Evaluation of contaminants in fluorosilicic acid used for public water fluoridation in the Santos region, Brazil

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ABSTRACT

Fluorosilicic acid is one of the main products used in water fluoridation. As a by-product of the phosphate fertilizer industry, it may contain contaminants that are harmful to human health. The aims of this study were to assess the quality control analysis of fluorosilicic acid; to detect the presence of contaminants, such as arsenic, lead, cadmium, aluminum, barium, strontium, cobalt, iron, and sulfur in fluorosilicic acid samples by using inductively coupled plasma–optical emission spectrometry; and to collect data for water analysis performed at a water treatment plant. The results show the presence of all contaminants mentioned previously, except for lead, in fluorosilicic acid samples from all sources. No quality control was carried out or required for this product at any time. Although the water analyses indicate the water is potable, there are no minimum safe limits for human consumption regarding carcinogenic elements such as cadmium and arsenic and both were detected and released in the water. Therefore, the purity of fluorosilicic acid used for water fluoridation should be required and monitored by public administrations to avoid long-term public health problems.

Key words | drinking water, fluorine, fresh water, toxicity, water treatment

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INTRODUCTION

Water fluoridation has been shown to be an important public health measure for reducing caries prevalence around the world (Armfield 2010) and has been recommended by the World Health Organization on account of its effectiveness and safety (Petersen & Lennon 2004). It is important that water fluoridation occur at appropriate levels; otherwise, it can cause fluorosis (Ramezani *et al.* 2015).

Grand Rapids (USA) was the first town around the world to use water fluoridation and that took place in 1945, decreasing the prevalence of caries by 60% to 65% among children and teenagers aged 4 to 16 years (Arnold *et al.* 1956). In Brazil, water fluoridation was initiated in Baixo Guando, a town in the state of Espírito Santo, in 1953 (Júnior & Narvai 2011). However, it was only in 1974 that water fluoridation was made obligatory at all public water treatment plants, pursuant to federal law no. 6,050 (Júnior & Narvai 2011).

The Brazilian Ministry of Health recommends a fluoride concentration in the water supply of 0.7 ppmF/L for most towns/cities, ranging from 0.6 to 1.5 ppmF/L, depending on local average temperatures (Resolution MS-GM-518, issued in 2005). The fluoride compounds most frequently used in Brazil are sodium fluorosilicate (Na_2SiF_6) and fluorosilicic acid (H_2SiF_6) (Buendia 1983). Both fluoride compounds are synthetic. Fluorosilicic acid is a waste product of the phosphate fertilizer industries and is widely used in São Paulo (Buendia 1983; Júnior & Narvai 2011) due to its financial advantages and easy handling by water treatment plants (Júnior & Narvai 2011).

Fluorine is found in nature, always associated with other elements, forming compounds such as fluorite, fluorapatite, and cryolite (Sampaio *et al.* 2005). It is also present in phosphate rocks, used to produce phosphate fertilizers and fluorosilicic acid. In addition to fluorine, almost every

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phosphate rock also contains toxic elements, such as aluminum (Al), arsenic (As), cadmium (Cd), lead (Pb), among other substances, or even radioactive elements such as uranium (U) and cesium (Cs) (Perez-Lopez *et al.* 2007). These contaminants can pose risks to and have adverse effects on human health, depending on their concentrations and on the conditions under which they are found (Jarup 2003). Some components such as cobalt, when present at high levels, cause systemic toxic effects on kidneys and liver (Lison 2015) whereas other elements such as Al, As, Cd, Cr, and Fe have a cumulative effect that can cause long-term health problems, (Flaten 2001; Brewer 2007; Satarug *et al.* 2010) especially arsenic and chrome, which are carcinogenic (Abdul *et al.* 2015; Sun *et al.* 2015). Nevertheless, no guidelines have been proposed by the Brazilian government to evaluate the purity and quality of the fluorosilicic acid used in public water fluoridation.

Therefore, the objectives of this study were to evaluate the water treatment system and the quality control performed by SABESP (a water and waste management company owned by the state of São Paulo) at Water Treatment Plant 3 (WTP 3) in the town of Cubatão; to analyze water quality data obtained from SABESP in the past 3 years; to assess the production of fertilizers which have fluorosilicic acid as a waste product; and to detect toxic elements in the fluorosilicic acid used by SABESP and produced by two major fertilizer industries in Cubatão. The research hypothesis is that neither fluorosilicic acid nor the water sampled from WTP 3 contains toxic contaminants.

MATERIALS AND METHODS

Water treatment and analysis

WTP 3, located in Cubatão, in the Santos region, state of São Paulo, Brazil, was visited and the water treatment stages and the inputs used during this process were identified. Water quality data obtained from SABESP in the past 3 years were collected. Fluorosilicic acid samples were also collected ($n = 3$) and analyzed by inductively coupled plasma–optical emission spectrometry (ICP-OES) as to their purity

Production of fluorosilicic acid by fertilizer industries

The production of fluorosilicic acid was assessed in two fertilizer industries in Cubatão's industrial region: Vale Fertilizantes (unit III) and Anglo American. These industries are the main manufacturers and suppliers of fluorosilicic acid for water fluoridation in the region.

The industries were visited and the steps for production of the fertilizers (simple and triple superphosphate) whose by-product is fluorosilicic acid were checked and the steps for collection and storage of fluorosilicic acid were identified. Fluorosilicic acid samples ($n = 3$) were collected from both industries and analyzed by ICP-OES.

ICP-OES analysis

Fluorosilicic acid samples were collected manually from three sources: Vale Fertilizantes, Anglo American, and SABESP. Fluorosilicic acid is stored in huge tanks and collected by employees wearing personal protection equipment. A total of nine samples were analyzed by ICP-OES in order to check for the presence of contaminants, namely arsenic (As), lead (Pb), cadmium (Cd), aluminum (Al), barium (Ba), cobalt (Co), strontium (Sr), iron (Fe), sulfur (S), and chrome (Cr).

This technique uses a source of argon plasma excitation at high temperatures (7,000–10,000 K or 6,727–9,727 °C) to produce excited atoms, which emit radiation in the range of 125 to 950 nm, according to the characteristics of the elements presented in the sample. These emitted radiations are selected according to their wavelengths by an optical system and their intensities are measured by specific radiation detectors. For each element, a calibration curve is used to correlate the radiation intensity with the concentration of the element in the sample.

Statistical analysis

Following normality and homoscedasticity requirements, the data of the concentration of each contaminant in the fluorosilicic acid samples were submitted to one-way analysis of variance (ANOVA) and Tukey's test, except for chrome, which was submitted to Student's *t*-test, given that only two groups showed measurable data. The global significance level was set at 95% ($\alpha = 0.05$).

RESULTS

Water treatment and analysis

The water treatment carried out at WTP 3 in SABESP is conventional and standardized for all SABESP plants. It consists of seven stages: pre-chlorination, coagulation, flocculation, sedimentation, filtration, post-chlorination, and fluoridation. Each water treatment stage and its description are displayed in Table 1.

Table 1 | Sequential water treatment stages and their objectives

Treatment stages	Objective
Pre-chlorination	Control of algae and microorganisms and oxidation of materials, removing flavor, smell, and color
Coagulation	Addition of coagulants to destabilize colloidal suspension, such as ferric chloride and calcium oxide; pH adjustment (operates in the pH range from 7.5 to 10.5)
Flocculation	Aggregation and compaction of coagulated particles with suspended particles in the water, forming flakes
Sedimentation	Dynamic process to separate suspended solid particles that are denser than water by force of gravity
Filtration (sand filters)	Organic matter and pathogenic microorganism removal
Post-chlorination	Water disinfection with free residual chlorine in the potable water distribution network
Fluoridation	Use of H_2SiF_6 at the mean concentration of 0.7 ppm/L for caries prevention

In order to monitor heavy metals in the water, SABESP analyzes the quality of the outlet water from WTP 3 every 6 months. The concentrations of elements (Al, As, Ba, Cd, Cr, Fe, Pb, S and F) in the past 3 years and the maximum allowable values (MAV) for human consumption, according to decree no. 2,914, of December 12, 2011, which regulates the procedures for control and monitoring of water quality for human consumption and potability standards (Brazil 2011), are presented in Table 2.

Production of fluorosilicic acid by fertilizer industries

Both companies used the same procedures to produce single superphosphate fertilizer, which has fluorosilicic acid as its by-product. In general, phosphate rocks are ground and acidulated with sulfuric acid (H_2SO_4) in the reactor and the reaction occurs in a closed environment at 125 °C. This exothermic reaction releases toxic gases (e.g., hydrofluoric acid (HF) and silicon tetrafluoride (SiF_4)), which react with water in a gas washer and form fluorosilicic acid at a concentration of 21%.

Even though both industries produce the single superphosphate fertilizer, as well as fluorosilicic acid, in a similar fashion, the operational factor and especially the origin and quality of raw materials and basic inputs vary widely, which can change the final product characteristics.

Table 2 | Concentrations of Al, As, Ba, Cd, Cr, Fe, Pb, S and F, in biannual water analysis at WTP 3, and MAV for human consumption, either in ppm/L or mg/L

	Concentration (mg/L)							
	January 2013	July 2013	January 2014	July 2014	January 2015	July 2015	MAV (Brazil 2011)	MAV (WHO 2011)
Al	<0.01	<0.01	<0.01	<0.01	0.03	0.04	0.2	–
As	<0.0012	<0.0012	<0.0012	<0.0012	<0.0012	<0.0012	0.01	0.01
Ba	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	0.7	0.7
Cd	<0.0040	<0.0012	<0.0012	<0.0012	<0.0012	<0.0012	0.005	0.003
Cr	<0.001	<0.001	<0.007	<0.001	0.004	<0.001	0.05	0.05
Fe	<0.05	<0.10	<0.09	<0.05	<0.05	<0.15	0.3	–
Pb	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	0.01	0.01
S (SO_4)	2.25	3.00	2.55	1.70	1.63	–	250	–
F	0.7	0.7	0.6	0.8	0.9	0.7	1.5	1.5

Furthermore, there was an important difference between the fertilizer industries regarding fluorosilicic acid production as Anglo American adds activated coal to fluorosilicic acid before storage. This removes some contaminants by adsorption and brings a clearer aspect to the final product. Also, Anglo American synthesizes triple superphosphate, which also generates fluorosilicic acid as a by-product. The fluorosilicic acid produced from either method is mixed and stored in the same tank.

ICP-OES analysis

The mean, minimum and maximum values of Al, As, Ba, Cd, Co, Cr, Fe, Pb, S, and Sr concentrations in fluorosilicic acid samples from SABESP's WTP 3, Vale Fertilizantes, and Anglo American and the maximum allowed concentration in fluorosilicic acid, according to the American Water Works Association (AWWA), are displayed in Table 3.

Note that the samples from Vale Fertilizantes showed a significantly higher concentration of Sr, Cr, Cd, and especially Al, which was around nine times higher than in the other groups. WTP 3 samples presented higher concentration of As and Ba while samples from Anglo American contained more Co and S when compared with the other groups. No groups or samples were free from contaminants. In all of the evaluated samples, As, Ba, and Cr are above the limit recommended by the AWWA standard. Cd from Vale Fertilizantes also exceeds this limit. Data obtained from other Cd samples and also from Pb samples are not precise enough to be compared with the AWWA standards due to the poor power of detection of the ICP-OES instrument.

DISCUSSION

One of the objectives of this study was to verify the presence of contaminants in fluorosilicic acid obtained from two manufacturers and also in that used by SABESP (WTP 3). The null research hypothesis was rejected since contaminants were found in all fluorosilicic acid samples. Vale Fertilizantes and Anglo American were selected because they are the main fertilizer manufacturers in the Santos region and because they sell their by-product, fluorosilicic acid, to SABESP which, in turn, uses it for public water fluoridation in the Santos region. There were significant differences concerning the contaminants found in the fluorosilicic acid collected from the three groups, especially with respect to aluminum ($p < 0.001$), arsenic ($p < 0.001$), cadmium (no statistics performed), and chrome ($p < 0.001$). Studies have warned that the consumption of these elements should be avoided since cumulative doses can cause long-term health disorders, especially arsenic and chrome, which are considered carcinogenic (Zhitkovich 2011; Abdul *et al.* 2015). Aluminum concentration was 10.5 and 164 mg/L in Anglo American and Vale Fertilizantes, respectively, showing over a tenfold increase. In turn, arsenic concentration was nine times

Table 3 | Mean and minimum–maximum values of the concentration of contaminants (mg/L) in fluorosilicic acid samples from three distinct sources and maximum allowed value (MAV) in fluorosilicic acid, according to the American Water Works Association guidelines (AWWA 2011)

	SABESP – WTP 3 (mg/L)	Vale Fertilizantes (mg/L)	Anglo American (mg/L)	MAV (AWWA 2011) (mg/L)
Al	17.7^b (17.6–17.8)	164.0^a (155.5–171.2)	10.5^b (10.4–10.5)	–
As	3.3^a (3.3–3.4)	0.37^b (0.3–0.4)	0.36^b (0.3–0.4)	0.001
Ba	7.1^a (7.1–7.2)	2.7^c (1.9–3.3)	4.7^b (4.6–4.7)	0.2
Cd	<0.01 (–)	0.44 (0.44–0.45)	<0.01 (–)	0.0005
Co	0.09^b (0.09–0.10)	<0.02 (–)	0.11^a (0.111–0.114)	–
Cr	0.17^c (0.16–0.17)	2.6^a (2.6–2.7)	0.28^b (0.26–0.29)	0.01
Fe	250.2^a (231.8–259.8)	196.6^b (193.1–201.9)	259.7^a (259.3–259.9)	–
Pb	<0.01 (–)	<0.01 (–)	<0.01 (–)	0.0015
S	293.5^b (265.1–308.0)	265.2^b (262.9–267.4)	330.6^a (329.2–331.4)	–
Sr	23.2^b (23.0–23.4)	93.6^a (91.3–97.1)	19.7^b (19.6–19.9)	–

For each element, a similar letter indicates absence of significant statistical difference.

higher in SABESP samples than in the other two groups. Cadmium was detected only in Vale Fertilizantes samples and chrome concentration in Vale Fertilizantes samples was about 15 times higher than in SABESP and nine times higher than in Anglo American samples. These huge differences in the concentration of contaminants occur due to the composition of the phosphate rocks used to produce the fertilizers and fluorosilicic acid; the rocks present random and unpredictable amounts of these elements, which are partially transferred to the by-product, fluorosilicic acid. There are no studies in the literature that analyze the concentrations of contaminants present in fluorosilicic acid; therefore, it is not possible to compare these concentrations with those of other studies. Despite the fact that there is no regulation of purity and quality for this product in Brazil, neither of the samples comply with the AWWA standard for As, Ba, and Cr concentrations (Table 3), which indicates the need for some treatment to decrease these levels and also serves as an important warning about their safety. In the present study, it was observed that only Anglo American treated the acid with activated coal in order to remove some contaminants. It was probably for this reason that lower concentrations of heavy metals such as Al, Cd, and As were found in the product of this industry and not in the samples from the other manufacturers. In fact, studies have shown effective adsorption of these elements by activated carbon (Panhwar *et al.* 2016; Pramanik *et al.* 2016). It is important to highlight that the samples submitted to activated coal adsorption presented significantly lower turbidity. However, this treatment was not effective in reducing Ba, Co, S, and Fe concentrations. As described in the literature, barium is not actually well adsorbed by activated coal (Sato *et al.* 2011); and although some studies have shown effective adsorption of Co, S and Fe by activated coal (Ben Hariz *et al.* 2014; Feist & Mikula 2014; Panhwar *et al.* 2016), this process relies on several factors that were not evaluated in this study, such as activated coal surface area and porosity, surface composition, time, and pH of the solution.

Table 3 shows that iron concentration was high in all samples, which could be caused by the corrosion of the storage tank, valves, and pipes by fluorosilicic acid and consequent incorporation of the released iron into the acid. Iron is an essential element for growth and development, but during the aging process, its levels, albeit normal, can worsen some diseases, such as Alzheimer's and arteriosclerosis, in elderly people (Brewer 2007). Sulfur was also found at high concentrations in the samples, possibly as residue of the sulfuric acid used in single superphosphate production.

The variability in the concentration of impurities can be attributed to several other factors, such as type and origin of the raw material and supplies and operating and maintenance procedures. According to the data from different manufacturers and suppliers of fluorosilicic acid, it is evident that there exists no regularity or predictability in the concentration of contaminants in fluorosilicic acid samples. However, no quality tests or certificates are applied to or required from these products, which are sold to the public water supply system.

According to some animal and human studies, these chemical compounds, under certain conditions, present risks to and have adverse effects on human health (Jarup 2003; Lison 2015; Tsuji *et al.* 2015). The main health problems caused by each contaminant are displayed in Table 4. Most of the elements, such as aluminum, arsenic, cadmium, chrome, iron, and lead, have a cumulative effect over time and can predispose to long-term diseases (Jarup 2003; Zhitkovich 2011; Willhite *et al.* 2012; Abdul *et al.* 2015), and thus any form of ingestion of these elements should be avoided, independently of their concentration. Health problems caused by other elements such as barium, cobalt, sulfur, and strontium are dose-dependent, and their ingestion is only safe in the recommended amounts (Cohen-Solal 2002; Serrato 2008; Lison 2015).

It should be noted that, despite the high level of some compounds in fluorosilicic acid, the concentration of contaminants in the water samples (Table 2) analyzed by SABESP is not hazardous and complies with Brazilian regulations and with World Health Organization recommendations in all the evaluations performed. These data should be viewed with caution since random variables such as location, time of collection, and system operation play an important role. The reason why contaminants in the fluorosilicic acid samples were at acceptable levels is due mainly to their dilution rather than to their removal by treatment since fluoridation is the last stage in the water treatment process (Table 1); hence all contaminants present in fluorosilicic acid are directly transferred to the

Table 4 | Long-term and dose-dependent health problems associated with several elements

Element	Main health problems	References
Cumulative effect		
Al	Neurodegenerative diseases; bone and hematopoietic disorders	Willhite *et al.* (2012)
As	Carcinogenic effect; anemia; skin lesions	Abdul *et al.* (2015), Tsuji *et al.* (2015)
Cd	Bone and kidney diseases, especially in more susceptible individuals	Nordberg (2009), Satarug *et al.* (2010)
Cr (VI)	Carcinogenic effect	Zhitkovich (2011), Sun *et al.* (2015)
Fe	Risk factor for myocardial infarction; worsening of aging-associated diseases such as neurodegenerative disorders, arteriosclerosis, and diabetes mellitus	Salonen *et al.* (1992), Brewer (2007)
Pb	hematopoietic disorders, liver and kidney diseases; encephalopathies	Jarup (2003)
Dose-dependent		
Ba	Heat-related problems; possible respiratory, hematologic, renal, hepatic, endocrine, and nervous system disorders	Kravchenko *et al.* (2014)
Co	Hepatic and renal disorders; pancreas and thyroid dysfunctions	Lison (2015)
S	Affect organism homeostasis; predisposition to diabetes mellitus, rheumatism, arthritis, and osteoporosis	Serrato (2008)
Sr	Bone diseases when associated with renal dysfunction; calcium homeostasis	Cohen-Solal (2002)

public water supply system. Depending on the initial fluorosilicic acid concentration and its degree of dilution in the water supply, people can ingest higher amounts of contaminants and, as described previously, some of these contaminants have a cumulative effect (Zhitkovich 2011; Abdul *et al.* 2015), and even if they do not cause acute toxicity, they can predispose to long-term diseases (Kravchenko *et al.* 2014; Lison 2015). Coagulants such as ferric chloride and calcium oxide can also contain some contaminants, but they were not reviewed in this study. Therefore the presence of contaminants pointed out in the water analyses cannot be attributed only to fluoridation.

Some limitations of this study included its small sample size, the monitoring of water treatment at only one water treatment plant, and analysis of fluorosilicic acid samples from only two manufacturers. Despite these limitations, this study warns about the safety and purity of fluorosilicic acid used in the public water fluoridation process given the high level of some contaminants and the absence of quality control analysis at the industry level and at water treatment plants. The example of other countries like the United States, which has already developed guidelines for quality control of fluorosilicic acid used in public water fluoridation and requires a certificate of analysis from the manufacturers (ADA 2005), should be followed.

Over the years, water fluoridation has been shown to be an effective and safe method for the prevention of dental caries (Petersen & Lennon 2004; Armfield 2010). To maintain these beneficial effects for the population, not only should water fluoridation be maintained in Brazil, but it must also be improved by treatment of fluorosilicic acid prior to its use in fluoridation to avoid other potential diseases. Furthermore, fluoride is essential to reduce caries prevalence, and the use of fluorine-containing products such as toothpastes and mouthwashes must continue and be incentivized in areas without water fluoridation.

CONCLUSIONS

The data presented here concern the Santos region, in the state of São Paulo, Brazil. Considering the limitations of this study, it may be concluded that manufacturers and water treatment plants do not conduct a quality control analysis of impurities in the fluorosilicic acid used for public water fluoridation in the Santos region; the fluorosilicic acid samples analyzed presented nine out of 10 contaminants evaluated, which are directly transferred to the public water supply; the contaminants in the fluorosilicic acid are from raw matter used in superphosphate fertilizer production. Data from the water analysis are in accordance with legal levels but these evaluations are only biannual and it occurs due the dilution of contaminants and not their removal; there are no rules for the concentrations of contaminants in the additives used in water treatment and fluoridation in water treatment stations.

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