Canada. The phosphate production portion of the fertilizer plant occupies 372 ha including cooling ponds, surge ponds and storage ponds. The PG stack has operated for approximately 50 years (since 1969), accumulating approximately 55 million tonnes of PG, stored in a 275 ha area.

The study region has a prairie type climate with annual mean precipitation at 58.8 mm/month and mean temperature at 12.6 ^{o}C during the growing season. Prevailing winds changed slightly over the years, mostly blowing from the west, northwest-west and north-west at approximately 11.3 km/h. Wind direction (degrees), wind speed (km/h), temperature (^{o}C) and precipitation (mm) data were collected over the period of 2008 to 2016 from two nearby meteorological stations (less than 5 km) to provide accurate information of the studied region.

Vegetation Monitoring:

An annual vegetation program (forage and non-forage species biomonitoring) and a biweekly vegetation sampling program (forage and crop species monitoring) were conducted from 2008 to 2016. Annual sampling spots were spread out in different directions to the emission source. Biweekly sampling occurred east of the emission source in a long term pasture. Sampling occurred in four main locations based on two wind directions (downwind, upwind) and two distances (D1 =1.6, D2 = 1.6–6 km). Downwind locations were south and east of the PG stack; upwind locations were north and west of the PG stack. Distance was from the closest PG stack boundary.

In each sample location, vegetation samples were cut 3 cm above ground surface to procure 100 to 150 g and were kept in coolers in the field, then stored in a laboratory refrigerator at 4 ± 2 ^{o}C before delivering to a commercial laboratory for analysis. Sampled plant species differed over the months and years. Forage species were a mix of common forage and crop species in the area, including *Leymus innovatus* (Beal) Pilg (hairy wild rye), *Bromus inermis* Leyss (smooth brome) and *Phalaris arundinacea* L. (reed canary forage), *Hordeum vulgare* L. (barley), *Triticum aestivum*

L. (wheat) and *Brassica napus* L. (canola). Tree species were *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).

Fluoride Analyses:

The biweekly sampling program collected total fluoride data and soluble fluoride data from PG ponds from 2008 to 2016. The annual sampling program collected vegetation accumulated internal fluoride data from shrubs and trees from 2008 to 2012. Total fluoride includes internal fluoride and any fluoride on the external part of the plant; total fluoride results 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. 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. A solution was prepared for washing (0.05 % liquinox and 0.05 % tetrasodium ethylenediamine tetraacetate) as surface residues were difficult to remove by simply washing with water. The wash process followed a standardized laboratory sample preparation procedure.[15] Washed and unwashed samples were delivered to a commercial laboratory and all samples were oven dried and finely ground in preparation for analysis. Washed and unwashed vegetation samples were analyzed by ion selective electrode after 0.1 M perchloric acid extraction at 80 ± 5 ^{o}C in a water bath.[16] A portion of samples were divided and analyzed by instrumental neutron activation analysis[17] to validate fluoride results.

Statistical Analyses:

All analyses were performed with R software (version 3.3.2). Natural logarithm transformation was performed to achieve normality and equal variances assumptions. A two-way ANOVA (type III sum of squares) was performed for testing main factor effects (species, location) and their interactions (function: Anova - package: car), followed by lsmean pairwise post-hoc tests (function: lsmeans - package: lsmeans). Pearson's correlation test (function: cor.test - package: stats) was applied to measure statistical linear dependence between monthly total fluorides and numeric variables (temperature, precipitation, wind speed, soluble fluorides in PG ponds). Significance was accepted at $p<0.05$. Multiple linear regression (function: lm – package: stats) was conducted to explain the relationship between fluoride concentrations and various meteorological variables. 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 (function: step – package: stats). Mean temperature, precipitation and soluble fluorides in PG ponds were regressed and partial sum of squares with their total of each independent variables were calculated to determine how much is accounted for (how important) by each factor.

RESULTS

Internal Fluoride In Forage, Shrubs, And Trees:

Mean internal fluoride concentrations were significantly different in groups of species (forage, shrub, tree) at all four locations. Internal fluoride accumulation was strongly affected by species ($p<0.001$) and locations ($p<0.001$). Fluoride accumulation in woody species (shrub, tree) was significantly higher for internal fluoride than forage species (Figure 1).

Since a significant interaction between species and location was detected ($p=0.002$), the mean differences of internal fluorides between species groups may depend on locations. Generally, closer locations (Upwind-D1, Downwind-D2) showed higher internal fluorides in forages, shrubs and trees; upwind locations (Upwind-D1, Upwind-D2) showed greater fluoride differences between species groups. Shrubs had the highest internal fluoride at all four locations, followed by trees.

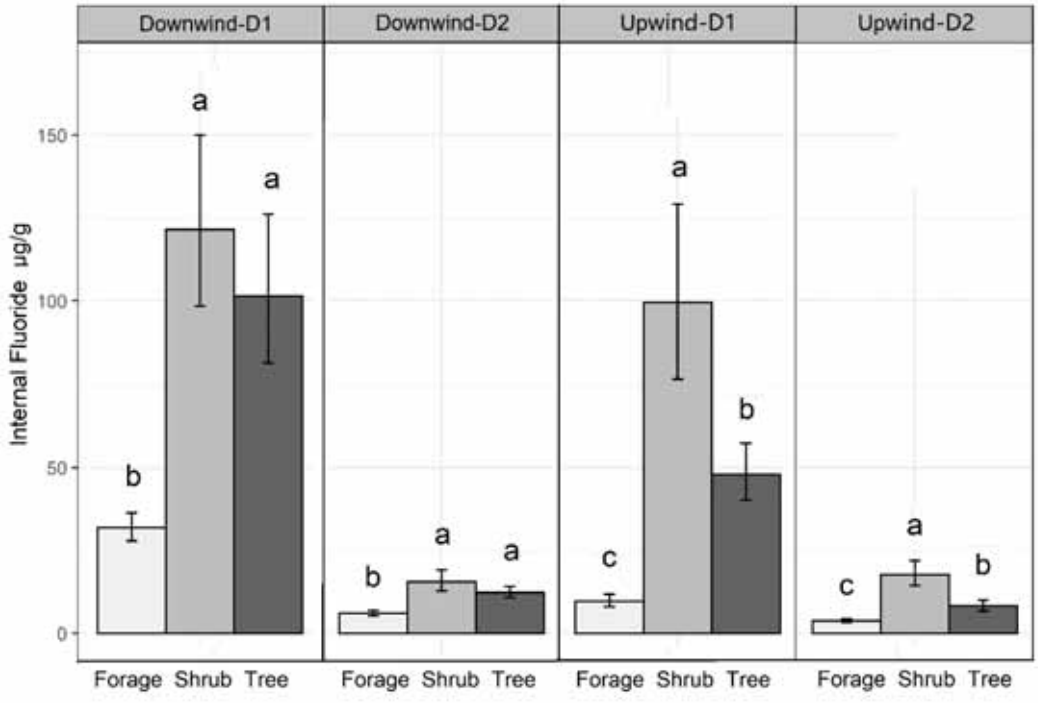

Figure 1. Mean internal fluoride (natural log back transformed) in forage, shrub and tree species at four sample locations. Error bars are standard errors. Different letters indicate significant differences within a location.

Total Fluoride Temporal Pattern In Forage:

Monthly patterns of total fluoride in forage was consistent among years (Table 1). Forage total fluoride concentrations generally trended upward throughout the growing season, with a marked decrease in late fall after the peaks except year 2008, 2012 and 2014. Seasonal mean concentrations for 2009 and 2010 were below regulatory levels (35 µg/g); 2008 and 2012 slightly exceeded it; other years greatly exceeded, varying from 54.5 to 86.8 µg/g (2011, 2013–2016).

Table 1. Mean total fluoride in forage from 2008 to 2016

Year	Monthly Mean Regulatory < 80 µg/g					Seasonal Mean Regulatory < 35 µg/g
	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

Total fluoride concentrations in forage fluctuated year to year which trended higher in recent (2013 to 2016) than more historic years (2008 to 2012) when comparing the frequency distribution of fluoride concentrations (Figure 2).

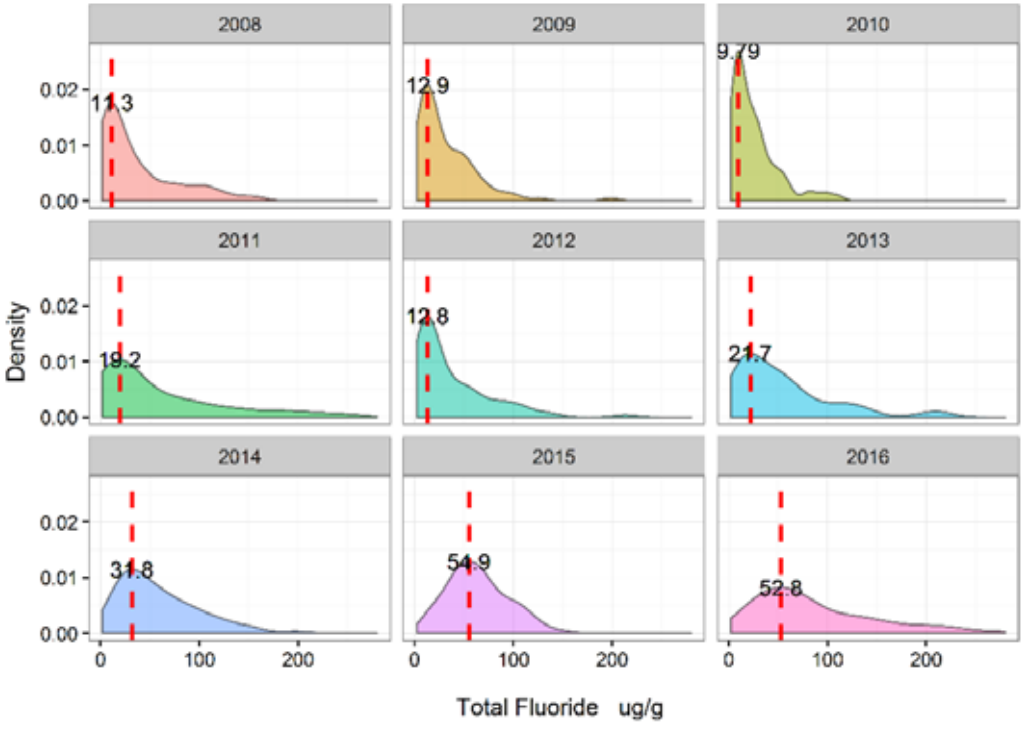

Figure 2. Relative frequency of seasonal mean total fluoride concentrations from 2008 to 2016 growing seasons. Density curves display fluoride concentration distribution. The area under the curve in a range of fluoride values indicates the proportion of values in that range. Density of the total area equals one. Red dashed lines refer to the major peak of concentrations.

The highest total fluoride occurred in 2015. The x-intercept of the major peak of 2015 (54.9 µg/g) was higher than that of 2016 (52.8 µg/g), although seasonal mean value of 2015 was lower than 2016.

Factors Affecting Total Fluoride Variation Over Time:

Pearson's correlation test showed that monthly total fluoride concentrations in forage were significantly negatively correlated with temperature ($p = 0.008$, $r = -0.393$) and mean precipitation ($p < 0.001$, $r = -0.515$); and significantly positively correlated with soluble fluorides in PG ponds ($p = 0.004$, $r = 0.419$). Wind speed did not show any strong relationship with total fluoride over the months. Soluble fluorides in PG ponds had the greatest influence on total fluoride monthly variation as it could approximately explain 23.4 % of the fluoride variation over the study period, followed by temperature (15.4 %) and precipitation (13.8 %). 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 ($p = 0.014$, $r = 0.777$). 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 3).

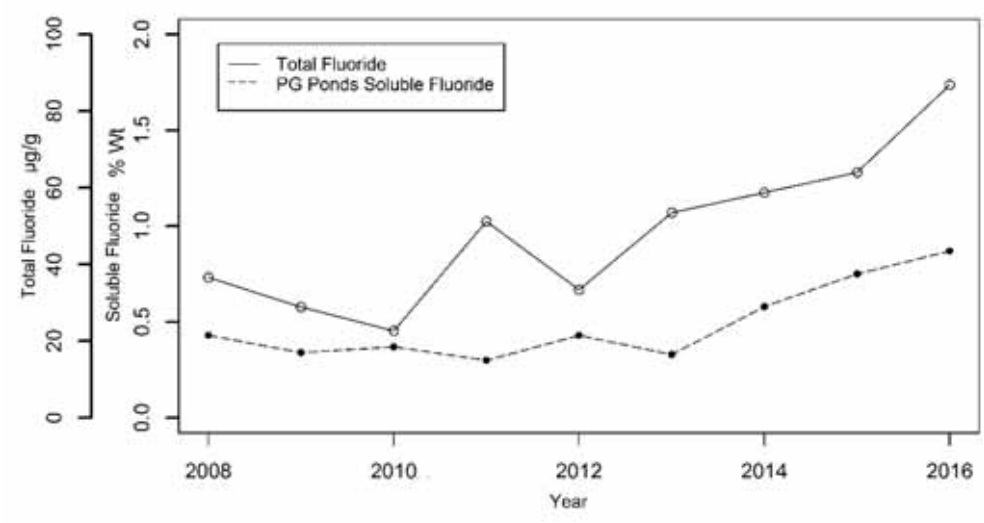

Figure 3. Total fluoride in forage and soluble fluoride in PG ponds Year to year variation.

Differentiating Internal And Total Fluorides:

On average, 32.3 % of fluoride can be washed off by water and considered an approximation of external fluoride. Series temperature ($p = 0.016$, $r = -0.477$) and precipitation ($p = 0.003$, $r = -0.576$) were strongly negatively correlated with external fluoride concentrations. Wind speed and soluble fluoride in PG ponds had no significant effects. Thus, temperature and precipitation may have affected external fluoride over time. The highest external fluoride was in the fall (September or October) when the 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.

DISCUSSION

Fluoride uptake of woody species in the vicinity of the PG stack may be more prone to volatility than forage species. This may be due to characteristics, such as height, leaf area, leaf shape and sensitivity to fluoride.[3] As woody species are generally taller than forage species, airborne fluoride transportation and deposition process might be less affected by blocking of buildings or taller plants.[3]

Total fluoride in forage was strongly affected by fluoride source, air temperature and precipitation. The latter two meteorological factors also 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 through stomatal pores.[3] External fluoride in the particle phase that remained on the leaf surface accumulated and had greater contribution to total fluoride. Therefore, more total fluoride was observed in fall than in summer.

The effects of precipitation are complex and conflictive based on previous studies. The negative correlation of precipitation with total and external fluoride in our study is similar to that of De Temmerman and Baeten[18] who found precipitation reduced 50 % fluoride concentrations in grass cultures. However, a wet surface can absorb more fluoride than a dry surface due to a higher fluoride up take capacity.[3] Less et al.[19] found artificial precipitation increased fluoride concentrations in plants two fold. The relationship between total fluoride and wind speed was not significant and this may be because mean wind speed varied slightly by 0.71 km/h (6.4 %) on average from June to October from 2008 to 2016.

According to our results, when soluble fluoride increased in PG ponds, total fluoride concentrations increased in forage. Approximately 0.15 % fluoride ion was found in the PG composition using Morocco phosphate rock during fertilizer production [20] 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. This could explain the increasing trend of fluoride in recent years (2013 to 2016) relative to previous years (2008 to 2012). As fluoride concentrations strongly vary with source rocks.[2] The increasing PG pond fluorides could be attributed to the change of phosphate rock used in phosphate fertilizer production over the study period. The phosphate rock used in study regions is likely a mix from various sources, but mainly sourced from Kapuskasing (Ontario, Canada) before 2013 and changed from Morocco (Africa) after that. Approximately 0.15 % fluoride ion was found in the PG composition using Morocco phosphate rock during fertilizer production[20] which was expected to cause higher fluoride in PG and process pond water. This might explain why seasonal mean total fluorides in forage increased notably since 2013.

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. In our study, 32.3 % total fluoride can be washed off on average. This indicated the highest proportion of fluoride in forage was internal, which may be coming from gaseous fluoride uptake and particle fluoride deposition. In other studies, approximately 22 % total fluoride can be removed by washing *Lolium multiflorum* cv. Lema (Italian rye forage)[6], 24 % from *Eucalyptus rostrata* Schlecht.

(gum tree), 39 % from *Populus hybridus* L. (hybrid poplar), and 51 % from *Pinus radiata* D. (radiata pine).[8] 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.

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REFERENCES

[1] Rutherford PM, Dudas MJ, Samek RA. Environmental impacts of phosphogypsum. The Science of the Total Environment 1994;149(1-2):1-38.

[2] Rutherford PM, Dudas MJ, Arocena JM. Radioactivity and elemental composition of phosphgypsum produced from three phosphate rock sources. Waste Management and Research 1995;13(5):407-423.

[3] Weinstein LH, Davison AW. Fluorides in the environment: effects on plants and animals. 1st ed. Cambridge, Massachusetts, USA: CABI Publishing; 2004.

[4] Wissa AEZ. Phosphogypsum disposal and the environment. [Proceedings of international workshop on current environmental issues of fertilizer production, 1999 June 7-9; Prague, Czech Republic.] In: Schultz JJ, Waggoner DR, editors. IFDC. Muscle Shoals, Alabama; 2002.

[5] Choubisa SL. Status of fluorosis in animals.Proceedings of the National Academy of Sciences India Section B: Biological Sciences 2012;82(3):331-339.

[6] Franzaring J, Klumpp A, Fangmeier A. Active biomonitoring of airborne fluoride near an HF producing factory using standardized grass cultures. Atmospheric Environment 2007;41(23):4828-4840.

[7] Junior AM, Oliva MA, Ferreira FA. 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 2008;8(5):454-461.

[8] Rodriguez JH, Wannaz ED, Pignata ML, Fangmeier A, Franzaring J. Fluoride biomonitoring around a large aluminium smelter using foliage from different tree species. Clean Soil, Air, Water 2012;40(12):1315-1319.

[9] Weinstein LH, Laurence JA, Mandl RH, Walti K. Use of native and cultivated plants as bioindicators and biomonitors of pollution damage. American Society for Testing and Materials 1990;117-126.

[10] Rey-Asensio A, Carballeira A. *Lolium perenne* as a biomonitor of atmospheric levels of fluoride. Environment International 2007;33(4):583-588.

[11] Hebelen RJ, Daniel WE, Jurgen F, Andreas K, Andreas F, Luisa PM. Biomonitoring of airborne fluoride and polycyclic aromatic hydrocarbons in industrial areas of Cordoba, Argentina, using standardized grass cultures of Lolium multiflorum. Atmospheric Pollution Research 2015; 6(3):444-453.

[12] Rozhkov AS, Mikhailova TA. The effects of fluorine-containing emissions on conifers. 1st ed. Berlin, Germany: Springer Verlag;1993. pp. 143.

[13] Mezghani I, Elloumi N, Abdallah FB, Chaieb M, Boukhris M. Fluoride accumulation by vegetation in the vicinity of a phosphate fertilizer plant in Tunisia. Fluoride 2005;38(1):69-75.

[14] Ahmad MN, van den Berg LJ, Shah HU, Masood T, Büker P, Emberson L, Ashmore M. Hydrogen fluoride damage to vegetation from peri-urban brick kilns in Asia: a growing but unrecognised problem? Environmental Pollution 2012;162:319-324.

;[15] Agrium Fertilizer Laboratory Services. 2012. Sample control procedures section (04) sample preparation – washing vegetation samples. Agrium Inc 2012; 1-4.

[16] Ontario Ministry of the Environment, W. (2012). The determination of fluoride in vegetation by ion selective electrode (ISE) version 4.0 (No. E3053). Ontario Ministry of the Environment. Laboratory Services Branch.

[17] Knight HG, Furr AK, Parkinson TF. Determination of fluorine by neutron activation analysis. Analytical Chemistry 1977;49(11):1507-1510.

[18] De Temmerman LM, Baeten H. The accumulation of airborne fluorides by perennial ryegrass cultures. Fluoride 1988;21:185-192.

[19] Less LN, McGregor A, Jones LHP, Cowling DW, Leafe EL. Fluoride uptake by gas from aluminium smelter fume. International Journal of Environmental Studies 1975;7(3):153–160.

[20] Sebbahi TS, Ould-Chameikh ML, Sahban F, Aride J, Benarafa L, Belkbir L. Thermal behaviour of Moroccan phosphogypsum. Thermochimica Acta 1997;302(1-2):69-75.