FLUORIDE ACCUMULATION IN LEAVES DUE TO BORON-CONTAINING FERTILIZERS

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Introduction

Fluoride damage to vegetation has been observed for a long time near chemical and metallurgical factories. Especially aluminum, glass and superphosphate fertilizer works emit pollutants which contain F^- compounds.

The tolerance of plants to the caustic action of F^- compounds varies greatly with each species. Apricot and peach trees, grape vines, gladiolus and iris plants are most susceptible to damage.

In the Rhone Valley (canton Valais, Switzerland) damage to grape vines and apricot trees has been reported as distant as 23 kilometers from the emission centers in the direction of the prevailing winds. The symptoms observed are typical of F^- damage, namely marginal and apical centripetal necroses in dicotyledons, apical progressive necroses in monocotyledons, twig defoliation in apricot and peach trees.

Fluoride assays of foliage of the damaged plants revealed very high F^- levels with values up to 600 ppm in dry matter (1 ppm = 1 part per million = 1 mg/kg).

Extensive necrosis of leaves as well as high F^- levels occurred several kilometers from the emission points. The damage was limited strictly to particular plots, belonging to the same proprietors, whereas neighboring plots did not show the above-mentioned symptoms.

Neither the composition of the soil, its F^- content, antiparasitic treatments nor irrigation by sprinkling, which is in common use in the Rhone Valley, could be implicated as the cause of the above-mentioned damage. Therefore, our attention was directed to fertilizers as its likely source.

Field Experiments

At first, investigations of the effect of a special form of potassium fertilizer, namely chlorinated and sulphated potassium fertilizer, indicated that the chlorinated type was responsible for the necroses.

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However, investigations conducted in 1968 in open fields as well as in pot-cultures proved that certain special types of fertilizers were exclusively instrumental in causing the high F^- accumulation in plant tissues and the characteristic features of F^- intoxication (Table 1).

TABLE 1

Typical Fluoride-Induced Necroses on Apricot Trees and Grape Vines (Rhone Valley)

Place	Type of Fertilizer Used	Plant Species	Foliage: Necroses*	Foliage: Fluoride ppm **	Soils: pH	Soils: $CaCO_3$ %	Soils: P_2O_5 Test	Soils: K_2O mg%	Soils: Total F^- ppm
Charrat	PKB	Apricot	3, 1	630, 0	8, 0	50, 0	250	29, 0	760
	PKB	Vine	3, 8	620, 0					
	NPKMg	Apricot	0	26, 4	7, 9	48, 0	132	19, 3	790
	NPKMg	Vine	0	31, 6					
	PKB	Apricot	2, 0	362, 0	7, 9	51, 0	145	20, 0	800
	NPKMg	Apricot	0, 1	12, 8	7, 8	28, 5	102	12, 7	660
Saxon	PKB	Apricot	2, 5	420, 0	7, 8	12, 0	43	3, 8	610
	PKMg	Apricot	0	16, 8	7, 6	14, 0	110	5, 6	450
Bieudron	PKB	Apricot	3, 0	524, 0	7, 6	3, 5	62	17, 0	650
	PKB	Vine	2, 5	213, 0					
	Manure	Apricot	0	38, 4	7, 7	3, 7	200	42, 0	620
	Manure	Vine	0	54, 4					
Fey	PKB	Apricot	2, 6	249, 0	7, 6	6, 8	47	46, 5	730
	NPK	Apricot	0, 7	11, 0	7, 3	4, 0	580	15, 5	810
Coor	PKB	Apricot	2, 6	127, 2	7, 2	----	230	100, 0	640
	NPK	Apricot	0, 6	12, 0	7, 1	0, 2	200	4, 6	720

*Estimated degree of damage **Dry matter

0 = without necroses

5 = all foliage necrotic

Boron-containing compounds are underlined.

Tests were conducted on a white grape vine in Luins on the shore of Lake Geneva, an area without any atmospheric pollution,and on apricot trees in Fey (Valais) in the Rhone Valley (Table 2). Additional experiments were carried out on forage cultures in Möhlin (Rhein Valley) in the North of Switzerland (Table 3). The special fertilizers were obtained by direct attack of strong acids, i. e. sulfuric or nitric acid, on the mixture of rough phosphates, potassium chloride and borax or boric acid. Only

TABLE 2

F⁻ Content of Grape Vines and Apricot Leaves from Experimental Plots

Type of Fertilizer	Grape Vine (Luins-Lake of Geneva)			Apricots (Fey-Rhone Valley)	
	5.6.	26.7. 1968	7.10	21.7	19.9 1968
1. Without fertilizer	3,0	11,8	16,5	13,7	18,5
2. Superphosphate + KCl	3,7	8,7	15,5	18,5	18,5
3. Super + KCl + Borax	3,3	8,0	18,5	----	----
4. Superphosphate + K_2SO_4	3,3	7,2	19,5	13,8	16,2
5. Super + K_2SO_4 + Borax	4,3	7,7	16,5	----	----
6. Combined fertilizer PK	3,3	9,0	13,0	9,7	12,5
7. Combined fertilizer PKB	9,7	53,4	45,5	200,1	161,0
8. Mixed fertilizer PKMg	5,3	10,8	16,0	14,5	12,0
9. Mixed fertilizer PKMgB	3,0	9,2	12,0	17,0	17,0

F⁻ concentrations in ppm, dry matter.

TABLE 3

Fluorine, Boron and Chlorine in Forage Plants
Experiment in Möhlin (Rhein Valley)

Type of Fertilizer	Experiment #1 Soil: pH 7,3 Fluorine:540 ppm Crops			Experiment #2 Soil: pH 6,1 Fluorine:260 ppm Crops		
	F⁻ ppm	Boron ppm	Cl. %	F⁻ ppm	Boron ppm	Cl. %
First Cutting (May 14, 1968)						
1. Without fertilizer	7,0	14,0	0,32	11,0	13,5	0,78
2. Superphosphate + KCl	21,5	13,8	1,87	26,5	14,0	1,29
3. Super + KCl + Borax	31,0	23,0	1,96	26,5	20,0	1,30
4. Superphosphate + K_2SO_4	25,5	11,0	0.77	37,5	18,0	0,89
5. Super + K_2SO_4 + Borax	29,0	18,0	0,89	32,5	17,5	0,27
6. Combined PK (chlorinated)	11,5	10,0	1,67	32,5	17,0	1,38
7. Combined PKB (chlorinated)	183,5	36,0	1,69	185,7	44,0	1,12
8. Mixed PKMg (sulphated)	12,5	14,0	0,66	17,0	16,0	0,87
9. Mixed PKMgB (sulphated)	13,0	13,8	0,71	21,5	17,5	0,66

the boron-containing combined fertilizers proved to be responsible for the high F^- content of the plants whereas fertilizers of the same formula, which were obtained by the same process but without addition of boron, failed to cause an increase in F^- uptake by plants. As Table 2 indicates, F^- levels in the leaves of apricot trees and grapevines do not exceed 20 ppm in the dry matter except in parcel No. 7 which received the PKB boron-containing fertilizer.

The same combined PKB fertilizer also caused a very high F^- accumulation in forage (Table 3). In the parcels where the PKB fertilizer was not used, the F^- content did not exceed 40 ppm although the experiments were located in a F^- polluted area near an aluminum factory.

TABLE 4

Pot-Cultures of Winter Rye (1968)
Relation of Type of Fertilizer to F^- and B Accumulation in Leaves

Tested Fertilizers	Fluoride ppm (dry)	Boron ppm (dry)
1. Without fertilizer	6, 0	10, 0
2. Calcium phosphate + KCl	9, 0	13, 7
3. Combined PK 13-26	7, 0	10, 0
4. Combined PKB 13-26-0, 35	34, 5	20, 0
5. Combined NPK 5-8-15	6, 0	13, 7
6. Combined NPKB 5-8-15-0, 35	51, 0	28, 7
7. Combined NPK 6-13-11	5, 0	10, 0
8. Combined NPKB 6-13-10-0, 34	55, 5	40, 0
9. Fertilizer NPK 13-13-21	6, 0	10, 0
10. Fertilizer NPKB 13-13-21-0, 2	7, 0	20, 0
11. Fertilizer NPK 13-13-27	7, 0	12, 5
12. Fertilizer NPKB 13-9-20-0, 12	9, 0	15, 0
13. Fertilizer NPK 9-9-18	10, 0	13, 7
14. Fertilizer NPKB 10-10-18-0, 3	8, 0	20, 0
15. Fertilizer NPKB 12-12-17-0, 1	10, 0	13, 7

"Combined" boron-containing compounds are underlined.

Greenhouse and Laboratory Experiments

Since in the field tests only the special combined boron-containing PKB fertilizer accounted for a marked F^- accumulation in plant tissues, we investigated 13 combined or mixed commercial fertilizers which are commonly used in Switzerland. These experiments were performed on winter rye in pot cultures.

Only 3 of the 13 fertilizers showed the above-mentioned reaction. They were the combined boron-containing type, namely PKB 13-26-0, 35, NPKB 5- 8-15-0, 35 and 6-13-10-0, 34. Mixed boron-containing fertilizers or combined fertilizers without boron (Table 4) failed to accumulate excess fluoride.

The penetration of F^- into plant tissues is obviously proportional to the amount of combined boron-containing fertilizer used in the cultures. A pot-culture experiment on winter barley proved that increasing proportions (from 0 up to 100%) of the combined NPKB boron-containing fertilizer in a NPK fertilizer without boron caused a progressive and parallel accumulation of F^- in the dry matter of barley leaves (Table 5).

TABLE 5

Pot-Cultures of Winter Barley
Relation of Combined Boron Fertilizers on F^- and B Penetration to Leaves

Type of Fertilizer	Fertilizer Ratio		Leaf Content	
	(a) with Boron %	(b) without Boron %	Fluoride ppm	Boron ppm
(a) NPKB 5-8-15-0, 35	0	100	23, 0	10. 0
(b) NPK 5-8-15	10	90	116, 0	18, 7
	25	75	237, 0	25, 0
	50	50	499, 5	60. 0
	75	25	807, 0	80, 0
	100	0	945, 0	80, 0
(a) NPKB 6-13-10-0, 34	0	100	9, 0	12, 2
(b) NPK 6-13-11	10	90	69, 5	18, 7
	25	75	153, 0	21, 2
	50	50	358, 0	45, 0
	75	25	508, 0	45, 0
	100	0	822, 0	45, 0

In order to determine the mode of action of the above-mentioned fertilizers on F^- accumulation in the cultures, several tests were made in a greenhouse with some commercial (technically improved) fluoride salts and two of the above-mentioned combined boron-containing fertilizers. Table 6 illustrates the striking analogy of the influence of the above-mentioned special fertilizers and the complex salt potassium fluoborate (KBF_4). Analysis of the combined boron-containing fertilizers proved that a high proportion of F^- in the form of fluoborate, namely 57% of the total F^- content of fertilizer PKB 13-26-0, 35 is indeed present as fluoborate. The total amount of fluoborate in this fertilizer is 1, 16%.

TABLE 6

Pot-Cultures of Goose-foot (Chenopodium)
F^- Penetration into Tissues Under the Influence of F^- Containing Salts Applied to the Soil

Treatment		Fluoride Content ppm (dry) Roots	Stems	Leaves
1. Without Treatment	(a)	76,0	8,0	24,0
2. Sodium Fluoride (NaF)	(a)	207,0	16,0	27,0
3. Sodium Fluoride + Boric Acid ($NaF + H_3BO_3$)	(a)	171,0	14,0	10,0
	(b)	87,0	11,0	14,0
4. Ammonium Fluosilicate $(NH4)\ _2SiF_6)$	(a)	215,0	18,0	28,0
	(b)	163,0	26,0	14.0
5. Ammonium Fluosilicate + Boric Acid $(NH_4)\ 2SiF_6 + H_3BO_3$	(a)	103,0	19,0	19,0
	(b)	110,0	18,0	28,0
6. Potassium Fluoborate (KBF_4)	(a)	67,0	66,0	475,0
	(b)	155,0	241,0	2365,0
7. Combined Fertilizer without Boron PK 13-26	(a)	70,0	16,0	33,0
	(b)	69,0	19,0	40,0
8. Combined Boron-containing Fertilizer	(a)	62,0	129,0	726,0
PKB 13-26-0,35	(b)	124,0	166,0	2196,0

(a) Temperature, humidity and lighting normal.
(b) Strong insulation, high temperatures and low relative humidity.

TABLE 7

Penetration of F and B into Stems, Grains and Leaves of Beans (Pot-Cultures)
Effect of Washing Leaves on their F and B Content

Type of Fertilizer	Fluoride ppm (dry) Stems	Grains	Leaves Not Washed	Leaves Washed	Boron ppm (dry) Stems	Grains	Leaves Not Washed	Leaves Washed
1. Without fertilizer	7,0	6,0	9,0	8,0	15,0	16,2	21,2	21,2
2. Superphosphate + KCl	6,0	6,0	9,0	6,0	22,5	30,0	22,5	30,0
3. Super + KCl + Borax	6,5	6,0	7,0	6,0	18,7	25,0	140,0	180,0
4. Superphosphate + K_2SO_4	7,0	6,0	10,0	5,5	12,5	13,7	13,7	13,7
5. Super + K_2SO_4 + Borax	5,0	5,0	6,0	5,5	35,0	15,0	223,5	200,0
6. Combined fertilizer PK	7,0	6,0	11,0	7,0	12,5	12,5	16,2	16,2
7, Combined fertilizer PKB	6,0	5,5	55,0	43,5	17,5	17,5	110,0	110,0
8. Mixed fertilizer PKMg	6,0	6,0	5,0	6,0	11,2	10,0	15,0	16,2
9. Mixed fertilizer PKMgB	4,0	4,0	10,0	6,0	11,2	15,0	200,0	190,0

Experiments on beans conducted in a greenhouse with several fertilizers including the special combined boron-containing fertilizer PKB 13-26-0, 35 proved that F^- could be partially eliminated by washing the leaves with water, whereas the boron content of the same tissues remained unchanged by washing (Table 7). Therefore, F^- must have penetrated the plant through the roots. Fluoride in plant tissues must be fairly water-soluble. This experiment further indicates that a part of F^- present inside the plant tissue might be eliminated when the leaves are being washed with water in order to carry away dust deposits. Our observations therefore agree with those of Venkateswarlu et al., who found that F^- is mainly localized in the extracellular spaces.

Summary

In Switzerland's Rhône Valley, apricot orchards and vineyards exposed to F^- emissions from aluminum and phosphate fertilizer factories displayed typical fluoride-induced necroses of the foliage. Up to 600 ppm F^- in dry matter was found in the plant tissue. The damage was limited to a few strictly circumscribed, individually owned parcels of land.

Experiments upon the land as well as in pot-cultures showed that the high F^- content in the plants resulted from certain fertilizers - the end product of a special factory process. These boron-containing combined fertilizers were obtained by direct reaction of sulphuric acid or nitric acid upon the raw products. A particular chemical combination containing fluorine and boron is formed in the fertilizer during the manufacturing process. The action of this special combination is similar to that of potassium fluorborate (KBF_4).

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