Impact of Fluoridation of the Municipal Drinking Water Supply: Results of Field and Laboratory Study and Supplement to Review of the Literature

Prepared for:

Escambia County Utilities Authority

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June 2001

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I. EXECUTIVE SUMMARY

The Escambia County Utilities Authority (ECUA) has approved addition of fluoride to the municipal drinking water system. Hydrofluosilicic acid will be added to deliver fluoride at a target concentrations of 0.8 mg/L. Citizens have raised questions and concerns about the safety and public health risks of this action. There is a tremendous body of literature addressing the pros and cons of drinking-water fluoridation, which we reviewed earlier for the ECUA (Lepo and Snyder, 2000).

This final report addresses our laboratory and field studies on several aspects of potential public health and environmental health effects of drinking water fluoridation. Individual laboratory studies reported here include:

1) **Assessment of regional environmental concentrations of fluoride in:**
   a) municipal water supplies (ground water wells);
   b) surface waters from the major rivers, bayous, and bays of the Pensacola Bay System;
   c) the municipal sewage treatment process (sludge vs. effluent concentrations).

2) **Analysis of the fluoride compound to be added** (hydrofluosilicic acid) for metals contamination and assessment of the levels of any such compounds delivered to end users of the water system.

3) **Estimation of the chemical complexes formed** in ground waters from supply wells:
   a) total amount of fluoride needed to reach the 0.8 mg/L free ion concentration before and after pH adjustment;
   b) stability of the free fluoride ion with time and exposure to metal pipes;
   c) potential for accumulation of fluoride complexes in "dead zones" of sediment accumulation within the delivery system;
   e) potential for added fluoride to interact with pipes to increase leaching of metals.

We have also provided a synopsis of scientific studies and updated reviews to supplement our original literature review.

Conclusions

The **updated literature review** supports our previous conclusions that the fluoridation of public water supply is a beneficial public health practice (Lepo and Snyder, 2000). However, a few new reviews suggest the wisdom of monitoring overall dose of fluoride in regions with higher levels of natural fluoride input, and that the availability of fluoride in the water used in infant formulas should be limited.

Our assessment of **fluoride in regional municipal water supplies** was consistent with ECUA-provided water quality analysis data. Our measures of **fluoride in regional surface waters** yielded results that were expected: we identified a descending gradient of fluoride from the Pensacola Bay inward into the bayous and freshwater areas; however, we also identified a reverse gradient of fluoride in the Bayou Texar that is probably the result of groundwater intrusion from the Agrico Superfund site.

We were able to obtain only one **commercial sample of hydrofluosilicic acid** and cannot make statements concerning the typical levels of metals contamination in a range of commercial products based on this one sample. Arsenic and cadmium were above detection limits, however, dilution of the product to the target concentration of 0.8 ppm fluoride, would make their concentrations in fluoridated water well below detection limits afforded by state-of-the-art analytical technology and below levels for any known toxicity. Likewise radioactivity was found to be well below background levels of radioactivity in the local environment and ECUA well waters, and below safety limits.

Our assessment of the **stability of the free fluoride ion with time** in ECUA well waters showed rapid loss for fluoride added at 0.4 ppm, but above that concentration, the loss rates appear to stabilize and are independent of dose concentration. For the target concentration of 0.8 ppm, the mean loss rates were: W & Avery 0.0295 ppm day^{-1}, McCrory 0.0198 ppm day^{-1}, and Airport 0.0173 ppm day^{-1}.

In our laboratory model to explore whether fluoride promotes **leaching of metals from pipes** both dissolved copper and lead were increased in water containing 10 ppm fluoride. This suggests that the standard warning issued to buyers/builders of new construction to let the water lines flush before using their water for human consumption should be emphasized in areas with fluoride in the water supply. These experimental results should not be over interpreted, since the high concentration of fluoride used (10 ppm) represents at least a ten-fold increase in effect over the concentration of fluoride targeted for the water system, and the long-term, static-incubation scenario of these experiments does not reflect most real-world situations.

To assess the **propensity of fluoride to concentrate in dead zones** of the water system, we tested precipitate from the City of Gulf Breeze, which operates a sand filter system to remove precipitate from ECUA water prior to distribution on Fairpoint Peninsula for free fluoride ion. The natural levels of fluoride in ECUA-supplied water to this facility range from 0.01 to 0.3 ppm. The back flushed material was not enriched in fluoride relative to the bulk water, suggesting that fluoride added to the water system should remain in dissolved form and not become enriched in dead zones where these precipitates may accumulate and periodically be flushed out to end users.

We analyzed **fluoride levels in treatment system influents and final effluents from ECUA sewage treatment facilities** and found a significant decrease in fluoride concentration in the final effluent at the Marcus Pointe facility (80% reduction). The levels of fluoride in the influent sewage at the Main Street facility were much higher than influent from those at the Marcus Pointe facility, and fluoride ion concentration was increased in the final effluent, perhaps reflecting differences in the treatment processes at the two plants. Reasons for the dramatic differences in fluoride ion concentration between the two waste streams are unknown. However, infiltration from the Agrico Superfund Site plume into the sewer collection system of the Main Street facility is a possible explanation.

A more intense and extended temporal sampling regime might have shed light on potential mechanisms for this anomaly. For instance, it is possible that sequestered fluoride in sediments might have been disturbed periodically, fortuitously coinciding with the sampling of the Main Street effluent, producing a spike in measured fluoride levels.

II. STUDY RESULTS AND DISCUSSION

A. Sampling and Analytical Methods

All sampling and analytical work was done under the Quality Assurance / Quality Control standards of the Center for Environmental Diagnostics and Bioremediation (CEDB) Wetlands Research Laboratory (WRL), which is an analytical arm of CEDB. The WRL is State of Florida Certified for environmental water analysis (Lab ID: E71176) and the laboratory complies with full chain of custody sample storage and handling practices (Comprehensive Quality Assurance Plan for Florida HRS: CompQAP #870431), conforming to Florida State Department of Environmental Protection and the U. S. Environmental Protection Agency standards.

General QA/QC

Samples were taken in certified-clean, new sample bottles in accord with surface water sampling standard operating procedures. All analytical glassware and other containers were either new, and certified clean, or else washed in accord with QA standards of the WRL. All analytical chemistry was performed with appropriate blanks, duplicate samples, duplicate analyses, matrix spikes, and controls, and using only certified standards for instrument calibration.

Fluoride analysis

Fluoride concentration was analyzed in accord with Standard Methods4500-F- C (Eaton et al., 1995), using an Orion model 720A pH/ISE meter and an Orion model 96-09 fluoride combination electrode. Five-point standard curves were generated using certified fluoride standards that ranged in concentration from 0.1 mg/L to 10 mg/L; the standards were diluted in distilled/deionized water unless indicated. When ion-specific electrode response (in mV) was plotted against the logarithm of fluoride concentration, the curve was linear over the 100-fold concentration range with a typical R^2 of over 0.99. Sample concentrations were computed from standard curves generated for each sample set using the curve formula from a regression analysis of the standard curve.

Metals analyses

Graphite Furnace Atomic Absorption Spectrophotometer Metals Analysis

Potable water samples (turbidity < 1 NTU) for total metals analysis were not digested prior to analysis. A representative aliquot of the sample was placed on the autosampler of the Varian 220Z graphite furnace atomic absorption spectrophotometer (GFAA) with Zeeman background correction. The furnace atomizes the metal in the sample and introduces it into the path of light from a lamp at a wavelength at which the metal will absorb light energy. The detector measures the light energy prior to and during the atomization. The difference between these is directly proportional to the mass of target metal in the sample. The instrument response to an unknown sample compared to a series of calibration standards of known concentration and the concentration of the target metal in the unknown sample is calculated.

Flame Atomic Absorption Spectrophotometer Metals Analysis

Potable water samples (turbidity < 1 NTU) for total metals analysis are not digested prior to analysis. A representative aliquot of the sample is introduced via sample pump into an acetylene or nitrous oxide flame of the Varian 220 flame atomic absorption spectrophotometer with deuterium background correction. The flame atomizes the metal in the sample and introduces it into the path of light from a lamp at a wavelength at which the metal will absorb light energy. The detector measures the light energy prior to and during the atomization. The difference between these is directly proportional to the mass of target metal in the sample. Instrument response to unknown is compared to response to certified calibration standards and the concentration of the target metal in the unknown sample is calculated.

Metals Quality Control

The calibration curve consists of four calibration standards containing concentrations of the target metal within the linear range of the method (dependant on sample volume introduced to the instrument and wavelength used). The calibration standards are made up from NIST-traceable source materials. A calibration verification standard is analyzed every 20 samples to verify the continued accuracy of the calibration curve. A blank is analyzed every 20 samples to verify the continued absence of carryover contamination from sample to sample.

B. Assessment of Fluoride in Regional Municipal Water Supplies

Although the ECUA has data available on the fluoride content of their water supply at the source, we conducted an independent corroboration of these data for inclusion in this final report. This study consisted of sampling the source water with the cooperation of the ECUA and testing for fluoride content. Samples from wells used by ECUA, as well as Pace, Milton, and Midway water systems were analyzed for fluoride ion concentrations. Past analyses and current sampling of these ground waters were compiled into this final report. Both pre-treated and post-treated (delivered water), were tested.

While no regional water utilities currently fluoridate their water in treating it for human use, differences in naturally occurring fluoride concentrations are evident (**Table 1**). ECUA wells in Escambia County have low concentrations of fluoride (0.01 parts per million (ppm) or below) with the exception of the East Well, which likely experiences elevated fluoride from the groundwater plume of the Agrico Superfund Site. Although the level reported (0.3 ppm) is below desired levels of fluoride, this well is no longer in service for public drinking water supply.

Consumer confidence reports from the regional water suppliers and the areas served provided the data presented in **Table 2**. Three of the regional systems did not report fluoride information. The other three all report levels of fluoride higher than any of the ECUA wells. The Midway water system reported a fluoride level (0.95 ppm) above the target concentration for fluoridating the ECUA drinking water supply (0.8 ppm). No adverse effects of this naturally occurring fluoride in the franchise area for Midway have been reported.

Table 3 shows our analyses of fluoride concentrations in three ECUA wells, Airport, McCrory, and W & Avery. All three had fluoride concentrations of less than 0.02 ppm. Water from these wells was selected for use in subsequent experiments described below in part because of distinguishing water quality parameters. McCrory has high iron (0.40 ppm), W & Avery is characterized by a relatively high nitrate level (4.4 ppm), and the Airport well has intermediate water quality (**Table 1**).

Table 1. ECUA Water Quality Data on Public Drinking Supply Wells.

	Nitrate	Fluoride	Aluminum	Iron	Manganese	Gross Alpha	Radium 226+Radium 228
EPA Standards							
Minimum Detection Level	0.10	0.01	0.10	0.05	0.01		
Maximum Contaminant Level	10.00	2.00	0.20	0.30	0.05	15 pCi/L	5 pCi/L
Well							
West	4.5	0.01	0.10		0.01	7.4	4.7
#6 Well	2.8	0.01		0.30		7.0	3.8
Montclair #2	2.8	0.01				2.5	3.7
#9 Well	8.0		0.27	0.08	0.09	15.7	7.6
McAllister	2.1		0.20		0.03	1.2	2.6
Ensley	2.1	0.01	0.05			2.0	1.3
East	5.1	0.3	0.41	0.21	0.10	9.00	5.40
Lillian	2.6		0.10	0.20		3.6	3.9
9th Avenue	2.0	0.01				0.9	0.8
Royce St.	2.3	0.01		0.20		8.4	3.0
West Pensacola	1.7	0.01		0.20		2.5	1.8
F & Scott	1.2	0.01		0.10		9.6	2.5
OLF 4A	1.8	0.01		0.10		3.7	3.9
Montclair #1	0.7	0.01			0.02	0.9	1.4
W & Avery	**4.4**	**0.01**		**0.10**		**1.8**	**3.0**
Davis	1.1	0.01	0.10	0.20		3.0	3.8
Sweeney	1.4					5.5	3.9
Airport north	**0.7**	**NA**		**NA**		**1.4**	**2.2**
Villa	0.5	0.01		0.20		1.3	1.7
Olive Road	2.5	0.02	0.20			4.9	3.9
Ellyson	2.4	0.01				3.7	3.5
Avondale	1.2	0				3.4	2.9
McCrory	**1.5**	**0.01**		**0.40**		**3.0**	**2.9**
Montclair #3	1.1					2.4	1.8
Broad St.	0.6					5.2	1.9
Dunaway	0.2	0.01	0.10			0.3	0.9
University	0.3	0.01				1.5	1.8
Carriage Hills	0.7	0.01				0.5	2.0
Cantonment	0.2	0.01				0.2	0.8
Tennant	1.5	0.01		0.10		1.7	1.7
Hagler	1.0	0.01				9.4	6.0
Bronson #1	0.7	0.01				1.7	4.0

Data source: Water Quality Data provided by ECUA;
All values are parts per million (ppm); NA = not available;
Boldface wells used as source water for experiments described later.

Table 2. Fluoride Ion Concentrations in Regional Water Systems.

Water System and Pop. Served	Date of Sampling	MCL Violation (Y/N)	Average Level Detected	Range of Results
			(ppm)	
CHUMUCKLA WATER SYSTEM, INC	Sept 1, 1999	N	0.069	ND-0.069
BAGDAD-GARCON POINT WATER SYSTEM	not provided			
MIDWAY WATER SYSTEM Fairpoint Peninsula, including South Santa Rosa Utilities, Inc. and Navarre	Mar 1, 1999	N	0.95	0.56-0.95
FARM HILL UTILITIES	not provided			
COTTAGE HILL WATER WORKS	not provided			
PACE WATER SYSTEM	Jan 1, 1999	N	0.121	ND-0.121

Table 3. Analysis of the Water from Three ECUA Wells.

Well ID	pH	F- (ppm)
Airport	8.22	0.017
McCrory	8.00	0.017
W & Avery	7.74	0.018

C. Assessment of Fluoride Levels in Regional Surface Waters

Potential environmental impacts of fluoridation of the municipal drinking water were assessed initially by a survey of fluoride levels currently in representative surface waters. Samples were taken within the major rivers, bayous, and bays of the Pensacola Bay System.

Water samples were taken at sampling locations (listed in **Table 4)** from the freshwater of the Escambia River, into Escambia Bay, in Bayou Texar, and in Pensacola Bay down to Pensacola Pass at Fort Pickens. Fluoride ion was measured by ion-selective electrode calibrated against certified fluoride standards. Free fluoride ion is naturally low in freshwaters and occurs at approximately 1 ppm in marine waters. The mixing of Gulf of Mexico marine waters with the fresh river water in the estuary results in a salinity gradient from the river to the pass at Fort Pickens, Santa Rosa Island. Using salinity as a conservative mixing tracer for seawater dilution, the occurrence of fluoride in the Pensacola Bay system follows a linear, conservative mixing trend ($R^2 = 0.924$) with the exception of Bayou Texar, which shows a reverse trend ($R^2 = 0.807$) (**Figure 1**). This indicates that the fluoride in the Pensacola Bay proper originates from the Gulf of Mexico. Extrapolating from these linear regression analyses, a concentration of 1.01 ppm is predicted for open Gulf waters at 36 parts-per-thousand (ppt) salinity, and 0.084 ppm is predicted for Escambia River water at 0.0 ppt salinity. Bayou Texar indicates a reverse trend, and this line-fit extrapolates to a freshwater source at 1.36 ppm, consistent with dilution of the Agrico Superfund site plume entering the upper reaches of Bayou Texar. These data indicate that free fluoride ion exists in the surrounding environment at levels in excess of that which will be added to the drinking water supply. The proposed level of fluoride addition at 0.8 ppm would be naturally found at a salinity of 27.9 ppt, or estuarine water commonly found on the surface well into Escambia Bay and on the bottom well above the Interstate Route 10 Bridge across Escambia Bay. No adverse environmental effects of the added fluoride are predicted.

Table 4. Water Sampling Locations for Fluoride Analysis.

Swamp House, north side of Route 90 at mouth of Escambia River
Smith's Fish Camp, south side of Route 90 at mouth of Escambia River
Westinghouse, on Scenic Highway
Bay Bluffs, on Scenic Highway
Scenic Heights, on Scenic Highway
Bayou Texar Stations (total of 18 stations)
West of Pensacola Bay (3-Mile) Bridge
Palafox Marina
Garden St. Bridge (Bayou Chico)
Pensacola Yacht Club
Bayou Grande Bridge
Ft. Pickens, Santa Rosa Island

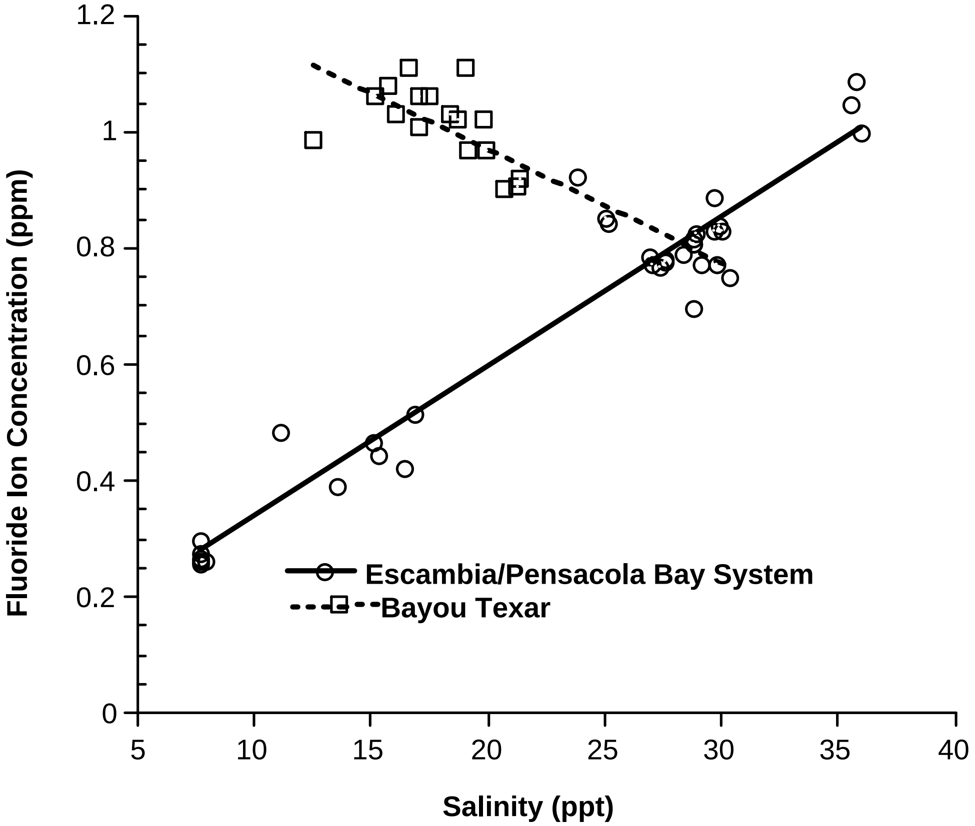


Figure 1. Fluoride concentrations in area surface waters. Circles are Escambia- and Pensacola Bay samples; squares are Bayou Texar samples.

D. Analysis of Hydrofluosilicic Acid for Metals.

The compositions of various commercially available sources of hydrofluosilicic acid are said to include a variety of contaminants, mostly metals. We examined the fluoride compound to be added (hydrofluosilicic acid) for potential impurities that may be introduced into the drinking water (Materials Safety Data Sheets that accompany preparations of hydrofluosilicic acid [**Materials Safety Data Sheet** http://www.hazard.com/msda/h/q249/q378.html**])**. These data were compiled with other analyses from the suppliers.

This compound is widely used in fluoridating municipal water supplies. Guidelines for its safe and effective use have been established (updated 1999) and are available in the CDC Engineering and Administrative Recommendations of Water Fluoridation, 1995. US Department of Health and Human Services, Public Health Service, Centers for Disease control and Prevention, Morbidity and Mortality Weekly Report Recommendations and Reports Vol. 44, No. RR-13 on the Internet at: http://www.cdc.gov/epo/mmwr/preview/mmwrhtml/00039178.htm.

Methods

Samples of hydrofluorosilicic acid for testing were requested from seven national suppliers of chemicals for municipal utility use. Only one company was able to supply a small quantity for testing purposes. The original source of the material was: Solvay Fluorides, Inc., 1630 Des Perres Road, Suite 210 St. Louis, MO 63131 (314) 965-7100. The compound was supplied as a 23% hydrofluorosilicic acid solution.

Hydrofluorosilicic acid contains two hydrogen atoms, one silicon atom, and six fluorine atoms (H_2SiF_6), with a molecular weight of 144.08. The weight of fluorine in one mole of the substance would be 113.99 g, making the concentration of fluorine in the concentrated 23% hydrofluorosilicic acid solution 262,180 ppm. The molecule disassociates in water to form free fluoride ions, silicate ions, and hydrogen ions. The dilution factor needed to achieve the target concentration of 0.8 ppm fluoride ion in the drinking water supply would be 1:327,800.

The product was tested for metals contamination using a *VARIAN SpectrAA* atomic absorption spectrometer (AA). Mercury was tested separately using a *CETAC Technologies M-6000A* Mercury analyzer. Metals analysis followed standard methods for the analysis of drinking water (see A. Sampling and Analytical Methods above, and Eaton et al., 1995).

Results

Table 5 lists the levels of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and mercury (Hg) in a solution of 1000 ppm hydrofluorosilicic acid (791 ppm F^-). At this concentration, Cu, Pb, and Hg were below the levels of detection. As and Cd were above detection limits. Dilution of this solution to the target concentration of 0.8 ppm, would make the concentration of added arsenic in the drinking supply 16.35 parts per trillion, and the concentration of added cadmium would be 0.689 parts per trillion. These concentrations are well below detection limits afforded by state-of-the-art analytical technology and below levels for any known toxicity.

Table 5. Analysis of trace metals in a commercial hydrofluorosilicic acid[a]

Analyte	Concn (ug/L) reported
Pb	non-detect
As	16.169
Cd	0.682
Cu	non-detect
Hg	non-detect

[a]Commercial product diluted to 1000 ppm.

The product was also tested for tested for radioactivity. Radioactive β decay measured as radon in the concentrated hydrofluorosilicic acid solution was 1,374 pCi L^{-1}. These levels of radioactivity, when diluted to the target fluoride ion concentration would be 0.0042 pCi L^{-1}, well below background levels of radioactivity in the local environment and ECUA well waters (**Table 1**), and below safety limits.

The Solvay hydrofluorosilicic acid product was also used in experiments to test stability of free fluoride ion in ECUA well waters and for interaction with metal pipe materials (reported below). Three ECUA wells were chosen for testing as representing relative extremes in the parameters for water quality: Airport, McCrory, and W & Avery (**Table 1**). McCrory was chosen for its high iron content, W & Avery was chosen for its high nitrate content, and Airport was chosen as an intermediate in water quality. Analysis of these waters after ECUA amendments (phosphate, lime) for pH and fluoride content provided the data presented in **Table 3.**

E. Stability of the Free Fluoride Ion with Time.

Addition of fluoride to ground water will result in chemical complexes that may reduce free fluoride concentration. The extent of these chemical reactions will depend on the chemistry of the ground water, which may change from well to well. The addition of lime to adjust pH will also affect these chemical reactions. Further chemical reactions in the water system downstream of the addition point during the residence time of the water in the system (pipes, storage tanks) are possible. We also examined the fate of fluoride with storage time with exposure to various metals used for piping in the system (copper, lead / tin solder).

Stability of fluoride ion added to ECUA well waters. Well water (200 ml) was dispensed into 250 ml flasks, 9 for each of three ECUA wells (McCrory, W & Avery, and Airport). Fluoride was added to each set of nine flasks ranging from 0.4 ppm to 1.2 ppm at 0.1-ppm increments. Flasks were tested daily for 8 days for free fluoride ion concentration. **Figure 2** shows representative data for the changes in fluoride concentration (only four concentrations are plotted) for the three well waters. A regression analysis was used to fit these data (**Figure 2**) and estimate slope values that indicate any loss of fluoride ion. These slope values (loss rates as ppm day^{-1}) were then plotted against the initial added concentration (**Figure 3**), to reveal any concentration-dependent loss behavior that might affect dosing for the water supply.

The analysis shows rapid loss for fluoride added at 0.4 ppm, but above that concentration, the loss rates appear to stabilize and are independent of dose concentration. For the target concentration of 0.8 ppm, the mean loss rates were: W & Avery 0.0295 ppm day^{-1}, McCrory 0.0198 ppm day^{-1}, and Airport 0.0173 ppm day^{-1}. These loss rates were not significantly different between W & Avery and McCrory, and McCrory and Airport, but were significantly different between W & Avery and Airport. The 95% confidence limits for the range of values for all three wells (0.0118 to 0.0395 ppm day^{-1}) are indicative of what might be expected of fluoride within the water system.

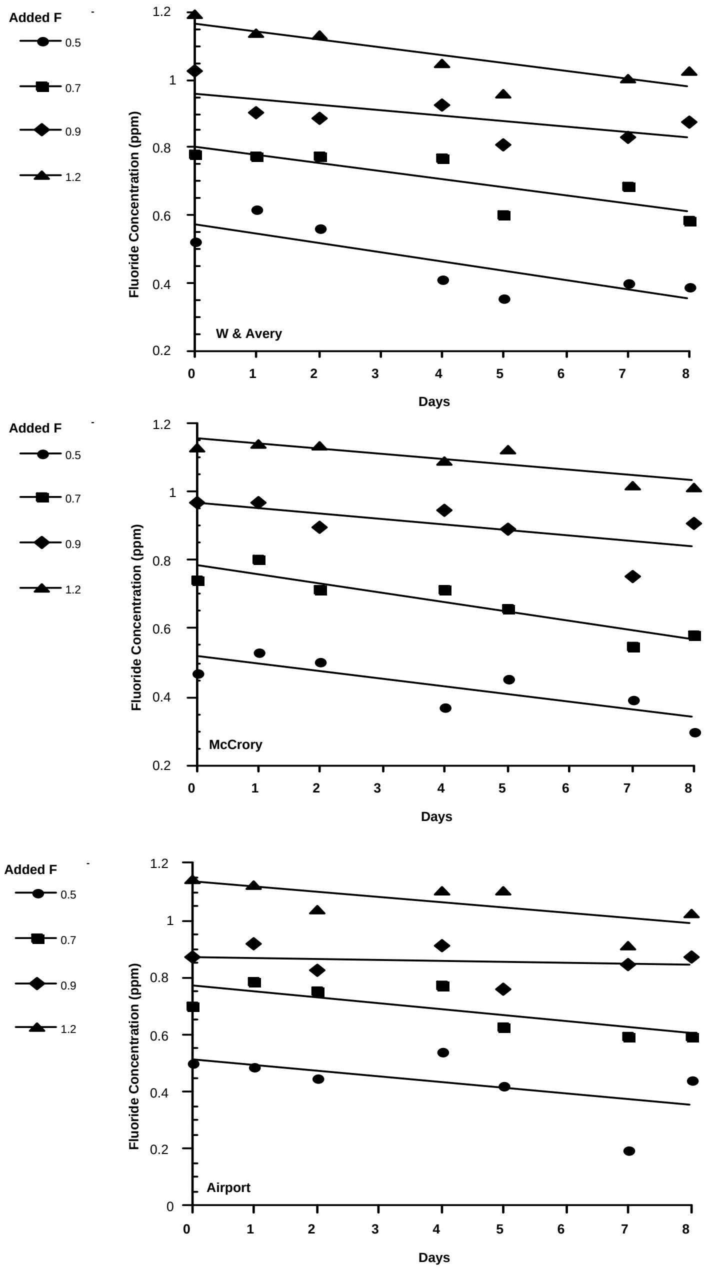


Figure 2. Loss of fluoride over time in three ECUA well waters.

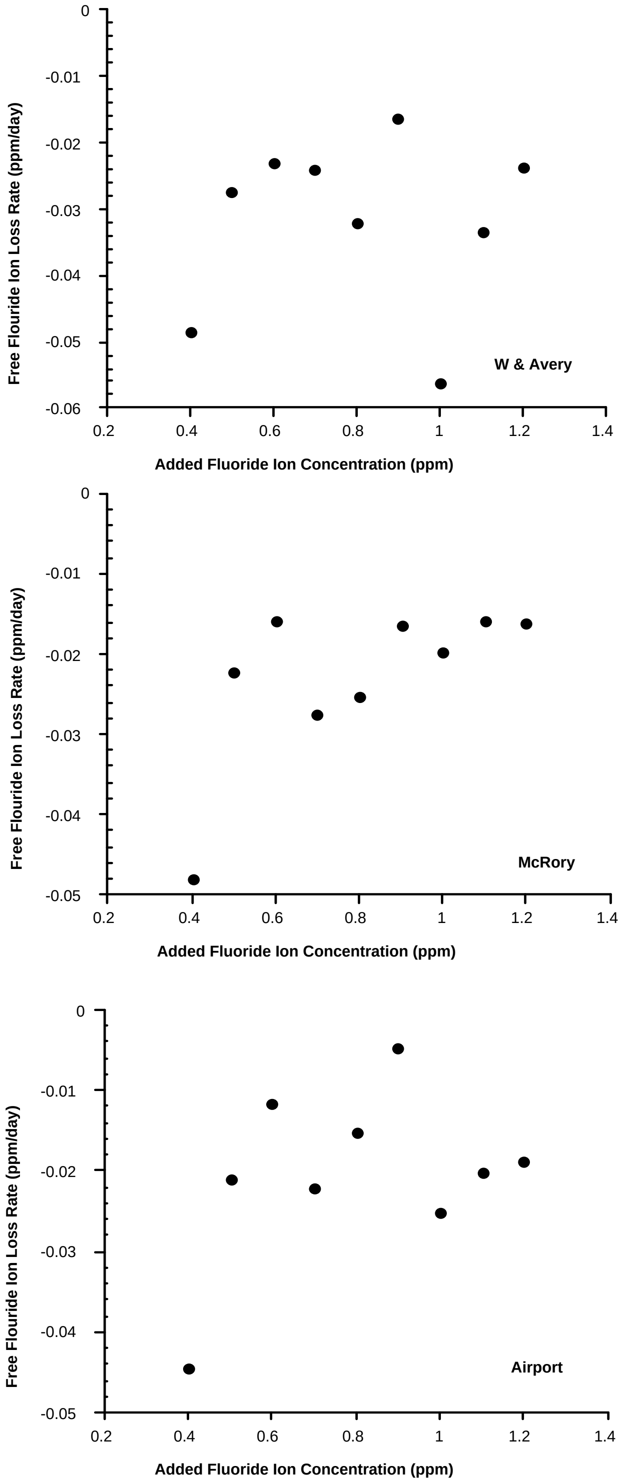


Figure 3. Loss rates of fluoride as a function of dose concentration.

F. Effects of Added Fluoride on the Leaching of Metals from New Pipes.

Reaction of the free fluoride ion with pipes would not only reduce free fluoride ion concentrations, but also has the potential to increase the leaching of metals from pipe materials into the drinking water supply.

In order to assess the effect of added fluoride on metals concentrations in the drinking water supply, we designed an experiment to monitor the solution of metal ions from copper and a lead/tin solder. This experiment would address situations where new construction or renovations involving unoxidized metal pipes and solder would be exposed to fluoridated drinking water.

Each of three ECUA water sources (W & Avery, Airport, and McCrory) was subjected to four treatments in flasks containing 500 ml of treated well water:

1) fluoride addition alone at 10 ppm,
2) added copper sheet representing 233 cm^2 of surface area,
3) added copper sheet and lead/tin solder representing 7.6 cm^2 surface area, and
4) fluoride and metals combined.

The fluoride addition at 10 ppm (in excess of 10-fold the concentration targeted for the drinking water supply, 0.8 ppm) was designed to maximize any effect of the added fluoride on metals dissolution. Each treatment was replicated three times for a total of 27 flasks. Flasks were sampled after one day and again after one month. Samples were analyzed for copper (Cu), tin (Sn), and lead (Pb) using a Varian atomic absorption spectrometer (AA). Metals analysis followed standard methods for the analysis of drinking water.

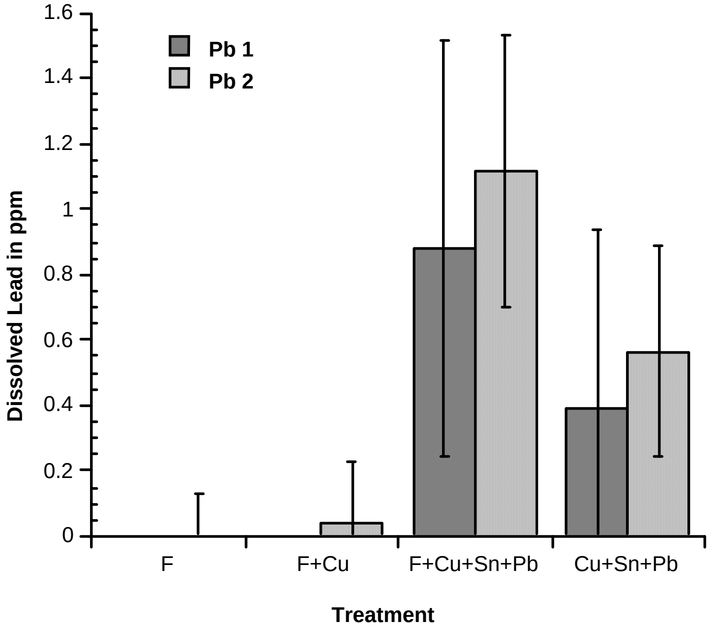
No significant differences ($P \geq 0.5$) were found between any of the three source well waters for any treatments. No significant loss of free fluoride ion was detected as result of the presence of metals. No dissolved tin was found in any of the treatment waters.

The combination of hydrofluorosilicic acid and copper or hydrofluorosilicic acid and copper and solder, increased the dissolved concentrations of copper significantly over treatments with metals and no fluoride added after one day of exposure (Cu 1, **Figure 4, bottom**). The combination of metals significantly reduced ($P \geq 0.5$) the amount of dissolved copper (**Figure 4, bottom)** in the copper + solder + fluoride treatment relative to the copper + fluoride treatment for both one day of exposure (Cu 1) and 27 days of exposure (Cu 2), suggesting a competitive effect between the metals and the fluoride. After 27 days of exposure, the dissolved copper concentration in the metals + fluoride treatment was not significantly different from zero (non-detect), suggesting a rebinding of copper ions previously in solution.

Dissolved lead (**Figure 4, top**) increased significantly ($P \geq 0.5$) after both 1 (Pb 1) and 27 (Pb 2) days of exposure in the presence of fluoride, over metals alone (0.491 ppm) and over treatments where no lead was added (0.878 ppm). Unlike the copper analysis, lead analysis did not indicate a decrease in dissolved lead after 27 days, but indicated an increase in lead content of water in treatments with and without fluoride.

The enhancement of metals solution from new metal exposed to 10 ppm fluoride suggests that the standard warning issued to buyers/builders of new construction to let the water lines flush before using their water for human consumption should be emphasized in areas with fluoride in the water supply. Once pipes become oxidized with use, the ability to leach metals would be greatly reduced.

These experimental results should not be over interpreted, since the high concentration of fluoride used (10 ppm) represents at least a ten-fold increase in effect over the concentration of fluoride targeted for the water system. Moreover, the long-term, static-incubation scenario of these experiments does not reflect most real-world situations, and the experimental model would be expected to greatly exacerbate leaching of metals into the water. Decreasing the enhanced dissolution effect by a factor of ten would result in a non-significant effect.



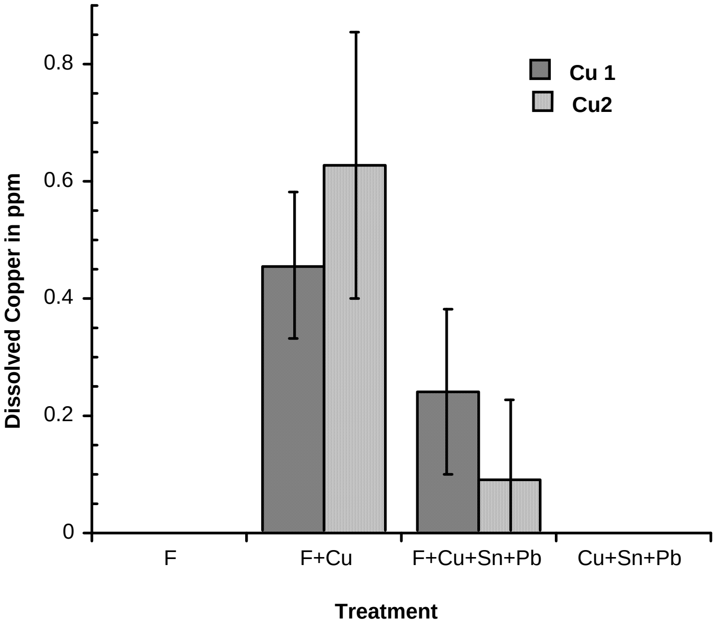


Figure 4. Leaching of metal ions from new copper sheet and solder. F = fluoride only added. F + Cu = fluoride and copper sheet. F + Cu + Sn + Pb = fluoride, copper sheet, and tin/lead solder. CU + Sn + Pb = metals with no added fluoride.

Table 6. Metal leaching: statistical difference between treatments[a]

Pb1	
F	A
F + Cu	A
F+Cu+Sn+Pb	B, C
Cu+Sn+Pb	A, C
Pb2	
F	A, D
F + Cu	A
F+Cu+Sn+Pb	B
Cu+Sn+Pb	C, D
Cu1	
F	A, D
F + Cu	B
F+Cu+Sn+Pb	C
Cu+Sn+Pb	D
Cu2	
F	A, D
F + Cu	B
F+Cu+Sn+Pb	C, D
Cu+Sn+Pb	C, D

[a] Treatments with the same letter were not significantly different ($P \geq 0.5$).

G. Propensity of Fluoride to Concentrate in Dead Zones of The Water System.

Areas of reduced water flow or hydrodynamic isolation "dead zones" within the delivery system have the potential to accumulate chemical flocculent that may be enriched in fluoride. Flushing of the system with increased usage periods could potentially deliver a pulse of water with enriched fluoride from resuspension of this flocculent.

To assess this potential problem, the natural precipitate that forms in the water system was tested for fluoride enrichment. Precipitate was acquired from the City of Gulf Breeze, which operates a sand filter system to remove precipitate from ECUA water prior to distribution on Fairpoint Peninsula. The natural levels of fluoride in ECUA-supplied water to this facility range from 0.01 to 0.3 ppm. Backflush from the sand filter was collected, acidified to dissolve the solids, and tested for free fluoride ion. This back flushed material was found to be not enriched in fluoride relative to the bulk water, suggesting that fluoride added to the water system should remain in dissolved form and not become enriched in dead zones where these precipitates may accumulate and periodically be flushed out to end users.

H. Analysis of Fluoride Levels in the Sewage Treatment Facilities

Samples were obtained from ECUA's Main Street and Bayou Marcus treatment plants and analyzed using a fluoride-ion-selective electrode calibrated against certified fluoride ion standards.

Fluoride levels in treatment system influents and final effluents from ECUA sewage treatment facilities are presented in **Table 5**. A significant decrease in fluoride concentration was observed in the final effluent at the Marcus Pointe facility (80% reduction) as a result of the treatment process. The levels of fluoride in the treated sewage at the Main Street facility were much higher than those at the influent from Marcus Pointe facility, and fluoride ion concentration was increased in the final effluent, perhaps reflecting differences in the treatment processes at the two plants.

Reasons for the dramatic differences in fluoride ion concentration between the two waste streams are unknown. However, infiltration from the Agrico Superfund Site plume into the sewer collection system of the Main Street facility is a possible explanation.

It is possible that sequestered fluoride in sediments was released periodically causing a spike in concentration in the Main Street effluent coinciding with the timing of the sampling. An experimental design incorporating more intense and extended temporal sampling regime might have shed light on potential mechanisms for this anomaly.

Table 7. Fluoride Ion Analysis in Waste Stream and Final Effluents at the ECUA Treatment Facilities.[a]

	pH	Fluoride Concentration (mg/L)
		Bayou Marcus Final Effluent
Sample 1:	**ND-**	0.070
Sample 2:	**ND**	0.073
Sample 3:	**ND**	0.073
		Bayou Marcus Influent
Sample 1:	7.98	0.254
Sample 2:	7.94	0.248
Sample 3:	7.24	0.177
		Main Street Final Effluent
Sample 1:	7.22	1.202
Sample 2:	7.06	1.184
Sample 3:	7.14	1.193
		Main Street Influent
Sample 1:	6.94	0.873
Sample 2:	6.86	0.860
Sample 3:	7.05	0.866

[a] The sampling date was 16 July 2001. ND = no data obtained.

III. UPDATE OF THE LITERATURE

The American Dietetic Association has recently strongly reaffirmed their position on the efficacy of fluoride supplementation to optimal levels either through the fluoridation of the community water supply or by other means (Anonymous, 2000). Earlier Position Papers on the status of fluoridation endorsed fluoridation of the water supply to an optimal concentration of 0.7 to 1.2 ppm with the expected result of a 40 to 60% reduction in dental caries. This report (2000) also addresses the current status of community water fluoridation, safety issues, and cost factors. The American Dietetic Association concludes that fluoride reduces dental caries and aids in the remineralization of teeth. The 2000 Position Paper relates the history of fluoridation practice and effect, and also describes the function of fluoride in dental health as follows:

A. promotes new mineralization of incipient lesions
B. increases resistance to acid demineralization
C. interferes in the formation of dental plaque microorganisms
D. increases the rate of posterruptive maturation and improves morphology.

The ADA concludes that fluoride is an important element for mineralization of body tissues. The use of topical and systemic fluoride for oral health has resulted in major reductions in dental caries and its associated disability. Fluoridation of public water supplies has been endorsed by over 90 professional health organizations as the most effective dental public health measure in existence. Still, about half of the US population fails to receive the maximum benefits possible from community water fluoridation and the use of fluoride products. Fluoride also plays a role in bone health. The role of high doses of fluoride for prevention of osteoporosis is undergoing active study and is considered experimental at this point. Dietetics professionals should routinely monitor and promote the use of systemic and topical fluorides, especially in children and adolescents. The American Dietetic Association strongly reaffirms its endorsement of the use of systemic and topical fluorides, including water fluoridation, at appropriate levels of intake, as an important public health measure. However, clients should be cautioned that experimental use of high intakes of fluoride should be avoided unless they are participating in clinical trials.

These Position Papers cite various surveys and case studies of fluoridation and conclude that fluoride use by either systemic or topical means promotes a healthy life.

Pratten and coworkers recently (2001) published their results of an *in vitro* study of the effect of fluoridated milk on oral bacterial biofilms in the peer-reviewed journal Applied and Environmental Microbiology. They established microcosms simulating dental habitats in which dental plaques were grown in artificial saliva and supplemented with either milk or fluoridated milk. The presence of fluoride in the milk increased the pH of the biofilms and reduced the proportions of streptococci, demonstrating that in this model, fluoridation of milk produces biofilms with reduced cariogenic potential. These results present additional circumstantial evidence for a mechanism we described in our previous literature review that fluoride ion effects a re-distribution of oral populations toward those less likely to promote tooth decay. However, care should be taken in the interpretation of such results as proof of mechanism for fluoridation benefits.

In a review of the chemistry of enamel caries, Robinson and coworkers **(**2000) provide particular focus on the mechanism of fluoride activity. They suggest that the role of fluoride is crucial in that it not only protects enamel per se but also promotes redeposition of enamel when present in solution by allowing more insoluble fluoridated species to form more easily. The role of organic material interacting with fluoride in caries formation needs further investigation, but they suggest a real possibility of both inhibition of repair and facilitation of redeposition. They suggest that delivering fluoride deep into the lesion would appear to offer the prospect of improved repair.

Although the predominant beneficial effect of fluoride occurs locally in the mouth, the adverse effect, dental fluorosis, occurs by the systemic route. Fomon et al. (2000) reviewed both aspects of fluoridation treatment. While the caries attack rate in industrialized countries, including the United States and Canada, has decreased dramatically over the past 40 years, the prevalence of dental fluorosis in the United States has increased during the last 30 years both in communities with fluoridated water as well as in communities with nonfluoridated water. Dental fluorosis is closely associated with fluoride intake during the period of tooth development. The authors reviewed the major changes in infant feeding practices that have occurred since 1930 and the changes in fluoride intakes by infants and young children associated with changes in feeding practices and concluded that fluoride intakes of infants and children have shown a rather steady increase since 1930, are likely to continue to increase, and will be associated with further increase in the prevalence of enamel fluorosis unless intervention measures are instituted. They recommend (1) using, when feasible, water low in fluoride for dilution of infant formulas; (2) adult supervision of toothbrushing by children younger than 5 years of age; and (3) changes in recommendations for administration of fluoride supplements so that such supplements are not given to infants and more stringent criteria are applied for administration to children.

McDonagh and coworkers (2000) provide an additional recent review of the safety and efficacy of drinking water fluoridation. They searched 25 electronic databases and the Internet, scientific journals and directly queried authors of publications. Criteria were established to assess validity and scientific integrity of the sources. For potential adverse effects, all outcomes reported were used. The review included 214 studies, which were judged low to moderate in quality. Water fluoridation was associated with an increased proportion of children without caries and a reduction in the number of teeth affected by caries. The range (median) of mean differences in the proportion of children without caries was -5.0% to 64% (14.6%). The range (median) of mean change in decayed, missing, and filled primary/permanent teeth was 0.5 to 4.4 (2.25) teeth. A dose-dependent increase in dental fluorosis was found. At a fluoride level of 1 ppm an estimated 12.5% (95% confidence interval 7.0% to 21.5%) of exposed people would have fluorosis that they would find aesthetically concerning. They conclude that the beneficial reduction in caries should be considered together with the increased prevalence of dental fluorosis, however they found no clear evidence of other potential adverse effects.

Mascarenhas (2000) reviewed recent scientific literature addressing risk factors for dental fluorosis. The review acknowledges that decline in dental caries prevalence and incidence in developed countries over the last two decades is largely due to the widespread use of fluoride. Simultaneously, he notes an increase in the prevalence of the mild and very mild forms of dental fluorosis, and is proportionally greater in non-fluoridated areas than in fluoridated areas. This is because of the increase in the mean fluoride intake from all sources since the 1940s. The literature over the last two decades has reported numerous studies with differing and confusing results. Only well conducted studies evaluating risk factors or indicators and quantifying the risk for dental fluorosis from the 1980s through the 1990s time period were included in this review. Four major risk factors were consistently identified: use of fluoridated drinking water, fluoride supplements, fluoride toothpaste, and infant formulas before the age of six years.

Featherstone (2000) has reviewed current science and practice of caries prevention and described protective factors of salivary calcium, phosphate and proteins, salivary flow, fluoride in saliva, and antibacterial components or agents. He reports that caries progression or reversal is determined by the balance between protective and pathological factors. Fluoride, a key agent in battling caries, works primarily via topical mechanisms: inhibition of demineralization, enhancement of remineralization and inhibition of bacterial enzymes. Fluoride in drinking water and in fluoride-containing products reduces caries via these topical mechanisms.

Oral health in the United States has improved in the post-fluoride generation according to a recent review by Milgrom and Reisine (2000). They cite reduced incidence of tooth decay, periodontal diseases, and associated loss of teeth in adults and children since the inception of community water fluoridation programs. Yet the disadvantaged and poor have not fully shared in the benefits and access to preventive and therapeutic dental care is far from universal. Public health programs similar in commitment to the approach of community water fluoridation programs initiated in the 1950s and 1960s are needed to address neglected oral health needs of underserved and high-risk populations in the United States.

IV. CONCLUSIONS

The **updated literature review** supports our previous conclusions that the fluoridation of public water supply is a beneficial public health practice (Lepo and Snyder, 2000). However, a few new reviews suggest the wisdom of monitoring overall dose of fluoride in regions with higher levels of natural fluoride input, and that the availability of fluoride in the water used in infant formulas should be limited.

Our assessment of **fluoride in regional municipal water supplies** yielded results consistent with ECUA-provided water quality analysis data. And our measures of **fluoride in regional surface waters** yielded results that were expected: we identified a descending gradient of fluoride from the Pensacola Bay inward into the bayous and freshwater areas; however, we also identified a reverse gradient of fluoride in the Bayou Texar that is probably the result of groundwater intrusion from the Agrico Superfund site.

We were able to obtain only one **commercial sample of hydrofluosilicic acid** and cannot make statements concerning the typical levels of metals contamination based on this one sample. Arsenic and cadmium were above detection limits. However, dilution of the product to the target concentration of 0.8 ppm, would make the concentration of added arsenic in the drinking supply 16.35 parts per trillion, and the concentration of added cadmium would be 0.689 parts per trillion. These concentrations are well below detection limits afforded by state-of-the-art analytical technology and below levels for any known toxicity. The product was also tested for radioactivity. Radioactive β decay measured as radon in the concentrated hydrofluorosilicic acid solution was 1,374 pCi L^{-1}. These levels of radioactivity, when diluted to the target fluoride ion concentration would be 0.0042 pCi L^{-1}, well below background levels of radioactivity in the local environment and ECUA well waters, and below safety limits.

Our assessment of the **stability of the free fluoride ion with time** in ECUA well waters showed rapid loss for fluoride added at 0.4 ppm, but above that concentration, the loss rates appear to stabilize and are independent of dose concentration. For the target concentration of 0.8 ppm, the mean loss rates were: W & Avery 0.0295 ppm day^{-1}, McCrory 0.0198 ppm day^{-1}, and Airport 0.0173 ppm day^{-1}. These loss rates were not significantly different between W & Avery and McCrory, and McCrory and Airport, but were significantly different between W & Avery and Airport. The 95% confidence limits for the range of values for all three wells (0.0118 to 0.0395 ppm day^{-1}) are indicative of what might be expected of fluoride within the water system.

In our laboratory model to explore whether fluoride promotes **leaching of metals from pipes** both dissolved copper and lead were increased in water containing 10 ppm fluoride. The enhancement of metals dissolution from new metal exposed to 10 ppm fluoride suggests that the standard warning issued to buyers/builders of new construction to let the water lines flush before using their water for human consumption should be emphasized in areas with fluoride in the water supply. Once pipes become oxidized with use, the ability to leach metals would be greatly reduced. These experimental results should not be over interpreted, since the high concentration of fluoride used (10 ppm) represents at least a ten-fold increase in effect over the concentration of fluoride targeted for the water system. Moreover, the long-term, static-incubation scenario of these experiments does not reflect most real-world situations, and the experimental model would be expected to greatly exacerbate leaching of metals into the water. Decreasing the enhanced dissolution effect by a factor of ten would result in a non-significant effect.

To assess the **propensity of fluoride to concentrate in dead zones** of the water system, we tested precipitate from the City of Gulf Breeze, which operates a sand filter system to remove precipitate from ECUA water prior to distribution on Fairpoint Peninsula for free fluoride ion (natural levels of fluoride in ECUA-supplied water to this facility range from 0.01 to 0.3 ppm). This back flushed material was found to be not enriched in fluoride relative to the bulk water, suggesting that fluoride added to the water system should remain in dissolved form and not become enriched in dead zones where these precipitates may accumulate and periodically be flushed out to end users.

We analyzed **fluoride levels in influents and final effluents from ECUA sewage treatment facilities** and found a significant decrease in fluoride concentration in the final effluent at the Marcus Point facility (80% reduction). The levels of fluoride in the influent sewage at the Main Street facility were much higher than those at the Marcus Point facility, and fluoride ion concentration was increased in the final effluent, perhaps reflecting differences in the treatment processes at the two plants. However, infiltration from the Agrico Superfund Site plume into the sewer collection system of the Main Street facility is a possible explanation. It is also possible that sequestered fluoride in sediments was released periodically causing a spike in concentration in the Main Street effluent coinciding with the timing of the sampling. An experimental design incorporating a more intense temporal sampling regime might have shed light on potential mechanisms for this anomaly.

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VI. ACKNOWLEDGMENTS

We thank Angela Harris and Natasha Rondon for sample collection and for technical services in performance of the fluoride analyses and conduct of the experiments described herein. Jan Macauley of the Wetlands Research Laboratory compiled data for the metals analyses of the hydrofluosilicic acid, which were performed by Melissa Rearick. We thank Dr. K. Ranga Rao for a critical reading of the draft report.