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The impact of aluminium smelter shut-down on the concentration of fluoride in vegetation and soils

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ABSTRACT

Although a great deal is known about the deposition of fluoride on vegetation, and the hazards associated with uptake by grazing herbivores, little is known about what happens to the concentration of fluoride in vegetation and soil at polluted sites once deposition ceases. The closure of Anglesey Aluminium Metals Ltd smelter, in September 2009, provided a unique opportunity to study fluoride loading once deposition stopped. Fluoride was monitored in plants and soil within 1 km of the former emission source. Fluoride concentrations in a range of plant material had decreased to background levels of 10 mg F kg^{-1} after 36 weeks. Concentrations of fluoride in mineral-rich soils decreased steadily demonstrating their limited potential to act as contaminating sources of fluoride for forage uptake. There were significant differences in the rate of decline of fluoride concentrations between plant species.

1. Introduction

Gaseous and particulate forms of fluoride are released into the atmosphere from a large number of sources including volcanoes, aluminium smelters and phosphate fertiliser factories (NAS, 1971; Weinstein and Davison, 2004). The most common gaseous form is hydrogen fluoride; one of the most phytotoxic of all air pollutants which, historically, has been responsible for large-scale economic and aesthetic damage (NAS, 1971; Weinstein and Davison, 2004). The deposition of fluoride on the surface of vegetation or the uptake by plants can cause fluorosis in mammalian herbivores if there is an excess in their diet. All of this is well documented (Weinstein and Davison, 2004), but questions about the long-term fate and cycling of deposited fluoride still arise when a new industrial source of fluoride is planned or when there is a volcanic eruption.

There is evidence that accumulated plant fluoride is sensitive to changes in ambient concentrations (Thompson et al., 1970), however, regulatory bodies and the public are often concerned about the potential for a build-up of fluoride in soils and, consequently, elevated plant fluoride even when a source ceases emission.

In general, the chemistry of soil fluorine and our understanding of the physiology of fluoride uptake suggest that there is little risk of accumulation from long-term deposition of fluoride on neutral to alkaline mineral soils, but uncultivated, acidic soils may be a greater risk (Davison and Weinstein, 2006; Weinstein and Davison, 2004). If the fluoride concentration in vegetation falls to background levels once emissions cease this would indicate that soil fluoride does not impact on the fluoride content of leaves. The problem is that very few studies of post-emission fluoride concentrations have been published and although work, such as that by Thompson et al. (1970), provides useful data, there is still a need for more information from a greater range of species and situations. The opportunity to obtain such information was presented when the Anglesey Aluminium Metals Ltd smelter (GB Grid Reference: SH 266 809) closed in September 2009. Samples of soil, leaves and lichens were collected and analysed to follow the changes in fluoride content over a 15 month period in order to examine the impact of site closure on fluoride concentrations in the environment.

2. Methods

2.1. Sampling locations and mapping

Vegetation and soil samples were collected regularly between 30th September 2009 (the day of smelter shutdown) and 6th January 2010 (14 weeks after shutdown). A collection of all material types was made on the 10th June 2010, the start of the following year's growing season (36 weeks after shutdown), and further samples

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of lichen were collected at the beginning of December 2010 in order to increase the size of the data set.

Each site was mapped (Fig. 1) using a Garmin Etrex H GPS system in combination with Memory Map software. All sampling locations were within 1 km of the smelter chimney and, with one exception; sites were within 1 km of the pot line roof, which were the main sources of fluoride emissions emanating from the smelter (Fig. 1). Table 1 shows the distance and direction of the sample types and locations from the smelter chimney from which the greatest volume of emissions emanated. The samples collected at the sites located North East of the chimney were downwind from the emission source.

2.2. Sampling

To avoid fluoride sinks in necrotic plant tissue, and in order to collect material representative of the current fluoride concentrations, all of the material sampled was from that year's growth. The first collection comprised samples of all the materials taken on the day the smelter was shutdown. Grass material of mixed swards, representative of forage for cattle, was sampled weekly for eight weeks from four sites situated around the smelter (Fig. 1). Further samples were then taken after a two week and then a four week period. At each site three sub-samples were collected from an area approximately 5 m^2 and cut to avoid fluoride contamination from roots and soil debris.

Three samples of the lichen, *Ramalina siliquosa*, were collected monthly from a location downwind from the smelter (Fig. 1) and three samples of coniferous needles were collected monthly from three trees at locations both upwind (*Pinus contorta*) and downwind (*Picea sitchensis*) from the smelter (Fig. 1). Three samples of sycamore leaves, *Acer pseudoplatanus*, were collected weekly, until leaf fall, from three trees located downwind from the smelter. Soil material was collected monthly from each of the four grass-collection sites. At each site, three samples of soil were removed from the top 2 cm of the soil layer. A further set of vegetation and soil samples were collected from all locations 36 weeks after site closure, at the start of the following year's growing season.

2.3. Chemical analyses

The fluoride content (mg F kg^{-1}) of both plant and soil material was measured using standard operating procedures employed by UK aluminium reduction plants in their routine fluoride monitoring programmes (Cooke et al., 1976).

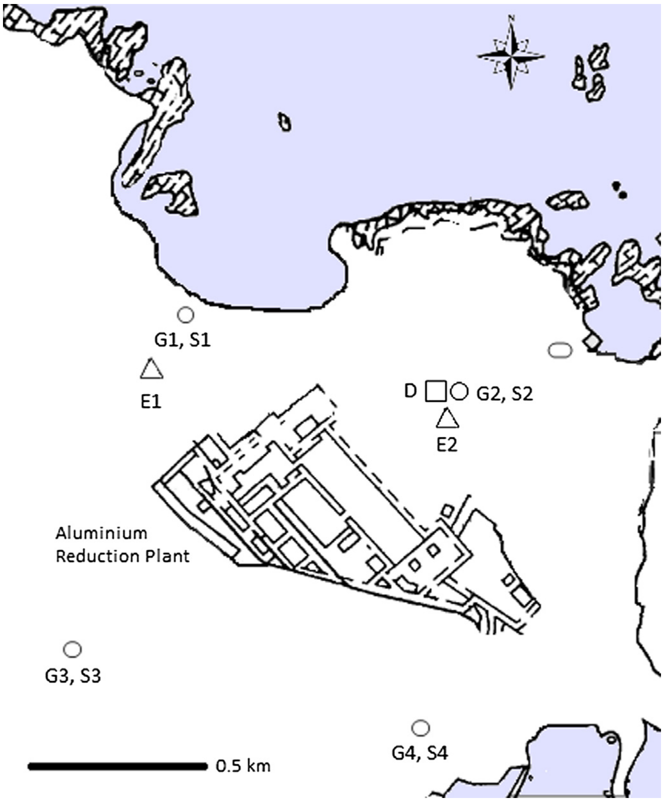

Fig. 1. Sampling sites near the Anglesey smelter for grass and soil (○, 1–4); Conifer sampling (Δ, 1–2); Sycamore leaf sampling (S2); and lichen (⬭). The chimney (c) and potroom roof (P) are the sources of fluoride emissions and are marked on the smelter site plan.

Table 1
The given name, the distance (metres) and the direction of each site from the source of the fluoride emissions at Anglesey Aluminium.

Material	Site name	Direction from the emission source	Distance from the emission source (metres)
Grass	G1	North west	596
	G2	North east	486
	G3	South west	943
	G4	South-south-east	932
Soil	S1	North west	596
	S2	North east	486
	S3	South west	943
	S4	South-south- east	932
Conifer	E1	North-west-west	542
	E2	North east	486
Sycamore	D	North east	486
Lichen	L	North-east-east	486

2.4. Plant material

Vegetation samples were dried for 24 h at 70 °C and then ground to a fine powder using a Cyclotec 1093 tissue grinding mill. Between 200 and 300 mg of each sample was added to 2 ml 0.25 M H_2SO_4, thoroughly wetted and left for two hours at room temperature to digest.

Six millilitres of trisodium citrate buffer was then added and stirred. The fluoride content of the solution was measured using an Elit 8221 fluoride-sensitive electrode coupled with an Orion potentiometer.

The calibration was made using sodium fluoride (NaF) standard solutions and the equipment was calibrated during every set of analyses. Three standard vegetation samples of 100 mg F kg^{-1} Assam tea were also included in each set of analyses to ensure the quality of the procedures. The tea samples came from a large batch of Assam tea that was milled using a Cyclotec 1093 tissue grinding mill. To ensure the quality of this standard material, the tea samples were included in round-robin inter-laboratory tests organised by the aluminium industry and in the Boyce Thompson inter-laboratory trials (Weinstein and Davison, 2004). Measurements of fluoride concentration were converted to mg F kg^{-1} (Cooke et al., 1976).

2.5. Soil material

The samples were air dried and sieved to remove debris and between 200 and 500 mg of sample was measured into a platinum crucible. Two hundred milligrams of anhydrous Analar sodium carbonate (Na_2CO_3) and drops of nanopure water (Sigma Aldrich) were added and mixed to form a slurry. This was then gently heated over a bunsen burner until samples were white and carbon-free.

The heat was increased and the residue was fused until it turned clear. It was then left to cool in a fluoride-free environment for 30 min. Ten millilitres of 0.25 M H_2SO_4 were added a few drops at a time and the mixture was allowed to digest for one hour. Six millilitres of trisodium citrate buffer were then added and the concentration of fluoride in the soils was measured using the fluoride-specific electrode.

The mean organic content of the soil samples was analysed for each site. A sample of each of the soil samples was dried and pre-weighed in to a platinum crucible before adding drops of nanopure water and mixing to form a slurry. Crucibles were heated over a bunsen burner for approximately 20 min until the water had evaporated and samples had thoroughly burnt. After cooling, the samples were then reweighed.

2.6. Statistical analyses

The mean fluoride concentration (mg F kg^{-1}) was calculated for each material on each sampling date. For each material and site, the mean fluoride concentration (mg F kg^{-1}) was plotted against the number of days since smelter closure. A power trend line was fitted to the data and the regression coefficient (R) calculated in Excel. Where the regression was significant ($P \leq 0.05$), the regression equation was used to calculate the half life of fluoride at each site, in each sample material. Where the concentration of fluoride in the grass samples exceeded 40 mg F kg^{-1} at the start of the analyses, the regression equation was also used to calculate the number of days it took for the fluoride concentration (mg F kg^{-1}) to fall to the Washington State standard of 40 mg F kg^{-1}; a twelve month moving mean not to exceed 40 mg F kg^{-1} in forage used to graze livestock.

3. Results

3.1. Interspecies variation

The mean concentration of fluoride from coniferous foliage, on the day of shutdown, was higher downwind from the source than