

## Analysis of Fluoride in Vegetation in the Vicinity of Wabash Smelting, Wabash, Indiana

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### *Abstract*

Wabash Smelting Corp., Wabash, Indiana, processes scrap and used aluminum for reuse. In a number of court actions Wabash Smelting has been accused of contaminating vegetation and gaseous fluorides emitted from their plant. Analyses run in 1969 showed high fluoride levels in both annuals and perennials near the plant. Our study was designed to test for current levels of fluoride in selected vegetation within a two mile radius of the plant. Analyses were carried out using ashing techniques and determination of fluoride was done using a fluoride ion electrode. Results of the analyses are given and conclusions are drawn.

### Introduction

Wabash Smelting Corp., Wabash, Indiana, is a secondary aluminum processor for the reclamation of aluminum from scrap. During this process, fluxing agents are added to scavenge impurities from the aluminum and remove dissolved gases. Also added are agents for reduction of magnesium (demagging agents) in the molten aluminum.  $\text{AlF}_3$  is a common fluxing and demagging agent. The chemical reactions leading to purification of the aluminum also lead to the formation of solids such as  $\text{MgF}_2$  and of gaseous products such as HF. Precipitators and scrubbers are used to remove the solids and gases. However, the possibility for environmental damage from poorly operating safeguards exists.

Wabash Smelting has been involved in a number of court actions dealing with exhausts from the plant. Fluoride analysis of vegetation collected around the plant were reported in late 1969 by J.E. Newman, Assoc. Prof. of Agronomy at Purdue University in a memorandum to the State Board of Health. All the samples tested showed fluoride levels ranging from 20-104 ppm. Of particular interest were high levels in sweet clover and alfalfa since these would reflect recent fluoride intake.

### Sampling Sites

To see if there was evidence of recent fluoride contamination, it was decided to sample plants within a two-mile radius of Wabash Smelting at half-mile intervals as shown on the map in Figure 1. Plants chosen were plantain (*Plantago major*), red clover, and annual grasses. Not all three were found at every site. Since much of the land around Wabash Smelting is crop land, sampling sites had to be somewhat scattered, especially to the southwest. To the north, a new highway was being constructed and samples were not taken near the new road as considerable dust was raised by the construction. It was thought that this might produce spurious results. Samples were taken from public access sites or permission was obtained from farm residents to take samples from their property. If samples were taken near roads, care was taken to find samples protected from the effects of passing traffic, although this would be an uncontrollable variable.

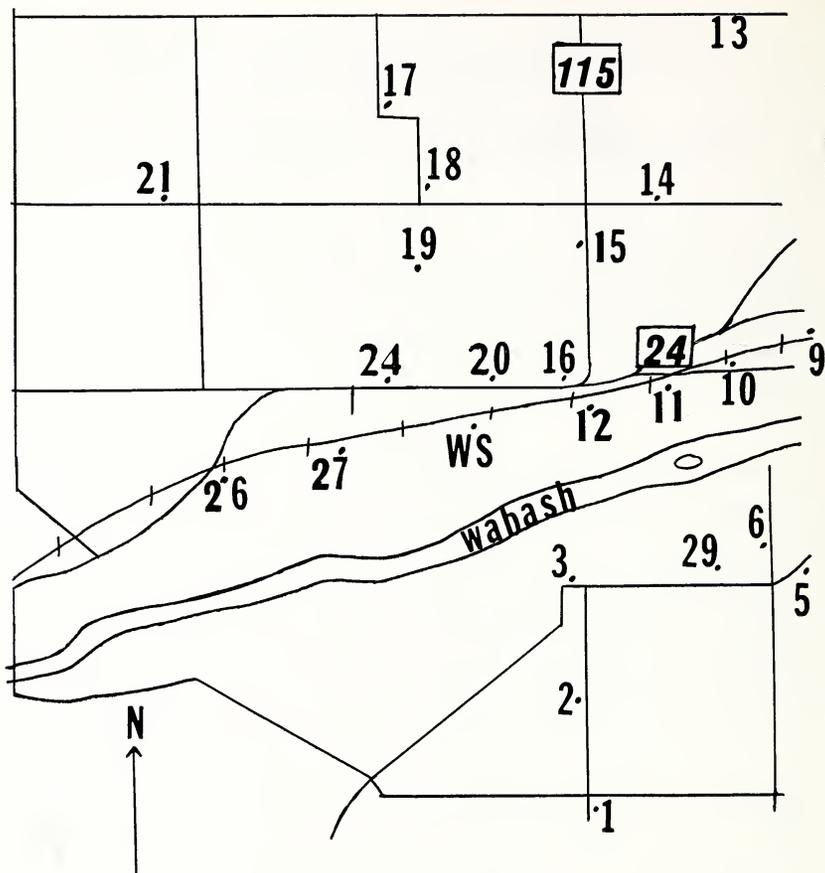


FIGURE 1. Collection sites surrounding Wabash Smelting (WS).

Only the leaves of the samples were tested. No attempt was made to wash off surface contamination so the results reflect both fluoride included in and on the plant tissue. It had rained lightly three days prior to sampling and the spring and summer weather prior to the time of sampling had not been unusually dry or wet. It was thought that wind patterns would be the most significant factor in determining fluoride concentrations although drainage patterns would probably also play a role.

#### Fluoride Analysis

The analysis used was a modification of procedures reported in references (1) and (2).

Vegetation was refrigerated as soon as possible. Samples were cut up and dried at 110°C for 24 hours. One gram samples were weighed into Pt crucibles and fused with base over a Fisher burner. The

charred material was then placed in a muffle furnace at 520°C for 45 minutes. The crucibles were removed from the oven and the residue was dissolved in 8.5M acetic acid to produce a solution of pH 5.5-6.5. An appropriate amount of ionic strength adjustment buffer (Hach 2589-01) was added and the fluoride level was determined using an Orion fluoride electrode.

No standard samples for fluoride analyses in vegetation were available at either NBS or EPA. Our method of testing the procedures was to add a known amount of fluoride to vegetation of supposedly low fluoride content and perform the analysis. Over 90% of the added fluoride was found in the final analyses. Duplicate analyses run on samples from the same plant indicated that our analyses were at least accurate to  $\pm 25\%$  for the lowest level fluoride and  $\pm 15\%$  for the highest level.

**Results**

The results of the analyses are shown in Table I. As can be seen, only four of the readings were above 10 ppm of dry weight and three of the four were in samples of plantain. Clover samples all contained less than 5 ppm which is considerably less than the 90 and 24 ppm reported by Dr. Newman in 1969. Levels reported in Table I more nearly compare with the control sample of Dr. Newman although direct comparison is difficult. Dr. Newman dried samples in the air at 45% relative humidity and 76°F and it is not clear what parts of the plant were used in his samples. The present work used only the leaves dried at 110°C and stored in a dessicator over CaCl<sub>2</sub>. However, given reason-

TABLE I. Results of analyses of the indicated plants—All results are reported in ppm dry weight. --- indicates that no samples of a particular plant were found at that site.

Site Number	Grass	Plantain	Red Clover
1	2.5	---	---
2	4.6	1.6	---
3	8.0	2.1	2.5
5	2.5	2.5	---
6	1.6	1.3	1.8
9	1.6	---	---
10	2.5	1.2	---
11	2.1	2.0	---
12	---	3.0	---
13	2.0	20.5	0.6
14	10.2	1.7	3.1
15	3.5	---	4.2
16	1.8	---	---
17	2.8	14.5	2.5
18	---	1.6	---
19	2.1	2.2	---
20	5.0	3.8	3.2
24	3.5	15.0	---
26	2.8	1.2	---
27	2.2	---	3.9
29	2.5	---	4.6

able errors for both analyses, the 9 ppm reported by Dr. Newman might roughly compare with our results.

It would seem reasonable to conclude that no significant pattern of fluoride levels was found and, with only one exception (plantain site 13), levels of fluoride would have to be considered as typical (3, 4). No evidence of fluoride pollution at ground level caused by emissions from the Wabash Smelting was found.

#### Literature Cited

1. BAKER, R. L., Determination of Fluoride in Vegetation Using the Specific Ion Electrode, *Analytical Chem.* 194:7 1327 (June 1972).
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3. NATIONAL ACADEMY OF SCIENCE, 1971 Fluoride N.A.S., Wash.
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