STATE OF NEW HAMPSHIRE

Department of Environmental Services

Air Resources Division

Memorandum

To: C. Beahm-SIP Planning Administrator **Date:** February 7, 2020

From: D. Larson, M.P.H. – EHP **Cc:** P. North, M.P.H.-EHP Administrator

RE: Review of Hydrogen fluoride (CASRN 7664-39-3) health risks

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The Environmental Health Program (EHP) has reviewed four (4) public comment documents [i,ii,iii,iv]submitted to the New Hampshire Department of Environmental Services (NHDES) Air Resources Division related to the Saint Gobain Performance Plastics (SGPP) draft air permit. In summary, a concern expressed in the documents is that hydrogen fluoride (HF) will be generated during the destruction of per- and polyfluoroalkyl substances (PFAS) that may have adverse health impacts in the surrounding area. Therefore, the public comments were that a scrubber should be added to the Regenerative Thermal Oxidizer (RTO) to limit potential HF exposure.

BACKGROUND

HF is a colorless, fuming liquid or gas that is lighter than air with a strong, irritating odor that is discernable at concentrations of about 0.04 ppm (32.7 µg/m^3) and readily dissolves in water to form colorless hydrofluoric acid (HA) solutions; with dilute solutions visibly indistinguishable from water. People breathing HF have complained of eye, nose, and skin irritation and breathing in a large amount can also harm the lungs and heart. Kidney and testes damage have been observed in animals breathing HF. Systemic effects can occur from all routes of exposure and may include nausea, vomiting, gastric pain, or cardiac arrhythmia. Symptoms may be delayed for several days, especially in the case of exposure to dilute solutions of HF (less than 20%). The systemic effects of HF are due to increased fluoride concentrations in the body which can change the levels of calcium, magnesium, and potassium in the blood. Children exposed to the same levels of HF as adults may receive larger doses because they have greater lung surface area: body weight ratios and increased minute volumes: weight ratios. Children may also be more vulnerable to corrosive agents than adults because of the relatively smaller diameter of their airways.[v]

Hydrofluoric acid (HA) is dangerous to humans because it can burn the eyes and skin. The initial exposure to HA may not look like a typical acid burn. Skin may only appear red and may not be painful at first. Damage to skin may happen over several hours or days, and deep, painful wounds may develop. When not treated properly, serious skin damage and tissue loss can occur. In the worst cases, getting a large amount of HF on your skin can lead to death caused by the fluoride affecting your lungs and heart. [v]

DISCUSSION

According to RSA 125-I, *Air Toxic Control Act*, NHDES must regulate "releases of toxic chemicals into the ambient air" and must adopt rules designating short-term and long-term ambient air limits (AALs) which "shall rely on threshold limit values, reference concentration (RfC) limits and such other generally accepted scientific data as may be available." The EHP reviews and evaluates changes to health information published by the United States Environmental Protection Agency (US EPA) in the Integrated Risk Information System (IRIS), and changes in the occupational exposure levels adopted by the American Conference of Governmental Industrial Hygienists (ACGIH) and other available scientific literature in formulating changes to the AALs. These requirements have been codified in Env-A 1400, *Regulated Toxic Air Pollutants*. Sections Env-A 1406 through Env-A 1410 dictate the methodology the EHP uses to derive the AALs and these calculations can be found in Appendix A. Using the methodology, the 24-hour AAL is 1.5 µg/m^3 and the Annual AAL is 0.98 µg/m^3. Below is a summary of the EHP approach and the basis for several comparison values.

The US EPA has not published a RfC for HF on IRIS which would be the basis for the AALs. A RfC is defined as an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. Because there is no RfC, the EHP based the calculation of the AALs on the ACGIH Threshold Limit Value (TLV) of 0.5 ppm (410 µg/m^3), measured as fluoride (F). The EHP reviewed the literature and assigned a Toxicity Class of 1 and a Time Adjustment Factor of D, resulting in the most conservative (lowest) Annual and 24-hour AALs possible according to the methodology. The TLV value is intended to minimize the potential for adverse effects in the respiratory tract, dermal or skeletal fluorosis, and irritation of the eyes and skin.[vi] Although the TLV is for an occupational scenario, the incorporation of the Toxicity Factor and Time Adjustment Factor reduces the TLV to concentrations below the California Environmental Protection Agency (Cal EPA) chronic Reference Exposure Level[1] (REL)[vii] of 14 µg/m^3 and the Agency for Toxic Substances & Disease Registry (ATSDR) acute Minimal Risk Level[2] (MRL)[viii] of 16 µg/m^3.

The respiratory tract appears to be the primary target of HF toxicity. Upper respiratory tract irritation and inflammation and lower respiratory tract inflammation have been observed in several human studies. Nasal irritation was reported by one subject exposed to 3.22 ppm (2,635 µg/m^3) fluoride as HF for 6 hours per day for 10 days. Very mild to moderate upper respiratory symptoms were reported by healthy men exposed to 0.5 ppm (409 µg/m^3) fluoride as HF for 1 hour. At higher concentrations, 4.2-4.5 ppm (3,437 -3,682 µg/m^3) fluoride as HF for 1 hour, more severe symptoms of upper respiratory irritation were noted. The MRL is based on the minimal lowest observed adverse effect level (LOAEL) of 0.5 ppm (410 µg/m^3) fluoride for upper respiratory tract irritation. An intermediate-duration study[ix] provides suggestive evidence that the severity of nasal irritation does not increase with increasing exposure duration. Three studies identified similar LOAEL values for different exposure durations, thus time scaling was not used to derive the acute inhalation MRL. There are limited data on the long-term toxicity of HF. Slight nasal irritation was reported by volunteers exposed to an average concentration of 2.98 ppm (2,439 µg/m^3) fluoride, 6 hours per day for 15-50 days.[vi] However, an intermediate-duration inhalation MRL was not derived for HF based on the study because the intermediate inhalation MRL would have been higher than the acute inhalation MRL. No chronic-duration studies were located for HF; thus a chronic-duration inhalation MRL was not derived by ATSDR for HF.[v] The Cal EPA has developed a chronic inhalation REL for HF based on impacts to bone and teeth.[viii]

CONCLUSION

As illustrated in the table below, Cal EPA has developed a chronic REL of 14 µg HF/m^3, 14x greater than the New Hampshire (NH) Annual AAL (0.98 µg/m^3). The ATSDR has developed an acute MRL of 16 µg/m^3 which is 10x greater than the NH 24-hour AAL. Based on the information in the above discussion, EHP concludes that concentrations of HF at or below the AALs are not anticipated to result in adverse health effects to potential receptors, including sensitive individuals.

Concentration (µg/m^3) of Hydrogen Fluoride Established by Various Agencies

Toxicity/Health Value		Regulatory or Advisory Value			
ATSDR MRL (acute)	**Cal EPA REL**	**OSHA PEL[x]**	**ACGIH TLV**	**NH 24-hour AAL**	**NH Annual AAL**
16[3]	14	2,500	410	1.5	0.98

[1] The chronic REL is similar to the US EPA RfC and is designed to address continuous exposures for up to a lifetime with no health effects anticipated; with the exposure metric being the annual average exposure.

[2] A MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure. These substance specific estimates, which are intended to serve as screening levels, are used by ATSDR health assessors and other responders to identify contaminants and potential health effects that may be of concern at hazardous waste sites. ATSDR uses the no observed adverse effect level/uncertainty factor approach to derive MRLs for hazardous substances. ATSDR has developed only an acute (1-14 days) MRL for HF.

[3] Human inhalation exposure at 0.5 ppm resulted in upper respiratory irritation. This LOAEL was used to derive an acute-duration minimal risk level (MRL) of 0.02 ppm; the concentration was divided by an uncertainty factor of 30 (3 for use of a minimal LOAEL and 10 to account for human variability). EHP converted ppm to µg/m^3 using formula: µg/m^3 = ((molecular weight x ppm) / 24.45)) x 1000

DEFINITIONS

Occupational Safety and Health Administration (OSHA) Permissible exposure limit (PEL): A time-weighted average; the concentration of a substance that should not be exceeded during any 8-hour work shift of a 40-hour workweek.

ACGIH TLV--American Conference of Governmental and Industrial Hygienists' threshold limit value; the concentration for a conventional 8-hour workday and a 40-hour workweek to which it is believed that nearly all workers may be repeatedly exposed, day after day, for a working lifetime, without adverse effect. For hydrogen fluoride, the TLV is a time-weighted average concentration.

APPENDIX A

Env-A 1400 AAL Example Calculations

$$AAL_{Annual} = \frac{OEL}{(SF \times 4.2)} \qquad AAL_{24-Hr} = \frac{OEL}{(SF \times TAF)}$$

Where:

OEL = Occupational exposure limit (µg/m^3)

SF = Safety factor determined by Env-A 1407 [Tox Class I = 100]

TAF = Time Adjustment Factor [D = 2.8]

Where: 4.2 = (24 hours per day / 8 hours per work day) * (7 days per week / 5 day work week)

Hydrogen fluoride

$$\boldsymbol{AAL_{Annual} = \frac{410^{\mu g}/_{m^3}}{100 \times 4.2} = 0.98\ \mu g/m^3} \qquad \boldsymbol{AAL_{24-Hr} = \frac{410^{\mu g}/_{m^3}}{(100 \times 2.8)} = 1.5\ \mu g/m^3}$$

REFERENCES

[i] Public Comment, Town of Merrimack, November 1, 2019

[ii] Public Comment, Rosemarie Rung, November 4, 2019

[iii] Public Comment, Carol DiPirro, November 9, 2019

[iv] Public Comment, Town of Merrimack, December 5, 2019

[v] Agency for Toxic Substances & Disease Registry. Public Health Statement for Fluorides, Hydrogen Fluoride, and Fluorine. September 2003. https://www.atsdr.cdc.gov/phs/phs.asp?id=210&tid=38

[vi] American Conference of Governmental Industrial Hygienists. 2005: Hydrogen fluoride

[vii] Cal EPA REL--California Environmental Protection Agency (Cal EPA). Technical Support Document for the Determination of Noncancer Chronic Reference Exposure Levels. Office of Environmental Health Hazard Assessment, Berkeley, CA. 2000.

[viii] ATSDR MRL (acute)—Agency for Toxic Substances & Disease Registry (ATSDR). Toxicological Profile for Fluorides, Hydrogen Fluoride and Fluorine. U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 2003, Minimal Risk Level (December 2019).

[ix] Largent EJ. 1960. The metabolism of fluorides in man. AMA Archives of Industrial Health 21:318-323.

[x] OSHA PEL—Occupational Safety and Health Administration (OSHA). Occupational Safety and Health Standards, Toxic and Hazardous Substances. Code of Federal Regulations. 29 CFR 1910.1000. 1998.