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Fluoride's Role in Acid Rain

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Fluoride Action Network | May 2008

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INTRODUCTION

Acid rain has been documente to cause widesprea damage to both fish and vegetation

According to conventior wisdom, acid rain causes adverse environme effects by increasing the acidity of both water and soils, thereby potentiating the toxicity of certain metals, particularly aluminum. Thus, it's not the acidity per se, but the enhanced toxicity of aluminum within the acidic medium, that causes the harm to both fish and vegetation.

One of the commonly overlooked facts of acid rain, however, is that the majority of aluminum found in acidic waters and soils is complexed with fluoride. Indeed, research has consistently found that when the pH of either water or soil decreases below 5, the majority of inorganic aluminum becomes bound with fluoride, resulting in aluminum fluoride complexes. Thus, the "aluminum" that has been linked to fish kills and vegetation damage exists primarily in the form of aluminum fluoride.

The predominance of aluminum fluoride in acidic environments has led to calls by some researchers for more focus on the contributing role of fluoride. As noted in 1984 by LaZerte: "The importance of the fluoride complex suggests that more detailed attention be paid to its toxicity." Later, in 1995, Hamilton warned that "aluminum-fluoride complexes could be a very important factor in the formation of inorganic complexes and consequently in the toxicity of aluminum to Atlantic salmon in some streams."

The possibility that fluoride may play a contributing role to the toxic effects attributed to "aluminum" is supported by laboratory research on both fish and vegetation. Hamilton (1995), for instance, found that the toxic effects of aluminum on fish were enhanced if 0.25 ppm fluoride was added to acidic water (5.5 pH). In addition, Hamilton also reported that gill damage among fish increased when he raised the fluoride concentration from 0.1 to 0.2 ppm, an effect which he suggests may result from fluoride's reported ability to increase the aluminum concentration at the gill surface.

In addition to research on aluminum fluoride's effect on fish, scientists have also investigated the impact of aluminum fluoride on vegetation. Most notably, Facanha in 2002 found that aluminum fluoride in acidic soils reduces the growth and yield of corn plants in a manner analagous to "phosphate starvation." Facanha makes a convincing case that aluminum fluoride complexes are able to cause this growth-suppressing effect through its "well-known phosphate-mimicking property." According to Facanha, the aluminum fluoride complex is treated as identical to phosphate by the corn's roots, thereby competing with phosphate uptake at the binding sites of the root. The end result is that less phosphate is absorbed into the plant, resulting in less energy and lower yields.

In summary, several lines of evidence (which are documented below) indicate that fluoride could be an important, yet overlooked, contributor to the environmental damage (fish kills and vegetation damage) associated with acid rain. This evidence includes:

1. Aluminum is widely believed to be the key toxic culprit in acidic soils and waters. Yet the majority of this aluminum is bound up in aluminum fluoride

complexes.
2. Laboratory experiments have found that low levels of fluoride (0.25 ppm) added to acidic water, increase the toxicity of aluminum to salmon.
3. Laboratory soil experiments have found that plants do not absorb fluoride from soils with a neutral pH. However, when the acidity increases, fluoride complexes with aluminum, and the rate of fluoride and aluminum uptake by plants greatly increases.
4. Laboratory soil experiments have found that aluminum fluoride complexes in acidic soils cause the very type of growth inhibitiion associated with acid rain damage.

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2) FLUORIDE'S ROLE IN FISH TOXICITY ASSOCIATED WITH ACID RAIN/ALUMINUM:

2a) In Acidified Water, Most Aluminum is Bound with Fluoride (and Vice Versa)

> **"As has been reported for many stream and surface waters, the fluoro-Al complexes were an important component of the inorganically complexed Al, ranging from 58% to 92% of the total inorganic Al fraction."**
> SOURCE: Bertsch, PM. (1989). Aluminum Speciation: Methodology and Applications. In: Norton SA, Lindbeg SE, Page AL. (1989). Acidic Precipitation: Soils, Aquatic Processes, and Lake Acidification. Volume 4. New York: Springer-Verlag.

> **"Fluoride readily complexed with Al, resulting in predominance of AlF complexes over AlOH complexes in our exposure waters. This pattern has been found in most other acidified streams in this area.** Similar results were reported by Driscoll et al (1980) for Canachagala Creek, Adirondack Mountains, NY."
> SOURCE: Clark KL, Hall RJ. (1985). Effects of elevated hydrogen ion and aluminum concentration on the survival of amphibian embryos and larvae. Can. J. Zool. 63: 116-123.

> "labile monomeric Al was the predominant form of Al in acidic Adirondack surface waters, although concentrations of nonlabile monomeric Al were also significant....**Fluoride complexed Al was the predominant form of labile monomeric Al in acidic surface waters, and at pH values below 5.5 essentially all aqueous F was complexed with Al.** Concentrations of aquo Al and OH-complexed Al

were less significant than F-complexed-Al. Sulfate complexes of Al were small in magnitude."
SOURCE: Driscoll CT. (1985). Aluminum in acidic surface waters: Chemistry, transport, and effects. Environmental Health Perspectives. 63: 93-104.

"...for three Atlantic salmon rivers on the Quebec North Shore, levels of dissolved inorganic Al increased by a factor of ≥ 3 during the spring pH depression (attaining values of ~2.4 uM); **up to 60% of this aluminum was present as Al(F)x species."**
SOURCE: Wilkinson KJ, Campbell PGC, Couture P. (1990). Effect of fluoride complexation on aluminum toxicity towards juvenile Atlantic salmon (Salmo salar). Can. J. Fish. Aquat. Sci. 47: 1446-1452.

"...the importance of the fluoride complex to inorganic monomeric Al is confirmed. The importance of the fluoride complex suggests that more detailed attention be paid to its toxicity."
SOURCE: LaZerte, BD. (1984). Forms of Aqueous Aluminum in Acidified Catchments of Central Ontario: A Methodological Analysis. Can. J. Fish. Aquat. Sci. 41: 766-776.

"Results for water samples, mainly from two streams in southern Norway, are discussed. **For most samples the labile monomeric Al-fraction dominates, the major species being either Al3+ or AlF2+."**
SOURCE: Seip HM, Muller L, Naas A. (1984). Aluminum Speciation: Comparison of Two Spectrophotometric Analytical Methods and Observed Concentrations in Some Acidic Aquatic Systems in Southern Norway. Water, Air, & Soil Pollution. 23: 81-95.

"Thermodynamic computations indicate that fluoride complexes are generally the dominant inorganic aluminum species. Free (aquo) aluminum and aluminum hydroxide complexes were predicted to be present in lesser amounts and aluminum sulphate complexes were generally insignificant."
SOURCE: Driscoll CT, Baker JP, Bisogni JJ, Schofield CL. (1980). Effect of aluminum speciation on fish in dilute acidified waters. Nature. 284: 161-164.

"Fluoride forms strong complexes with aluminum in water, and F chemistry in water is largely regulated by Al concentration and pH. At pH < 5, F is almost entirely complexed with Al. As a consequence, free F levels are generally low."
SOURCE: Skjelkvale BL. (1994). Factors Influencing Fluoride Concentrations in Norwegian Lakes. Water, Air, and Soil Pollution. 77: 151-167.

"Fluoro-Al complexes are particularly sensitive to pH changes, with the relative proportion of AlF2+ and [AlF2]+ increasing markedly in the pH range 4.5-5.5."
SOURCE: Wilkinson KJ, et al. (1993). Surface Complexation of Aluminum on Isolated Fish Gill Cells. Environ Sci Tech. 27: 1132-1138

"Fluoride is a ligand which forms complexes with Al3+ in natural waters with relatively low pH, and may play a role in processes causing dead fish." - Saether OM, Andreassen BT. (1995). Amounts and sources of fluoride in precipitation over southern Norway. Atmospheric Environment. 29: 1785-1793.

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2b) Implications of Aluminum Fluoride Complexes in Acidified Water:

"Fluoride is a ligand which forms complexes with Al3+ in natural waters with relatively low pH, and may play a role in processes

causing dead fish." - Saether OM, Andreassen BT. (1995). Amounts and sources of fluoride in precipitation over southern Norway. Atmospheric Environment. 29: 1785-1793.

"Fluoride concentrations were highest, and pH lowest, during high flow periods in these streams. **Therefore, aluminum-fluoride complexes could be a very important factor in the formation of inorganic complexes and consequently in the toxicity of aluminum to Atlantic salmon in some streams."**
SOURCE: Hamilton SJ, Haines TA. (1995). Influence of fluoride on aluminum toxicity to Atlantic Salmon. Can. J. Fish. Aquat. Sci. 52: 2432-2444.

"...the importance of the fluoride complex to inorganic monomeric Al is confirmed. **The importance of the fluoride complex suggests that more detailed attention be paid to its toxicity."**
SOURCE: LaZerte, BD. (1984). Forms of Aqueous Aluminum in Acidified Catchments of Central Ontario: A Methodological Analysis. Can. J. Fish. Aquat. Sci. 41: 766-776.

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2c) In Acidic Water, Fluoride May Enhance Aluminum's Toxicity to Fish:

"Our results indicate that at pH 5.5, low fluoride addition (50 ug/L) did not influence the acute toxicity of aluminum, but at high fluoride (250 or 500 ug/L) aluminum toxicity was increased."
SOURCE: Hamilton SJ, Haines TA. (1995). Influence of fluoride on aluminum toxicity to Atlantic Salmon. Can. J. Fish. Aquat. Sci. 52: 2432-2444.

"Wilkinson and Campbell (1993) reported that for given equivalent Al3+ concentrations, sorption of aluminum to the gill surface was higher in the presence of fluoride than in its absence, which further indicates the formation of mixed ligand complexes at the gill surface. **This increased aluminum accumulation at the gill in the presence of fluoride may explain the greater gill damage in our study at 200 ug/L fluoride than at 100 ug/L fluoride."**
SOURCE: Hamilton SJ, Haines TA. (1995). Influence of fluoride on aluminum toxicity to Atlantic Salmon. Can. J. Fish. Aquat. Sci. 52: 2432-2444.

"The best prediction of fish mortality was obtained as a function of the species Al3+ and AlF2+."
SOURCE: Wilkinson KJ, Campbell PGC, Couture P. (1990). Effect of fluoride complexation on aluminum toxicity towards juvenile Atlantic salmon (Salmo salar). Can. J. Fish. Aquat. Sci. 47: 1446-1452.

"Our experiments suggest that the toxic Al species were AlF compexes... Thus, AlF complexes in the natural acidic environment may be important toxic agents where AlOH complexes are not prevalent."
SOURCE: Clark KL, Hall RJ. (1985). Effects of elevated hydrogen ion and aluminum concentration on the survival of amphibian embryos and larvae. Can. J. Zool. 63: 116-123.

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3) FLUORIDE'S ROLE IN VEGETATION DAMAGE ASSOCIATED WITH ACID RAIN/ALUMINUM:

3a) Acid Rain Increases the Availability/Toxicity of Soil-bound Fluoride to Plants:

"This study has provided the first documented evidence that acid rain and fluoride may act synergistically in inhibiting plant growth via soil deposition." - Horner JM, Bell JNB. (1995). Effects of fluoride and acidity on early plant growth. Agriculture, Ecosystems and Environment. 52: 205-211.

"Recent work in this laboratory shows that both microorganisms and **acid rain have the ability to liberate F- from water insoluble particulates... thereby increasing the availability of this potentially toxic ion in polluted soils."**
SOURCE: Supharungsun S, Wainwright M. (1982). Determination, Distribution, and Adsorption of Fluoride in Atmospheric-polluted Soils. Bulletin of Environmental Contamination and Toxicology. 28: 632-636.

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3b) Fluoride Uptake By Plants Increases When Soil's Acidity Increases:

"Our experiment showed clearly that, when enough calcium was available to give a pH of about 6.5, the fluorine absorption through the roots was very low, but **the important thing is pH, it seems. We had high absorption of fluorine at low pH. We must know the pH of the soil."**
SOURCE: Daines RH, Leone I, Brennan E. (1949). The Effect of Fluorine on Plants as Determined by Soil Nutrition and Fumigation Studies. In: Air Pollution. Proceedings of the United States Technical Conference on Air Pollution. McGraw-Hill Book Co, New York. pp. 97-105.

"Soil pH is a determinant factor for fluorine solubility, but there exist different explanation models."
SOURCE: Wenzel W, Blum W. (1992). Fluorine Speciation and Mobility in F-Contaminated Soils. Soil Science. 153(5): 357-364.

"Soil reaction, or pH, is a factor in the movement of fluorides from soil into plant tops, and hence acid-loving vegetation may contain fluorine well beyond the 4 to 7 ppm content that is usual in forage vegetation devoid of fluoric contamination."
SOURCE: MacIntire WH. (1949). Air Versus Soil as Channels for Fluoric Contamination of Vegetation in Two Tennessee Locales. In: Air Pollution. Proceedings of the United States Technical Conference on Air Pollution. McGraw-Hill Book Co, New York. pp. 53-58.

"The effect of fluoride pollution of soils on plants has generally been discounted, primarily because it is well known that F adsorbs strongly to most soils at neutral pH and is, therefore, assumed to be unavailable to plants."
SOURCE: Stevens DP, McLaughlin MJ, Randall PJ, Keerthisinghe G. (2000). Effect of fluoride supply on fluoride concentrations in five pasture species: Levels required to reach phytotoxic or potentially zootoxic concentrations in plant tissue. Plant and Soil. 227: 223-233.

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3c) In Acidic Soils, Most Fluoride and Aluminum Exists as Aluminum Fluoride Complexes:

"In acid soils fluoride binds mainly to aluminum."
SOURCE: Gago C, Fernandez Marcos ML, Alvarez E. (2002). Aqueous Aluminum Species in Forest Soils Affected by Fluoride Emissions from an Aluminum Smelter in NW Spain. Fluoride. 35(2): 110-121.

"The main form of F in soils with pH below 6 are different AlFx complexes."
SOURCE: Arnesen AKM. (1997). Availability of fluoride to plants grown in contaminated soils. Plant and Soil. 191: 13-25.

"Aluminum is the most prevalent cation with which F complexes in acid soils."
SOURCE: Stephens, McLaughlin MJ, Alston AM. (1997). Phytoxicity of aluminum-fluoride complexes and their uptake from solution culture by Avena sativa and Lycopersicon esculentum. Plant and Soil. 192: 81-93.

"A comparison between metal contents and the amount of complexed fluorine...leads to the conclusion that **below pH 5.5 AlFx complexes are the predominant species due to their high stability under acid conditions."**
SOURCE: Wenzel W, Blum W. (1992). Fluorine Speciation and Mobility in F-Contaminated Soils. Soil Science. 153(5): 357-364.

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3d) In Acidic Soils, Aluminum Fluoride Complexes Facilitate the Uptake of Both Aluminum & Fluoride:

"The linkage of fluoride and aluminum accumulation can be explained by the formation of stable soluble aluminum-fluoride complexes in the soil, particularly under acid conditions, and the resulting increase of uptake of both elements."
SOURCE: Klumpp A, Klumpp G, Domingos M, Dias Da Silva M. (1996). Fluoride impact on native tree species of the Atlantic forest near Cubatao, Brazil. Water Air and Soil Pollution. 87: 57-71.

"The high solubility of fluorine under acid conditions can be explained by the occurrence of cationic [AlF]2+ and [AlF2]+ complexes... Aluminum solubility is increased by fluoride."
SOURCE: Wenzel W, Blum W. (1992). Fluorine Speciation and Mobility in F-Contaminated Soils. Soil Science. 153(5): 357-364.

"The increased solubility of fluoride at lower pH is attributable to formation of soluble AlFx3-x complexes..."
SOURCE: Gago C, Fernandez Marcos ML, Alvarez E. (2002). Aqueous Aluminum Species in Forest Soils Affected by Fluoride Emissions from an Aluminum Smelter in NW Spain. Fluoride. 35(2): 110-121.

"The degree of [fluoride] accumulation depends on several factors,

including soil type and, most prominently, pH. **At acidic pH (below pH 5.5), fluoride becomes more phytoavailable through complexation with soluble aluminium fluoride species**, which are themselves taken up by plants or increase the potential for the fluoride ion to be taken up by the plant."
SOURCE: World Health Organization. (2002). FLUORIDES. Environmental Health Criteria 227. World Health Organization, Geneva

"The uptake of positively charged AlFx complexes may explain the positive correlations between F and Al concentrations in the shoot."
SOURCE: Arnesen AKM. (1997). Availability of fluoride to plants grown in contaminated soils. Plant and Soil. 191: 13-25.

"Aluminum increased fluoride concentrations in roots and shoots but the pattern of distribution between root and successive leaves was not substantially altered... **Aluminum might affect the uptake and transport of fluoride in several ways."**
SOURCE: Takmaz-Nisancioglu S, Davison AW. (1988). Effects of aluminum on fluoride uptake by plants. New Phytol. 109: 149-155.

"Increasing the AlCl3 concentration caused a very marked increase in soluble fluoride in Soils 1 and 2, probably due to formation of soluble aluminum fluoride complexes."
SOURCE: Larsen S, Widdowson AE. (1971). Soil Fluorine. Journal of Soil Science. 22: 210-221.

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3e) In Acidified Soils, Aluminum-Fluoride Complexes Reduce Plant Growth and Yield:

"Results obtained in this study showed that high levels of F in acid soils reduce crop yield due to increasing aluminum and depressing phosphate uptake."
SOURCE: Elrashidi M, Persaud N, Baligar VC. (1997). Effect of fluoride and phosphate on yield and mineral composition of barley grown on three soils. Agricultural Research Service. United States Department of Agriculture. Approved date: March 4, 1997.

"The results of this study support our hypothesis that the toxicity of Al is enhanced in acidic environment contaminated with fluoride."
SOURCE: Rai LC, Husaini Y, Mallick N. (1996). Physiological and biochemical responses of *Nostoc Linckia* to combined effects of aluminum, fluoride and acidification. Environmental and Experimental Botany. 36: 1-12.

"the strong inhibition of H+ -ATPase observed in medium containing fluoride and aluminum may suggest that fluoroaluminate could play a role in the mechanism of aluminum toxicity and inhibition of plant growth observed in acid soils. However, at present we do not know whether fluoroaluminate is able to penetrate the cells of the corn roots."
SOURCE: Facanha AR, Meis L. (1995). Inhibition of Maize Root H+ -ATPase by Fluoride and Fluoroaluminate Complexes. Plant Physiology. 108: 241-246.

"fluoroaluminum complexes have been shown in the present study to be toxic to root elongation, but sulfatoaluminum species appear to have little or no toxicity."
SOURCE: Kinrade, TB. (1996). Reconsidering the rhizotoxicity of hydroxyl, sulfate, and fluoride complexes of aluminum. Agricultural Research Service. United States Department of Agriculture. Approved

date: August 14, 1996.

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3f) Mechanism of Aluminum Fluoride's Toxicity to Plants:

AlF mimics phosphate, reduces root uptake of phosphate, and causes a reduction in the plant's energy and yield similar to the effects seen in cases of "phosphate starvation")

"Contrary to prior expectations, Al-F complexes have been shown to be toxic to plants. Although several hypotheses for the mechanism of Al-F toxicity have been considered, so far all of them have been rejected. The present study focuses on the description of an alternative mechanism for the toxicity of AlFx through a well-known phosphate-mimicking property attributed to these complexes. **Phosphorus is acquired by plant roots primarily via high-affinity Pi transporters. Several pieces of evidence support a model where AlFx complexes can mimic the tetrahedral phosphate group competing with it for the same binding sites on the Pi carriers and possibly stabilizing an inactive conformation.** First, AlFx-induced inhibition of Pi uptake was antagonized by raising the Pi concentration in the reaction medium. Second, the stimulation of Pi uptake in corn roots after AlFx pretreatment is similar to that observed after Pi starvation... This supports the model where the fluoroaluminates act as physiological Pi analogs by competing directly for the same binding sites of Pi transport rather than any indirect effect on the proton motive force of the process... These evidences support the proposal that **the property of AlFx to mimic Pi may describe the most important mechanism of AlFx toxicity whenever AlF3 and AlF4 are the dominant species."**
SOURCE: Facanha AR, Okorokova-Facanha AL. (2002). Inhibition of Phosphate Uptake in Corn Roots by Aluminum-Fluoride Complexes. Plant Physiology. 179: 1763-1772.

"Results obtained in this study showed that **high levels of F in acid soils reduce crop yield due to increasing aluminum and depressing phosphate uptake."**
SOURCE: Elrashidi M, Persaud N, Baligar VC. (1997). Effect of fluoride and phosphate on yield and mineral composition of barley grown on three soils. Agricultural Research Service. United States Department of Agriculture. Approved date: March 4, 1997.

"The possibility remains that **Al-F is an effective vehicle for the intracelluar uptake of Al and F where these elements, once dissociated from each other, may exert a toxic effect."**
SOURCE: Kinraide TB. (1997). Reconsidering the rhizotoxicity of hydoxyl, sulphate, and fluoride complexes of aluminum. Journal of Experimental Botany. 48(310): 1115-1124

"Higher intracellular Al uptake from the media containing AlF3 and NaF+AlCl3 as opposed to that with only AlCl3 in the presence of phosphate indicates the existence of different modes of entry for Al in the presence and absence of fluoride."
SOURCE: Rai LC, Husaini Y, Mallick N. (1996). Physiological and biochemical responses of *Nostoc Linckia* to combined effects of aluminum, fluoride and acidification. Environmental and Experimental Botany. 36: 1-12.

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