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Determination, Distribution, and Adsorption of Fluoride in Atmospheric-polluted Soils

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Fluorine is widely regarded as the third most important air-pollutant after SO_2 and O_3 (ROSE & MARRIER 1977). High concentrations of the element occur, as the F^--ion, in soils which are contaminated with pollutants released during the manufacture of aluminium; bricks; glass and steel. Fluoride pollution is of concern because it can damage vegetation and cause fluorosis in cattle and sheep (ROSE & MARRIER 1977).

Despite the importance of F^- as a pollutant, no consensus has yet been arrived at as to what is the best method of extracting the ion from atmospheric-polluted soils, and as a result little is known about the distribution of the element in such soils. Our aim was therefore to evaluate methods used to determine F^- in non-polluted soils and assess their applicability to determine the content and distribution of F^- in soils exposed to air pollution from a variety of sources.

MATERIALS AND METHODS

Soils : Soils were sampled approximately 0.5 km downwind of the following sources of atmospheric pollution: aluminium smelter (Anglesey, N. Wales); glass factory (Barnsley, Yorks, England), and a refractory brickworks (Loxley, Sheffield, England). A relatively unpolluted soil was obtained from Fitzwilliam W. Yorks, England.

F^- analysis : F^- was determined using a Philips F^- specific ion electrode connected to a Philips PW9414 ion activity meter. All extracts were diluted 1:1 with a total ionic strength adjustment buffer (TISAB). The buffer was prepared by dissolving 57 mL acetic acid, 58 g NaCl, 0.3 g sodium citrate, and 1 g of trans-1-2,-Diaminocyclohexane-NNN'N' tetra-acetic acid (CDTA) in 800 mL of water, adjusting the pH of the resulting solution to 5.8 with 50% (w/v) NaOH, and diluting the solution with water to 1 L.

Extractants evaluated

(1) Available (water extractable)F^-. Air-dried soil (16 g), sieved to < 2mm, was shaken in deionized water (50 mL) for 16 h. The suspension was then filtered through Whatman No. 1 filter paper and the filtrate (10 mL) was diluted with TISAB (10 mL), and the F^- concentration determined.

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(2) Soluble ($CaCl_2$-extractable)F^-. The above method was used, except that $CaCl_2$ solution (0.01M, 50 mL) was used instead of water.

(3) Resin-extractable F^-. Resin-extractable fluoride was measured using the method of LARSEN & WIDDOWSON (1971). A strongly basic anion exchange resin (Amberlite IRA-40, 20-50 mesh) was added to the soil slurry (5 mL resin to 1 g soil in 50 mL deionized water) which was then shaken for 16 h in polyethylene bottles. The resin was separated from the slurry by sieving (60 mesh) and washing with deionized water. Exchangeable F^- was then leached from the resin with 0.6 N Na_2SO_4 (50 mL) at a flow-rate of 2.5 mL min^{-1}.

RESULTS AND DISCUSSION

The amount of F^- extracted from Anglesey (aluminium smelter) and Barnsley (glass works) soils using $CaCl_2$ and H_2O respectively, increased with increasing weight of soil to extractant up to 8 g, when the amount extracted began to level off. (Figs. 1, 2). Only small increases in F^--extraction efficiency were achieved by increasing the shaking period (up to 16 h) when water was used to extract the ion from the Barnsley soils (Fig. 1).

Table 1. Efficiency of the extractants (µg F^- g^{-1} soil)[a]

Soil	Extractants		
	Available (H_2O)	Soluble ($CaCl_2$)	Resin-extractable
Al-smelter (Anglesey)	25.6 ± 0.08	10.1 ± 0.13	199 ± 61
Glassworks (Barnsley)	6.2 ± 0.05	3.3 ± 0.09	39.8 ± 9.5
Control (Fitzwilliam)	1.1 ± 0.3	0.8 ± 0.03	8.7 ± 0.1

[a] 16 g soil shaken for 16 h in 50 mL extractant, means of 3 replicates, ± SD

Short extraction times can be safely employed therefore to achieve equilibrium and extract F^- from atmospheric-polluted soils. In the subsequent studies however, we used a 16 h shaking time, with 16 g of soil added to 50 mL of extractant; this length of shaking being chosen for convenience as it could be done overnight. Similar findings to these were reported by LARSEN & WIDDOWSON (1971) for maximum extraction of F^- from non-polluted agricultural soils.

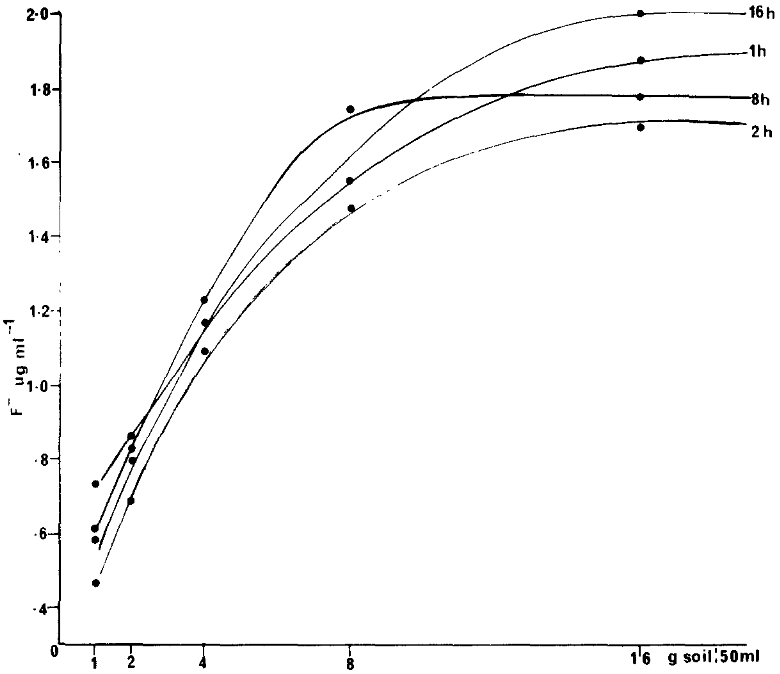

Fig. 1. Effect of shaking period and soil extractant ratio on F^- extraction by water from glassworks-polluted (Barnsley) soils.

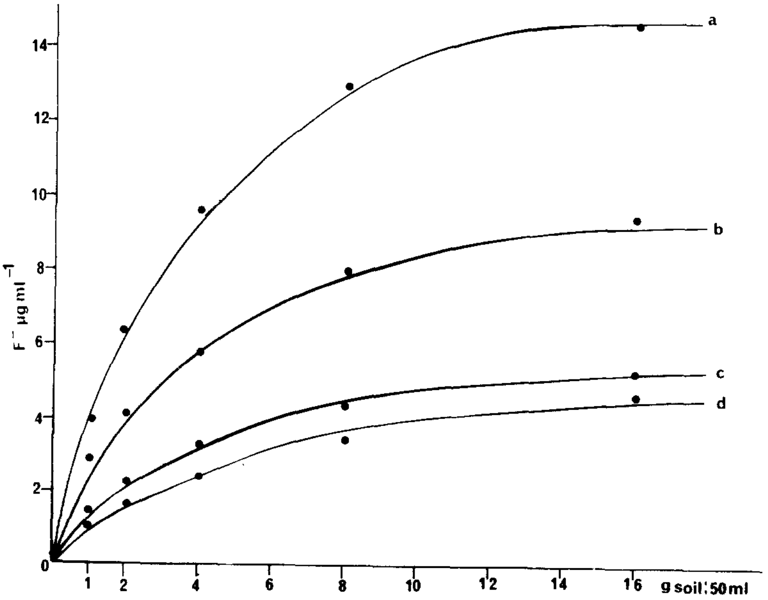

Fig. 2. Effect of soil:extractant ratio on F^- extraction by $CaCl_2$ solution (0.01M) from four aluminium smelter-polluted soils (Anglesey).

Table 2. Distribution of F^- ($\mu g\ F^-\ g^{-1}$ soil) in soils exposed to refractory brick pollution (Loxley)[a]

Distance from effluent source (m)	Available (H_2O)	Soluble ($CaCl_2$)	Resin-extractable
100	1.5 ± 0.01	6.5 ± 0.1	20.0 ± 1.6
250	1.3 ± 0.01	5.6 ± 0.07	24.3 ± 0.4
500	1.3 ± 0.4	1.4 ± 0.07	33.0 ± 2.1
750	3.7 ± 0.1	10.0 ± 0.03	67.5 ± 7.0
1000	1.0 ± 0.03	3.0 ± 0.07	8.1 ± 2.3

[a] 16 g soil shaken for 16 h in 50 mL extractant. Means of 3 replicates, ± SD.

Distribution of F^- in atmospheric polluted soils

The amount of total fluoride in soils has frequently been reported, but since 90% of this is bound, such figures tell us little about the amount of biologically-available F^- present. The concentration of F^- in the atmospheric-polluted soils studied, using the three extractants, is shown in Tables 1 and 2. Highest F^- concentrations were found in soils sampled adjacent to an aluminium smelter (Anglesey), followed by the glass (Barnsley) and refractory brick (Loxley) factories. All F^- values are clearly in excess of those reported for unpolluted soils. LARSEN & WIDDOWSON (1971) for example, showed that of the 100 United Kingdom soil samples tested, most were in the range 0-0.2 $\mu g\ mL^{-1}$ F^- (0.01M $CaCl_2$ extractable), while in only two of these 100 samples did the F^- concentration exceed 1 $\mu g\ ml^{-1}$; resin extractable values averaged 26 $\mu g\ mL^{-1}$. Similar results were obtained for non-polluted, agricultural soils in Pennsylvania, U.S.A. (GILPIN & JOHNSON (1980) (0.05 - 1.5 $\mu g\ F^-\ mL^{-1}$ $CaCl_2$-extractable, and a mean of 21.7 $\mu g\ F^-\ mL^{-1}$ for resin extractable). Values for water soluble F^- in soils exposed to pollution from a Canadian phosphorus works were, not surprisingly, found to be higher at 3.8 - 5.8 $\mu g\ F^-\ mL^{-1}$, compared with 2.4 $\mu g\ F^-\ mL^{-1}$ for unpolluted controls (THOMPSON et al. 1979).

The order of efficiency of extraction for the aluminium smelter and glass factory polluted soils was, resin extractable > water extractable > $CaCl_2$ extractable (Table 1), while $CaCl_2$ was generally more efficient than water at extracting F^- from soils exposed to brickwork effluents (Loxley) (Table 2).

Resin and $CaCl_2$ extractable F^- was high in soils sampled within 750 and 250 m of the refractory brickworks (Table 2), but fell off dramatically with distance from the source; the concentration of water soluble F^- on the other hand remained relatively constant (Table 2).

Table 3. F^- adsorption by soil (Loxley, refractory brickworks)

Distance from effluent source (m)	Total soil Carbon (% w/w)	Soil pH	F^- adsorbed $\mu g\ mL^{-1}$
100	3.0 ± 0.1		8.5 ± 0.08
250	4.1 ± 0.3		8.8 ± 0.05
500	3.0 ± 0.06		9.0 ± 0.05
750	3.6 ± 0.4		8.5 ± 0.15
1000	7.8 ± 1.0		8.4 ± 0.37

a 16 g soil shaken with 50 ml of F^- solution containing 10 $\mu g\ mL^{-1}$ F^- as NaF. Means of 3 replicates, ± SD.

BREWER (1966) concluded that water extractable F^- was of primary interest because this is the sole source of the element which is available to plants. LARSEN & WIDDOWSON (1971) however, point out that F^-, like phosphate, is largely adsorbed by soils, and that the amount of the ion which is taken up by plants will not be controlled by the concentration of water soluble F^- alone. The adsorption of F^- to soil is illustrated by data shown in Table 3. Soil (16 g) (Brickworks, Loxley) was shaken with 50 mL of a 10 $\mu g\ F^-\ mL^{-1}$ solution (NaF) for 2 h, then filtered and the concentration of F^- in solution determined. Only a little more than 10% of the added F^- was generally recovered in the filtrate.

The results presented here show that techniques used to determine the F^- content of unpolluted soils (LARSEN & WIDDOWSON 1971) are applicable to soils exposed to atmospheric pollution which contain much higher concentrations of F^- than non-polluted soils. Because of adsorption of the F^- onto soil however, much of the ion will be unavailable to inhibit plants and microorganisms, but may subsequently become available. Recent work in this laboratory shows that both microorganisms and acid rain have the ability to liberate F^- from water insoluble particulates, which are often a major form of fluoride released into the atmosphere from industrial sources, thereby increasing the availability of this potentially toxic ion in polluted soils.

REFERENCES

BREWER, R. F. : In Diagnostic Criteria for Plants and Soils. H. S. Chapman Ed. Univ. California Press (1966).

GILPIN, L. and A. H. JOHNSON : Soil Sci. Soc. Amer. J. 44, 25 (1980).

LARSEN, S. and A. E. WIDDOWSON : J. Soil Sci. 22, 210 (1971).

ROSE, D. amd J. R. MARRIER : Environmental Fluoride, Natural Res. Council, Canada, Rep. 16081 (1977).

THOMPSON, L. K., S. S. SIDHU and B. A. ROBERTS : Environ. Pollut. 18, 221 (1979).