UPTAKE OF FLUORIDE AND ALUMINUM BY PLANTS GROWN IN CONTAMINATED SOILS

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Abstract. Soils collected from areas at different distances from an aluminum smelter were studied to determine the soluble and labile F and soluble Al contents and availabilities to selected plants. Red maple seedlings (*Acer rubrum* L.) and orchard grass (*Dactylis glomerata* L.) were grown in pots containing the soils and after 3 mo foliar tissues were sampled and analyzed for the two elements. The soluble and labile contents of soil F as predictors of foliar F were compared.

Significant decreases in soluble and labile F and soluble Al in soils were found with increasing distance from the smelter. As F levels in the soils increased, the F in the foliage of both orchard grass and maple increased. As Al in the soil increased, Al in maple foliage increased. Overall, F concentrations in plant foliage were below those considered as background. The results imply that, at least in the soils studied, the soil F content is not an important source of F to plants and therefore to herbivores in the area.

Labile F values in the soils were significantly greater than soluble F at all sites, but, contrary to previous studies, soluble F was a better predictor of foliar F than was labile F.

1. Introduction

Compounds released into the atmosphere during the process of Al smelting ultimately enter the soil either directly in precipitation and dry deposition or indirectly through contaminated litter. Gaseous compounds emitted include HF, which has been extensively studied due to its phytotoxicity. Emissions in particulate form may include NaF, CaF_2, AlF_3, and several Na-Al-fluoride compounds such as Na_3AlF_6 (cryolite), $Na_5Al_3F_{14}$ (chiolite), and $NaAlF_4$ (Drury *et al.*, 1980; Flühler *et al.*, 1982). The soil in the vicinity of a smelter may act as a sink and provide a long term source of pollutants to soil-dwelling organisms and to plants. This paper focuses two of the elements (F and Al) emitted during the process of Al smelting.

Fluoride is not only the most phytotoxic of the common air pollutants, but it is also accumulated by plants. High concentrations of F in plant foliage, when ingested by vertebrates may result in fluorosis, a dental and skeletal disease. Fluorosis has been most extensively studied in cattle (NAS, 1971), but elevated levels of F in bones of wildlife have also been reported (e.g., Kay, 1974; Suttie, 1977; Murray, 1981).

Background concentrations of F in plant tissues range from 2 to 20 ppm (Weinstein, 1977). However, higher amounts of F can be accumulated from soils under some

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circumstances (Prince *et al.*, 1949; Lalonde, 1976; McClenahen and Weidensaul, 1977). In the vicinity of a F-emitting industry, direct uptake by plant foliage of airborne F would mask any accumulation from the soil. In areas having high concentrations of F in the soil but low concentrations of airborne F, soilborne F may be a major source of F to plants.

Because the total F concentration in soils varies greatly from area to area, it is considered a poor indicator of either soil F contamination or soil F available to plants (Flühler *et al.*, 1982). Soluble soil F has been correlated with accumulation in plants on sodic soils, but the relationship is not as clear in acid soils (Davison, 1984). Labile soil F (i.e., that fraction extracted with an anion exchange resin) has been suggested as a better estimate of soil F that is available to plants (Larsen and Widdowson, 1971; Davison, 1984), but the method has not been tested in a wide range of soils.

High concentrations of F in soil can increase concentrations of organic matter and metals, including Al, in leachates (Polomski *et al.*, 1982) and also increase Al accumulation and toxicity in plants (Hani, 1978), as well as a possible source of F to plants. Increases in Al were greater from acid soils than from calcareous soils and were attributed to breakdown and removal of Al- and Fe-hydroxides and organometallic compounds (Hani, 1978).

Much of the information on F uptake from soils by plants is based upon the result of controlled additions of NaF to the soil (Davison, 1984). Only a few studies in the vicinity of F-emitting industries have examined uptake of F from contaminated soils in the absence of any airborne contribution (Sidhu, 1976). Therefore, the uptake of soilborne F and Al by plants was studied using soils collected from three locations downwind from an Al smelter. Red maple (*Acer rubrum* L.) and orchard grass (*Dactylis glomerata* L.) were grown in the different soils and analyzed for the two elements. The objectives were to:

(1) determine the relationship of the concentration of F and Al in soil with distance from the smelter,
(2) determine availability of soluble or labile F and soluble Al to plants, and
(3) compare the relationship of labile and soluble F in soil to foliar F.

2. Materials and Methods

Three locations, approximately 1.2, 6.5, and 16.1 km from an Al smelter (hereafter referred to as locations A, B, and C, respectively) were selected (Figure 1). The area is in the unglaciated portion of the Alleghany Plateau in Ohio. The locations had similar soil characteristics and vegetation cover of secondary growth hardwoods.

Soils at all three locations were classified as the Gilpin–Upshur association (Kunkle *et al.*, 1957; Hayhurst *et al.*, 1974). The Gilpin soil type is classified as a fine, loamy mixed mesic typic Hapludalt and the Upshur soil type is described as a fine, mesic typic Hapludalt (Soil Survey Staff, 1975).

At each of the three locations, five sample sites were selected. The sites were approximately 3 × 6 m and were within a 0.25 ha area. Because F from anthropogenic sources would probably accumulate in the upper horizons (McClenahen and Weidensaul, 1977), the A horizon and the litter layer only were collected. To eliminate possible masking effects of airborne HF, soils collected from the three locations above were transported to Ithaca, New York. Soil from each sample site was homogenized separately using a cement mixer. Samples taken for analysis were kept moist, sieved to <4 mm, placed in plastic bags, and stored under refrigeration (4 °C).

Seedlings (8 to 12 inches tall) of red maple were transplanted and seeds of orchard grass were sown in pots containing the different soils, with four replications of each sample site/species combination. Red maple was chosen because it is common in the area around the smelter and orchard grass because it is a common forage grass. Litter collected from each site was replaced on the soil surface of each pot. The plants were

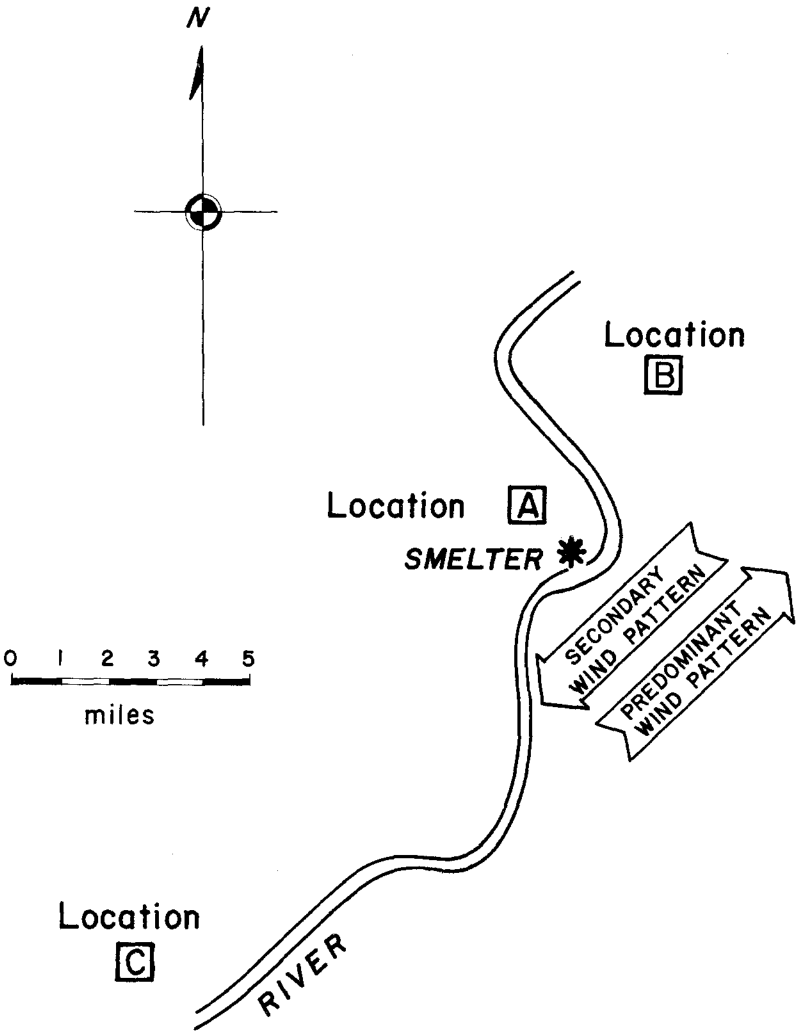

Fig. 1. Diagram of sample area.

maintained in the field for approximately 3 mo. The foliage was then harvested, washed to remove superficial materials (McCune *et al.*, 1965), dried for 24 h at 80 °C, and milled to pass a 40-mesh screen.

Foliar F was determined in duplicate samples using the AOAC (1975) First Action acid-base extraction procedure. Foliar Al was assayed by neutron activation analysis. Approximately 50 mg dried and milled sample was placed in a polyvial. The vials were irradiated in the TRIGA nuclear reactor at Cornell University for 1 min at a flux of 5.0×10^{11} neutrons cm^{-2} s^{-1}. Gamma ray activities were measured using an EG&G Ortec High Purity Germanium (HPGe) solid state detector, and were analyzed using the Nuclear Data Inc. ND-66 gamma-spectrometer (4096 channels). The detector has a relative efficiency of 24.2%. The absolute efficiency for the distance and peak used (1778.9 keV) is 0.1%. Full width at half maximum resolution is 1.70 keV. Peaks at the area of interest were integrated by the automatic analyzer.

To determine soluble F, 15 g soil in 25 ml 0.01 M $CaCl_2$ were shaken overnight. The mixture was decanted and centrifuged. The supernatant liquid was filtered through a 0.45 μm micropore filter and the extract mixed 1 : 1 with Orion TISAB II. Fluoride in three replicate soil samples from each site was measured using a F-specific electrode. Labile or resin-extractable F was determined in triplicate samples of soil using a method described by Larsen and Widdowson (1971). Fluoride was extracted from the soil using Dowex 1-X8 (Cl^-), 20 to 50 mesh. Total soluble (0.01M $CaCl_2$ extractable) Al was assayed in triplicate using a modification of the 8-hydroxyquinoline and butyl acetate extraction method (Bloom *et al.*, 1978). A digestion procedure was used first to eliminate F, Mn, and Fe interferences (James *et al.*, 1983). Soil pH was measured in 0.01M $CaCl_2$ (1 : 2 dilution).

The statistical analysis for concentrations of F and Al in soils was treated as a nested design with levels of location, site within location, and determination within site. The latter two effects were considered to be random, permitting the mean square value for site within location to be used to test location differences.

Covariate analysis was performed to determine whether increases in the concentrations of F and Al in foliage were due solely to differences in F and Al in soils, or whether there were additional differences due to location. Means for location were compared after variation attributed to soil F or Al in soils (the covariate) was omitted. After fitting the covariate, there were still significant differences among the location means, suggesting that there are factors other than soil F and Al contributing to foliar F and Al.

A nested analysis for concentrations of F and Al in foliage was used with levels of location, site within location, plant within site, and determination within plant. Because site, plant within site, and determination within plant were random effects, the mean square value for site within location was used as an error term to test location differences. Orthogonal contrasts and the Newman-Keuls multiple range test were used at the $\alpha = 0.05$ level of significance to further test differences in the means.

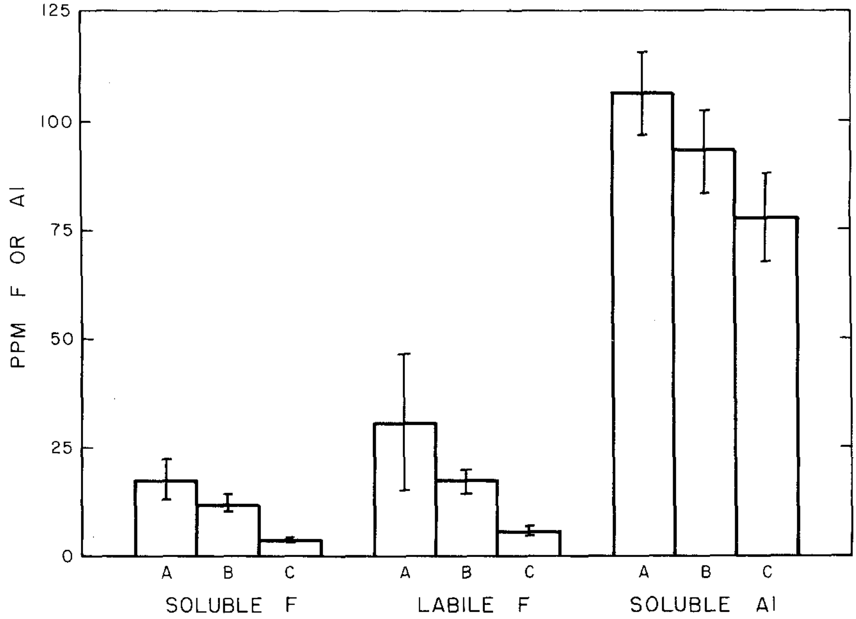

Fig. 2. Soluble and labile F and soluble Al concentrations in soils. Letters are location designations (see text). Bars are 95% confidence intervals for the means.

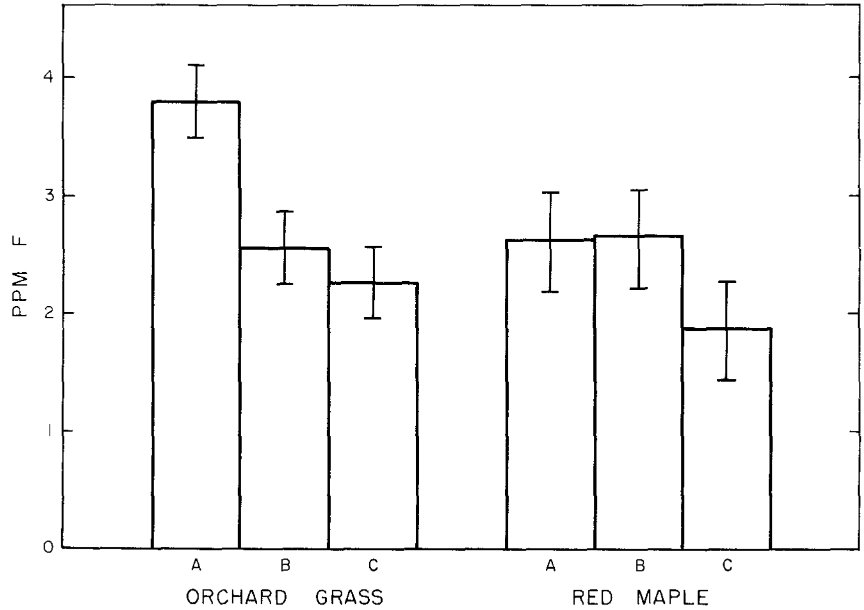

Fig. 3. Fluoride in red maple and orchard grass foliage grown in soils from different distances from a source. Letters are location designations (see text). Bars are 95% confidence intervals for the means.

3. Results

There were significant decreases in the concentrations of soluble and labile F, and of total soluble Al in soils with increasing distance from the smelter (Figure 2). Between locations B and C, there were significant reductions in all three measures, whereas between locations A and B, only the concentrations of soluble F were reduced.

Differences in soil pH between the different locations were tested to estimate a variable that would not have been expected to change as a result of smelter emissions and thus support the assumption that soils taken from the three locations had similar characteristics. The pH values ranged from 3.6 to 4.8, with a mean of 3.9, and did not vary significantly between the three locations.

In all three soils, the concentration of labile F was significantly higher than that of soluble F. The two measures, however, were not highly correlated with each other; the adjusted R-squared value was 0.206.

Concentrations of F in foliage of orchard grass and red maple grown in soils from the three locations tended to decrease with distance from the smelter (Figure 3). For orchard grass, a significant reduction occurred between locations A and B, but there was no further reduction for plants grown in soils from location C. In maple foliage the concentration of F were significantly reduced for seedlings grown in soil from locations C relative to those grown in soils from locations A and B which were not different from each other.

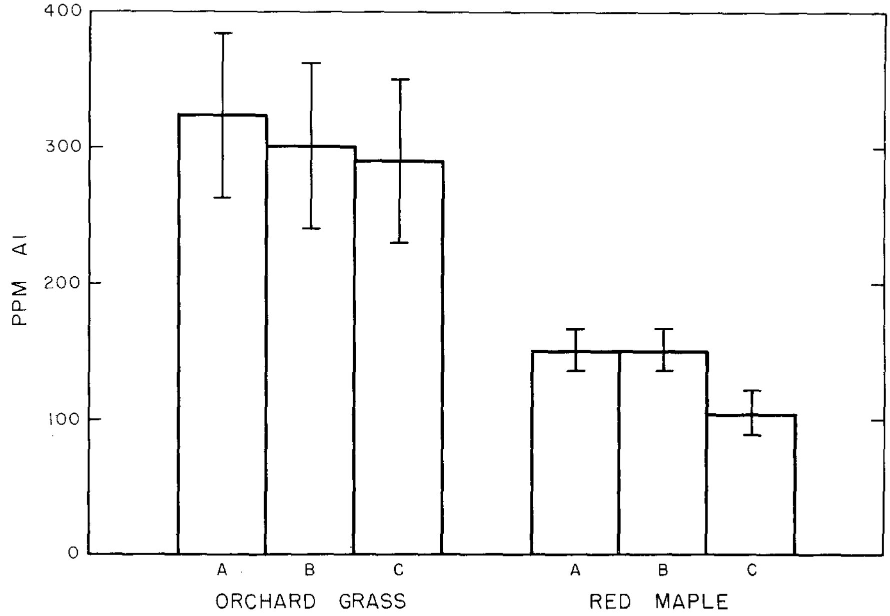

Fig. 4. Aluminum concentration in orchard grass and red maple foliage grown in soils from different distances from a source. Letters are location designations (see text). Bars are 95% confidence intervals for the means.

Foliar Al decreased in maples grown in soil from location C as compared with locations closer to the smelter (Figure 4). Neither foliar F nor foliar Al were significantly different when comparing maples grown in soils from locations A and B. As a result of high variation, differences in mean values for Al in orchard grass at the three locations were not significant.

Linear, first-degree regressions (Foliar F = $a_1 \times$ soil F + a_0) using either soluble or labile soil F as the independent variable were used to compare the validity of the two kinds of measures for soil F to predict foliar F. Although the correlations were low, soluble F was a better predictor of foliar F values than was labile F (with R-squared values of 0.302 and 0.124 for soluble and labile F in red maple, and 0.540 and 0.252 for soluble and labile F in orchard grass).

4. Discussion

Increases in the level of F in soil nearest the smelter probably resulted from deposition of F-containing particulate matter and from plant litter. The increase in soluble Al may have resulted from the accumulation of Al-containing particulate matter, or, perhaps, as a result of solubilization of Al by increased levels of F.

Several different effects on the ecosystem could result from increased levels of F and Al. Litter has been shown to accumulate near aluminum smelters, implying that there is an adverse effect of smelter emissions on decomposing microorganisms (Rao and Pal, 1978). Seed germination of sensitive species of plants can be reduced after imbibing F as NaF at levels as low as 20 to 25 ppm (Navara *et al.*, 1966; Soni and Mohnot, 1979). Although F in soils is surely not present solely as NaF, soluble concentrations of up to 23 ppm were found at sampling sites close to the smelter. Although no specific measures of germination were made, there were no apparent differences in germination of orchard grass in the three soils used in these investigations. Aluminum in the soil solution can inhibit growth of sensitive plants at levels as low as 1 ppm (Foy, 1974) and there is evidence that high concentrations of soil Al may be important in determining plant succession in noncultivated areas (Clarkson, 1966).

All of the F analyses of maple and orchard grass tissues gave relatively low values, including samples from plants grown in soils collected nearest the smelter. Our results, which ranged from ca. 1.5 to 4.1 ppm F are withing the range considered to be background (up to 20 ppm, but generally below 10 ppm) (Weinstein, 1977). Our conclusion, that the soil is not an important source of toxic levels of F to most plants, and therefore to herbivores, supports the observations of others. In the vicinity of a closed P fertilizer plant where high concentrations of both foliar F and airborne HF had occurred for many years, Sidhu (1976) found low concentrations of F in foliage and concluded that there was little uptake of F by plants from soil. In the vicinity of a closed Al smelter in the Ohio Valley, low concentrations of F were found in conifer needles that emerged during the growing season after the smelter closed (Braen and MacLean, 1983).

The increase in Al in maple foliage would not indicate the presence or degree of

Al-induced injury, since toxicity to plants occurs primarily in the roots (Foy *et al.*, 1978). However, the increase does imply that there was more Al transported to the maple leaves when grown in soils closer to the smelter than in those more remote.

Although the chemical nature of the labile fraction of F in soil is not known, it provides an estimate of F on the soil matrix in addition to that in the soil solution (Larsen and Widdowson, 1971). It was not surprising, then, to find that soil labile F values were significantly greater than soil soluble F at all sites. Because availability and subsequent accumulation of F by plants depends on the amounts of F in solution that can be replaced by F associated with the soil matrix, it has been reported that labile F may be a better estimate of the F fraction available to plant roots (Davison, 1984). In this study, however, the reverse was true: the concentrations of soluble F in soils were more correlated with foliar F values than were the concentrations of labile F. Further work is needed to characterize the chemical nature of both fractions in the soil and how they relate to the absorption of F by plant roots.

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