THE EFFECT OF TEMPERATURE, WATER HARDNESS, AND EXPOSURE TIME ON FLUORIDE TOXICITY IN THE AQUATIC ENVIRONMENT

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SUMMARY: Many studies have measured fluoride toxicity for aquatic organisms with various levels of water quality including the examination of spot samples and the presence of interfering factors. In the present study, the actual fluoride toxicity, the fluoride LC_{50}, was determined without interfering factors present and then after modelling the effects of changes in temperature, water hardness, and exposure time. Fluoride toxicity decreased with increased water hardness and increased with increased temperature and exposure time. This information may help with industrial effluent discharge planning in recipient waters that have a high fluoride content so that fluoride toxicity can be avoided.

Key words: *Daphnia magna*; Fluoride bioassay; Fluoride LC_{50}; Fluoride toxicity.

INTRODUCTION

In the bodies of water, the toxicity of the fluoride ion (F) is related to several parameters, such as pH, temperature, and water hardness.[1-2] In unpolluted surface waters, F concentrations are usually 0.01–0.3 mg/L, although higher concentrations may occur in waters in volcanic areas.[3-7] Moreover, human activities can increase F in water resources by the discharge of industrial wastewaters into recipient waters.[4,8-9] The ingestion of high levels of F can cause dental and skeletal fluorosis[10] as well as damaging other organs including the kidney, liver, and brain.[7] In aquatic environments, a high level of F has acute and chronic toxic effects (e.g., growth reduction and even death) on organisms such as algae, plants, fish, and marine crustaceans.[3,11-12] Many studies have used bioassay methods with different aquatic organisms to determine F toxicity. The fluoride LC_{50} was determined in these studies in the presence of constant amounts of various interfering factors.[3, 13-14] In the present study, the maximum toxicity of F in an aquatic environment was measured with and without the interfering factors of temperature, water hardness, and exposure time.

MATERIALS AND METHODS

In determining the interactions between the interfering parameters, of temperature, water hardness, and exposure time, the study was performed in an aquatic environment at three different temperatures and four different levels of water hardness. The standard method was used for the measurement of hardness in

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the prepared solutions.[15] *Daphnia magna* were collected from an aquatic environment and bred under standard conditions.[15] To measure the maximum toxicity of F (LC_{50} and LC_{99}), F solutions were prepared in ten concentrations from a stock solution by dissolving the desired amounts of stock solution in 100 mL Milli Q water. The stock solution was prepared by dissolving 2.21 g of NaF (99.99% purity) in 1 L Milli Q water. For each concentration, three 100 mL containers were prepared, comprising a control container and 2 test containers. Ten 10 *Daphnia* were then added to each container. The *Daphnia* mortality was recorded after 24, 48, and 72 hours of exposure. The pH values for all the solutions were 5.65–6.12. The toxicity test was repeated for the determination on F toxicity of temperature changes (12, 15 and 18ºC) and water hardness (50, 100, 200, and 400 mg/L hardness as $CaCO_3$). The selected levels for hardness and temperature were in the natural ranges of hardness and temperature occurring in water bodies.

The LC_{50} and LC_{99} of F were measured by probit analysis with SPSS software. The simultaneous influence of temperature, exposure time and water hardness changes on F toxicity were analyzed by 3 way ANOVA.

RESULTS AND DISCUSSION

The LC_{50} and LC_{99} of F were initially measured after 24, 48, and 72 hours of exposure to F solution without any hardness. (Table 1.)

Table 1. LC_{50} and LC_{99} for *Daphnia* of fluoride (mg F/L) without the interference factor of water hardness

Exposure time in hours	LC_{50} and LC_{99} for fluoride	
	LC_{50} (mg F/L)	LC_{99} (mg F/L)
24 hr	54.9	126.3
48 hr	46.5	108.4
72 hr	38.7	92

The effect on the LC_{50} of the interfering factors of water hardness and temperature are shown in Table 2.

Table 2. LC_{50} for *Daphnia* of fluoride (mg F/L) in the presence of the interference factors of duration of exposure (24, 48, and 72 hr), temperature (12, 15, and 18 °C) and water hardness (50, 100, 200, and 400 mg/L $CaCO_3$)

*Temperature	12°C			
**Water hardness	50	100	200	400
LC_{50} 24 hr (mg F/L)	43.78	83.65	103.45	99.88
LC_{50} 48 hr (mg F/L)	38.42	76.7	94.63	89.23
LC_{50} 72 hr (mg F/L)	33.86	64.33	83.56	78.37
Temperature	15°C			
**Water hardness	50	100	200	400
LC_{50} 24 hr (mg F/L)	38.54	72.5	86.10	103.86
LC_{50} 48 hr (mg F/L)	34.42	65.38	77.52	96.74
LC_{50} 72 hr (mg F/L)	30.52	58.36	65.08	85.13
*Temperature	18°C			
**Water hardness	50	100	200	400
LC_{50} 24 hr (mg F/L)	31.71	58.09	55.92	66.45
LC_{50} 48 hr (mg F/L)	29.24	47.52	49.79	59.4
LC_{50} 72 hr (mg F/L)	27.37	37.23	42.46	52.97

* Temperature in °C; **Water hardness in mg/L $CaCO_3$.

The interfering factors of temperature, exposure time, and water hardness interacted significantly ($p< 0.001$) in their effects on the LC_{50} (Table 3). The trends of their effects on F toxicity are shown in Figures 1–3.

Table 3. The effects on the LC_{50} for fluoride of simultaneous exposure to the interfering factors of temperature, water hardness, and exposure time. The data were obtained from 3 way ANOVA

Parameters	Levels	Mean LC_{50} (mg F/L)	SD (mg F/L)	Meaningful coefficients	p value
Temperature (°C)	12	75.77	24.93	-	<0.001
	15	67.85	24.03	–7.923	
	18	49.07	15.25	–26.698	
Hardness (mg/L $CaCO_3$)	50	34.21	5.24	-	<0.001
	100	62.64	14.40	28.433	
	200	76.58	18.01	42.373	
	400	83.49	19.17	49.282	
Exposure time (hr)	24	72.01	25.04	-	<0.001
	48	64.12	24.97	–7.892	
	72	56.56	21.48	–15.446	

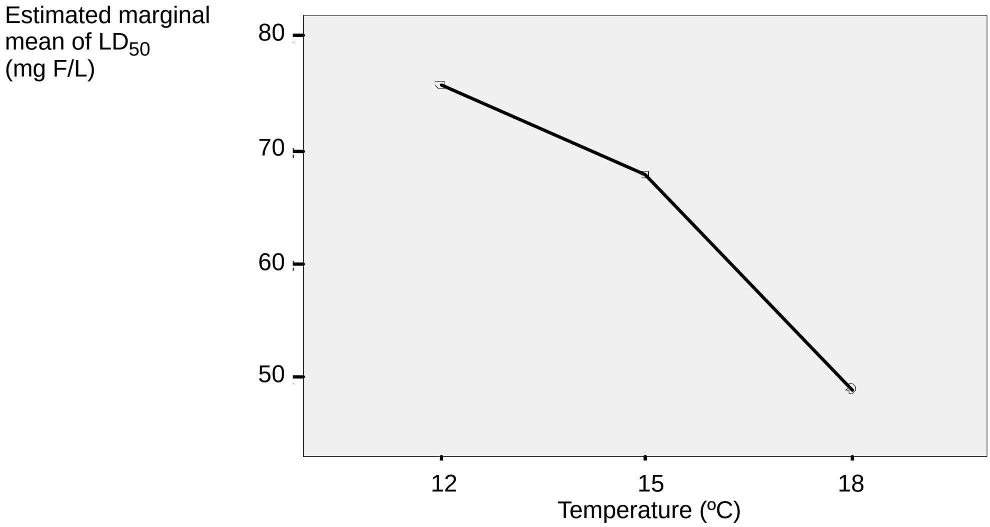

Figure 1. Trend of the effect of the interference factor of temperature (ºC) on fluoride LC_{50} (mg F/L).

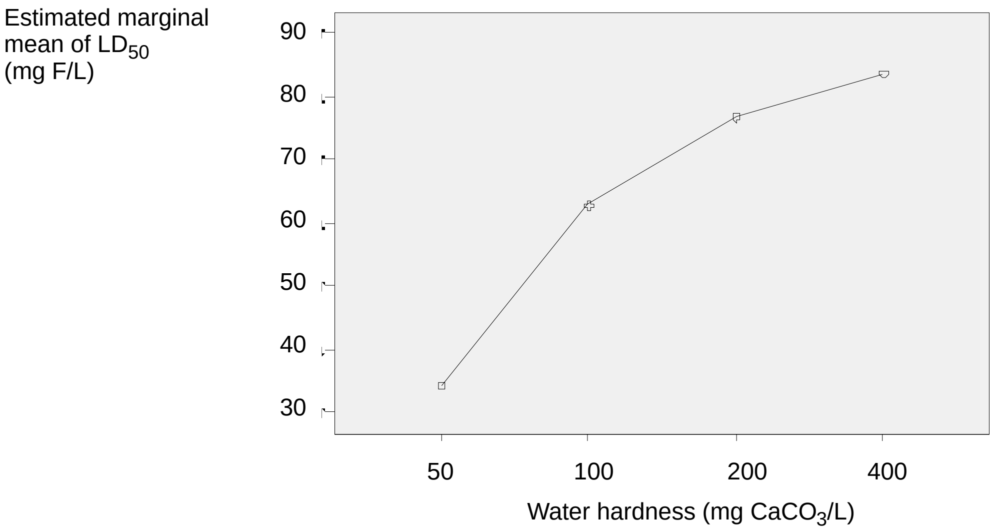

Figure 2. Trend of the effect of the interference factor of water hardness (mg $CaCO_3$/L) on fluoride LC_{50} (mg F/L).

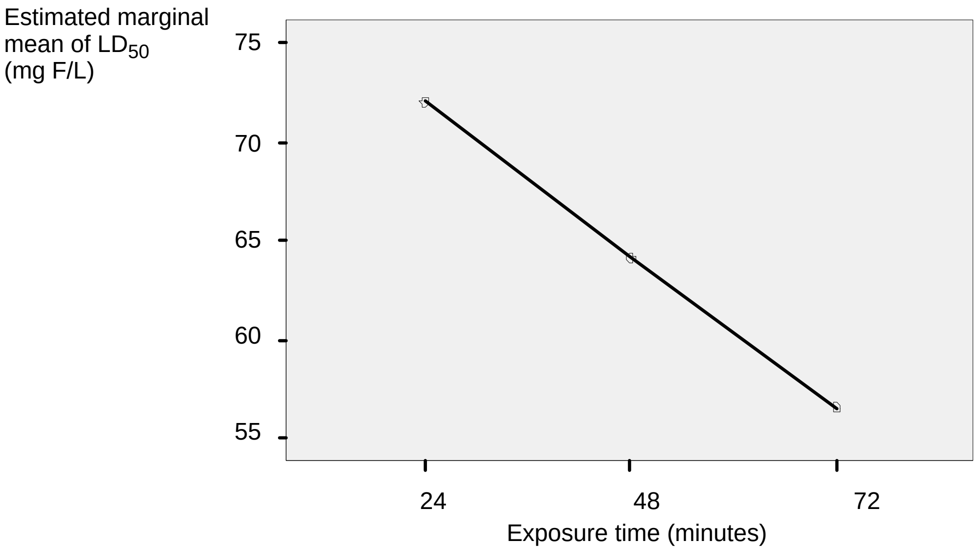

Figure 3. Trend of the effect of the interference factor of exposure time (minutes) on fluoride LC_{50} (mg F/L).

As shown in Figure 3, an increase in exposure time led to an increase in F toxicity and a reduction in LC_{50} values. A direct relationship was also present between water temperature and F toxicity (Figure 1). This direct relation can be explained by the increase in the degree of ionic dissociation (α) of sodium fluoride with increased temperature. The resulting increase in the effective concentration of fluoride anions in solution leads to increased F toxicity. An inverse relationship was present between water hardness and F toxicity with the fluoride LC_{50} increasing with increased water hardness (Figure 2). The formation of CaF_2 from the solution decreases the effective concentration of fluoride anions.

In the first part of the study, water hardness as an interfering factor was removed from the test solution so the determined toxicity level was the actual F toxicity. In the second part, the simultaneous influence of the interfering factors of temperature, water hardness, and exposure time on fluoride LC_{50} were determined.

Most studies on F toxicity have often surveyed hardness and temperature affects on toxicity using spot samples.[16-17] In the presence of a constant level of hardness and temperature, fluoride LC_{50} at 24 and 48 hours were reported to be 308 and 154 mg/L, respectively.[12] In a similar study, Dave et al. determined fluoride LC_{50} values of 205 and 93 mg/L at 24 and 48 hours, respectively.[18] Also, Fieser et al. determined the influence of temperature on F toxicity after 24, 48, and 72 hours of exposure in the presence of a constant degree of hardness.[19]

Identifying conditions that maximize or minimize F toxicity is one of the capabilities of this method. In the present study, F toxicity was determined by applying interfering factors and studying their interactions. This is useful for industrial effluent discharge planning into recipient waters that have a high F content. Having knowledge of the features of the recipient water that affect F toxicity (e.g., temperature and hardness) can help in the determination of the local effluent discharge limits required for avoiding F toxicity effects. Also, some periodic or seasonal variations in water body features, such as water temperature, can cause major variations in the F toxicity level in the recipient water. Seasonal variations in the effluent discharge limits may be appropriate in order to allow for these seasonal changes.

ACKNOWLEDGMENT

The authors would like to thank the Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran, for their financial support.

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