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CONTENTS

GUEST EDITORIAL

ORIGINAL ARTICLES:

SPECIAL REPORT

ABSTRACTS

The Fourth Annual Conference of the I.S.F.R. will take place at The Hague, Holland, at the Royal Institute for Engineers Sunday, October 24 to Wednesday, October 27, 1971.

The Program Committee is soliciting abstracts in English, French and German of papers to be presented dealing with any phase of fluoride research. The deadline is July 15, 1971.

Kindly mail abstracts confined to 300 words or less to Dr. Philip Zanfagna, 163 Lawrence St., Lawrence, Massachusetts 01841. Reservations for the conference will be made through the secretary's office.

As of Jan. 1 the offices
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MANUSCRIPTS for publication should be submitted in English, double-spaced with generous margins. References should be arranged according to the order in which they are cited in the text, and written as follows: Author, title, journal, volume, pages and year. Each paper must contain a summary of not more than 20 lines.

Contributors will receive 10 copies of the issue of FLUORIDE containing their paper, free of charge.

FLUORIDE is listed in
Current Contents Agricultural
Food and Veterinary Sciences

GUEST EDITORIAL

DIETARY FLUORIDE INTAKE IN THE USA

During the past two decades the dietary F^- intake in North America appears to have increased four or five fold.

In the 1940's and early 1950's the total F^- intake* in North American communities using low F^- water was estimated to average 0.3 to 0.4 mg or less per person per day (1, 2, 3). In essence this value represents the estimated baseline F^- intake prior to, or coinciding with, the post World War II industrial boom and with the inception of community water fluoridation programs. (A range of 0.5 to 1.5 mg for the "normal" daily dietary F^- intake was reported in 1939 by Machle, et al. (4); however, subsequent investigations indicated those F^- analyses to be unusually high (5).)

A 1954 report noted the F^- intake from food (by actual analysis) in Toronto, Canada to be as high as 0.79 mg per person per day (6). In 1965, it was estimated that the normal daily dietary intake in the U.S.A. ranged up to 1.5 mg for areas with no appreciable F^- in their water supplies (7). The progressive four to five fold increase in the maximum clearly suggests that increasing amounts of F^- are entering the food chain of communities where water supplies contain little or no F^-.

At first glance it would appear that fluoridated water would add 1 mg per day to an individual's total dietary F^- intake. This value is based upon the assumption that one liter per day of fluoridated water is consumed in addition to the diet. The problem is not so simple, however, because home or commercial processing of food in fluoridated water greatly increases its F^- content. As recently shown by Marier and Rose (8) such processing may increase the F^- content of some foods about three times the initial value, as an average. Marier and Rose estimated that the preparation and processing of food in fluoridated water would add, on the average, an additional 0.5 mg per day to an individual's F^- intake. Thus the maximum intake for a person in a fluoridated community, assuming he drank only one liter of water or beverages prepared with fluoridated water, should be 3 mg (Table 1).

Marier and Rose (8) determined that some healthy individuals among the seven laboratory workers in their study group consumed as much as two to three liters of beverages per day. Thus these individuals had an estimated intake of

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*Total F^- intake is here defined as arising from food plus water. Fluoride intake from breathing F^- polluted air or occupational exposure is not included for lack of data. Such intake is probably small for the majority of the population. However, under appropriate conditions, these sources may be major contributors to total F^- intake.

TABLE 1

Maximum Intake for a Person in Fluoridated Community Drinking One Liter of Water or Beverages Prepared with Fluoridated Water

F^- Contained in	mg
Food	1.5
Food processed and prepared in F^- water	0.5
Drinking one quart of F^- water	1.0
Total Daily Intake (mg)	3.0

4.0 to 5.0 mg of F^- per day. Of the seven persons, the estimated average maximum intake was 3.6 mg per day. This estimated level of maximum total F^- intake in fluoridated Ottawa, Canada is nine to twelve times that of the base for a non-fluoridated city in the late 1940's and early 1950's.

At this point, the major identifiable single contributor to the increasing F^- intake is fluoridated water. The Food and Drug Administration cautions against the prescription of 1 mg F^- tablets to children in areas where the F^- level in water is above 0.7 ppm (0.7 mg per liter). It limits to 0.5 mg per day the quantity of F^- that can be added to food (9), and to 7 ppm the F^- insecticidal residues on foods (10). Krepkogorsky has recommended that the total adult F^- intake should not exceed 3.2 mg per day (11). His suggestion is based upon a review of worldwide intake data (water plus food) collected by himself and others.

A recent study by Spencer, et al. (12) has confirmed the level of total F^- intake estimated for fluoridated communities as outlined above. They obtained by actual dietary analysis a range of 3.6 to 5.4 mg (average 4.4 mg) per day F^- intake in fluoridated Chicago.

The question arises: Can the F^- content in water any longer be used as a baseline for our daily F^- intake? Indeed, in fluoridated communities, the previous assumption that the major portion of the total F^- intake would arise from the consumption of one liter of water no longer holds true. In such communities food now either equals or exceeds water in its contribution to the total F^- intake.

Even in nonfluoridated communities the baseline F^- level in food appears to be rising. Factors which influence the F^- content of the diet are contamination of food plants and animal forage due to release of F^- into the environment by industrial activities, use of F^- containing pesticides on food crops, the processing of foods with F^- containing water, and an individual's choice of foods. Fertilizer use is also an important factor (13).

As more cities of North America are fluoridated, an increasing percentage of the food will be processed with fluoridated water, thus adding substantially to the dietary F⁻ intake. In addition, the dramatic increase since the 1940's in the number and size of aluminum reduction and phosphate fertilizer plants along with other F⁻ emitting industries are adding to the F⁻ burden of food crops. There have been numerous reports of F⁻ damage to vegetation (14, 15,16). Marketing of F⁻ polluted crops would certainly increase the amount of F⁻ in the food chain. Examples of such high values are presented in Table 2.

TABLE 2

Examples of Fluoride Values in Food Grown in Polluted Areas*

Food	F⁻ levels (ppm) Contaminated (fresh wt)	Normal** (fresh wt)	Source
San Jose Raspberries	54	0.3***	(17)
Spinach	16	0.2 - 1.8	(18)
Lettuce	62	0.3 - 1.92	(18)
Beans (cooked)	17.3	0.11-0.13	(19)
Lettuce	44	0.3 - 1.92	(19)
Potatoes	20-30	0.07 - 0.2	(13)
Sugar beets	30-50	3.3 (dry wt)	(13)
Peaches	3.1-21.9 (dry wt)	0.21	(20)

*The water content of these foods ranged from 75 to 90%. Conversion of a fresh weight value to dry weight for comparison purposes may be approximated by multiplying the fresh weight value by seven.

**From F.J. McClure, Fluoride in Foods, Survey of Recent Data, Pub. Health Reports, 64:1061, 1949.

***From W. Oelschläger, Fluoride, 3:6, 1970.

In industrialized Germany Oelschläger (14) estimated the average daily F⁻ consumption through food, based upon his current analyses, to be 0.3 to 0.4 mg. The samples were selected so as to exclude those that might be contaminated by industrial and coal burning sources. Moreover, food processed in fluoridated water was not included. When samples were taken in the vicinity of F⁻ emitting industries or from coal burning areas their F⁻ content was considerably elevated.

Over the past two decades changes in food processing in North America may be partially responsible for increased total F⁻ intake. Diets now contain a higher proportion of processed foods, especially foods requiring either reconstitution with water or the addition of water for preparation. The use of fluoridated water in the processing or reconstitution procedures will obviously increase the F⁻ content beyond the original amount.

The evidence indicates that a F⁻ build-up is in progress in the North American food chain which is exposing considerable number of citizens to an intake above safe levels. There is a genuine need for more data to help determine the magnitude and extent of the upward shift in total F⁻ intake. The contributory factors need to be identified and the extent of their influence determined.

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DETERMINATION OF FLUORIDES IN POLLUTED AIR BY USE OF AN ION SPECIFIC ELECTRODE

by

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Rome, Italy

SUMMARY: The analytical determination of fluoride in samples of various nature has been greatly simplified by the use of an ion membrane electrode, which is selective and specific for fluoride ion. Its main advantage is the elimination of a lengthy distillation procedure for the separation of fluoride. The determination of fluoride is performed either by direct potentiometry or by a potentiometric titration.

In the application of this method to air pollution, the air is filtered through a suitable medium. The collected material is dissolved in water. According to the amount of air which is pumped and the extent of pollution, a fluoride concentration in the range 0.1 ppm up to several ppm is obtained.

In this range, the ion selective electrode yields a linear response proportional to the fluoride activity. With respect to the total fluoride concentration, the direct potentiometric measurement is not satisfactory due to interference of other ions which affect the fluoride activity. In assays of polluted air, particulate matter which collects on a filter contains fairly large amounts of aluminum, iron, calcium and other ions which form complexes with fluoride. A precise and convenient procedure, in very dilute solutions, is the potentiometric titration with a standard solution of NaF and the plotting of the experimental values with the Gran's function. By the use of the Gran's plot it is possible to obtain information on the amount of interfering actions. The operational details of the method are discussed.

The availability of ion selective electrodes, indicators of the activity of the corresponding ions, offers the possibility to develop fast and accurate analytical procedures.

The analytical determination of fluoride in samples of different nature, such as tap water (1), phosphate rock(2), biological samples (3), bone (4), tungsten (5), chromium plating baths (6), enamel of teeth (7), saliva (8) and air and stack gases (9) has become greatly simplified by the use of a membrane selective electrode specific for the fluoride ion.

From the Istituto di Chimica Analitica, Universita, Direttore Prof. Arnaldo Liberti, Rome, Italy. ****

Presented at the Third Annual Conference of the I. S. F. R., Vienna, 3/22-25/70.

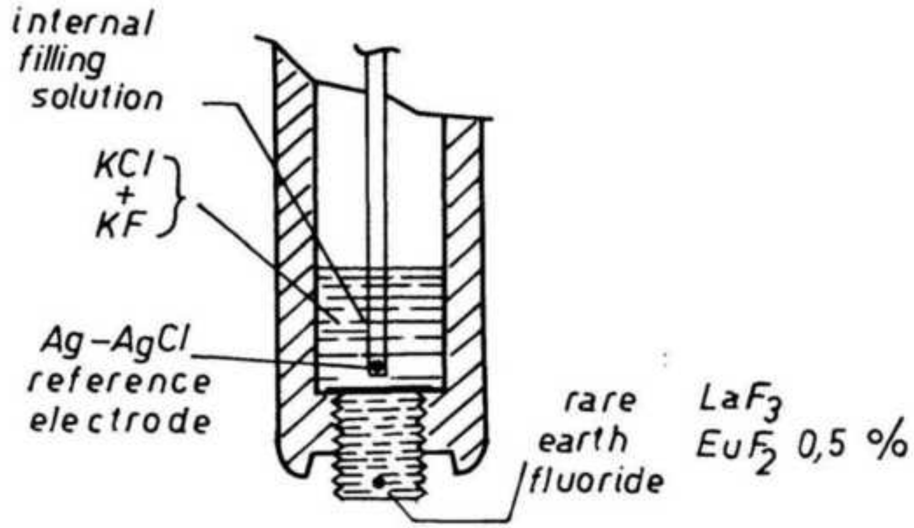
This research deals with an improved procedure for fluoride evaluation in air and stacks and shows how polluted air can be continuously monitored by the above procedure.

The main advantage of the electrometric determination with this electrode is the elimination of time-consuming steps such as the fluoride distillation from perchloric or sulfuric acid to remove interferences. Moreover, the analysis can be carried out in the presence of large amounts of foreign substances.

The Orion-fluoride electrode is constructed using a single crystal membrane of lanthanumfluoride doped with about 0,5% (mole) of EuF_2 (Fig. 1); the membrane is sealed in the end of a rigid epoxy tube. Within the tube there is a silver-silver chloride electrode and a 0,1M NaF and 0,1M KCl electrolyte as reference.

Fig. 1

Fluoride Ion Activity Electrode



The electrode responds to variations of activity of the fluoride ion of the liquid sample in which it is dipped and the potential measured, depends upon the fluoride activity of the sample solution. The potential values are measured with an external reference electrode such as a saturated calomel electrode on an expanded scale pH meter. The potential measured follows the Nernst law, and at 25°C,

$$E = E^o - 0,059 \log a_{F^-}$$

where E is the measured potential of the total system, E^o the standard potential of the system which depends upon the reference system (internal and external) and a_F is the fluoride ion activity in aqueous solution.

The response of this electrode to fluoride concentrations is linear to the range 5×10^{-6} M to 1×10^{-1} M (0.1 - 1,900 ppm).

Three major points should be considered for proper use of the electrode:

a) the ionic strength of the solution affects the activity of the F^- ion, and is thus a primary interference;

b) the electrode response is also pH dependent as hydroxyl ion may pass through the crystal membrane. By working in the pH range 5 to 8, the OH^- concentration is however sufficiently suppressed to prevent its interference.

c) The presence of species in solution which may complex F^- such as iron and aluminum ions affect the electrode response, which indicates only the free F^- ion.

The procedure commonly adopted to minimize these interferences and to determine the total concentration of F^- is the dilution of the sample with a buffered solution of a high ionic strength and a high concentration of ligands ions, e.g., sodium citrate 1M (10).

Furthermore, to obtain a higher precision namely in very dilute fluoride solution, it has been suggested (11) to carry out the potentiometric titration with a standard solution of NaF and to obtain the equivalence point by plotting the Gran's function (Fig. 2). (For details of this calculation consult reference 11).

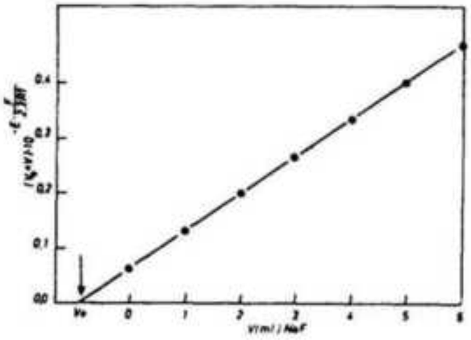
The fluoride determination in the air and in stack gases is of great importance in order to control pollution and prevent damage to animals, vegetation and to working people. The most common sources of fluoride pollution are the phosphate fertilizers, the aluminum, steel, and ceramics manufacturing plants. In some cases, the fluoride emission in the atmosphere occurs together with large amounts of aluminum or iron. This necessitates taking into account the above-mentioned limitations on the use of the fluoride electrode.

Experimental

Total fluoride, gaseous and particulate in ambient air or in stack effluents can be sampled by drawing air on membrane filters impregnated with sodium formate. They were prepared by immersing cellulose acetate filter sheet in 50% ethanol solution containing 10% sodium formate. By means of a high volume pump about 200 m^3 are drawn through the filter to obtain 2-100/µg fluoride; by dissolving this amount in 20 ml of an aqueous solution, a concentration in the range 0.1 to 5 ppm fluoride ($5 . 10^{-6}$ to 10^{-4}M) is obtained which can be satisfactorily measured by the fluoride electrode.

Fig. 2

Determination of Fluoride of 20 ml of 5.5 x 10^{-5} M Fluoride
Fluoride Standard Solution Added was 10^{-3} M NaF



As the aluminum or iron concentration is (in weight) 10-100 times larger than fluoride, a variety of solutions have been tried to overcome the limitation due to the binding of fluoride by the mentioned cations.

Figure 3 presents the results obtained by titration of 20 ml of a sample solution containing 0.5 ppm of fluoride in the presence of 0; 0.5; 5; 50; 500 ppm of Al; the titration was carried (a) in the absence of any complexing agents (b) in the presence of TISAB (total ionic strength adjustment buffer consisting of NaCl 1M, Sodium citrate 10^{-3}M, acetate 0.5M) and (c) in the presence of 1M monosodium citrate and sodium hydroxide.

The plot of the experimental values of the potentiometric titration with the Gran's function should be a straight line. If the experimental points do not lie on a straight line, fluoride is bound to the cations present in the solution. In the presence of a solution with a high concentration of citrate, deviations from linearity are negligible. This solution is the most satisfactory for determining fluoride and can be used up to a ratio Al:F of about 100:1; 0.1 ppm fluoride can be determined with about 5% error.

The fluoride content of stack gases can be determined with the same procedure, a shorter sampling time being required because of the higher concentration which is measured.

The fluoride electrode may be used as well to monitor continuously the fluoride concentration of stacks. Stack gases are made to bubble into a cell containing the citrate solution where the fluoride membrane electrode and a saturated calomel electrode connected to a recorder are located.

In order to obtain the higher sensitivity from the detecting device, a fresh absorbing solution is always used, which is continuously fed by a proportioning pump. The experimental set is shown in Fig. 4.

Fig. 3

Titration with Gran's Plot of 20 ml Containing 0, 5 ppm of Fluoride in the Presence of 0, 5; 5; 50; 500 ppm of Al, (a) Without Any Complexing Agent, (b) With TISAB and (c) With Buffer Monosodium Citrate and Sodium Hydroxide.

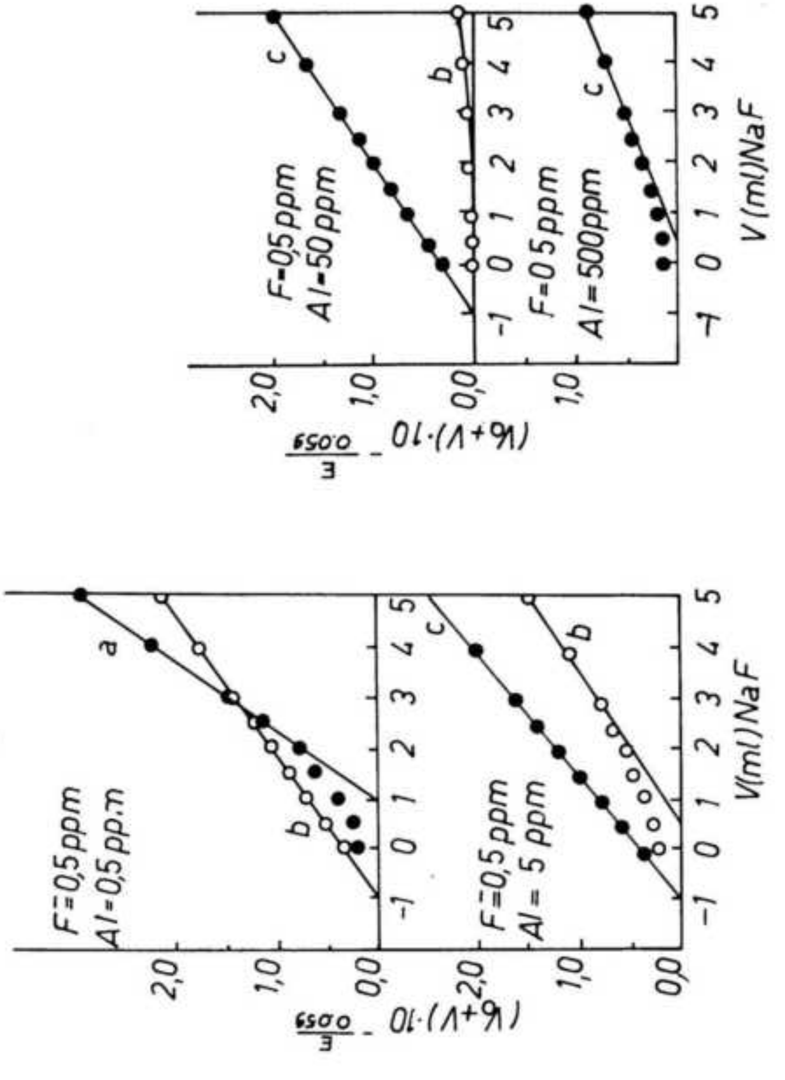
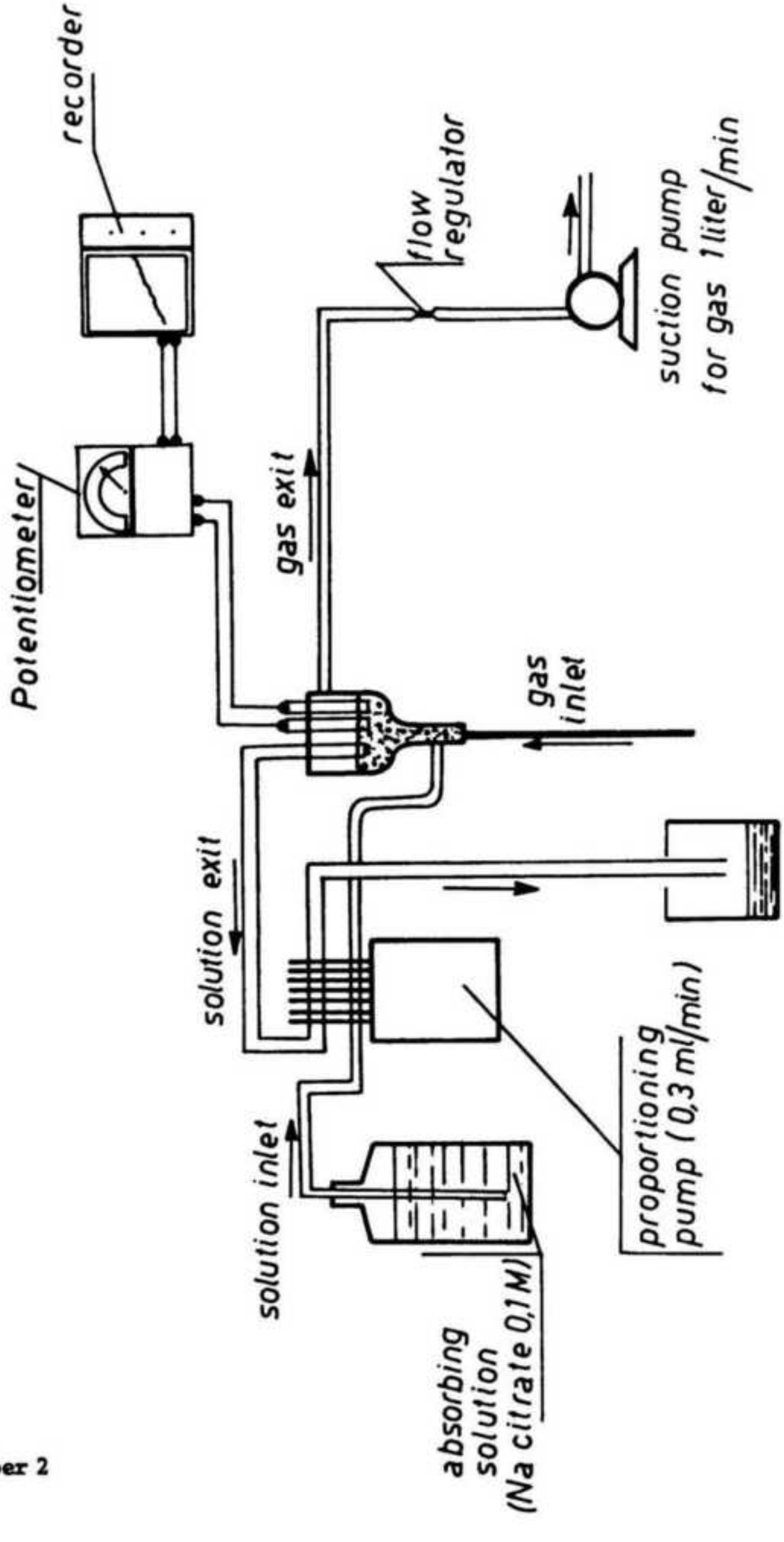


Fig. 4

Apparatus for Continuous Monitoring of Fluoride, Adsorption Solution Flows Continuously at Constant Speed

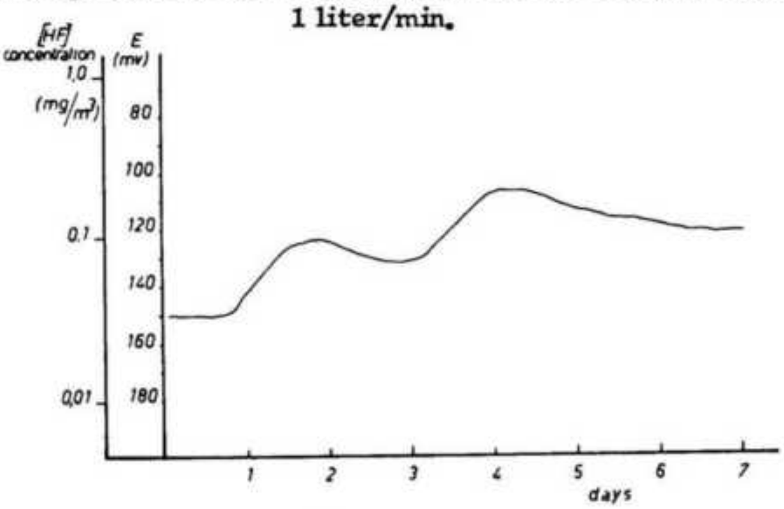


The solution concentration is maintained around 10^{-5} to 10^{-4}M, varying the ratio between gas and liquid flows. A fluoride concentration in the range 30 to 1000 $\mu g/m^3$ can be measured in stack effluent.

The recorded potential can be expressed directly in milligram of fluoride per cubic meter of stack gas, as shown in Fig. 5.

Fig. 5

Continuous Monitoring of Stack Gases. The Recorded Potential is Expressed in Fluoride Concentration of Gaseous Flow. The Absorbing Solution Flow is 0.3 ml/min and the Gaseous Flow is 1 liter/min.



Discussion

The following are the advantages of analysis by means of the ion specific electrode.

a) The use of an ion specific electrode greatly simplifies the determination of fluoride in polluted air and in stacks.

b) The time of analysis is much shorter as neither fusion nor distillation are required.

c) The accuracy of the determination is greatly increased by carrying a potentiometric titration with a standard fluoride solution and using a Gran's Plot.

d) The interference due to cations which may bind the bound fluoride ion is eliminated by using a sodium monocitrate-sodium hydroxide buffer 1M.

e) The determination of fluoride can be carried automatically and continuously recording the potential of a cell where stack gases are continuously analyzed.

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DISCUSSION PERTAINING TO PAPERS PRESENTED

by Drs. G. Reusmann and M. Buck* and by Prof. A. Liberti

Dr. E. Moser, Aluminum-Hütte Rheinfelden GmbH: The new method is usable for many cases, but will not give absolutely exact results. The interference by other elements depends on the kind and the amount of these elements present in the samples. Therefore it is necessary to know the amount of the interfering elements in order to calculate the exact amount of fluorine. The interference of aluminum can be practically eliminated by keeping the pH at 8.

The method is especially suitable when a large number of biological samples are to be analyzed, provided one takes into account a certain inaccuracy in results. For exact determinations, the Willard-Winter method of distillation modified by Oelschläger is preferable. Copies are obtainable from Dr. W. Oelschläger, Chemisches Institut, Universität Hohenheim, D-7 Stuttgart - Hohenheim, Germany

Dr. G. Reusmann: Under the described conditions a systematic error was found only in the presence of Mg^{++} and Al^{+++} ions. Interference by Al^{+++} ions can be eliminated by increasing the pH value to 8 but also by the addition of CDTA (pH-value 5.7).

The small negative error due to the presence of Mg^{++} ions can be calculated with sufficient accuracy by taking a median value of the well known and published Mg- content of the plant material.

We asked several other institutions to determine the F^- content of several kinds of plant materials which we had already analyzed. Our results corresponded excellently with those of the other laboratories. In this interlaboratory study we also compared the electrometic method with the photometric one which is used in Hohenheim.

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*FLUORIDE 4:1, January, 1971

OBSERVATIONS WITH A "SCANNING" ELECTRON MICROSCOPE ON DENTAL ENAMEL TREATED WITH FLUORIDES

by

L. Capozzi and F. Marci
Rome, Italy

Attempts to demonstrate the efficacy of topical applications of F^- in the prevention of dental decay show, in a convincing manner, that enrichment of enamel by F^- enhances resistance to the action of decaying agents. This resistance is attributed to a modification of the crystalline structure by absorption or by ionic exchange (2, 3, 5, 6)

To obtain explicit data on the action of the topically applied F^-, we employed a scanning microscope. Thus it was possible to obtain images at a particular depth very similar to the conventional image which would be observed by the human eye were it capable of enlarging objects 40,000 times.

It was of interest to investigate the effect of the demineralizing action of lactic acid solution, buffered at pH 4, on the morphology of normal enamel surfaces and upon those which had been treated "in vivo" with topical applications of different F^- compounds.

Organic acids, lactic and pyruvic acid in particular, which are liberated following the breakdown of carbohydrates, have the capacity to disintegrate the enamel structure which, according to Miller (1-4), may be the beginning of the decay process.

To obtain clearer information on this aspect, the experiments were conducted on teeth which had been covered by fenestrated crowns before the F^- applications. Thus, it was possible to have adjacent "treated" and "untreated" zones on the same tooth.

Method

Several fragments of the external enamel surface of the permanent, mono-rooted, caries-free teeth of ten subjects residing in a low-F^- locality (Perugia: F 0.2/1 mg) were examined. We carried out two kinds of studies:

(a) Six subjects brushed their teeth twice daily for 5 minutes "in vivo" for 22 days with two different toothpastes; one contained an amine fluoride, the other sodium monofluorophosphate. One tooth for each subject was examined both in the natural state and post avulsionem after demineralization for three hours in a solution of lactic acid, buffered at pH 4.

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(b) Four teeth were shielded by fenestrated metallic crowns so that during brushing "in vivo" with a tooth paste containing a fluorinated amine, only a restricted portion of the enamel surface would come into contact with the halogen. After treatment, which for this group consisted of two daily brushings for 5 minutes during a 12 day period, the teeth were extracted. The metallic crowns were removed and the teeth were immersed for 3 hours in a solution of lactic acid buffered at pH 4.

All fragments of the external surface of the enamel corresponding to the vestibular surface of the dental crowns were removed, and reduced to 3 x 3 mm squares. Care was taken not to damage the surface which was to be examined.

The different fragments were glued on special aluminum supports and prepared for microscopic examination by metallization under vacuum.

The samples were examined with a Stereoscan MK II electron microscope (Cambridge Scientific Instruments Ltd.); a 45° angle was used between the electron beam and the sample surface.

Results

The findings relative to the morphology of the external surface of the enamel of caries-free teeth of subjects residing in low-F^- areas, confirm the observations already accepted in the literature by other authors. They show, both at low and high magnification, honeycomb-like appearance in recently extracted teeth (Fig. 1), or, a uniformly compact or slightly wrinkled appearance in teeth of adult subjects (Fig. 1A).

When the enamel surface of these teeth was treated for three hours with a solution of lactic acid buffered at pH 4, a remarkable morphological modification of the external surface of the enamel was noted. At low magnification it appeared wrinkled; at higher magnifications it had a crater-like appearance due to loss of mineral components (Fig. 2A and B). These data agree with those described by Poole et al. (7).

The enamel surfaces of teeth treated "in vivo" with topical applications of F^- compounds, and immersed post avulsionem for three hours in lactic acid buffered at pH 4, appeared to be slightly wrinkled at low magnification (Fig. 3A). At the high magnification (Fig. 3B) the enamel appeared irregular and indented, a morphological picture quite different from the one observed in teeth which had not been treated with F^-.

The enamel surfaces of teeth protected by partial metallic crowns, treated "in vivo" with F^- and then demineralized, showed a totally different morphology in the protected zones compared to the unprotected ones. The enamel zones which came into contact with the halogen showed, even after demineralization, a rather smooth surface at low magnification (Fig. 4A, D), and a slightly wrinkled one at the high magnification (Fig. 4C), not very different from that of dental enamel not treated with demineralizing agents.

Fig. 1A

Vestibular Surface of Tooth No. 3
Decay Free, Barely Worn

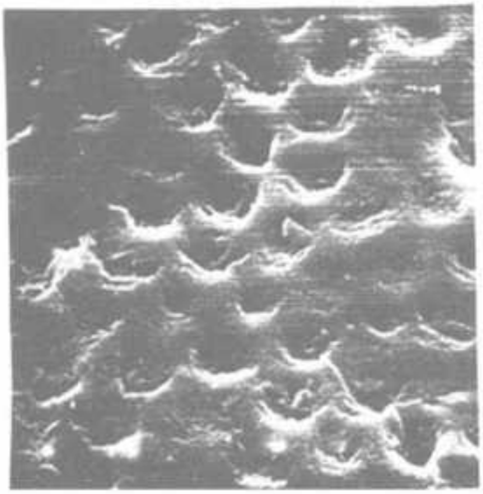


Fig. 1B

Vestibular Surface of Tooth No. 5
Decay Free, Barely Worn

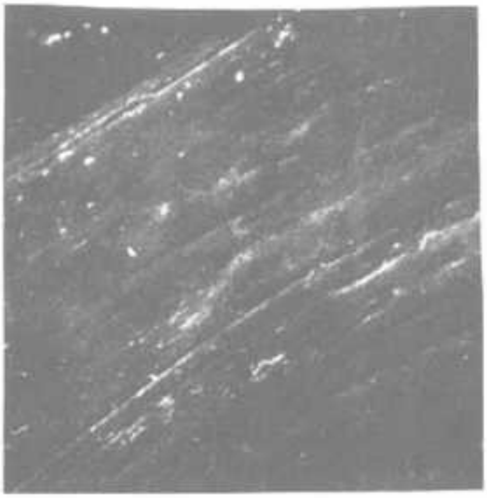
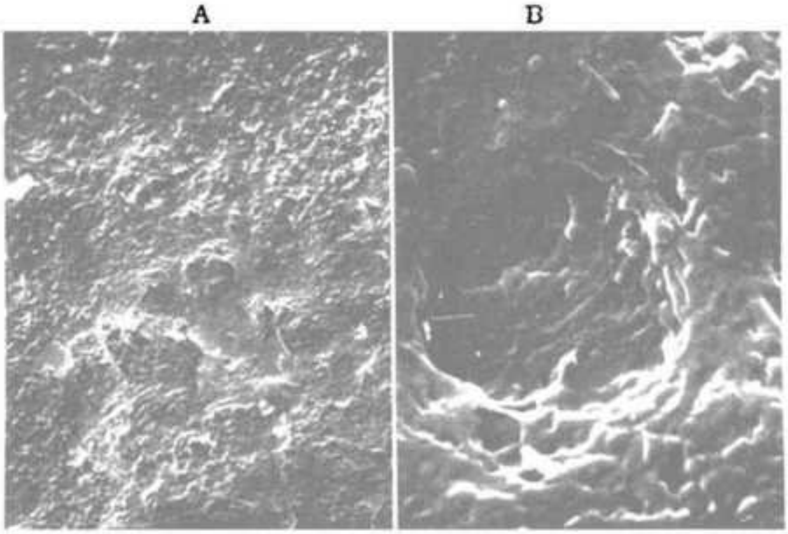


Fig. 2A, B

Same Surface as in Fig. 1A
After Immersion of Tooth for Three Hours in Lactic Acid Solution

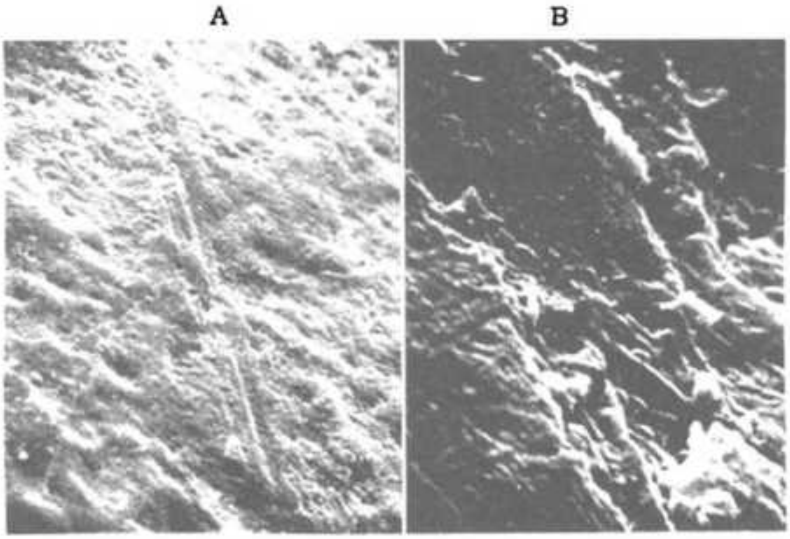


Magnification × 1, 500

Magnification × 7, 000

Fig. 3A, B

Vestibular Surface of a Tooth No. 3, Decay Free
Patient in a low F¯ area treated for 22 days with twice daily brushings with F¯ toothpaste and immersed post avulsionem for three hours in lactic acid solution (pH4)



Magnification x 1,100 Magnification x 7,500

On the other hand, the zones which had been protected by the metallic crown and therefore had not been in contact with the F¯ containing tooth paste showed serious alterations, characterized by a crater-like appearance (Fig. 4A, S; 4B).

Discussion

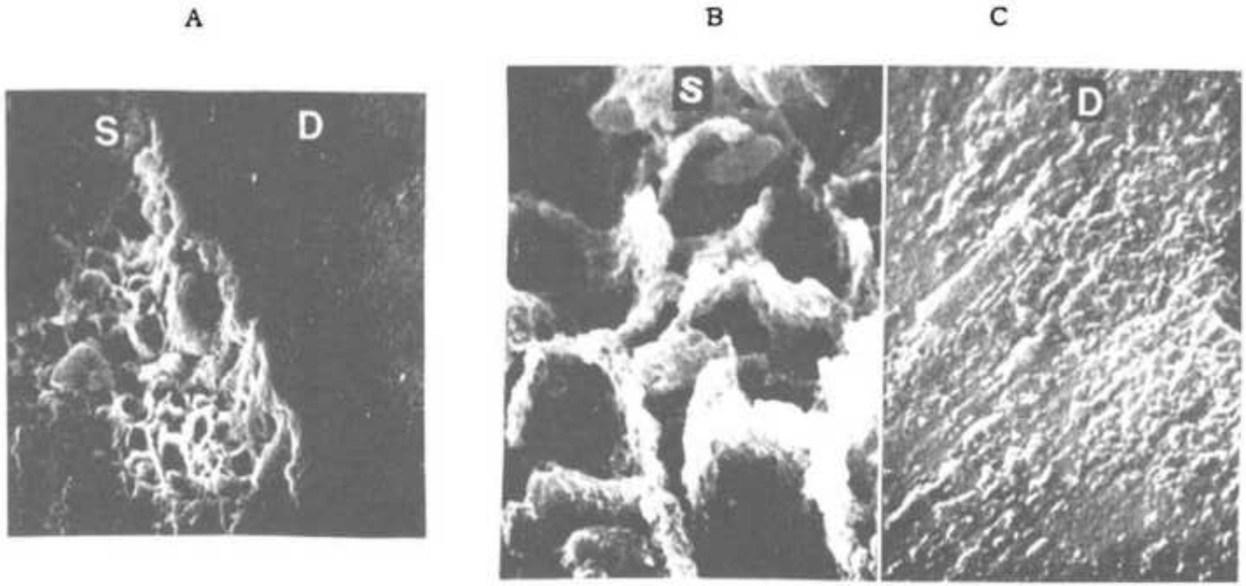
The data collected, even if the range of sampling should be suitably enlarged, are worth further consideration.

1. By the use of a scanning electron microscope, the deep structural alterations of the enamel surfaces following treatment by demineralizing agents (lactic acid buffered at pH 4) have been demonstrated.

2. These changes were considerably less pronounced in teeth treated by topical applications of F¯ containing toothpastes than in untreated ones. The value of such methods in the prevention of dental decay is thus supported and confirmed by a comparison of the morphology of two portions of the enamel of the same dental crown, one of which had not been in contact with the F¯, the other of which had received F¯ treatment. In the former deep alterations, in the latter nearly normal images were found.

Fig. 4A, B, C

Vestibular Surface of Tooth No. 5 Treated "in vivo" for 12 Days with Twice Daily Brushings with a F⁻ Toothpaste



During this period, the vestibular surface of the crown protected by a fenestrated metallic crown; only a limited area of enamel had direct contact with F⁻. A) Enamel surface after three hours of immersion in lactic acid solution (pH 4).

Note: Much greater demineralization in the area not exposed to F⁻ (S). Greater than in treated area (D) (magnification x 1, 400). (B, C) Details of the areas S and D at higher magnification (magnification x 7, 000).

Conclusions

It can therefore be concluded that topical application of different F$^-$ compounds inhibits the solubility of the external surface of the enamel. This confirms and consolidates the results already obtained on this subject by other methods and investigations.

We intend to complete these initial observations by checking the external surface of the enamel after interruption of the topical treatment with F$^-$ for a period as well as by using other demineralizing agents in order to preclude possible specific action shown by lactic acid.

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HUMAN FLUORIDE INTOXICATION IN PUNJAB

by

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SUMMARY: In an epidemiological survey on fluorosis in India, the most extensive one available to date, the following facts were established:

The incidence of dental fluorosis (46,000 children surveyed) is not related to that of skeletal fluorosis. Periapical tooth resorption and premature loss of teeth is a feature of dental fluorosis in adults. Dental fluorosis occurs where water contains less than 1 ppm F^-.

Skeletal fluorosis develops after 10 to 30 years of residency in endemic areas at F^- levels of drinking water as low as 1.5 ppm. Of 1300 radiologically demonstrable cases, 309 were asymptomatic, 742 had rheumatic and arthritic complaints, 144 exhibited crippling deformities, and 125 showed neurological complications.

Detailed neurological studies on 80 cases (73 males and 7 females) revealed myeloradiculopathy of the cervical and dorsal spine with acroparaesthesias, muscular wasting and neuritic pains. Spastic quadriplegia was noted in several cases. The authors encountered no evidence of visceral involvement in the endemic area.

Mean F^- levels were recorded as follows: Blood 2.8 ppm; urine 5.3 ppm; bones 3187 ppm (700 to 7000 ppm in dry fat-free bone); teeth 1960 ppm, urinary calculae 22 ppm. In 15 soil samples collected in the endemic areas F^- values ranged from 166 to 389 ppm. Cereals contained from .22 to 4.40 ppm F^-. Serum calcium, inorganic phosphates, phosphorus clearance and calcium deprivation tests showed no significant differences from those of controls. Serum alkaline phosphatase levels were elevated in fluorotic patients. Adrenal functions were normal. Excessive urinary tyrosine excretion was noted.

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Though dental mottling had been reported by Eager (1) as early as 1901, it required some 30 years until F^- was identified as the cause of this defect by three groups of workers (2, 3, 4,) independent of each other. Skeletal involvement due to F^- was reported by Moller and Gudjonsson in 1932 (5) and by Roholm in 1937 (6) in industrial fluorosis. About the same time skeletal fluorosis due to ingestion of excessive amounts of F^- in water was first described by Shortt et al. (7) from India. Subsequently endemic fluorosis has been reported from many countries of the world (8-15).

Ingestion of excessive quantities of F^- produces characteristic changes on teeth and bones. The skeletal changes when they become extensive can lead to invalidism due to crippling and neurological complications.

Punjab in its southwestern region has an extensive endemic belt where the disease has occurred in a very severe form. This area of Punjab has a hot summer, the temperature going as high as 116-120°F, and scanty rainfall. The soil is sandy. Population in this area consists mostly of farmers who do hard manual labor. There is no significant nutritional deficiency in this group. Because of the nature of their work and hot atmospheric conditions in summer, they consume excessive amounts of water. Their diet consists mainly of cereals, pulses (a cereal) and foods of animal origin like milk, butter-milk curd.

The object of this paper is to summarize our observations in cases of endemic fluorosis in this area where the natural F^- content of drinking water may be the highest in the world. The following subjects will be discussed:

1. Dental fluorosis
2. Skeletal fluorosis
3. Neurological complications
4. Visceral involvement
5. Fluoride bearing water
6. Biochemical data: a) F^- in different body tissues; b) F^- in soil and food stuffs, c) Serum enzymes, 3) Parathyroid function, f) Thyroid function, g) Adrenal assessment, h) Chromatographic studies, i) Calcium balance studies

Dental Manifestations

Mottled enamel is one of the earliest, most delicate and easily distinguishable signs of excessive intake of F^- in childhood. It has been utilized in epidemiological surveys as an index of endemicity of fluorosis in a particular area. Generally three grades are recognized (16).

1. White chalky opacities or patches on enamel with or without faint yellow lines,

2. Distinct brownish pigmentation,

3. Pitting of the enamel, sometimes with chipped-off edges in addition to pigmentation.

We have studied dental fluorosis in school age children using this grading in endemic areas which were formerly Punjab. Over 46,000 children have been examined. Generally the concentration of F^- in drinking water is directly related to the incidence of dental fluorosis (Table 1).

TABLE 1

Dental Mottling in Endemic Villages

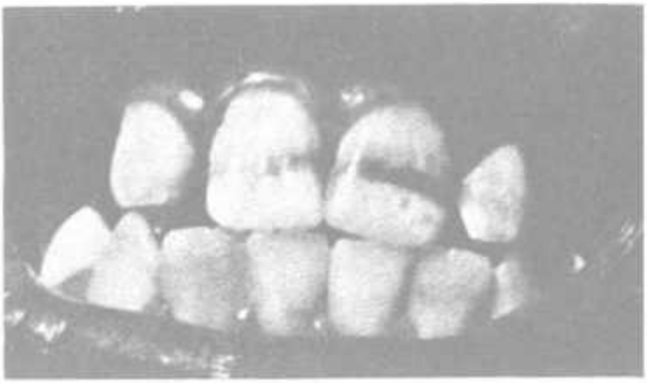
Village	Mean F^- ppm	% Mottling children (5-15 yrs.)	% Mottling Adults (21 years)	% Incidence of skeletal fluorosis
*Mandi Bareta	0.7	81.2	80.6	3.6
Gharachon	1.4	22.6	13.8	2.4
Gurney Kalan	2.4	44.6	77.4	17.0
Laluana	2.4	30.6	60.2	23.0
Kooriwala	2.5	48.8	52.2	33.0
Dhaipai	3.0	24.5	47.6	19.6
Bhodipura	3.0	55.9	31.2	42.2
Rajthal	3.3	47.0	10.0	10.0
Bhikhi	3.3	53.4	52.2	45.0
Sanghera	3.6	27.4	29.4	33.1
Ganjadhaneula	4.3	67.4	81.5	19.4
Ramuana	5.0	52.7	56.6	60.0
Bajakhana	5.09	76.9	80.3	44.5
Village Bareta	5.49	70.0	87.5	31.3
Rorki	7.02	47.08	65.0	47.4
Ganjigulab Singh	8.5	81.4	55.6	58.9
Khara	9.4	80.0	85.3	70.1

*The extraordinarily high incidence of dental fluorosis in this township is under investigation.

In western countries less than 2 ppm F^- in water is said to produce no toxicity to dental structures (17) and in some regions of the world 1 ppm F^- is being added to community water to reduce the incidence of dental caries. We have observed well marked dental mottling to be associated with waters containing 0.7 to 1 ppm F^- (Table 1). Similar findings have also been encountered by other Indian workers (18, 19, 20).

Fig. 1

Typical Dental Pigmentation Associated with Pitting of Enamel Surfaces



Dental fluorosis in adults differs slightly from that observed in children. In some adults, characteristic pigmentation of enamel has been replaced by diffuse light yellowish discoloration. That this stage is difficult to recognize may account for reported absence of dental fluorosis in advanced cases of skeletal fluorosis.

Though dental fluorosis in children may be taken as an index of endemicity of the disease, it has no direct relationship with the incidence of skeletal fluorosis. However, where ever the incidence of skeletal fluorosis is high, there is a significant incidence of dental fluorosis.

Our intensive epidemiological surveys demonstrated premature loss of teeth in endemic areas. The increased incidence of lost teeth paralleled that of skeletal fluorosis. Therefore, we consider loss of teeth in adults to be an advanced manifestation of dental fluorosis.

Radiological changes have also been observed in some of the teeth (21). The root portion of each tooth was irregular and rough. In the apical region a calcified mass composed of excessive amounts of F^- osteocementum was found. Periapical tooth resorption was noted in a few cases.

Skeletal Fluorosis

In general, the development of skeletal fluorosis demonstrable by X-ray requires 10 to 30 years and comparatively large doses of F^-. On the other hand, in India skeletal fluorosis has been reported from as little as 1.2 ppm F^- in drinking waters (20, 22). During the last 12 years, we examined a total of 1320 radiologically proven cases of skeletal fluorosis during epidemiological surveys or through inpatient hospital admissions. The details are given in Table 2.

Fig. 2

Calcification of Interosseous Membrane of Forearm

An early radiological feature of skeletal fluorosis.

Fig. 3

Osteosclerosis of Thoracic Bony Cage

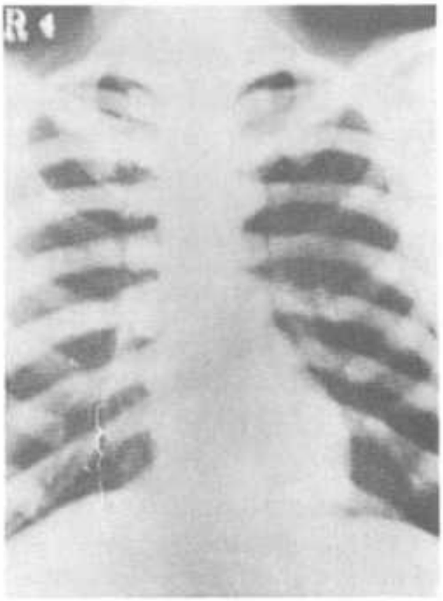


Fig. 4

Osteosclerosis, Extensive Osteophytosis and Calcification of Ligaments in Lumbar Spine.

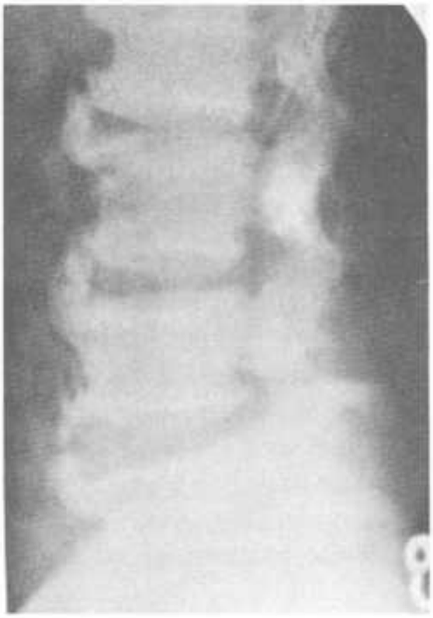


Fig. 5

Osteosclerosis, Extensive Osteophytosis and Calcification of Ligaments in Lumbar Spine.

TABLE 2

Incidence of Skeletal Fluorosis

Total cases detected on radiological examination	1320	Percentage		
a) Latent or subclinical without symptoms	309	23.4		
b) Symptomatic	1011	76.6		
			Male	Female
Non-crippled	742	73.4	70.5	29.5
With crippling deformities	144	14.3	91.0	9.0
With neurological complications	125	12.3	91.2	3.8

Without radiological studies, early skeletal involvement evades detection. Whereas in early stages the subjects may be asymptomatic, sooner or later they develop rheumatic complaints. They complain of pain and stiffness of spine. Subsequently the joints of both limbs become similarly affected. Paraesthesiae in the extremities occur. The incidence of rheumatic complaints rises with the endemicity of skeletal fluorosis. In later stages stiffness of the spine increases, movements become limited and such deformities as kyphosis appear. The patient loses his ability to walk as crippling deformities, contractures and neurological complications appear.

One of the useful diagnostic signs is the presence of exostoses resulting from irregular new bone formation. These exostoses are mostly palpable along the anterior border of the tibia, along the soleal line of the tibia and near the olecranon. These exostotic masses occur most commonly along the soleal line on back of the tibia where they can be readily palpated along the medial border of the tibia. These exostoses are mostly encountered in males, particularly in persons doing hard manual labor

The radiological, histopathological and gross changes of the skeleton are quite distinctive and have been described in detail in our previous publications (21, 23, 24, 25, 26). On gross examination the bones are of dull white color. They show extensive layers of new bone along the attachments of muscles and tendons, and in the interosseous membrane of forearm and leg bones. Considerable new bone is laid down in the pelvis and in the whole axial skeleton. The vertebrae show altered measurements in all planes. In some cases the antero-posterior diameter of the spinal canal is considerably reduced. The intervertebral foramina are also narrowed. These changes account for the neurological features observed in advanced cases.

Radiologically there is a combination of osteosclerosis, osteophytosis and of calcification of ligaments and tendon insertions in all bones. These changes are particularly striking in spine, pelvis and ribs. Calcification of interosseous membrane of forearm bones is a very helpful radiological sign, particularly in cases of borderline osteosclerosis. In our epidemiological work we have used this sign as an index of skeletal fluorosis.

The histopathological changes in human skeletal fluorosis have been studied very infrequently, although considerable data is available in animal experiments. Some of the more recent observations of Baylink and Bernstein (27) in cases of osteoporosis due to F^- used therapeutically provide interesting data for comparison with fluorosis from F^- in water naturally. The various changes which have been described by different workers are disorientation of the Haversion system (26, 28), increased osteoid tissue (6, 26, 29, 30), irregular mineral deposition (6, 25, 31), altered properties of bone matrix (6, 31, 32) a brown discoloration of the mineralized bone (31), globular bodies in bone and vascular spaces (6, 29, 31) changes in bone cell number (6, 28, 29) and cytological abnormalities (6, 31).

Neurological Complications

Almost all cases of neurological fluorosis have been reported from India. Credit for the earliest description of neurological features should go to Shortt et al. (7). Subsequently, sporadic reports from the different parts of India have appeared (33-39).

TABLE 3

Pattern of Neurological Deficit in Fluorosis

	Male	Female
Cervical myeloradiculopathy	39	1
Cervical myeloradiculopathy with deafness.	1	-
Cervical myeloradiculopathy with cerebellar signs.	1	-
Cervical myelopathy	6	1
Cervicodorsal myelopathy	2	1
Dorsal myelopathy	16	4
Cervical radiculopathy	2	-
Peripheral neuritic type	4	-
Fluorosis associated with cerebrovascular accidents.	2	-
Total	73	7

As far as could be ascertained, only two cases with neurological complications have been reported from outside India (40, 41). The majority of cases have been observed from Punjab which is one of the most hyperendemic areas in the world. Our recently compiled series of hospitalized cases now totals 80. Singh and Jolly (37) designated the neurological complication to be essentially a radiculomyelopathy due to compression of spinal cord and nerve roots by the protruding osteophytes. The details of the 80 neurological cases as observed by us is shown in Table 3.

The important radicular manifestations were wasting, acroparaesthesia, and pains referred along the nerve roots in the upper limbs. Weakness and muscular wasting was usually asymmetrical and involved mainly the small muscles of the hands. Subjective complaints like acroparaesthesia, and pains were universally present.

The earliest and most common myelopathic involvement was shown by the weakness of the lower limbs. In some cases a spastic quadriplegia occurred. In most cases lower limb reflexes were exaggerated and plantar reflex was positive in 61 patients.

Two patients had suffered a cerebrovascular accident with hemiplegia. Another case manifested cerebellar signs such as ataxia, tremor and disdiadokokinesis also. This condition is thought to be the result of compression of the vertebral artery during its passage through the cervical spine.

Sensory involvement, though quite common, was patchy in distribution. Four cases had peripheral neuritic type of involvement. Headache, tetaniform convulsions (43, 44) auditory nerve function impairment (42) and meralgia paraesthetica (38) have also been encountered by some workers.

Visceral Involvement

In addition to skeletal and dental structures, other organs of the body have also been reported to be affected by excessive ingestion of F^-.

Next to calcified tissues, the thyroid gland contains the highest level of F^-. Both iodides and fluorides are said to have an affinity for this gland. Some workers (45, 46, 47) have reported F^-'s goitrogenic nature. However, Leone et al. (48) in the Bartlett-Cameron survey found no significant incidence of thyroid goitre. In Switzerland, addition of F^- to children's diet did not lead to the reappearance of goitre (49, 50). Siddiqui (51) also observed no significant incidence of goiter in an endemic area. Our surveys in Punjab failed to reveal an undue incidence of goiter. Thyroid function tests discussed elsewhere in this paper were also normal in cases of skeletal fluorosis.

In kidneys, which are the major source of F^- excretion, high concentrations of F^- have been noted. There have been reports of undue incidence of kidney involvement in cases of fluorosis (6, 7, 16, 52). The association of kidney disease with fluorosis is of particular importance in view of possible hazard in the use of fluoridated water in long term hemodialysis in chronic renal failure (53). Increased retention of F^- in subjects with impaired kidney function has been noted.

Vascular calcifications of the Menkeburg type have been observed in cases of fluorosis (52, 55). Increased incidence of mongolism has been reported in high F^- areas (56). A number of allergic reactions have been associated with exposure to fluoridated water (57, 58).

Fluoride Bearing Water

More than seven thousand water samples have been analyzed for F^- concentration from different parts of Punjab. Variation of F^- levels in endemic areas ranged from 0.2 to 40.0 ppm. However, it needs to be emphasized that waters containing more than 20 ppm, as reported from South Africa, are not used in India for drinking because of their bad and brackish taste.

Biochemical Investigations

a) Fluoride Estimations in Various Body Tissues: In addition to water, we analyzed blood, urine, bones, teeth and kidney stones from fluorotic subjects for their F^- content. In all specimens we invariably found higher F^- concentrations than in normal individuals (Table 4).

TABLE 4

Fluoride Assays in Body Tissues

Tissue	Range	Mean	Normal
Blood (mgm%) (48)*	0.05 - 0.8	0.28	Traces
Urine (mgm %) (94)*	0.1 - 2.57	0.528	Less than 0.185
Bone (mgm/100 g dry fat free bone) 20*	70-700	318.7	110 ± 20
Teeth (gm %) (20)*	0.05-0.69	0.196	0.009-0.034
Urinary calculi (mgm/100 g) stone ash) (25)*	0.85-4.15	2.2	0.62

*Denotes number of specimens analyzed.

Of particular interest is the F^- content of tooth enamel in fluorotic patients. In enamel of ten mottled teeth, the F^- levels ranged between 0.05 - 0.67 gm percent (500 to 6700 ppm); in teeth without mottling from persons residing in endemic areas, from 0.06 to 0.69gm percent (600 to 6900 ppm). The F^- content of normal enamel ranged from 0.009 to 0.034 gm percent (90 to 340 ppm). Thus, the amount of F^- was considerably elevated both in mottled as well as non-mottled teeth in endemic areas. The ash content of enamel of fluorotic persons ranged from 96.0 to 97.1 percent compared to normal values of 95.4 percent.

Fluoride values of urinary calculi were considerably higher in most cases of the present series than in those reported by Zipkin et al. (60).

b) Soil and Food Stuff: Fifteen soil samples collected from villages of the endemic area were assayed for F^-. The values varied from 166 to 389 ppm with a mean of 241 ppm. Table 5 presents a comparison of the soil analysis from different countries.

Forty samples of pulses and other cereals grown in an endemic area also have been analyzed. Whole wheat contained 0.48 to 2.4 ppm F^-, maize 1.95 to 2.5 ppm, whereas in various pulses F^- content varies from 0.22 to 4.40 ppm. These readings are high compared to those presented by McClure (63).

c) Serum Enzymes: Serum enzymes were determined in the hospitalized patients since F^- is known to be a general metabolic poison which interferes with many enzymes systems.

TABLE 5

Fluoride Content of Soils

Country	Number of samples	Mean ppm	Range ppm
U.S.S.R (61)	46	200	30-320
U.S.A. (62)	137	290	10-7070
New Zealand (62)	23	200	68-740
India (present study)	15	241	166-389

Table 6 shows that, in patients with endemic fluorosis, significantly higher than normal values of serum alkaline phosphatase occur. However, no correlation between the severity of the clinical picture and the alkaline phosphatase levels could be established nor did blood F^- levels correlate with the alkaline phosphatase values.

TABLE 6

Serum Enzymes in Fluososis

	Alkaline Phosphatase	Acid Phosphatase	S.G.P.T.	S.G.O.T.	Cholinestrase
No. of cases	30	17	30	30	30
Range (units)	6-26	0.5-2.5	5-26	6-29	35-115
Mean	13.3	1.26	13	15.5	70.2
S.D.	± 5.8	± 0.64	± 5.97	± 5.55	± 21.1
Normal	8.3	1.02	14	16.3	74

The remaining serum enzymes studied were within normal limits.

Parathyroid Function Tests

An attempt was made to assess the parathyroid function in view of a possible antagonism between F^- and calcium in bones which might be related to F^- retention in bones and an increased rate and amount of calcium elimination. Twenty-five proven cases of endemic fluorosis and an equal number of normal persons were studied (Table 7).

TABLE 7

Parathyroid Function in Fluorotics

Test	Normals		Fluorotics	
	Mean	Range	Mean	Range
Serum calcium (mgm %)	9.97	8.7-11.0	10.1	8.8-13.2
Serum phosphorus (mg%)	3.37	2.6-4.3	3.31	2.5-4.5
Serum Alkaline Phosphatase (K.A. units)	8.7	5-14	13.3	5-26
Phosphate clearance (ml/min)	11.8	5.60-19.7	9.8	3.2-23.1
Calcium deprivation test	-----------Normal-----------------			

Serum calcium, inorganic phosphorus, phosphate clearance and calcium deprivation tests did not show a statistically significant difference between normal controls and fluorotic patients. However, serum alkaline phosphatase levels in fluorotic patients were significantly higher than in the control group.

TABLE 8

Thyroid Function Test in Endemic Fluorosis

Test	Controls		Fluorotics	
	Mean	Range	Mean	Range
PBI (µg%) (26 cases)	5.4	4.0-7.8	4.77	2.8 - 7.2
BMR (14 cases)		-15 to + 12		-18 to +6
Serum Cholesterol (mg %) (26 cases)	142.2	112.0-172.0	134.5	100-165.0

Serum cholesterol and BMR values in fluorotics were within normal limits. A slight difference in PBI values in fluorotics compared to normal values was not of statistical significance.

Thyroid Function Test

The thyroid glands contain high F^- concentrations. The discovery of F^- derivatives of thyroxine has thrown new light on the inter-relationship between various members of the halogen group and their interference with thyroid function.

Assessment of PBI, BMR and Serum Cholesterol made in cases of fluorosis as well as in normal individuals is shown in Table 8.

Suprarenal Function Tests

Certain parameters concerned with suprarenal function were studied in 14 hospitalized patients (Table 9).

TABLE 9

Adrenal Function Tests

	Normals	Fluorotics	
		Mean	Range
Serum Na (mgm %)	310-340	334.5	299-348
Serum K (mgm %)	14-20	16.6	11.3-19.0
Plasma Cl (mgm %)	500-620	592.1	520-630
Thorn's Test	Normal	Normal	
Kepler's Test	Normal	Normal	

Table 9 shows that these results pointed to a normal adrenal function in cases of fluorosis.

Chromatographic Study of Phenolic Acid Excretion

In our preliminary studies we noted that the color of urine from patients with endemic fluorosis and from monkeys with experimental fluorosis, turned dark brown on standing. We suspected that this was due to excessive amounts of phenolic compounds. At that time 24 hour urinary excretion studies in 35 cases of fluorosis were conducted, the results of which are given in Table 10.

Seven monkeys artificially fluoridated for 3 weeks gave somewhat similar results as compared to controls (64).

We, therefore, extended our studies to the urinary excretion of phenolic acids in fluorotics employing paper chromatography.

TABLE 10

	Fluorotics	Controls
Total N	8.72 ± 1.25 g	5 - 10 g
Alpha amino N	272 ± 57.77 mg	100 - 150 mg
$\frac{\text{Alpha amino N}}{\text{Total N}}$ Indes	3.11 ± 0.67	1 - 2
Tyrosine and its metabolites	274 ± 39.95 mg	48.1 - 189.5 mg

Eighty normal subjects and fifty radiologically and biochemically proven cases of fluorosis were studied (65). No definite disturbance in urinary excretory patterns was observed among the fluorotic patients. Alkaline solvents, used in this study, are known to destroy easily oxidizable dihydroxy phenolic compounds, which are known to be changed to melanins. It is, therefore, important to use neutral or acidic solvents if one desires to investigate the occurrence of phenolic compounds, which may give rise to darkening of urine in air. It may be added here that all extracts of urine from fluorotics are darker than the usual normal extracts. Hence further studies with acidic or neutral solvents are indicated.

Calcium Balance Studies

The role of calcium ion in the production of F^- osteosclerosis and conversely the effects of F^- in calcium metabolism have been controversial. In order to investigate calcium metabolism in fluorotics, calcium balance studies were undertaken in 22 hospitalized cases of different grades of fluorosis along with 15 normal controls. Patients were stabilized on a daily calcium intake of 1 gram at least 10 days prior to the commencement of the study. 24 hour urine and stools for 3 consecutive days were analyzed for their calcium content. Serum calcium, phosphorus, alkaline phosphatase were also determined. Fluorotic patients retained an average of 377.4 mgm of calcium daily compared to 29.7 mgm in controls. Similar findings have also been observed by other workers (66, 67). This avid retention of calcium in fluorotics was associated with a decreased excretion by kidneys and greater absorption from the G.I. tract. Serum alkaline phosphatase levels were consistently raised, whereas serum calcium and phosphorus were within normal limits. Urinary F^- excretion averaged 2.93 mgm daily, although osteosclerosis was evident in one case with urinary F^- excretion of 1.2 mgm per day.

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FLUORIDE UPTAKE IN SOIL AND ITS DEPLETION

by

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SUMMARY: The author determined the magnitude of F^- uptake by soil from polluted air and from artificial fertilizers. These values were compared to the amount of F^- removed through harvesting crops and through seepage water. Fertilization, with superphosphates, of cereals, potatoes, grass, fodder, beets and sugar beets added from 8 to 20 kg F^-/hectar to soil. On the other hand these plants, when harvested, contained only between 5 to 80 g F^-/hectar or 0.1 to 0.4% of the added F^-. The F^- accumulation in soil containing 200 ppm F^- - a general average - after fertilization with superphosphate ranged from 1.3 to 4.5% annually. Excess F^- is also being added to soils in industrial regions in the neighborhood of F^- emitting factories. Average yearly F^- emmissions in a highly industrialized area have been 2.1 kg F^-/ha, in another adjacent to a big metallurgical factory 7.3 to 21.9 kg F^-/ha, in the neighborhood of an aluminum plant 10.3 kg F^-/ha.

Removal of F^- from soil by seepage water was estimated at thirty widely separated agricultural and wooded areas. Fluoride loss through seepage water averaged between 52 and 208 µg/l depending upon the levels of clay and lime in the soils, and upon the marked relation between the F^- content of the water and the runoff. From 0.5% to 6% of the yearly added increment was thus removed. In a non-polluted area, therefore, considerable amounts of F^- accumulate in soil from fertilizers. In some instances, they constitute up to 90% of the amounts which are added to the ground.

F^- Uptake by Soil

In view of emissions in a large industrial area, where several industrial facilities are emitting F^- compounds, eight different stations were selected for F^- determinations.

During the course of 224 days we established that 2.1 kg F^- per hectar per year were deposited in soil. The sampling was done by the Technical Surveillance Organization, Rheinland ("Technisches Uberwachungs Verein, Rheinland). Even larger amounts of F^- were noted by Graue and Nagel (3) during a three year study of emissions near a large smelter. These authors found 7.3 to 21.9 kg F^-/ha/year. These levels were similar to those encountered near

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to 21.9 kg F⁻/ha/year. These levels were similar to those encountered near an aluminum smelter in CSSR during a survey extending over a 7 year period (4) which yielded an average of 10.3 kg F⁻/ha/year.

Through Fertilizer

Fertilizers constitute another source of relatively high F⁻ uptake by soil. Table 1 presents the F⁻ levels of some of the most widely used artificial fertilizers. Except for Thomasphosphate which is preferred for adding phosphates to acid soils because of its relatively high content of CaO, all other phosphate fertilizers contain considerable F⁻ levels. The F⁻ content of the Hüttenkalk is especially high. The most frequently used phosphate fertilizers in Germany are superphosphate, Rhenania phosphate and hyperphosphate which contain from 15.0 to 36.0 gF/kg. Table 2 reveals that a considerable amount of F⁻ is taken up by the soil annually through superphosphate fertilization. Addition of hyperphosphate and raw phosphates leads to even larger uptake of F⁻ by the soil. Between 8 and 20 kg F⁻/ha are being added yearly by applying fertilizer to such crops as grain, hay, potatoes and sugar beets.

TABLE 1

F⁻ Content of the Principal German Fertilizers

Fertilizer	g/F⁻/kg
Rohphosphate	33.4 - 41.1
Hyperphos	31.0 - 36.4
Rhenaniaphosphat	15.0 - 27.7
Superphosphat	14.6 - 25.7
Thomasphosphat	0.01 - 0.14
Branntkalk	0.05 - 0.19
Mergel	0.06 - 0.27
Dolomitkalk	0.22
Hüttenkalk	3.9 - 10.2
Kalidüngesalz 40%	0.02 - 0.03
Kainit	0.01 - 0.02
Schwefelsaures Ammoniak	0.003
Kalkammonsalpeter	0.01
Kalkstickstoff	0.58
Stallmist, (Fresh manure)	0.003

TABLE 2

Fluoride Added to Soil by Superphosphates

Crop	Fertilization with phosphate kg/ha	F^- added to soil kg/ha
Grain	400 - 800	8 - 16
Potatoes	400 - 800	8 - 16
Hay (grain)	400 - 800	8 - 16
Turnips	600 - 1000	12 - 20
Sugar beets	600 - 1000	12 - 20

Fluoride Removal from the Soil

Through Harvest: In order to determine the extent of F^- removal from the soil through the harvest, the above-names crops and their average yields in tons (1000 kg) per hectar are listed in Table 3. The last column shows the amounts of F^- removed by each crop in mg/kg. This table demonstrates

TABLE 3

Average Crop Yields and Their Removal of F^- from Soil

Crops	Harvested Tons per Hectar 3 to 4 grains	Average F^- per kg
Grain	3 - 4 Grains	0.8 FS*
	+3 - 7 Straw	0.9 DS**
Potatoes	20 - 30 Tubers	0.2 FS
	+7 - 10 Leaves	1.2 FS
Hay grass	5 - 12 Hay	6.8 DS
Beets	50 - 80 Beet	0.2 FS
	+15 - 20 Leaves	1.0 FS
Sugar beet	30 - 50 Beets	1.1 FS
	+18 - 25 Leaves	1.0 FS

* FS = Fresh Substance ** DS = Dry Substance

that the amount of F^- removed from the soil through the harvest is very minute. Only Thomas phosphate fertilizer is an exception among the phosphate containing fertilizers. Between 0.1 to 0.4% of the amount of F^- added to soil is removed with the harvest. In a soil with an F^- content of 200 mg/kg which constitutes the mean F^- level of soil containing 20% water, we calculated a yearly increment of F^- to be 1.3% to 4.5% without considering the washout of F^- by rain.

Through Seepage Water: The amount of F^- removed from soil through seepage water is also relatively small. We assayed water samples for F^- from 30 widely separated agricultural and forest areas. In twenty-seven the water was derived from artesian wells and in 3 from drainage from fields. Fifteen waters from nearly calcium-free areas averaged 0.080 mg F^- per liter. Twelve from areas containing calcium had an average F^- content of 0.128 mg F^- per liter. The latter soils were rich in clay. Serial assays of drainage waters flowing out of a Para-Braunerde Pseudogley formation revealed that the F^- concentration is in reverse proportion to the flow of the water. Table 4 presents the amount of the F^- removal from the soils through seepage with different quantities of ground water.

TABLE 4

Estimated Fluoride Removal from Soil by Ground Water

Yearly Amounts of Ground Water	Amount of F in Seepage Water (ha/years)		
	Minimal	Maximal	Averages
mm	0.034 µg/l	0.220 µg/l	0.104 µg/l
50	17	110	52
100	34	220	104
200	64	440	208

According to this table the F^- withdrawal from soil by seepage varies from 20 to 400 grams per hectar, or approximately 0.5 to 6%.

The above studies demonstrate that in areas where the air is not polluted by F^-, a considerable amount of F^- from fertilizers, as for example 90% of F^- superphosphate, accumulates in the soil.

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LONG TERM EFFECT OF FLUORIDE EMISSION UPON CHILDREN

by

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SUMMARY: After the start of operation of an aluminum smelter the health status of children living in close proximity was followed up for 8 years. In the area under investigation the daily F^- intake from food averaged 1.4 mg, that from inhaled air 0.4 to 0.7 mg F^-, from water 0.1 to 0.31 mg/l. In a control area the daily F^- intake from food was 0.8 mg, that from the air was negligible.

To date, no evidence of skeletal fluorosis has been found in the children. Nevertheless, the average hemoglobin had decreased and the F^- content of teeth, nails, hair, and urine had increased in the exposed children. In teeth, the average F^- value was 45.02 mg/100 g (450 ppm) of the original weight, compared with 15.71 mg in controls. Children's nails averaged 20.9 mg/100 g (209 ppm) in the exposed area, 14.3 mg/100 g (143 ppm) in the controls. Fluoride in hair averaged 1.6 mg/100 g (16 ppm) in the exposed children, 0.75 mg/100 g (7.5 ppm) in the controls. The 24 hour F^- assays of the urine were consistently higher in the exposed children compared with those of the control area, namely 0.8 ppm and 0.4 ppm respectively.

The establishment of an aluminum smelter and the serious effect of F^- emission upon the surrounding biolife which it created, made it necessary to take measures to trap and neutralize the pollutant agents. Thus far, it has not been possible to solve completely the problem of pollution control.

It has been recognized both through animal experiments and clinical observations that F^- accumulates at any level of intake and that the skeleton of a growing organism retains more F^- than that of adults. Persistent F^- uptake results in greater retention than interrupted uptake.

In view of the sparsity of data concerning the effect of F^- emission upon surrounding life and upon the human organism, we studied throughout an 8 year period the long-term health status of 6 to 14 year old children living in the immediate surroundings of the smelter (1). The study was initiated 5 years after the start of production of the plant. The sources of F^- uptake in the affected area were F^- contaminated food and F^- in the atmosphere. On the

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basis of actual F⁻ values of the ambient air and of F⁻ assays of agricultural products, we calculated that the daily F⁻ uptake from contaminated food averaged 1.2 mg and that from atmospheric inhalation 0.4 mg to 0.7 mg. Daily F⁻ uptake from food was 0.8 mg in the control area; F⁻ uptake from inhalation from the air was practically negligible. In both areas the F⁻ content of drinking water ranged between 0.1 to 0.3 mg per liter.

The children who were covered by this study had been living continuously in the exposed area for approximately 12 years. History and examination findings showed no major significant changes in the exposed children as compared with the control group. A statistically significant increase, however, was noted in the following clinical features: perspiration, abdominal pains, loss of appetite, parasthesias, alopecia, rhinitis, pharyngitis, tonsilitis, conjunctivitis and white streaking of nails (leukonychia). The examination of the children, after 6 years, revealed a higher than normal degree of perspiration and loss of appetite.

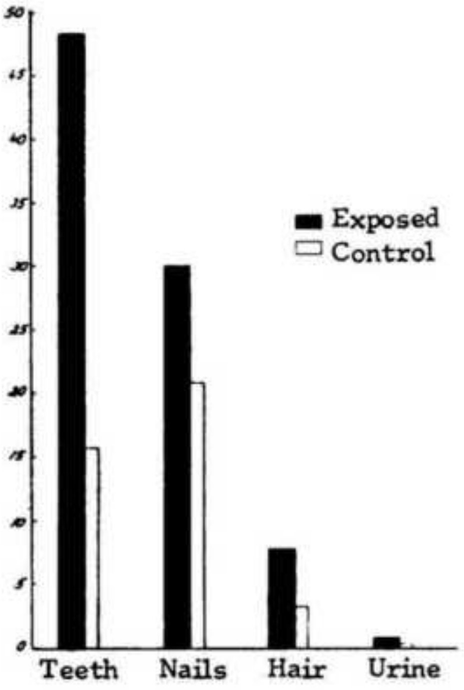
The incidence of pharyngitis and tonsilitis ranged in the three age groups of children from 42.5 to 77.1% with a mean of 50.3% in all children of the affected area after 6 years and 55.9% after 8 years. In the exposed areas there was a distinct increase in leukonychia during the intervals between the two examinations, namely from 12.4% to 54.2%. Skin lesions of the kind described near the aluminum plants in Chizzola (2) and Bolzano (3, 4) were not observed.

Of particular interest were the F⁻ levels in teeth, nails, hair and urine of the children, since they furnish some indication as to the F⁻ uptake into the organism. In all four parameters the values were higher among the exposed children than in the control group (Fig. 1). The F⁻ content of hair averaged 1.6 mg/100 gram (16 ppm) in the affected region as compared to 0.75 mg/100 gram (7.5 ppm) in the control group. The corresponding values for fingernails were 20.9 mg/100 gram (209 ppm) as compared to 14.3 mg/100 gram (143 ppm).

Stomatological examinations revealed slightly better teeth in the children residing in the exposed community than elsewhere, suggestive of a favorable effect of minute amounts of F⁻ upon the development of teeth and resistance against dental caries. Chemical analysis of the teeth showed an increase of F⁻ levels in all children with values ranging between 13.5 and 131.4 mg F⁻/100 gram (135 to 1314 ppm) of the original weight and an average of 45.02 mg F⁻/100 (450 ppm). In the control group these values ranged from 9.2 to 25.4 mg F⁻/100 (92 to 254 ppm) of the original weight with an average of 15.71 mg F⁻/100 (151.1 ppm). These results suggest that teeth are sensitive indicators of increased F⁻ uptake into the children's organism.

Fig. 1

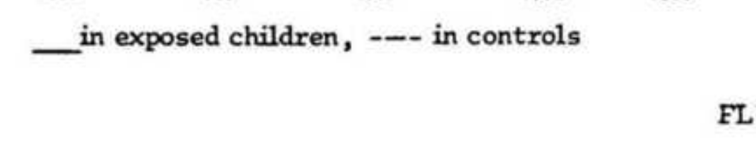
Average F^- Values in Teeth, Nails, Hair and Urine in Children Age 6-12 (mg% F^-)



The children of the affected community showed higher urinary F^- values than the "control" children with averages of 0.8 ppm F^- and 0.4 ppm respectively (Fig. 2). On two occasions during the period of observation, a marked elevation in the urinary F^- excretion in the exposed children correlated with a simultaneous marked increase of F^- in the atmosphere. These findings tend to confirm the view of those who believe that urinary F^- excretion may serve as an indicator of increased F^- uptake.

Fig. 2

MONTHLY Average Urinary Fluoride Levels

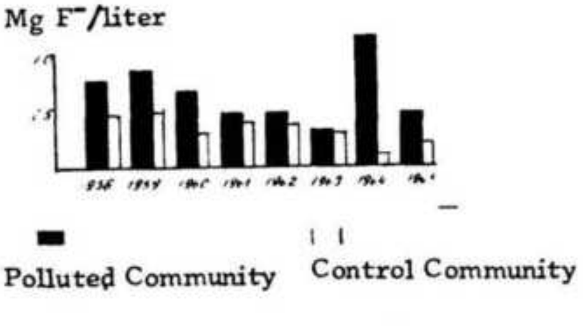


___ in exposed children, --- in controls

Figure 3 presents the yearly averages of urinary F^- in the children during the eight year study period which ranged from 0.3 to 1.2 ppm in the studied communities. The highest value was 4.75 ppm. We calculated that in the exposed area with an average total daily F^- uptake of 2.15 mg the children excreted 0.7 mg in the urine. In the age group 12 to 14 the urinary excretion was lower than in children aged 6 to 11. This can be explained by the enhanced skeletal growth following the 13th year and therefore a relatively higher capacity of the skeleton to retain F^- associated with a lower urine excretion.

Fig. 3

YEARLY Average Urinary Excretion



Our studies prompted introduction of measures for the protection of the life and health of the population which is undoubtedly endangered by F^- emissions from the aluminum smelter. Preventative health measures of the population are indicated with special consideration for children and teen-agers particularly with respect to adequate nutrition and to regular removal of school children to a recreational center away from the exposed area.

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EFFECT OF FLUORIDE EMISSION ON ANIMAL PRODUCTS

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SUMMARY: This paper is a part of an 8 year study concerning the effect of F⁻ emissions in the vicinity of an aluminum smelter.

Fluoride assays were made on milk and eggs produced by animals within a distance of 100 m of an aluminum plant where they were continually exposed to F⁻ emissions. One young heifer and 8 cows, 4 to 9 years old, raised and continuously stabled in the exposed area, produced milk with an average F⁻ content of 0.6 mg/l. The milk obtained in the morning averaged 0.5 ppm F⁻, that in the evening 0.7 ppm. The highest F⁻ content was found in the heifer's milk namely, an average of 0.94 ppm during the 18 months' investigation.

In eggs produced in the factory area, the F⁻ in yolk averaged 1.2 ppm. This value was only slightly higher than that of the controls (1.1 ppm). However, F⁻ content of egg shells in the exposed area was 9 times higher than that in the control eggs.

The composition of milk plays an important part in the protection of children against noxious effects of chemicals. Normally cows milk contains relatively little F⁻. Most authors consider 0.2 mg/l a representative average value in milk.

During intensive observations concerned with the changes of the biological life near an aluminum smelter, we determined F⁻ levels in agricultural products. In addition to fruit, vegetables and grains we made F⁻ assays for a three year period on milk and eggs produced by animals raised in the immediate surrounding of the aluminum smelter. The F⁻ determinations were made according to the Willard-Winter Method (1), as modified by Szokolay and Rippel (2).

Most of the cattle had developed fluorosis and had to be transferred to a different area. However, we were able to obtain data on the F⁻ content of milk from a young cow which was raised and kept constantly in a barn 200 meters from the source of the emission. Subsequently a group of 8 tuberculous cows, 4 to 9 years old, were temporarily housed near the factory. Also a permanent establishment for raising chickens was close to the factory.

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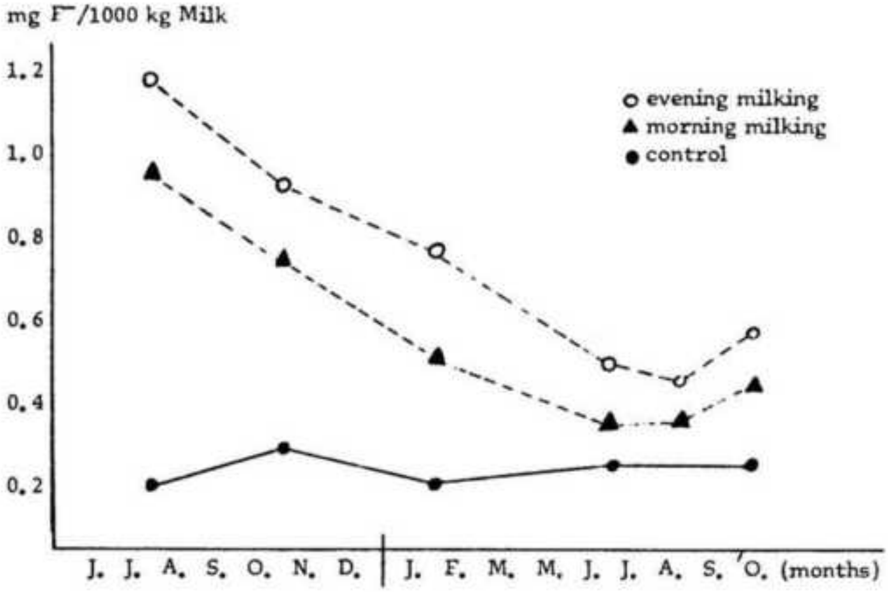
The F⁻ levels of a common water supply used by all animals averaged 0.2 mg/l (0.07 to 0.3). The total atmospheric F⁻ compounds in that area during the 8 year period of observation (1958 to 1965) amounted to 0.1 mg F⁻/l m^3 (3). During the same time the F⁻ content of the hay in the pasture of the same area amounted to 4.0 to 1,000 mg/kg in dry substance with an average of about 100 mg/kg. The dust present on the forage was calculated to range between 1 to 25% of this amount. Fluoride present in grain averaged 6 times the normal amount (4).

Parallel F⁻ determinations of milk from a creamery which constituted a control, averaged 0.2 mg/l. The average F⁻ content of milk of the heard of 8 cows varied considerably. Milk produced in the morning contained an average of 0.5 mg F⁻/l whereas the evening milking contained 0.7 mg F⁻/l (Fig. 1) Because the latter is richer in fat and albumin, it shows a higher F⁻ content. The detailed results are presented in Table 1.

Fig. 1

Mean Fluoride Content in Milk of Group of 8 Cows



A relatively high F⁻ content namely an average of 0.94 mg/l was noted in the milk of a heifer during 18 months' observation (Fig. 2). Such an increment of F⁻ in milk in young cows agrees with the generally accepted fact that the young growing organism is less resistent to the effect of F⁻ than are adult animals.

Several authors (5, 6) maintain that a daily and persistent F⁻ intake of 500 mg does not induce any morbid changes in a cow.

TABLE 1

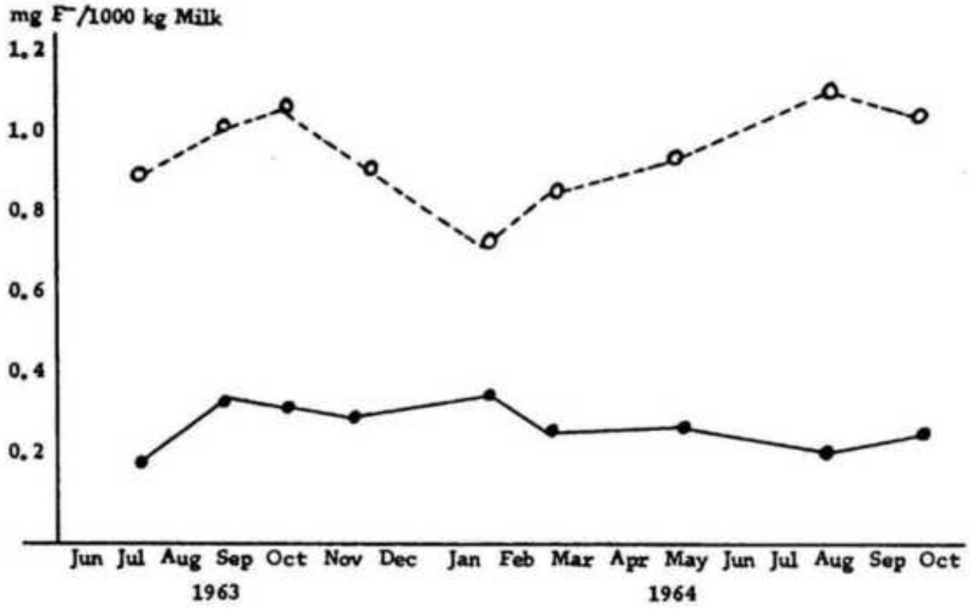
Fluoride Content in Milk and Eggs

Animal Products	Number of Samples	ppm (fresh weight)		
		Minimum	Average	Maximum
Milk from 8 cows	24	0.26	0.60	1.8
Milk of young cow	26	0.68	0.94	1.16
Control (milk)	28	0.12	0.25	0.31
Yolk of hens	8	1.0	1.2	1.6
Control (yolk)	6	0.8	1.0	1.4
Shell of eggs	6	38.0	45.0	56.0
Control (shell)	6	4.2	5.0	14.0

Our observations indicate that the daily F^- uptake from the air (10 mg) and that from the drinking water (10 mg) represents only a relatively small portion of the total daily F^- consumption. The major portion of F^- compounds reaches the organism from forage, especially from hay which also contains a significant percentage of F^- compounds derived from dust. Since most of the forage in our animals was imported from distant areas, the F^- excretion in the milk of our cows which were housed near the factory was relatively low.

Fig. 2

Fluoride Content in Milk of a Heifer



The main portion of F⁻ is excreted through the kidneys with the urine (7). The average F⁻ content in the milk of 0.6 mg/l of the 8 cows was within the limits of the maximum admissable F⁻ levels recommended by Truhaut (8).

In the yoke of eggs from chicken the F⁻ content of 0.2 mg/kg was only slightly higher than in the control eggs. The shells, however, contained about 9 times as much F⁻ in the exposed area as in the controls (Fig. 2).

This increment pointed to an unusual excretion of what appeared to be air-borne F⁻, since the chicken feed had been obtained from a non-contaminated area.

In comparing the results of the F⁻ content of the milk and eggs derived from a highly contaminated area we confirmed the fact that poultry is relatively more resistent to F⁻ emissions than cattle.

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SPECIAL REPORT

AIRBORNE FLUORIDE IN THE LAKE ST. CLAIR - DETROIT RIVER AREAS

by

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SUMMARY: A study concerned with air pollution in the Lake St. Clair - Detroit River area was undertaken by a special board at the request of the "International Joint Commission" representing the governments of U.S.A. and Canada

A limited survey for atmospheric F^- yielded concentrations of 0.16 to 2.9 ppb. In comparison, the highest level obtained by the National Air Sampling Network in 1966 and 1967 was 2.4 ppb. Gladioli planted at five locations showed F^- levels up to 50 ppm. Tip and margin burns occurred within 5 weeks after the gladioli were planted. The sources of F^- emission were not determined.

The author suggests that such variables as duration and continuity of sampling, heighth of sampling stations and their distance from the emitting sources, F^- levels in soil and edibles grown in the respective area should be considered in order to apply the above findings to the evaluation of health effects of F^- emissions upon humans.

In September 1966 the governments of Canada and of the United States requested the International Joint Commission to "inquire into Air Pollution in the Detroit/Windsor and Sarnia/Port Huron areas and to report to them with recommendations for corrective action".

The Commission established the International St. Clair - Detroit Air Pollution Board composed of federal, state and provincial officials to "undertake the necessary technical and scientific investigations". This Board, composed of three members from each country was advised by three committees: The Committee on Transboundary Flow of Air Pollution, The Committee on Sources and Their Control and The Committee on Effects of Air Pollution.

On February 4, 1971 the Board released its report (1). It concluded that "the transboundary flow of air pollutants produced pollution levels that are in excess of the air quality standards established in Ontario and about to be established in Michigan".

Eighty aerometric sampling stations were set up on public property such as schools, police stations, airports, roads and in a few factories in the communities bordering the river. Mainly sulfur dioxide concentrations and suspended particulates were monitored.

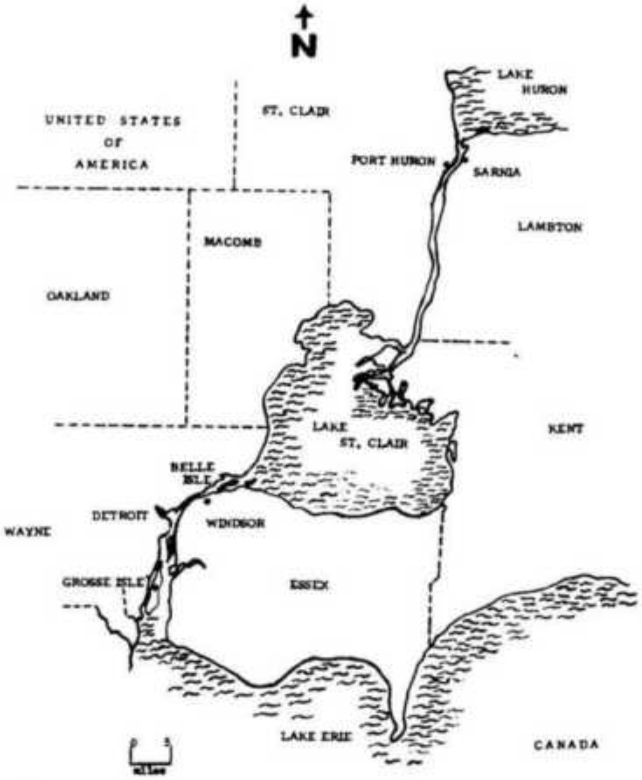
Only five of the 80 stations sampled for fluorides, namely two in the Port Huron/ Sarnia area and three in the Detroit / Windsor area. Specially designed sequential samplers which contained filterpaper impregnated with sodium formate for chemical adsorption of hydrogen fluoride were used. Sampling was carried out every third day for six four hour periods. Analysis of air samples for their F⁻ content, both adsorbed and particulate, was done by means of the specific ion electrode. The results were reported as four-hour averages in parts per billion (ppb) F⁻ at 25°C and 760 mm pressure.

Results of F⁻ Sampling

In the two Port Huron/Sarnia samplings, maximum concentrations of 2.2 ppb (1.8 $\mu g/m^3$) and 1.3 ppb (1.0 $\mu g/m^3$) were recorded. The arithmetic mean, however, was much lower namely, 0.3 ppb (.24 $\mu g/m^3$) at one station and 0.2 ppb (0.16 $\mu g/m^3$) at the other. Winter values were not available.

In the three Detroit/Windsor area stations, the maximum values were also above the 1 ppb level, which constitutes the Ontario government's standard. At the Windsor station higher F⁻ concentrations were detected during the summer than during spring and fall. At the Grosse Isle Michigan station which is located close to the Wyandotte Chemical Corporation and to power and steel plants, the maximum concentration was 2.9 ppb (2.3 $\mu g/m^3$). At this station the concentrations exceeded 2.7 ppb (2.16 $\mu g/m^3$) for 1% of the observations.

Fig. 1



These values are higher than those obtained in numerous U.S. cities by Yunghans and McMullen (2) in 1966 and 1967. They found less than 0.6 ppb (0.5 $\mu g/m^3$) in 87% of urban stations with a maximum of 2.4 ppm (1.89 $\mu g/m^3$). In 97% of non-urban stations they noted no detectable amounts of F^-.

Sources

The Board's report presented a detailed inventory of the possible sources of F^- emissions, without specifying the distances of the sampling stations from the respective factories. No aluminum smelters and only one fertilizer factory, which are considered to be the principal sources of F^- emissions, are located in the areas. Therefore, steel and electric power plants, a fiber glass factory and oil refineries must be considered the most likely sources of F^- emissions.

Location of Sampling Stations

The report does not specify at what heights the samplings were made. At the level of breathing, 5 to 6 feet above the earth's surface, conditions are likely to differ materially from those at the roof of a building. At higher altitudes there is a greater dispersion of contaminants than close to the earth's surface, particularly at times of inversions.

Duration of Exposure

Besides the location at which the sampling is made, the periods of time when monitoring is carried out are of importance in detecting pollutants. Sampling every third day does not disclose air quality during the two-day interval between samplings. A sudden burst of pollution, even if it lasts for only a few hours, could conceivably induce more damage to the health of a person than the average levels of pollution throughout a whole year.

Test Plants

The Board placed F^- sensitive plants at 5 locations. They chose the snow princess variety of gladioli as an indicator of the degree of air pollution. Tip and margin burns developed on the leaves within 5 weeks after the gladioli were planted at shelter sites. Leaves, which were sampled, showed F^- levels ranging from 25 to 50 ppm. The accumulations were highest in plants grown in Port Huron, Grosse Isle, Belle Isle, Windsor and Sarnia, in the order mentioned. Unfortunately, the polluting sources in these areas were not identified.

F^- Levels in Soil and Edible Vegetation

The Board has not as yet presented F^- levels in soil and produce grown in the areas. Fruit, vegetables and grain are produced not far distant from the urban areas. The question arises to what extent such edibles are contaminated by F⁻ and how much of the contaminated food is consumed by the local population. Consumption of polluted forage by cattle and other domestic animals could contribute materially to the total F⁻ burden of the population. Useful models for such studies have been presented in FLUORIDE by Balazova et al. (3), Oelschläger (4) and Gisiger (5).

Human Health

On page XXI, The Report concludes that "Transboundary and local pollution both exceed the level that is detrimental to the health, safety and general welfare of citizens...". So far, no data are available on what damage to health has occurred at pollution levels which are obviously excessive.

Discussion

In view of the wealth of data already available to the investigating team, a study on how F⁻ affects the health of the residents in the Detroit- St. Clair river area is indicated. Such a survey should include a review of records in hospitals which are situated near sources of pollution and a house to house canvass of persons residing in close proximity to factories which are known to emanate F⁻. Individuals in whom adverse effects are suspected should undergo careful evaluation of their organ functions (liver, kidney, etc.) before and after test doses of F⁻. The symptomatology of nonskeletal fluorosis outlined by Roholm (6) could serve as a guide. Body fluids (urine, blood, saliva, etc.) and biopsy material should be examined for their F⁻ content. Autopsy material could be assessed for the kind of pathological changes which are encountered following protracted low grade F⁻ intake. Emphasis must be placed on studies of individual persons rather than on statistical surveys of population groups, because adequate controls for the latter are difficult, if not impossible, to obtain. In samplings of populations, unless many thousands or millions are involved, it is rarely possible to detect persons whose health is adversely affected by F⁻.

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STUDIES OF AIR POLLUTION IN THE GRAZ AREA

by

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Abstracted from Arch. Fur Hygiene und Bacteriologie 153:114-118, 1969

This is the third part of a study concerned with the effect of the air pollution due to F^- emission from a brick factory near Graz. It relates urinary F^- excretion to F^- uptake from various sources.

The authors assayed urinary F^- values in mg/liter in persons residing in the vicinity of two brick manufacturing industries. One of the factories (Z1) is situated at the southern edge of the city of Graz, an area characterized by stagnant air and lack of wind. During half of the year hardly any movement of air currents was recorded; during the balance of the year the wind velocity ranged from 2 to 7 km per hour. The second brick factory (Z2) is situated in northeastern Austria in a wide, well-ventilated valley free from fog and stagnant air throughout the entire year.

In area Z1 residents had been complaining of illness; wild flowers and garden plants showed damage attributable to emanations from the factory. Fluoride levels, in the vegetation which was under study, were excessively high.

Near factory Z1 five groups of subjects were studied. Their urine showed the following F^- values in ppm.

Group A - Brick workers residing in the immediate vicinity of the factory: 0.74 ± 0.024 ppm.
Group B - Brick workers in same factory but living in a rural area in open country: 0.67 ± 0.032 ppm.
Group C - Persons living in an institution 4 km south of the factory (control group): 0.47 ± 0.027 ppm.
Group D - Workers and employees of a shoe factory in an industrial zone in the vicinity of Graz where high SO_2 levels prevailed: 0.63 ± 0.025 ppm.
Group E - Residents of Radegund located 400 to 500 meters above the Graz polluted area, surrounded by woods, away from industry: 0.29 ± 0.028 ppm.

Factory Z2 is situated in an atmosphere where no stagnation of pollutants occurred. The five subgroups, which were similar to those of the subgroups near factory Z1, yielded the following urinary averages.

Group A - Brick workers residing close to factory Z2: 0.5 ± 0.081 ppm.
Group B - Brick workers residing in open country away from the factory: 0.031 ± 0.045 ppm.

Group C - Persons living near the factory but working in the fields: 0.36 ± 0.071 ppm.

Group D - Control group of persons living 4 to 12 km from factory Z2: 0.27 ± 0.023 ppm.

Group E - Employees of a hospital situated at 1340 m above sea level in a non-polluted wooded area, similar to that in the corresponding Group E of factory Z1: 0.41 ± 0.025 ppm.

At factory Z2 little damage to plants was noted. More distant than 20 meters from the factory no damage occurred.

Urinary levels of workers in factory Z2 were significantly lower than those in factory Z1 located in the more polluted area. In fact, the urinary excretion of group A workers in factory Z2 was nearly of the same level as those of the control group in factory Z1 (Group C).

The authors cautioned against drawing conclusions concerning possible damage to health in the emission areas based upon the urinary F^- values particularly since no total daily urinary values are recorded. Considering an average urinary excretion of 1500 ml and the highest F^- excretion as 0.98 mg/l/day, they estimated a daily F^- output of 1.5 mg and a mean of 1 mg. They suggested that those who recommend F^- for caries prophylaxis should take into account an intake 1 mg to 1.5 mg daily through sources other than water.

AN ATTEMPT TO EVALUATE EXPOSURE TO FLUORIDES BASED UPON FLUORIDE LEVELS IN HAIR

by

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Abstracted from Chemii Toksykologicznej, 2:11-16, 1969

Fluoride accumulates in the skin as well as in hair and nails. This fact prompted an investigation of the F^- content in hair of persons with long-term exposure to F^- in air and water.

A total of 91 men, 18 to 60 years of age, were divided into three groups according to the duration of their exposure to F^-.

From the Zakladn Stomatology Zachowawdzsy, Poland.

TABLE 1

Fluoride Content in Hair

Fluoride in mg/100 g	Control group* Gdansk	Residents of Malbork**	Welders of working period		
			<5 yrs.	6-10 yrs.	>10 yrs.
0.301 - 0.400	10				
0.401 - 0.500	9	4			
0.501 - 0.600	1	7	1		
0.601 - 0.700		3	1	2	
0.701 - 0.800		3	3	3	1
0.801 - 0.900		2	3	2	3
0.901 - 1.000		1	2	1	1
1.001 - 1.100					3
1.101 - 1.200			3	2	1
1.201 - 1.300			1		3
1.301 - 1.400			3	1	
1.401 - 1.500				1	
1.501 - 1.600				1	
1.801 - 1.900				1	1
2.201 - 2.300				2	
2.301 - 2.400				1	1
2.401 - 2.500					2
2.701 - 2.800					1
No. of persons examined	20	20	17	17	17
Mean F^- values	0.408	0.628	0.994	1.265	1.428
Stand. Deviation	0.0638	0.137	0.258	0.588	0.669

* F^- in drinking water 0.5 ppm ** F^- in drinking water 1.2 ppm

Group 1, which constituted the controls, were residents of Gdansk without occupational contact with F^- compounds. Their drinking water contained 0.5 mg F^-/l.

Group 2 were residents of Malbork, where the F^- content in drinking water was 1.2 mg F^-/l.

Group 3 consisted of welders from Gdansk who had occupational exposure to F^- compounds. Group 3 was divided into three subgroups according to the length of time the welders had been employed. Those in Group 3a had been working less than 5 years, in 3b from 5 to 10 years, in 3c more than 10 years. The F^- content in hair was determined according to Fabre's method with the authors' modification.

Results

A statistically significant difference was found between the control group (mean F^- value of hair 0.41 mg% or 4.1 ppm) and all other groups (Table 1). A similar difference was noted between the residents of Malbork with mean F^- values of 0.63 mg% or 6.3 ppm and all the other groups. Lastly, a significant difference was observed between the two extremes, according to the duration of their employment namely 0.99 mg% (9.9 ppm) in those employed less than 5 years and 1.43 mg% (14.3 ppm) in those employed up to 10 years (Table 2).

TABLE 2

Values of "t" Test Calculated on the Basis of All Examined Groups

		Control Group	Residents of Malbork	Welders' Working Period		
				<5 yrs.	6-10yrs	>10 yrs
Control Group		0				
Residents of Malbork		6.67*	0			
Welders' working period	<5 yrs.	9.17*	5.62*	0		
	6 - 10 yrs.	5.96*	4.36*	1.74	0	
	>10 yrs.	6.15*	4.85*	2.49	0.75	0

*Statistically significant

The results indicate a direct relationship between the F^- levels in hair and their concentration in air and drinking water.

Due to the fact that welders are not constantly exposed to F^- compounds, their F^- uptake is best evaluated by the F^- content in their urine, which according to previous investigations by one of us ranged between 1.2 to 1.4 mg/l as compared to 0.3 mg/l of the control group.

The simultaneous occurrence of elevated F^- levels in hair and urine of exposed persons calls for further investigations to establish a relationship between the absorbed dose and the F^- content in hair.

Jerzy Krechniak

THE INFLUENCE OF CHEMICAL FACTORS ON THE ORAL CAVITY IN WORKERS OF THE SZCZECIN PHOSPHORUS FERTILIZER FACTORY

by

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(Abstracted from Czasopismo Stomatologiczne 21:1081-7, 1968)

Workers of a fertilizer plant were exposed to hydrogen fluoride, silicotetrafluoride, sulfur dioxide, sulfur trioxide, carbon monoxide and dust of apatites and phosphorites. The concentrations of hydrogen fluoride and dusts exceeded the MAC values by factors of 3 and 4 respectively.

In 1965, 146 workers (39 women, 107 men) were examined. One hundred persons (44 women, 56 men) employed in a furniture plant served as controls. Both groups were divided into three sub-groups according to the duration of their working period. Group I had been employed from 0 to 5 years, Group II from 6 to 10 years, Group III from 11 to 20 years.

The incidence of dental caries and of periodontal disease, the condition of the oral mucosa, as well as the pH of saliva and of the oral mucosa were recorded.

A statistically significant decrease of the caries incidence was noted in the workers employed for a period of 11 years or more in the fertilizer plant. The authors explained this finding by the action of F^- compounds on hydroxyapatite in enamel and on the inhibition of the enzyme enolase which metabolizes carbohydrates.

Almost 38% of the workers employed at the fertilizer plant had periodontal disease compared to 26% of the control group. However, no significant difference was observed as measured by the Klötzschke index pertaining to the severity of the periodontal disease.

In 14 workers at the fertilizer plant, pathological changes in the oral mucosa were observed which did not occur in the control group. In nine individuals dark-gray lesions were noted on the mucosa and in 5 cases the mucosa had become thickened and scaly. These changes could have been caused by the action of sulfur oxides.

No significant differences were found between the pH values of the oral mucosa and those of saliva in the two groups.

Jerzy Krechniak

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