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EFFECTS OF FLUORINE DEPOSITION ON THE CHEMISTRY OF ACID LUVISOLS

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The deposition of airborne fluorine by an aluminum smelter in Upper Austria (Central Europe) during 50 years caused a storage of fluorine in the soils up to 170 g m^{-2} , corresponding to an annual deposition up to 3.7 g m^{-2} . The proportion of 1:50 water extractable fluorine increased with total fluorine and ranges from 25% to 37% of the total deposition, indicating an increasing risk of groundwater pollution through further fluorine input. The deposited fluorine increased the solubility of exchangeable and ammonium oxalate soluble aluminum. This is explained by ligand exchange of OH^- -groups at the surface of amorphous Al-oxides with consequent dissolution of Al. Subsequently, aluminum was leached and the contents of exchangeable and oxidic aluminum in the topsoils decreased. The released OH^- neutralized protons (H^+) dissociating from organic matter, causing a significant decrease of the base neutralization capacity, and raising the pH of the soils.

KEY WORDS: Fluorine, aluminum chemistry, pH, base neutralization capacity, acid Luvisols, soil contamination.

INTRODUCTION

Soil contamination near industrial plants is a serious problem for soil conservation.¹ Several authors have reported on soil pollution with fluorine,^{2,3} and on interactions of fluorine and aluminum in soils.^{4–7} Results from laboratory studies showed that fluorine releases aluminum from crystal surfaces through complexation after replacement of OH^- by ligand exchange.^{7,8} Treatment of soil columns with fluorine solutions induced a significant loss of Al, Fe, and C.⁹ On the other hand, an increase of exchangeable aluminum was found in calcaric Regosols, caused by fluorine deposition.⁹

An increase of the base neutralization capacity (BNC) of silicates and oxides treated with neutral fluorine solutions was detected by Huang and Jackson.⁷ They concluded that fluorine increased the number of weak functional acid groups through dissolution of mineral surfaces. Polomski *et al.* found a decrease of pH in calcaric Regosols ($\text{pH} > 7$) by increasing fluorine contamination of the soil.⁹ Conversely, fluorine treatment raised the pH of acid soils through release of OH^- .^{10–12}

As most of these results, in part contradictory, were gained from short term laboratory studies, we analysed long term effects of fluorine deposition in acid Luvisols near an aluminum smelter with special regard to changes in soil acidity, base neutralization capacity and aluminum chemistry.

MATERIALS AND METHODS

Study area and soils

The aluminum smelter is located near Ranshofen (Innviertel, Upper Austria) on the Wuermian terrace of the Inn river. The deposition area is covered by forests. The soils are Chromic and Orthic Luvisols.¹³ The mean values for some physical and chemical soil characteristics in six profiles are shown in Table 1.

Soil material was sampled according to Arbeitsgemeinschaft Bodenkunde.¹⁴ For the calculation of profile balances for fluorine soil samples were taken at eight depth intervals as shown in Table 1. For the study of fluorine-induced changes in soil chemistry we sampled topsoils (0–5 cm, corresponding to Ah-horizons) at distances of 25 m along a transect with a length of 1250 m in the main wind direction (ENE of the aluminum smelter). Some characteristics of these samples are given in Table 2. The soil texture for each of the forty samples was silt loam.¹³

Aluminum Smelter

The electrolysis plant of the aluminum smelter has been in operation since 1939 with an annual capacity (1982) of about 80 000 t raw aluminum. It emits annually about 170 t fluorine (1982), mainly in form of gaseous HF (about 80%) and aerosols of cryolite (Na_3AlF_6), NaF, AlF_3 or similar compounds. Annual fluorine input in the vicinity of the smelter is higher than 2 g m^{-2} , natural input in this area is reported to be lower than $0.035 \text{ g m}^{-2} \text{ y}^{-1}$.¹⁵

Table 1 Characteristics of six Luvisols under forest (mean values = \bar{x} , standard deviations = s)

Depth (cm)		Clay %	pH(H_2O)	OC ^a %	CEC ^b meq, kg^{-1}	Fed ^c %	Al ^d %
5–0	\bar{x}	—	4.60	27.2	11.0	—	—
	s	—	0.34	8.1	2.8	—	—
0–5	\bar{x}	17.6	4.23	9.5	7.7	0.85	0.26
	s	2.8	0.17	7.1	2.6	0.10	0.07
5–10	\bar{x}	19.3	4.49	2.4	5.0	0.84	0.32
	s	2.5	0.39	1.1	2.2	0.14	0.05
10–20	\bar{x}	18.7	4.56	1.1	3.3	0.77	0.28
	s	1.6	0.34	0.1	0.7	0.11	0.05
20–40	\bar{x}	21.2	4.50	0.6	3.4	0.89	0.25
	s	2.3	0.35	0.1	0.7	0.08	0.04
40–70	\bar{x}	25.1	4.48	0.29	5.9	1.28	0.24
	s	5.4	0.22	0.14	1.3	0.27	0.05
70–100	\bar{x}	15.0	6.01	0.11	6.9	1.10	0.13
	s	3.5	1.32	0.06	2.1	0.19	0.03
100–130	\bar{x}	8.4	7.25	0.09	5.4	0.67	0.05
	s	0.4	0.71	0.01	0.8	0.30	0.02

^a Organic carbon.

^b Cation exchange capacity.

^c Dithionite—citrate—bicarbonate soluble iron.

^d Oxalate soluble aluminum.

Table 2 Selected properties of the topsoils (0–5 cm) used for the study of fluorine effects on soil chemistry

Sample number	pH(H ₂ O)	OC ^a %	ECEC ^b meq kg ⁻¹
702	4.72	5.26	111
703	4.63	4.22	116
704	4.77	5.59	93
705	4.43	17.14	145
706	4.32	10.57	155
707	4.29	9.85	138
708	4.47	10.71	169
709	4.24	8.26	132
710	5.10	4.75	204
711	4.28	4.17	99
712	4.52	3.68	99
713	5.14	4.36	119
714	4.26	5.15	120
715	3.89	10.35	150
716	4.16	5.12	121
717	4.05	8.91	140
718	4.04	6.93	143
719	4.04	8.22	139
720	4.57	3.58	103
721	4.12	7.16	130
722	3.74	17.94	186
723	3.99	7.19	121
724	4.25	6.03	111
725	3.82	7.43	150
726	4.00	9.18	135
728	4.27	6.65	118
729	5.07	7.12	127
730	3.85	6.48	124
731	3.93	3.77	118
732	4.30	5.45	81
733	4.33	9.90	112
734	4.05	9.75	137
735	3.78	9.86	145
736	3.94	6.37	152
737	4.06	12.93	107
738	4.17	8.51	130
739	4.13	8.94	121
740	4.09	8.47	159
741	4.15	8.56	166
742	4.02	6.33	162

^a OC = Organic carbon.^b ECEC = Effective cation exchange capacity.*Analytical procedures*

Soil analyses were carried out on air dried soil samples. All data are based on oven dry (105°C) matter.

Bulk density was determined on 200 cm³ cores, particle size distribution with combined sieve and pipette method (skeleton > 2 mm, sand 2000 µm–63 µm, silt 63 µm–2 µm, clay < 2 µm).

Total organic carbon (OC) was determined by dry combustion and IR-detection of CO_2 ,¹⁶ total iron oxides (Fe_d) by dissolution in dithionite–citrate–bicarbonate,¹⁷ amorphous aluminum oxides (Al_o) by dissolution in ammonium oxalate,¹⁸ exchangeable cations (Ca, Mg, K, Na, Al, Fe, Mn) and ECEC by extraction with 0.1 M BaCl_2 -solution (soil:solution ratio 1:20) after 2 hours extraction, base neutralization capacity (BNC) by discontinuous titration with $\text{Ca}(\text{OH})_2$ and measurement of pH, pH in distilled water (1:2.5) after 24 hours with ORION glass electrode.¹⁶ Soluble fluorine was determined by extraction with water 1:5 during 2 hours¹⁶ and water 1:50 during 16 hours.²

Fluorine determination was carried out using a combination fluoride electrode ORION 96-09 and TISAB II; all other elements were measured by plasma emission (DCP) or atomic absorption (AAS).

Calculation of profile balances

Because of the vertical variability (loess cover above fluvial gravelly sediments), profile balances of fluorine and heavy metals could not be based on the contents of C-horizons as reference. Therefore we calculated horizontal balances for each depth and summed them up to profile balances.

Statistical procedures

Linear regression and correlation analyses was carried out following McPherson.¹⁹

RESULTS AND DISCUSSION

Accumulation of fluorine

The accumulation of total and 1:50 water extractable fluorine in acid Luvisols to a depth of 70 cm at distances of 100, 150, 350 and 6200 m from the aluminum smelter is shown in Figure 1.

The soil without significant contamination at a distance of 6200 m from the smelter was chosen as reference. In the most highly contaminated soil about 170 g m^{-2} within 70 cm depth were stored over a period of 50 years, corresponding to an average annual deposition of about 3.7 g m^{-2} . This compares well with fluorine deposition data measured in 1982.¹⁵ Therefore, nearly all deposited fluorine must have been stored in the soil.

Water extractable fluorine (1:50) shows the same distribution as total fluorine (Figure 1). About two thirds of the deposited fluorine is not extractable by water and must be firmly bound in the soil, although fluorine mobility in these acid soils is relatively high.²⁰ The high proportion of water-extractable fluorine in polluted soils (up to 37%) compared to unpolluted ones (about 25%) indicates that mobility of fluorine increases with increasing deposition.

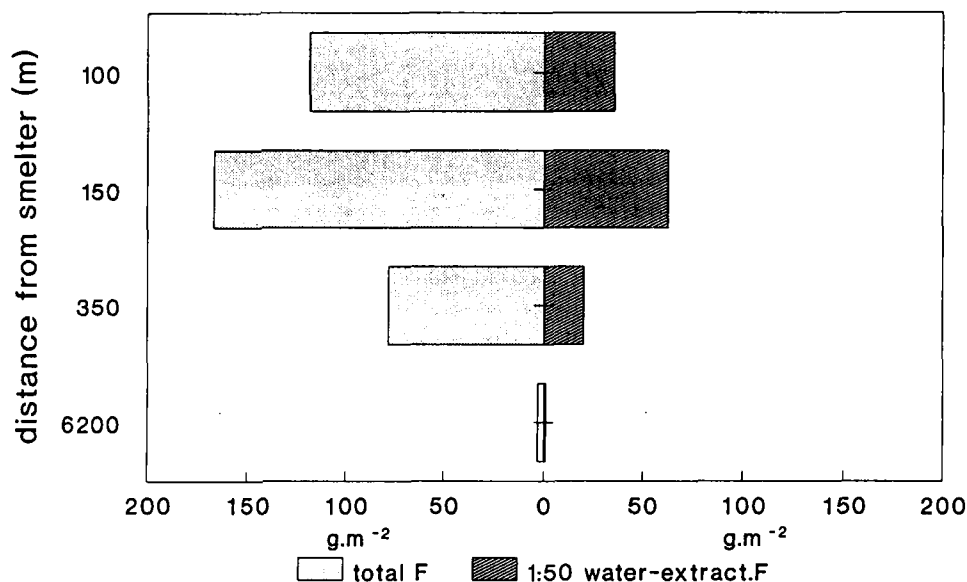


Figure 1 Storage of total and 1:50 water extractable fluorine (in g m^{-2} within 70 cm of depth) in Luvisols under forest at four different distances from the smelter.

Effects of fluorine on aluminum chemistry

The effect of fluorine deposition on aluminum chemistry was studied on different contaminated topsoil samples (Ah-horizons, 0–5 cm). Aluminum and fluorine soluble in water 1:5 were significantly correlated ($r = 0.930^{***}$, Figure 2), due to strong complexation of aluminum by fluorine.²⁰ Conversely, there exists a negative correlation ($r = -0.464^{**}$) between exchangeable aluminum and water soluble (1:5) fluorine (Figure 3) as well as between NH_4 -oxalate soluble aluminum (Al_0) and water soluble fluorine (Figure 4, $r = -0.520^{**}$).

Based on these results and the cited literature data we explain the effects of fluorine on aluminum chemistry of the acid Luvisols as follows. On the one hand, deposited fluorine complexes exchangeable aluminum, bringing it into soil solution.⁵ On the other hand, fluorine substitutes OH^- at the surface of amorphous aluminum oxides (Al_0) by ligand exchange,^{7,8} subsequently causing a breakdown of tetrahedral Al–O–bonds, due to the high electronegativity of fluorine. In consequence, aluminum in the soil solution increases and is partly leached into deeper horizons. Therefore, in highly contaminated areas exchangeable and oxalate soluble aluminum are significantly lower in the topsoils.

Effect of fluorine on soil pH and base neutralization capacity

Because of the presumed release of OH^- from aluminum oxides, changes in soil pH can be expected.^{7,8,10,12} Indeed, a significant increase in soil $\text{pH}(\text{H}_2\text{O})$ with 1:5 water extractable fluorine ($r = 0.611^{***}$) is shown in Figure 5.

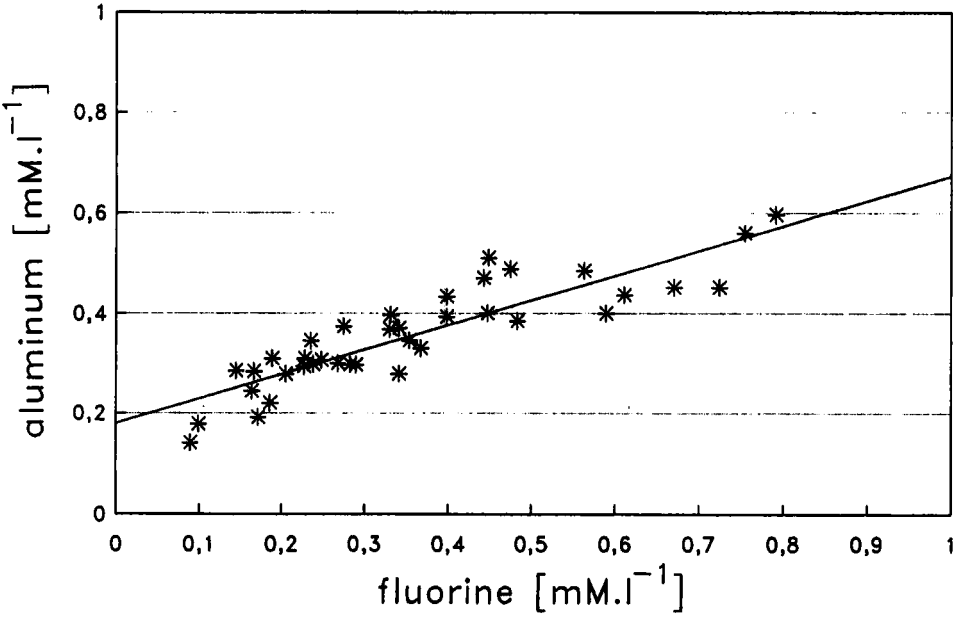


Figure 2 Correlation between 1:5 water soluble aluminum and fluorine in the top horizon (0–5 cm) of acid Luvisols (N = 39, $r = 0.930^{***}$).

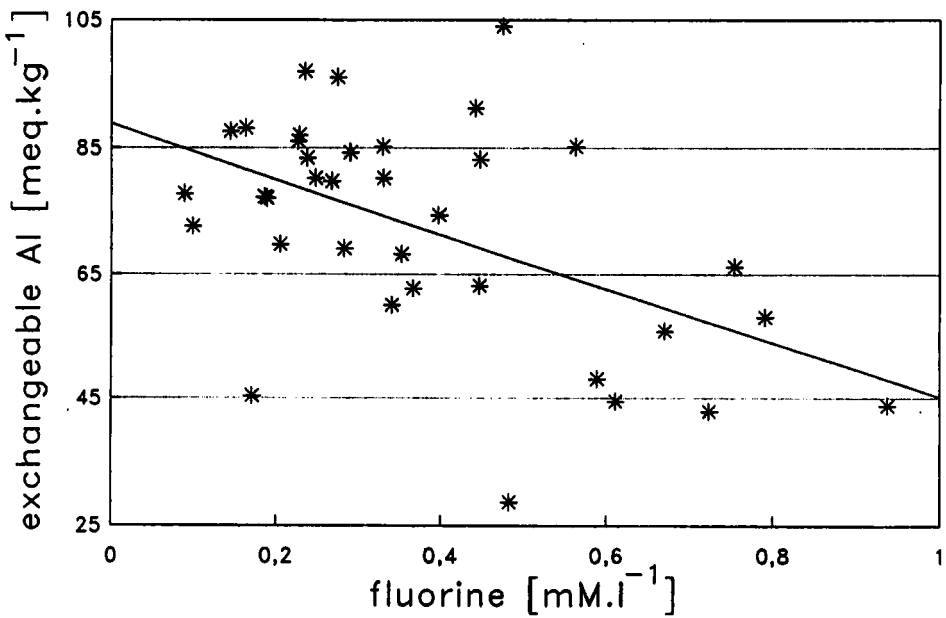


Figure 3 Correlation between exchangeable aluminum and 1:5 water soluble fluorine in the top horizon (0–5 cm) of acid Luvisols (N = 37, $r = -0.464^{**}$).

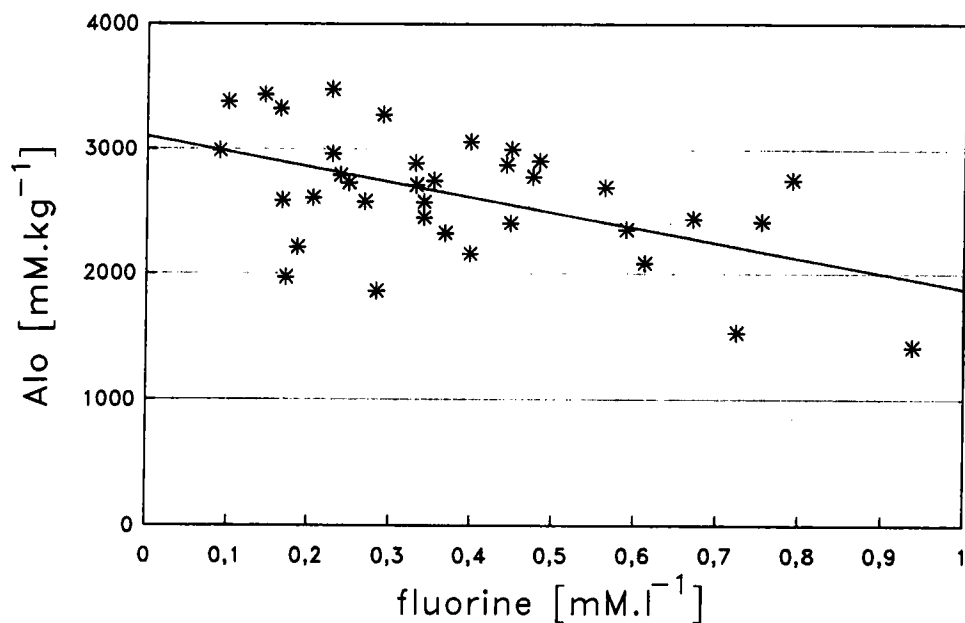


Figure 4 Ammonium oxalate soluble aluminum (Al_0) and 1:50 water soluble fluorine in the top horizon (0–5 cm) of acid Luvisols ($N = 36$, $r = -0.520^{**}$).

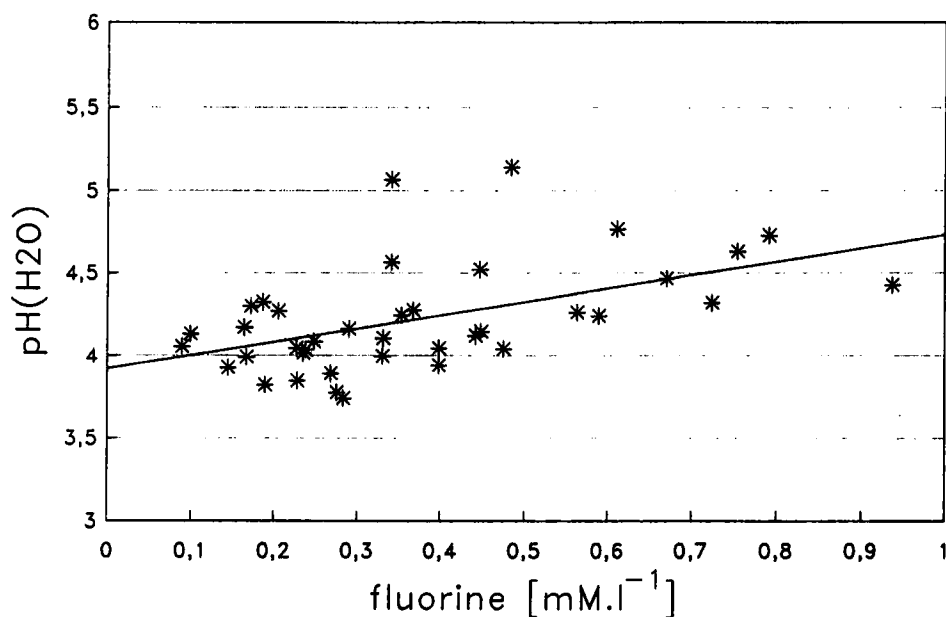


Figure 5 Correlation between soil pH and 1:5 water extractable fluorine in the top horizon (0–5 cm) of acid Luvisols ($N = 40$, $r = 0.611^{***}$).

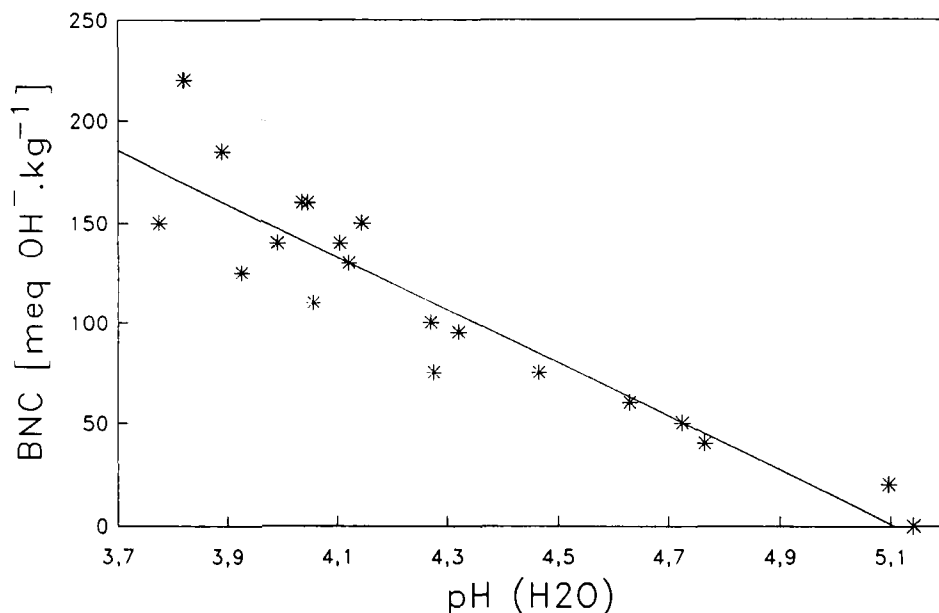


Figure 6 Correlation between soil pH and base neutralization capacity in the top horizon (0–5 cm) of acid Luvisols ($N = 23$, $r = -0.919^{***}$).

Because the soils of this study were contaminated continuously during 50 years, the measured pH values (intensity factor of acidification) should express the OH^- -storage or buffering of airborne H^+ during this time. This is supported by the correlation ($r = 0.919^{***}$) between the pH and the base neutralization capacity (capacity factor of acidification), see Figure 6.

The increase of BNC (up to 180 meq kg^{-1} , Figure 6) is of the same magnitude as the decrease of Al_{ex} (exchangeable Al) and Al_0 (together up to 170 meq kg^{-1} , Figures 3 and 4), indicating the release of 3 OH^- per Al^{3+} . Deposited fluorine, which passed the here considered Ah-horizon (0–5 cm), amounts up to 170 g m^{-2} (Figure 1), corresponding to about 250 meq kg^{-1} . A comparison with the decrease of Al_0 and Al_{ex} indicates that about two thirds of the deposited fluorine reacted with these compounds within the layer 0–5 cm. The increase of BNC can be explained by neutralization of H^+ dissociating from organic matter through released OH^- .

CONCLUSIONS

Our investigations on long term contaminated soils support the hypothesis derived from results of the cited laboratory studies^{7,8,10–12} about the effects of fluorine on the chemistry of acid soil. In calcareous soils the decrease of soil pH and increase of exchangeable aluminum⁹ can be explained by the dissolution of carbonates, and the increase of weak functional acid groups with a pK about 8 at mineral surfaces by exposure to HF.⁷ Conversely, due to the high pK of these groups they cannot exist

in acid soils thus supporting our proposed reaction mechanism for fluorine in acid soils.

The high proportions of water soluble fluorine still found at a distance of 300 m from the aluminum smelter raises the question of whether further deposition could exhaust the buffer capacity of these soils in the long run, endangering ground water quality. Moreover, further dissolution of Al from amorphous oxides could cause a decrease of the cation exchange capacity and the stability of soil structure.²¹

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