Fluoridation of Drinking Water
Questioning the Accepted Chemistry

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Executive Summary

This document is based a review of a large body of literature, pertaining to the use of solutions of hexafluorosilicic acid and its sodium salt in the fluoridation of drinking water. It offers the conclusion that neither compound is the active ingredient in providing the fluoride ion. Rather it is concluded that the active ingredient, in the use of either mixture, is hydrogen fluoride, and that both hexafluorosilicic acid and its sodium salt are "contaminants" in the fluoridation process. This conclusion is considered to be significant because there is evidence in the literature that those "contaminants" are associated with lung and bladder cancers.

Introduction

It is currently accepted throughout the world that the presence of fluoride ion, F^-, in drinking water, helps prevent tooth decay. One mechanism, for how this is achieved, is its reaction with hydroxyapatite, $Ca_5(PO_4)_3OH$ on the teeth, and the production of fluoroapatite, $Ca_5(PO_4)_3F$, which is reported to be more resistant to acidic solutions.

Drinking water consists of concentrations of most ions found on the periodic table. In order to ensure that the water is safe to drink, a great many measurements are routinely conducted to ensure that each parameter is within quality guidelines established by Health Canada. Measurements are also made of organic compounds that are considered to be contaminants Appendix A contains a list of measurements typically conducted by the City of Calgary.

All of the listed parameters are important to ensuring health, but the general population is usually most aware of those describing hardness, alkalinity, toxic metal ions and pH (the negative log of the hydrogen ion concentration). Drinking water is considered to have equal concentrations of hydrogen ion and hydroxide concentration when the pH is 7; each concentration being 10^{-7} M. As a result of the natural presence of carbonate and bicarbonate, typically drinking water will have a pH of between 8 and 9.

Through the mechanism described above, it is widely believed that the concentration of fluoride ion in drinking water plays a role in the prevention of tooth cavities in young children. The average in Calgary water is 0.1 mg/L and it is believed that, if its concentration could be increased, its effectiveness as a cavity preventer would be increased.

Literature Review

Fluorine is the most electronegative element in the Periodic Table. This means that it accepts other element's electrons and bonds very strongly with most metals and nonmetals. It can even form molecules with noble gases like Xenon. As stated above, its high electronegativity is the property that, almost certainly, allows it to help reduce tooth decay in children.

There are three compound additives that are proposed as sources of additional fluoride ion for drinking water. They are sodium fluoride, NaF, hexafluorosilicic acid, $H_2(SiF_6)$, and, thirdly, its sodium salt, sodium hexafluorosilicate. Of the three compounds, NaF is the most obvious source because when mixed with water, it disassociates rapidly into Na+ ion and the active species, F^-. Hexafluorosilicic acid, $H_2(SiF_6)$, is delivered to municipal water treatment systems as approximately a 22% aqueous solution and is claimed to be a good source of fluoride ions.

Past literature have claimed that $H_2(SiF_6)$ {HFSA}, a waste product[1] of the phosphate fertilizer industry, has been found to be contaminated with significant amounts of heavy metals which include arsenic, lead and radioactive species , radium -226 and lead-210. Research has reported that these contaminants can lead to lung and bladder cancer. Currently, it is reported that approximately 90% of drinking water systems that augment fluoride ion content, use HFSA or its sodium salt. This product is reported to be currently used by 49 US states and 9 provinces of Canada.

Of significance in this regard, it has been reported that when chloramine is used as a disinfectant in water systems, together with hexafluorosilicates, leaching of lead from brass/lead water pipes takes place. It has been suggested that the result is elevated blood lead levels in children (see Appendix B)

On first glance, HFSA appears to be a typical weak acid and as such, in water, it would not dissociate into large quantities of H^+ ions and its anion SiF_6^{--} ions. The literature states that its dissociation[2] constant, Kd, is 10^{-30}. Comparison of this Kd with those of known organic acids like benzoic (6.2×10^{-5}), acetic acid (1.8×10^{-5}) and fluoroacetic acid (2.6×10^{-3}) suggests just how weak it is. The dissociation reaction may be expressed as:

$$H_2(SiF_6) + 2H_2O \overset{Kd}{\rightleftharpoons} 2H_3O^+ + SiF_6^{--} \tag{1}$$

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[1] Phosphate ores, containing fluoride and silicon compounds are heated with sulfuric acid. The resulting chemical reaction produces the gases SiF_4 and HF. Both are combined to form a 22% solution of HFSA.

[2] Kd, Dissociation Constant, is a measure of the strength of an acid in solution. It is a ratio of dissociation products to the original species.

$Kd = 10^{-30} = [H_3O^+]^2[SiF_6^{--}]/ [H_2(SiF_6)]$

In other words, in solution, the concentration of $H_2(SiF_6)$ is much larger than its dissociated products, H^+ and SiF_6^{--}. There is no suggestion of the presence of fluoride ions.

In spite of this knowledge, it has been suggested by proponents for its use that HFSA is rapidly hydrolyzed, in drinking water, to fluoride ions, according to the pathway

$$H_2(SiF_6) + 6OH^- \longrightarrow 6F^- + Si(OH)_4 + 2H_2O \qquad (2)$$

A second pathway that has been suggested is

$$H_2(SiF_6) + 2H_2O^- \longrightarrow 6HF +^- SiO2 \qquad (3)$$

These reactions are considered to be unusual (especially considering the fluoride electronegativity) and are not based on known chemistry of drinking water (pH 9), having a hydroxide concentration of 10^{-5} M. It suggests a reaction between a strong base and $H_2(SiF_6)$ and is not a reaction that would normally be expected in drinking water. A more likely reaction that could be expected would be

$$H_2(SiF_6) + 2Na^+ + 2OH^- \rightleftarrows Na_2(SiF_6) + 2H_2O$$

Or (see reference 3)

$$2H^+ + SiF_6^{--} + 2Na^+ + 2OH^- \rightleftarrows Na_2(SiF_6) + 2H_2O \qquad (4)$$

In 2006, a study by Finney et al, using 19F NMR (reference 1), repudiates the claim, in equation 2, that hexafluorosilicic acid completely dissociates in water. Those experiments, conducted to examine the possible presence of fluorosilicate intermediates produced during the believed hydrolysis of $H_2(SiF_6)$, found no intermediates. *One species, identified as* $SiF_6^{--,}$ *or its hydrate, is suggested to be more likely, based on known chemistry, to have been the un-dissociated* $H_2(SiF_6)$. Perhaps of more significance is that the result did not prove the presence of F ions as suggested by equation 2. The conclusion that there must be complete dissociation into F ions is a conclusion that raises doubt. since there were no intermediates.

The sodium salt of hexafluorosilicic acid is the third compound that is often used to fluoridate drinking water. The same arguments, presented above for the acid, apply to its consideration as a source of F ions in drinking water. The main difference between use of either the acid or its salt is that one is available as an aqueous solution while the latter is a solid. Both are understood to be byproducts of the phosphate mining industry and concerns have been expressed that they may contain some impurities such as HF and heavy metals such as arsenic, lead, mercury and cadmium. Proponents of their use for fluoridation do not dispute that contaminants may be present but have concluded that, based on the amounts added to the drinking water, that the contributions of resulting contaminants are limited to more than two orders of magnitude below Health Canada drinking water guidelines.

It is understood that the main supplier of 22% HFSA solution is located in Europe, while a supplier located in Florida is inconsistent .

Pharmaceutical or food grade NaF is reported to contain approximately 100 times less heavy metals contaminants than HFSA. If its cost can be supported it appears to be a logical replacement for HFSA. However, since it is a powder, it would first need to be put into solution for ease of addition to Calgary's drinking water. Additional problems may also include the difficulty in handling a powder, bulk storage and assurance of consistent supply.

Conclusions

1. It has been claimed that 22% solution of HFSA can be used to fluoridate drinking water if it meets the guidelines of NSF/ANSI/CAN60. These are understood to be the mandatory guidelines accepted throughout the world. According to the latest Association of State Drinking Water Administrations Survey, 49 US States and 9 Canadian provinces use chemicals that meet that Certification.

2. It has been claimed, by its proponents, that HFSA is a strong acid and dissociates in water according to reactions 2 or 3, above. The literature review, in this study, states that it is a weak acid and would be expected to dissociate according to reaction 1 above. In other words, the correct chemistry does not support the conclusion that HSFA is the source of fluoride ions.

3. What is the source of the fluoride ions in the 22% mixture of HFSA that meets NSF/ANSI/CAN60 certification? It is stated (reference 2) that in the production of HF, for the phosphate mining industry, 50 kg of HFSA is produced per 1000 kg of HF. HFSA is also produced as a product of the reaction of HF with silicate minerals. It is therefore suggested that one possible explanation for the presence of fluoride ions is that the 22% solution of HFSA is really a solution of HF and contains HFSA as a "contaminant".

4. If HFSA is a "contaminant" in the 22% solution of HFSA and if the main active fluoridation agent is in fact HF, then consideration would be given to adding its measurement to the parameter list shown in Appendix A.

5. Support for the conclusion 4 seems to be the observation by the city of Calgary that the 22% HFSA solution has similar chemical properties as HF alone. For example, it is understood that storage containers, tank liners have been selected based on those properties. It is understood that, in the past, the use of the 22% HFSA, during the fluoridation process included dilution to prevent excess wear on other infrastructure pumps and lines.

6. ***The overall conclusion of this document is that while the use of 22% HFSA for the purposes of fluoridating Calgary's water probably meets international guidelines, the fact cannot be ignored that contaminants other than fluoride are also added, which are reported in the literature to be associated with lung and bladder cancers.***

Recommendations

This review concludes that HFSA in the fluoridation solution will not dissociate when added to Calgary's drinking water. The source of the fluoride ion is concluded to be HF. It is recommended that the City of Calgary Water Treatment department conduct an in depth analysis of the purchased solution for the concentration of HF and trace metals (including radium -226 and lead-210). As in Reference 1, It would be useful to measure undissociated HFSA in the drinking water after fluoridation.

References

1. Finney et al, Environmental Science and Technology, 40(8), 2572-7, "Re- examination of Hexafluorosilicate Hydrolysis by 19F NMR and pH Measurement".
2. USGS Fluorospar
3. "Sodium Hexafluorosilicate (CASRN 16893-85-9) anf Fluorosilicic Acid (CASRN 16961-83-4) Review of Toxicology Literature" pdf ntp.niehs.nih.gov

APPENDIX A

City of Calgary Bearspaw Water Treatment Plant Summary

January 1, 2019 to December 31, 2019

		Bearspaw Treated Water (Entering the Distribution System)			Maximum Acceptable Concentration or Guideline[1]	
PARAMETER	**UNITS**	**Minimum**	**Maximum**	**Average**		**Common Source**
Alkalinity, Total	mg/L as $CaCO_3$	81	140	122	No Guidelines	Erosion of natural deposits in watershed
Aluminum	mg/L			0.058	0.100 (O) (Annual Average)	Naturally occuring and plant treatment
Ammonia	mg/L as N	<0.05			No Guidelines	Naturally occurring; released from agricultural or industrial wastes
Antimony	mg/L	<0.0005			0.006	Erosion of natural deposits in watershed
Arsenic	mg/L	<0.0005			0.010	Erosion of natural deposits in watershed
Atrazine + metabolites	mg/L	<0.001			0.005	Leaching and/or runoff from agricultural use
Azinphos - methyl	mg/L	<0.001			0.02	Leaching and/or runoff from agricultural use
Barium	mg/L	0.031	0.043	0.036	1.0	Erosion of natural deposits in watershed
Benzene	mg/L	<0.0005			0.005	Releases or spills from industrial use
Benzo[a]pyrene	mg/L	<0.000005			0.00004	Distribution System materials
Beryllium	mg/L	<0.0005			No Guidelines	Contamination from ceramic applications and manufacturing of aerospace, electronics and mechanical industries
Bicarbonate	mg/L as $CaCO_3$	81	140	122	No Guidelines	Erosion of natural deposits in watershed
Boron	mg/L	0.004	0.008	0.006	5	Naturally occurring; leaching or runoff from industrial use
Bromate	mg/L	<0.01			0.01	Possible contamination in hypochlorite solution
Bromoxynil	mg/L	<0.0002			0.005	Leaching and/or runoff from agricultural use
Cadmium	mg/L	<0.0005			0.005	Erosion of natural deposits in watershed
Calcium	mg/L	37	52	44	No Guidelines	Erosion of natural deposits in watershed
Carbaryl	mg/L	<0.002			0.09	Leaching and/or runoff from agricultural use
Carbofuran	mg/L	<0.0005			0.09	Leaching and/or runoff from agricultural use
Carbonate	mg/L as CaCO3	<20			No Guidelines	Erosion of natural deposits in watershed
Carbon Tetrachloride	mg/L	<0.0005			0.002	Industrial effluents and leaching from hazardous waste sites
Chloramines, Total[3]	mg/L	<0.09			3	Formed in the presence of both chlorine and ammonia
Chlorate	mg/L	<0.10			1	Possible contamination in hypochlorite solution
γ-Chlordane	mg/L	<0.00001			No Guidelines	Leaching and/or runoff from agricultural use
Chloride	mg/L	3.1	6	4.7	250 (A)	Naturally occurring, dissolved salt deposits, highway salt
Chlorine, free	mg/L	0.76	1.34	1.06	No Guidelines	Plant treatment
Chlorite	mg/L	<0.10			1	Possible contamination in hypochlorite solution
Chlorpyrifos	mg/L	<0.001			0.09	Leaching and/or runoff from agricultural use
Chromium	mg/L	<0.0005	0.002	<0.0005	0.05	Erosion of natural deposits in watershed

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PARAMETER	**UNITS**	**Minimum**	**Maximum**	**Average**		**Common Source**
Cobalt	mg/L	<0.0005			No Guidelines	Erosion of natural deposits in watershed
Coliforms, *E.coli*	MPN/100mL	<1			0	Domestic animals, wildlife and human waste
Coliforms, Total	MPN/100mL	<1			0	Soil, domestic animals and wildlife.
Color	TCU	<2			15 (A)	Erosion of natural deposits in watershed
Conductivity at 25°C	uS/cm	290	376	343	No Guidelines	Leaching and/or runoff from agricultural use
Copper	mg/L	<0.0005	0.0168	0.0007	2 1.0 (A)	Erosion of natural deposits in watershed
Cryptosporidium	oocysts/100L	Not Tested			Treatment Goal	Domestic animals, wildlife and human waste
Cryptosporidium, Min. Log Reduction Ratio[3]	no units	1.33			Treatment Goal	Domestic animals, wildlife and human waste
Cyanazine	mg/L	<0.001			No Guidelines	Run off from agricultural or other uses
Cyanide	mg/L	<0.002			0.2	Industrial and mining effluents; Release from organic compounds
Cyanobacterial toxins – total microcystin	mg/L	0.00014	0.00016	0.00015	0.0015	Naturally occurring; released from blooms of blue-green algae
Diazinon	mg/L	<0.001			0.02	Run off from agricultural or other uses
Dicamba	mg/L	<0.0002			0.12	Leaching and/or runoff from agricultural use
1,2-Dichlorobenzene	mg/L	<0.0005			0.2	Releases or spills from industrial use
1,4-Dichlorobenzene	mg/L	<0.0005			0.005	Releases or spills from industrial use
2,4-DDT	mg/L	<0.00001			No Guidelines	Leaching and/or runoff from agricultural use
4,4'-DDT	mg/L	<0.00001			No Guidelines	Leaching and/or runoff from agricultural use
1,1-Dichloroethylene	mg/L	<0.0005			0.014	Releases or spills from industrial use
1,2-Dichloroethane	mg/L	<0.0005			0.005	Releases or spills from industrial use
Dichloromethane	mg/L	<0.005			0.05	Industrial and municipal wastewater discharges
2,4-Dichlorophenol	mg/L	<0.0005			0.9	By-product of chlorination
2,4-D	mg/L	<0.0002			0.1	Leaching and/or runoff from use as a weed controller
Diclofop-methyl	mg/L	<0.0001			0.009	Leaching and/or runoff from use as a weed controller
Dimethoate	mg/L	<0.001			0.02	Leaching and/or runoff from agricultural use
Diquat	mg/L	<0.007			0.07	Leaching and/or runoff from agricultural use
Diuron	mg/L	<0.001			0.15	Leaching and/or runoff from use in controlling vegetation
Endrin	mg/L	<0.00001			No Guidelines	Leaching and/or runoff from agricultural use

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PARAMETER	**UNITS**	**Minimum**	**Maximum**	**Average**		**Common Source**
Ethylbenzene	mg/L	<0.0005			0.14 0.0016 (A)	Emissions, effluents or spills from petroleum and chemical industries
Extractable Hydrocarbons	mg/L	<0.01			No Guidelines	Releases or spills from industrial use
Fluoride	mg/L	0.07	0.14	0.10	1.5	Erosion of natural deposits in watershed[2]
Giardia	cysts/100L	Not Tested			Treatment Goal	Domestic animals, wildlife and human waste
Giardia, Min. Log Reduction Ratio[3]	no units	1.08	2.57	1.57	Treatment Goal	Domestic animals, wildlife and human waste
Glyphosate	mg/L	<0.005			0.28	Leaching and/or runoff from use as a weed controller
Gross Alpha	Bq/L	<0.13	0.22	0.14	0.5	Naturally occurring; emissions from nuclear reactors
Gross Beta	Bq/L	<0.05	0.1	0.06	1.0	Naturally occurring; emissions from nuclear reactors
Haloacetic Acids, Total	mg/L			0.0095	0.08 (Annual Average)	By-product of chlorination
Hardness	mg/L as CaCO3	143	191	173	No Guidelines	Erosion of natural deposits in watershed
Heptachlor + heptachlor epoxide	mg/L	<0.0001			No Guidelines	Leaching and/or runoff from agricultural use
Iron	mg/L	<0.010	0.012	<0.010	0.3 (A)	Erosion of natural deposits in watershed.
Lead	mg/L	<0.0005			0.005	Leaching from plumbing (pipes, solders, brass fittings, and lead service lines)
Lindane	mg/L	<0.00001			No Guidelines	Leaching and/or runoff from agricultural use
Lithium	mg/L	0.0020	0.0045	0.0031	No Guidelines	Releases or spills from industrial use
Magnesium	mg/L	11.4	16.3	14.0	No Guidelines	Erosion of natural deposits in watershed
Malathion	mg/L	<0.001			0.19	Leaching and/or runoff from agricultural and other uses
Manganese	mg/L	<0.0005	0.0015	<0.0005	0.12 0.02 (A)	Erosion of natural deposits in watershed.
MCPA (2-methyl-4-chlorophenoxyacetic acid)	mg/L	<0.00002			0.1	Leaching and/or runoff from agricultural and other uses
MCPP (methylchlorophenoxy propionic acid)	mg/L	<0.00008			0.015 (A)	Leaching and/or runoff from agricultural and other uses
Mercury	mg/L	<0.000002			0.001	Erosion of natural deposits in watershed
Methyl parathion	mg/L	<0.001			No Guidelines	Leaching and/or runoff from agricultural use
Methoxychlor	mg/L	<0.00001			No Guidelines	Leaching and/or runoff from agricultural and other uses
Metolachlor	mg/L	<0.001			0.05	Leaching and/or runoff from agricultural and other uses
Metribuzin	mg/L	<0.001			0.08	Leaching and/or runoff from agricultural use

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PARAMETER	**UNITS**	**Minimum**	**Maximum**	**Average**		**Common Source**
Mirex	mg/L	<0.00001			No Guidelines	Leaching and/or runoff from agricultural use
Molybdenum	mg/L	0.0005	0.0008	0.0007	No Guidelines	Leaching and/or runoff from industrial, agricultural and other uses
Monochlorobenzene	mg/L	<0.0005			0.08	Releases or spills from industrial effluents
MTBE (methyl tertiary-butyl ether)	mg/L	<0.0005			0.015 (A)	Spills from gasoline refineries, filling stations and gasoline powered boats; seepage into groundwater from leaking storage tanks
Nickel	mg/L	<0.0005	0.0011	<0.0005	No Guidelines	Leaching from plumbing (pipes, solders, and brass fittings)
Nitrate	mg/L as N	0.08	0.15	0.11	10	Erosion of natural deposits in watershed
Nitrite	mg/L as N	<0.005			1	Erosion of natural deposits in watershed
Nitrilotriacetic acid (NTA)	mg/L	<0.0002			0.4	Sewage contamination
N-Nitrosodimethylamine (NDMA)	mg/L	<0.0000022			0.00004	By-product of chlorination; industrial and sewage treatment plant
Nitrogen, total (TKN)	mg/L	<0.10	0.20	<0.10	No Guidelines	Erosion of natural deposits in watershed
Odour	Scale = 0-12	6	10	8	Inoffensive	Biological, industrial, or treatment disinfection sources
Paraquat	mg/L	<0.001			0.01	Leaching and/or runoff from agricultural and other uses
Parathion	mg/L	<0.002			0.05	Leaching and/or runoff from agricultural use
Pentachlorophenol	mg/L	<0.0005			0.06	By-product of chlorination
Perfluorooctane Sulfonate (PFOS)	mg/L	<0.00001			0.0006	Synthetic chemical used in consumer products and fire-fighting foams for their water and oil repellant properties
Perfluorooactanoic Acid (PFOA)	mg/L	<0.00001			0.0002	Synthetic chemical used in consumer products and fire-fighting foams for their water and oil repellant properties
Pesticides, total	mg/L	<0.01			No Guidelines	Leaching and/or runoff from agricultural use
pH	pH units	7.0	8.2	7.6	7.0 - 10.5 (O) 6.5-8.5 (AEP)	Influenced by the dissolved minerals in the water, temperature and water treatment processes
Phorate	mg/L	<0.0005			0.002	Leaching and/or runoff from agricultural and other uses
Phosphorus, Total	mg/L	<0.001	0.004	0.002	No Guidelines	Leaching and/or runoff from agricultural and other uses
Phthalate Esters	mg/L	<0.01			No Guidelines	Industrial effluents or spills
Picloram	mg/L	<0.0002			0.19	Leaching and/or runoff from agricultural and other uses
Potassium	mg/L	0.5	0.6	0.5	No Guidelines	Erosion of natural deposits in watershed
Polycyclic Aromatic Hydrocarbons[3] (PAH)	mg/L	<0.0001			No Guidelines	Industrial sources

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PARAMETER	**UNITS**	**Minimum**	**Maximum**	**Average**		**Common Source**
Selenium	mg/L	<0.0005	0.0010	<0.0005	0.05	Naturally occurring (erosion and weathering of rocks and soils) and release from coal ash from coal-fired power plants and mining, refining of copper and other metals
Silicon, dissolved	mg/L	1.33	1.86	1.59	No Guidelines	Erosion of natural deposits in watershed
Silver	mg/L	<0.001			No Guidelines	Naturally occurring (erosion and weathering of rocks and soils)
Simazine	mg/L	<0.001			0.01	Leaching and/or runoff from agricultural and other uses
Sodium	mg/L	2.6	5.5	4.6	200 (A)	Erosion of natural deposits in watershed
Strontium	mg/L	0.143	0.213	0.184	7.0	Erosion of natural deposits in watershed
Sulphate	mg/L	42	62	52	500 (A)	Erosion of natural deposits in watershed
Sulphide	mg/L as H_2S	<0.002			0.05 (A)	Can occur in the distribution system from the reduction of sulphates by sulphate-reducing bacteria; industrial wastes
Taste	mg/L	Not Tested			Inoffensive (A)	Biological or industrial sources
Temperature	°C	1.2	9.1	7.1	15 (A)	Surface water temperature
Terbufos	mg/L	<0.0005			0.001	Leaching and/or runoff from agricultural and other uses
Tetrachloroethylene	mg/L	<0.0005			0.01	Industrial effluents or spills
2,3,4,6-Tetrachlorophenol	mg/L	<0.0005			0.1	By-product of chlorination; industrial effluents and use of pesticides
Thallium	mg/L	<0.0005			No Guidelines	Erosion of natural deposits in watershed.
Tin	mg/L	<0.0005			No Guidelines	Industrial effluents or spills
Titanium	mg/L	<0.0005			No Guidelines	Industrial effluents or spills
Toluene	mg/L	<0.0005	0.0021	<0.0005	0.06	Emissions, effluents or spills from petroleum and chemical industries
Total Dissolved Solids	mg/L	176	220	200	500 (A)	Erosion of natural deposits in watershed
Total Organic Carbon	mg/L	0.5	1.2	0.7	No Guidelines	Erosion of natural deposits in watershed
Triallate	mg/L	<0.001			No Guidelines	Leaching and/or runoff from agricultural and other uses
Trichloroethylene	mg/L	<0.0005			0.005	Industrial effluents and spills from improper disposals
2,4,6-Trichlorophenol	mg/L	<0.0005			0.005 0.002 (A)	By-product of chlorination; industrial effluents and spills
2,4,5-T	mg/L	<0.0002			No Guidelines	Leaching and/or runoff from agricultural and other uses
Trichlorophenoxypropionic Acid (2,4,5-TP)	mg/L	<0.0002			No Guidelines	Leaching and/or runoff from use in controlling vegetation
Trifluralin	mg/L	<0.001			0.045	Runoff from agricultural uses

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PARAMETER	UNITS	Bearspaw Treated Water (Entering the Distribution System)			Maximum Acceptable Concentration or Guideline[1]	Common Source
		Minimum	Maximum	Average		
Total Trihalomethanes[3] (TTHMs)	mg/L			0.0088	0.1 (Annual Average)	By-product of chlorination
Turbidity	NTU	<0.05	0.08	<0.05	0.15	Suspended particles in solution
Uranium	mg/L	<0.0005	0.0006	<0.0005	0.02	Industrial effluents or spills
Vanadium	mg/L	<0.0005	0.0012	<0.0005	No Guideline	Naturally occurring (erosion and weathering of rocks and soils)
Vinyl Chloride	mg/L	<0.0005			0.002	Industrial effluents; degradation product from organic solvents in groundwater; leaching from polyvinyl chloride pipes
Virus, Min. Log Reduction Ratio[3]	no units	1.5			Treatment Goal	Domestic animals, wildlife and human waste
Xylenes, total[3]	mg/L	<0.001			0.09 0.02 (A)	Emissions, effluents or spills from petroleum and chemical industries
Zinc	mg/L	<0.003	0.003	<0.003	5.0 (A)	Erosion of natural deposits in watershed. Leaching may occur from galvanized pipes, hot water tanks and brass fittings

Legend

[1] Maximum acceptable concentrations and

Information hyperlinks

Health Canada Guidelines for Canadian Drinking

Health Canada Water Quality - Reports and

Alberta Environment & Parks

[2] The City of Calgary ceased fluoridation of its drinking water on May 19, 2011.

[3] Calculated parameter based on individual analytes

(O) Operating guidance as determined by Health Canada

(A) Aesthetic Objective as determined by Health Canada

(AEP) Alberta Environment and Parks provincial guidance

< Indicates not detected above the specified value

Bq/L = Becquerel per litre

mg/L = milligrams per litre, or parts per million (ppm)

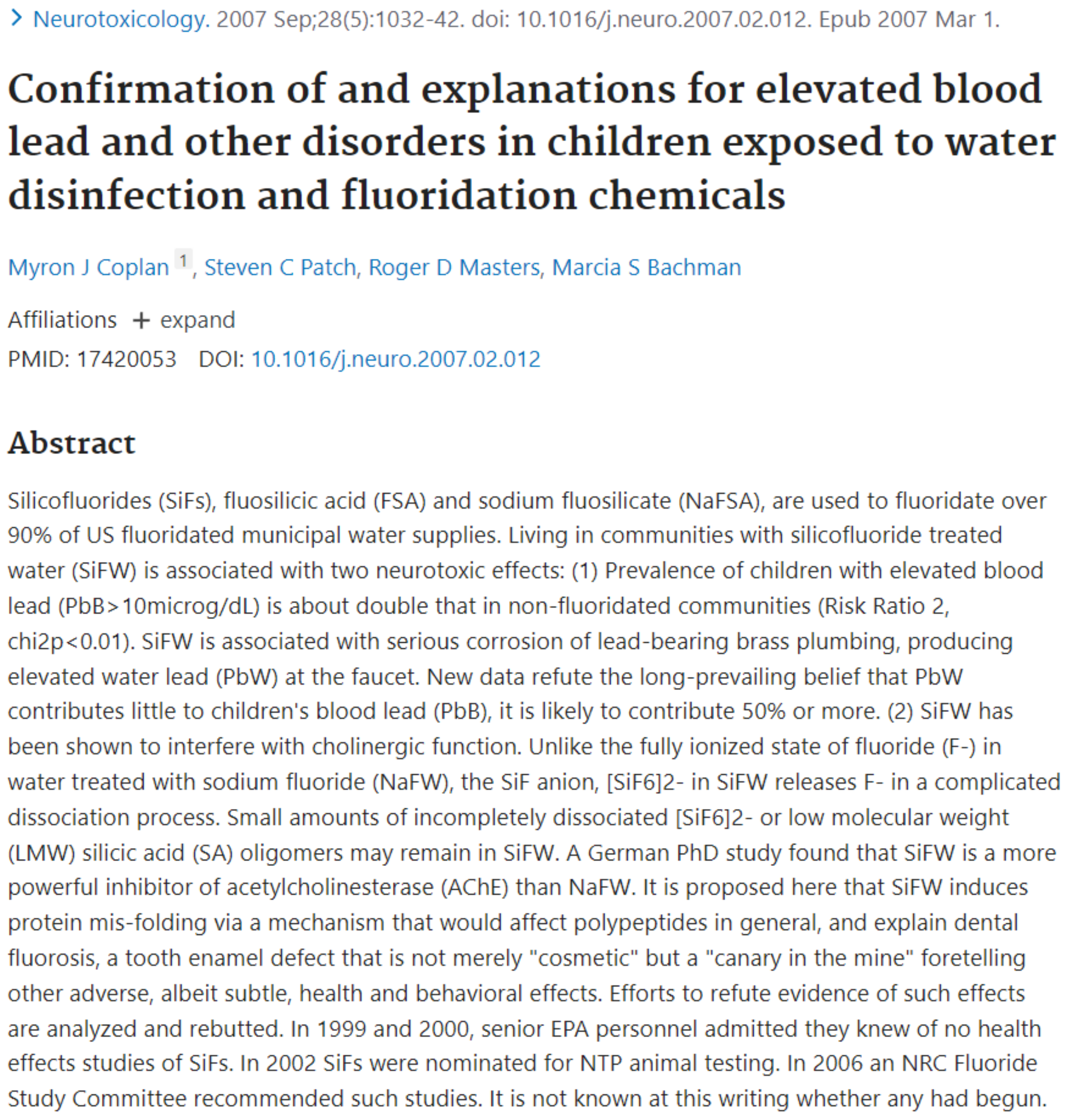
MPN = Most-Probable Number

NTU = Nephelometric Turbidity Units

TCU = True Colour Units

Treatment Goal = Calculated log removals are health based treatment goals for enteric protozoa and viruses as determined by Health Canada.

APPENDIX B



› Neurotoxicology. 2007 Sep;28(5):1032-42. doi: 10.1016/j.neuro.2007.02.012. Epub 2007 Mar 1.

Confirmation of and explanations for elevated blood lead and other disorders in children exposed to water disinfection and fluoridation chemicals

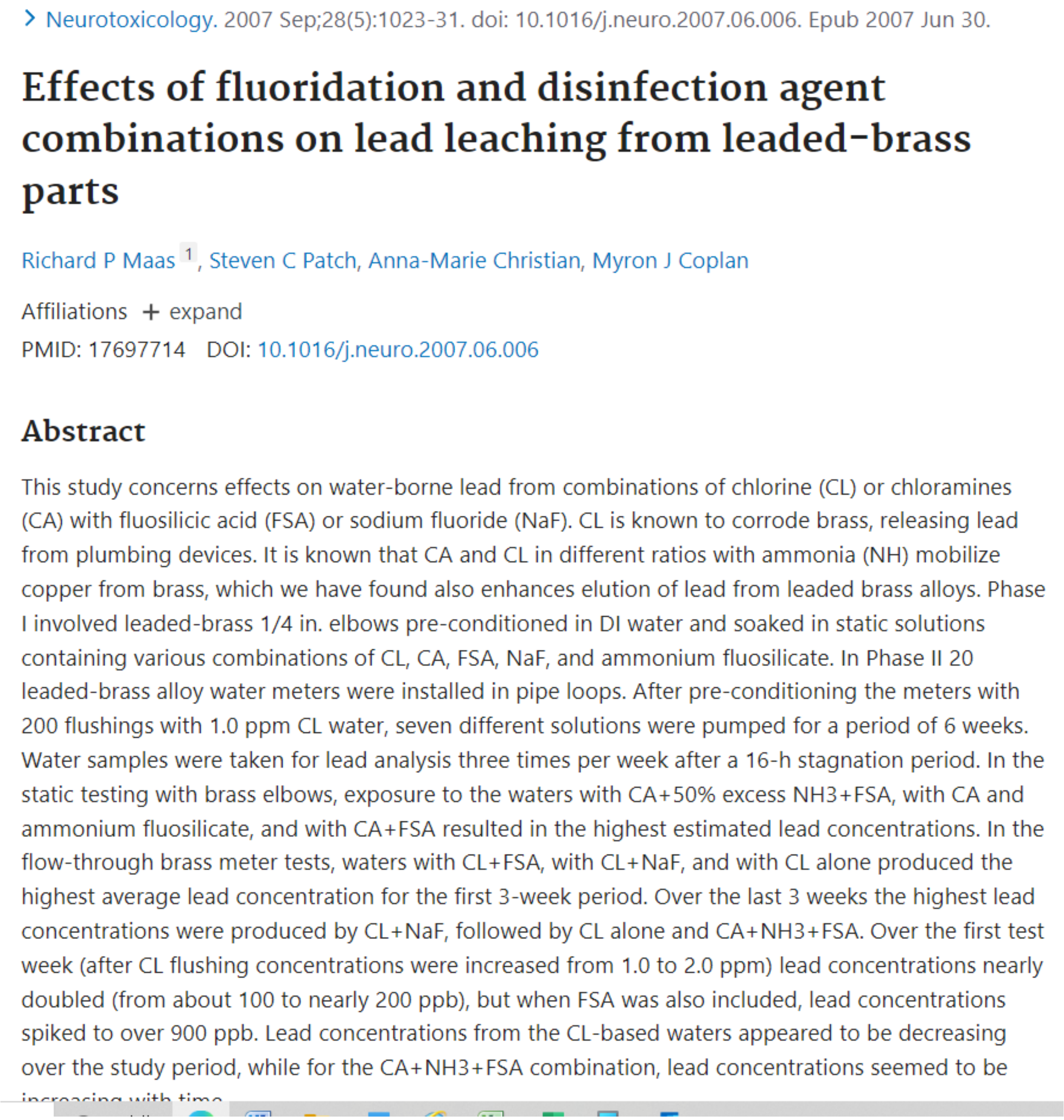
Myron J Coplan [1], Steven C Patch, Roger D Masters, Marcia S Bachman

Affiliations + expand

PMID: 17420053 DOI: 10.1016/j.neuro.2007.02.012

Abstract

Silicofluorides (SiFs), fluosilicic acid (FSA) and sodium fluosilicate (NaFSA), are used to fluoridate over 90% of US fluoridated municipal water supplies. Living in communities with silicofluoride treated water (SiFW) is associated with two neurotoxic effects: (1) Prevalence of children with elevated blood lead (PbB>10microg/dL) is about double that in non-fluoridated communities (Risk Ratio 2, chi2p<0.01). SiFW is associated with serious corrosion of lead-bearing brass plumbing, producing elevated water lead (PbW) at the faucet. New data refute the long-prevailing belief that PbW contributes little to children's blood lead (PbB), it is likely to contribute 50% or more. (2) SiFW has been shown to interfere with cholinergic function. Unlike the fully ionized state of fluoride (F-) in water treated with sodium fluoride (NaFW), the SiF anion, [SiF6]2- in SiFW releases F- in a complicated dissociation process. Small amounts of incompletely dissociated [SiF6]2- or low molecular weight (LMW) silicic acid (SA) oligomers may remain in SiFW. A German PhD study found that SiFW is a more powerful inhibitor of acetylcholinesterase (AChE) than NaFW. It is proposed here that SiFW induces protein mis-folding via a mechanism that would affect polypeptides in general, and explain dental fluorosis, a tooth enamel defect that is not merely "cosmetic" but a "canary in the mine" foretelling other adverse, albeit subtle, health and behavioral effects. Efforts to refute evidence of such effects are analyzed and rebutted. In 1999 and 2000, senior EPA personnel admitted they knew of no health effects studies of SiFs. In 2002 SiFs were nominated for NTP animal testing. In 2006 an NRC Fluoride Study Committee recommended such studies. It is not known at this writing whether any had begun.



› Neurotoxicology. 2007 Sep;28(5):1023-31. doi: 10.1016/j.neuro.2007.06.006. Epub 2007 Jun 30.

Effects of fluoridation and disinfection agent combinations on lead leaching from leaded-brass parts

Richard P Maas [1], Steven C Patch, Anna-Marie Christian, Myron J Coplan

Affiliations + expand

PMID: 17697714 DOI: 10.1016/j.neuro.2007.06.006

Abstract

This study concerns effects on water-borne lead from combinations of chlorine (CL) or chloramines (CA) with fluosilicic acid (FSA) or sodium fluoride (NaF). CL is known to corrode brass, releasing lead from plumbing devices. It is known that CA and CL in different ratios with ammonia (NH) mobilize copper from brass, which we have found also enhances elution of lead from leaded brass alloys. Phase I involved leaded-brass 1/4 in. elbows pre-conditioned in DI water and soaked in static solutions containing various combinations of CL, CA, FSA, NaF, and ammonium fluosilicate. In Phase II 20 leaded-brass alloy water meters were installed in pipe loops. After pre-conditioning the meters with 200 flushings with 1.0 ppm CL water, seven different solutions were pumped for a period of 6 weeks. Water samples were taken for lead analysis three times per week after a 16-h stagnation period. In the static testing with brass elbows, exposure to the waters with CA+50% excess NH3+FSA, with CA and ammonium fluosilicate, and with CA+FSA resulted in the highest estimated lead concentrations. In the flow-through brass meter tests, waters with CL+FSA, with CL+NaF, and with CL alone produced the highest average lead concentration for the first 3-week period. Over the last 3 weeks the highest lead concentrations were produced by CL+NaF, followed by CL alone and CA+NH3+FSA. Over the first test week (after CL flushing concentrations were increased from 1.0 to 2.0 ppm) lead concentrations nearly doubled (from about 100 to nearly 200 ppb), but when FSA was also included, lead concentrations spiked to over 900 ppb. Lead concentrations from the CL-based waters appeared to be decreasing over the study period, while for the CA+NH3+FSA combination, lead concentrations seemed to be increasing with time.

APPENDIX C

FLUOROSILICIC ACID, 23-25%

1. PRODUCT AND COMPANY IDENTIFICATION

1.1. Identification of the substance or preparation

Product name : FLUOROSILICIC ACID, 23-25%
Synonyms : Fluorosilicic Acid, Fluosilicic Acid, Hydrofluorosilicic Acid
Molecular formula : H_2SiF_6

1.2. Use of the Substance/Preparation

Recommended use :
- Chemical intermediate
- Water treatment

1.3. Company/Undertaking Identification

Address :
SOLVAY FLUORIDES, LLC
3333 RICHMOND AVENUE
HOUSTON TX 77098-3099
United States

1.4. Emergency and contact telephone numbers

Emergency telephone : **1 (800) 424-9300 CHEMTREC ® (USA & Canada)**
01-800-00-214-00 (MEX. REPUBLIC)

Contact telephone number (product information): : **US: +1-800-765-8292 (Product information)**
US: +1-713-525-6500 (Product information)

2. HAZARDS IDENTIFICATION

2.1. Emergency Overview:

NFPA : H= 3 F= 0 I= 0 S= None
HMIS : H= 3 F= 0 R= 0 PPE = Supplied by User; dependent on local conditions

General Information

Appearance : liquid
Colour : colourless
Odour : pungent

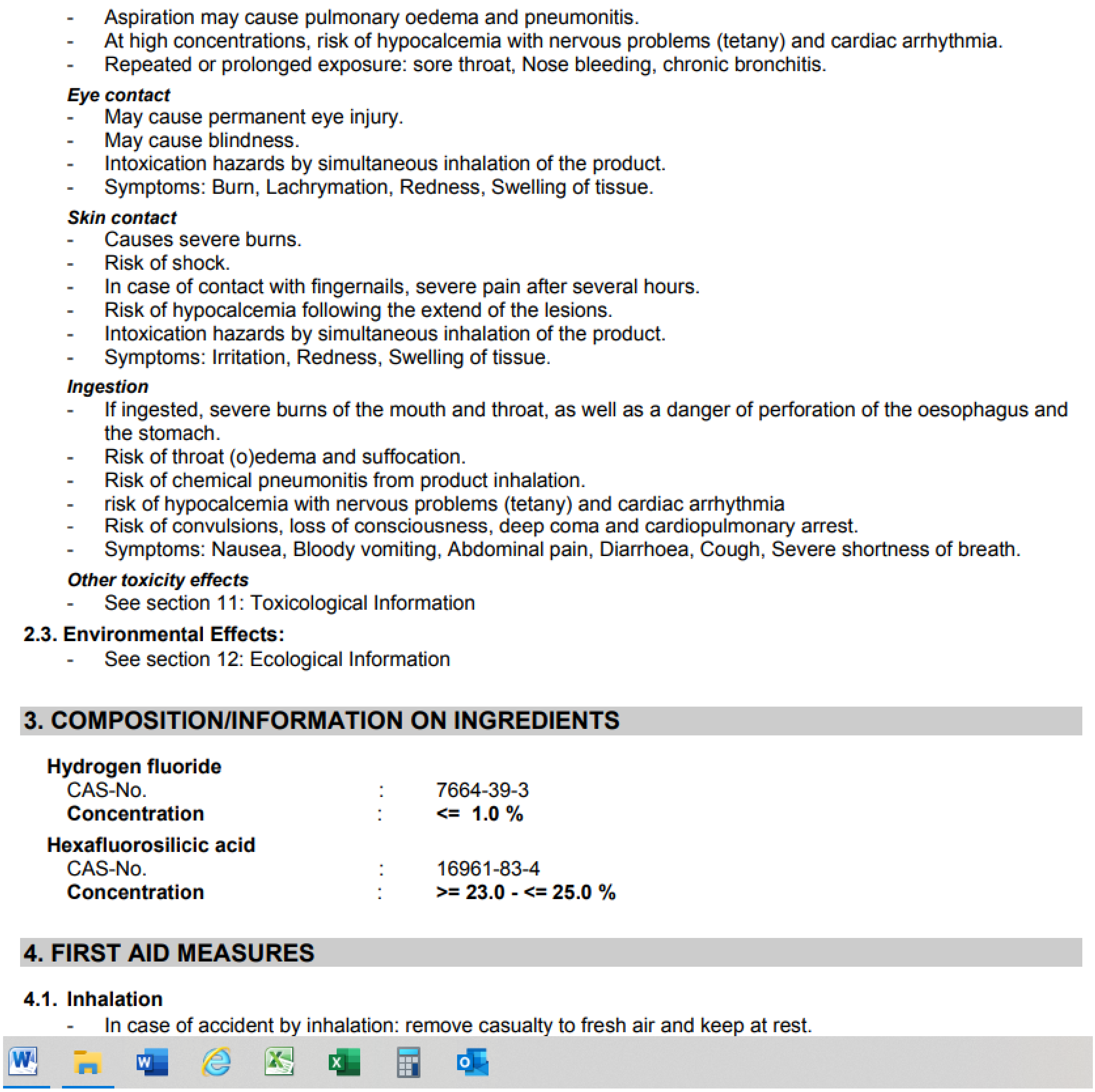
Main effects

- Hazardous decomposition products formed under fire conditions.
- Corrosive
- Harmful by inhalation, in contact with skin and if swallowed.

2.2. Potential Health Effects:

Inhalation

- Inhalation of vapours is irritating to the respiratory system, may cause throat pain and cough.
- Breathing difficulties



- Aspiration may cause pulmonary oedema and pneumonitis.
- At high concentrations, risk of hypocalcemia with nervous problems (tetany) and cardiac arrhythmia.
- Repeated or prolonged exposure: sore throat, Nose bleeding, chronic bronchitis.

Eye contact

- May cause permanent eye injury.
- May cause blindness.
- Intoxication hazards by simultaneous inhalation of the product.
- Symptoms: Burn, Lachrymation, Redness, Swelling of tissue.

Skin contact

- Causes severe burns.
- Risk of shock.
- In case of contact with fingernails, severe pain after several hours.
- Risk of hypocalcemia following the extend of the lesions.
- Intoxication hazards by simultaneous inhalation of the product.
- Symptoms: Irritation, Redness, Swelling of tissue.

Ingestion

- If ingested, severe burns of the mouth and throat, as well as a danger of perforation of the oesophagus and the stomach.
- Risk of throat (o)edema and suffocation.
- Risk of chemical pneumonitis from product inhalation.
- risk of hypocalcemia with nervous problems (tetany) and cardiac arrhythmia
- Risk of convulsions, loss of consciousness, deep coma and cardiopulmonary arrest.
- Symptoms: Nausea, Bloody vomiting, Abdominal pain, Diarrhoea, Cough, Severe shortness of breath.

Other toxicity effects

- See section 11: Toxicological Information

2.3. Environmental Effects:

- See section 12: Ecological Information

3. COMPOSITION/INFORMATION ON INGREDIENTS

Hydrogen fluoride
CAS-No. : 7664-39-3
Concentration : <= 1.0 %

Hexafluorosilicic acid
CAS-No. : 16961-83-4
Concentration : >= 23.0 - <= 25.0 %

4. FIRST AID MEASURES

4.1. Inhalation

- In case of accident by inhalation: remove casualty to fresh air and keep at rest.

NEW JERSEY DEPARTMENT of HEALTH and SENIOR SERVICES

New Jersey Department of Health and Senior Services

HAZARDOUS SUBSTANCE FACT SHEET

Common Name: **SODIUM FLUOROSILICATE**

CAS Number: 16893-85-9
DOT Number: UN 2674

RTK Substance number: 1701
Date: August 1999

HAZARD SUMMARY

- **Sodium Fluorosilicate** can affect you when breathed in.
- **Sodium Fluorosilicate** can irritate the skin causing a rash or burning feeling on contact.
- **Sodium Fluorosilicate** can irritate the eyes on contact.
- Breathing **Sodium Fluorosilicate** can irritate the nose, throat and lungs causing coughing, wheezing and/or shortness of breath.
- High exposure to **Sodium Fluorosilicate** can cause a salty or soapy taste in the mouth, nausea, vomiting, abdominal cramps and diarrhea, muscle weakness, tremors, loss of consciousness, convulsions and death.
- Repeated high exposure can cause deposits of *Fluorides* in the bones and teeth, a condition called "*Fluorosis.*" This can cause pain, disability and mottling of the teeth.
- The above health effects do NOT occur at the level of *Fluoride* used in water for preventing cavities in teeth.
- *CONSULT THE NEW JERSEY DEPARTMENT OF HEALTH AND SENIOR SERVICES HAZARDOUS SUBSTANCE FACT SHEET ON FLUORIDES.*

IDENTIFICATION

Sodium Fluorosilicate is a white granular powder. It is used as a fluoridation agent for drinking water and in enamels for china and porcelain. It is also used as an insecticide, rodenticide and a veterinary treatment for lice.

REASON FOR CITATION

- **Sodium Fluorosilicate** is on the Hazardous Substance List because it is regulated by OSHA and cited by ACGIH, DOT, NIOSH, IARC, HHAG and EPA.
- Definitions are provided on page 5.

HOW TO DETERMINE IF YOU ARE BEING EXPOSED

The New Jersey Right to Know Act requires most employers to label chemicals in the workplace and requires public employers to provide their employees with information and training concerning chemical hazards and controls. The federal OSHA Hazard Communication Standard, 1910.1200, requires private employers to provide similar training and information to their employees.

- Exposure to hazardous substances should be routinely evaluated. This may include collecting personal and area air samples. You can obtain copies of sampling results from your employer. You have a legal right to this information under OSHA 1910.1020.
- If you think you are experiencing any work-related health problems, see a doctor trained to recognize occupational diseases. Take this Fact Sheet with you.

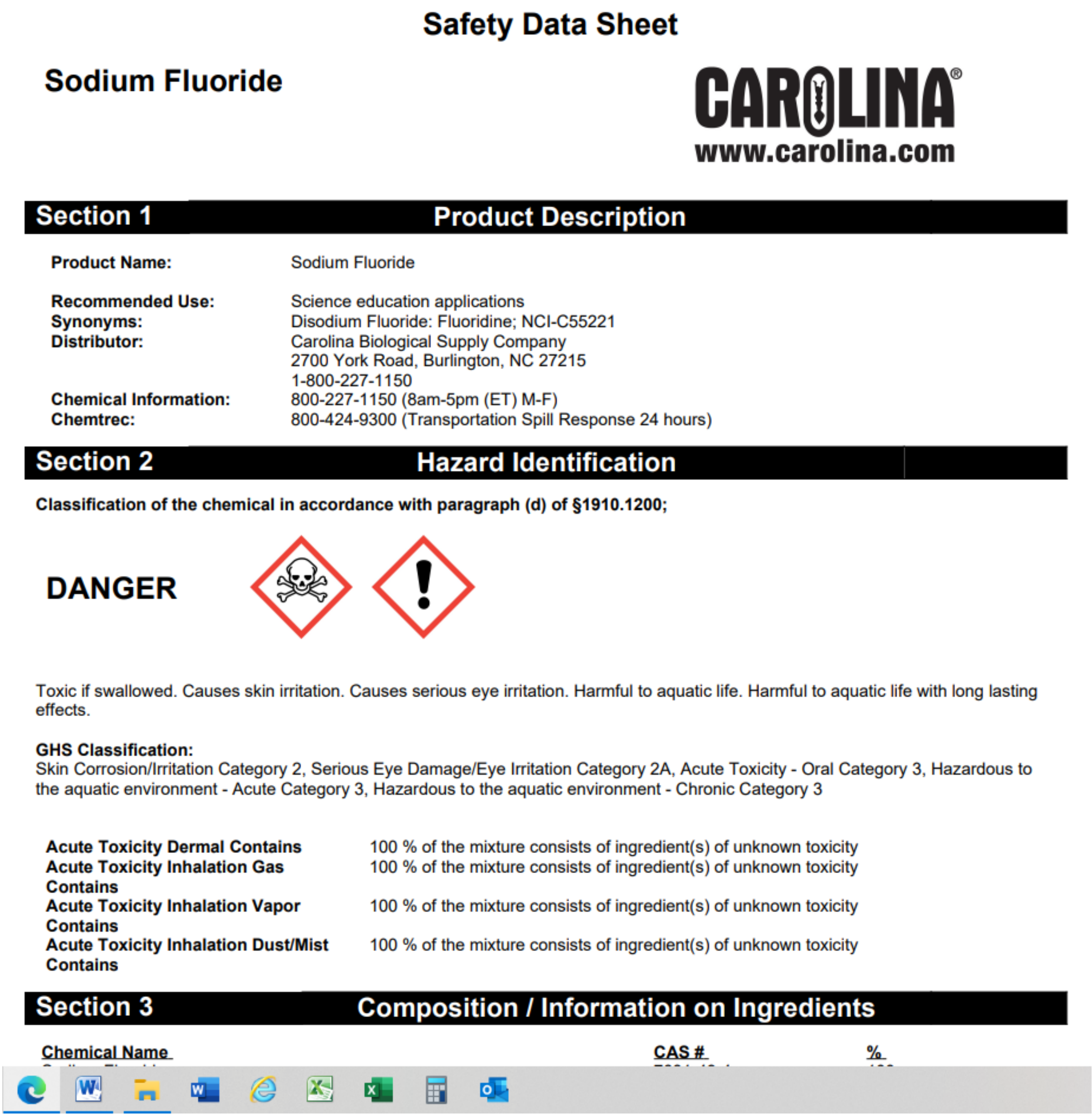
WORKPLACE EXPOSURE LIMITS

The following exposure limits are for *Fluorides* (measured as *Fluoride*):

OSHA:	The legal airborne permissible exposure limit (PEL) is **2.5 mg/m^3** averaged over an 8-hour workshift.
NIOSH:	The recommended airborne exposure limit is **2.5 mg/m^3** averaged over a 10-hour workshift.
ACGIH:	The recommended airborne exposure limit is **2.5 mg/m^3** averaged over an 8-hour workshift.

WAYS OF REDUCING EXPOSURE

- Where possible, enclose operations and use local exhaust ventilation at the site of chemical release. If local exhaust ventilation or enclosure is not used, respirators should be worn.
- Wear protective work clothing.
- Wash thoroughly immediately after exposure to **Sodium Fluorosilicate** and at the end of the workshift.
- Post hazard and warning information in the work area. In addition, as part of an ongoing education and training effort, communicate all information on the health and safety hazards of **Sodium Fluorosilicate** to potentially exposed workers.



Safety Data Sheet

Sodium Fluoride

Section 1 Product Description

Product Name:	Sodium Fluoride
Recommended Use:	Science education applications
Synonyms:	Disodium Fluoride: Fluoridine; NCI-C55221
Distributor:	Carolina Biological Supply Company 2700 York Road, Burlington, NC 27215 1-800-227-1150
Chemical Information:	800-227-1150 (8am-5pm (ET) M-F)
Chemtrec:	800-424-9300 (Transportation Spill Response 24 hours)

Section 2 Hazard Identification

Classification of the chemical in accordance with paragraph (d) of §1910.1200;

DANGER

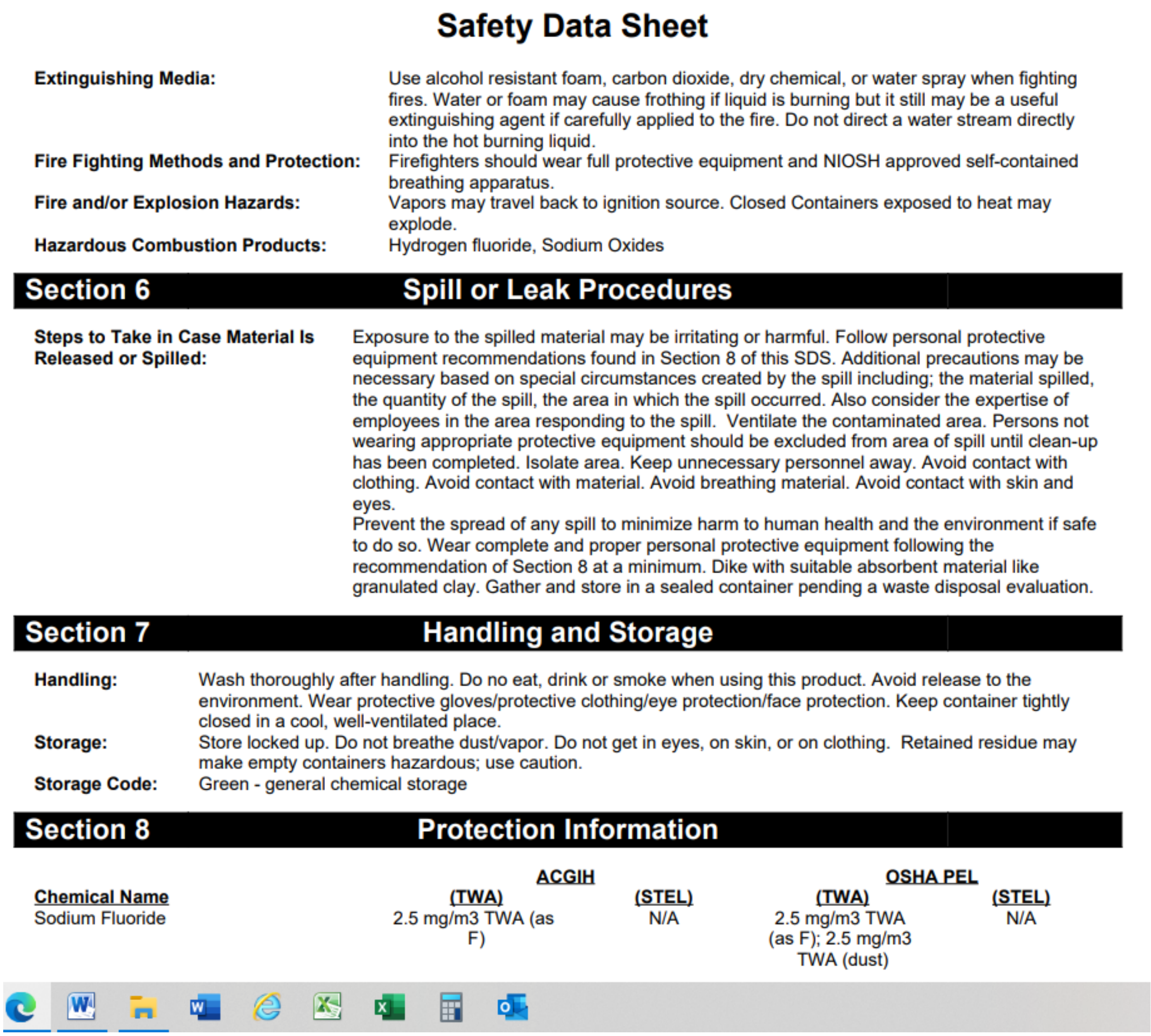
Toxic if swallowed. Causes skin irritation. Causes serious eye irritation. Harmful to aquatic life. Harmful to aquatic life with long lasting effects.

GHS Classification:
Skin Corrosion/Irritation Category 2, Serious Eye Damage/Eye Irritation Category 2A, Acute Toxicity - Oral Category 3, Hazardous to the aquatic environment - Acute Category 3, Hazardous to the aquatic environment - Chronic Category 3

Acute Toxicity Dermal Contains	100 % of the mixture consists of ingredient(s) of unknown toxicity
Acute Toxicity Inhalation Gas Contains	100 % of the mixture consists of ingredient(s) of unknown toxicity
Acute Toxicity Inhalation Vapor Contains	100 % of the mixture consists of ingredient(s) of unknown toxicity
Acute Toxicity Inhalation Dust/Mist Contains	100 % of the mixture consists of ingredient(s) of unknown toxicity

Section 3 Composition / Information on Ingredients

Chemical Name	**CAS #**	**%**



Safety Data Sheet

Extinguishing Media:	Use alcohol resistant foam, carbon dioxide, dry chemical, or water spray when fighting fires. Water or foam may cause frothing if liquid is burning but it still may be a useful extinguishing agent if carefully applied to the fire. Do not direct a water stream directly into the hot burning liquid.
Fire Fighting Methods and Protection:	Firefighters should wear full protective equipment and NIOSH approved self-contained breathing apparatus.
Fire and/or Explosion Hazards:	Vapors may travel back to ignition source. Closed Containers exposed to heat may explode.
Hazardous Combustion Products:	Hydrogen fluoride, Sodium Oxides

Section 6 Spill or Leak Procedures

Steps to Take in Case Material Is Released or Spilled:

Exposure to the spilled material may be irritating or harmful. Follow personal protective equipment recommendations found in Section 8 of this SDS. Additional precautions may be necessary based on special circumstances created by the spill including; the material spilled, the quantity of the spill, the area in which the spill occurred. Also consider the expertise of employees in the area responding to the spill. Ventilate the contaminated area. Persons not wearing appropriate protective equipment should be excluded from area of spill until clean-up has been completed. Isolate area. Keep unnecessary personnel away. Avoid contact with clothing. Avoid contact with material. Avoid breathing material. Avoid contact with skin and eyes.

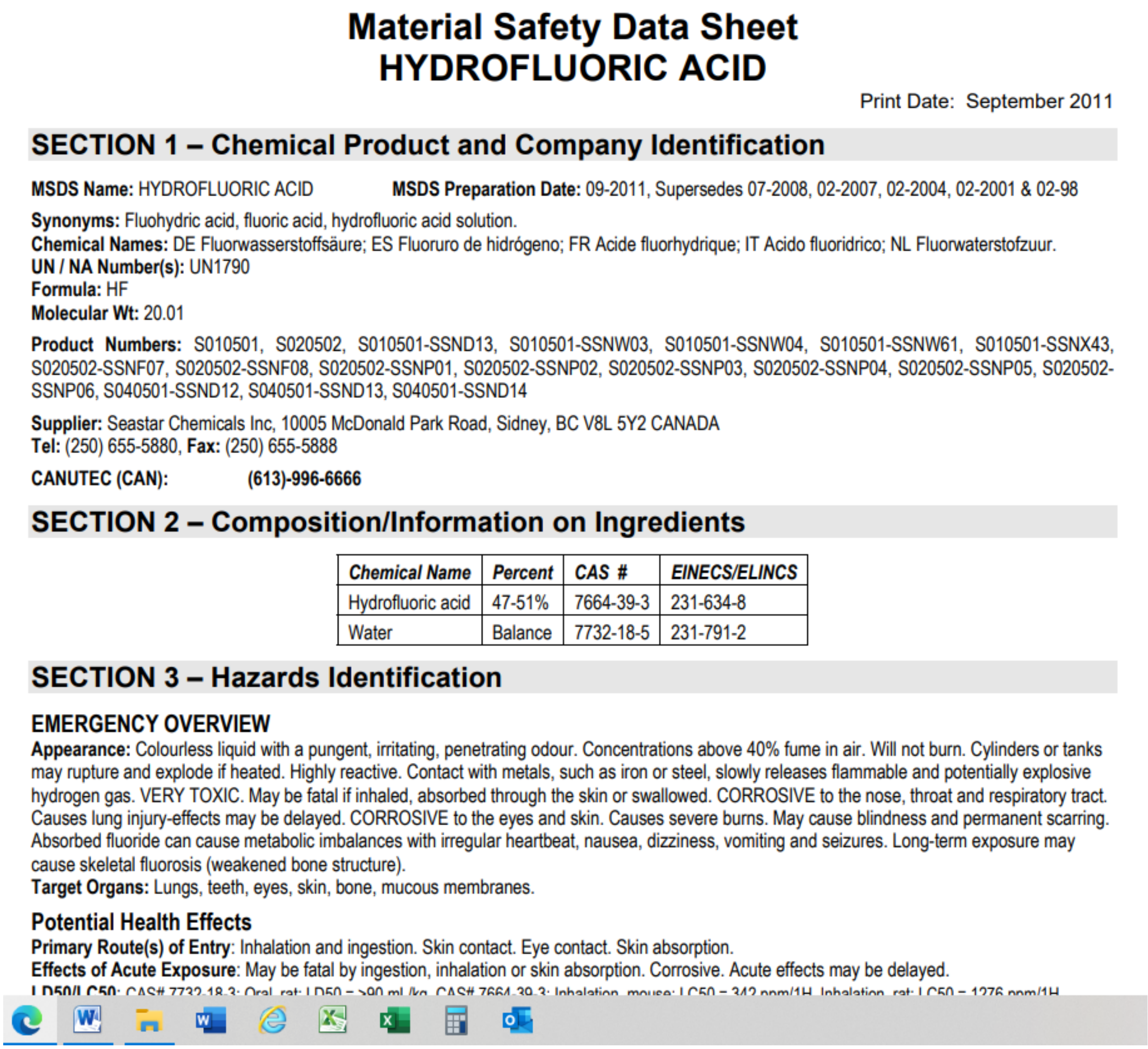
Prevent the spread of any spill to minimize harm to human health and the environment if safe to do so. Wear complete and proper personal protective equipment following the recommendation of Section 8 at a minimum. Dike with suitable absorbent material like granulated clay. Gather and store in a sealed container pending a waste disposal evaluation.

Section 7 Handling and Storage

Handling:	Wash thoroughly after handling. Do no eat, drink or smoke when using this product. Avoid release to the environment. Wear protective gloves/protective clothing/eye protection/face protection. Keep container tightly closed in a cool, well-ventilated place.
Storage:	Store locked up. Do not breathe dust/vapor. Do not get in eyes, on skin, or on clothing. Retained residue may make empty containers hazardous; use caution.
Storage Code:	Green - general chemical storage

Section 8 Protection Information

	ACGIH		OSHA PEL	
Chemical Name	**(TWA)**	**(STEL)**	**(TWA)**	**(STEL)**
Sodium Fluoride	2.5 mg/m3 TWA (as F)	N/A	2.5 mg/m3 TWA (as F); 2.5 mg/m3 TWA (dust)	N/A



Material Safety Data Sheet
HYDROFLUORIC ACID

Print Date: September 2011

SECTION 1 – Chemical Product and Company Identification

MSDS Name: HYDROFLUORIC ACID **MSDS Preparation Date:** 09-2011, Supersedes 07-2008, 02-2007, 02-2004, 02-2001 & 02-98

Synonyms: Fluohydric acid, fluoric acid, hydrofluoric acid solution.
Chemical Names: DE Fluorwasserstoffsäure; ES Fluoruro de hidrógeno; FR Acide fluorhydrique; IT Acido fluoridrico; NL Fluorwaterstofzuur.
UN / NA Number(s): UN1790
Formula: HF
Molecular Wt: 20.01

Product Numbers: S010501, S020502, S010501-SSND13, S010501-SSNW03, S010501-SSNW04, S010501-SSNW61, S010501-SSNX43, S020502-SSNF07, S020502-SSNF08, S020502-SSNP01, S020502-SSNP02, S020502-SSNP03, S020502-SSNP04, S020502-SSNP05, S020502-SSNP06, S040501-SSND12, S040501-SSND13, S040501-SSND14

Supplier: Seastar Chemicals Inc, 10005 McDonald Park Road, Sidney, BC V8L 5Y2 CANADA
Tel: (250) 655-5880, **Fax:** (250) 655-5888

CANUTEC (CAN): **(613)-996-6666**

SECTION 2 – Composition/Information on Ingredients

Chemical Name	***Percent***	***CAS #***	***EINECS/ELINCS***
Hydrofluoric acid	47-51%	7664-39-3	231-634-8
Water	Balance	7732-18-5	231-791-2

SECTION 3 – Hazards Identification

EMERGENCY OVERVIEW

Appearance: Colourless liquid with a pungent, irritating, penetrating odour. Concentrations above 40% fume in air. Will not burn. Cylinders or tanks may rupture and explode if heated. Highly reactive. Contact with metals, such as iron or steel, slowly releases flammable and potentially explosive hydrogen gas. VERY TOXIC. May be fatal if inhaled, absorbed through the skin or swallowed. CORROSIVE to the nose, throat and respiratory tract. Causes lung injury-effects may be delayed. CORROSIVE to the eyes and skin. Causes severe burns. May cause blindness and permanent scarring. Absorbed fluoride can cause metabolic imbalances with irregular heartbeat, nausea, dizziness, vomiting and seizures. Long-term exposure may cause skeletal fluorosis (weakened bone structure).
Target Organs: Lungs, teeth, eyes, skin, bone, mucous membranes.

Potential Health Effects

Primary Route(s) of Entry: Inhalation and ingestion. Skin contact. Eye contact. Skin absorption.
Effects of Acute Exposure: May be fatal by ingestion, inhalation or skin absorption. Corrosive. Acute effects may be delayed.
LD50/LC50: CAS# 7732-18-3: Oral, rat: LD50 = >90 ml /kg, CAS# 7664-39-3: Inhalation, mouse: LC50 = 342 ppm/1H, Inhalation, rat: LC50 = 1276 ppm/1H