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TABLE OF CONTENTS

Corrected Version

The International Society for Fluoride Research (ISFR) extends a special invitation to you to participate in the 16th Conference. This will be held in the Conference Hall of Zyma at Nyon (30 km from Geneva) Monday, August 31st through Wednesday, September 2nd, 1987. Professor C.A. Baud will host this Conference and he has nominated Christiane Demeurisse as secretary of the Conference. The Fluoride journal will carry information about the Conference in future issues.

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Guest Editorial

WATER FLUORIDATION AND OSTEOPOROSIS

In a widely-quoted report, Simonen and Laitinen (1) postulated that the incidence of osteoporotic hip fractures can be significantly reduced by water fluoridation at a level of 1 mg/L. This conclusion was based on data from the fluoridated city of Kuopio, Finland, which we also studied in our epidemiological investigation (2). However, in contrast to their results, we found no evidence that fluoridated water is associated with less osteoporosis or a lower rate of attendant hip fractures.

As pointed out by Burgstahler (3) in his discussion of these contradictory findings, there is a major inconsistency between the results of Simonen and Laitinen and those of other investigators, namely the relatively high incidence of hip fractures among men compared to women reported by Simonen and Laitinen for their low-fluoride (0-0.1 mg/L) control city of Jyväskylä. Independently, Sutton (4) also questioned the findings of Simonen and Laitinen and wondered why these authors had not cited our conflicting results. In their reply to Sutton, Simonen and Laitinen (5) stated they felt that our "histomorphometric studies are valid and acceptable" but not our epidemiological findings. The latter they rejected on various methodological grounds, principally because we had not reported hip fracture incidence according to sex.

We had not presented this information primarily because the number of fracture cases in some of the age groups, especially among men, is rather small. As seen in Table 1, however, when our results are expressed by sex, there are still no statistically significant differences in incidence rates between the low-fluoride (0-0.3 mg/L), fluoridated (1 mg/L), and high-fluoride (above 1.5 mg/L) areas. Furthermore, with but one exception in one age group, fracture rates in all three areas are consistently higher for women than for men, in agreement with the large-scale survey results of Madans et al. (6) in the USA.

Simonen and Laitinen (1) found a relatively high incidence of hip fractures among men aged 50-59, in low-fluoride Jyväskylä compared to fluoridated Kuopio. This finding can be explained by a larger number of high-energy (severe trauma) fractures in Jyväskylä, which is more industrialized than Kuopio. In compiling their cases, Simonen and Laitinen used codes 820.00 and 820.10 in the International Classification of Diseases, based on hospital discharge data for Finland for residents of the two communities. However, only the central area of Kuopio is supplied with fluoridated water; people living in other parts of the city have their own water sources, which are very low in fluoride.

In our Kuopio survey, we examined individually the files of all hip fracture patients and checked to make sure they actually had lived in the fluoridated area for at least 10 years prior to the fracture. Moreover, all patients with high-energy accidents, pathological fractures, metabolic bone disease, etc., were excluded. In some cases the international code designations were found to be completely incorrect. Obviously it is not possible to make such distinctions simply on the basis of hospital discharge data. Although less important in a large population, these factors cannot be ignored in a study such as this one.

Finally, in our histomorphometric study we found no increase in trabecular

Table 1

Annual Mean Incidence of Low-Energy Hip Fractures by Age and Sex during the 10-year Period 1972-1981 in Three Areas of Finland with Different Concentrations of Fluoride in the Drinking Water (cf. ref. 2).

	Age group	Population (in 1980)			Number of Fractures			10-year incidence/100,000		
		Men	Women	Total	Men	Women	Total	Men	Women	Total
	50-59	2141	2225	4366	3	2	5	14.0	9.0	11.5
Low-	60-69	1560	1923	3483	7	20	27	44.9	104.0	77.5
fluoride	70-79	915	1458	2373	7	32	39	76.5	219.5	164.3
area[a]	80-	231	456	687	10	54	64	432.9	1184.2	931.6
	Total	4847	6062	10909	27	108	135	55.7	178.2	123.8
	50-59	2932	3767	6699	5	8	13	17.1	21.2	19.4
Fluoridated	60-69	1867	3056	4923	10	28	38	53.6	91.6	77.2
water area	70-79	955	2105	3060	8	42	50	83.8	200.0	163.4
(Kuopio)	80-	230	678	908	13	72	85	562.5	1061.9	936.1
	Total	5984	9606	15590	36	150	186	60.2	156.2	119.3
	50-59	2143	2344	4487	1	2	3	4.7	8.5	6.7
High-	60-69	1494	2020	3514	11	17	28	73.6	84.2	79.7
fluoride	70-79	925	1612	2537	13	39	52	140.5	241.9	205.0
area[b]	80-	239	531	770	14	43	57	585.8	809.8	740.3
	Total	4801	6507	11308	39	101	140	81.2	155.2	123.8

[a] Centrally located communities of Kaavi, Keitele, Lepävirta, Suonenjoki, and Vieremä.

[b] Southeast communities of Hamina, Pyhtää, Ruotsinpyhtää, Vehkalahti, and Virolahti.

bone mass even in the high-fluoride area where, however, the amount of unmineralized osteoid was increased. The absence of increased bone mass in a high-fluoride (4 mg/L) community in northwest Iowa, along with no decrease in bone fractures, has also been reported recently (7). In our study no differences in the histomorphometric parameters as well as fracture incidence between the low-fluoride and fluoridated water areas was observed. Consequently, and in view of the relatively small number of cases, it is unwarranted to conclude from the study of Simonen and Laitinen that fluoridated water can prevent osteoporotic hip fractures. The same applies to a recent study in Hungary by Fazekas (8) who, like Simonen and Laitinen, found a higher incidence of hospital-recorded hip fractures of all types among men — but not among women — in a small low-fluoride (0.2 mg/L) community than in a nearby community with a fluoride level of 1 mg/L in drinking water.

It would indeed be ideal if some dominating factor could be discovered that does prevent osteoporosis and its complications, especially hip fractures. But osteoporosis is too complex and not well-enough understood to be solved simply by the addition of a single chemical element to community water supplies. To date no incontrovertible evidence that fluoridation of drinking water is an effective prophylaxis against osteoporosis is available.

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HYDROGEOCHEMISTRY OF FLUORIDE IN THE DROUGHT-PRONE HARD-ROCK REGIONS OF PENINSULAR INDIA

by

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SUMMARY: Fluorosis is a crippling disease affecting the teeth and/or bones of humans and livestock in many parts of peninsular India. Such endemic areas were studied to understand the fluoride hydrogeochemistry in the rain-shadow region where mean annual rainfall is around 600 mm and the climate is arid. Analyses of over 3000 water samples coming from Archaean rocks (gneisses, granites, schists, etc.) and experiments on soil leachates indicate that the fluoride content in water is not related to the amount of fluoride in bulk rock but rather to weathering conditions. Fluoride (aq) is highly variable spatially and exhibits a normal distribution unlike other dissolved species which are log-normal.

The calcite and fluorite equilibria modified by biological agencies govern the amount of fluoride in natural waters. Depending on the typography, equations of the type:

$$F^- = 1.2 \cdot \sqrt[3]{Na}$$

$$[F^-] = 0.37 \cdot \sqrt[5]{[Na]^2}$$

where F^- is the fluoride content and Na^+ is the excess sodium over and above that of chloride present in the water sample

are obtained for different slope conditions with distinct characteristics in erosional features and chemistry. These equations are found to be valid in different river basins like Vedavati, Pennar, etc.

KEY WORDS: F^- in groundwater; Fluorosis, crippling; Hydrogeochemistry of F; India.

Introduction

The occurrence of fluoride-rich ground waters has been known in peninsular India for over four decades (1). Parts of Nalgonda, Kurnool, Anantpur and other districts in the state of Andhra Predesh, Bellary, Chitradurga, etc. in Karnataka state in India have been endemic areas with dental and skeletal fluorosis in both humans and livestock. In order to help in possibly locating fluoride-low water sources, it was felt desirable to understand the geochemistry of the fluoride ion and the mechanism of its occurrence in ground waters. The high variability in the fluoride content in ground waters spatially and the inadequacy of the available hypothesis of the solution-evaporation-ion-exchange process to explain the fluoride content further underlined the need for a closer look.

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Study Area

The area studied is in the central portion of peninsular India and forms parts of the Vedavati and Pennar river basins (Lat. 13°05' - 15°44'N; Long. 75°43' - 78°E). It is a typically drought-prone hard-rock terrain of Dharwar schists, Peninsular gneisses and later granites of Archaean age. Recent Alluvium occupies the stream valleys. The long-term mean annual rainfall is about 612 mm in the Vedavati basin and about 583 mm in the Pennar basin. Physiographically, the area is characterized by rolling topography. Higher elevations are generally made up of granitic rocks. The principal soil types occurring in this area are red sandy loams and clayey loams. The lower reaches of the Vedavati basin are occupied by black cotton soils.

Sampling and Chemical Analysis

The Vedavati river basin was studied intensively during 1976-79 and the Pennar basin during 1981. Water samples were collected from village open wells used for either domestic water supply or irrigation as part of a well-inventory by teams of officers. Deep bore well samples were collected as part of the water balance study of the Vedavati river basin. Field determinations of chemical constituents were done in selected experimental study areas; otherwise, the chemical analyses were carried out in the laboratory. Local ponds and streams were also selectively sampled for chemical quality.

The chemical constitutents determined were pH, HCO_3^-, Cl^-, Ca^{++}, Mg^{++}, Na^+, K^+, and specific conductivity. Fluoride was determined using Spadns method or ion specific electrode. Standard procedures as per APHA, (2) were followed for chemical analyses. Nearly 3000 water samples were analyzed in the total study period.

Occurrence and Distribution of Fluoride Ion

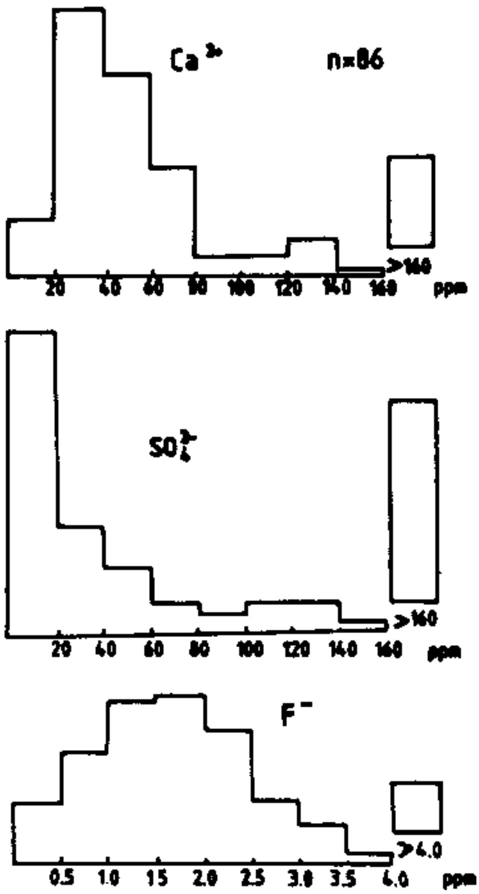
Shallow Groundwater Zone: The unconfined or top groundwater zone showed a variation from less than one ppm (parts per million) to as high as 11 ppm of fluoride. In the upper reaches of the Vedavati basin the fluoride level in groundwater was lower than the lower reaches. The high fluoride regions occur mostly in gneissic and granitic areas. There was no statistically significant distinction in the fluoride content of domestic water supply wells and irrigation wells although from the other chemical species like K^+ and NO_3^-, it could be seen that the domestic wells were more polluted.

The fluoride content did not vary much in the vertical direction or, in other words, shallow groundwater and deeper waters in the same locality contain almost the same amount of fluoride. There was however a large variation laterally even within short distances. In order to observe the frequency distribution of the fluoride ion, the results from 86 bore well water samples were plotted on histograms. To avoid extraneous sources of pollution, dug well water samples were not used. Fluoride exhibited a normal distribution unlike the log-normal or skewed distribution which is usually found in the case of most other ions (Figure 1). One can perhaps infer that the geochemical processes are further modified to give a complete random distribution as per the bell-shaped curve in the case of fluoride.

The high spatial variability of fluoride in groundwaters poses a problem in representing the fluoride content on maps. The normal technique of contours of equal value of fluoride on the geochemical maps would be misleading. Therefore, the fluoride content is represented by the mean as a dot and standard deviation as a bar on the map. Water samples falling in a 5' x 5' grid of the topsheet (i.e. an area of about 83 Km^2) are treated as one cluster for the calculation of the mean and standard deviation. The data density of the number of water samples being considered in each cluster is indicated by an inset map (3).

Figure 1

Frequency Distribution of Fluoride in Groundwater



Geochemistry of Fluoride

Calcium fluoride (fluorite) is the most common form of fluoride occurring in igneous, metamorphic and sedimentary rocks; apatite [$Ca_5(Cl\text{-}OH\text{-}F)\text{-}(PO_4^{3-})_3$] the next common mineral. Cryolite [Na_3AlF_6] and the solid-solution series of ralstonite [$NaMgAl\text{-}(F\text{-}OH)_6 \cdot H_2O$ to $Al_2(F\text{-}OH)_6 \cdot H_2O$] are the other though less important sources. Fluoride ion, similar in size to hydroxyl, may be found replacing $(OH)^-$ in many common rock forming minerals like amphiboles, micas, etc. Aluminium fluoride complexes to some extent are likely to exist in waters whose pH is below neutrality (4). In certain areas, where calcium is very low and sodium is high, fluoride can be as high as 30-40 ppm. Low pH will also facilitate high fluoride.

Calcite and fluorite equilibria are given by the following equations.

$$CaCO_3 + H^+ \rightleftharpoons Ca^{++} + HCO_3^- \quad \ldots 1$$

$$K_{CaCO_3} = 97$$

$$CaF_2 \rightleftharpoons Ca^{++} + 2F^- \quad \ldots 2$$

$$K_{CaF_2} = 10^{-10.96}$$

Dividing the first equation by the second, we obtain

$$\frac{[HCO_3^-]}{[H^+]\,[F^-]^{2-}} = 97 \times 10^{10.96} \qquad \ldots 3$$

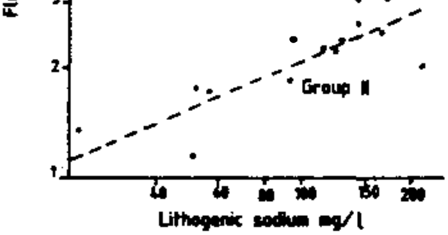
where the rectangular brackets indicate the activities.

It is clear from equation 3 that the activity of the fluoride ion is proportional to that of $[HCO_3]^-$ under constant pH. Because of the low solubility product of CaF_2, saturation is easily reached with respect to calcium fluorite and further presence of calcium changes the system because of the interaction with bicarbonate. The positive correlation between HCO_3^- and F^-, negative correlation between Ca^{++} and F^- have been observed earlier in high fluoride ground waters (5,6). Conditions of close to saturation in respect of CaF_2 and saturation with respect to $CO_3^=$ were also reported by these authors who supported a solution-evaporation-ion exchange hypothesis for the genesis of fluoride waters. The observations in both Vedavati and Pennar river basins deviated from the above findings.

The granitic rocks in the upper reaches of the Vedavati river basin contain more than 0.13% of fluoride. Fluorite mineral was also reported in thin-sections of the rock to the extent of 1.25% in modal composition. But groundwaters in the immediate surrounding area did not contain more than one or two ppm of fluoride. Detailed analyses of the rock and water samples from representative wells showed no correlation between fluorite content in waters and bulk rock. On the other hand there was good correlation between the fluoride content in soil leachates and that of even surface water bodies like tanks, ponds, etc (3). These results clearly establish that the leachable fluoride in the soil rather than the total fluoride in the bulk rock or soil govern the amount of dissolved F^- in natural waters. Therefore, the weathering condition or the degree of weathering, rather than the mere presence of fluoride-bearing minerals, is more important in controlling F^-(aq).

Figure 2

Plot of F^-(aq) with respect to Lithogenic Na^{++}(aq)



As the rock minerals weather to montmorillonite in dry climates, Na^+ and other cations are released from the minerals of the rocks. Hence the amount of sodium thus acquired by the groundwaters can be an approximate index of the degree of weathering. But Na^+ as sodium chloride also comes through anthropogenic activities or by the agency of wind. Because of the high solubility of NaCl, subtration of the equivalent weight of chloride from Na^+(aq) values stoichiometrically gives the residual or lithogenic sodium which can be considered as the input from mineral weathering only.

A plot of the lithogenic sodium and fluoride in the waters of the upper Pennar basin on a log-log graph showed (Figure 2) two distinct suites of samples with the following regression equations:

$$[F^-] = 1.2 \cdot \sqrt[3]{[Na]} \quad \ldots 4$$

$$[F^-] = 0.37 \cdot \sqrt[3]{[Na]^2} \quad \ldots 5$$

where $[F^-]$ and $[Na^+]$ are expressed in mg/l.

The correlation coefficients of the two suites are 0.71 and 0.83, the sample sizes being 9 and 16. The two groups come from distinct topographic environments as shown in Table 1.

Table 1

Characteristics of the Two Groups of Water Samples from Upper Pennar Basin

	Group I	Group II
1. Erosional feature	Gully erosion, low valley development	Stream valley is better developed
2. Gradient	Comparatively steeper surface slopes	Surface slopes are gentler
3. Fluoride	Minimum 3 mg/l	May be very low (less than 3 mg/l)
4. Saturation with respect to CaF_2	Saturated/over-saturated	Under-saturated
5. Saturation with respect to $CaCO_3$	Over-saturated	Over-saturated
6. Alkalinity	Lower for a given F^-	Relatively higher for the same F^-
7. P_{CO_2}	Range: 1.79 to 2.44 Mean: 2.09	Range: 1.82 to 3.28 Mean: 2.17
8. Regression	$[F^-] = 1.2 \cdot \sqrt[3]{[Na]}$	$[F^-] = 0.37 \cdot \sqrt[3]{[Na^+]^2}$

In the Vedavati river basin, where the stream valley is better developed, the following relationship was obtained between lithogenic sodium and fluoride (r = 0.7, n = 26)

$$[F^-] = 0.29 \cdot \sqrt[3]{[Na^+]^2} \quad \ldots 6$$

The equation has a close resenblance to that of the upper Pennar basin with similar topographic conditions. The structure of the above equations shows that the increase in fluoride is very low beyond 16 ppm of lithogenic sodium in the first group (gully erosion) and beyond 12 ppm of sodium in the case of the second group (better valley development). The equations are not applicable to a different environment, such as thermal springs.

The Fluoride Migration

Jacks et al (7) showed through a series of laboratory studies and field examination that the Ca-Mg carbonate concretions (Kankar), which form in the arid and semi-arid areas, accumulate fluoride leached out of rock minerals. The dissolution of fluoride from concretions and/or soil is controlled by pH of the draining solution, alkalinity and dissolved CO_2 and P_{CO_2} in the soil zone. In view of the fact that many of the water samples show supersaturation with respect to CaF_2, Ca^{++} may not be playing a decisive role in controlling F^-(aq). Hence weathering conditions and topographic development play a greater role.

The fluoride so accumulated by waters is further modified by the plant species growing in the area. Davison and others (8) cite several plants which accumulate fluoride of a few hundred ppm. The fluoride content of plants varies and does not remain constant over a period of time. In view of this, a closer interrelationship exists between the plant species in general and the other biota on one hand and the physico-chemical and weathering conditions on the other hand in controlling the dissolved fluoride in groundwaters. Thus, the mechanism of fluoride accumulation occurring in natural waters may be summarized as shown in Figure 3.

Conclusion

Studies on the chemistry of natural waters conducted in the Vedavati and Pennar river basins in peninsular India, a drought-prone, hard rock region, revealed that fluoride was highly variable spatially. Hence fluoride maps must show mean, standard deviation, and data density for meaningful understanding. Unlike the other chemical constituents, fluoride ion is normally distributed. Rather than the mere presence of fluoride-bearing minerals, fluoride ion in a leachable state controls the amount accruing to the groundwater. Weathering conditions govern and biota modify the fluoride content of ground waters. Certain equations relating valley development due to weathering (through lithogenic sodium as an index) to fluoride content can be developed. These equations appear to be characteristically valid in a given set of physiographic conditions.

Acknowledgements

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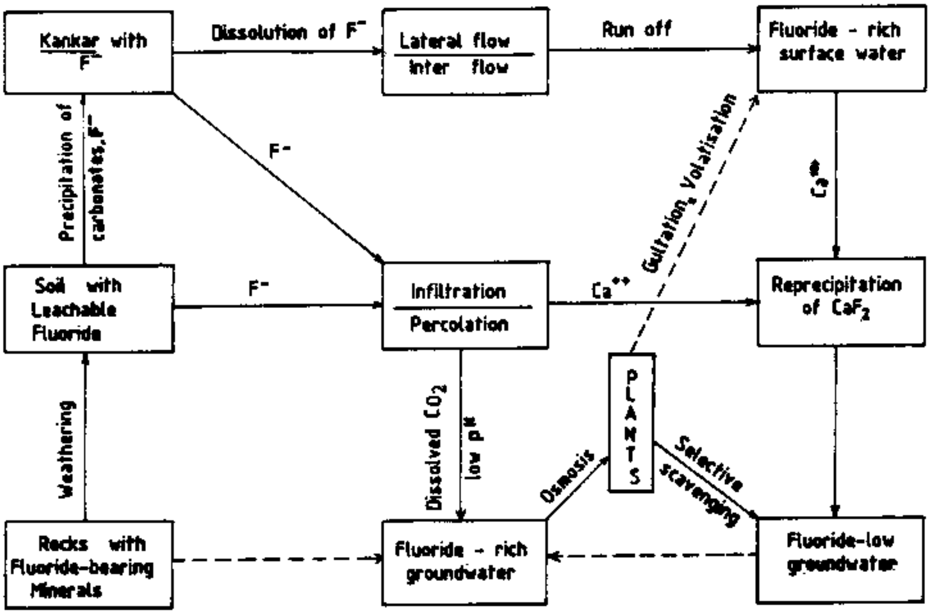
Figure 3

A Model for the Migration of F^-



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CASE HISTORY OF ACUTE POISONING BY SODIUM FLUOROSILICATE

by

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SUMMARY: A *rare case of acute poisoning by sodium fluorosilicate* is presented in the treatment of which calcium preparations administered intravenously played an important role.

KEY WORDS: Acute poisoning; Fluoride; Fluorosilicate

Introduction

Acute poisoning by fluorine compounds is less frequent than chronic forms and may be difficult to differentiate from other kinds of acute poisoning (1). It has been studied in humans and animals (2). In humans it has resulted from carelessness at coming in contact with fluorine compounds or by ingestion, either accidental or by intent to commit suicide (3). Acute fluorine poisoning has been previously described and documented by laboratory and clinical results (4). One feature of fluorine poisoning is cardiac dysrhythmia and the possibility of ventricular fibrillation (5). Acute poisoning may cause sudden death (3). Of great importance in the treatment of fluorine poisoning is the administration of calcium compounds, *without which the binding of fluorine with calcium* may cause a deepening hypocalcemia (4,6) with all its morbid consequences.

Case History

A 32-year-old female chemical plant worker, in a suicide attempt, ingested three teaspoonsful of sodium fluorosilicate. Almost immediately vomiting ensued. Despite prompt gastric irrigation by the first aid physician, the patient exhibited diarrhea, diaphoresis, weakness, facial numbness, cramps of the palms, feet and legs, muscular spasms, abdominal pain, shallow breathing and dyspnea. Physical examination revealed tachycardia (104/min), tachypnea (22/min), and generalized muscle spasms. On admission to the Intensive Care Unit, the following were administered: Calcium carbonate, 10 g dissolved in 20 cc of H_2O, gastric lavage and repeated in 6 hours; Pipolphen (promethazine-HCl) 50 mg per IV and repeated in 4 hours; Calcium carbonate solution 20 cc per IV; Bretylium tosilate 100 mg IM every 4 hours; Lidocaine 200 mg IV every 4 hours; Fenicort 200 mg IV every 6 hours for 24 hours. Physiological *multielectrolytic fluid (containing, in* g/dm^3: *NaCl,* 5.75; KCl, 0.38; $CaCl_2$, 0.394; $MgCl_2$, 0.20; Na acetate, 4.62; Na citrate, 0.90) was administered in 500 cc volume IV every 8 hours. The patient also received 500 cc of 5% glucose IV every 8 hours.

After 12 hours and subsidence of life-threatening symptoms, the patient was transferred to the Clinical Department of Occupational Diseases. There persisted a generalized weakness and liver enlargement to 3 cm below the right costal margin. Intravenous 5% glucose was continued and a single dose of multielectrolytic fluid of 500 cc was administered. Orally, the patient

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received Calcium lactogluconate 4 g t.i.d. for 10 days and aluminum phosphate 4.5% gel 15 cc q.i.d. throughout the period of hospitalization.

Laboratory testing revealed the following: 1] Erythrocyte sedimentation rate: 11 mm after 1 hour and 40 after 2 hours; 2] Blood count: Hb, 12.9 g/dl; RBC, 5.0 x 10^6; WBC, 4.1 x 10^3; PLTS, 211 x 10^3; 3] Urinanalysis: specific gravity 1.024; protein, 0.295%; no sugar was detected, leukocytes 10 to 15 in visible field, fresh erythrocytes 1 to 2 in visible field, desiccated erythrocytes 12 to 15 in visible field; 4] Gasometry: pH, 7.41; pO_2, 68.6 mm Hg; pCO_2, 37.0 mm Hg, HCO_3, 23.8 mmol/dm^3; BE, 0.4 mmol/dm^3; 5] GOT, 60 uJ/ml; GPT, 40 uJ/ml; LDH, 152 U/L; 6] Calcium level: 1.7 mmol/dm^3. Gasometry concerns the first 24 h in capilliary blood. (The normal values in this laboratory were: pH 7.35-7.45; pO_2, 80-100 mm Hg; pCO_2, 35-45 mm Hg; HCO_3, 21-27 mmol/dm^3; BE 3 mmol/dm^3; GOT, 5-40 uJ/ml; GPT, 5-30 uJ/ml; LDH, 120-230 U/L; Calcium level 2.2-2.5 mmol/dm^3).

The glucose tolerance curve was normal. However, galactose was detected in serum and urine for 2 weeks. Fluoride determination of urine and serum using the Radelkis fluoride ion meter are shown in Table 1. Fluoride in fingernails was determined by the gas chromatographic method (7). Twenty-one days after admission, the patient was discharged from the Department with no evidence of pathology. A follow-up examination 21 days after discharge also was negative.

Figure 1

Fluoride Level in Serum, Urine and the Nails

Day of hospitalization	F^- in serum (mg/dm^3)	F^- in fresh urine (mg/dm^3)	F^- in urine (24 hr collection) mg/dm^3
2	5.130	235.60	not investigated
3	0.399	15.39	not investigated
4	0.257	11.02	not investigated
5	0.156	1.71	4.56
7	0.057	1.71	1.03
11	0.072	0.54	0.80
13	0.038	1.10	0.29
15	0.049	2.09	1.67
20	0.067	0.87	0.72

Fluoride in nails determined after 15 days of hospitalization; 6.7 ppm F^-. After 32 days since poisoning, the level was 5.0 ppm F^-.

Discussion

As is apparent from the present case history, the level of fluorides in serum and urine rapidly returns to normal after calcium therapy was initiated. This is comparable with the observation made by Yolken et al, who have described a case of sodium fluorosilicate poisoning in a 2.5 year-old girl (4). Urine fluoride decreased more slowly than that of serum; only by the fifth day did stabilization of urine fluoride take place. Lack of significant changes in the fluoride level of nails is understandable since accumulation of nail fluoride is a slow process (8). Interestingly, acute fluoride poisoning does not include abnormalities of the glucose tolerance test whereas chronic poisoning has been observed to lead to hyperglycemia (9). An unusual feature of fluorine poisoning seems to be the presence of galactose in urine and serum. Further studies will establish whether or not the presence of free galactose in urine and serum are characteristic of such poisoning.

Conclusion

Prompt medical intervention in acute fluorine poisoning is necessary to prevent 1] sudden death from cardiac arrhythmia induced by calcium displacement from the heart muscle cell, and 2] the blocking of hemoglobine and formation of fluoromethemoglobin, pulmonary edema, tetany and, in consequence, respiratory complications and metabolic alkalosis.

Treatment should include the earliest possible gastric lavage and administration of calcium compounds. Cardiologic monitoring is indispensable because of the likelihood of cardiac dysrhythmias.

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SOIL RESPONSE AND ALFALFA FLUORIDE CONTENT AS AFFECTED BY IRRIGATION WATER

by

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SUMMARY: Fluoride containing irrigation water used on soil and crops during six years caused soil soluble F^- to increase linearly as irrigation proceeded. Total F^- increased only in the surface of the soil where it appears to reach a plateau. Further studies showed a decrease in F^- retention capacity and a CaF_2 soil solution saturation. The deep horizon showed no detectable F^- retention capacity. Soil properties favor persistence of added F^- in soil solution. The danger of F^- toxicity increases as irrigation progresses. With increase in water soluble F^-, alfalfa F^- content increases.

KEY WORDS: Alfalfa; Irrigation water; Soil fluoride; Soil fluoride retention; Soluble fluoride.

Introduction

The Central Provinces of Argentina are located in a typical temperate semiarid region. Devoted to cattle fattening on pastures, seeded with wheat, rye, sorghum and corn crops, the main agricultural problem is total rainfall (600 mm yearly) and its distribution. Rainfall is maximum in spring and minimum in winter; in dry and windy summers rain does not usually cover the high atmospheric water demand; periodic droughts may occur.

Irrigation would solve the shortage of water during the summer months. But surface water resources in this area are insufficient; underground water, usually high in salinity and alkalinity, would have to be used for irrigation; several aquifers are also F^- enriched (1).

The response of a typical soil and crop irrigated with such water is presented.

Materials and Methods

The field work was carried out on the Facultad de Agronomía (Universidad de La Pampa) farm located in Santa Rosa, La Pampa province. On the University Farm, one of several complementary irrigation plots, sprinkling irrigation was studied.

The soil is sandy loam entic Haplustoll, the characteristics of which have been published elsewhere (2). Soil samples were taken at 30 cm intervals, to a 1.20 m depth, where a caliche crust locally called "tosca," is almost impervious.

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Samples were taken from plots, where alfalfa (Medicago sativa) had been grown as a] control which was never irrigated, b] under irrigation for one year, c] under irrigation two years, d] under irrigation six years.

During the work period rainfall was average (600 mm yearly) or slightly more. Irrigation water, supplied to meet high summer water transpiration, was equivalent to 400 mm annually or less. Irrigation proceeded during the alfalfa growing period. Plant material was sampled from mature plants in spring.

F^- was determined in triplicate by a colorimetric method; soluble F^- (water extract 1:1); total F^- through digestion with H_2SO_4 and distillation with $HClO_4$; F^- in plants through NaOH digestion (1); soil F^- retention by the Gilpin method. Ammonium acetate exractable Fe was also measured (3).

Results and Discussion

Composition of the irrigation water, shown in Table 1, resembled that found 10 years ago (2) showing a composition constancy with time. The water is not well suited for irrigation and, as seen earlier (2), soil salinity and alkalinity increased. Soluble salts had accumulated in the C_2 horizon just over the calcareous crust, which abruptly impedes deep percolation. In this short irrigation time, exchangeable Na, conversely, accumulated on the surface (Table 2).

Table 1

Irrigation Water Composition

meq L^{-1}								d Sm^{-1}		ppm
Cl	SO_4	CO_3	CO_3H	Na	Ca	Mg	K	EC	Sodium adsorption ratio	F
11.26	7.84	2.30	3.68	21.82	1.55	2.63	----	2.48	18.5	9.1

Table 2

Soil Salinity and Alkalinity

	Control		1 yr irrigated		2 yrs irrigated		6 yrs irrigated	
depth (cm)	pH	EC	pH	EC	pH	EC	pH	EC
0-30	6.8	0.30	7.1	0.69	7.0	0.58	8.0	0.79
30-60	7.2	0.40	7.6	0.26	7.5	0.79	8.5	1.09
60-90	7.7	0.51	7.8	1.03	7.9	1.78	8.7	1.31
90-120	8.0	0.78	7.9	1.72	8.0	2.61	8.2	5.21

F^- content of water was far higher than maximum values given in irrigation standards (4,5), but irrigation water added on the average, annually, only about 40% of the total input of water to the soil, which would be similar to the use of water having 3 to 4 ppm F^- for a full irrigation area. Average values of both soluble and total F^- are shown in Table 3. In non-irrigated soil both are low in accordance with environmental conditions (6). As irrigation

Table 3

Total and Soluble Fluoride (mgK^{-1})

	Control		1 yr irrigated		2 yrs irrigated		6 yrs irrigated	
Depth (cm)	sol.F	tot.F	sol.F	tot.F	sol.F	tot.F	sol.F	tot.F
0-30	0.38	44.55	0.95	69.96	1.93	73.99	6.30	80.39
30-60	0.12	52.56	0.65	59.33	1.09	65.14	3.09	62.83
60-90	0.69	61.30	1.28	69.39	2.43	63.21	3.45	76.66
90-120	----	----	1.92	66.00	2.98	----	4.10	75.27

Figure 1

Total and Soluble F^- in A_1 Horizon

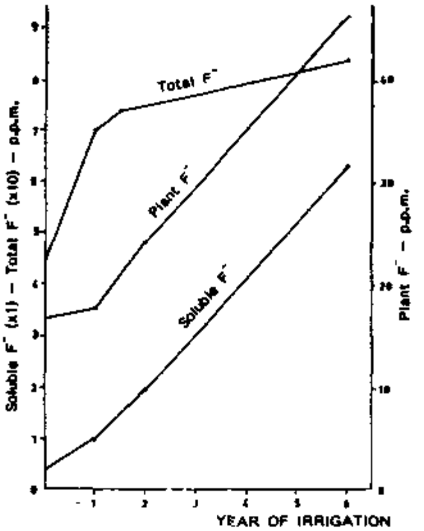

Table 4

F^- Retention and NH_4Ac extractable Fe

Depth (cm)	% retention	Fe ppm
0-30	49.49	0.42
30-60	22.90	0.20
60-90	0	0
90-120	0	0

time increased, both soluble and total F^- increased. Soluble F^- appeared not to accumulate in any horizon, but total F^- accumulated mainly in top soil. Figure 1 shows both total and soluble F^- in A_1 horizon and in alfalfa tissues. Soluble F^- increased linearly as irrigation progressed. Total F^- increased rapidly at first and then more slowly. Thus, the upper soil horizon would have been saturated in F^- retention capacity and, after a period of time under irrigation, soil retention would be very low or nil; all F^- from the irrigation water would not precipitate in top soil.

Reduction of F^- retention along with depth was marked (Table 4). It is associated with the ammonium acetate pH 4.8 extractable Fe, was described earlier (3). In the A_1 horizon from 6 year-old irrigated soil, F^- retention dropped from 50% to 38.8%. Accordingly, the ionic activity product (IAP) of CaF_2 (7) in the top horizon of the 6-year irrigated soil was 8.513; in the C_1 horizon it was 16.001 which shows that the soil surface is already saturated with CaF_2 and no more F insolubilization through the effect of Ca would be expected (7). The soil solution is not as yet CaF_2 saturated in depth but its retention properties are poor.

Most soils, even sandy ones, have high F^- retention capacity (6-10) which is also true for a neighboring soil (3). In the present case the soil can only retain some F^- in the upper horizons although it is swiftly losing this property. In deep horizons, F^- retention is not significant and soil soluble F^- increases as irrigation progresses.

Conclusion

For this soil, use of irrigation water, containing even less F^-, has to be carefully studied because the soluble F^- content of the soil rises abruptly. Further, the subsuperficial caliche crust represents a barrier for deep percolation of this F^- enriched soil solution, increasing the speed of contamination and reducing the rate of F^- elimination.

F^- in alfalfa plants, growing in 6-year irrigated soil, is high and would be harmful for crops; unfortunately data on yields, to measure the impact on production is lacking.

Plant F^- content was highly correlated with soluble F^- in the A_1 horizon or soluble F^- averaged in the whole soil profile ($r = 0.99$ in both cases). The regression equations were linear: $y = 2.666 \pm 1.195\ x$ and $y = -1.339 + 0.123\ x$, respectively. Although some authors found that sprinkling irrigation favored leaf absorption (11), apparently, in this particular situation, rainfall is enough to leach alfalfa leaves; significant F^- entrance was avoided in this way.

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THE FLUORIDE CONTENT OF CHINESE AND BLACK TEAS AVAILABLE IN HONG KONG

by

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SUMMARY: An experimental method of preparing a tea infusion was devised to simulate the situation in Chinese restaurants. The total fluoride content of Chinese and black teas was of the same magnitude (0.199-0.422 mg per ml tea). However, the dissolvable fluoride content of black teas was consistently higher than that of Chinese teas.

KEY WORDS: Tea infusion, fluoride content; tea solution.

Introduction

Traditionally tea has been an important constituent of the Chinese diet. In Hong Kong per capita tea consumption increased by 8.2% between 1981 and 1983 (Table 1) (1). The majority of the teas drunk by Chinese members of the community are grown in Mainland China, whereas those consumed by the much smaller expatriate community are grown in China, India, Sri Lanka and New Guinea. Published studies, which have been carried out in China on teas grown there, are few and data available on teas consumed in Hong Kong are limited.

Table 1

Tea Consumption in Hong Kong from 1981 to 1983

Year	Population in millions	Consumption of Tea Leaves per Annum	
		Total in million Kg	Per capita in Kg
1981	5.15	10.67	2.07
1982	5.23	11.04	2.11
1983	5.31	11.88	2.24

The results obtained by workers studying the fluoride content of tea infustions have varied, possibly due in part, to the different methods used to determine the fluoride ion concentrations (2-4) and to the fact that different brands of commercially available black teas are blended. The subjective quality of Chinese teas is determined by such factors as, seasons, age of tea leaves when they were harvested, and the region in which the plant was grown. The regions may vary in altitude, in amounts of sunshine, in sources of water and hence in fluoride content, timing and quantities of rainfall. The method of processing is also an important factor. Published results, although indicating the available fluoride content of tea leaves obtained by experimental techniques, do not necessarily reflect the amount of fluoride that an individual

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who drinks the tea will receive, as the domestic method of preparation is not reproduced in the scientific investigation.

The purpose of this study was to determine the amount of available fluoride in Chinese and black teas and the dietary intake from this source by people living in Hong Kong.

Materials and Methods

Six different varieties of Chinese tea and four different types of branded black teas were used in this study. For each of the six types of Chinese tea three differently priced samples were obtained to reflect differing qualities. In Tables 2, 3 and 4 the cost of each tea is indicated by the suffix 1, 2, or 3; 3 was the most expensive, and 1 the least expensive.

When preparing the infusions, 2.0 g of tea leaves were infused with 300 ml of boiling tap water (0.67%, w/v tea infusion). Three samples of each tea were prepared and three readings taken. Only mean values are reported.

The fluoride content of each tea was determined from infusions prepared in two different ways:

Method 1 – Continuous Infusion (English style). The fluoride content of the infusion was determined after 5 minutes, 20 minutes and 24 hours. The solution was allowed to remain in contact with the leaves throughout the experimental period.

Method 2 – Repeated Infusion (Chinese style). After the fluoride content of the infusion had been determined at 20 minutes the entire solution was decanted. A freshly boiled 300 ml volume of water was added to the used tea leaves. At the end of one hour the solution was decanted and its fluoride content determined. The process was then repeated and the fluoride ion concentration again measured after the water had been in contact with the leaves for five hours.

Fluoride Determination: The available dissolvable fluoride in the tea infusions was determined by the combination fluoride specific electrode method.

Determination of the total fluoride content of the tea leaves was performed using alkaline reflux. The tea leaves were refluxed in 50% NaOH for 2 hours. The filtrate was neutralized and the pH adjusted until it was 5-6 by using 4M buffered potassium acetate solution. The residue was then fused with zinc oxide and sodium carbonate to remove any remaining fluoride. Finally, the total fluoride content of the leaves was determined by the sum of the fluoride content in all the filtrates and the vapor from the reflux of the residues.

Results

After 20 minutes of infusion using the continuous infusion method, 55.3% of the dissolvable fluoride was obtained from the sample of Lu-an 3, compared with 92.7% of that of the Shui-hsien 2. For black teas a higher percentage of dissolvable fluoride was constantly obtained in this time period; it was 94.5% for Rickshaw and 97.7% for the Yellow Label Lipton tea (Table 2). The

Table 2

Dissolvable F^- in 0.67% Tea Solution by Continuous Infusion Method

Types of tea	Dissolvable F^- in mg/L tea solution — Infusion Time			Percentage of dissolvable F^- in 20 min
	5 min	20 min	24 hr	
Pu-erh 1	0.14	0.22	0.27	82.5
Pu-erh 2	0.19	0.27	0.40	66.7
Pu-erh 3	0.22	0.37	0.40	91.7
Lung-ching 1	0.34	0.41	0.51	85.5
Lung-ching 2	0.21	0.27	0.30	88.9
Lung-ching 3	0.17	0.24	0.28	85.7
Jasmin 1	0.26	0.31	0.39	81.0
Jasmin 2	0.32	0.35	0.45	77.6
Jasmin 3	0.28	0.31	0.41	75.4
Lu-an 1	0.21	0.29	0.43	67.7
Lu-an 2	0.32	0.47	0.67	69.3
Lu-an 3	0.32	0.38	0.69	55.3
Shui-hsien 1	0.25	0.43	0.53	81.0
Shui-hsien 2	0.42	0.77	0.83	92.7
Shui-hsien 3	0.34	0.46	0.62	74.2
Shou-mei 1	0.23	0.38	0.59	64.8
Shou-mei 2	0.26	0.44	0.61	72.5
Shou-mei 3	0.18	0.24	0.30	80.0
Rickshaw	1.00	1.04	1.10	94.5
Liptons Yellow Label	1.11	1.13	1.16	97.7
Liptons Ceylon Tea	0.74	0.79	0.81	97.5
Twinings Breakfast Blend	1.44	1.58	1.67	94.8

1,2,3 indicate cost: 1, least expensive; 3, most expensive.

results of the technique in which all of the infusion was decanted off and the fluoride content determined showed that the majority of the fluoride was obtained after 20 minutes (Table 3). The total dissolvable fluoride in Chinese teas ranged from 0.045-0.136 mg per gram tea leaves, whereas for black teas the range was from 0.120-0.244 mg per gram of tea leaves (Table 4).

The total fluoride content as determined by the alkaline extraction technique showed the fluoride level to range from 0.199-0.422 mg per gram tea leaves for the Chinese teas. The black teas in this range had a much higher profile (0.357-0.387 mg per gram of tea leaves). Percentage of dissolvable fluoride to total fluoride content was 11.1%-39.9% in Chinese teas; for black teas the range was from 32.9%-67.0% (Table 4).

Table 3

Dissolvable F^- in 0.67% Tea Solution Determined by Repeated Infusions After Decantation of All the Solution

Types of Tea	Dissolvable F^- in mg/L tea solution			
	Infusion Time			
	20 min	1 hr	5 hr	Total F^-
Pu-erh 1	0.22	0.07	0.05	0.34
Pu-erh 2	0.27	0.06	0.00	0.33
Pu-erh 3	0.37	0.17	0.09	0.63
Lung-ching 1	0.41	0.07	0.02	0.50
Lung-ching 2	0.27	0.05	0.01	0.33
Lung-ching 3	0.24	0.03	0.00	0.27
Jasmin 1	0.31	0.05	0.00	0.36
Jasmin 2	0.35	0.13	0.00	0.48
Jasmin 3	0.31	0.09	0.00	0.40
Lu-an 1	0.29	0.04	0.11	0.44
Lu-an 2	0.47	0.17	0.09	0.73
Lu-an 3	0.38	0.19	0.05	0.62
Shui-hsien 1	0.43	0.11	0.11	0.65
Shui-hsien 2	0.77	0.21	0.00	0.98
Shui-hsien 3	0.46	0.11	0.05	0.62
Shou-mei 1	0.38	0.06	0.13	0.57
Shou-mei 2	0.44	0.11	0.00	0.55
Shou-mei 3	0.24	0.03	0.03	
Rickshaw	0.94	0.09	0.01	1.04
Liptons Yellow Label	1.06	0.08	0.01	1.15
Liptons Ceylon tea	0.69	0.09	0.01	0.79
Twinings Breakfast Blend	1.47	0.10	0.01	1.58

Discussion

In Hong Kong the majority of the population eat at restaurants rather than at home. Tea is the most popular beverage among the Chinese and is almost exclusively consumed in restaurants. The experimental methods used in this study simulated the traditional method of preparing Chinese tea. The quantity of tea, 2.0 g in 300 ml of water (0.67% solution) is the average quantity of leaves placed in a standard size Chinese teapot. When all of the infusion has been drunk fresh water is added and this process is continued until the meal is finished. Method 2 recreates this social situation.

Chinese teas are of many different qualities. An attempt was made to account for this variation in quality by using three different types of tea within each group. Unfortunately, no obvious trend was found between the quality of tea and the quantity of dissolvable fluoride. To determine whether any correlation exists it would be necessary to perform an investigation on all teas

Table 4

Comparison of F^- Obtained by Alkaline Reflux with that by Infusion Methods

Types of Tea	Total F^- Content Obtainable in mg/gm tea leaves				Percentage of dissolvable F^- to total F^-
	Alkaline extract	Infusion			
		continuous	successive	average	
Pu-erh 1	0.302	0.040	0.050	0.045	14.9
Pu-erh 2	0.223	0.060	0.049	0.055	24.7
Pu-erh 3	0.400	0.060	0.095	0.078	19.5
Lung-ching 1	0.282	0.077	0.075	0.076	27.0
Lung-ching 2	0.263	0.045	0.049	0.047	17.9
Lung-ching 3	0.368	0.042	0.040	0.041	11.1
Jasmin 1	0.199	0.058	0.055	0.057	28.6
Jasmin 2	0.217	0.067	0.071	0.069	31.8
Jasmin 3	0.200	0.061	0.059	0.060	30.0
Lu-an 1	0.382	0.065	0.066	0.066	17.3
Lu-an 2	0.323	0.101	0.108	0.105	32.5
Lu-an 3	0.320	0.103	0.093	0.098	30.6
Shui-hsien 1	0.254	0.079	0.098	0.089	35.0
Shui-hsien 2	0.422	0.124	0.147	0.136	32.2
Shui-hsien 3	0.233	0.093	0.093	0.093	39.9
Shou-mei 1	0.272	0.088	0.085	0.087	32.0
Shou-mei 2	0.254	0.091	0.082	0.087	34.3
Shou-mei 3	0.354	0.045	0.045	0.045	12.7
Rickshaw	0.387	0.165	0.156	0.161	41.6
Liptons Yellow Label	0.357	0.174	0.173	0.174	48.7
Liptons Ceylon tea	0.365	0.121	0.118	0.120	32.9
Twinings Breakfast Blend	0.364	0.250	0.237	0.244	67.0

within each group. The total fluoride content of all Chinese and black teas under investigation as determined by alkaline reflux was of the same magnitude and fell within the range of 0.199-0.422 mg per gm tea leaves. However, the amount of dissolvable fluoride was consistently greater in the black teas whatever method of extraction was used. The largest proportion of the dissolvable fluoride was obtained within the first 20 minutes (Tables 2, 3).

The results obtained for black teas compared favorably with those of Louw and Grobler (4), but were slightly higher than reported elsewhere (2,3). This may be because other workers used a 1% tea infusion and determined the fluoride content after only 5 minutes rather than 20 minutes, the optimum time period. By comparison Chinese teas were found to have a fluoride content similar to South African Rooibos tea, but have a much lower value than Camillia sinensis (4), as the tea plant is known to accumulate fluoride in its leaves (2).

Chinese teas contained less fluoride than European style black teas. In itself this would suggest that it is better to drink Chinese tea prepared in the traditional way. However, consideration must be given to the total dietary fluoride intake from all types of food (7,8) as well as from Chinese tea consumed by an individual living in Hong Kong. According to the 1983 population census figures (1), the annual consumption of dry tea leaves was 2.24 kg per capita (1). At a concentration of tea equivalent to 0.67%, each individual would consume 0.92 litres of tea solution per day, giving a minimum daily fluoride intake from tea of 0.49 ppm or 0.45 mg of fluoride.

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EFFECT OF BORAX IN TREATMENT OF SKELETAL FLUOROSIS

by

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SUMMARY: Borax was used during 1981-1982 for treatment of 31 patients suffering from skeletal fluorosis. The amount administered was gradually increased from 300-1100 mg/day during a three month period, with one week resting period each month.

Experimental criteria included observation of symptoms, of physical signs such as movement of joints, and urinary excretion of F^- and BF_4^-. Findings in patients given borax were compared with data obtained from controls to whom no borax was administered. The borax group experienced a good effect rate.

KEY WORDS: Borax; Defluoridating agent (fluoride removal by borax); Skeletal fluorosis.

Introduction

Borax is one of a number of defluoridating agents as shown by animal experiments conducted in China and in other countries; an effective short period remedy for fluoride poisoning. Although toxicity has not been exhibited, application to skeletal fluorosis in humans has not been reported (1). When used for a sudden attack of epilepsy (2) a dose from 0.9-4.0 mg borax caused no adverse reaction. Since 1981, 31 of our patients have been treated with borax.

Materials and Methods

In 31 patients aged 35-55 years who had always resided in an endemic fluorosis area, physical signs and symptoms of fluorosis were manifest. Skeletal fluorosis was proven by X-ray. In 1981, 10 patients were administered 90-135 mg/day borax for 95 days which we designated The First Observation. In 1982, we made The Second Observation: 21 patients were divided into two groups; to one, borax was administered; the other was used as control. The experimental group received 300 mg/day for 15 days, 600 mg/day for 15 days, 900 mg/day for 45 days and 1100 mg/day for 15 days. One week resting period was provided each month. The control group received yeast instead of borax.

The following observations were made on borax and control groups: symptoms, physical signs, X-ray films, duration of treatment, urinary BF_4^- excretion, liver and kidney function. Urinary F^- and BF_4^- were determined by ionic sensitive electrodes.

1. In those in whom borax made a significant effect, clinical symptoms basically disappeared (Table 1); physical signs improved and both urinary F^- and urinary BF_4^- increased.

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Table 1

The Improvement of the Symptoms and Signs

Symptoms	First Observation, 1981 Before Therapy	First Observation, 1981 Good Effect	Second Observation, 1982 Before Therapy	Second Observation, 1982 Good Effect
Headache	1	1	9	8
Dizziness	8	6	10	10
Numbness	6	3	7	4
Tinnitus	5	4	8	7
Pain in Arms	7	7	7	5
Pain in Legs	10	6	10	7
Backache	10	8	11	6
Fatigue	6	4	12	7
Palpitation	6	5	8	8
Abdominal pain			8	8
Activity of Shoulder Joint	10	3	15	13
Squatting and Sitting test	10	3	15	11

Table 2

Variations in Urinary BF_4^- (mg/24 hr) of Patients

Group	Cases	0	I	II	III	IV	V
BORAX GROUP	1	22.4	23.9	32.1	37.8	51.1	75.1
	2	49.6	20.4	15.7	42.3	77.9	34.5
	3	50.1	40.3	38.3	40.7	53.6	46.3
	4	57.6	82.6	35.2	90.8	98.0	97.9
	5	14.5	7.8	11.6	20.1	25.4	20.0
	6	63.3	54.2	54.8	76.6	99.6	66.8
	7	54.1	21.2	34.9	31.4	23.3	21.8
	8	17.0	9.2	8.6	17.8	25.0	19.9
	9	48.2	48.8	33.1	44.2	48.1	21.0
	10	51.4	59.1	28.7	53.8	81.0	73.0
	11	57.2	65.4	66.6	68.0	84.6	76.4
	12	8.4	15.3	7.5	14.0	31.3	26.5
	13	55.2	28.3	49.2	42.5	53.4	41.7
	14	15.4	15.0	10.8	13.0	15.4	8.7
	15	24.2	18.4	30.3	24.0	41.7	28.1
						$P<0.01$	$P>0.05$
CONTROL	1	33.8	7.9	12.6	24.9	33.4	24.1
	2	63.4	67.9	35.8	80.9	60.9	66.1
	3	24.9	13.9	20.0	23.3	30.6	35.7
	4	60.3	73.2	76.7	71.8	101.0	50.0
						$P>0.05$	$P>0.05$

Note: 0 = Before Therapy; I = 300 mg/day; II = 600 mg/day; III = 900 mg/day; IV = 1100 mg/day; V = Therapy Discontinued.

2. In those who improved, clinical symptoms were somewhat better; urinary F^- and urinary BF_4^- increased but not markedly.

3. In the control group no change occurred; signs and X-ray films were the same as before treatment.

Results

For improvement of symptoms and signs after treatment see Table 1. Upon increasing the dosage, physical signs decreased more than from the primary dose, especially after 1100 mg/day borax was administered in 1982, based on activity of shoulder joint, squatting and sitting tests. Urinary excretion of BF_4^- is shown in Table 2; 1100 mg/day of borax caused marked increase in urinary BF_4^- ($p < 0.01$) which decreased when borax was stopped. In the control group little difference was observed before and after treatment, only some symptoms were alleviated.

Table 3

Comparison of Therapeutic Effect

Group	Total Cases	Good Effect Cases	Rate %
First Therapy	10	5	50
Second Therapy	15	12	80
Control	4	0	0

No significant changes in liver and kidney function were observed before or after treatment. Table 3 shows the therapeutic effect: the larger the dosage of borax, the better the effect.

Discussion

Since the element fluorine was first isolated in 1886, scientists have been trying to find a method to relieve its toxic effect by using calcium, aluminum, etc. Recently scholars observed that Ca and Al, in excess, are harmful to the organism. In 1975, Indian scientists reported that serpentine possesses therapeutic value but its constituents are quite complicated. Since serpentine is not always the same its effect varies (3-6).

In 1978, Grunewald and others reported in rabbit experiments that borax is a good anti-fluoride agent, without toxic side-effects. Use of borax for skeletal fluorosis in humans has not as yet been reported either in China or elsewhere (7-14).

In our experiments, dosage of borax was gradually increased from 300-1100 mg/day; excretion of BF_4^- was compared with controls. When dosage increased, urinary F^- and BF_4^- also increased, whereas in the control group no difference was observed, indicating that borax has a general therapeutic effect on skeletal fluorosis patients. During treatment no neuritis occurred; liver and kidney function remained normal.

The therapeutic mechanism of borax is not as yet clear. Seffner's experiment on pigs indicates that long bones from both fluoride groups were longer and thicker; in the high borax group they were reduced (11).

Conclusion

Additional studies are necessary to elucidate the mechanism involved in borax therapy as well as to determine whether high doses of borax can be administered to humans over an extended period without causing subtle adverse effects to liver and kidneys.

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SPINAL CORD STUDIES IN FLUOROTIC DOGS

by

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SUMMARY: No studies are available of spinal cord examination in cases of fluorotic spinal compression. Only one report in the literature is concerned with the spinal cord in a case of industrial fluorosis. The findings in this patient, who died of glioblastoma multiform, indicate the presence of anterior horn cell disease in fluorosis.

In the present study, spinal cords in five fluorotic dogs from the endemic area were studied histologically; in none of the spinal cord sections was evidence of anterior horn cell lesion observed.

KEY WORDS: Spinal cord; Anterior horn cells

Material and Methods

Five fluorotic dogs, otherwise neurologically normal, from the endemic area and five healthy dogs from a nonendemic area were used for the study of spinal cords. Twenty-four hour urinary fluoride of fluorotic as well as healthy dogs was estimated using Orion fluoride electrode method (1). Roentgenograms, taken in both groups, were tabulated in one of three grades (2). Myelograms were done on fluorotic dogs. Only those whose myelogram was normal were used for the study.

Under intraperitoneal anesthesia, wide laminectory was performed in all dogs. Spinal cords which were removed were fixed in formalin. Spinal cord sections, made at the level of cervical, dorsal and lumbar regions — taken at almost the same level in all — were stained with hemotoxylin and eosin; Nisels staining was done for the study of anterior horn cell structure.

Results

The roentgenograms of the spine of fluorotic dogs showed grade I changes in four and grade III in one. Myelograms did not reveal any block in all five fluorotic dogs. The urinary and bone fluoride levels were several times higher in fluorotic dogs compared to normal dogs.

Spinal cord sections revealed no abnormality in the grey matter histologically to suggest anterior horn cell pathology. All sections showed normal architecture and neuronal population.

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Discussion

In this study fluorotic dogs, otherwise neurologically normal with normal myelograms, were used specifically to exclude the possibility of changes in anterior horn cells secondary to radiculopathy and myelopathy. None of the spinal cord sections studied showed any abnormality to suggest anterior horn cell disease. It was practially impossible to do quantitative study to determine the density of anterior horn cells. Thus this study shows no clear cut evidence of anterior horn cell disease in fluorosis. However in the spinal cord case of industrial fluorosis who died of glioblastoma multiform features in the grey matter of the spinal cord suggested anterior horn cell disease (1,2). According to histological studies (4,5) of muscle and nerve in endemic fluorosis the nerve root "F" waves and "H" reflex abnormalities were recorded by electromyography in skeletal fluorosis patients without obvious neurological deficit indicating subclinical entrapment of nerve roots (6). In light of the above facts it is likely that the changes observed by Franke in anterior horn cells of the spinal cord are secondary due to spinal root entrapment. Subclinical entrapment of nerve root in fluorosis without obvious clinical signs is possible.

Conclusion

Thus fluoride does not seem to have a direct toxic action on anterior horn cells.

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FLUORIDE ANALYSIS OF MILK IN JAPAN

by

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SUMMARY: To determine the total and ionizable fluorine levels in milk, we applied and examined the optimum working conditions for each of the following three methods: 1] gas chromatographic method after pretreatment with low temperature oxygen plasma ashing; 2] separation of fluorine by microdiffusion followed by gas chromatographic analysis; and 3] direct measurement of ionizable fluoride in milk by the fluoride ion-selective electrode method.

Total and ionizable fluoride levels of 20 kinds of milk obtained from different districts of production in Japan, which were determined and compared, varied according to different districts of production. The ratio of total fluoride to ionizable fluoride was not always in agreement.

KEY WORDS: Fluoride analysis; Japan; Low temperature ashing; Microdiffusion; Milk.

Introduction

Determination of the fluoride in foods is important in estimating our daily fluoride intake. In recent years, the total and ionizable fluoride levels in milk have been determined separately (1) in the same manner as fluoride levels in blood serum are determined. On examining the practicality of using low temperature oxygen plasma ashing (2) for the pretreatment of biological samples we decided to use the low temperature ashing method for milk.

After investigating the optimum working conditions of the low temperature ashing method, the microdiffusion method and the fluoride ion-selective electrode method for the determination of fluoride in milk, we analyzed the total and ionizable fluoride levels of 20 kinds of milk produced and marketed from different districts in Japan.

Materials and Methods

Shaking apparatus (Thomas scientific T-22S). 20 milk samples were obtained from different districts of production in Japan. Total and ionizable fluoride levels were determined by use of the three methods described in the following:

The Low Temperature Ashing Method: A mixture consisting of 1 mL of milk and 1 mL of distilled water was subjected to low temperature ashing. Optimum working conditions were found to be as follows: 1 mL of milk; electric power at 100 watts; oxygen flow rate: 100 mL/min; and ashing time of 6 hours. The final extract in hexane was then analyzed by gas chromatography.

The Microdiffusion Method: This is a combination of microdiffusion and gas

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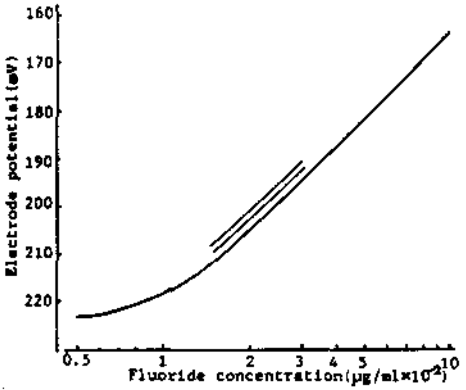
chromatography. Strong perchloric acid was used to simultaneously decompose and diffuse milk as in the case of blood serum. Since milk contains higher amounts of organic matter than blood serum, we examined such factors as the concentration and amount of both the trapping solution, sodium hydroxide, and the perchloric acid in order to find optimum working conditions of micro-diffusion of milk.

As with blood serum, a Tupper Ware minicup was used as a diffusion bottle. A polyethylene tube containing a trapping solution of 100 μL of 5 M sodium hydroxide and a 2 mL sample were placed into the minicup. Addition of 2 mL of 60% perchoric acid solution saturated with HMDS (hexamethyldisiloxane) followed. The last-mentioned was added as a releasing solution. The fluorine was released then analyzed by gas chromatography.

The Fluoride Ion-Selective Electrode Method: In this procedure, milk samples without any prior treatment were subjected to determination by the fluoride electrode method.

Figure 1

Calibration Curve for Fluoride



The fluoride ion-selective electrode has been widely used to determine ionizable fluorine. Recently however, it has been reported that the electrode method can give false results, particularly when the fluoride concentration in the solution is low (3). To solve this problem, just before measurement was to be taken, a low-level TISAB (4) was added to the sample and standard solutions in a ratio of one to one. This was followed by addition of 0.6 mL of lactic acid and the pH of the solution was adjusted to 5. A calibration curve was contructed on semilogarithmic paper which has twice as wide a scale as ordinary semilogarithmic paper (Figure 1).

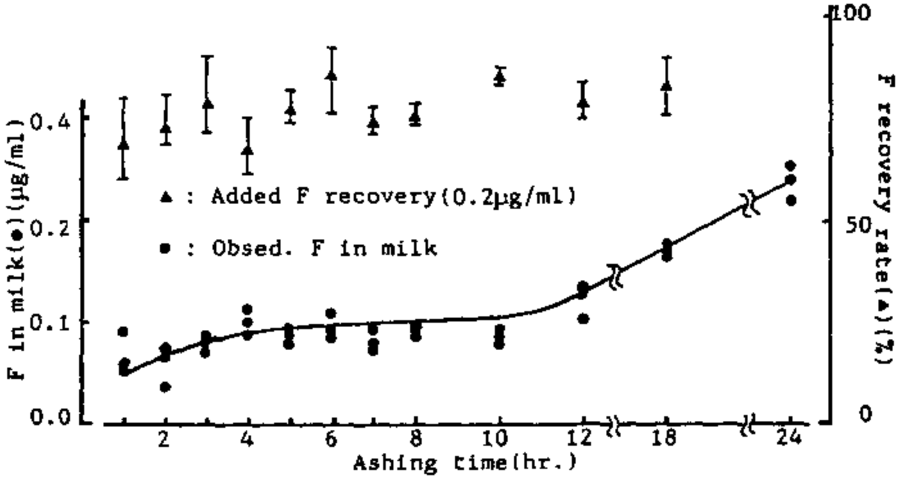
The electrode potentials of the standard solutions were measured and plotted on a linear axis against their concentrations on a log axis. As the memory effect (5) of the electrode influences the measurement of subsequent samples, we corrected the calibration curve with a 0.02 μg/mL standard solution between each measurement. From our experience the ionizable fluorine level of milk is around 0.02 μg/mL. The electrode potentials had to be read exactly ten minutes after the electrode made contact with the sample or the standard solution. This method made it possible to measure the fluoride concentration down to a third decimal place with good reproducibility.

Results and Discussion

Figure 2 illustrates the relationship between the time taken for ashing and the fluoride concentrations determined by gas chromatography. Consistent values were obtained within 4 and 8 hours of ashing. Ashing beyond 8 hours resulted in a gradual increase in fluoride with increase in ashing time.

Figure 2

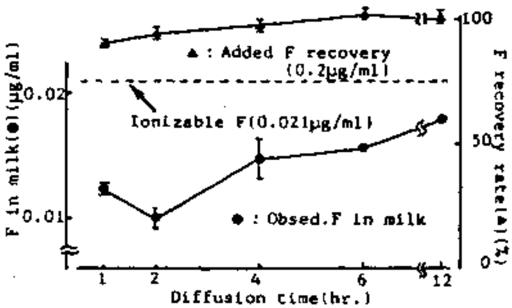
Effects of Ashing Time on F Determination



The mechanisms involved in oxidation and decomposition of plasma samples during ashing are not clear. The reasons for the above increase in fluoride levels may be that the amount of calcium in milk is about 1000 ppm, ten times as high as that in blood serum. When ashing time is short and decomposition is not complete, calcium is covered with organic matter that remains in the ash. This calcium is unable to absorb fluorine in the oxygen inside the chambers of the low temperature ashing apparatus. As the ashing time is extended and the ashing is completed, calcium will exist as calcium carbonate or calcium oxide. These may adsorb small quantities of fluorine in the oxygen inside the chambers.

Figure 3

Effects of Diffusion Time on F Determination



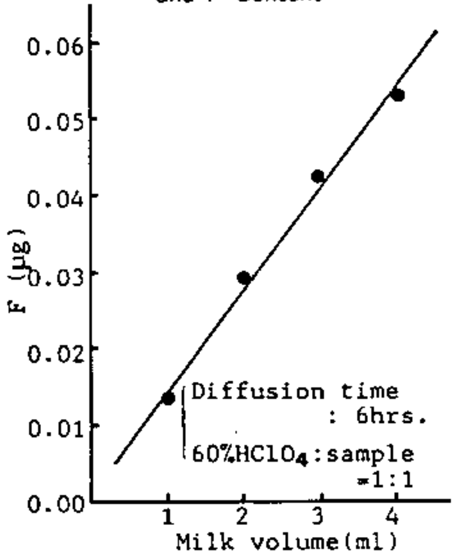
Sodium fluoride was added to milk at a level of 0.2 μg/mL and a recovery rate of about 85% was obtained with an ashing time of 6 hours. Even at an ashing time of 8 hours, the recovery rate was above 80%.

Figure 3 illustrates the effect of diffusion time on the fluoride content and the recovery of added fluoride. The recovery rate of fluoride added to milk as sodium fluoride was around 100% after a diffusion time of 3 hours or more, the same rate as that of blood serum.

The levels of fluoride in milk obtained in this study showed a gradual increase as diffusion time was increased. After 12 hours diffusion, the fluoride level obtained by microdiffusion was about the same as that of ionizable fluoride obtained by the electrode method. Our method requires a longer

Figure 4

Relation between Sample Volume and F Content



diffusion time than Sara's method (6) due to use of a different type of diffusion container which lowers the loss of fluorine although diffusion time is longer. A good linear relationship exists between the sample volume and the fluoride value determined (Figure 4).

The results obtained from determination of 20 kinds of milk produced and marketed from different districts in Japan are summarized in Table 1. The mean value for ionizable fluoride, measured by the direct electrode method, was 0.020 μg/mL. With gas chromatography, following pretreatment with microdiffusion, the mean value obtained was 0.018 μg/mL. The difference between the two figures was small. The mean total fluoride level in milk samples determined by the low temperature ashing method followed by gas chromatography was 0.080 μg/mL.

Figure 5

The Districts of Production of 20 Kinds of Milk in Japan

The total fluoride level was slightly lower than those reported by Duff (7) and Dirks et al. (1). Although the value for ionizable fluoride was about the same as that reported by Dirks et al. This may be due to the fact that the samples were obtained from different dairy producers. Daily variations may also exist.

The ionizable fluoride content of sample No. 9 from Nakakanbara (* in Figure 5) is almost twice as high as that of other samples, which may be related to geographical characteristics influencing the fluorine content in milk produced in certain areas.

The ratios of total fluoride to ionizable fluoride varied from 3.2 to 6.1. Milk with a higher concentration of ionizable fluoride did not always show higher concentration of total fluoride.

Table 1

Total and Ionizable F Levels in Milk

Sample No.	Districts of Production	F detected (μg/mL)			Ratio
		Diff.-GC	I.E.[1] (ionizable F)	Ashing-GC	Ashing-GC / I.E.
1	Ashahikawa	0.011	0.017	0.078	4.6
2	Akita	0.017	0.018	0.062	3.4
3	Ninohe	0.012	0.015	0.062	4.1
4	Koga	0.012	0.017	0.064	3.8
5	Higashiyamato	0.014	0.017	0.076	4.5
6	Numazu	0.031	0.026	0.108	4.2
7	Shizuoka	0.022	0.022	0.103	4.7
8	Toyohashi	0.015	0.015	0.091	6.1
9	Nakakanbara	0.025	0.029	0.110	3.8
10	Minamikanbara	0.021	0.027	0.090	3.3
11	Nagaoka	0.034	0.027	0.091	3.4
12	Mihara	0.016	0.019	0.068	3.6
13	Takamatsu	0.017	0.022	0.074	3.4
14	Takamatsu	0.016	0.022	0.072	3.3
15	Zentsūji	0.018	0.020	0.086	4.3
16	Kasuga	0.023	0.023	0.073	3.2
17	Kikuchi	0.010	0.015	0.079	5.3
18	Kumamoto	0.022	0.021	0.075	3.6
19	Ōita	0.013	0.014	0.065	4.6
20	Miyakonojō	0.016	0.015	0.072	4.8
	Mean	0.018	0.020	0.080	4.1
	S.D.	0.006	0.005	0.015	0.8

[1] F ion electrode

Conclusion

Total and ionizable fluoride levels varied with sources of milk. The ratio of total to ionizable fluoride levels was not always in agreement. It is apparent that fluoride determination in milk is difficult because it deals with extremely low levels of fluorine. Further research is required. Knowledge of fluorine content in food is important to ascertain fluoride intake especially that of babies and young children.

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THE RELATIONSHIP OF BONE MASS AND FRACTURE HISTORY TO FLUORIDE AND CALCIUM INTAKE: A STUDY OF THREE COMMUNITIES

by

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(Abstracted from American Journal of Nutrition 44:889-898, 1986)

Stimulated by the suggestion that water fluoride >1 mg/L may protect against osteoporosis, we studied bone mass of women in three rural communities with differing mineral content of the water supply. Mean fluoride and calcium of community drinking waters were 4 mg/L and 16 mg/L, respectively, in the high fluoride community; 1 mg/L and 375 mg/L, respectively, in the high calcium community; and 1 mg/L and 65 mg/L, respectively, in the low calcium community. Bone mass was measured by single photon absorptionmetry, and women were interviewed about fracture history, dietary intake, and other important covariates.

We observed no protective effect with higher fluoride intake. Bone mass was lower in older women from the high fluoride community although not statistically so; these women reported significantly more fractures. There was no observed community difference in young women's bone mass or fracture history. Young women in the high fluoride community consuming calcium and vitamin D in excess of 800 mg/day and 400 IU/day, respectively, had significantly better bone mass ($p < 0.05$) than their peers.

KEY WORDS: Bone mass, Dietary calcium intake, Fractures, Fluoride, Osteoporosis.

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HIP FRACTURE INCIDENCE NOT AFFECTED BY FLUORIDATION

by

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(Abstracted from Acta Orthop. Scand. 57:344-348, 1986)

Illiac crest biopsies were taken from patients with hip fractures from a low-fluoride area (<0.3 ppm), from an area with fluoridated drinking water (1.0-1.2 ppm), and from a high-fluoride area (>1.5 ppm). Fluoride content analysis and histomorphometry of bone were performed. The hip fracture incidence during 1972-1981 was studied in the same areas.

The fluoride content of the bone samples correlated with drinking water fluoride. In patients with hip fractures, both osteomalacia and osteoporosis were common. In the high-fluoride area also osteofluorosis was found in many patients. Osteofluorosis may occur if the fluoride content of trabecular bone exceeds 4,000 ppm and either the volumetric density of osteoid or the osteoid-covered trabecular bone surface is abnormally increased. There was no difference in incidence of hip fracture in the three areas.

KEY WORDS: Hip fractures; Osteofluorosis; Osteomalacia; Osteoporosis.

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VARIATIONS AMONG FLUORIDE CONCENTRATIONS OF WATER FROM DOMESTIC WELLS IN A FOUR-COUNTY AREA

by

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(Abstracted from Journal of Dentistry for Children 52:347-352, 1985)

Of the 229.8 million U.S. residents in 1980, an estimated 195.6 million (85 percent) received water from public water systems, 34.2 million (15 percent) did not. Most private water supplies are domestic wells, the fluoride content of which may vary considerably, requiring laboratory analysis.

During the 24 months from March 1982 through February 1984, 503 non-randomly selected water samples in New Mexico's Bernalillo, Sandoval, Torrance and Valencia counties were analyzed for fluoride, using a specific ion electrode. Of these 33 (6.6 percent) had less than 0.3 ppm, 372 (73.9 percent) had between 0.3 and 0.7 ppm, and 98 (19.5 percent) had greater than 0.7 ppm of fluoride. Fluoride concentrations ranged from 0.1 to 6.4 ppm. The mean fluoride concentration of water samples tested was 0.6 ppm (S.D. = 0.6) and the median was 0.5 ppm. Of special interest is the considerable variation in a relatively small area (20 x 28 miles). Differing fluoride concentrations were found at all intervals of well-depth reported.

It is important for dentists, physicians, and nurse practitioners to be aware of the potential for variation of fluoride concentrations among domestic wells, and that the water from them must be assayed on an individual basis before prescribing a supplement.

KEY WORDS: Domestic wells, F^- in; New Mexico well water; Variable F^- in wells.

REPRINTS: Dr. M.D. Siegel, Dental Director, Columbus City Health Department, Columbus, Ohio

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THE EFFECT OF FLUORIDE ON FERTILIZED EGGS OF A FRESHWATER FISH, CATLA CATLA (HAMILITON)

by

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(Abstracted from Toxicology Letters, 22:139-144, 1984)

The present study was undertaken to determine the effect of fluoride — both that discharged as effluent from a fluorine industry and that in a prepared NaF solution — on the fertilized eggs of the freshwater fish, Catla catla (Hamiltion).

The control eggs and those exposed to 1.86 ppm fluoride (effluent dilutions and NaF solution) hatched at the end of 6 hrs. Hatching occurred at the end of 7 hrs. in effluent and NaF solution containing 3.21 and 3.56 ppm fluoride, respectively. Eggs exposed to 7.12, 9.56 and 16.23 ppm fluoride (effluent) and 7.34, 10.01 and 16.68 ppm fluoride (NaF) hatched at the end of 8 hrs.

A significant increase in fluoride was observed in eggs exposed to effluent and NaF, compared to controls. Assimilation of fluoride in eggs exposed to NaF solutions was significantly higher than in those exposed to effluent dilutions. Fluoride accumulation was more dependent on the source of fluoride in the medium (effluent or NaF) than the amount of fluoride in it. Accumulation increased with the increase in exposure time; it was more pronounced in exposure media containing 1.86 ppm fluoride at all exposure hours and for the rest of media up to 4 hours. Fluoride accumulation was highest in eggs exposed to 16.68 ppm NaF and 16.23 ppm effluent at the end of 4 hrs. Fluoride estimated in controls ranged from 0.09 to 0.14 ppm.

A significant decrease in weight compared to controls was observed from 2 hrs onwards in eggs exposed to 7.34, 10.01 and 16.68 ppm NaF and 7.12, 9.56 and 16.23 ppm effluent. The weight of eggs exposed to fluoride (in both media) decreased considerably with the increase in fluoride in the media and exposure time. The weight of eggs from controls was 117.70-119.30 mg.

Protein decreased significantly in eggs exposed to 3.56 and 7.34 ppm NaF and 3.21 and 7.12 ppm effluent 4 hrs. and more. Decrease in protein was significant in eggs exposed to 10.01 and 16.68 ppm NaF and 9.56 and 16.23 ppm effluent 3 hrs. and more. Eggs from controls showed a protein content of 230.1-236.0 mg/g.

KEY WORDS: Egg weight; Fertilized eggs; Fluoride accumulation; Fluoride effluent; India; Protein; Sodium fluoride.

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EFFECT OF FLUORIDE ON MORPHOLOGICAL AND METABOLIC MODIFICATIONS IN HELA CELL CULTURE

by

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(Abstracted from Tsitologiya 26:299-306, 1984)

Treatment of HeLa cell monolayers with subtoxic permissible concentration (1.5 μg/mL) and toxic concentration (12 μg/mL) of fluoride affected mitosis, DNA, RNA, and protein synthesis by cell cultures. The lower concentrations inhibited the protein and RNA synthesis more strongly than the 12 μg/mL concentration, especially during the early days of the experiment. The decrease in mitotic activity at the lower dose of fluoride was contrary to some of the data in the literature. The duration of individual phases of mitosis, quality and quantity changes of the pathological form of mitosis, especially with respect to K-mitosis, may be related to decreased synthesis of tubulins. The paradoxical effects of fluoride, seen at the 2 concentrations, are discussed with reference to the literature.

KEY WORDS: Fluoride effects; HeLa cell cultures; Mitosis; Morphology.

REPRINTS: Institute of Human Morphology, Moscow, USSR.

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THE CONCENTRATION OF FLUORIDE IN DIFFERENT DAIRY PRODUCTS

by

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(Abstracted from Sci. of Tot. Environment, 50:183-189, 1986)

The total fluoride levels in milk from cows grazing in fluoride-contaminated pastures (0.26 μg/g) are about twice as high as those in milk from cows on a "normal" grass diet (0.11 μg/g).

Among dairy products from contaminated milk, the fluoride concentrations in cream and cheese are the highest. They are about three times those of milk (0.80 μg/g). During processing, large amounts of fluoride accumulate in these products.

KEY WORDS: Cows's milk; Dairy products; F^- content; F^- contaminated pastures.

REPRINTS: DRF/Laboratoire de Biologie Végétale, Centre d'Etudes Nucléaires de Grenoble, 85X-38041 Grenoble Cedex, France.

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ACUTE FLUORIDE POISONING AFTER INGESTION OF SODIUM FLUORIDE TABLETS

by

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(Abstracted from the Medical Journal of Australia 141:503-505, 1984)

Numerous acute fluoride poisonings, mostly from the USA and West Germany have been reported in the literature. The first fatality, that of a 35-year-old man who died within 35 minutes after ingestion of 15 ml of hydrofluoric acid, was recorded in 1873. Seventy years later, in 1943, 163 patients became ill and 46 of them died in a U.S. hospital after a meal of scrambled eggs. The poison, identified as roach powder, contained 90% sodium fluoride. Many of the patients had rejected the food because of its salty, soapy taste; some complained of numbness of the mouth as soon as they had eaten it.

In the past six years, at least 20 children were admitted to two major children's hospitals in Brisbane Australia after ingestion of fluoride tablets. The highest recorded dose ingested was approximately 176 mg of sodium fluoride (about 6.3 mg fluorine/kg of body weight). The majority of the children had ingested 50 or more tablets, but the F content was not always recorded. The ages of the patients ranged from 1 to 5 years; numbers of both sexes were roughly equal.

Fourteen children were admitted to Adelaide Children's Hospital between 1978 and 1982 after ingestion of fluoride tablets; 231 acute fluoride poisonings were reported in 1982, 173 in the first nine months of 1983; most of the victims were less than 14 years of age. Two cases of poisonings in 1982 were those of attempted suicide.

Data on more serious fluoride toxicity, necessitating admission to the hospital, obtained only for Brisbane and Adelaide, suggest that, in any year, one child in 50,000 will be hospitalized for the treatment of acute fluoride poisoning. Queensland has the highest prevalence of children ingesting an excessive number of fluoride tablets. In Brisbane, on the other hand, the number of calls per head of population is approximately twice as large as those in Sydney and Melbourne.

One reported fatality in Queensland, after the ingestion of fluoride tablets, occurred in 1973 when a 2-year-old child, alleged to have swallowed fewer than fifty 2.2 mg sodium fluoride tablets, died five days after admission to the hospital. Very young children will often swallow large numbers of tablets. A lethal dose for humans is reported to be 30-65 mg of fluorine per kg of body weight. Fluoride toxicity is directly related to the plasma concentration of fluoride.

The symptoms of acute fluoride poisoning, like many other kinds of acute poisoning, usually include nausea, vomiting, excessive salivation, cramps in the abdomen and diarrhea. Vomiting usually occurs abruptly and, at times, simultaneously with diarrhea, although diarrhea may not develop for several hours after ingestion of fluoride. In the early stages of acute fluoride poisoning, depending on the prevailing gastric acidity, highly corrosive hydrofluoric acid may be produced in the stomach. The gastric mucosa of infants can easily be damaged by this acid, causing ulceration and hemorrhage, usually demonstrated by the presence of blood in the vomitus and stool. Due to the sudden fall in blood calcium level which follows fluoride ingestion, there may be an increase in skeletal muscle excitability, hyperactive reflexes, painful spasm, weakness and tetanic contractures, paresis of affected muscle groups, especially of eyes, face, hands and lower extremities. Dysphagia and uncoördinated eye movements may also occur. A fall in blood pressure due to central vasomotor depression as well as to a direct toxic effect on cardiac muscle may subsequently occur. The presence of cyanosis; tachycardia; shallow, irregular respiration (respiration may be stimulated in the early stages); faint cardiac sounds; pallor; diaphoresis and thick muccoid discharge from the mouth and nose suggest cardiac and respiratory involvement. Extreme muscular weakness is a characteristic feature of the condition. Death usually results from respiratory depression and, in some cases, cardiac failure may be involved.

In medical management of patients with symptoms, immediate attention to the maintenance of airways and cardiovascular circulation is essential and may be the first requisite.

KEY WORDS: Acute F poisoning; Australia; Fluoride fatalities; Fluoride tablets.

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EXPERIMENTAL ACUTE SODIUM FLUORIDE POISONING IN SHEEP: RENAL, HEPATIC, AND METABOLIC EFFECTS

by

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(Abstracted from Fundam. Appl. Toxicol. 5:1025-33, 1985)

In sheep, which received a single intragastric dose of 0.5, 1.0, 1.5, or 2.0 mmol F^-/kg, mild toxic signs occurred at 1.5 mmol F^-/kg; the animals recovered 2 days later. Animals given 2.0 mmol F^-/kg dose all showed dullness, anorexia, and mild diarrhea which decreased after the third day. Dose-related congestion of duodenum, liver, kidney, and lung was observed in all animals. For the two higher doses, kidney degeneration and tubular necrosis were associated with glomerular inflammation. In serum, fluoride had a dose-related increase. It was still significantly elevated on day 7 for sheep given doses higher than or equal to 1.0 mmol F^-/kg. Serum calcium and glucose levels were significantly lower for all doses on the first day; the decrease was dose-related. In sheep given 2.0 mmol F^-/kg, total proteins and sodium were significantly lowered, whereas potassium and urea were increased ($p < 0.05$); alkaline phosphatase (ALP) and lactic dehydrogenase (LDH) were both lowered (p < 0.01) on the first day and ALP was still lowered on day 7. For the highest dose, glutamate dehyrodgenase (GDH) was increased on days 1 and 7; γ-glutamyl transferase (GGT) was increased on day 1 and lowered on day 7. Diuresis was increased for the two higher doses on day 3 or 4 following dosage. A dose-related increase of daily fluoride excretion occurred for all doses on day 1; fluoride excretion was still significantly elevated on day 7 except for the lowest dose.

KEY WORDS: Acute F effects; Kidney degeneration; Liver enzymes; Metabolic effects; Morocco; Sheep, F effects on.

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FLUORIDES AND FLUOROSIS IN KENYA
PART 1: THE OCCURRENCE OF FLUORIDES

by

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(Abstracted from Odontostomatol. Trop. 9:15-20, 1986)

Part 1 deals with the occurrence of fluoride and possible sources of dietary fluoride.

Lake Nakuru – in the Rift Valley – contains 2800 ppm fluoride, probably the highest recorded level in natural waters. The highest level of fluoride obtained from groundwaters was 39.0 ppm from wells, and 43.5 ppm from boreholes. In over 60 per cent of that from boreholes fluoride is above 1.0 ppm; nearly 20 per cent, above 5.0 ppm. The highest level, 57 ppm, was found in a borehole in the Rift Valley.

Most foods are low in fluoride; their dry weight content is 0.1 to 1.0 ppm; foods grown in high fluoride areas may contain much higher levels of fluoride. The flesh of Tilapia, Nile Perch and Distochodus contain 15.0 ppm, 7.0 ppm and 35.0 ppm respectively. Bones of fish contain up to 1050.0 ppm. In neighboring Tanzania, bananas contain 5.3 to 8.1 ppm, maize 12.4 to 17.6 ppm, coffee seeds 18.1 to 24.6 ppm and whole fish 30.5 to 39.1 ppm. Tea leaves may contain up to 400.0 ppm fluoride although infusions release only about 0.5 to 1.5 ppm. African teas contain between 290 to 656 mg/kg; about two-thirds goes into solution on infusion. Loose Kenyan tea (3.9 g in 195 mL of deionized water) provided a fluoride ion concentration of 5 ppm in solution, Kenyan tea bags with a mean weight of 1.8 g, 1.9 ppm fluoride in solution. When this tea was boiled for 30 seconds and 5 minutes the concentration increased to 4.2 ppm and 16 ppm respectively.

Dust containing high levels of fluoride has been implicated in the occurrence of fluorosis — both skeletal and dental. Skeletal fluorosis has been reported in a factory in Magadi dealing with soda ash containing 18,000 ppm fluoride. Not only such special high risk groups may obtain fluoride from dusts, but also those living in the surrounding areas. The incidence of fluorosis and the proximity to phosphate mines where dust was reported to contain about 20,000 ppm fluoride was positively correlated. Around Lake Nakuru dust contained 5,600 ppm fluoride; in the Nakuru Municipality 1240 ppm and samples of dust on shelves on various houses contained 150 ppm. Pasture samples, up to a mile from Lake Nakuru have been reported to contain 22 ppm fluoride at 3/4 of a mile, 6.7 ppm, one mile away. Such dust may not only be inhaled, but also ingested on foods and vegetables which are not washed.

Further research is required to estimate the relative contributions of these potential sources of fluoride. From evidence obtained in other parts of the world, water is likely to be the most important source of fluoride in the human diet in Kenya.

KEY WORDS: F-containing dusts; F in food; Fluoride occurrence; Kenya, fluorosis in.

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FLUORIDE UPTAKE AND RETENTION AT VARIOUS STAGES OF RAT MOLAR ENAMEL DEVELOPMENT

by

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(Abstracted from J. Dent. Res., 65:34-38, 1986)

To study fluoride uptake in enamel of maxillary first molar at various stages of enamel development plasma fluoride levels in six-day-old and 11-day-old pups were monitored following intraperitoneal injection of fluoride. Fluoride was more easily taken up and retained during the early stages of enamel formation. However fluoride uptake can occur during all stages of enamel formation. When injections were started early in enamel formation, more fluoride was contained in enamel of the maxillary first molar at 13 days of age. The same dose of fluoride per gram body weight resulted in greater exposure to elevated plasma fluoride levels in six-day-old pups than in 11-day-old pups.

KEY WORDS: F uptake; Rat molars; Enamel fluoride.

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THE INFLUENCE OF FLUORIDE RECOVERY ALUMINA ON THE WORK ENVIRONMENT AND HEALTH OF ALUMINUM POTROOM WORKERS

by

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(Abstracted in Med. Lavoro, 4:313-317, 1981)

The aim of this investigation was to study the influence of fluoride recovery alumina on the dust exposure and on the short-term health effects of the aluminum potroom operator. The study was carried out during two periods, each lasting eight days, using recovery alumina during the first period and pure alumina during the second period. The same employees were working day shift during both investigatory periods.

The prevalence of work-related symptoms was significantly higher during the recovery alumina period. The percentage of participants having a symptom code of 4 or more, the result of answers to 7 questions regarding acute work-related health complaints and other factors, was higher during the recovery alumina period. Pot-operators were relatively more bothered due to recovery alumina than other potroom workers. Workers reporting chronic pulmonary symptoms had a much higher prevalence of acute complaints than other workers. Elimination of selection factors by comparing each worker to himself during the two periods, revealed a correlation between dust exposure and acute health complaints.

Not only was dust exposure and the prevalence of acute health complaints higher during the operating period when recovery alumina was used, but prevalence of chronic pulmonary complaints was significantly higher than expected.

KEY WORDS: Aluminum workers; Fluoride recovery; Respiratory illness.

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CHANGES IN THE FLUORIDE-INDUCED MODULATION OF MATURATION STAGE AMELOBLASTS OF RATS

by

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(Abstracted from J. Dent. Res., 64:1365-1370, 1985)

The present study was undertaken to determine whether the ameloblast modulation in the maturation stages of enamel development was altered in animals given chronic high levels of fluoride in their drinking water. Calcein staining of and ^{45}Ca incorporation into maturation enamel were compared in fluorosed and control rat incisor enamel.

The calcein staining pattern in the maturation enamel was disrupted in animals given 75, 100, or 150 ppm fluoride in drinking water for five weeks. In the incisors from animals given 75 ppm fluoride in drinking water, the most apical stripe fluoresced strongly. However, the more incisal stripes were shorter than those in the control enamel. The more incisal stripes from animals given 75 ppm fluoride in drinking water did not have a distinct double-banded appearance. In animals given 100 and 150 ppm fluoride in drinking water, only one stripe was evident, incisal to the white opaque boundary. Direct histological observation of the ameloblast pattern of modulation in the enamel organ confirmed that the number of smooth-ended ameloblast regions correlated with the number of calcein-stained bands in the enamel.

In the control enamel, there were five or six cycles of ^{45}Ca uptake in the maturation stage. Only two cylces of ^{45}Ca incorporation were present in enamel from animals given 100 ppm fluoride in their drinking water. In both control and experimental animals, the number of cycles of ^{45}Ca incorporation was correlated with the calcein staining. Moderate uptake began with the calcein-stained bands (smooth-ended ameloblasts). Uptake continued with heaviest uptake in the apical portion of the unstained bands (ruffle-ended ameloblasts).

In animals which had been given 100 ppm fluoride in drinking water for two weeks, and three days after the animals were given deionized water, the maturation enamel had three rather than two calcein-labeled stripes. After 12 days without fluoride, the stripe pattern had returned to the typical five or six stripes found in the enamel of control animals of the same age.

KEY WORDS: Ameloblast modulation; Ameloblast maturation; Dental fluorosis; enamel; Rat dentition.

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FLUORIDE ABSORPTION: INDEPENDENCE FROM PLASMA FLUORIDE LEVELS

by

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(Abstracted from the Society for Experimental Biology and Medicine 181:550-554, 1986)

Four different methods were used to evaluate the effect of plasma fluoride levels on the absorption of the ion in rats: (1) the percentage of daily fluoride intake that was excreted in the urine; (2) the concentration of fluoride in femur epiphyses; (3) the net areas under time-plasma fluoride concentration curves after intragastric fluoride doses; and (4) the residual amounts of fluoride in gastrointestinal tracts after the intragastric fluoride doses. These methods failed to indicate that plasma fluoride levels influence the rate or degree of fluoride absorption. Unless extremely high plasma fluoride levels are involved (pharmacologic or toxic doses) it was concluded that absorption of the fluoride ion is independent of plasma levels. These results provide further evidence that plasma fluoride concentrations are not homeostatically regulated.

KEY WORDS: Intragastric F^- doses; Plasma F^-; Rats.

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EFFECT OF ENDOGENOUS PHOSPHOENOLPYRUVATE POTENTIAL ON FLUORIDE INHIBITION OF GLUCOSE UPTAKE BY STREPTOCOCCUS MUTANS

by

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(Abstracted from Infect. Immun., 51:119-124, 1986)

The fluoride sensitivity of glucose uptake by whole cell suspensions of *Streptococcus mutans* was studied. Preincubation of the organism with up to 1 mM glucose markedly reduced the fluoride sensitivity of subsequent glucose uptake at pH 7.0 and 5.5. Glucose preincubation was shown to result in the establishment of a stable pool of three-carbon glycolytic intermediates. On the basis of inhibition studies and thin-layer chromatography of cell extracts, we suggest that 3- and 2-phosphoglycerate are the principal constituents of the pool. Increased concentrations of glucose used in preincubation mixtures were associated with increased pool sizes of the glycolytic intermediates and increased fluoride resistance. Transport of 2-deoxy-D-glucose by permeabilized cells was inhibited by fluoride when 2-phosphoglycerate served as the energy

source. Increased concentrations of 2-phosphoglycerate overcame fluoride inhibition of transport. Establishment of a stable pool of glycolytic intermediates that includes 2-phosphoglycerate (or its progenitors) may contribute significantly to apparent refractoriness of plaque microbes to fluoride in vivo.

KEY WORDS: Fluoride resistance; glucose in plaque; Glycolysis; Phosphoglycerates; Streptococcus mutans.

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THE INHIBITION OF RAT AND GUINEA PIG CHOLINESTERASES BY ANIONIC HYDROLYSIS PRODUCTS OF METHYLPHOSPHONIC DIFLUORIDE (DIFLUORO)

by

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Methylphosphonic difluoride (difluoro) and its hydrolysis products, methylphosphonfluoridate (MF) and fluoride, were examined for cholinesterase-inhibiting ability in rats and guinea pigs by both inhalation and intraperitoneal exposure routes. In vivo inhibition was compared to in vitro inhibition. In the whole animal, MF was the active chemical but in vitro under special conditions, difluoro was more potent than MF and fluoride. Rats and guinea pig blood cholinesterases were equally sensitive to inhibition by MF, and only the guinea pigs displayed cholinergic signs leading to death from MF toxicity. Data imply that MF is responsible for the cholinesterase inhibition resulting from exposure to DF vapor. MF may be the first example of a moderately strong acid shown to inhibit cholinesterase and cause death from cholinergic effects.

KEY WORDS: Guinea pigs; Methylphosphonfluoridate; Methylphosphonic difluoride; Rats

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FEATURES OF THE MODIFYING CAPACITY OF MUTATIONS IN AEGILOPS SEEDS PRODUCED UNDER VARIOUS ECOLOGICAL CONDITIONS

by

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(Abstracted from Izv. Akad. Nauk. Az., SSr., Ser. Biol. Nauk, 4:21-24, 1984)

To examine the antimutagenic effects of alpha-tocopherol (59-02-9), A. triuncialis seeds collected at various altitudes (80, 870, and 1100 m above sea level) were treated with NaF and γ rays. The highest antimutagenic effect in all 3 populations was observed when tocopherol concentration was > 10^{-1} γ/mL. The exogenous factor altitude had a definite antimutagenic effect namely 0.44, 0.75 and 0.82 at the same 3 heights (30, 870 and 1100 m) respectively.

When the mutation inducer was NaF, antimutagenic effects of α-tocopherol at the 3 altitudes were 0.41, 0.75, and 0.68 respectively. Thus α-tocopherol was most effective at 870 m above sea level. Ecological conditions also play a role in the adaptation mechanism and the stability of the genetic apparatus.

KEY WORDS: Aegilops seeds; Alpha-tocopherol; F^- mutations; USSR.

REPRINTS: Institute of Botany, Baku, USSR.

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The International Society for Fluoride Research (ISFR) extends a special invitation to you to participate in the 16th Conference. This will be held in the Conference Hall of Zyma at Nyon (30 km from Geneva) Monday, Austust 31st through Wednesday, September 2nd, 1987. Professor C.A. Baud will host this Conference and he has nominated Christiane Demeurisse as secretary of the Conference. The Fluoride journal will carry information about the Conference in future issues.

REPORT ON THE THIRD FLUORINE SYMPOSIUM IN SZCZECIN (POLAND)

by

Z. Machoy
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The Third Fluorine Symposium in Szczecin, May 30-31, 1986, entitled "Effect of Air Fluoride on Plants and Foodstuffs" was attended by over 70 persons from 11 native areas and 6 foreign lands namely, GDR, GFR, Czechoslovakia and Denmark. Papers by the latter were presented in English. Seventeen papers and 27 poster communications were presented. The introductory lecture, by Z. Machoy (Szczecin) entitled, "Significance of Studies on Fluorine Compounds in the Area of Western Pomerania" familiarized participants with environmental pollution by fluorine compounds in Poland, with special reference to West Pomerania.

Three papers presented by U. Glabisz (Szczecin) "Fluorine Problem in the Fertilizer Industry," I. Pollo (Lublin) "Reactivity and Emission of Fluorine Compounds," K. Prawdzic (Szczecin) "Meteorological Conditions Prevailing Around the Police Chemical Plant" dealt with the fluorine problem in the chemical-fertilizer industry, reactivity of fluorine compounds in industrial emissions and meteorological conditions prevalent in the surroundings of a big chemical plant, Police, the production profile of which is phosphorite and apatite processing. Unfavorable meteorological conditions are associated with the presence of a huge water reservoir in the vicinity of said plant.

Three additional papers, by S. Borowiec and Z. Zabłocki (Szczecin) "Fluorine in Plants in the Area Affected by Emissions of the Police Chemical Plant," A. Sienkiewicz and I. Cichocka (Poznań) "Influence of Industrial Emissions on the Content of Fluorine in Selected Forest Plant Species," S. Kmiecik (Szczecin) "Impact of the Industrial Fluorine Emissions on Forests" covered the influence of industrial emissions on vegetation to a much greater extent than they did on foodstuff produced by technological processes. The effect of fluorides from industrial emissions upon plants is quite different from that on forests. Cultivation of food crops, in general, is limited to a short period of time, whereas forests form a kind of protective umbrella for undergrowth and a variety of game.

The forests in Europe are dying fast, and Poland is not being spared even in regions far distant from big industries. Due to even higher and higher factory chimneys industrial emissions are being spread over increasing areas. Moreover, because rain- and snowfalls from polluted zones are acid, they are causing colossal damage to forests. Leaf-trees, due to renewal of leaves in seasonal rotation are less sensitive to pollution than coniferous trees. The highest accumulation of fluoride is detected in the assimilation apparatus of trees, which may elucidate the diminution in wood mass growth. Every sort of soil has a limited acidity capacity; its transgression leads to unpredictable consequences. For instance, in acidified soil there is a cessation in the exchange of Mg and Ca cations — important compounds whose metabolic role is of paramount significance. In his paper, entitled "Studies on the Daily Intake of Selected Population Segments Living in Different Fluoride-polluted Areas in a District of GDR," Dr. Melde dwelt on what the fluoride load looked like in the natural environment within industrialized areas of Cottbus, GDR.

The main topic of the symposium summed-up in the lecture by Dr. Valach of Czechoslovakia, entitled "Rise in Fluorine Contents of Foodstuffs and Consequences Thereof" discussed not only the negative effects of fluorine influence upon the metabolic processes, but also the need to combine our efforts for preparing a memorandum on the imminent danger arising from the constant increase in the amount of fluorine in the environment.

Other papers were principally concerned with the most recent achievements in the fields of therapy, toxicology, prophylaxis and analysis of fluorine compounds. J. Franke (GDR) reported the results of osteoporosis treatment with sodium fluoride. P. Grandjean (Denmark) in his report "Long-term Health Effects of Occupational Exposure to Fluoride," depicted the fate of workers and pensioners at an aluminium mill in Denmark, with reference to the incidence rate of cancer. M. Guminska (Kraków), "In Vitro and In Vivo Interactions of Fluorine with Magnesium" focussed her attention on the mechanisms of the toxic effects of fluoride upon cells, highlighting the role played by magnesium ions. J. Markiewicz (Kraków) in his lecture, "Some Toxicological Aspects of Fluorine Compounds," pointed out the necessity to promote studies on biochemical toxicology, which may facilitate a better understanding of the bases in toxicology of fluorine connection. T. Juszkiewicz's paper linked with the fluorine content in foodstuff headed, "Fluorosis in Domestic Animals" emphasized the fact that at certain periods of animal breeding (e.g. lard-hogs) a great variety of fodder components are used (phosphate feed), which contain a considerable amount of fluorine known to influence the value of meat and its products.

The report by M. Kobylańska (Poznań), "Fluorides in Caries Prevention. A Survey of Problems," was concerned with the effect of fluoridated water upon the level of fluorides in saliva, on the anatomical shape of the teeth and their physical, chemical and biological properties with reference to the metabolic activity of the dental plate bacteria. E. Gabriel of GFR in his paper, "Modifying Influences of Fluorine on Mechanical and Chemical Properties in Micro-regions of Biological Hard Tissue: New Methods of Determination and Some Results" pointed to the dynamic development of physical methods for determination of trace elements in osseous tissue, with particular emphasis on the so-called LAMMA method (Laser Microprobe Mass Analyzer), whereas H. Bem (Łódź) reported "Radiometric Methods for Determination of Fluorine."

The poster sessions covered the effect of fluorine on plants, foodstuffs, bones, teeth, and the biochemical metabolic processes in living organism. Two films were projected. One referred to the Szczecin agglomeration; the second, was entitled "Adverse Effects of Topical Fluorinated Steroids." Titles and summaries of the poster communications were bilingual — Polish and English; summaries were presented in English.

The Fourth Fluorine Symposium is scheduled to take place in Szczecin on September 1-2, 1988.

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