Environmental and health risk analysis of nitrogen trifluoride (NF$_3$), a toxic and potent greenhouse gas

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ABSTRACT

This article aimed at the introduction of nitrogen trifluoride (NF$_3$) and its decomposition products into its hazards to the environment and health because this perfluorocompound is a toxic and potent greenhouse gas not blanketed into the Kyoto Protocol. This paper also predicted the global NF$_3$ emissions from the electronics industry on the basis of the methodologies recommended by the Intergovernmental Panel on Climate Change (IPCC), and further discussed its atmospheric implications according to the estimation of environmental fate for NF$_3$. It showed that the vaporization of NF$_3$ from the water bodies to the atmosphere is very high according to its predicted value (*ca.* 6.0×10^5 MPa) of Henry's law constant (K_H). Furthermore, NF$_3$ emitted from the electronics industry around the world in 2006 was estimated to be between 3.6 and 56 metric tonnes and it will be on increasing trend in the near future. Although the accumulative amount of NF$_3$ in the atmosphere currently should be very negligible based on the predicted ratio (the order of 10^{-6} to 10^{-7}) of equivalent CO$_2$ emission from NF$_3$ to total equivalent CO$_2$ emissions from potent greenhouse gases, it is necessary to adopt the available abatement and also monitor the concentration of NF$_3$ in the workplaces for reducing the overall environmental and health impacts of various semiconductor processes.

1. Introduction

Prior to the middle of 1990s, perfluorocompounds such as tetrafluoromethane (CF$_4$), hexafluoroethane (C$_2$F$_6$) and sulfur hexafluoride (SF$_6$) are commonly used in the processes of etching silicon materials and cleaning plasma enhanced chemical vapor deposition (PECVD) chamber [1,2]. In order to reach the goals of reducing these gases by the Kyoto Protocol, several specialty gases have been used as replacements for perfluorocompounds. Because of its high etching rate, higher effectiveness, relatively chemical stability and excellent electrical characteristics [3,4], nitrogen trifluoride (NF$_3$) has been enormously used as a fluorine source in the electronics industry [5]. Therefore, its usage has been more and more common over the last decade. In comparison with the global production of less than 100 metric tonnes per year in the early 1990s [6], current global production levels are believed to be about 2300 metric tonnes per year [7]. In Taiwan, the rapid growth of the semiconductor and thin film transistor liquid crystal display (TFT-LCD) manufacturing industries has resulted in the consumption of large quantities of NF$_3$ since the early 2000s. According to the industry figures by the Taiwan Semiconductor Industry Association (TSIA)

and the Taiwan TFT-LCD Association (TTLA), the demand for NF$_3$ was estimated to be over 1000 metric tonnes per year due to the local investment in the 12-in. wafer and the sixth generation TFT-LCD manufacturing fabs in recent years [8,9]. As a result, Taiwan is expected to become the largest market for NF$_3$ in the world.

It should be noted that NF$_3$ is still a radiatively active gas although it was not blanketed into one of the six target greenhouse gases under the Kyoto Protocol in 1997. According to the data adopted by the Intergovernmental Panel on Climate Change (IPCC) [10], its atmospheric lifetime and 100 year time horizon-global warming potentials (GWP) are 740 year and 17,200 (relative to CO$_2$), respectively. Furthermore, it is also a hazardous compound with slight solubility in water and inhalation toxicity by inducing the methemoglobin [11]. Consequently its occupational exposure limit (OEL), based on 8-h time-weighted average (TWA), has been set at 10 ppm by the American Conference of Governmental Industrial Hygienists (ACGIH), the Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), etc. As compared to the OEL value (i.e., 1000 ppm) of SF$_6$ and most of hydrofluorocarbons (HFCs) by the ACGIH [12] and the American Industrial Hygiene Association (AIHA) [13], it shows that NF$_3$ should be more toxic than those perfluorocompounds. Therefore, its emissions from the manufacturing processes used in the semiconductor and optoelectronic industries can pose serious hazards to occupation and environment. On the other hand,

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NF_3 has been recognized as a stable gas at room temperature [14], but its toxic decomposition products while applying and/or abating by electrical discharge (e.g., plasma) or other destruction methods have aroused the concern about their potential hazard, especially in fluorides and nitrogen oxides emissions [15]. The toxic products containing fluorine and/or nitrogen in the NF_3 decomposition probably include NF_3O, F_2, HF, SiF_4, NO_2, NO, N_2O, HNO_2, and HNO_3 [15–23]. Although these highly reactive and toxic species are well known as water-soluble products, small quantities of these products, not completely solved in the wet scrubbing, are probably found in the vent gas. Furthermore, the discharges via the best available control technology system still pose a potential hazard to health due to the exposure to the removed fluorides in water bodies and vented exhausts.

Recently, many researches have addressed the decomposition technologies of NF_3 and the formation mechanism of its decomposed products [18,21,23], the published information on the hazard to occupational health and on environmental risks of exposing to these toxic substances and the fluorides probably produced from the exhaust control in the destruction–wet scrubbing system was scarcely addressed or reviewed in the literature. The manuscript is based on the previous works [24,25] that addressed the analysis of the environmental and health risk of sulfur hexafluoride (SF_6) and its decomposition products in detail. This paper aimed at presenting the information on the emissions estimation on the basis of the methodologies recommended by the Intergovernmental Panel on Climate Change, and the hazards to the environment and health caused by its toxic decomposition products while applying and/or abating by destruction methods. According to the prediction/calculation values of its water solubility, Henry's law constant and current emissions, the environmental fate of NF_3 and its atmospheric implications were further addressed in this manuscript.

2. Theory

2.1. Estimation of NF_3 emissions

With respect to the estimation of NF_3 emissions from the electronic industry, it becomes a more significant environmental issue, even if NF_3 has not been blanketed into the Kyoto Protocol. Due to the great demand for the electronic products, NF_3 consumption in Taiwan ranged from 1200 to 1500 metric tonnes on average each year [8,9], one-third of the total NF_3 consumption in the world. NF_3 emissions are dependent on a variety of process parameters and emission reduction technologies. In the methodologies recommended by the Intergovernmental Panel on Climate Change, the Tier 1 method uses default values for all parameters and does not account for the use of emission control technology. The Tier 3 method, the most rigorous method, requires a complete set of process-specific values rather than default values. The Tier 2a method calculates NF_3 emissions on the basis of industry-wide default values for the fraction of the purchased gas remaining in the shipping container after use. As compared to the Tier 2b method of requiring data on the aggregate quantities of each NF_3, the fraction of the gas destroyed or transformed in the electronics manufacturing processes fed into all etching processes and all cleaning processes. In the present study, the Tier 2a has been adopted for calculating NF_3 emissions from the electronic industry because the default values have been developed for the parameters used in the Tier 2 method on the basis of convinced data [26].

$$E = (1 - h) \times FC \times (1 - U) \times (1 - a \times d)$$

where E = NF_3 emissions (metric tonnes); FC = NF_3 consumption (metric tonnes); the value of 4000 metric tonnes adopted in this study according to current status of the semiconductor and TFT-LCD industries in Taiwan and other countries (i.e., South Korea, Japan, and China). h = fraction of NF_3 remaining in shipping container (heel) after use; the value of 0.1 adopted in this study. U = fraction of NF_3 destroyed or transformed in process; the values of ranging 0.7–0.98 adopted in this study. a = fraction of NF_3 volume used in processes with emission control technologies; the value of 1.0 assumed by the author and adopted in this study. d = fraction of NF_3 destroyed by the emission control technology; the value of 0.95 adopted in this study.

2.2. Health risk of NF_3 and its decomposition products

NF_3 has extremely attractive properties, particularly non-flammability, non-corrosiveness and high etch rate as compared to common perfluorocompounds such as CF_4, C_2F_6 and SF_6, even if it is a moderately toxic substance. It should be noted, however, that its decomposition products, produced by electrical and thermal decomposition of NF_3 in the presences of other molecules or substances (e.g., H_2O, Si, O_2, H_2), are probably toxic and even corrosive. The toxic products containing fluorine and/or nitrogen in the NF_3 decomposition probably include NF_3O, F_2, HF, SiF_4, NO_2, NO, N_2O, HNO_2, and HNO_3.

From the viewpoints of molecular structures and physical properties, perfluoroamines such as NF_3 are chemically related to high stability and low reactivity. Hence, NF_3 is insoluble in water. Following release into the environment, the compound possibly reacts with oxidizing molecule (e.g., H_2O) at extreme conditions and produces a variety of degradation products. The reactivity of NF_3 with water has been investigated at 373 K for 7 days [14]. The results showed that the decomposition reaction was assumed to lead to the formation of hydrogen fluoride and nitrous acid.

$$NF_3 + 2\,H_2O \rightarrow 3\,HF + HNO_2$$
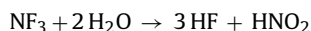
It should be noted that the compound does not react with water at room temperature [27]. Further, the gaseous mixture containing NF_3 and water vapor was ignited by sparking and then reacted according to the following equation [27,28]:

$$2\,NF_3 + 3\,H_2O \rightarrow 6\,HF + NO + NO_2$$
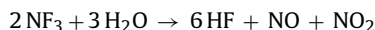
On the other hand, the reaction of hydrogen and NF_3 has been studied to obtain the heat of reaction [29], which can be stoichimetrically shown in the following equation:
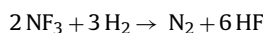
$$2\,NF_3 + 3\,H_2 \rightarrow N_2 + 6\,HF$$

Table 1 listed chemical and physical information on NF_3 decomposition products, which were mainly compiled from the Lange's Handbook of Chemistry [30] and the Sax's Dangerous Properties of Industrial Materials [31].

2.3. Estimation of environmental fate for NF_3

In the discussion of environmental distribution among phases of a given compound, it is hypothetical that the target is not chemically transformed. In this respect, NF_3, which is an inorganic gas and chemically similar to SF_6, has been considered to be relatively stable, highly inert and unlikely decomposed under the normal environmental conditions [32]. It means that the environmental fate of the molecule if released or emitted is only transported from a phase to another without changing its identities until the equilibrium approached. Therefore, the properties regarding the environmental distribution among air, water, and solid phases are significantly important, not only to understand its movement between media, but also to evaluate its behavior

Table 1
Chemical and physical information on NF$_3$ and its decomposition products

Compound	CAS no.	Molecular formula	Molecular weight	Melting point (°C)	Boiling point (°C)	Solubility
Nitrogen trifluoride	7783–54–2	NF$_3$	71.01	−208.5	−129	Slightly soluble
Fluorine	7782–41–4	F$_2$	38.00	−218	−187	(HF formed)
Hydrogen fluoride	7664–39–3	HF	20.01	−83.1	19.54	Very soluble
Nitric acid	7697–37–21	HNO$_3$	63.02	−42	83	Very soluble[b]
Nitric oxide	10102–43–9	NO	30.01	−161	−151.18	Slightly soluble
Nitrogen dioxide	10102–44–0	NO$_2$	46.01	−11.2	21.15	Reacts with H$_2$O giving HNO$_3$ + NO
Nitrogen trifluoride oxide	13847–65–9	NF$_3$O	87.01	−160	−87	Resistant to hydrolysis
Nitrous acid	7782–77–6	HNO$_2$	47.02	(Stable only in solution)		
Nitrous oxide	10024–97–2	N$_2$O	44.01	−90.8	−88.49	Slightly soluble
Silicon tetrafluoride	7783–61–1	SiF$_4$	104.09	−77	−65	(Rapidly hydrolyzed)

The data are from the references [30,31].

within a single medium. These distribution properties commonly include octanol–water partition coefficient (K_{ow}), water solubility (S), Henry's law constant (K_H), and vapor pressure (P). K_{ow}, however, is only used to describe an organic compound about the partition between water phase and oil phase at equilibrium, suggesting that there is no information on K_{ow}. Recent studies on these properties of NF$_3$ experimentally measured were limited to its vapor pressure [33,34], and water solubility [35,36].

2.3.1. Water solubility

Of the various fate and transport properties that affect the environmental distribution between air and water, water solubility is one of the most important parameters. Generally, water solubility is much less important for gases, as compared to liquids or solids, on the basis of environment because it is usually measured when the partial pressure of the gas above the aqueous solution is one atmosphere, an unlikely condition in the environment. Henry's law constant (discussed later), another fate property for gases, is a more important parameter, which describes the ratio of the concentrations of a given gas in the phases of water and air (at low partial pressure) under equilibrium conditions.

2.3.2. Henry's law constant

Interface transfer between the gas phase (i.e., atmospheric air) and water bodies is one of the fate processes affecting the transport of many chemical compounds in the environment because the vaporization of them from aqueous solutions is an important pathway to air from water. In this regard, Henry's law is used to describe the partition of a gas in two different phases, such as water and air, under equilibrium conditions. Therefore, the Henry's law constant (K_H) is a partition coefficient, which is usually defined as the ratio of a chemical's concentration in air to its concentration in water at equilibrium, or mathematically described as the following form [37]:

$$\lim \left(\frac{f_2}{x_2} \right) x_{2-0} = K_H$$

where x_2 is the mole fraction of the solute gas in aqueous solution and f_2 is the fugacity of the solute gas. For dilute solution at low pressure, the above equation is then written as

$$K_H = \frac{P_2}{x_2}$$

where P_2 is the partial pressure of the solute gas over the solution.

3. Results and discussion

3.1. Health hazards of NF$_3$ and its decomposition products

Based on the previous description, the identified products in the NF$_3$ decomposition system were NF$_3$O, F$_2$, HF, SiF$_4$, NO$_2$, NO, N$_2$O, HNO$_2$, and HNO$_3$. For example [14], ignition of a mixture of NF$_3$ and water vapor gives a slow reaction, resulting in the production of HF and HNO$_2$. The latter product may react further to form HNO$_3$ and nitrogen monoxide (NO) in the oxidative medium. It is well known that airborne HNO$_3$ is a potent irritant with both acute and chronic effects [38]. On the other hand, HF is a colorless, corrosive gas or liquid (it boils at 293 K). It is well known for its ability to cause severe chemical burns on contact with skin and even develop skeletal fluorosis in workers heavily exposed to high levels of fluorspar [39]. It should be noted that these decomposition and/or reaction products seemed to be only formed in the thermal reactor and the electrolytic cell because they are not likely to be formed in the destruction–scrubbing abatement process under normal conditions and emitted NF$_3$ is very stable in the atmosphere. Human exposure to these toxic compounds, however, may occur via inhalation from accidental leaks and/or spills from the plasma CVD chamber and destruction system.

Table 2 summarized the hazards of NF$_3$ to health and its main decomposition products [12,39]. These decomposition products show similarities in hazards to health in the chemical properties such as corrosiveness (highly acidic) and their reactivity is obvious in the physiological effects. With the exception of NF$_3$ and NO$_2$ and NO, the gases and the vapors of these decomposed chemicals are irritants to the respiratory system and skin and/or eye contact. Thus, the inhalation of relatively low concentration of these gases and vapors will cause an unpleasant, and pungent sensation, which is followed by a feeling of suffocation, coughing, and a sensation of constriction in the chest [38]. The skin or eye contact with them will immediately cause significant burns and severe irritations. Due to the harmful hazards to human health and environmental quality, some chemicals from NF$_3$ decomposition have been regulated by a series of recently enacted laws such as Toxic Substances Control Act (TSCA), Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Emergency Planning and Community Right-to-Know Act (EPCRA), and Clean Air Act Amendments (CAAA) in the USA, as listed in Table 3 [31].

In the rat experiments studied by Dost et al. [11], NF$_3$ has been demonstrated to induce the production of methemoglobin, which will reduce the level of oxygen transferred to the body tissues. Unfortunately, the decomposition products from NF$_3$ destruction processes are also reactive, corrosive and toxic. Inhalation is the most potential way of exposure to these toxic gases. Thus, its occupational exposure limit (OEL), such as the American Conference of Governmental Industrial Hygienists (ACGIH)–threshold limit value (TLV), the Occupational Safety and Health Administration (OSHA)–permissible exposure limit (PEL), and the National Institute for Occupational Safety and Health (NIOSH)–recommended exposure limit (REL), basically based on 8-h time-weighted average (TWA), has been set at 10 ppm, as listed in Table 4 [12,39–43]. It should be noted, however, that overexposure to NF$_3$ may have adverse effects on blood, liver, and kidney.

Table 2
Hazards of NF_3 to health and its decomposition products

Compound	UN NIOSH[a]		TLV basis-critical effect[b]
	Exposure routes	Target organs	
Nitrogen trifluoride	Inhalation	Blood, liver, kidneys	Anoxia; blood; liver; kidney
Fluorides (as F)			Irritation; bone; fluorosis
Fluorine	Inhalation, skin and/or eye contact	Eyes, skin, respiratory system, liver, kidneys	Irritation
Hydrogen fluoride	Inhalation, skin absorption (liquid), ingestion (solution), skin and/or eye contact	Eyes, skin, respiratory system, bones	Irritation; bone; teeth; fluorosis
Nitrogen dioxide	Inhalation, skin and/or eye contact	Eyes, respiratory system, central nervous system	Irritation; pulmonary edema
Nitric oxide	Inhalation	Blood, liver, kidneys	Anoxia; irritation; cyanosis
Nitrous oxide	Inhalation, skin and/or eye contact	Eyes, skin, respiratory system	Reproduction; blood; CNS
Nitric acid	Inhalation, ingestion, skin and/or eye contact	Eyes, skin, respiratory system, central nervous system	Irritation; corrosion; pulmonary edema

[a] The data are from the reference [39].
[b] The data are from the reference [12].

Table 3
NF_3 and its decomposition products designated as toxic/hazardous substances for specific regulatory purpose[a]

Compound	TSCA[b]/inventory	CERCLA[b]/extremely hazardous substance	EPCRA[b]/toxics release inventory	CAAA[b]/hazardous air pollutant
Nitrogen trifluoride	Listed	–	–	–
Fluorine	Listed	Listed	Listed	–
Hydrogen fluoride	Listed	Listed	Listed	Listed
Nitric acid	Listed	Listed	Listed	–
Nitric oxide	Listed	Listed	–	–
Nitrogen dioxide	Listed	Listed	–	–
Nitrogen trifluoride oxide	Listed	–	–	–
Nitrous acid	Listed	–	–	–
Silicon tetrafluoride	Listed	–	–	–

[a] The data were mainly compiled from the reference [31].
[b] TSCA: Toxic Substances Control Act; CERCLA: Comprehensive Environmental Response, Compensation, and Liability Act; EPCRA: Emergency Planning and Community Right-to-Know Act; CAAA: Clean Air Act Amendments.

Since the equipment or facility using NF_3 is usually sealed or well-ventilated, and even designed with the exhaust control system (residual abatement) such as plasma-scrubber, the occupational exposure to its decomposition toxic products should be at a minimum. However, it should be noted that the repair or maintenance of the related compartments could involve welding operations and possibly cause the occupational exposure to final decomposition toxic products including hydrogen fluoride (HF) and nitrogen dioxide (NO_2) or nitric acid (HNO_3). In order to display a relative health risk of personnel emergency exposure to NF_3 decomposition products, also listed in Table 4 were the available data on the "Immediately Dangerous to Life or Health" (IDLH), it is a situation "that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment" [39].

Table 4
Occupational exposure limits/levels of NF_3 and its probable decomposition products based on the time-weighted average (TWA) concentration for 8-h (or up to a 10-h) workday and a 40-h workweek

Compound	TLV[a]	PEL[b]	REL[c]	OEL[d]	MAK[e]	PCS[f]	IDLH[g]
Nitrogen trifluoride (NF_3)	10 ppm	10 ppm	10 ppm	–[i]	–	10 ppm	1000 ppm
Fluorides (as F)	2.5 mg m^{-3}	2.5 mg m^{-3}			2.5 mg m^{-3}	2.5 mg m^{-3}	–
Fluorine (F_2)	1 ppm	0.1 ppm			0.1 ppm	1 ppm	25 ppm
Nitric acid (HNO_3)	2 ppm	2 ppm	2 ppm	2 ppm	2 ppm	2 ppm	25 ppm
Nitric oxide (NO)	25 ppm	25 ppm			25 ppm	25 ppm	100 ppm
Nitrogen dioxide (NO_2)	3 ppm	1 ppm (STEL)[j]	1 ppm (Ceiling)	(Pending)	5 ppm	5 ppm	1000 ppm
Nitrous oxide (N_2O)	50 ppm	–	25 ppm	–	100 ppm	–	–
Silicon tetrafluoride (SiF_4)[h]	2.5 mg m^{-3}	2.5 mg m^{-3}	2.5 mg m^{-3}	–	–	–	–

[a] Threshold limit value, American Conference of Governmental Industrial Hygienists [12].
[b] Permissible exposure limit, Occupational Safety and Health Administration [42].
[c] Recommended exposure limit, National Institute for Occupational Safety and Health [39].
[d] Occupational exposure limit, Japan Society for Occupational Health [43].
[e] Maximum allowable concentration, Deutsche Forschungsgemeinschaft [40].
[f] Permissible Concentration Standard, Council of Labor Affairs [41].
[g] Immediately Dangerous to Life or Health [39].
[h] The limit (i.e., 2.5 mg m^{-3}) for SiF_4 was adopted because fluorides will be emitted when it is applied.
[i] Not available.
[j] Short-term exposure limit, which is defined as a 15-min time-weighted average (TWA) exposure that should be exceeded at any time during a workday.

On first insight (Table 2) and the information described above, most of NF_3 decomposition products are gases and have very high solubility and/or reactivity in water and humid air at room temperature, just like SF_6 decomposition products in the previous work [24]. Therefore, they are likely to remain in water and atmospheric air as fluorides, which may exist in the forms of hydrogen fluoride, fluoride ion, and hydrofluoric acid. The fluorosis or chronic fluorine intoxication has been correlated with fluoride deposition in skeletal tissues (i.e., teeth and bone) of both animals and humans on the basis of clinical and epidemic studies [44,45]. Generally, the most significant pathway to exposure to all sources of fluoride is via ingestion [45], including fluoridated public drinking water, soft drinks and fruit juices (beverages), infant formula, cow's milk, foodstuffs, fluoride supplement tablets, incidental ingestions of soil (by children), and toothpaste containing fluoride. Although atmospheric air was considered as only a small part of total fluoride exposure sources, the fluoride concentration in the workplace environment could be elevated in the industrial areas such as semiconductors and TFT-LCD manufacturing processes, and even in the workplace air owing to the combustion and spark sources, leading to increased exposure by the inhalation route. Notably, human exposure to fluoride may occur via inhalation from accidental leaks and/or spills from the industries using NF_3 as processing gases.

3.2. Estimation of NF$_3$ emissions

The data used to estimate the NF_3 emissions were based on the default values suggested and adopted by the IPCC method. Thus, estimating NF_3 emissions from the electronics industry sector by the IPCC method was calculated as follows:

$$E_{max} = (1 - 0.1) \times 4000 \times (1 - 0.7) \times (1 - 1.0 \times 0.95) = 56 \quad \text{metric tonnes}$$

$$E_{min} = (1 - 0.1) \times 3000 \times (1 - 0.98) \times (1 - 1.0 \times 0.95) = 3.6 \quad \text{metric tonnes}$$

The results showed that annual NF_3 emissions from the industrial processes in the world during the year of 2006 amounted to about 3.6–56 metric tonnes, indicating that the PFC emissions was significantly lower than other GHGs such as CO_2 and CH_4 [10]. It should also be noted that the emission source will be on the increasing trend in the near future because of the enormous investment in the 12-in. (300 mm) wafer and over 6-generation TFT-LCD manufacturing fabs in response to the fast demand in the world.

3.3. Environmental fate of NF$_3$

3.3.1. Water solubility

With respect to the studies on water solubility of NF_3 in the literature, the data on the temperature ranging from 273 to 323 K has been first determined by Ashton et al. [35]. The results showed that NF_3 has remarkably low solubility in water, which has been correlated with temperature (expressed as the absolute temperature, K) as follows:

$$x = \frac{5785.95}{T} + 38.2556 \log T - 18.9122$$

where x is water solubility expressed as a mole fraction. With comparison with other perfluorocarbons like SF_6, the aqueous solubility of NF_3 is significantly higher than that of SF_6. For example, the water solubility of NF_3 at 298 K is as compared to for that of SF_6. Another work investigated by Dean et al. [36] had a similar correlation:

$$x = \frac{4596.4}{T} + 29.558 \log T - 3.404$$

Table 5
Atmospheric status and global warming properties for some perfluorocarbons and hydrofluorocarbons commonly used in semiconductor industry[a]

Compound	Atmospheric conc. in 2005 (ppt)	Conc. Change since 1998 (ppt)	Annual emission in late 1990s (Gg)[b]	Radiative efficiency (W/m²-ppbv)	Lifetime (year)	GWP[c]
CF_4	74	–	~15	0.10	50,000	7,390
C_2F_6	2.9	+0.5	~2	0.26	10,000	12,200
CHF_3	18	+4	~7	0.19	270	14,800
SF_6[a]	5.6	+1.5	~6	0.52	3,200	22,800
NF_3	<0.1[d]	–[e]	~2.3[d]	0.21	740	17,200

[a] Most of the data were compiled from the reference [10].
[b] The data were compiled from the reference [47].
[c] Global warming potential (GWP) for 100-year time horizon.
[d] The data were compiled from the reference [7].
[e] Not available.

where x and T have been defined above, but T ranges between 298 and 318 K. In brief, NF_3 is negligibly soluble at ambient temperature.

3.3.2. Henry's law constant

For very stable gases, K_H can be approximately estimated by dividing the vapor pressure of a target gas according to its water solubility at the same temperature (e.g., 298 K) if it has not yet been measured or observed in the literature [46]. The predicted value of $\ln (K_H/MPa)$ for NF_3 was thus obtained to be about 13.3 based on its vapor pressure (i.e., 511 kPa, at 298 K) calculated from the correlation from the literature [34] and the solubility in water described above. The predicted value implied that the vaporization of NF_3 from the water bodies to the atmosphere is very high. It should be also noted that NF_3 is very stable in the atmosphere, and does not exactly react with highly oxidative species (e.g., O_3) and free radicals such as hydroxyl radical and not be decomposed by direct or sensitized photolysis [32]. Therefore, there is no sink for this potent greenhouse gas in the troposphere and even in the stratosphere.

3.3.3. Environmental implications of NF_3

From the data on the infrared (IR) absorption spectrum of NF_3 [32], there are two integrated absorption cross-sections (intensities) significantly observed in the spectral bands of 840–60 and 970–085 cm^{-1}, leading to an atmospheric lifetime of more than 500 years and a 100 year time horizon GWP value of the order of 8000. Afterward, the calculated radiative efficiency (0.13 W/m^2-ppbv) was adopted by the Intergovernmental Panel on Climate Change based on its information on atmospheric lifetime (i.e., >500 years) and 100 year-time horizon global warming potential (i.e., 10,800) [47]. Based on the updated data on the radiative efficiency of 0.21 W/m^2-ppbv, atmospheric lifetime of 740 years and 100 year-time horizon GWP of 17,200 relative to CO_2 [7,10], it is clear that NF_3 is a potent greenhouse gas as compared to other perfluorocarbons currently used in the semiconductor and TFT-LCD industries. Table 5 listed some atmospheric status and global warming properties of NF_3 and perfluorocarbons because the chemistry of the former resembles that of the latter. Because of its long atmospheric lifetime of approximately 800 years, NF_3 is expected not to be degraded in the tropospheric environment by reactions with highly oxidative species (e.g., O_3) and free radicals such as hydroxyl radical [32].

It should be remarked that the current atmospheric concentrations of NF_3 is probably at an approximate level of 0.1 pptv [7]. Its contribution to radiative forcing of climate change seemed to be so negligible at present ($<0^{-4}$ W m^{-2}) [7], and may be also extremely small in the future based on the predicted ratio (the order of 10^{-6} to 10^{-7}) of equivalent CO_2 emission from NF_3 to total amounts of potent greenhouse gases emitted into the atmosphere [10]. However, it is necessary to adopt the best available abatement technology and also monitor the concentration of NF_3 in the workplaces for reducing the environmental and health impacts from emitted NF_3 and its toxic decomposition products due to its atmospheric lifetime of 740 years and the potential for its essentially irreversible accumulation in the atmosphere.

4. Conclusions

Though NF_3 addressed in this paper have not been included in the basket of the six major greenhouse gases in Kyoto Protocol, the perfluorocompound gas still possesses some hazards to environment and health, especially in global warming, and adverse effect of exposure to its toxic decomposition products, including NF_3O, F_2, HF, SiF_4, NO_2, NO, N_2O, HNO_2, and HNO_3. In this respect, NF_3 emissions from the electronics industry amounted to be around 3.6–56 metric tonnes annually based on the industrial activities (i.e., NF_3

consumption in 2006) and the IPCC recommended emission factors/fractions. For the protection of the environmental quality and of human health, the emission of inorganic vapors containing these toxic (irritating) and corrosive species in the workplace environment still needs to be controlled using various wet capture methods to reduce the exposure risk. However, the discharges of fluorides from the controlled vents and effluents could be expected. It is necessary to monitor and evaluate its long-term emissions, because fluoride is moderately toxic to human on contact with moist body tissues through inhalation, causing fluorosis in skeletal tissues (i.e., teeth and bone). On the other hand, NF_3, a potent greenhouse gas, could be emitted from the process due to leak, spill, or unreacted vent. The environmental fate of NF_3 and its atmospheric implications were also analyzed in the paper, indicating that there are no environmental sinks of it at normal conditions. However, its impacts on the global climate change would be more significant in the future because of its long lifetime in the atmosphere and the rampant production of meeting a demand in industrial uses.

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