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EDITORIAL

FLUORIDE INTAKE THROUGH FOOD

One of the most important questions concerned with fluoride research which is far from being resolved at this time is the amount and nature of F^- present in our daily food.

In 1937, Roholm (1) attributed to contamination of food much of the damage to health of Danish cryolite workers afflicted with chronic F^- poisoning. Since then only a few papers have appeared which elucidate the possibility of chronic poisoning due to F^- contaminated food. Articles by Wilson and Murray on neighborhood fluorosis (2), by Fradà et al. on hydrofluorosis (3) and the reports on endemic fluorosis in India raised the question to what extent F^- contaminated food contributed to the illness, but little information is available on the amounts of F^- consumed by the victims.

More recently several investigators have associated clinical symptoms in humans with food polluted by industrial F^- emission. Balazova et al. (4) noted anemia in children, Columbini et al. (5) changes in serum alkaline phosphatase in the vicinity of F^- emitting factories. Waldbott and Cecilioni (6) related acute and chronic gastro-intestinal upsets to consumption of food contaminated up to 10 times the usual level by F^- emissions from a phosphate fertilizer factory.

In food of animal origin F^- accumulates when domestic animals graze on F^- contaminated forage and when animals are fed F^- containing mineral supplements. In vegetation, F^- uptake occurs mainly through the pores of leaves from F^- contaminated air. Lesser amounts enter vegetation, especially tuber vegetables, from soil contaminated either by F^- emitting factories, by burning coal or by phosphate fertilizers. Fluoride-containing sprays have also accounted for the presence of F^- in fruit and vegetables (7).

Fluoride consumption through food under "normal" conditions has been subjected to studies with varying results. Bredemann (8) recorded a wide range in the F^- content of food. Fluoride levels vary even from sample to sample in the same batch. In 1949 McClure (9) estimated the daily F^- intake from a typical diet at 0.25 to 0.3 mg on the basis of his personal analyses and his survey of the literature.

More recently, Marier and Rose (10) have shown that McClure's figures no longer apply. Now the daily F^- intake through food can be as high as 1 to 2 mg due to food being processed with fluoridated water.

In the current issue of "Fluoride" Oelschlager (page 6) estimated the daily average F^- intake from food at between 0.3 to 0.4 mg. Under certain conditions it may rise to 2 mg and more. His data are based on extensive experience with F^- analysis and on careful avoidance of the many errors to which F^- assays are subject.

Cook (page 12) has made a valuable contribution to the subject by analyzing tea for F^-. He computed that the daily F^- intake through tea ia 1.26 mg in children and 2.55 in adults in the United Kingdom where tea is a major staple drink. He has also shown that about 96% of F^- in the tea infusion is in an ionized form which renders it readily absorbable in the human organism.

Oelschlager's data are particularly significant because he, like Rippel (11), Garber (12) and Gisiger (13), has demonstrated that F^- levels of a particular food grown in an industrial area are usually many times higher than those of the same food grown in an uncontaminated region. He has also confirmed what has been recognized by other authors that in coal burning nonindustrial regions enough F^- is liberated into the air to cause a substantial increase of F^- in food.

Tea ranks first among foods high in F^-. Seafood and salt-water fish contain high F^- levels. Sea water, their natural habitat, contains about 1 ppm F^-. In the Persian Gulf a concentration as high as 7 ppm has been reported. Likewise, fresh water fish may be high in F^-, especially those which receive food supplements containing calcium phosphates.

Oelschlager adds polished rice and polished peas to the list of "high fluoride" foods. Their F^- content is between 50 and 100 times higher than that of unpolished rice and peas. Small amounts of F^- present in talcum powder $(Mg_3(Si_4O_{10})(OH)_2$ is used in the polishing process.

Gelatin, named by Bartlett (14), as a "high fluoride" food, normally contains 1 to 25 ppm F^- with a median of 6.5 ppm, but in 8 samples prepared with water containing 1 ppm F^-, it ranged from 29 to 34 ppm. Marier et al. demonstrated that the problem becomes further complicated by the fact that foods cooked in fluoridated water pick up additional F^- causing their F^- levels to be increased by a factor 3 to 5 (10).

With much new information now available on the F^- content of food two major questions need to be given attention. Lovelace and Welkie (15) showed that vegetation grown near an F^- emitting factory contains F^- in the highly toxic form of fluoroacetate and fluorocitrate. Because of the tendency of the fluoride ion to combine with numerous chemical agents, the question arises whether similar, unusually toxic compounds in food are consumed by humans or whether the toxicity of F^- in food is of a lesser degree as for instance that of sodium fluoride, the F^- salt on which most studies concerned with F^-'s biological action are based.

The other question concerns the role of F^- in producing illness both from occasional ingestion of a single large dose or from persistent intake of F^- contaminated food. Because of the many difficulties encountered in clearly pinpointing such illness, the medical profession is likely to be unaware of its existence.

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"CHIZZOLA" MACULAE

In 1957 Colombini et al. (1) described an unusual skin disease resembling traumatic suffusions in the vicinity of an aluminum factory near Chizzola, Italy. Steinegger (2) reported the same condition from an area near Bolzano, Italy, where another aluminum factory is located.

The lesions are macular, indolent, not raised above the surface of the skin, grayish-brown to blue, round or oval in shape, 1 to 2 cm in diameter and not sharply delineated. Upon digital pressure and diascopy they remain unchanged. They are fleeting in character, lasting between 3 to 7 days. After they fade, new lesions appear on other parts of the body. In none was there a history of trauma.

In both areas, the occurrence of the lesions was linked with the activity of the aluminum plants. The shorter the distance from the plant, the higher was the incidence of the disease. In some communities, as much as one-third of the population manifested the lesions.

Waldbott and Cecilioni (3) observed the same lesions in 9 out of 32 cases of incipient fluorosis near a fertilizer factory and in another case near a steel foundry. Both industries emit F^- through their chimneys. Near a Czechoslovakian factory Balazova et al. (4) failed to detect the lesions among children and women.

Histologically, Waldbott noted peri-capillary infiltrations with lymphocytes and mast cells,and slight melanin deposition near capillaries. Others (5) observed an unusual degree of capillary permeability.

The following criteria permit a differentiation of the lesions from traumatic suffusions: Their size rarely exceeds that of a quarter. Their shape is round or oval. In contrast to suffusions their color does not change to brown and yellow as they disappear.

Experimentally the lesions could not be reproduced by Colombini et al. (5) in animals fed forage grown in the polluted area. Injections of sodium fluoride and injections of an extract of pollutant flydust into pregnant animals by Cavagna et al. (6) did not produce the lesions in the offspring. Significantly, the skin of the experimental animals contained more than twice as much F^- as that of the control animals, namely 8.39 ppm in animals whose mothers received NaF; 7.02 ppm in the offspring of those which received dust extract; 3.11 ppm in controls. Cavagna et al. found no change in capillary permeability as shown by the suction cup test in their experiments.

Whereas there are strong indications that F^- is responsible for the lesions, it is certain that this unusual skin disease is not an obligatory feature of F^- intoxication.

Several questions arise in connection with the above-described dermatosis:

Do other chemicals, in association with F^- emitted from the factories, precipitate the lesions? Might certain F^- complexes be formed in the human organism under specific conditions which pertain to a patient's individual make-up and predispose him to the lesions? Are the maculae the precursor of inflammatory capillary changes observed by Khan and Wig (7) in their description of one of their cases of skeletal fluorosis? Can the lesions be linked with the calcification of arteries described by several authors in advanced skeletal fluorosis? Indeed, the fact that thus far the lesions have not been reproduced experimentally even raises doubt as to whether they are in fact F^- induced.

If F^- can be confirmed as the cause of Chizzola Maculae they would constitute a specific diagnostic criterion of fluorosis as significant as, or more so than, mottled teeth and F^- osteosclerosis: They would make it possible to pinpoint the disease in its early stage prior to the development of dental and skeletal changes.

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FLUORIDE IN FOOD

by

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SUMMARY: Food from animal and plant life was analyzed for F^-. The average daily F^- consumption through food in Germany ranged between 0.2 and 0.4 mg. Addition of such "high fluoride" foods as polished peas and rice, tea and fish may raise the daily average intake to 2 mg and above. Food originating in an air-contaminated area contains much higher F^- levels than food grown in non-polluted areas.

During studies on the biological effect of F^- in domestic animals we have carried out numerous F^- assays in food, both in the vicinity of F^- emitting factories and under so-called normal conditions. The results of these assays are herewith presented.

Method

Fluoride was determined by the distillation procedure of Willard and Winter (1). In employing this method we have taken precautions against possible errors which we have outlined in previous papers (2). These errors pertain to collecting of specimens, to grinding, ashing, distillation and condensing the distillate. Recently we acquired an automatic distillation apparatus which is useful in all our assays of animal and plant products and of inorganic substances.

Tables 1 and 2 show F^- levels in food substances derived from plant and animal life, tables 3 and 4 in beverages, tables 5 and 6 present the F^- content of food from areas exposed to fluoride emissions.

"Normal" Values of Food and Beverages

According to table 1, lettuce and spinach contain more F^- than other vegetables; sweet cherries more than other fruits. No essential difference is noted in the F^- content of potatoes which are cooked in their jackets and those which are peeled and then cooked. Peapods contain 9 times more F^- than the peas. 200 times more F^- was found in polished peas than in unpolished ones. Similarly the F^- content of polished rice was 50 times higher than that of unpolished rice.

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No essential difference exists in the F^- content of various kinds of bread. This finding is contrary to the popular belief that rye bread contains more F^- than white bread.

As an interesting experiment, we determined the F^- content of noodles, unpolished and polished rice, potatoes and cauliflower which had been boiled in fluoridated (1 ppm) water. Whereas the noodles and the unpolished rice took up little F^- from water, polished rice accumulated 11%, potatoes 7% and cauliflower 32% of the total F^- present in the water.

TABLE 1

"Normal" Values of Food and Beverages

	Average F^- Values mg/kg		Average F^- Values mg/kg
FRUIT			
Apple	0.08	Red cabbage	0.06
Pear	0.11	Cabbage (round)	0.06
Prune	0.14	Celery cabbage	0.07
Cherry	0.72	Potato peeled, raw	0.16
Grape	0.11	Potato for salad	0.12
Current	0.35	Beans	0.66
Gooseberry	0.31	Lentils (dry)	0.52
Blackberry	0.07	Peas with pod	0.35
Strawberry	0.29	Peapods	1.00
VEGETABLES		Peas peeled	0.12
Lettuce	0.63	Peas polished	14.06
Head lettuce	0.38	BREAD	
Endive	0.14	White bread	0.11
Spinach	1.05	Buns	0.06
Beet	0.09	Mixed wheat	0.06
Celery	0.11	Rye	0.13
Carrot	0.09	Rye, whole	0.08
Onion	0.14	Pumpernickel	0.04
Leek	0.25	"Knicke" bread	0.18
Tomato	0.28	MISCELLANEOUS	
Cucumber	0.08	Rice, wild	0.18
Cauliflower	0.09	Rice, peeled	0.24
Brussel Sprouts	0.12	Rice, polished	10.67
Kohlrabi	0.18	Noodles	0.11

Food derived from animal life (table 2), with exception of egg, was higher in F^- than food which originated from plant life. Beef kidneys contained twice as much F^- as pork kidneys. The largest amounts of F^- were found in fish. Fish also contained the highest levels of selenium, an element which tends to promote dental caries. Fluoride assays in trout were higher than in other fish, probably because trout are raised with phosphate supplements which are usually high in F^- (3).

TABLE 2

F^- in Food of Animal Origin (1 to 4 Samples)

F^- fresh wt. mg/kg		F^- fresh wt. mg/kg	
BEEF		**FISH** (boiled bones removed)	
Meat	0.19	Herring	1.37
Liver	0.25	Bass	1.30
Heart	0.48	Caviar	1.40
Kidney	0.51	Trout	5.21
Spleen	0.34		
Bone (ash)	820.00		
PORK		**MISCELLANEOUS**	
Meat	0.27	Egg	0.05
Liver	0.32	Cheese	0.25
Heart	0.29	Sausage	0.34
Kidney	0.34	Meat broth	0.12 mg/600 ml
Lung	0.25		
Spleen	0.26		

Prior to assaying the cooked trout all bones were carefully removed. When the high F^--containing bones were boiled in distilled water, only minute amounts of F^- were transferred into the broth.

Beer produced with Stuttgart city water (0.12 ppm) and milk contained little F^- (table 3). Our findings pertaining to beer contradict those of an Australian investigation (4), which suggested beer for prevention of dental caries because of its presumed high F^- content. In two kinds of mineral water the F^- levels ranged up to 1.5 and 2.1 ppm respectively. F^- levels in coffee and cocoa (table 4) were relatively low but those of tea unusually high. In tea infusions between 81 and 89% of F^- was transferred from the leaves into the solution. This compares with 29% of F^- which was found in infusions of peppermint tea in boiling water, 20% F^- in infusions of rose hips and 5% in camomile tea. Little F^- was noted in coffee beans, whereas coffee substitutes contained much larger amounts. As much as 80% of the F^- content of coffee substitutes goes into solution.

On the basis of the above findings we calculated that a person eating an average daily diet would consume between 0.3 and 0.4 mg. This amount rises to 0.5 mg when spinach is included in one of the meals and to 0.7 mg when fish is added. Consumption of polished peas with one of the meals (65 to 100 mg) raises the daily F^- intake to between 1.2 and 1.7 mg. This value is further exceeded when polished rice (150 g) is eaten with the meal.

TABLE 3

F⁻ in Mineral Water, Beer and Milk

	mg F⁻/Liter
Sutttgart City Water	0.13
Stuttgart Beer	0.01
Milk	0.07
Remstalsprudel	0.84
Teinachersprudel	0.78
Bad Mergentheim Albert Spring	0.83
Bad Mergentheim Karls Spring	0.36
Bad Mergentheim Wilhelms Spring	0.82
Mineral Water Nurtingen	0.63
Mineral Water Cannstatt, Mountain	1.52
Mineral Water Cannstatt, Valley	2.13

TABLE 4

F⁻ in Coffee, Tea, Cocoa

	before Infusion mg	after Infusion mg	liter	mgF⁻/l
Coffee Substitute	0.64*	0.13	4.5	0.23
Bean Coffee	0.04	0.04	1.5	0.13
Nescafe	0.14		1.5	0.23
Black Tea				
Assam-Tea	14.36	2.26	8.3	1.59
Ceylon-Assam-Tea	10.08	1.12	4.8	1.92
Indian-Ceylon-Tea	10.78	2.07	5.0	1.87
Peppermint	2.39	1.69	5.0	0.27
Malven Tea	0.31	0.25	5.0	0.14
Rose Hips Tea	0.23	0.18	3.2	0.15
Camomile Tea	0.61	0.58	8.3	0.13
Cocoa				
Nesquick, Instant	0.02		1.5	0.08

*F⁻ in 100 gm dry substance

In Germany, where much mineral water with an average F⁻ content of 1 ppm is consumed even among children, another 1 to 1.5 mg of F⁻ per day is added to the daily F⁻ intake.

The above considerations do not take into account the high F⁻ levels of food in air-contaminated areas near hydrofluoric acid, aluminum, glass,

TABLE 5

F⁻ in Food near HF Factories I and II

	No. of Samples	Average F⁻/kg fresh wt. Near Factory	Normal
Head lettuce	1	7.7	0.4
Leek	1	28.0	0.7
Parsley	1	18.5	0.9
Carrot	1	1.2	0.1
Milk (cow)	369	0.22 (0.04 - 3.65)	0.05
Blood (beef)	214	0.19 (0.06 - 1.55)	0.06
Pear (fruit)	2	1.6	0.1
Sweet cherry (fruit)	1	4.0	0.7
Raspberries (fruit)	1	2.7	0.3
Current (fruit)	1	2.3	0.3
Gooseberry (fruit)	1	3.2	0.3

TABLE 6

F⁻ in Animal and Plant Products in Vicinity of F⁻ Emitting Sources

Contaminated Area		No. of Samples	Average F⁻ mg/kg F⁻ Dry	Normal
Weisweiler Area	Turnip leaf	17	19	8
	Grass	22	15	7
	Red clover	6	20	7
Mannheim Area	Digitalis *	1	31	8
Brick I	Pine Needles *	4	54	3
	Vine	16	295	12
Brick II	Pine Needles *	3	37	3
Brick III	Turnip Leaf	2	40	8
Brick IV	Red Clover	1	46	7
Glass I	Pine Needles *	3	85	3
Glass II	Beech Leaves *	1	2585	10
Enamel I	Red clover	1	1503	7
	Red clover washed	1	101	7
Enamel II	Linden Leaf ●	7	317	14
	Chestnut leaf *	4	408	19
	Sycamore *	3	211	7
	Red beech *	2	316	11
Aluminum I	Grass	30	39	7
	Pelvic bone (beef)	70	2730(A)(36)	150-180(A)
	Bone (beef)	124	5724(A)(37)	800(A)
Aluminum II	Vine leaves *	2	1733	12
	Rib (beef)	1	11300(A)	800(A)
	Pelvic Bone (beef)	1	10700(A)	800(A)
Aluminum III	Tail bone (beef)	1	7085(A)	800(A)
	Thoracic Vertebra	1	7848(A(	800(A)

A = Ash *Visible damage

superphosphate, enamel, ceramic, steel, cement factories and in regions with unusually high coal consumption. Here F^- values proved to be much higher than in uncontaminated areas, as indicated in Table. 5.

In order to obtain accurate results all samples were washed prior to analysis since F^- containing dust present on the surface of leaves and fruit may produce erroneous results. It is generally recognized that F^- uptake through the roots is smaller than that through the leaves. Near a hydrofluoric acid factory, milk contained as much as 5.7 ppm F^- compared with 0.05 ppm in non-contaminated areas.

Fluoride levels in animal and plant products in the vicinity of F^- emitting sources presented in Table 6 show considerably higher levels than normal. In the two industrial areas of Mannheim and Weisweiler no factory with F^- emission is known to exist but the F^- content of the samples from these areas are considerably above normal. This fact can be explained on the basis of air pollution due to burning of F^- containing coal.

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FLUORIDE INTAKE THROUGH TEA IN BRITISH CHILDREN

by

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SUMMARY: In a survey on 662 British school children between 5 and 15 years of age, 92.5% were found to drink tea regularly. The total daily fluid intake per child is 1924 ml. Thirty varieties of tea consumed in Great Britain ranged from 121 to 260 mgF$^-$/kg with an average of 186.1 mgF$^-$/kg or 0.52 mg per cup. The daily fluoride intake from tea in children up to age 15 was calculated to be 1.26 mg as compared to 2.55 mg in adults. The average daily fluoride intake from all other beverages when prepared with fluoridated water is 2.05 mg.

Webb-Peploe and Bradley (1) reported a case of crippling fluorosis with neurological complications in a Hampshire man whose only known exposure to F$^-$ intake was through consumption of tea. Cook (2) observed dental fluorosis in a woman who had been drinking tea since the age of 2. She had never resided where the water had contained an appreciable quantity of F$^-$.

According to Reid (3) F$^-$ in teas ranges from 37.5 mg to 398.9 mg/kg, according to Wang (4) from 57 to 355 mg/kg, according to McClure (5) from 75 to 100 mg/kg, according to Longwell (6) from 66 to 258 mg/kg. Reid determined that in a 2% infusion 81 to 96% of the F$^-$ was extracted from the tea leaves. Longwell found 80% whereas Wang found only 29.1 to 50.5% in the infusion.

Fluoride fed to pregnant rats (7) either as tea infusions or as sodium fluoride passed the placental barrier to the fetus. The F$^-$ levels of the young carcasses at weaning were 2 to 8 times higher than those in controls. The incisors of the young were the only teeth which exhibited minor changes.

According to Clifford (8) tea infusions contain 1.19 ppm F$^-$. Analysis of tea by Harrison (9) yielded 92 to 147 mg F$^-$ per kg. She estimated the daily F$^-$ consumption from tea as 0.45 to 0.93 mg on the basis of 8.1 gm of dry tea consumed per day. She also showed (10) that urinary F$^-$ excretion correlated with tea consumption. The mean daily urinary F$^-$ excretion was 0.52 mg among tea drinkers, 0.27 mg among non-tea-drinkers.

14, St. Alban's Street, Jermyn Street, London, S.W.I., England.

Ham and Smith (11) found 0.92 to 1.26 ppm F^- in tea infusions. Fabre and Campos (12) who determined the ionizable F^- in teas by means of electrodialysis found F^- values of the order of 161.5 to 197.3 mg/kg tea for ionizable F^-. These values correspond closely with those obtained by calcination. They support the fact that the F^- is mainly in an ionized condition. They correspond to 1.62 to 1.97 ppm in a 1% tea infusion. In Sao Paulo teas, Compos found 87.5 to 90.8 mg/kg, but only two-thirds of the F^- was present in infusions. This amount yielded values of 0.4 to 0.6 ppm F^- in a 1% infusion after 6 minutes' contact.

Procedure

In nine schools a pilot survey was carried out on 662 children by means of a questionnaire pertaining to fluid intake, drinking habits, tea consumption and F^- ingestion. In order to avoid undue emphasis on any particular drink the sole information given to the teachers of each class which cooperated in this study was that childrens' drinking habits were being surveyed.

TABLE 1

Drinking Habits in 662 Children

Beverage	Total No. of Children	Children Drinking Beverages Number	%
Water	662	651	98.5
Tea	662	612	92.5
Coffee	662	490	74.0
Lemonade	601	513	85.3
Cola	631	415	65.7
Squashes	606	522	86.1
Milk	628	581	92.5
Others	603	470	78.0

Table 1 presents the percentage of the 662 children who were imbibing the various kinds of drinks. 92.5% of the children were in a habit of drinking as much tea as milk and nearly as much tea as water (98.5%). In computing this table a surprisingly high intake of beer and cider, which was included in the column designated "other drinks", was noted in the Hampstead children at age 9 during the 7 day period covered in the questionnaire.

Table 2 presents the total daily fluid intake of the children. The estimated figures (in brackets) were based on rough averages whenever the returns were incomplete. Incompleteness was taken into account in determining the daily average for each child as indicated in the table.

TABLE 2

Total Daily Fluid Intake

Place	Age	No. of Children	Water	Tea	Coffee	Lemon-ade	Cola	Squa-shes	Milk	Others
			Total Number of Cups (200 ml) per day.							
Gloucester	11-12	31	(74)	74.00	30.00	(30)	(10)	39.14	30.00	25.00
Tonbridge	5	33	(50) 11.50*	50.00	17.00	15.00	15.00	31.00	54.00	(10)
Hackney	10	26	46.14	48.43	18.71	6.71	6.71	(30)	64.00	(20)
Portsmouth	7^3 - 8^3	34	60.00	58.43	27.43	32.00	24.71	35.43	(50)	(25) 74.20**
Hampstead	9^3-10^2	37	89.52	71.80	20.36	20.50	22.50	26.29	76.80	30.57
Consett	10^3	37	174.00	87.43	13.50	19.25	7.11	26.92	82.32	13.89
Annfield	13^3-15^3	66	137.96	170.56	50.98	29.88	30.70	45.07	82.22	37.91
S.E. London	10	30	60.84	45.30	17.71	(17)	20.00	(20)	27.70	17.14
Stanley Jr.	7^4-11^3	92	229.73	201.28	52.98	54.55	33.10	35.87	199.48	61.12
Stanley Sr.	11^4-16^3	313	584.39	791.20	291.20	188.93	109.56	216.63	396.21	221.35
Totals		662	1394.08	1597.84	539.87	366.82	269.39	456.35	1012.73	478.18
Adjusted Totals		662	1506.58	1597.84	539.87	413.82	279.39	506.35	1062.73	459.18
Average /child/day			2.28	2.41	0.82	0.62	0.42	0.77	1.61	0.69

Total fluid intake/child/day = 9.62 Cups = 1924 ml.

Total of beverages made by adding water (water, tea, coffee, squashes) = 6.28 Cups
= 1256 ml

*Incomplete return **Including milk

Figures in brackets included as adjustment to allow for incomplete returns.

At ages 5 to 15 children imbibe an average of 2.41 cups of tea per day, an average of 6.28 cups (1256 ml) of drinks made with water, and an average of 9.62 cups (1924 ml) total fluids per day.

Method of F^- Analysis

In determining the ionized F^- in the tea infusion the following method was employed. A standard means of extraction was set up for the F^- assay in order to obtain a 1% infusion although a 1.65% infusion is customarily used in British households. A weighed quantity of dry tea leaves was added to a measured quantity of F^- free water which was just coming to a boil. It was then kept standing on a suitable hot-plate at the boiling temperature, without boiling. The tea was stirred twice during a ten minute period and the hot infusion poured off through a standard nylon tea strainer into a cup in which it was allowed to cool. A number of measurements indicated that in the average British family, tea was allowed to stand for 10 minutes. The ionized F^- content of the infusion was then determined with an Orion F^- selectrode and a phosphate-citrate-edetate buffer (Electrode and P.C.E. Buffer, Electronic Instruments Ltd.). This instrument was calibrated against pure NaF standard solutions similarly buffered.

Results

Table 3 presents the ionized F^- contents determined by this method. The average F^- levels were 186.1 ppm, 0.32 ppm in a 1% infusion and 0.52 ppm in a 1.65% infusion. With an average daily tea consumption of 2.41 cups for each child, and with an average F^- content of the dry tea of 186 ppm as noted in Table 3, each child ingests an average of 1.26 mg of F^- daily from tea alone, with a range from nil to 4.7 mg. This figure is derived on the basis of a 170 ml infusion per cup to which milk is added to bring the volume up to 200 ml.

Tea consumption in Great Britain is increasing steadily. According to the International Tea Committee, it reached more than 500 million pounds in 1967. With a population at 55,200,000 at mid-year estimate, 9.20 lbs or 4.152 kg were imbibed per head per annum. Based on an available F^- content of 186 ppm, the overall average F^- intake from tea is therefore 2.125 mg per person per day (exclusive of F^- in the water used in preparing the tea).

In children with an average tea consumption of 2.41 cups/day/child, the annual consumption per child is 5.456 lb or 2.471 kg. Since the number of children aged 5 to 15 is 16.48% of the total population, according to the 1966 sample census, this age group which comprises 9.095 million children consumes 49.60 million lbs of tea per year.

We thus arrive at F^- intake in the 5 to 15 year old children of 1.26 mg whereas persons over 15 years consumed 2.55 mg daily from tea alone. Where drinking water is fluoridated at 1.0 ppm children aged 5 to 15 ingest 1.26 mg of F^- from tea plus 1.26 mg from the 1256 ml or 6.28 cups (table 2) of fluoridated water contained in their water-made drinks (water, tea, coffee, squashes), or a daily total of 2.52 mg.

TABLE 3

Available, Ionized Fluoride in Teas, as Drunk

Brand Name	mg F^-/kg or ppm F^-	mg Fluoride per Cup* Infusion 1%	1.65%
Lyons Red Label	121	0.21	0.34
Lyons Green Label	152	0.26	0.43
Lyons Quick Brew	156	0.27	0.44
Lyons Premium	190	0.32	0.54
Typhoo Tea	172	0.29	0.48
Brooke Bond Dividend	128	0.22	0.36
Brooke Bond P.G. Tips	139	0.24	0.39
Brooke Bond Choicest	155	0.26	0.44
Brooke Bond 1/2 Tea	198	0.34	0.56
Brooke Bond 1/- Tea	230	0.39	0.65
Brooke Bond 10^d Tea	241	0.41	0.68
Hornimans Dividend	228	0.39	0.64
Hornimans Home Brew Dividend	228	0.39	0.64
Hornimans Strong Tea	164	0.28	0.46
Co-op 99 Tea	217	0.37	0.61
Co-op Prize Tea	235	0.40	0.66
Co-op Oriental Tips	260	0.44	0.73
Co-op Economy Tea	217	0.37	0.61
Co-op Indian Prince	140	0.24	0.39
Twinings Blu Tips	223	0.38	0.63
Ridgways Country House Tea	167	0.38	0.47
Ceylon Uva Tea	187	0.32	0.53
Ceylon Kandy Tea	162	0.28	0.46
Ceylon Dimbula Tea	128	0.22	0.36
Ceylon Nuwara Eliya Tea	205	0.35	0.58
Tetleys Tea Bags	205	0.35	0.58
Brooke Bond Tea Bags	167	0.28	0.47
Co-op Tea Bags	194	0.33	0.55
Liptons Tea Bags	229	0.39	0.64
St. Michael Tea Bags	157	0.27	0.44
Average	186.1	0.32	0.52

TABLE 4

Available, Ionized Fluoride in Beverages other than Tea

Coffee, fresh ground	0.06
Nescafe Instant Coffee (1%)	0.01
St. Michael Instant Coffee (1%)	0.03
Cadbury's Drinking Chocolate	0.04
Ovaltine	0.07
Coca Cola	0.61
Pepsi Cola	0.10
Schweppes Lemonade	0.07
Schweppes Bitter Lemon	0.49
Kia-Ora Orange Squash	0.07
Rose's Lime Juice Cordial	0.06
Minster Shandy	0.05
Inde Coope Long Life Beer	0.19
Inde Coope Double Diamond Beer	0.41
Inde Coope Light Ale	0.50
Inde Coope Brown Peter Beer	1.02
Inde Coope Nightcap Stout	0.92
Inde Coope John Bull Beer	0.40
Inde Coope Jubiles Stout	0.46
Inde Coope Arctic Barley Wine	0.84
Skol International Lager	0.18
Skol International 2000 Lager	0.20
Skol Liqueur Lager	0.22
Benskins Draught Bitter Beer	0.68
Benskins Colne Spring Ale	0.84
Benskins India Pale Ale	1.00
Worthington India Pale Ale	0.40
Guiness Extra Stout	0.16
Mackeson Beer	0.13
Trumans Trubrown Beer	0.14
Whitbreads Forest Brown Beer	0.15

Individuals above age 15 ingest 2.55 mg F^- from tea plus that in the water used for preparing the tea, namely 0.13 mg if unfluoridated and 0.84 mg if fluoridated at 1 ppm when the tea infusion contains 1.65% of the F^-. In addition they consume F^- in other beverages such as beers, in water drunk as such and in foods. Thus, F^- in tea contributes materially to the daily F^- intake in the British population and might well constitute a hazard to health.

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LONG TERM EFFECT OF FLUORIDE EMISSIONS UPON VEGETATION

by

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SUMMARY: Fluoride determinations over an eight year period in the vicinity of an aluminum factory showed levels 6 times higher in vegetables, 5 times higher in fruit and 2.6 times higher in grain than in normal controls.

For 8 years we have been studying the F^- content of agricultural products near an aluminum factory. Assays were carried out according to the Willard-Winter's titration method (1) which was modified by us (2). Simultaneously we studied the prevailing atmospheric conditions namely F^-

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levels of the air in both solid and gaseous form, F^- in dust, soil and drinking water. Some of our data were recorded elsewhere (3). In children residing near the factory, the average daily F^- intake from air, food and drinking water (4) was 2.1 mg as compared to only 1 mg in a non-exposed group of children.

By determining the F^- content of agricultural plants, we were able to establish the degree of food poisoning in a community. Furthermore, we established at what distance from the factory and in what manner food grown in a contaminated area can affect the health status of a community.

TABLE 1

Total Average F^- Content in Plants 1958-1963

	Controls 12-22 km mgF^-/kg*	3 Villages 2-2.5 km mgF^-/kg	1 Village 0.2-1.0 km mgF^-/kg
Fruit			
Apple	0.3 (60)**	0.7 (70)	1.5 (52)
Pear	0.3 (40)	0.5 (48)	1.3 (36)
Grape	0.5 (32)	- -	2.1 (36)
Cherry	0.6 (40)	0.8 (48)	2.0 (30)
Prunes	0.2 (64)	1.0 (72)	4.1 (32)
Vegetables			
Potato	0.5 (40)	0.5 (40)	0.6 (30)
Carrot	0.6 (64)	0.8 (70)	1.2 (52)
Onion	0.9 (10)	- -	1.5 (10)
Paprika	0.6 (6)	- -	1.4 (6)
Tomato	0.4 (34)	0.5 (20)	1.0 (20)
Cucumber	0.4 (40)	0.4 (50)	0.7 (30)
Cabbage	0.6 (50)	1.0 (46)	5.0 (40)
Head lettuce	1.0 (64)	1.1 (60)	6.4 (40)
Parsley	0.6 (10)	- -	0.7 (10)
Grain			
Barley	1.8 (8)	2.5 (10)	7.8 (16)
Rye	1.9 (36)	2.4 (20)	4.5 (36)
Wheat	2.0 (66)	2.5 (78)	4.0 (86)

*Fresh weight **Numbers of samples in brackets

In this communication we wish to present the results of F^- assays in fruit, vegetables and grain grown in four communities situated near the aluminum factory. Our observations covered the years 1958 to 1965. Control values were obtained simultaneously by examining samples from a non-exposed area about 20 km distant from the factory.

Fluoride values in plants pertain only to a portion of the product. F^- values of dust present on the plant's surface exceed those of the central portion of the plant by 10 times. The specimens of grain were collected at a location between the four communities situated north and south of the source of contamination.

Table 1 shows that the F^- levels in fruit in the community nearest to the factory were 5 times as high as those of controls; in vegetables, they were 6 times as high but in grain only 2.6 times as high as in the controls. In the root vegetables, especially potatoes, only minor changes in the F^- content occurred. This observation agrees with that of Garber (5) who noted that F^- uptake by plants is independent of F^- levels in soil.

In comparing F^- accumulation in tuber vegetables with those of other vegetables and fruit, it was found that in the polluted areas F^- accumulated in the portions of the plants which were growing above the soil rather than in the tubers. This fact points to F^- uptake from the air since the leaves showed higher F^- levels than the portions covered by soil (Table 2).

TABLE 2

Fluoride Content in Different Portions of Plants
(mg% Dry Weight)

	In Peelings		In Fruit		In Seeds	
	Control	In Emission Area	Control	In Emission Area	Control	In Emission Area
Apple	0.28	0.75	0.11	0.18	-	-
Pears	0.24	0.75	0.12	0.15	-	-
Cherry	-	-	0.60	2.20	0.72	0.93
Prunes	-	-	0.24	1.85	0.40	0.48
Cucumber	0.40	1.20	0.14	0.28	-	-
Potato	0.92	1.12	0.37	0.32	-	-
Parsley	0.42	1.00	0.29	0.51	-	-

In plums the average yearly F^- values during 1958 to 1963 ranged from 2.0 to 7.5 mg/kg, in head lettuce and cabbage from 2.6 to 9.2 mg/kg (Table 3). Control specimens of plums contained only from 0.2 to 0.5, those of head lettuce from 0.7 to 1.5 and those of cabbage from 0.4 to 1.0 mg F^-/kg (fresh weight).

TABLE 3

Average Yearly F⁻ Content in Plants in the Most Exposed Community

Year	Fresh Weight mgF⁻/kg Plums	Head Lettuce	Cabbage
1958	7.5 (6)*	6.5 (6)	- -
1959	3.8 (8)	3.0 (8)	7.4 (8)
1960	2.6 (8)	5.0 (8)	9.0 (8)
1961	2.1 (8)	4.1 (8)	9.2 (8)
1962	2.1 (8)	2.6 (8)	8.9 (14)
1963	2.0 (6)	8.4 (6)	4.2 (8)

*Number of samples in brackets

Long-term F⁻ emissions affected fruit and plants in the following manner: 1. There was a distinct decrease in the biological and organoleptic values of the agricultural product (4). 2. The productivity of agricultural plants decreased (5). 3. Fluoride levels of the plants were above normal. 4. Fruit trees deteriorated progressively, particularly those most sensitive to F⁻ such as plum trees and grape vines (7).

We concluded that agricultural plants growing near polluting industries show evidence of damage. Trees as well as fruit are adversely affected by F⁻ emissions.

Our observations formed the basis for remedial agricultural measures taken in the affected area.

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FLUORIDE IN RAINWATER AND VEGETATION

by

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SUMMARY: Fluoride levels of rainwater in industrial areas of Germany ranged from 0.28 mg/l to 14.1 mg/l depending on the kind of industry, the distance from the industrial complexes, and the extent to which coal is used. There was a direct correlation between the magnitudes of F^- in rainwater and F^- in test plants. Plants grown near industrial complexes which process F^- containing raw materials contain as much as 50 to 185 mg/100 grams of F^- (dry) compared to normal averages of 0.7 to 1.5 mg.

The fluoride content of rainwater correlates directly with that of vegetation. Both are largely dependent upon emissions of gaseous and soluble F^- compounds from industrial complexes which employ F^- compounds in their manufacturing processes and use F^- containing raw materials. Furthermore, much F^- reaches the atmosphere through burning of coal which contains from 50 to 550 ppm F^-. Rainwater precipitates F^- from the air and deposits it in the soil. In an area where much coal is being burned, McIntyre et al. (1) calculated that rainwater adds approximately 170 grams of F^- per ha (0.15 lbs. per acre).

At the Bern (Switzerland) railroad station, Von Fellenberg(2) found 0.026 mg/l of F^- in rainwater after a light rainfall as compared with only 0.016 mg/l in a suburb. The soot of a chimney yielded as much as 4.9 mg% water-soluble F^-. He concluded that burning coal emits significant amounts of F^-.

Garber (3) demonstrated that the analysis of rainwater can serve as an indicator of the deleterious effects of F^- emissions upon vegetation. Near metal smelters and fertilizer factories 2 mg/l of F^- were found in rainwater and approximately 10 mg F/100 mg dry substance in the filtered residue. With increasing distance from this industrial complex the F^- levels of rainwater decreased. At a distance of about 2 km, rainwater contained only 0.7 mg F/l.

Fluoride assays of rainwater have proved to be valuable in expert testimony in litigation due to F^- damage. They also constitute a valuable diagnostic tool in the recognition of F^- damage.

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Method

For the collection of rainwater we use a funnel about 30 cm in diameter attached to a 10 liter polyethylene flask which is partially buried in soil or is protected through another appliance from effect of storms (Fig. 1). This equipment is similar to that of Löbner and Liesegang (Wabolu or Hibernia). The fact that only 60 cm can protrude above the surface of the soil instead of 150 cm does not disturb comparative studies.

Result

With the aid of this equipment F^- levels in rainwater were determined in various areas and compared with the F^- content of vegetation. Near a fertilizer factory a sharp increase in F^- values in rainwater was established, especially during the fall and winter months. Table 1 demonstrates the correlation of F^- levels in vegetation with those of rainwater.

TABLE 1

Fluoride in Rainwater and Plants
(Near a Fertilizer Factory)

	Station 1 ca. 500 m ENE *	Station 2 ca 500 m SW**	Station 3 ca 1000 m NE***
	mg F/1 Rainwater		
January	10, 4	2, 5	6, 3
February/March	12, 1	3, 3	6, 0
April/June	6, 8	1, 0	3, 4
August/September	5, 3	0, 79	3, 1
October/November	11, 3	1, 9	5, 3
December/January	14, 1	1, 6	6, 3
Mean	10, 0	1, 85	5, 1
	mg F^- in 100 g plant substance (dry)		
Averages of several plant species	185, 0	20, 5	53, 1

* East North East ** South West *** North East

At Station I, situated near the factory in the direction of the prevailing wind (Fig. 2), the yearly average of F^- in rainwater was 10 mg/l, an unusually high value. At Station II, located at exactly the same distance from the factory as Station I but in the opposite direction, F^- in rainwater was only 1/5 that found at Station 1. At Station III, at a distance of 1000 meter but also in the direction of the prevailing winds, F^- levels in rainwater averaged approximately 1/2 those of Station. I.

The F^- assays of various plant species at the three stations showed the same trend as those in rainwater. Here too, the high F^- content of the air accounted for the increase of F^- in plants. In a hothouse experiment (4) using soil with a high F^- content from the contaminated area, F^- uptake in plants was only 4 times higher than in control plants (5), in contrast to a 22 to 200 fold increase in the F^- values of the plants exposed to airborne F^- near the factory.

Fig. 1

Rainwater Collecting Unit.

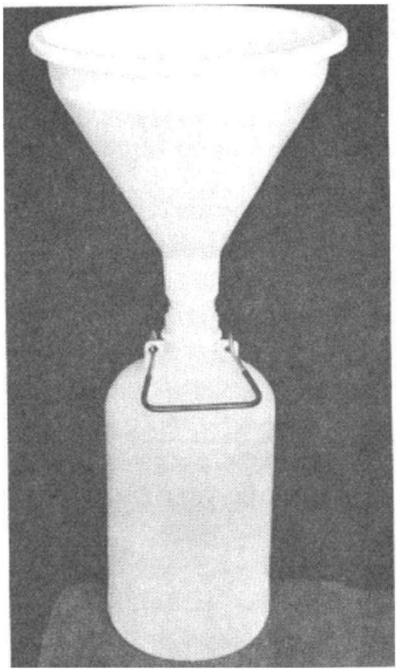


Fig. 2

Station I

Near another fertilizer factory with somewhat different manufacturing processes rainwater gathered close to the factory complex was high in F^- (Table 2), although much lower than in the area shown in Fig. 2. The test plants, mainly bush-beans of the species phaseolus vulgaris, cultivated near the rainwater testing stations showed marked damage by F^- emission. At Station I (Fig. 3) the test plants were completely destroyed in spite of the fact that F^- levels in rainwater were only 10 times higher than those considered normal. These findings suggest that high concentrations of F^- compounds must have entered the plants during brief periods on short-term exposure. The F^- values of the test plants obtained at Station II confirmed this observation. They were unusually high in spite of the relatively low F^- values in rainwater compared to those of Station III. High F^- concentrations in the air, which prevailed temporarily, accounted for the increase in F^- uptake by these plants. In spite of the high F^- content of the test plants at Station II, the necroses were not as extensive as those at Station I. The total magnitude of F^- in rainwater did not increase materially as the result of the short-term high F^- levels in the air.

In industrial areas where no F^- emitting factories are located, F^- values of rainwater were slightly higher than in non-industrial regions. The burning of coal probably accounts for the higher F^- values. In these areas, however, the vegetation showed significantly lower F^- levels than in areas with F^- emitting factories.

TABLE 2

F^- in Rainwater and Vegetation Near a Fertilizer Factory

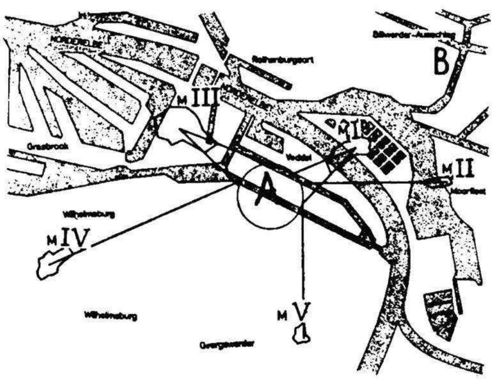
Station	mg F/l Rainwater (3 months)	mg/100 g (F^- Content of Check-Plants)
1	1, 60	----*
2	0, 63	36, 3
3	0, 82	10, 6
4	0, 61	5, 3
Control Point	0, 16	1, 5

*Complete necrosis

Table 3, for instance, presents the F^- values in rainwater and vegetation in one of the most industrialized areas of the city of Hamburg, Germany. Several industrial complexes are located in area A (Fig. 3). Whereas considerable sulphur compounds are being emitted from these factories F^- levels in rainwater as well as in plants are relatively low, considering the high industrial activity in that area. According to table 3, F^- in rainwater collected at Station I is only twice as high as that of the control station.

Fig. 3

Industrial Complexes Located in Hamburg



M: Sampling Stations (Messstelle)

TABLE 3

F^- in Rainwater and Test Plants in Industrial Hamburg

Stations	mg F/l Rainwater (12 months)	mg F/l 100 g (dry matter of 4 plant species)
Station I near area A	0, 41	2, 92
ca. 1000 m NE of industrial area	0, 41	2, 92
Station II (ca. 1800 m from industrial area A)	0, 28	2, 02
Station III Control point out of the industrial and town area)	0, 19	1, 50
Station B (ca. 3000 m North from industrial area A but near several factories)	0, 61	2, 52

The same is true with respect to the F^- content of the test plants (cabbage, broccoli, turnip leaves and spinach). At Station III no correlation between F^- in rainwater and in vegetation was noted.

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HIGH FLUORIDE LEVELS IN A CITRUS GROVE DUE TO A GYPSUM POND DYKE BREAK

by

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SUMMARY: The break of the dam of an artificial lagoon constructed to accumulate the effluents from a fertilizer factory induced F^- contamination in the surrounding area. The effluent water contained up to 5150 ppm of F^- and up to 21,500 phosphates. Levels in soil ranged up to 384 ppm, in leaves of citrus trees from 45 to 86 ppm, in roots of citrus trees up to 1656 ppm.

During the manufacture of phosphoric acid at a phosphate fertilizer plant, calcium sulfate (gypsum) is discharged into large lagoons. The characteristics of this waste are listed in Table 1.

TABLE 1

Characteristics of Gypsum Pond Water

pH	1.6 to 1.8
Fluorides	2810 to 5150 ppm
Phosphates	4260 to 21,500 ppm
Acidity	12,100 to 15,200
Temperature	86 to 96° F.

In addition to its high acidity, this waste contains large quantities of fluorides and phosphates. The ponds, several hundred acres in surface area, usually discharge water through a waste treatment facility during periods of heavy rainfall.

One such facility, located in southwest Florida, had an accidental dam break in August 1967. There are two ponds in the system, a gypsum pond of 160 acres and a cooling pond of 100 acres. The ponds have earthen walls. Their average water depth ranges from 5 to 8 feet. Normally excess water is discharged through a waste treatment facility in which the acid water is neutralized by addition of lime ($Ca(OH)_2$).

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As the result of the dam break, water was discharged from the ponds into an area known as Bishop's Harbor. During this time the phosphate company added lime to the ditch adjacent to the plant at the rate of 10 tons per hour in an attempt to neutralize the waste.

TABLE 2

Fluoride Analysis of Environmental Samples

Location	Fluoride In			
	Soil ppm	Leaves ppm(dry)	Tree Roots ppm(dry)	Tree Roots average size
1	---	46	111	feeder
Live tree	---	--	21	2-4 mmø
adjacent to				
injured trees	---	--	12	5-7 mmø
2	384	58	118	feeder
Injured tree	---	--	15	2-4 mmø
east edge of				
flooded area	---	--	15	5-10 mmø
5	---	70	1, 555	feeder
Tree almost	---	--	538	2-4 mmø
dead, East				
side flooded	---	--	363	5-9 mmø
area				
6	---	--	1, 656	feeder
Dead citrus	---	--	240	2-4 mmø
tree, flooded				
area, near	---	--	59	5-10 mmø
scum 3-4"				
7	155	45	451	feeder
Healthy	---	--	52	2-4 mmø
tree north				
of ditch	---	--	22	5-15 mmø
8	93	142	38	feeder
Skyway	---	86**	11	2-4 mmø
Grove	---	---	11	5-13 mmø

*Summer Flush **Fall Flush
All stations 1/2 mile from the pond.

After the overflow had subsided, samples were collected in a grove approximately 1/4 mile from the phosphate facility. We assayed soil core samples for fluoride from the surface to a depth of 1 foot and samples of roots and leaves of citrus trees in the affected area (Table 2).

The fluoride content of soil samples ranged from 93 to 384 ppm. This level is primarily dependent upon the relation of the sampling station to the depth of the water which covered the ground and the retention of the scum layer in some areas after the water had receded.

At the same locations, samples were taken from the root feeder stock of citrus trees, from roots 2 to 4 mm in diameter, and from roots 5 to 7 mm in diameter.

Table 2 presents the F^- values of the soil of the tree roots and of the tree leaves from eight locations on the property. As the roots increase in size, their F^- contents decreased. Fluoride levels in feeder stock ranged from 38 to 1600 ppm. Root stock 2 to 4 mm in diameter contained from 11 to 538 ppm, and root stock 5 to 7 mm in diameter from 11 to 363 ppm. At stations 5 and 6, exceptionally high F^- values were found in tree root feeder stock due to the higher water depths, to the retention of scum after the water had receded, and to the condition of the trees: one was almost dead and the other was dead.

Fig. 1

Aerial Photo Showing Area of Seepage Wall Break

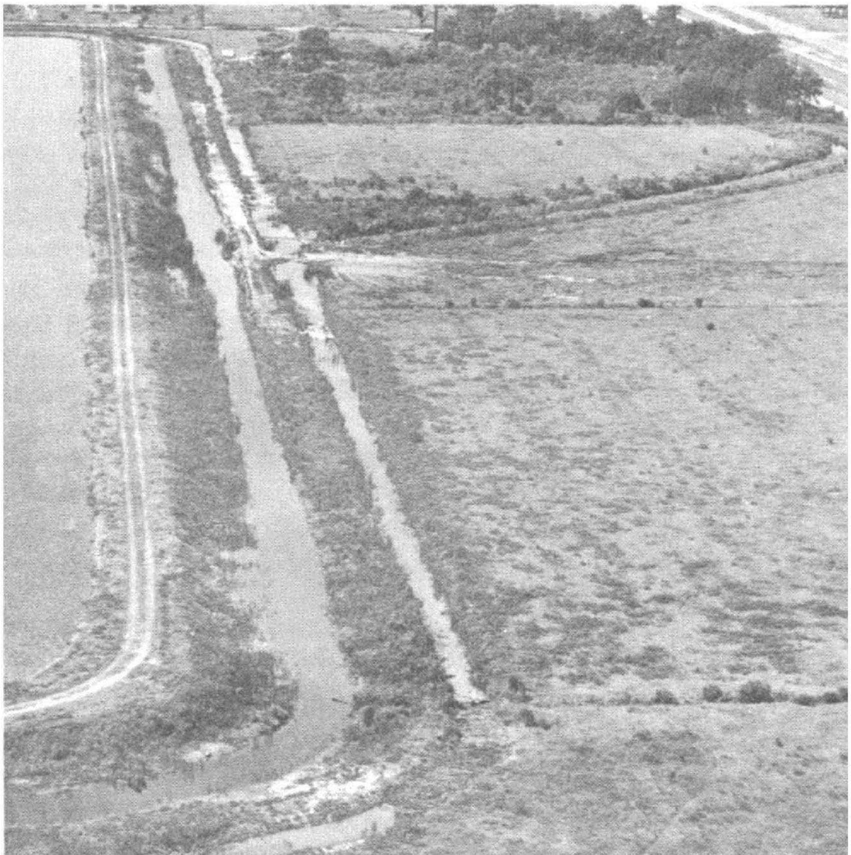

Photo by Tim Murphy

In addition to the sampling of citrus trees, specimens were collected from ornamental trees in the area as shown in Table 3. Fluoride levels of their leaves ranged from 187 to 1222 ppm.

TABLE 3

Fluoride Levels in Ornamental Trees

Total F^- Values in ppm (dry basis)	Ornamental Trees	Leaf Condition
346	Norfolk Island Pine	All green
338	Norfolk Island Pine	Some turning brown
436	Norfolk Island Pine	All dead
567	Papershell Pecan	Mostly green
344	Stewart Pecan	Mostly green
530	Cedar	Some partly dead, mostly green
1222	Cedar	All dead leaves
187	Magnolia	Mostly green
761	Palm	All dead
375	Palm	All green

F^- values in citrus leaves and leaves of ornamental trees are considered normal at levels of 10-30 ppm in spring flush and 30-50 ppm in older leaves.

This incident points up the importance of carefully reviewing plans for the installation of waste treatment facilities for phosphate plants. In addition to the chemical treatment of the effluent waste material, care should be taken in the construction of the dams and in the structural arrangements of the lagoons.

DOMESTIC DEFLUORIDATION OF WATER IN AREAS OF ENDEMIC FLUOROSIS

by

A. H. Siddiqui
Hyderabad, India

SUMMARY: An inexpensive method of defluoridation of water is described at the domestic level in areas of endemic fluorosis. Alum impregnated sulphonated saw dust carbon is used as an ion-exchanger. The saw dust carbon can be easily reactivated at nominal cost after its fluoride removal capacity is exhausted. The exchange unit can defluoridate water (containing 5 mg/l of fluoride) for a family of 5 for about 15 days at the rate of 15 gallons per day.

Removal of fluorides from naturally fluoridated water has been achieved in India with several aluminum treated ion-exchange carbons and anion exchange resins of the quarternary ammonium type. Alum impregnated paddy husk carbon digested with alkali, sulfonated ion-exchange carbons prepared from saw dust, spent coffee grounds, and powdered coconut shell have been employed by various workers in India with a fair amount of success (1-5).

Preparation of Ion Exchange Carbon

Saw dust, a waste material from saw mills is used as a starting material. The saw dust is mixed with concentrated sulphuric acid and left overnight at room temperature to be completely carbonized. The material is then washed free of acid, dried in a hot air oven and sieved (20 to 40 mesh-British Sieve Specification). Active carbon is prepared by treating it with a 2% solution of alum overnight. It is then washed free of excess impregnating ion. Filtered alum is chosen as a regenerant because of its good regenerating capacity and non-corrosiveness. Carbon from saw dust developed by the Central Public Health Engineering Research Institute (CPHERI), Nagpur, India, removes fluoride to the extent of 1600-2400 mg/kg as against 500-600 mg/kg of material in the case of other carbons.

The Unit

An inexpensive defluoridating unit costing about $7.00 has been designed and fabricated by the Central Public Health Engineering Research Institute, Nagpur, for use at domestic level in areas of endemic fluorosis (Fig. 1). The exchange unit is sufficient to defluoridate water containing

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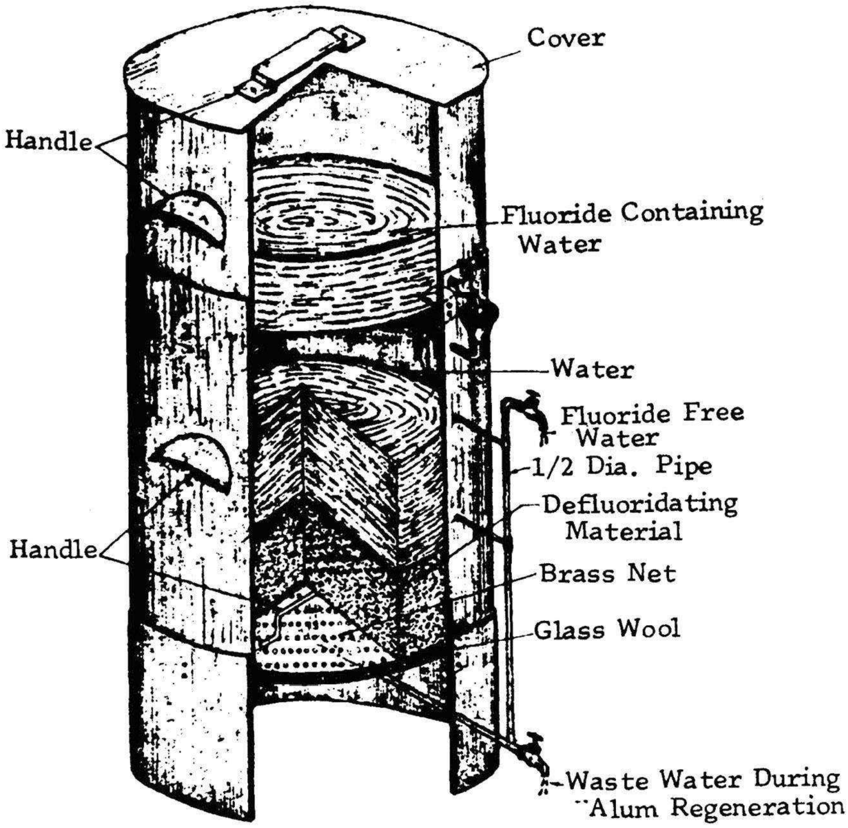
From the Osmania Medical College and Osmania General Hospital.

5 mg/l of fluoride for a family of five for about 15 days at the rate of 3 gallons per day per each member. The material can be easily reactivated after its fluoride removing capacity is exhausted by passing a 1 to 2% filtered alum solution over it. Regeneration cost is nominal.

The unit consists of two vessels made of sheet metal placed one above the other. The upper vessel capacity (approximately 25 liter) is designed to hold the fluoride bearing raw water which is allowed to flow down to the lower vessel at a regulated flow-rate through a tap provided for the purpose. The lower vessel with a capacity of 30 liters contains activated carbon developed and prepared in CPHERI laboratory. The carbon rests on a fine net. A thin layer of glass wool underneath the net acts as a screen and prevents the carbon particles from passing into the filtered water. The treated water can be tapped through a siphon tube which insures the carbon bed to be always covered by water. The total height of the unit is about 40", its diameter 16".

Fig. 1

Defluoridating Unit



Operation

Step 1 - Ion Exchange: About 25 liters of activated carbon is pre-treated with 2 bed-volumes* (50 lit.) of filter alum solution and then washed with 3 bed-volumes of clean water. The carbon is filled in the lower vessel after sufficient glass wool and the screen are put in place. Raw water is allowed to run from the vessel at a flow rate of 300 ml/min. The treated water is collected through a tap on the siphon. The above volume of carbon can treat about 200 gallons of water containing fluoride up to 5 mg/l.

Step 2-Regeneration: The spent carbon can be regenerated by passing 60 liters of 1% filter alum solution through the bed. The solution should be prepared in partially defluoridated water. Its flow rate can be adjusted so that 60 liters are passed through in about 2 hours. Excess alum solution is washed with 3 bed-volumes of clean raw water (fluoride containing water should be used). During regeneration and washing, the bottom tap should be operated. The washed bed can be re-used for defluoridation as before.

The sulphonated saw dust carbon acts as a cation exchanger. Besides the reduction of fluoride content, the pH and alkalinity are lowered and the hardness of water is also removed.

TABLE 1

Composition of Water

	Treatment	
	Before	After
Dissolved solids	718	600
Calcium (Ca)	13	1.2 - 5.0
Magnesium (Mg)	8	0.5 - 2.0
Total hardness as $CaCO_3$	65.5	11.5
Methyl orange	332	120
Alkalinity ($CaCO_3$)		11.5
Phenolphthalein ($CaCO_3$)	60	nil
Fluorides (F^-)	5	0.8
	1	nil
pH	9.1	6.0 - 7.5

Concentration of fluorides can be reduced from 5 to 0.8 ppm and from 1 ppm to nil (1). After a few runs when the carbon is used repeatedly following alum regeneration, the cation exchange character of the carbon will not remain active and the removal of hardness and neutralization of alkalinity will be negligible.

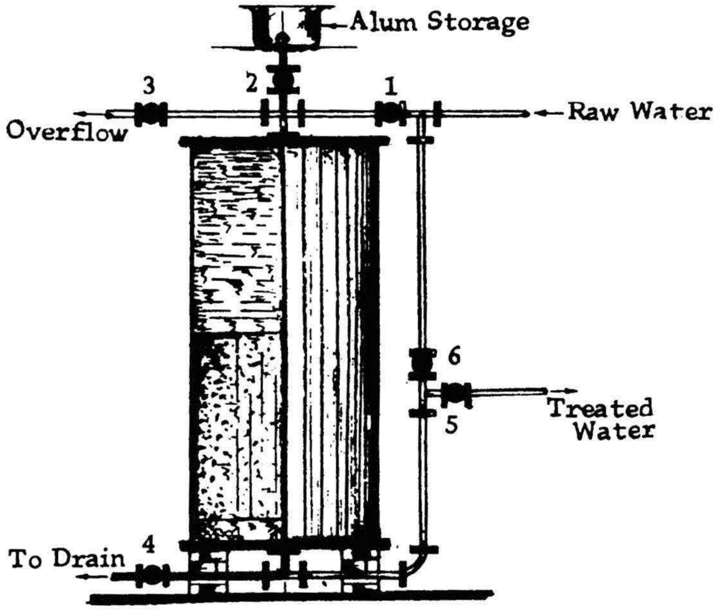
* "bed-volume" is the volume of water needed to fill the carbon bed.

It is remarkable that the fluoride removal capacity of the carbon in the second and subsequent cycles remains at the same level after regeneration.

An improved model of the defluoridating unit manufactured by CPHERI is shown in Fig. 2.

Fig. 2

CPHERI
Domestic Defluoridation Unit



Regeneration	Close Valves	1	3	5	6
Back Wash	Close "	1	2	4	5
Service	Close "	2	3	4	6

Discussion

Alum impregnated sulphonated saw dust carbon is an inexpensive ion exchanger and has been successfully employed for fluoride removal in areas of endemic fluorosis in India. Its fluoride removal capacity is more than 3 times that of other carbons.

The mechanism of fluoride removal is interesting. When soaked in alum, the aluminum ions are retained by the carbon by adsorption. These ions form an insoluble complex with the fluoride ions in the influent water in the exhaustion or the treatment phase. The nature of the complex has been studied by potentiometric titration of alum with fluorides and is formally deduced as $(AlF_6)Al$. The Complex which remains adsorbed on the carbon, is soluble in excess alum. Thus, when the excess alum is run through the bed, during the regeneration phase, the fluorides are removed and the new aluminum ions,which are being adsorbed, render the bed once again capable of removing fluorides.

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I wish to thank the Director, Central Public Health Engineering Research Institute, Nagpur, for his assistance in the preparation of this paper through the Hyderabad Zonal Centre.

FLUORIDE IN POULTRY NUTRITION - A REVIEW

by

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SUMMARY: Relatively high F^- levels in the diet of chickens and turkeys have been shown to decrease growth rate, decrease feed consumption, increase F^- content of egg yolk, decrease the metabolizable energy value of the feed, produce changes in the intestinal tract, increase the iodine content of the thyroid gland with diets low in iodine, decrease or increase bone-ash depending upon the phosphorus level of the diet and F^- level used, and increase the alkaline phosphatase activity of some tissues.

A Mg/F^- interaction has been reported which results in a characteristic leg weakness, depressed growth, reduced bone-ash, and decreased incorporation of ^{45}Ca and ^{32}P into femurs from young chicks. This interaction has not been completely explained.

The basic interest in F^- in poultry nutrition stems from the fact that certain phosphate supplements contain relatively large quantities of this element. A study of the principal phosphate deposits of the world showed F^- to be present in amounts ranging from 2.62 to 4.08% (1).

Early research (2-7) established that a level of dietary sodium fluoride that supplied 0.06% of F^-, or more, reduced the growth rate of chickens. These studies also indicated that a relatively high level of calcium fluoride (0.27% F^-) could be added to the diet without adverse effects. In addition, small amounts of F^- tended to increase bone-ash. Feeding F^- from rock phosphate to laying hens resulted in a distinct increase in the fluorine content of eggs, most of which was in the yolk. These workers felt that growth was inhibited through restriction of feed consumption.

Gardiner et al. (8) reported that 0.08% of dietary F^- from sodium fluoride caused cellular changes in the proventriculus of the chicken. These changes included hypertrophy and hyperplasia of the columnar epithelium of the gland surface. No work was done on any other portion of the digestive system. Creek et al. (9) investigated possible interactions between iodine and fluorine and indicated that high dietary F^- levels appeared to reduce growth and increased the iodine content of the thyroid gland when the diet was low in iodine (below 150 parts per billion).

From Canada Department of Agriculture, Research Station, Lethbridge, Alberta.

Summers et al. (10) concluded that fat enhanced F^- toxicity and that F^- decreased percentage bone-ash at low dietary phosphorus levels but increased bone-ash when the diet contained adequate levels of phosphorus.

Motzok and Branion (11) studied the effect of 0.096% dietary F^- from sodium fluoride on the alkaline phosphatase activity of bone, plasma, liver, kidney, and intestinal mucosa. The phosphatase activity of the plasma and bone was significantly increased, whereas there was no measurable effect on the other tissues studied.

Using turkeys as the experimental animal, Anderson et al. (12) found that growth rate decreased with dietary F^- levels of 200 ppm or more. They also noted a thickening of the duodenal wall, the severity of which depended upon the level of F^- fed. In addition, they found broken feathers on turkeys fed 1600 ppm F^-.

Raica et al. (13) found that F^- administered by water was not more toxic to chickens than F^- added directly to the diet.

In 1961, Gardiner et al. (14) reported that the inclusion of 0.08% F^- and 0.25% Mg in the same diet caused a greater depression in growth rate than the inclusion of F^- alone. Furthermore, the addition of both F^- and magnesium to the diet resulted in a characteristic leg weakness, reduced bone-ash, and a reduction in both the calcium and phosphorus content of the bone. The leg weakness and bone changes were not observed when fluoride or magnesium was added singly to the diet. An increase of the phosphorus content of the diet was without effect upon the toxicity of F^- or the Mg/F^- interrelationship. These findings were confirmed by Griffith et al. (15), who also reported that an increase of the dietary calcium level reduced, but did not prevent, the Mg/F^- interrelationship. In addition, the Mg/F^- interrelationship occurred only when one-day old chicks were fed the experimental diets. Plasma alkaline phosphatase activity in chicks was increased about twofold by added F^- regardless of the dietary magnesium or calcium levels. Dietary Mg or F^- levels did not influence the conversion of 3-phosphoglycerate to phosphoenolpyruvate by muscle homogenates.

Later, Griffith et al. (16) reported on the influence of dietary Mg and F^- on the Mg content of tissues from growing chicks. Their data indicated that bone and liver Mg and total and diffusible plasma Mg were greater in birds fed diets containing high levels of both Mg and F^- than in birds fed diets high in either Mg or F^- alone. Muscle Mg did not vary greatly with the dietary treatment and the Mg content of the heart was remarkably constant.

Spierto et al. (17) studied the Mg/F^- relationship relative to its effect on bone mineralization in young chicks. At an early age (2 to 6 days) chicks fed the high Mg, high F^- diet incorporated less ^{45}Ca and ^{32}P into their femurs 4 hours after intraperitoneal injection than chicks maintained on control, high F^- or high Mg diets. In chicks, 8 to 10 days old, incorporation of injected ^{32}P into femurs was not affected by dietary treatment, but ^{45}Ca incorporation was elevated in the high Mg, high F^- group.

Gardiner et al. (18) using a pair feeding technique observed a significant reduction in growth rate of chickens by feeding F^-. They accounted for the reduction in growth rate by reduced feed consumption (51.4%), decreased metabolizable energy value of the feed (13.3%), and lower efficiency of energy metabolism (33.3%). The remaining 2.0% was not accounted for.

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The Third Annual Conference of the I. S. F. R. will be held at the Botany Institute of the University of Vienna, March 22-25, 1970. Approximately 30 papers are scheduled for the 3 day session.

Registration will start Sunday, March 22, 1970 at 2:00 p.m. at Hotel Michelbeuren, 1180 Wien. A business meeting and reception will be held in the afternoon. Films on fluorosis in cattle and in humans will be shown in the evening.

The morning session of Monday, March 23, will feature papers dealing with new advances in fluoride analysis, physical properties of fluoride compounds and experimental retinitis. During the afternoon session a symposium on Fluoride and Bone Metabolism will take place.

Papers on endemic fluorosis and acute fluoride intoxication are scheduled for the morning session of Tuesday, March 24. The afternoon session will feature papers on poisoning of animals and humans by organofluorides and papers on hydrofluoric acid burns.

Wednesday morning, March 25, will be devoted to fluoride as air pollutant with contributions on its effect upon vegetation, animal life and humans. The sessions will close on Wednesday at 1 PM.

Hotel reservations should be made promptly through Dr. Gottfried Halbwachs, Botanisches Institut XVIII Gregor-Mendel Str. 33, Wien.

ACCUMULATION OF FLUORIDE BY FORAGE CROPS

by

D. C. MacLean, R. E. Schneider and L. H. Weinstein
Yonkers, N. Y.

(Abstract)

The authors studied the relationship between the concentration of gaseous HF in air and accumulation of F^- in timothy grass and red clover.

Method: Portions of an established mixed planting of the two forage plants were covered with 4 portable Mylar-covered fumigation chambers. Each chamber was placed over an area of about 6 m^2. Four kinds of fumigation treatment were employed for a 14-day period:

1. "Low treatment": Continuous HF exposure averaging 1.6 $\mu g/m^3$, with daily averages ranging from 1.1 to 2.5 μg F^-/m^3.

2. "High treatment": Continuous HF exposure averaging 7 μg F^-/m^3 with daily averages from 4.1 to 11.1 μg F^-/m^3.

3. "Intermittent treatment": HF was injected into the chamber and then withheld at alternate 48-hour periods. This resulted in a total of four 2-day exposures during the 14-day period. The average daily concentrations during the periods of HF exposure ranged from 2.2 to 6.4 μg F^-/m^3, with a mean concentration for the entire 14-day period of 1.9 μg F^-/m^3.

4. "Control treatment": Exposure of the two forage crops to filtered ambient air with an HF level of less than 0.2 μg F^-/m^3.

Forage samples were analyzed for F^- just prior to HF exposure and at 2 to 3 day intervals thereafter. The composite unwashed samples from each chamber were analyzed for F^- at each of the sampling dates by means of a semi-automated method of analysis.

Results: Forage exposed to the high HF treatment accumulated F^- rapidly, namely more than 100 ppm within three days and about 400 ppm by the end of the 14-day exposure period. The F^- content of the control plants never exceeded 6 ppm.

Intermittent F^- fumigation caused greater F^- accumulation by the forage plants than continuous low exposure. The peak concentrations in the intermittent exposure were much more influential in the accumulation of F^- in the forage than chronic exposure with comparable concentrations.

From the Boyce Thompson Institute for Plant Research, Yonkers, New York.

The plants exposed to the high exposure which accumulated relatively high F^- concentrations, also showed severe HF induced leaf symptoms whereas forage given the "low treatment" showed mild injury and contained the lowest amount of F^-. However, there was a dissimilarity in the rate of F^- accumulation between the continuous low and the intermittent HF exposures at the end of the exposure period. The plants exposed to intermittent HF fumigation accumulated more F^- than those subjected to the low fumigation but showed no greater leaf damage. In both treatments the leaf blades exhibited mild tip necrosis and moderate marginal chlorosis which was more pronounced in leaves of timothy than of red clover. These changes were most severe after the high F^- treatment.

The authors felt that the intermittent exposure may have provided sufficient time for detoxification of absorbed F^-. During periods when the HF fumigation was discontinued, absorbed F^- was possibly complexed at cationic sites and thus accounted for less toxic F^- concentrations within the plant tissue.

RESORPTION AND RETENTION OF FLUORIDE PRESENT IN MINERAL WATERS AND SOFT DRINKS IN HUMANS AND EXPERIMENTAL RATS

by

K. Rub
Bukarest, Romania

(Abstracted from Inaugural Dissertation, Medical Faculty, Würzburg, 1968)

The author reported F^- assays on 101 mineral waters and 9 soft drinks which are in general use in the German Federal Republic. The soft drinks averaged less than 0.4 ppm F^-. Of the mineral waters, 72.5% contained from 0.10 to 0.69 ppm F^-, 10% from 0.7 to 1 ppm F^- and 17.5% above 1 ppm F^-. In two springs in Bad Aachen the F^- levels were as high as 4.81 and 6.27 ppm F^- respectively and spring water of the well-known spa of Baden Baden contained 9.98 ppm F^-.

On the basis of available figures the author estimated that in Germany the average yearly consumption of mineral water with more than 0.7 ppm amounts to 6000 ml/head.

In 11 adults the author examined 24-hour specimens for F^- during a four week period. She concluded that F^- absorption from these drinks is as prompt as absorption from tap water. After drinking F^- containing mineral water, rats accumulated as much F^- in bones and teeth as control rats which were given tap water with the same F^- concentrations. In general, alkaline waters showed higher F^- values than water rich in carbon dioxide. The highest F^- concentrations were noted in waters of thermal springs.

The mineral waters with the highest F^- content presented by the authors appear in the following table:

Springs of	F^- Content
Zurzach	9.8 ppm
Stabio (Tessin)	2.5 to 7.4 ppm
Baden (Switzerland)	3.3 ppm
Leukerbad	2.1 to 3.1 ppm
Plombière (France)	9 to 12 ppm
Vichy, Hauterix, Saint Yorre	5 to 8.7 ppm
Labassere	6 ppm
Saint Honoré, LaPrest and Eaux-Bonne	4 ppm approx.

EFFECT OF EMISSIONS FROM AN ALUMINUM PLANT ON CHILDREN'S HEALTH

by

Kvartovkina, L.K., Kazanskaya, R.M., Kantemirova, A.E., Kryukov, A.S., Kuleva, N.P., Meerson, E.A. and Tarannikova, O.I.
Volgograd, U.S.S.R.

(Abstracted from Gigiena i Sanitariya 33:94-96, 1968)

This paper presents an account of the health of children living withinin 500, 1000 and 1,500 meters of a Russian Aluminum Plant. In addition to F^-, SO_2, CO, tar and coal dust were emitted from the plant. Air samples showed F^- levels 15 times higher than the maximum allowable concentration. Pollution was detectable at distances 5 to 9 km from the plant. Vegetation in the area had died. Growth of fruit trees and production of fruit was reduced.

The main complaints of persons living within 500 to 1000 meters were headaches, nausea and cough. Particularly the children of the area showed a high incidence of upper respiratory disease, especially bronchitis, pneumonia and laryngitis. In children four and five years of age born before the aluminum plant began to operate, the incidence of respiratory diseases was 3 to 7 times higher than in the control group in a non-polluted area. As the children grew older, the incidence of respiratory diseases decreased.

From the Volgograd Institute of Medicine, U.S.S.R.

Altogether, 113 nursery school, 186 preschool and 150 school children up to age 12 residing in the polluted area, were examined and their health compared with that of a similar control group. The exposed nursery school children showed an increase in RBC values, significantly lower hemoglobulin levels and higher eosinophil counts (the last-mentioned only in winter). The 3 to 7 year old exposed children manifested a decrease of the RBC and hemoglobin throughout the year, but a higher eosinophilia and ESR. In the children above age 7 no difference between the two groups in the RBC and WBC was noted. The exposed children had lower blood sugar values. The phagocytic activity of leukocytes was suppressed by 18 to 30% in the 4 to 12 year old children of the exposed group.

In general, exposure to F^- resulted in a higher morbidity among the younger children whereas in the older age group functional changes were more apparent.

THE ACTION OF PHENYLMETHYLSULFONYL FLUORIDE ON HUMAN ACETYLCHOLINESTERASE, CHYMOTRYPSIN AND TRYPSIN

by

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San Francisco, California

(Abstracted from J. of Pharm. and Experimental Therapeutics 167:98-104, 1969)

Acute hemorrhagic pancreatitis is believed to be associated with autodigestion of pancreas tissue by prematurely activated pancreatic proteolytic enzymes. Reports in the literature indicate that phenylmethylsulfonyl fluoride (PMSF, formula: $C_6H_5CH_2SO_2F$) and related compounds inactivate trypsin and chymotrypsin (from bovine tissues) without affecting acetylcholinesterase. The authors studied the action of PMSF on human enzymes and its toxicity in vivo.

Purified human chymotrypsin (5.1 μg in 3 ml total volume isopropanol-water), isolated from fresh cadaver pancreas, was rapidly deactivated (100% after pre-incubation for 60 min. at 30°C) by 10^{-3} M PMSF. Under similar conditions human trypsin activity (0.46 μg) was only 30% inhibited, but acetylcholinesterase (0.83 U in isopropanol(from human erythrocytes showed marked inhibition, detectable even at 10^{-7} M PMSF as shown in the following table.

From the Molecular Biology Division, Veterans Administration Hospital, 4150 Clement Street, San Francisco, California 94121, and from the Department of Bio-chemistry, School of Medicine, University of California, VA Hospital; and the Department of Pharmacology, School of Dentistry, University of the Pacific.

Concentration of PMSF ($\underline{M}$)	% Inhibition of Acetylcholinesterase	
	30 min	60 min
10^{-3}	100%	100%
10^{-4}	75	92
10^{-5}	25	40
10^{-6}	6	15
10^{-7}	0	5

After pre-incubation with PMSF at 30°C for: (assays at 25° with acetylcholine substrate)

Similar data are presented for crystalline bovine trypsin (4.9 μg) and chymotrypsin (9.0 μg), each in a total volume of 3 ml isopropanol-water:

Concentration of PMSF ($\underline{M}$)	% Inhibition of trypsin after pre-incubation for:		% Inhibition of chymotrypsin after pre-incubation for:	
	30 min	60 min	30 min	60 min
10^{-3}	96%	98%	100%	100%
10^{-4}	60	74	100	100
10^{-5}	16	27	79	79
10^{-6}	0	0	21	40

In agreement with previous findings by A. M. Gold and D. E. Fahrney (Biochemistry 3:783-791, 1964), 0.01 ug (1.73 U) of acetylcholinesterase from the electric eel, the classic source of this enzyme, showed no detectable inhibition when pre-incubated with 10^{-3} $\underline{M}$ PMSF for 90 min. at 30°. This is one of the first major differences to be demonstrated between acetylcholinesterase sources and from the electric eel. The sensitivity of mammalian esterases to PMSF is in the order: bovine chymotrypsin human red cell acetylcholinesterase bovine trypsin.

Experiments with C^{14}-labeled PMSF indicated that the inhibitor reacts readily with membrane-bound cholinesterase in intact erythrocytes and freely passes the blood-brain barrier. In toxicity studies, PMSF showed an LD_{50} in mice i.p. of 200 mg/kg. * In addition, in an *in vitro* test on rat phrenic nerve-diaphragm preparation, it showed no neuromuscular blocking effects i.e. no interference with synaptic transmission.

*Abstractor's note: This amount of PMSF contains 22 mg of fluoride, which is in the range commonly accepted for the acute i.p. lethal dose of F^- in mice (c.f. N.C. Leone, F.E. Geever and N.C. Moran, Pub. Health Rep. 71:459, 1956).

The authors conclude that the strong inhibitory effect of PMSF on human acetylcholinesterase together with its relatively low affinity for human trypsin create serious limitations to its potential use as a therapeutic agent for the treatment of acute pancreatitus.

A.W.B.

INFLUENCE OF WELL WATER SALINITY AND FLUORIDES ON KEEPING QUALITY OF "TROPICANA" ROSES

by

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The authors investigated the influence of dissolved salts ($MgSO_4$ and NaCl) and fluorides (F^-) on the keeping quality of "Tropicana" roses.

Roses harvested in the tight bud stage were cut to 9 inches in length and the stems placed immediately in 500 or 800 ml of solution at $75^oF \pm 4^o$ under a light intensity of 100 foot-candles. Each experimental unit consisted of 3 stems and was replicated 3 times. Total soluble salt contents of well waters were estimated by means of a solu-bridge and conversion chart based on KCl as a standard. F^- was determined by the method of E. Bellack and P.S. Schouboe (Anal. Chem. 30:2032-2034, 1958).

Effects of holding solutions were estimated after 4 days by a toxicity index based on the following scale:

10.0 - normal bud opening with no marginal petal discoloration
7.5 - moderate petal discoloration and slight retardation in opening
5.0 - 50% reduction in opening ability and marked petal discoloration
1.0 - little floral development with severe petal burn

For commercial purposes a rating of 8.5 or greater was considered desirable. Results are summarized as follows:

Well water sources.- The degree of toxicity of well waters appeared to be more closely associated with F^- content than with salinity levels. For example, roses in water from Oneca well No. 1 with 275 ppm salts and 3.0 ppm F^- had a rating of 4.9 on the toxicity scale whereas roses in water from the Palm Sola well with 1540 ppm salts and 2.7 ppm F^- had a rating of 5.3.

Effects of salinity. - In contrast to its appreciable effect on chrysanthemums (W. E. Waters, Proc. Am. Soc. Hort. Sci. 92:633-640, 1968), water salinity appeared to be a minor factor in reducing the keeping quality of cut roses. Factorial combinations of $MgSO_4$ and NaCl in distilled water showed only slight reduction in bud opening ability and mild discoloration of petals, visible after 3 to 4 days. Water uptake was not significantly affected by either salt.

Effects of fluoride. - As indicated in the table below, the keeping quality of cut "Tropicana" roses decreased markedly as F^- levels in the holding solutions increased from 0 to 7 ppm F^-. Because the toxicity associated with F^- in well water was significantly more severe than from F^- in distilled water or in laboratory-prepared salt solutions, evidently other factors in the well waters enhance F^- toxicity symptoms. In distilled water the uptake of water decreased in the presence of F^- independently of its concentration.

Influence of F^- in Holding Solutions on Rose Quality Index

	Quality Index (see above)	Water Uptake (ml/100 g)
Distilled Water	9.8	253
1 ppm F^- in Dist. Water	8.2	200
3 ppm F^- in Dist. Water	6.5	207
5 ppm F^- in Dist. Water	6.0	210
7 ppm F^- in Dist. Water	5.5	200
Oneca No. 1 Well (3 ppm F^-)	4.2	147

Combined effects of F^- and salinity. - Factorial combinations of F^- (0, 1.5, and 3.0 ppm) and salinity levels (0, 600, and 1200 ppm total salts in a ratio of 1:1:2!4 $CaSO_4$, $CaCl_2$, $MgSO_4$, and NaCl, respectively) showed that F^- was the main factor in reducing the keeping quality index of cut roses in water. In these experiments the depression in water uptake by F^- was not satistically significant.

In summary, it was found that the keeping quality of cut "Tropicana" roses decreased greatly as the dissolved F^- level increased in the holding solutions but decreased only slightly as the total salts increased. F^- induced marginal petal discoloration and deterioration and retarded the opening and development of buds. Similar findings are cited for cut gladiolus flowers (W. E. Waters, Proc. Am. Soc. Hort. Sci. 92:633-640, 1968).

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