

## CAN FLUORIDATION AFFECT LEAD(II) IN POTABLE WATER? HEXAFLUOROSILICATE AND FLUORIDE EQUILIBRIA IN AQUEOUS SOLUTION\*

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Recent reports have attempted to show that fluoridating potable water is linked to increased levels of lead(II) in the blood. We examine these claims in light of the established science and critically evaluate their significance. The completeness of hexafluoro-silicate hydrolysis is of paramount importance in ensuring that total water quality is maintained. The possible impacts of such complexes as  $Pb^{II}-F-SiF_5$  or  $PbF_2^{(2-2)}$  are discussed as are the contributions of fluoridation byproducts to total acid content. We calculate the fractional distribution of aqueous species based on known chemical equilibria and show the species concentrations for several different model tap waters. We discuss and quantitatively show the effects of other complexing anions, such as carbonate or hydroxide. Overall, we conclude that no credible evidence exists to show that water fluoridation has any quantifiable effects on the solubility, bioavailability, bio-accumulation, or reactivity of lead(0) or lead(II) compounds. The governing factors are the concentrations of a number of other species, such as (bi)carbonate, hydroxide, or chloride, whose effects far exceed those of fluoride or fluorosilicates under drinking water conditions. Lastly, we consider some previous epidemiological studies of lead(II) exposure and how recent papers fare methodologically.

**Keywords:** Fluoridation; fluoride; fluosilicic acid; hexafluorosilicate; hexafluorosilicic acid; lead(II); potable water; silicofluoride; water treatment

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## 1. INTRODUCTION

Controversy over water fluoridation varies in nature and intensity. Recent papers have implications for water fluoridation since they suggest that certain adverse health or social conditions may stem from interactions between lead(II) and inorganic fluoro-compounds, specifically, fluorosilicates and fluoride [1-3]. In order to assess the validity of these assertions, it is necessary to have a firm foundation of the aqueous chemistry of  $\text{H}_2\text{SiF}_6$  and HF. There is a considerable body of fundamental chemical literature on these species. Nonetheless, some gaps do remain, and little effort has been expended in combining the known chemistry into one comprehensive and authoritative volume. Accordingly, we believe it to be worthwhile to revisit the concepts involved in water fluoridation at a fundamental level and to examine some of the relationship suggested by recent papers in light of well-established science.

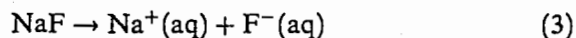
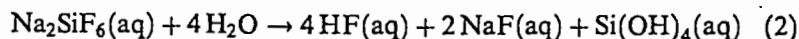
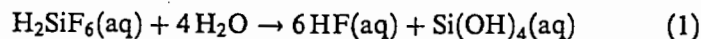
The sheer number of people consuming fluoridated potable water makes fluoridation issues relevant. In 1992, the Centers for Disease Control Fluoridation Census found that 62.1% of the U.S. population served by public suppliers drank fluoridated water [4]. The CDC also surveyed utilities regarding fluoridating agents (see Tab. I). Most commonly used are hexafluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) or its sodium salt ( $\text{Na}_2\text{SiF}_6$ ), which hydrolyze to produce fluoride ion upon dilution (1)-(2). However, sodium fluoride (NaF) is sometimes used as a direct fluoride source (3).

TABLE I Water fluoridation chemicals used by U.S. public water suppliers in 1992\*

	<i>Hexafluorosilicic acid</i>	<i>Sodium hexafluorosilicate</i>	<i>Sodium fluoride</i>
formula	$\text{H}_2\text{SiF}_6$	$\text{Na}_2\text{SiF}_6$	NaF
common synonyms	fluosilicic acid fluorosilicic acid hydrofluosilicic acid	sodium silicofluoride sodium fluorosilicate	-
population served	80,019,175 62.6% <sup>†</sup>	36,084,896 28.2% <sup>†</sup>	11,701,979 9.2% <sup>†</sup>
utilities using	5876	1635	2491

\* Total US population: 258,544,000. Population and utility data were taken from Ref. [4].

<sup>†</sup> Percentages are based on total population of 127.8 million persons drinking fluoride-fortified public water and does not include those drinking water naturally high in fluoride.



Hexafluorosilicic acid is a cheap and readily available source of fluoride. However, it is difficult to handle and the handling costs can only be offset by the volume discount in large water treatment plants. Although more systems rely on sodium fluoride than sodium hexafluorosilicate, these serve only 9.2% of the U.S. population. Because sodium fluoride is the easiest of the three to handle and dispense, small systems are the primary users of NaF. Although the EPA regulates drinking water, the US Public Health Service has been involved in water fluoridation for historical reasons (primarily because the practice of fluoridation pre-dates EPA). The purpose of fluoridating water is the prevention of dental caries; therefore, the publication of water fluoridation how to manuals falls under the purview of the CDC. These manuals discuss dosing and other practical matters of concern to the treatment plant operator [5].

## 2. CAUSE FOR CONCERN?

Potable water from large public water supplies contains a large number of compounds, including disinfection byproducts (such as trihalomethanes or haloacetic acids), residual oxidants (such as chlorine or chloramine), nonspecific dissolved organic matter, trace metals, minerals (such as sodium chloride or calcium carbonate), and additives (such as fluoride). Consequently, drinking water science is a complicated interplay among the chemical constituents as well as the physical conditions, such as temperature.

This paper evolved in large part as a response to relationships (posited in the literature [1-3]) between the practice of water fluoridation and human blood concentrations of lead(II). It is instructive to address the issues regarding water fluoridation and lead(II) by

posing a series of questions regarding the fundamental behaviors of fluoride, silicon and lead. We will explore the answers to these questions in the sections that follow.

1. What is the residual concentration of hexafluorosilicate ion ( $\text{SiF}_6^{2-}$ ) after the hydrolysis reaction (2) takes place?
2. How fast does reaction (2) occur?
3. Do fluoridation additives affect the pH of the finished water at the plant or at the tap? If there is a pH change, does it matter? Can  $\text{H}^+$  from hydrolysis of residual  $\text{SiF}_6^{2-}$  promote the solubilization of lead(II) from the distribution system, thereby increasing the lead(II) concentration at the tap?
4. Can  $\text{F}^-$  or residual  $\text{SiF}_6^{2-}$  complex with lead(II) and make it more bioavailable? In other words, do fluoro-species complex with Pb(II), promoting permeation of the gastric mucosa and absorption into the bloodstream.
5. Can residual  $\text{SiF}_6^{2-}$  lower gastric pH and therefore convert particulate Pb or lead compounds to bioavailable aqueous lead(II) ion?
6. How do the lead(II) drinking water regulations and sampling schemes relate to human health effects?
7. How is human lead exposure measured? What are the weaknesses in its quantitation?
8. What quality controls exist for drinking water additives? Can the additives themselves be responsible for contaminants in the water supply? Specifically, can they be a source of lead exposure?
9. What are the routes and nature of human lead exposure? What sorts of factors are linked to human lead exposure?
10. When all of the chemical and physical phenomena are considered together, what is the magnitude of the effect? That is, what species represent the greatest fractions of total lead(II) and fluoride concentrations under potable water conditions?

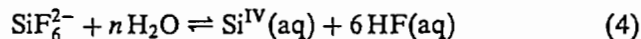
Certainly, we cannot fully answer all of these questions in one paper. However, we can summarize the principal findings and refine our understanding of the role drinking water plays. Let us begin to answer these questions at the molecular level by examining what takes place when sodium hexafluorosilicate is added to the water stream inside a utility plant.

### 3. THE CHEMISTRY OF HEXAFLUROSILICATE AND FLUORIDE IN AQUEOUS SOLUTION

#### 3.1. Equilibria and Kinetics of Hexafluorosilicate Hydrolysis

##### 3.1.1. Equilibria

Hexafluorosilicate ion reacts with water to produce fluoride ion and an assortment of silicon oxyanions [6, 7], e.g.,  $\text{SiO}_3^{2-}$ ,  $\text{SiO}_4^{4-}$ ,  $\text{Si}(\text{OH})\text{O}_3^{3-}$ . We represent the oxyanions as  $\text{Si}^{\text{IV}}(\text{aq})$  without further speciation at this time.



A principal issue (Q1) at stake is how much residual fluorosilicate is present, that is, whether Eq. (4) proceeds to completion. Of course, we must define completion. What fraction of total silicon(IV) is present as a fluoro-species? Is it 1%, 0.1%, or lower?

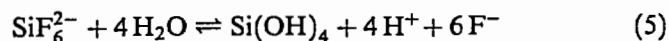
The actual speciation of silicon oxyanions is a function of acidity, *i.e.*  $[\text{H}^+]$ . Busey *et al.* [8] showed that virtually 100% of the hexafluorosilicate is hydrolyzed to silicon oxyanions at pH 6, even when there is a free fluoride concentration of 0.01 M. Meanwhile, fluoridated drinking water contains only  $\sim 1$  ppm fluoride, which equates to  $5 \times 10^{-5}$  M. Previous investigations [9, 10] found a non-negligible concentration of residual  $\text{SiF}_4$ <sup>1</sup> when this gas was passed through water. Ciavatta *et al.* [9] investigated fluorosilicate equilibria with  $0.3 \leq [\text{H}^+] \leq 3 \text{ m} [\text{mol F}^- (\text{kg water})^{-1}]$  and ionic strength fixed at 3 M, adjusted with  $\text{LiClO}_4$ . They concluded that the mixed ligand species<sup>2</sup>  $\text{SiF}(\text{OH})_3$  and  $\text{SiF}(\text{OH})_2(\text{H}_2\text{O})^+$  are significant contributors to total silicon(IV) in

<sup>1</sup>When dissolved in water, it is probably reasonable to view silicon(IV) compounds as hexacoordinated so that  $\text{SiF}_4(\text{aq})$  is actually better represented as  $\text{SiF}_4(\text{H}_2\text{O})_2(\text{aq})$ . Possible exceptions to this would involve the formation of pi bonds, such as  $\text{Si}(d\pi) \leftarrow \text{O}(p\pi)$  back donation. However, even  $\text{Si}(\text{OH})_4$  can be thought of as having two weakly attached axial  $\text{H}_2\text{O}$  molecules.

<sup>2</sup>Choosing a nomenclature system for the mixed ligand species is somewhat complicated. Any name is likely to impart a certain amount of confusion since the naming of these compounds has historically been lax. For example,  $\text{SiF}(\text{OH})_3$  might be called (mono)fluorotrihydroxysilane or (mono)fluorosilanetriol (organic), silicon (mono)fluoride trihydroxide (inorganic salt), monofluorosilicic acid (nonmetal oxyacid), or fluorotrihydroxosilicon(IV) (coordination complex). A particular name might be more suited to one context, but there is no truly preferable name. Naming as derivatives of silicic acid is problematic because there is confusion over whether silicic acid means  $\text{Si}(\text{OH})_4$  or  $\text{SiO}(\text{OH})_2$ .  $\text{SiF}(\text{OH})_2(\text{H}_2\text{O})^+$  seems best named as a coordination complex, aquofluorodihydroxosilicon(IV). Even though that name is cumbersome, the other nomenclature systems are incapable of describing such a species.

addition to  $\text{SiF}_4$ ,  $\text{SiF}_6^{2-}$  and  $\text{HSiF}_6^-$  under these conditions. Nonetheless, their results showed that fluoro-complexes comprised less than 5 mol% of the total silicon(IV) in  $0.01 \text{ m H}^+$  and  $10^{-4} \text{ m F}^-$ . Korobitsyn *et al.* [10] examined the hydrolysis of sodium hexafluorosilicate in sodium carbonate solution. Their work was geared towards an industrial process for producing sodium fluoride and is not directly applicable here.

The use of chemical shift information derived from  $^{19}\text{F}$  NMR spectrometry in understanding the formation of fluoro-ligated species is well-established [11–16]. Fluoride ligand exchange occurs rapidly between HF and  $\text{SiF}_6^{2-}$  at temperatures above  $-10^\circ\text{C}$  [13], and the identification of aqueous fluorosilicate species and the measurement of the concomitant equilibrium constants has been done almost entirely by  $^{19}\text{F}$  NMR spectroscopy and spectrophotometry [14–16]. The *Gmelin Handbook of Inorganic Chemistry* tabulates values for the equilibrium constants expression (6) of the hydrolysis reaction (5) at temperatures from 0 to  $60^\circ\text{C}$  [17].



$$K = \frac{[\text{Si}(\text{OH})_4][\text{H}^+]^4[\text{F}^-]^6}{[\text{SiF}_6^{2-}]} \quad (6)$$

The *smallest* value at ambient temperature reported for  $K$  is  $10^{-31.6}$ . Using this value at  $[\text{H}^+] = 10^{-6} \text{ M}$  and  $[\text{F}^-] = 5 \times 10^{-5} \text{ M}$ , the ratio  $[\text{Si}(\text{OH})_4]/[\text{SiF}_6^{2-}] = 1.6 \times 10^{18}$ . Note that less than 1% of fluoride exists as HF at drinking water acid levels (*i.e.*,  $\text{pH} > 5.2$ ) since  $\text{p}K_a^{\text{HF}} = 3.17$  [18]. Even if the hydrolysis constant were off by a factor of 1000, it would not matter. There would still be essentially no hexafluorosilicate ion. A fractional distribution plot in *Gmelin* [17] shows that other fluorosilicates (*i.e.*,  $\text{SiF}_4$  and  $\text{SiF}_5^-$ ) also drop off dramatically as free fluoride concentration, and not  $[\text{F}^-]_{\text{T}}$ , decreases towards  $10^{-4} \text{ M}$ , even in silica-saturated 4 M perchloric acid. For this solution, total fluoride concentration is expressible as (7), neglecting any mixed fluorohydroxo-ligated species:

$$[\text{F}^-]_{\text{T}} = [\text{HF}] + [\text{F}^-] + 4[\text{SiF}_4] + 5[\text{SiF}_5^-] + 6[\text{SiF}_6^{2-}] \quad (7)$$

Crosby studied the dissociation of sodium hexafluorosilicate and hexafluorosilicic acid in deionized water [19]. He found that about 99 mol% of the hexafluorosilicate had hydrolyzed when added to water to produce a 1 ppm fluoride solution; however, the pH of this solution was 4.20, considerably below a potable water pH. An important factor must be considered in potable water fluoridation as Crosby explains:

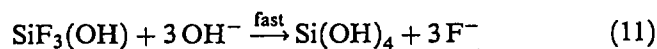
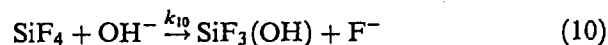
It should be remembered that the actual ionic population of most public drinking-water supplies is somewhat different from the experimental conditions used in the present and previous studies. Thus, the pH is normally adjusted to about 7 to 8, and the presence of additional salts may further influence the equilibrium owing to the formation of complexes with calcium and other metals.

If the pH of a treated drinking water is too low, it is adjusted to comply with regulations and minimize corrosion. We do not dispute Crosby's results. His water was demineralized and completely devoid of buffering agents. Consequently, the dissociation of hexafluorosilicate was hindered by the drop in pH. Crosby's fractional dissociation data cannot be applied directly to a potable water supply without correcting them for pH. Of course, that correction is the effect we have computed above, namely, the complete hydrolysis of fluorosilicates. This is precisely what Crosby was emphasizing. This observation hints at the answer to Q3 (effect on pH), which we shall come back to shortly.

Interestingly enough, a number of species actually promote the dissociation of hexafluorosilicate, including ferric ion [20]. While the compound  $\text{PbSiF}_6 \cdot 2\text{H}_2\text{O}$  can be synthesized, it decomposes quickly in moist air and slowly when dry [21]. Perhaps then lead(II) itself promotes hexafluorosilicate decomposition, such as through the formation of plumbous fluoride. Because moist air promotes this compound's destruction, we can infer that it would not be stable in aqueous solution at all. Based on the above computations and observations, we can dispense with the issue of incomplete hydrolysis entirely. There is essentially no hexafluorosilicate remaining in drinking water at equilibrium.

### 3.1.2. Kinetics and Mechanisms

Now that we have answered Q1 by concluding that the hydrolysis reaction (4) does in fact proceed to completion, we must consider how fast it reaches that state (Q2). The first major kinetics studies were performed in the early 20th century by Hudleston and Bassett [22], who studied the reaction between hexafluorosilicic acid and sodium hydroxide by adding an excess of the acid to a known volume of base and measuring the time for the phenolphthalein color to fade, and then titrating to the end point with more base. The problem with such a design is that excess acid stabilizes the hexafluorosilicate and the silicon tetrafluoride from hydrolyzing. Hudleston and Bassett did conclude that  $\text{SiF}_4$  hydrolysis was fast; however, it was not favored under their conditions. Rees and Hudleston added various volumes of standard  $\text{NaOH}(\text{aq})$  solution to a set volume of hexafluorosilicic acid solution [23]. There was no difference in the time required for the phenolphthalein color to fade. Consequently, they concluded that reaction was zeroth order in  $[\text{OH}^-]$  and first order in  $[\text{SiF}_6^{2-}]$ . At the time, the study of chemical kinetics was in its infancy, and the concepts of rapid pre-equilibrium and steady-state intermediates were not well-established. Suppose the reaction mechanism proceeds along these lines:



This mechanism immediately suggests a steady state in the concentration of tetrafluorosilane. The steady state approximation requires an unstable intermediate of limited lifetime, capable of remaining present at very low levels as it is simultaneously produced in (9) and consumed by (-9) and (10). Applying the steady state approximation, we set the rate of change of this species to zero, *i.e.*,  $d[\text{SiF}_4]_{ss}/dt = 0$ .



The net reaction rate is expressible as (12):

$$\text{rate} = k_{10}[\text{SiF}_4]_{ss}[\text{OH}^-] \quad (12)$$

Making use of the steady state approximation, we obtain the following differential rate expression (13):

$$\text{rate} = k_{10}k_9K_8[\text{SiF}_6^{2-}][\text{OH}^-]/\{[\text{F}^-](k_{-9}[\text{F}^-] + k_{10}[\text{OH}^-])\} \quad (13)$$

At sufficiently high hydroxide concentrations where  $k_{10}[\text{OH}^-] \gg k_{-9}[\text{F}^-]$ , the dependence of the rate on hydroxide concentration would disappear. Although an inverse variation with fluoride concentration would exist, Rees and Hudleston did not vary fluoride concentration. Note that we do not advocate this mechanism *per se*, but point out that it is consistent with Rees and Hudleston's data. Since they did not vary fluoride concentration, it is impossible to say whether their data support the inverse dependence suggested by Eq. (13). To our knowledge, the kinetics and mechanisms of hexafluorosilicate hydrolysis have not been adequately investigated at this time other than to suggest that the rate is fast enough for equilibrium to be achieved in a period of less than 30 minutes. Given the limits of laboratory apparatus and computing/data analysis technology in the 1920s and 1930s, it is unsurprising that the authors did not carry the work further.

In the 1970s, Plakhotnik conducted studies into the effects of lithium and calcium cations on the rate of hexafluorosilicate (and tetrafluoroborate) hydrolysis [24,25]. Plakhotnik concluded that a rapid pre-equilibrium existed between the hexafluorosilicate and the metal cation with a fluoride ion acting as an inner sphere bridging ligand to both the  $\text{Si}^{\text{IV}}$  and the  $\text{Li}^+$  or  $\text{Ca}^{2+}$ . Plakhotnik found that the reaction was catalyzed by both metal cations. He allowed for contributions from hydroxide assistance, but did not quantitate these. Although solutions were reported to have been made alkaline, neither a pH nor a hydroxide concentration is given. Presumably, all reactions were carried out at the same base concentration. Calcium accelerated the reaction by a factor of more than 10, while lithium accelerated it by a factor of perhaps 1.2. Based on Plakhotnik's results, we calculate that the hydrolysis would be 99 mol% complete in 12 minutes *if carried entirely by the uncatalyzed pathway*. That notwithstanding, natural water supplies do contain calcium and other divalent metals as well as

trivalent metal cations (e.g.,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ) either native or introduced during other treatment processes, such as agglutination (coagulation). Therefore, we can state that the actual hydrolysis rate would be even faster. And so we have answered Q2: the hydrolysis of hexafluorosilicate proceeds to completion before water reaches the consumer's tap.

Based on the above information on both the thermodynamics of the hydrolysis reaction and its kinetics, we can safely conclude that there is essentially no hexafluorosilicate remaining in drinking water at equilibrium and that equilibrium is rapidly reached from the combined uncatalyzed and metal-catalyzed reactions.

### 3.1.3. Significance of Common Practices in Analytical Chemistry

Having spent so much time demonstrating the completeness of hexafluorosilicate hydrolysis, we fear that someone who is familiar with two common practices in fluoride measurement, but not the chemical logic behind them, may now be puzzled. Accordingly, we take a moment to explain.

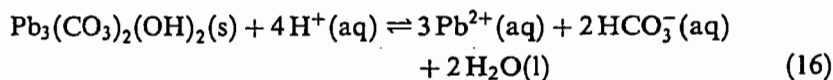
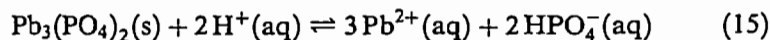
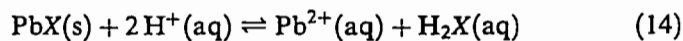
*3.1.3.1. On the Determination of Fluoride in Potable Water* One might wonder about the sample pre-treatment steps used in the potentiometric measurement of fluoride in potable water as one basis for concluding that hydrolysis is incomplete. In the procedure, several reagents are added to a potable water sample in the form of a total ionic strength adjustment buffer (TISAB). The TISAB contains sodium chloride, acetic acid, and cyclohexanediaminetetraacetic acid (CyDTA) which forms more stable and less labile complexes than the more common EDTA. As a chelating agent, CyDTA binds up metal cations (e.g.,  $\text{Al}^{3+}$ ) that might otherwise complex with fluoride and thereby interfere in the titration. Complexation of fluoride with silicon(IV) is not a concern.

*3.1.3.2. On the Determination of Total Fluoride in Sodium Hexafluorosilicate* In this procedure, the analyte is total fluoride. Since most of the fluoride is in the form of  $\text{SiF}_6^{2-}$ ,  $[\text{F}^-]_{\text{T}} \approx 6[\text{SiF}_6^{2-}]_0$  (the initial

concentration of hexafluorosilicate). In the sample of reagent material,  $[\text{SiF}_6^{2-}]_0$  is presumed to be at a concentration of 0.01 M or higher, and is titrated with 0.2 M NaOH(aq) solution while boiling. Because these conditions are far more forcing than what occurs in water treatment, do these standard practices constitute a basis for concluding that hexafluorosilicate hydrolysis is incomplete? Yes. Of course the hydrolysis will be incomplete in the raw material. The total fluoride and total acid are much higher than drinking water conditions. In fact, these conditions approach (or possibly exceed) Crosby's (*vide supra*). As with any titrimetric method, one strives for a very rapid reaction that occurs immediately upon addition of a drop of titrant. Boiling accomplishes this and it minimizes carbon dioxide introduction. With a phenolphthalein end point, it is necessary that the reaction reach completion on a millisecond time scale; otherwise, a falsely low end point could result.

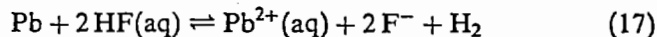
### 3.2. Potential for Solubilizing and Concentrating Plumbous Ion in the Distribution System

In Q3, we inquired whether additives could affect pH. Since Eq. (2) produces hydrogen ions, a pH drop is the only possibility. Consequently, we would like to ascertain whether this pH drop is capable of either dissolving otherwise insoluble lead(II) compounds that coat pipe walls (14)–(16) or dissolving metallic lead (as from solder or brass), specifically particulate lead(0)?



where  $X^{2-}$  is some anion that forms an insoluble lead(II) compound which exists at least partly as particulate matter (*i.e.*, in the solid state and not a soluble complex), for example,  $\text{CO}_3^{2-}$ ,  $\text{O}^{2-}$ , or  $\text{SO}_4^{2-}$ . Hydrogen ion can react with metallic lead in a redox reaction (17), but this direct reaction is not observable under drinking water

conditions. Other species that affect lead(II) solubility, such as carbonate and hydroxide, are affected by  $[H^+]$ , but this is not *via* a redox phenomenon.



The solubilizing effects of hydroxide, bicarbonate, carbonate and even chloride (though to a lesser extent) far outweigh the effect of this small amount of acid. In addition, we must not ignore the buffering capacity of a natural water resulting predominantly from bicarbonate and carbonate and to a lesser degree from organic matter, silicates, and hydrolytic (Lewis acidic) metal cations (*e.g.*,  $Fe^{3+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ). Moreover, the oxidizing capacity of the residual chlorine, which may be as high as  $1 \text{ mg L}^{-1}$  ( $= 14 \mu\text{M} = 28 \mu\text{N}$ ) is about half that of the HF, which is present at  $53 \mu\text{M}$  ( $= 53 \mu\text{N}$ ).

A later section will describe the speciation of lead(II) in drinking water using a model constructed from multiple simultaneous equilibria. The concentrations of  $PbF^+(aq)$  and  $PbF_2(aq)$  will be shown to be negligible compared to carbonate-, hydroxo- and other ligand complexes of the plumbous cation.

A more quantitative treatment of buffer capacity will come later. To answer Q3 for now, we can say that pH is controlled by many factors of greater magnitude than the hydrogen ion produced by (2). Furthermore, the small change in pH induced by (2) cannot solubilize lead(II) to the extent that the basic ligands, such as carbonate can.

### 3.3. Potential Effects on Lead(II) Bioavailability

Now we will consider chemistry under some physiological conditions. Even though we have demonstrated that there is no hexafluorosilicate remaining by the time water reaches the consumer's tap, let us assume momentarily that this is not the case. The following beyond-worst-case scenarios nicely illustrate the magnitude of the effects on lead(II).

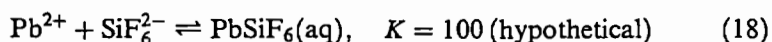
#### 3.3.1. Possible $\mu$ -fluoro Complexes of $Pb^{II}$ and $SiF_6^{2-}$

In Q4, we ask whether fluoride or hexafluorosilicate could complex with lead(II). Let us first consider  $SiF_6^{2-}$ . The only coordination option

for  $\text{Pb}^{\text{II}}$  and  $\text{SiF}_6^{2-}$  is a bridging fluoride ion (symbolized by  $\mu\text{-F}$ ) attached to both the lead(II) and the silicon(IV).

To produce 1.0 ppm fluoride requires an initial hexafluorosilicate concentration of  $8.8 \mu\text{M}$ . The hydrolysis reaction (2) is a reversible equilibrium, and in the most acidic gastric conditions, the pH could be as low as 1.5 so that  $[\text{H}^+] = 10^{-1.5} \text{M}$ .<sup>3</sup> Using this hydrogen ion concentration, we calculate the ratio  $[\text{Si}(\text{OH})_4]/[\text{SiF}_6^{2-}] = 4.5 \times 10^5$ . This means that only 0.00022% of the total silicon(IV) is present as the hexafluorosilicate ion so that  $[\text{SiF}_6^{2-}] = 1.9 \times 10^{-11} \text{M} = 19 \text{ picomolar (pM)}$ .

Haque and Cyr showed that hexafluorosilicate anion forms complexes with several metal cations:  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Fe}^{\text{III}}$  [26]. The largest stability constant they obtained was for the reaction with ferrous ion, with  $K = 1.2 = 10^{0.08}$ . Let us assume that the lead(II) ion forms a stabler complex and set the stability constant for Eq. (18) to an arbitrarily high value of 100. In addition, we shall *pretend* that the hydrolysis computed above has not occurred, that all  $8.8 \mu\text{M}$  of the silicon(IV) remains in the form of hexafluorosilicate ion.



In this worst case, only 0.088 mol% of the total lead(II) would be in the form of a hexafluorosilicate complex. The  $\mu\text{-fluoro}$  ligand would serve as a link between the silicon(IV) and lead(II). How significant is 0.088 mol% of the lead(II)?

Now consider the actual case where  $[\text{SiF}_6^{2-}] = 19 \text{ pM}$ . If the equilibrium constant for (18) were larger, say  $10^6$ , so that the reaction could be treated as going to near completion, there would still be less than 19 pM  $\text{Pb}-\mu\text{-F}-\text{SiF}_5$ . Because of the magnitude of the equilibrium constant for (6), the equilibrium constant for (18) would have to exceed  $10^{25}$  in order to have a quantifiable effect by preventing hexafluorosilicate hydrolysis. There is no basis in fact for such

<sup>3</sup>We assume activity coefficients of unity so that activities and molar concentrations are approximately equal. Although one could attempt to account for the differences by an extended Debye-Hückel treatment, there is little point since there is rarely more than 0.4 logarithm unit variation. Given the uncertainties in the equilibrium constants and the magnitude of the concentrations, a variation of even a factor of 100 is not especially significant, let alone what would be expected from the activity coefficient corrections. The same applies to differences in temperature.

an assertion. As a final point, we note that the national primary drinking water standards are intentionally predicated on the assumption that all lead is bioavailable, and the water utilities should be complying with these standards.

Before we deal with the other part of Q4, fluoro-complexes of lead(II), let us consider how residual hexafluorosilicate might affect gastric pH (Q5).

### 3.3.2. Post-ingestion Gastrointestinal Chemistry

Imagine that the hexafluorosilicate ion has escaped hydrolysis up to the moment of consumption of a glass of water. Imagine further that it is suddenly hydrolyzed upon entering the stomach, where it now forms hydrofluoric acid.

How does the pH drop from the hexafluorosilicate hydrolysis compare with that from other sources of acidity? In other words, how many protons (hydrogen ions) are produced? Drinking water treated to contain 1 ppm fluoride would contain  $53 \mu\text{M HF(aq)}$ . If one were to drink this solution of  $53 \mu\text{M HF(aq)}$ , which is 93 mol% dissociated to hydrogen and fluoride ions, it would contain  $49 \mu\text{M H}^+$  and its solution would have a pH of 4.3. Meanwhile, the high extreme for stomach pH (lowest acidity) is about 3 ( $1000 \mu\text{M H}^+$ ); the lowest stomach pH is about 1.5 (for optimal pepsin enzymatic activity in the digestion of protein). At pH 3, roughly half of the HF will not ionize since it is a weak acid. Meanwhile, some foods are equally or more acidic, for example, apple (pH 2.9) or tomato juice (pH 4.4). Using this logic, we would expect those persons who consume large amounts of acidic foods or drinks to suffer from lead toxicity.

One might be tempted to counterargue that a person consuming fruit juices has excluded particulate lead (from the distribution system) except that many fruit drinks are reconstituted using tap water, and soda fountain drinks are prepared likewise. Thus, consumers of soft drinks should be at especially higher risk, given the high concentrations of complexing organic acids (*e.g.*, citric and tartaric acids in powdered fruit drink mixes) or inorganic acids (*e.g.*, phosphoric and carbonic acids in colas). In fact, Coleman *et al.*, showed that chelating organic bases (*e.g.*, citrate<sup>3-</sup>, ascorbate, EDTA) promote the transport of lead(II) in the small intestine [27]. The acidic components of these

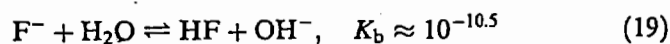
beverages completely overwhelm the contribution from HF in the water used to prepare them. Whether any of these other species is present in sufficient concentration to influence bioavailability is unknown. Regardless, acid from hexafluorosilicate-based fluoridation is negligible compared to other sources of acid in the American diet. Consequently, one cannot demonstrate that an increase in blood lead(II) ion levels can be linked to acidity from  $\text{SiF}_6^{2-}$  hydrolysis as opposed to consuming fruit drinks, carbonated beverages, or frozen orange juice on a city-wide scale. Since we expect consumption of these products to occur without respect to water utility, suggestions of effects due to  $\text{SiF}_6^{2-}$  within the digestive tract cannot play an important role in lead(II) gastroenterochemistry.

A pH effect—if it actually existed—would only pertain to the stomach. The small intestine does not absorb divalent ions well. In addition, bile (from the gall bladder) and bicarbonate (secreted by the pancreas) raise the pH and effectively buffer against pH change. Partly digested food in the chyme will also act as a buffer. Moreover, normal gastric biophysiology resists changes in acidity by a mechanism involving gastrin secretion and activity for which a detailed description is beyond the scope of this work. In conclusion, the production of acid from fluoridation of water is insignificant when compared to other acids and bases supplied by a normal diet or physiological mechanisms.

### 3.3.3. Fluoro-complexes of the Plumbous Ion

What about the effect of the fluoride itself (Q5)? Can it promote lead(II) bioabsorption? Is there an association between lead(II) and fluoride?

HF is a weak acid with a  $\text{p}K_a$  of 3.17 [18]. Therefore, NaF does affect pH *via* (19). However, its effect can generally be neglected since the pH of drinking water is controlled by many different buffering species.



While it may be calculated, the very small association [28, 29] between  $\text{Na}^+$  and  $\text{F}^-$  (20) would be insignificant, and can be safely ignored.

The magnitude of this stability constant is so small as to be negligible; however it can still be calculated. On the other hand, other cations present in reasonably high concentrations, most notably aluminum, bind to fluoride much more strongly (21)–(32). Table II summarizes these chemical equilibria and their stability constants.

There are many metal cations competing for the fluoride; therefore, the free fluoride available to complex with the lead(II) ion is very small. In addition, most, if not all, of the competing metal cations are in greater abundance than lead(II) by orders of magnitude. Further reducing the lead(II) are such ligands as hydroxide, chloride, carbonate, bicarbonate, and sulfate, all of which compete with fluoride for the lead(II) and are present in far greater concentrations. Table III summarizes these equilibria and their stability constants. For  $\text{pH} > 6$ , the free lead(II) concentration drops off dramatically from hydroxo- and (bi)carbonato-complexation. That drinking water contains a substantial fraction of fluoro-aluminum complexes (21)–(26) rather than free fluoride was highlighted by Pitter as a concern because free fluoride is more effective in protecting against tooth decay [30]. We shall take these and other factors into account in speciating the lead(II).

TABLE II Cumulative stability constants for formation of fluoro-complexes\*

Fluoro-complexation	Equations	$\log \beta$
$\text{Na}^+ + \text{F}^- \rightleftharpoons \text{NaF}(\text{aq})$	(20)	-0.24 <sup>†</sup>
$\text{Al}^{3+} + \text{F}^- \rightleftharpoons \text{AlF}^{2+}$	(21)	7.0 <sup>†</sup>
$\text{Al}^{3+} + 2 \text{F}^- \rightleftharpoons \text{AlF}_2^+$	(22)	12.7 <sup>†</sup>
$\text{Al}^{3+} + 3 \text{F}^- \rightleftharpoons \text{AlF}_3(\text{aq})$	(23)	16.8 <sup>†</sup>
$\text{Al}^{3+} + 4 \text{F}^- \rightleftharpoons \text{AlF}_4^-$	(24)	19.4 <sup>†</sup>
$\text{Al}^{3+} + 5 \text{F}^- \rightleftharpoons \text{AlF}_5^{2-}$	(25)	20.6 <sup>†</sup>
$\text{Al}^{3+} + 6 \text{F}^- \rightleftharpoons \text{AlF}_6^{3-}$	(26)	20.6 <sup>†</sup>
$\text{Fe}^{3+} + \text{F}^- \rightleftharpoons \text{FeF}^{2+}$	(27)	5.2 <sup>‡</sup>
$\text{Fe}^{3+} + 2 \text{F}^- \rightleftharpoons \text{FeF}_2^+$	(28)	9.1 <sup>‡</sup>
$\text{Fe}^{3+} + 3 \text{F}^- \rightleftharpoons \text{FeF}_3(\text{aq})$	(29)	11.9 <sup>‡</sup>
$\text{Ca}^{2+} + \text{F}^- \rightleftharpoons \text{CaF}^+$	(30)	0.94 <sup>†</sup>
$\text{Mg}^{2+} + \text{F}^- \rightleftharpoons \text{MgF}^+$	(31)	1.82 <sup>†</sup>
$\text{Cu}^+ + \text{F}^- \rightleftharpoons \text{CuF}^+$	(32)	1.2 <sup>†</sup>
$\text{H}^+ + \text{F}^- \rightleftharpoons \text{HF}(\text{aq})$	(33)	3.18 <sup>†</sup>
$\text{H}^+ + 2 \text{F}^- \rightleftharpoons \text{HF}_2^-$	(34)	3.76 <sup>†</sup>

\* These stability constants are used for the construction of Figures 3, 4 with the exception of Eqs. (27)–(29) and (32).

<sup>†</sup> Values taken from Ref. [29].

<sup>‡</sup> Values taken from Ref. [18].



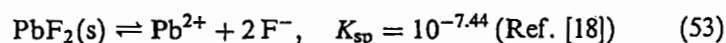
TABLE III Lead(II) equilibria and constants\*

Equilibrium	Equations	log $\beta$
$\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PbOH}^+$	(35)	-7.22
$\text{Pb}^{2+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_2(\text{aq}) + 2 \text{H}^+$	(36)	-16.91
$\text{Pb}^{2+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_3^- + 3 \text{H}^+$	(37)	-28.08
$\text{Pb}^{2+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_4^{2-} + 4 \text{H}^+$	(38)	-39.72
$2 \text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Pb}_2\text{OH}^{3+} + \text{H}^+$	(39)	-6.36
$3 \text{Pb}^{2+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Pb}_3(\text{OH})_4^{2+} + 4 \text{H}^+$	(40)	-23.86
$\text{Pb}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{PbCO}_3(\text{aq})$	(41)	7.10
$\text{Pb}^{2+} + 2 \text{CO}_3^{2-} \rightleftharpoons \text{Pb}(\text{CO}_3)_2^{2-}$	(42)	10.33
$\text{Pb}^{2+} + \text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{PbHCO}_3^+$	(43)	12.59
$\text{Pb}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{PbSO}_4(\text{aq})$	(44)	2.73
$\text{Pb}^{2+} + 2 \text{SO}_4^{2-} \rightleftharpoons \text{Pb}(\text{SO}_4)_2^{2-}$	(45)	3.50
$\text{Pb}^{2+} + \text{Cl}^- \rightleftharpoons \text{PbCl}^+$	(46)	1.6
$\text{Pb}^{2+} + 2 \text{Cl}^- \rightleftharpoons \text{PbCl}_2(\text{aq})$	(47)	1.8
$\text{Pb}^{2+} + 3 \text{Cl}^- \rightleftharpoons \text{PbCl}_3^-$	(48)	1.7
$\text{Pb}^{2+} + 4 \text{Cl}^- \rightleftharpoons \text{PbCl}_4^{2-}$	(49)	1.4
$\text{Pb}^{2+} + \text{F}^- \rightleftharpoons \text{PbF}^+$	(50)	2.06
$\text{Pb}^{2+} + 2 \text{F}^- \rightleftharpoons \text{PbF}_2(\text{aq})$	(51)	3.42
$\text{Pb}^{2+} + \text{H}_4\text{SiO}_4(\text{aq}) + 4 \text{H}^+ + 6 \text{F}^- \rightleftharpoons$ $\text{Pb-F-SiF}_3(\text{aq}) + 4 \text{H}_2\text{O}$	(52)	32.18 <sup>†</sup>

\*Values derived from Tables IV-XVI in Ref. [31] at 25°C and zero ionic strength. These equilibria are used in the construction of Figures 1-4.

<sup>†</sup> Computed from combining the dissociation constant for the reaction  $\text{Si}(\text{OH})_4 + 4 \text{H}^+ + 6 \text{F}^- \rightleftharpoons \text{SiF}_6^{2-} + 4 \text{H}_2\text{O}$ ,  $\log K = 30.18$  (from Ref. [29]) with Eq. (18). We believe this value to be an intentional overestimate by a factor of at least 10-20 over the likely value of the true stability constant, which has not been measured.

One might logically inquire whether  $\text{PbF}_2$  can precipitate under drinking water or physiological conditions. Combining Eqs. (51) and (53) gives the solubility of the aqueous uncharged difluorolead(II) coordination complex:  $[\text{PbF}_2(\text{aq})]_{\text{max}} = 9.5 \times 10^{-5} \text{ M}$ .



Recall that a 1.0 ppm fluoride solution contains only  $5.3 \times 10^{-5} \text{ M}$  fluoride ion. Even if the equilibrium constants have some error in them, the competing equilibria ensure that plumbous fluoride does not precipitate. Aluminum, iron(III), calcium, magnesium, and copper(II) compete with lead(II) for fluoride. Meanwhile hydroxide, carbonate, phosphate, and sulfate compete with fluoride for lead(II). The net result of these simultaneous competitions is that  $\text{PbF}_2$  cannot precipitate as a solid. Even with 90th percentile lead(II) levels of  $\sim 210 \mu\text{g L}^{-1}$  ( $\sim 1 \mu\text{M}$ ), no plumbous fluoride would precipitate. The formation of soluble fluoro-complexes of Pb(II) is governed solely by

the stability equilibria of (50)–(51). Therefore, no simple stoichiometric ratio exists among the concentrations of lead(II), fluoride, and the fluoro-complexes.

*Pretending that there are no competing metal cations and no competing coordinating ligands*, the total Pb(II) concentration is given by (54):

$$[\text{Pb}^{\text{II}}]_{\text{T}} = [\text{Pb}^{2+}] + [\text{PbF}^+] + [\text{PbF}_2] = [\text{Pb}^{2+}](1 + \beta_1[\text{F}^-] + \beta_2[\text{F}^-]^2) \quad (54)$$

where  $\beta_1$  and  $\beta_2$  come from (50) and (51), respectively. In 1.0 ppm free fluoride ( $5.3 \times 10^{-5}$  M) solution, the fractional speciation is as follows:  $f_{\text{Pb}^{2+}} = 99.904\%$ ,  $f_{\text{PbF}^+} = 0.096\%$  and  $f_{\text{PbF}_2(\text{aq})} = 0.000099\%$ . We draw attention to the fact that, in fluoridated tap water, the number  $5.3 \times 10^{-5}$  M really refers to the total fluoride, which is expressible as (55):

$$[\text{F}^-]_{\text{T}} = [\text{F}^-] + [\text{PbF}^+] + 2[\text{PbF}_2] = 5.3 \times 10^{-5} \text{ M} \quad (55)$$

Nevertheless, because  $[\text{F}^-]_{\text{T}} \approx [\text{F}^-]$  (less than 0.1% difference), there is no point in distinguishing between these two concentrations. However, in a real water, the competition of other metal cations for fluoride would substantially reduce free fluoride. We will shortly demonstrate this fact and that  $[\text{Pb}^{\text{II}}]_{\text{T}} \gg [\text{Pb}^{2+}]$  in any real potable water.

We emphasize that – for practical purposes – there is no endless supply of lead(0/II) awaiting complexation by fluoride (or anything else for that matter). In other words, one cannot argue that the reaction between lead(II) and complexing anions is driven forwards by a readily available reservoir of lead that provides as much as the ligands can react with. The dissolution of lead is confounded by three possible barriers: (1) the kinetics of the oxidation of lead(0) are insufficiently facile for equilibrium to be approached, (2) the reaction is limited by the total oxidizing capacity of the water, and (3) the presence of passivating films such as  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2(\text{s})$ ,  $\text{Pb}_3(\text{PO}_4)_2(\text{s})$ ,  $\text{PbCO}_3(\text{s})$ , or  $\text{Pb}_5(\text{PO}_4)_3(\text{OH})(\text{s})$  controls solubility [29].

If ligand availability alone were the determining factor, chloride itself would be far more important than fluoride. A chloride concentration of 50 ppm ( $= 1.4 \text{ mM} = 1400 \mu\text{M}$ ) is about 26 times the

fluoride concentration. Between the chloride concentration and the chloro-complex formation constants in (46)–(49), concentrations of lead(II) complexes with chloride exceed those of fluoride in drinking water.

We feel strongly that there is no scientific justification for asserting that water fluoridation chemicals can have any quantifiable impact on human health *via* lead(II) exposure. There is no sound chemical explanation for invoking any interactions between plumbous species and hexafluorosilicic acid, hexafluorosilicate, or fluoride.

#### 4. METHODOLOGICAL CONSIDERATIONS IN STUDYING THE IMPACT OF FLUORIDATION ON LEAD(II)

##### 4.1. Measurement and Significance of Lead(II) Concentrations in Tap Water

The total lead in a first draw sample tells more about the quality and construction of a building plumbing system than it does about the quality of the post-treatment water. Comprehensive water sampling for epidemiological and other health effects studies for lead(II) is logistically complicated and expensive; therefore, it is very tempting to try to use available regulatory tap water monitoring data for this purpose. The temptation must be resisted, however as the monitoring program specified in the United States drinking water regulations is both statistically and physically invalid for this purpose. The vast preponderance of the lead(II) in nearly all tap waters originates from the plumbing materials located between the water distribution mains and the end of the faucet used by the consumer. Individuals consume water under innumerable combinations of volumes of water, interior plumbing system configurations and ages, and lengths of stagnation of the water in the plumbing between uses. Data reported from many tap water sampling experiences throughout the US and Europe indicate tap water lead levels tended to follow a log-normal distribution, and both within-site and between-site variability tended to be large relative to the lead(II) concentrations. Keeping this in mind, the American standard for lead in drinking water was crafted to focus

on the lowering of lead(II) levels by central water treatment for the plumbing configurations most likely to represent nearly the worst cases for the most vulnerable humans, *i.e.*, infants, children, pregnant women (Q6). After a cursory examination of the requirements for a statistically valid sampling program accounting for needed levels of predictive confidence across all sources of variability observed, one realizes that it would take literally hundreds or thousands of samples at great frequency from cities of all sizes to try to adequately characterize tap water lead levels for even a single uniformly applied national sampling protocol.

Obviously, the water chemistry at the point the distributed finished water enters the domestic or commercial building plumbing system plays a very significant role in affecting lead release into the water, but many other physical factors also operate [31-40]. The water at this point may have undergone chemical changes during its passage through the distribution system from the treatment plant or well, and changes in treatment or changes in water sources may also cause the chemical characteristics of the water to change periodically, especially in such important aspects as pH, and concentrations of alkalinity, natural organic matter, oxidant levels, and a variety of potentially aggressive anions. Even the season may influence lead levels in complicated ways, by changes in ground temperature, or temperatures in buildings where pipes run through basements, unheated crawl spaces, concrete slabs, or nearby heating or air conditioning ducts. A single snapshot sampling event cannot capture this.

The drinking water literature is full of papers that show how difficult it is to correlate lead levels with any one or even a mix of several water quality parameters, and a complete discussion of the matter is beyond the scope of this article. There may be countless other physical or chemical quantities that may be statistically correlated with lead(II) levels but nonetheless be totally unrelated mechanistically. Clearly, aggregate measures such as a small number of first-draw or fully-flushed water samples taken infrequently from an intentionally biased relatively small pool of sampling sites throughout a water system cannot quantitatively and precisely predict the exposure of any individuals to lead from drinking water. To accurately determine lead(II) intake, sampling schemes using diverters or proportional sampling devices that capture a representative fraction of the water

actually drawn at the faucet by the consumer seem to be the only feasible approach [31]. Informed speculation suggests that other water and plumbing characteristics, which were not measured in the studies of Ref. [2] could correlate with lead(II) levels with equal or greater statistical significance than those relationships that were put forth.

#### 4.2. Measurement and Significance of Lead(II) Concentrations in Blood

How is lead exposure assayed? How should it be measured? These are complicated questions, and whole volumes can be dedicated just to Q7. The discussion here will be confined to certain techniques and their weaknesses.

We suggest that the apparent link between hexafluorosilicate usage and children's blood lead(II) concentrations is the result of an unfortunate coincidence. The use of blood lead(II) levels is problematic for a number of reasons. Masters and Coplan [2] report these results (reproduced here in Tab. IV); however, they do not report the uncertainties associated with measurement or the variation of the sample space.

A recent paper by Skerfving *et al.*, reports that blood lead levels are not linked in a linear fashion with exposure or risk and that biological monitoring is complicated by these factors [41]. Consequently, it is unclear whether a difference of  $7.1 \mu\text{g L}^{-1}$  is truly significant.

Blood lead(II) levels were reported in a previous study conducted by the Dartmouth-Hitchcock Medical Center [42, 43]. We have some concerns regarding the secondary use of these data. Samples were collected by a wide variety of personnel with undocumented training and experience in the matter of collecting samples for trace metal analysis and collection conditions were unspecified. Without a protocol that

TABLE IV Blood lead(II) concentrations and fluoridating agents\*

Treatment	$[\text{Pb}^{II}]_{\text{blood}} \mu\text{g L}^{-1}$
$\text{H}_2\text{SiF}_6$	27.8
$\text{Na}_2\text{SiF}_6$	26.6
NaF	20.7
none	20.2

\* Taken from Ref. [2].

includes the collection of spiked samples or recovery check standards, it is impossible to know if an individual collection site may be responsible for a determinate error in all of the samples in a particular region. Trace metals are extremely susceptible to surface adsorption, and lead(II) is notorious for plating out (reduction to  $\text{Pb}^0$ ) under nonacidic conditions. Because the procedure was unspecified, sample preservation and integrity are unknown.

The subsequent determination of lead(II) in blood was carried out by the semi-quantitative method of Piomelli [44]. In this method, a moderately linear relationship is found to exist between free erythrocyte porphyrins and total lead(II) concentration (as determined by atomic absorption photometry). A plot of FEP concentration against blood total lead(II) concentration in the original reference shows so much scatter that the uncertainty in any blood lead concentration must be at least  $\pm 10 \mu\text{g L}^{-1}$ , and Piomelli gives an estimate of  $\pm 15 \mu\text{g L}^{-1}$  at a concentration of  $50 \mu\text{g L}^{-1}$ . Accordingly, we feel that there is no statistical difference in the blood total lead values for any set of conditions. Piomelli does not list any interferences other than iron-deficiency anemia and erythropoietic protoporphyria; however, we suspect that other elevated levels of other metals may also bring about elevated levels of free porphyrins in the blood.

In defense of the Sargent *et al.*, studies, we want to emphasize that the original authors never intended for their lead(II) screening data to be used in the way that Masters and Coplan have used them. The original studies did not attempt to construct the sort of hard and fast links of the Masters and Coplan papers, and they made no mention of tap water whatsoever. In fact, senior authors Sargent and Bailey have specifically stated that they do not agree with the Masters and Coplan thesis (personal communication). To be sufficiently rigorous for a study of drinking water and blood, more accurate, precise, and rugged techniques than the FEP test are required, for instance, inductively-coupled plasma or atomic absorption spectrophotometry.

#### 4.3. Difficulties in Correlating Lead(II) Concentrations in Water and Blood

The authors did not give the total lead concentrations in the first draw water samples, so we cannot directly compare blood lead levels with

water lead levels [2]. They did give blood lead levels divided up by those water systems where first draw samples were divided by a cut-off of  $15 \mu\text{g L}^{-1}$  of lead(II); see Table V.<sup>4</sup>

Because the sodium hexafluorosilicate data are based on one system with  $[\text{Pb}^{\text{II}}]_{\text{water}} > 15 \mu\text{g L}^{-1}$ , we discount it as an outlier without further consideration. Without some estimation of the uncertainties of  $[\text{Pb}^{\text{II}}]_{\text{blood}}$ , we cannot be assured that  $23 \mu\text{g L}^{-1}$  is distinct from  $33 \mu\text{g L}^{-1}$ . Also, we do not believe that it is possible to report 3 significant digits in the blood lead level. We expect that the numbers are probably good to about 10–15%. Masters and Coplan also failed to include the possibility of naturally occurring fluoride and silicates in the unfluoridated water systems, which would be necessary to substantiate their thesis, as the effects should be the same whether the fluoride is an additive or native constituent. The authors themselves acknowledge the poor correlation between blood and water lead(II) levels [2]:

Whereas a community's average uptake of lead by children is weakly associated with the so-called "90th percentile first draw" lead levels of lead in public water supplies (adjusted  $r^2=0.02$ ), the fluoridation agents used in water treatment have a major effect on lead levels in children's blood.

There appears to have been no effort to correlate an individual building or house with blood lead levels. From the details in the paper, there is no indication that there is any connection between sampled taps and sampled persons. In other words, nothing indicates that a person living in the sampled house had his blood drawn. Instead, the

TABLE V  $[\text{Pb}^{\text{II}}]_{\text{blood}}$  ( $\mu\text{g L}^{-1}$ ) for fluoridation processes\*

$[\text{Pb}^{\text{II}}]_{\text{water}}$	none	NaF	$\text{Na}_2\text{SiF}_6$	$\text{H}_2\text{SiF}_6$
$< 15 \mu\text{g L}^{-1}$	19.7	21.1	23.7	23.1
<i>n</i> =	86	31	6	26
$> 15 \mu\text{g L}^{-1}$	21.8	19	43.8	32.7
<i>n</i> =	29	8	1	25

\*Taken from Ref. [2].

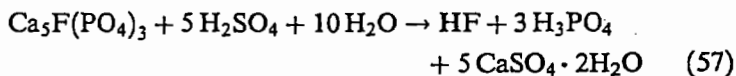
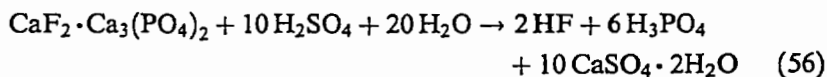
<sup>4</sup>It is unclear from where these numbers originated. Reference [2] mentions averaged 90th percentile values. We take this to mean that 90th percentile values from two or more rounds of regulatory testing were averaged.

authors rely on quartile divisions of both water lead levels and blood lead levels. For there to be a correlation between the lead(II) levels in blood and water, there must be a link between the samples. It is possible that the highest blood levels of lead(II) are closely linked to other exposures, such as paint, soil, or mine run-off. It would appear that the authors did not believe their own correlation coefficient of 0.02. When these methodological problems are coupled with the failure to account for fundamental chemical interactions, the relationships posed between lead(II) and water fluoridation become unsubstantiatable.

### 5. PURITY AND INTEGRITY OF WATER FLUORIDATING AGENTS

Water treatment chemicals are subject to National Sanitation Foundation specifications, which require that additives contain a *maximum allowable level* (MAL) less than or equal to 10% of the *maximum contaminant level* (MCL) for any regulated contaminant in the national primary drinking water standards [45]. This third-party standard sets the limits for quality control (Q8). Nevertheless, one might ask if there is a possibility that the materials purchased by utilities could be contaminated in some way. Let us consider how these compounds are produced and handled.

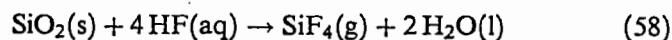
Most hexafluorosilicate and fluorosilicic acid are derived from the processing of phosphate rock by the fertilizer industry [46]. In this process, apatite and fluorapatite (which can be thought of as a blend of fluorite and apatite for this purpose) are decomposed with sulfuric acid:



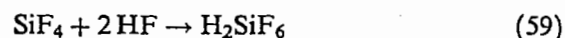
After the mined rock is ground, it is mixed with dilute phosphoric acid. The wet crushed rock is moved to a reactor, treated with sulfuric



acid, and heated to 75–80°C for several hours. The phosphate and fluoride minerals make up only a portion of the rock. Part of the remainder is silica, which reacts with the hydrofluoric acid:



Both the silicon tetrafluoride (tetrafluorosilane) and hydrofluoric acid are swept away by an air stream into an absorption tower where hexafluorosilicic acid is generated.



The resulting material is stored in containers of high density polyethylene or other unreactive materials. Because the HF and SiF<sub>4</sub> are removed as gases, there is little chance of lead contamination from the crushed rock. However, 23% w/w hexafluorosilicic acid is a strong acid and quite corrosive; therefore, any lead would have to be the result of improper storage or handling. While it is possible for this to be a source of lead in drinking water, there is no evidence to suggest contamination. A service draw of water should contain the same concentration of lead(II) as a first draw if such contamination occurs, and the authors themselves admit that service draws are characteristically much lower in lead. Testing either the water at the plant or the stock fluoridating agent itself would also be sufficient to rule out this possible route of exposure.

## 6. EPIDEMIOLOGY OF LEAD EXPOSURE AND ABSORPTION

Exposure to lead can occur in many ways (Q9). The varying contributions of these exposure routes have been the subject of multiple studies. The problem is further complicated by incomplete understanding of subacute toxicity and dose-response [47]. Much of the exposure to lead occurs through dust, air-borne particulates, soil, paint, ceramic glazes, and sundry other sources, including drinking water [48–51]. One of the special concerns for drinking water is that the lead(II) appears to be far more bioavailable [48]. This is probably because aqueous lead(II) is far more likely to pass through mucous membranes than insoluble plumbous minerals. However, there is

some evidence to suggest that even insoluble minerals can release lead(II) when ingested under the right conditions [52]. A number of studies<sup>5</sup> have concentrated on other factors affecting bioavailability and bioabsorption, including other nutrients, alcohol, cigarettes, water hardness, plumbing, and lifestyle [53–59]. The main conclusion that can be drawn from these studies is that the biological availability, absorption, and accumulation of lead and its compounds depend on a wide variety of factors, making this a very complicated puzzle to solve [60, 61].

## 7. FRACTIONAL SPECIATION MODELING

While many of the conclusions reached thus far have been based on calculations, the complicated interplay of multiple species, which was alluded to in the introduction, has heretofore been avoided. It is now time to rigorously account for all of these interactions in a quantitative fashion (Q10).

We have taken into account equilibria of lead(II), aluminum, calcium, and other metals for such ligands as carbonate, chloride, hydroxide, sulfate, and, of course, fluoride. These were given earlier in Tables II and III. Other necessary equilibria and their constants that we have used for this modeling exercise are shown in Table VI. From the following graphs, it is immediately clear that hexafluorosilicate and fluoride complexes play no role in the chemistry of lead(II) in a drinking water matrix. They are of inconsequential concentration under the conditions encountered in treated potable water.

To test different hypotheses about the impacts of fluoride ligands on lead solubility, several solutions were modeled using the computer program MINEQL + [62]. The effect of various background ions such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{PO}_4^{3-}$  and water quality parameters such as pH have been extensively investigated and reported in the water treatment literature [29, 31, 35, 59–68]. Free lead(II) ion,  $\text{Pb}^{2+}$ , is a very minor fraction of the soluble lead in most drinking water systems;

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<sup>5</sup>The references cited here include a representative sampling over the last two decades of the kinds of work that have been done. These references are not intended to comprise a complete listing or review of the studies in this area.

TABLE VI Other equilibria used to calculate the fractional distribution of aqueous species\*

Equilibrium	Equations	log $\beta$
$\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$	(60)	-1.468
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	(61)	-6.352
$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	(62)	-10.329
$\text{Na}^+ + \text{HCO}_3^- \rightleftharpoons \text{NaHCO}_3(\text{aq})$	(63)	-0.25
$\text{Na}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NaCO}_3^-$	(64)	1.27
$\text{Ca}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CaHCO}_3^+$	(65)	1.106
$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{aq})$	(66)	3.224
$\text{Mg}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{MgHCO}_3^+$	(67)	1.07
$\text{Mg}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{MgCO}_3(\text{aq})$	(68)	2.98
$\text{Si}(\text{OH})_4(\text{aq}) \rightleftharpoons \text{SiO}(\text{OH})_3^- + \text{H}^+$	(69)	-9.83
$\text{Si}(\text{OH})_4(\text{aq}) \rightleftharpoons \text{SiO}_2(\text{OH})_2^{2-} + 2\text{H}^+$	(70)	-23.0
$\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$	(71)	-1.988
$\text{Ca}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CaSO}_4(\text{aq})$	(72)	2.30
$\text{Mg}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{MgSO}_4(\text{aq})$	(73)	2.37
$\text{Al}^{3+} + \text{SO}_4^{2-} \rightleftharpoons \text{AlSO}_4^+$	(74)	3.02
$\text{Al}^{3+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Al}(\text{SO}_4)_2^-$	(75)	4.92
$\text{Al}^{3+} + \text{HSO}_4^- \rightleftharpoons \text{AlHSO}_4^+$	(76)	0.46
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	(77)	-14.00
$\text{Na}^+ + \text{H}_2\text{O} \rightleftharpoons \text{NaOH}(\text{aq}) + \text{H}^+$	(78)	-14.18
$\text{Ca}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CaOH}^+ + \text{H}^+$	(79)	-12.78
$\text{Mg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{MgOH}^+ + \text{H}^+$	(80)	-11.44
$\text{Al}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^{2+} + \text{H}^+$	(81)	-5.00
$\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	(82)	-10.1
$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3(\text{aq}) + 3\text{H}^+$	(83)	-16.9
$\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_4^- + 4\text{H}^+$	(84)	-22.7

\* Values taken from Ref. [29]. These equilibria are used in the construction of Figures 3, 4. Equations (59), (60), (67), (68) and (75) are used for Figure 5.

therefore, sophisticated methods must be used to determine the overall distribution of lead species in the water.

Calculations were performed for the following hypothetical water solutions, as a means to test some plausible limits on when fluoride or fluorosilicate complexes might be of consequence with respect to solubility. Conditions are summarized in Tables VII and VIII. The lead(II) concentration used for Figures 1 and 2 is 1000 times the 90th percentile action level for public water supplies. For all modeling, temperature was set to 25°C, and an ionic strength of 0.005 M was assumed. This is characteristic of many New England waters and close enough that small differences will not significantly affect lead solubility and speciation projections. Test calculations showed this was very close to the actual ionic strength of the hypothetical waters for which other major constituents were included.

TABLE VII Water quality parameters for speciation modeling\*

Species		Concentration, mg L <sup>-1</sup>	Concentration, mol L <sup>-1</sup>
[SiO <sub>2</sub> ] <sub>T</sub> <sup>†</sup>		5.0	8.3 × 10 <sup>-5</sup>
[Pb <sup>2+</sup> ] <sub>T</sub> <sup>‡</sup>	Figures 1, 2	15	7.2 × 10 <sup>-5</sup>
	Figures 3, 4	0.015	7.2 × 10 <sup>-8</sup>
[F <sup>-</sup> ] <sub>T</sub> <sup>¶</sup>		1.0	5.3 × 10 <sup>-5</sup>
[CO <sub>2</sub> ] <sub>T</sub> <sup>°</sup>	Figures 1, 3, 4	5.0	4.2 × 10 <sup>-4</sup>
	Figure 2	50	4.2 × 10 <sup>-3</sup>

\*These concentrations used for Figures 1-4 except as noted.

<sup>†</sup>[SiO<sub>2</sub>]<sub>T</sub> = total silicon(IV) concentration, expressed as silicon dioxide.

<sup>‡</sup>[Pb<sup>2+</sup>]<sub>T</sub> = total lead(II) concentration, all species.

<sup>¶</sup>[F<sup>-</sup>]<sub>T</sub> = total fluoride concentration [F<sup>-</sup>] + [HF] + Σ n[MF<sub>n</sub><sup>(s-n)</sup>].

<sup>°</sup>[CO<sub>2</sub>]<sub>T</sub> = [CO<sub>2</sub>(aq)] + [H<sub>2</sub>CO<sub>3</sub>] + [HCO<sub>3</sub><sup>-</sup>] + [CO<sub>3</sub><sup>2-</sup>] (dissolved inorganic carbon). Mass-based concentration is expressed as C not CO<sub>2</sub>.

TABLE VIII Concentrations of background ions used in speciation modeling\*

Ion	Concentration, mg L <sup>-1</sup>	Concentration, mol L <sup>-1</sup>
Ca <sup>2+</sup>	5.0	1.2 × 10 <sup>-4</sup>
Mg <sup>2+</sup>	2.0	8.2 × 10 <sup>-5</sup>
Na <sup>+</sup>	10.0	4.4 × 10 <sup>-4</sup>
Al <sup>3+</sup>	0.20	7.4 × 10 <sup>-6</sup>
Cl <sup>-</sup>	10.0	2.8 × 10 <sup>-4</sup>
SO <sub>4</sub> <sup>2-</sup>	5.0	5.2 × 10 <sup>-5</sup>

\*These values used for Figures 3, 4.

Figures 1, 2 show the fractional distribution of species in water that contains only dissolved lead(II), inorganic silicates, fluoride, and carbonates, where we find that the principal lead(II) species are the aquo ion, hydroxo-complexes, and carbonato-complexes. We note that there is less than one molecule of PbSiF<sub>6</sub> per liter of water even though there is no competition for fluoride by aluminum or other metal cations and competition for lead(II) by only the predominant complexing species (but not minor ones). Figure 1 shows that Pb<sup>2+</sup>(aq) is the dominant species for pH < 6.8, at which point the carbonatolead(II) complex begins to dominate. By pH ≈ 7.2, the hydroxolead(II) ion also exceeds the free lead(II). As pH increases to ~8.4, only ~1% of the total lead is the free aquated ion. In Figures 1 and 2, we see that the mono- and difluorolead(II) complexes always account for less than 1% of the total lead(II). Note that the species PbSiF<sub>6</sub> is present at such low concentrations that we would expect to find only one molecule of this complex in 1000 liters of tap water at pH 6. Note the broken ordinate.

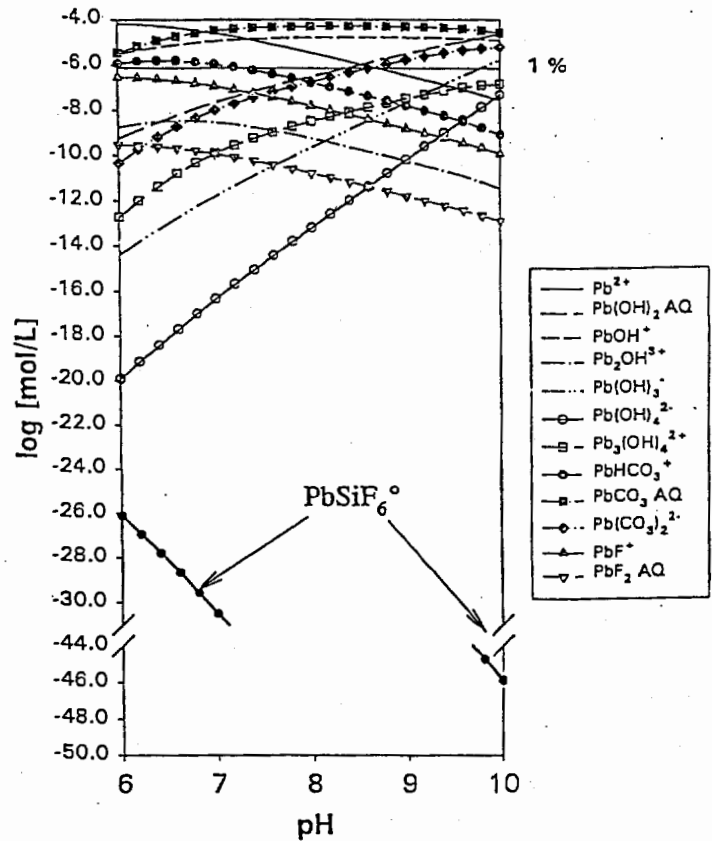


FIGURE 1 Species distribution for lead in system containing only carbonate (5 mg C/L), silicate (5 mg SiO<sub>2</sub>/L), and fluoride (1 mg/L) at 25°C, *I* = 0.005. PbSiF<sub>6</sub><sup>°</sup> complex was included in the model, with assumption of log β = 2.

In Figure 3, we show the minor species, including the sulfato-, fluoro-, and chloro-complexes under the influences of other common background ions (Tab. VIII). The carbonato-complexes of lead(II) are much stronger than the halo-complexes – as reflected by their stability constants, which are 5–8 orders of magnitude higher than those of the comparable halide complexes. As a consequence, we did not consider higher [CO<sub>2</sub>]<sub>T</sub> concentrations where the fluoro-complexes become even less significant.

The concentration of aluminum in Table VIII represents a moderate to somewhat high residual carried over from agglutination

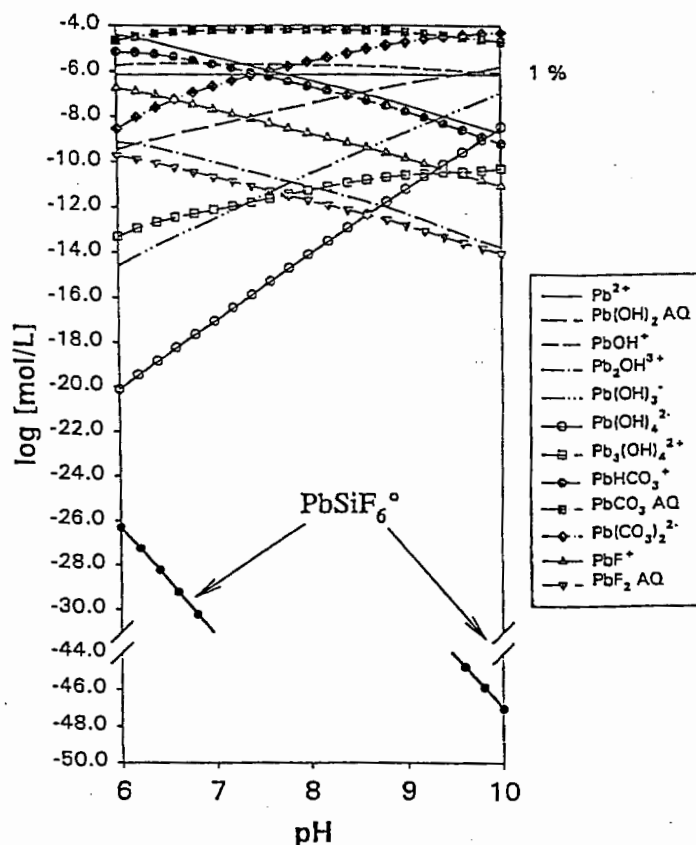


FIGURE 2 Species distribution for lead in system containing only carbonate (50 mg C/L), silicate (5 mg  $\text{SiO}_2/\text{L}$ ), and fluoride (1 mg/L) at  $25^\circ\text{C}$ ,  $I=0.005$ .  $\text{PbSiF}_6^0$  complex was included in the model, with assumption of  $\log \beta=2$ .

(coagulation) with potassium aluminum sulfate (alum), as commonly occurs with surface water treatment plants adjusted for corrosion control and the Lead and Copper Rule. Pertinent results with respect to lead speciation and the impact of fluoride and  $\text{SiF}_6^{2-}$  complex formation on it, are shown in Figures 1–3.

The insignificance of any  $\text{SiF}_6^{2-}$  can be logically determined another way. Even if the formation constant for a hypothetical  $\text{PbSiF}_6(\text{aq})$  complex were ten times higher than the strongest complex found by Haque and Cyr [26], it would have a similar stability to  $\text{PbF}^+$ . Assuming all of the fluoride present in drinking water were  $\text{SiF}_6^{2-}$ ,

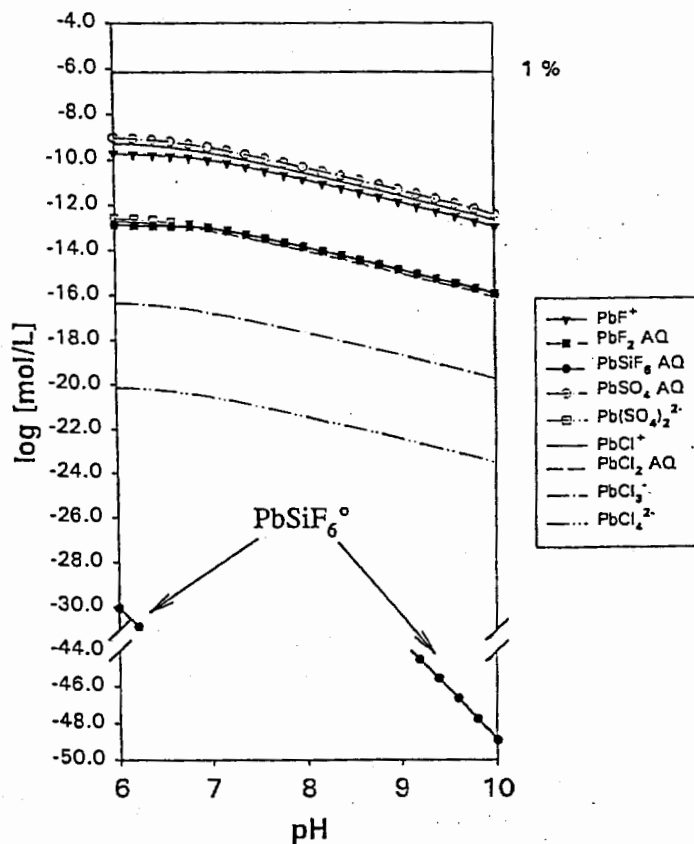


FIGURE 3 Minor lead species distribution for lead in hypothetical "New England" water described in Table VII. Computations were done for 25°C,  $I=0.005$ .  $PbSiF_6^0$  complex was included in the model, assuming of  $\log \beta=2$ .

Figures 1–3 show that it would still be approximately 3 (pH 6) to more than 6 (pH 10) orders of magnitude lower than the soluble lead level, which is governed by the concentrations of other Lewis bases. Because complexation with carbonate and bicarbonate dominates aqueous lead speciation at drinking water pH, the increased  $[CO_2]_T$  level of  $50 \text{ mg L}^{-1}$  (Fig. 2) makes contribution of the fluoro-complexes to  $[Pb^{II}]_T$  even less significant. The bar graph in Figure 4 clearly illustrates how free lead(II), hydroxo-, and (bi)carbonato-complexes dominate the speciation of lead(II) at all drinking water pH values while fluoro-complexes are always in the minority.

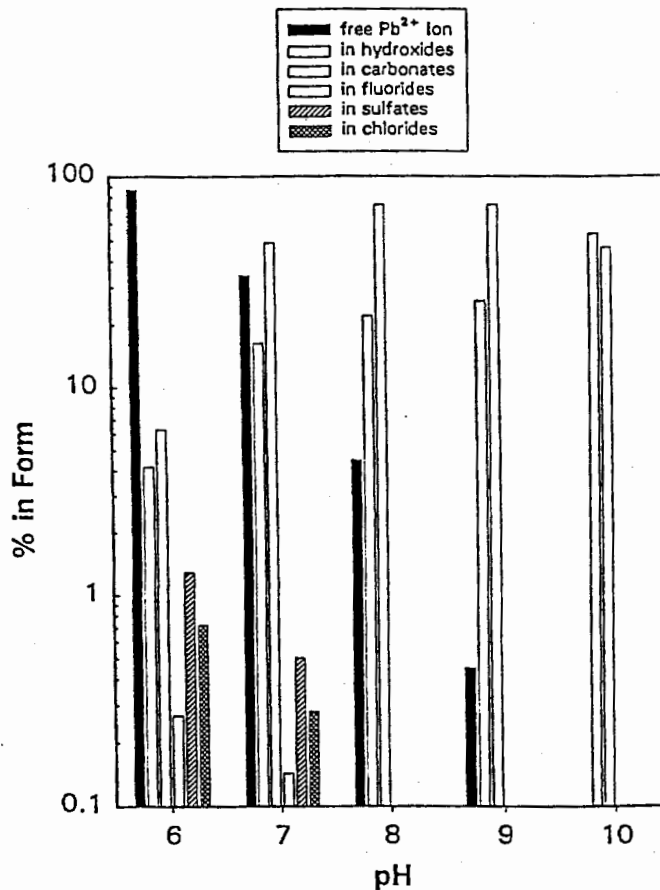


FIGURE 4 Illustration of fractions of soluble lead bound to different ligand groups for hypothetical representative "New England" water, assuming  $15 \mu\text{g/L Pb}$  and background ion concentrations given in Table VII of the text.

### 7.1. Buffer Intensity (Buffer Capacity)

We have previously stated that naturally occurring buffers have a significant impact on drinking water chemistry. At this point, we will quantitatively illustrate the magnitude of this impact. Figure 5 shows the buffer intensity (capacity)  $\mathcal{B}$  as a function of pH.<sup>6</sup> The buffer

<sup>6</sup> Buffer intensity is usually represented by the symbol  $\beta$ , which we find to be an unfortunate coincidence as it leads to confusion between this quantity and cumulative stability constants, for which  $\beta$  is often used simultaneously. As a result, we have broken with convention and used the symbol  $\mathcal{B}$  to stand for buffer intensity.



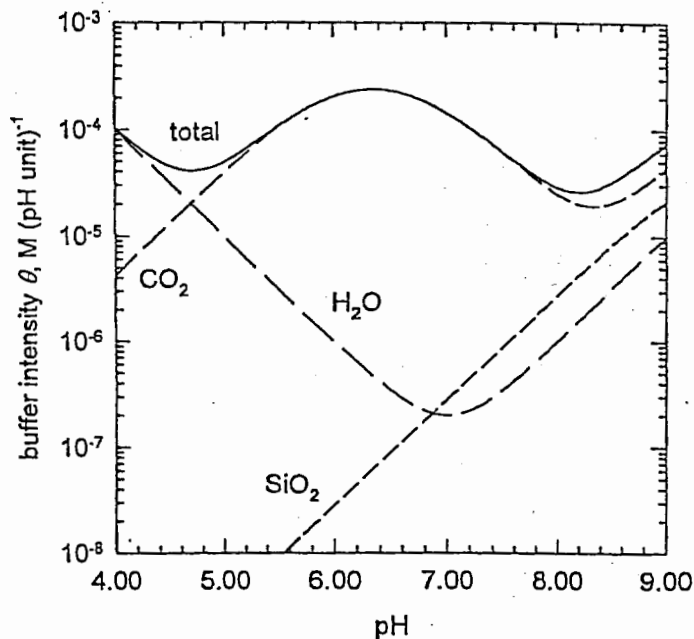


FIGURE 5 Buffer intensity as a function of pH for an aqueous solution containing  $[\text{CO}_2]_{\text{T}} = 42 \mu\text{M}$  and  $[\text{SiO}_2]_{\text{T}} = 83 \mu\text{M}$  with  $I = 0.005 \text{ M}$ ,  $T = 25^\circ\text{C}$ .

intensity is a quantitative description of a solution's resistance to changes in pH upon addition of acid or base and is defined as (85):

$$B = -dC_a/d(\text{pH}) = dC_b/d(\text{pH}) \quad (85)$$

where  $C_a$  is the *formal* concentration (formality) of added acid and  $C_b$  is the formality of added base. Because we are discussing infinitesimal (differential) quantities of added acid or base, the effects are equal and opposite for added acid *versus* added base. Note that the derivative described in (83) is the slope of a curve of  $C_b$  *versus* pH, which is the inverse of a "titration curve" where base molecules are added directly to a solution of acid so that the titer is zero and there is no change in volume, only changes in concentration. In terms of a real system, one can imagine dropping NaOH pellets or bubbling HCl into a pond. Alternately, a large body of water into which small volumes of acidic or alkaline solution are added experiences essentially no change in volume and can be represented in this fashion.

Virtually all potable waters contain some dissolved inorganic carbon, represented here as  $[\text{CO}_2]_{\text{T}}$ ; therefore, the buffer intensity will

be controlled by the simultaneous conjugate acid-base equilibria of the carbon dioxide-carbonic acid-bicarbonate-carbonate system. Although not conceptually difficult to understand, the derivation of a quantitative definition of the buffer intensity  $\beta$  for a given system can be cumbersome due to the lengthy algebraic expressions and differential calculus. For this reason, we include the derivation for this system. Let us consider the situation where the system resists a change in pH upon addition of an infinitesimal (differential) amount of alkali. The same thought processes would apply for the introduction of a small amount of acid.

We begin with the charge balance (86) and mass balance (87) expressions:

$$[\text{H}^+] + [\text{M}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (86)$$

$$[\text{CO}_2]_{\text{T}} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2] \quad (87)$$

where  $\text{M}^+$  represents the cation of some monohydroxide base (MOH). Because  $\text{H}_2\text{CO}_3$  can be thought of as  $\text{CO}_2 \cdot \text{H}_2\text{O}$  and water has activity equal to unity, there is no need to include carbonic acid separately in this process,  $K_{a1}$  includes both  $\text{CO}_2$  and  $\text{CO}_2 \cdot \text{H}_2\text{O}$ . As we are adding portions of base directly, there is assumed to be no change in volume. For this exercise, it is convenient to express the carbon dioxide acid equilibria in terms of the cumulative protonation constants rather than the stepwise acid dissociation constants given in Table VI.<sup>7</sup>

$$\beta_1 = 1/K_{a2} = [\text{HCO}_3^-]/([\text{H}^+][\text{CO}_3^{2-}]) \quad (88)$$

$$\beta_2 = 1/(K_{a2}K_{a1}) = [\text{CO}_2]/([\text{H}^+]^2[\text{CO}_3^{2-}]) \quad (89)$$

Making use of (88) and (89), we obtain the following expression for the total carbon dioxide concentration (dissolved inorganic carbon):

$$[\text{CO}_2]_{\text{T}} = [\text{CO}_3^{2-}](1 + \beta_1[\text{H}^+] + \beta_2[\text{H}^+]^2) \quad (90)$$

<sup>7</sup>Because our equilibrium constants are adjusted for ionic strength and temperature, we have not included correction factors or activity coefficients; however, we emphasize that one cannot simply substitute any values into these equations without appropriate consideration of relevant conditions.

Since  $[M^+]$  is equal to the *formal* concentration of the added base, we replace  $[M^+]$  with  $C_b$ . We express the bicarbonate and carbonate concentrations in (86) in terms of  $[\text{CO}_2]_T$ , using (88)–(90). Lastly, we substitute  $K_w/[\text{H}^+]$  for  $[\text{OH}^-]$  and rearrange, solving for  $C_b$ :

$$C_b = K_w/[\text{H}^+] - [\text{H}^+] + (\beta_1[\text{H}^+] + 2)[\text{CO}_2]_T / (1 + \beta_1[\text{H}^+] + \beta_2[\text{H}^+]^2) \quad (91)$$

Differentiating with respect to the hydrogen ion concentration and combining like terms yields (92):

$$\frac{dC_b}{d[\text{H}^+]} = \frac{-K_w}{[\text{H}^+]^2} - 1 + [\text{CO}_2]_T \left( \frac{-\beta_1 - 4\beta_2[\text{H}^+] - \beta_1\beta_2[\text{H}^+]^2}{(1 + \beta_1[\text{H}^+] + \beta_2[\text{H}^+]^2)^2} \right) \quad (92)$$

Since  $d[\text{H}^+]/d(\text{pH}) = -[\text{H}^+](\ln 10)$ , we make use of the chain rule for composite functions to obtain the buffer intensity  $\mathcal{B}$ , which is given by (93) after simplification:

$$\begin{aligned} \mathcal{B} &= dC_b/d(\text{pH}) = dC_b/d[\text{H}^+] \cdot d[\text{H}^+]/d(\text{pH}) \\ &= \{dC_b/d[\text{H}^+]\} \cdot \{-[\text{H}^+](\ln 10)\} \\ &= (\ln 10) \left[ \frac{K_w}{[\text{H}^+]} + [\text{H}^+] + [\text{CO}_2]_T \left( \frac{\beta_1[\text{H}^+] + 4\beta_2[\text{H}^+]^2 + \beta_1\beta_2[\text{H}^+]^3}{(1 + \beta_1[\text{H}^+] + \beta_2[\text{H}^+]^2)^2} \right) \right] \end{aligned} \quad (93)$$

where  $\mathcal{B}$  has units of  $\text{M} (\text{pH unit})^{-1}$  when all concentrations are expressed in molarities. Upon inspection of (93), it can be seen that the buffer intensity can readily be divided into contributions from  $[\text{OH}^-]$ ,  $[\text{H}^+]$  and  $[\text{CO}_2]_T$ . As Butler [68] notes, the cubic terms are negligible under most conditions and are often dropped from these expressions. Contributions from additional buffers,  $\mathcal{B}_i$ , may be accounted for by additional terms. For example,  $\mathcal{B}_{\text{SiO}_2}$  is given by (94):

$$\mathcal{B}_{\text{SiO}_2} = (\ln 10)[\text{SiO}_2]_T (K_1[\text{H}^+]^3 + 4K_2[\text{H}^+]^2 + K_1K_2[\text{H}^+]) / ([\text{H}^+]^2 + K_1[\text{H}^+] + K_2)^{-2} \quad (94)$$

where  $[\text{SiO}_2]_T = [\text{Si}(\text{OH})_4] + [\text{SiO}(\text{OH})_3^-] + [\text{SiO}_2(\text{OH})_2^{2-}]$  and  $K_1$  and  $K_2$  take their forms from Eqs. (69) and (70), respectively. Note that the multiplier of  $[\text{buffer}]_T$  is unitless as it represents the active

fraction of the total buffer. The inclusion of other components, including other weak Brønsted-Lowry bases (silicates, phosphates, *etc.*), or Lewis acidic (hydrolytic) metal cations ( $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ , *etc.*), serves to add terms and complicates the mathematics. However, the same fundamental principles and logic used here apply equally to such derivations.

Figure 5 shows that much of the buffer intensity is derived from the carbon dioxide-bicarbonate-carbonate system.<sup>8</sup> For the example New England water used in the calculations, the minimum buffer intensity contributed by the  $[\text{CO}_2]_T$  and water is  $\mathcal{B} = 0.25 \text{ mM (pH unit)}^{-1}$ . The contribution of acid from undissociated  $\text{SiF}_6^{2-}$  can again be proved negligible from the following extreme example. Even if 10% of the total fluoride input were as  $\text{SiF}_6^{2-}$  at pH 7, the acid input would be  $\Delta C_a = 5 \times 10^{-6} \text{ M}$ .  $I \approx 0.005 \text{ M}$ ,  $T = 25^\circ\text{C}$ . Thus, we can compute the change in pH directly using the buffer intensity calculated above:  $\Delta(\text{pH}) \approx -\Delta C_a / \mathcal{B} = -0.0050 \text{ mM} / [0.25 \text{ mM (pH unit)}^{-1}] = -0.020 \text{ pH unit}$ . This value is within the limits of a linear approximation of buffer capacity. Such a small effect on pH is undetectable and inconsequential with respect to other sources of variability in factors affecting lead release from plumbing materials. The concepts of chemical equilibria are well-established and measured equilibrium constants are sufficiently accurate and precise to show that fluoride and fluoro-silicate essentially do not affect the distribution of lead(II) species under potable water conditions.

## 8. CONCLUSION

Recent reports on the possible effects of water fluoridating agents, such as hexafluorosilicic acid, sodium hexafluorosilicate, and sodium fluoride are inconsistent with accepted scientific knowledge, and the authors fail to identify or account for these inconsistencies. Many of the chemical assumptions are scientifically unjustified, and alternate explanations (such as multiple routes of  $\text{Pb}^{\text{II}}$  exposure) have not been satisfactorily addressed. At present, there is no evidence to suggest

<sup>8</sup>The atomic mass of carbon is  $12.011 \text{ g mol}^{-1}$ , so concentrations of  $[\text{CO}_2]_T$  expressed as  $\text{mg CL}^{-1}$  can be converted to units of  $\text{mol L}^{-1}$  by dividing by 12,011.

that the common practice of fluoridating drinking water has any untoward health impacts *via* effects on lead(II) when done properly under established guidelines so as to maintain total water quality. Our conclusion supports both EPA and PHS/CDC policies on water fluoridation.

#### LIST OF SYMBOLS

$\mathcal{B}$	buffer capacity
$\mathcal{B}_{\text{CO}_2}$	buffer capacity of carbon dioxide
$\mathcal{B}_{\text{SiO}_2}$	buffer capacity of silicon dioxide
$\beta$	stability constant
$\mu$	micro, bridging ligand
$m$	molality
$[X]_{\text{T}}$	total concentration of $X$
$f_{\text{Pb}^{2+}}$	fraction of lead(II) ion
$f_{\text{PbF}^+}$	fraction of lead(II) ion
$f_{\text{PbF}_2(\text{aq})}$	fraction of lead(II) fluoride
$K_{\text{sp}}$	solubility product

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