Review

Environmental risk assessment of hydrofluoropolyethers (HFPEs)

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Abstract

Hydrofluoropolyethers (HFPEs), a new family of linear oligomeric fluorinated fluids, are being used as potential replacements for halon, hydrochlorofluorocarbons (HCFCs) and perfluorocarbons (PFCs) that have been listed as ozone depleting substances and/or greenhouse gases. Because of their physicochemical properties, these substances may be industrially used as cleaning solvents in the electronic components, fire suppression agents in the fire protection, and heat transfer fluids in the heat exchangers. From the environmental, ecological, and healthy points of view, it is urgent to understand their environmental risks of these HFPEs. This article aimed at introducing these HFPEs in physiochemical properties and potential uses, and evaluating their environmental risks (i.e., global warming, photochemical potential, and environmental partition). Further, the updated data on their toxicological profiles and potential exposure hazards from their degradation products were also addressed in this paper. It is indicated that HFPEs still pose some significant hazards, especially global warming and photochemical potentials, to the atmosphere. Regarding the estimation of partition properties (i.e., vapor pressure, octanol–water partition coefficient and bioconcentration) of HFPEs, the predicted values of log K_{ow} for several HFPEs were found to be below zero, suggesting that they should possess very low potential for bioaccumulation in the environment.
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Keywords: Hydrofluoropolyethers (HFPEs); Environmental risk; Global warming; Photochemical potential; Exposure hazard

Contents

1. Introduction

In the last century, chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbons (HCFCs) were widely used for commercial and industrial purposes, including refrigerant, cleaning solvent, blowing agent, propellant and fire extinguishing agent. However,

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Table 1
Chemical identifications of selected HFPEs

HFPE notation[a]	Chemical structure	Formula	CAS registry no.
HG-00[a]	$HF_2C–OCF_2H$	$C_2H_2F_4O$	1691-17-4
HG-10	$HF_2C–OCF_2–OCF_2H$	$C_3H_2F_6O_2$	78522-47-1
HG-01	$HF_2C–OCF_2CF_2O–CF_2H$	$C_4H_2F_8O_2$	188690-78-0
HG-20	$HF_2C–(OCF_2)_2–OCF_2H$	$C_4H_2F_8O_3$	249932-25-0
HG-11	$HF_2C–OCF_2CF_2–OCF_2–OCF_2H$	$C_5H_2F_{10}O_3$	188690-77-9
HG-02	$HF_2C–(OCF_2CF_2)_2–OCF_2H$	$C_6H_2F_{12}O_3$	205367-61-9
HG-21	$HF_2C–(OCF_2CF_2)–(OCF_2)_2–OCF_2H$	$C_6H_2F_{12}O_4$	249932-26-1
HG'-00[b]	$H_3C–OCH_3$	C_2H_6O	115-10-6
HG'-01	$H_3C–OCF_2CF_2–OCH_3$	$C_4H_6F_4O_2$	73287-23-7
HG'-02	$H_3C–(OCF_2CF_2)_2–OCH_3$	$C_6H_6F_8O_3$	485399-46-0
HG'-03	$H_3C–(OCF_2CF_2)_3–OCH_3$	$C_8H_6F_{12}O_4$	485399-48-2

[a] The general formula of HFPE with the trade name of H-Galden is: $HF_2C–(OCF_2CF_2)_p(OCF_2)_q–OCF_2H$. In the present study, the notation of HFPE is thus denoted as HG-qp.

[b] Another form of HFPE is: $H_3C–(OCF_2CF_2)_p(OCF_2)_q–OCH_3$, which is denoted as HG'-qp in the present study.

these volatile organics were found to be the so-called ozone depleting substances (ODS), which will cause the depletion of the ozone layer, shields the earth from the harmful effects of the sun's ultraviolet (UV) radiation. Under a treaty known as the Montreal Protocol on Substances that Deplete the Ozone Layer which was first established in 1987 and thereafter revised several times, CFCs and HCFCs need to be completely phased out for non-article countries by the years 1995 and 2030, respectively [1]. In addition to causing the destruction of stratospheric ozone, the release of CFCs and HCFCs contributes to global warming and changes in global climate. It means that they possess significant absorbing potentials for the infrared (IR) radiation reflected from the surface on earth and are thus called the greenhouse gases (GHGs) [2,3]. The development of environmentally friendly replacements for CFCs and HCFCs has thus become an urgent priority since the early 1990s.

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), because of their similarity to CFCs and HCFCs in physiochemical, environmental and toxicological properties, have been used as interim replacements for them. However, there are some environmental hazards and health risks to be pointed out while using HFCs and PFCs [4,5]. For example, they have been considered as one of the six target GHGs under the Kyoto Protocol of the United Nations' Framework Convention on Climate Change (UNFCCC) in 1997 [6]. According to the Kyoto Protocol effective on 16 February 2005, the governments around the world are voluntarily committed to reducing target GHGs emissions to atmosphere by 2012. Notably, these interim substances generally have high volatility and very low solubility in water. Following their releases into the environment, these compounds almost reside in the atmosphere. Toxic degradation products are possibly generated in the tropospheric atmosphere by the photolytic and photochemical processes [7]. On the other hand, hydrofluoroethers (HFEs) are being used as third-generation replacements for CFCs, HCFCs and PFCs because of their nearly zero stratospheric ozone depletion and relatively low global warming potential [7–9]. However, there are few HFEs still possessing some environmental hazards (i.e., global warming, flammability hazard and adverse effect of exposure), which were described in the previous study [10]. In the meantime, other potential alternatives like hydrofluoropolyethers (HFPEs) have been developed to replace them (especially in PFCs) because of their strong similarity in the chemical and physical properties [11].

Like other CFCs substitutes, HFPEs have a controlled number of hydrogen atoms in the molecules, which consist of a perfluoropolyether chain terminated at both ends with functional groups, $–OCF_2H$ or $–OCH_3$, i.e.

$$HF_2C–(OCF_2CF_2)_p(OCF_2)_q–OCF_2H \tag{1}$$

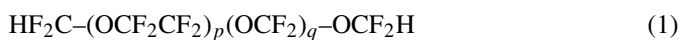$$H_3C–(OCF_2CF_2)_p(OCF_2)_q–OCH_3 \tag{2}$$

Table 1 lists the chemical identifications of some HFPEs, which will be further discussed in the study. As shown in Table 1, CHF_2OCHF_2 (bis(difluoromethyl) ether or HFE-134) and CH_3OCH_3 (dimethyl ether) are also included in the HFPEs as the two simplest model molecules for the purpose of comparing them with other HFPEs. This paper aims to present the predicted physical properties, potentially commercial/industrial uses, and environmental hazards (e.g., global warming, photochemical potential, and environmental partition) of selected HFPEs. In addition, recent studies on the toxicological profiles of HFPEs in the literature are also summarized and further discussed in this paper [12].

2. Properties and potential uses of HFPEs

2.1. Estimation of critical property

The vapor–liquid behavior of pure component can be described in terms of critical temperature (T_c), critical pressure (P_c), critical volume (V_c), and acentric factor (ω) because they are used in many corresponding state correlations for thermodynamic properties of gases and liquids [13]. The critical properties of HFPEs were calculated by using three different methods (i.e., Ambrise, Lydersen and Joback) in the Marchionni's study [14]. In the present study, the values (i.e., T_c, P_c, and V_c) of HFPEs were determined with precision by using the Marrero–Pardillo method [15], which considers the contributions of interactions between bonding groups in the molecule. In the method, T_c, P_c

Table 2
Critical parameters of selected HFPEs estimated by the method of group contribution[a]

HFPEs	Critical temperature (T_c, K)	Critical pressure (P_c, MPa)	Critical volume (V_c, cm^3/mol)	Acentric factor (ω)
HG-00[b]	411.2	3.664	223.3	0.393
HG-10	428.6	2.646	364.9	0.561
HG-01	452.1	2.296	447.6	0.612
HG-20	453.3	2.000	506.5	0.710
HG-11	469.7	1.767	589.2	0.744
HG-02	480.7	1.572	671.9	0.768
HG-21	487.0	1.402	730.8	0.817
HG′-00[c]	399.7	5.131	157.1	0.202
HG′-01	472.7	2.983	381.4	0.411
HG′-02	515.7	1.948	545.7	0.618
HG′-03	526.2	1.095	896.0	0.645

[a] Estimated by the Marrero–Pardillo method [15].
[b] The experimental data in the literature [20]: $T_c = 420.25$ K; $P_c = 4.228$ MPa; $V_c = 223$ cm^3/mol; $\omega = 0.3764$.
[c] The reported data in the literature [20]: $T_c = 400.2$ K; $P_c = 5.340$ MPa; $V_c = 168.0$ cm^3/mol, $\omega = 0.204$.

and V_c were estimated by the following equations:

$$T_c = \frac{T_b}{\left\{0.5851 - 0.9286\left[\sum N_k(\text{tcbk})\right] - \left[\sum N_k(\text{tcbk})\right]^2\right\}} \tag{3}$$

$$P_c = \left[0.1285 - 0.0059 N_{\text{atoms}} - \sum N_k(\text{pcbk})\right]^{-2} \tag{4}$$

$$V_c = 25.1 + \sum N_k(\text{vcbk}) \tag{5}$$

where N_{atoms} is the number of atoms in the molecule of HFPEs, N_k is the number of atoms of type k with the contributions tcbk, pcbk, and vcbk for the estimations of T_c, P_c, and V_c, respectively. It is noted that the estimation of T_c requires the data on the normal boiling point (i.e., T_b), which was also estimated by the Marrero–Pardillo method as follows:

$$T_b = M^{-0.404}\sum N_k(\text{tbbk}) + 156.00 \tag{6}$$

where M is the molecular weight, and N_k is the number of atoms of type k with the contributions tbbk. In addition to the critical properties of pure substance, the acentric factor (ω) is commonly used to predict the physical properties. As a reliable approximation, the property, which is related to T_b, P_c, and T_c, was carried out the calculation by the following equation [13]:

$$\omega = -\frac{\ln P_c/1.01325 + f^{(0)}(T_{\text{br}})}{f^{(1)}(T_{\text{br}})} \tag{7}$$

where P_c is in bars while T_b and T_c are both absolute temperatures. The functions $f^{(0)}$ and $f^{(1)}$ have been defined and given in the reference [16,17]. The data on T_c, P_c, V_c, and ω of HFPEs have been calculated and listed in Table 2. To validate the accuracy of the method in the estimation of critical properties of HFPEs, bis(difluoromethyl) ether (CHF$_2$–O–CHF$_2$, denoted as HG-00) and dimethyl ether (CH$_3$–O–CH$_3$, denoted as HG′-00) that are similar in chemical structure to these HFPEs were estimated to obtain their critical properties, which were then compared to those reported or measured in the literature [13,18–20].

2.2. Physicochemical property

It has been recognized that HFPEs are characterized by their excellent thermal and chemical stability, good compatibility with contact materials, high electrical resistance, and no formation of decomposition products in use [11,12]. It was

Table 3
Main physicochemical properties of selected HFPEs

HFPEs	Molecular weight (g/mol)	Boiling point (K)	Density (g/cm^3, 25 °C)	Refractive index[a]	Dipole moment (Debye, D)[a]	Viscosity (mPa s, 25 °C)	Reference(s)
HG-00[b]	118	278.3	1.375	1.230 (at 30 °C)	1.739 (at 36 °C)	0.310	[21,23,24]
HG-10	184	308.2	1.4695	1.2577	1.77	0.391	[14]
HG-01	234	331.7	1.5516	1.2638	1.77	0.590	[14]
HG-20	250	341.2	1.5747	1.2669	1.90	0.580	[14]
HG-11	300	358.7	1.6012	1.2689	1.97	0.805	[14]
HG-02	350	371.7	–[b]	–	2.00	–	[14]
HG-21	366	382.2	1.6400	1.2730	2.05	1.091	[14]
HG′-00	46	248.3	0.655	1.2984	1.30 (gas)	0.149	[19,20]
HG′-01	162	327.0[c]	–	–	–	–	
HG′-02	278	384.0[c]	–	–	–	–	
HG′-03	394	434.2	1.52	–	–	1.07	[27]

[a] At 20 °C (except for HG-00).
[b] Not available in the literature.
[c] Estimated by the Marrero–Pardillo method [13].

reported that no degradation or structural change was detected on HFPEs under the acidic (H_2SO_4, HNO_3, and HCl) and alkaline (40% KOH in water) conditions by prolonged treatment at high temperature (20 h, 150 °C) [11]. HFPEs are insoluble in water. However, they can be miscible with common organic solvents because of their terminal groups possessing significant polarity. On the other hand, HFPEs can mix with water and alcohol (e.g., isopropyl alcohol) to form a ternary aqueous system HFPE–water–alcohol, which has been found to be useful as cleaning agents [11]. The main physicochemial properties of some HFPEs in Table 3 are mainly compiled from the available monographs or books [19,20], and references from multidisciplinary journals such as *Fluid Phase Equilibria* [21,22], *J. Chem. Eng. Data* [23,24], *J. Fluor. Chem.* [14,25–27].

2.3. Potential uses

It has been shown that HFPEs can be partly used as replacements for halons and PFCs because many of their similar physical and thermochemical properties. These fluorocarbons maintain the chemical and thermal properties of perfluorinated polyethers (PFPEs, known in the lubricating oils) [28]. Because of their chemical inertness, low toxicity, non-flammability, zero ozone depleting potential (ODP) and thermal stability, HFPEs have promised to be applied to the following products:

1. Fire extinguisher or fire suppression agent

   In the past decades, halons have been used extensively as effective fire extinguishers in fixed, total flooding systems for protecting sensitive electrical equipments. The Montreal Protocol stimulated tremendous efforts to search for acceptable replacements and alternatives. There are two broad categories to be currently developed as clean fire suppression agents. One is inert gases or their mixtures (e.g., argon, nitrogen). The other is the halocarbon compounds. Recently, HPFEs have been approved of for limited use (i.e., only in non-residential applications) as streaming agents (as a halon 1211 substitute) under the U.S. EPA Significant New Alternatives Policy (SNAP) [29].

2. Heat exchange fluid

   Generally, there are two categories of heat transfer (exchange) fluids for offering superior heat transfer efficiency and optimal thermal stability throughout its operation temperature range: aqueous and non-aqueous systems. The latter includes silicones and hydrocarbon oils. Because of the similarity in physicochemical properties between PFCs and HFPEs, HFPEs may be applied to the electronic, electromechanical, chemical, nuclear, and pharmaceutical industries as heat exchange fluids. Many industrial applications to ion implanters, etchers, radar, transformer power supplies, and freeze dryer have been made [30].

3. Cleaning solvent

   It is well known that the most common organic cleaning solvents applied to the electronic components, precision cleaning and metal finishing were chlorinated solvents (i.e., CFC-113 and 1,1,1-trichloroethane) and HCFCs (i.e., HCFC-141b and HCFC-225ca/cb). However, all these substances will be completely phased out according to the Montreal Protocol. It was previously mentioned that an outstanding feature of HFPEs is their abilities to form the ternary HFPEs–water–alcohol system, which can be used as a powerful cleaning solvent in the aqueous phase without the degreasing additives [11].

3. Environmental risks of HFPEs

The manufacture and use of any organic chemical may pose potential risks to environmental and health if it is released into the environment, and/or its degradation product is generated. Although it is not possible to evaluate all environmental risks of new chemicals, it is necessary to do a preliminary screening based on the available and/or limited information in the literature. HFPEs, also considered as volatile organic compounds (VOCs), have extremely attractive properties, including zero ODP, non-flammability, low toxicity, mediate-high volatility and hydrophilicity compared to similar chemicals such as ethers and HFEs. It means that they are most likely to accumulate in the atmosphere if released. Therefore, they seem to inherently pose different environmental risks, such as global warming, photochemical potential, and environmental distributions (i.e., vapor pressure, partition coefficient and bioconcentration), which are further discussed below.

3.1. Global warming

If several anthropogenic compounds including all VOCs are once emitted into the atmosphere, they may cause the earth's average temperature to elevate, which is called global warm-

Table 4

Atmospheric lifetimes, global warming potentials and gas-phase atmospheric degradation products for selected HFPEs

HFPE	Atmospheric lifetime (year)[a]	GWP[b]	Degradation products	Reference(s)
HG-00	14, 24.8, 29.7, 26	3699, 5800, 5720, 6220, 6300	$CHF_2OC(O)F$, CF_2O	[35–39]
HG-10	13.6, 12.1	2780, 3692, 7000	CF_2O	[25,32,33,37,39]
HG-01	6.2, 7.0	1480, 1725, 3900	CF_2O	[25,32,33,37,39]
HG-11	6.3, 7.1, 48	1840, 4900, 8700	CF_2O	[25,32,33,37,39,40]
HG′-00	0.015	0.3	$H_3COC(O)H$, HCHO	[36,41]
HG′-01	2	230	$H_3C–OCF_2CF_2–OC(O)H$, CF_2O, HCHO	[34]
HG′-02	2	270	$H_3C–O(CF_2CF_2O)_2–C(O)H$, CF_2O, HCHO	[34]
HG′-03	2	250	$H_3C–O(CF_2CF_2O)_3–C(O)H$, CF_2O, HCHO	[34]

[a] Estimated values, which can be mainly calculated by the reciprocal of the pseudo-first order rate constant for its removal by OH radicals in the troposphere.

[b] Global warming potential with 100-year time horizon (relative to GWP of $CO_2 = 1$).

ing, or greenhouse effect. According to the Kyoto Protocol, the governments around the world are voluntarily committed reducing target greenhouse gases (GHGs) emissions to atmosphere. Global warming potential (GWP) shows the relative increase in earthward IR radiation flux due to the emission of GHGs. As described above, HFPEs possess the terminal hydrogen atoms, thus resulting in the increase in the chain reactivity and the reduction in their atmospheric lifetimes. Thus, HFPEs have relatively smaller values of atmospheric lifetime and GWP (Table 4) compared to CFCs and HCFCs because these replacements contain one C–O bond, and one or more C–H bonds, which are susceptible to attack from hydroxyl radicals and hence shorten atmospheric lifetimes in the troposphere [7]. It is noted that the GWP values of some HFPEs (i.e., HG-01, HG-10, and HG-11) are substantially greater than CO_2 as seen in Table 4. Hence, though they are currently used in much smaller quantities than HFCs, PFCs and HCFCs, it is possible at this point to eliminate or reduce these HFPEs emissions.

3.2. Photochemical potential

From the viewpoints of chemical structure and physical property, HFPEs belong to volatile organic compounds (VOCs) like ethers, which possess a mediate-high volatility that allows them to evaporate quickly. Following release into the atmosphere, these compounds possibly reside in the lower atmosphere (i.e., troposphere) due to the heavier vapor density than that of air, where they are photochemically oxidized, photolyzed and/or subsequently hydrolyzed as a result of a variety of primary and secondary degradation products. As mentioned above, HFPEs do not contain chlorine and are hence not a class of ODS. Also, the presence of C–H bonds in HFPEs means that they can contribute to photochemical oxidants formation in the troposphere, in a similar manner to those of typical VOCs. It has been recognized that hydrocarbon compounds are liable to react with •OH radical to convert them into carbonyl species, which are then removed by wet deposition via rainfall and dry deposition to the surface [31].

With respect to the gas-phase photochemistry of HFPEs, it has been recently established by limited researches [11,25,32–34]. Table 4 summarizes tropospheric degradation products of some HFPEs. As described above, the presence of C–O bonds in the HFPEs molecule provides the reaction of hydrogen abstraction by the atmospheric •OH radicals, resulting in their decreases in atmospheric lifetimes and reducing their potential transport to the stratosphere. It was concluded that the Cl• atom or •OH radical- initiated photooxidations of selected HFPEs (i.e., HG-10, HG-01 and HG-11) in atmospheric air predominantly produced carbonyl fluoride (CF_2O) as the only carbon-containing product. Because of the high potential hydrolysis of CF_2O in the aqueous phase, the environmental fate of the product in the atmosphere will be rapidly incorporated into raindrops/aerosols, where it eventually degrades to HF (as fluorides) and CO_2. It is also noted that the reaction of these HFPEs with Cl• atoms yields another product HCl. Due to the extremely high solubility of HCl in liquid water, its lifetime in the atmosphere is very short because it is almost absorbed by raindrops/aerosols. On the other hand, the atmospheric oxidation of selected HFPEs (i.e., HG′-01, HG′-02 and HG′-03) in air will be initiated by the reaction of hydrogen abstraction with •OH radicals or Cl• atoms. In the case of $CH_3O(CF_2CF_2O)_nCH_3$ ($n = 1$–3), it was found that the predominant carbonyl fluoride (CF_2O) was formed by the atmospheric reaction as described above [34]. Other carbon-containing products (i.e., fluorinated formates $CH_3O(CF_2CF_2O)_nC(O)H$, and formaldehyde), however, were also formed by degradation reaction of $CH_3O(CF_2CF_2O)_nCH_2O•$ radical. The former may pose potential hazards to the environment because their environmental fates may be removal mechanisms such as photolysis, hydrolysis and dry deposition [34].

3.3. Vapor pressure

The vapor pressure of an organic compound at the room temperature plays a significant role in its environmental

Table 5
Environmental hazards of selected HFPEs

HFPE	Vapor pressure[a] (mmHg, 25 °C)	$\log K_{ow}$[b]	Bioconcentration factor[c]
HG-00	1476[d]	−0.317	0.338
HG-10	511	−1.574	0.038
HG-01	184	−1.051	0.094
HG-20	118	−2.308	0.010
HG-11	53	−2.046	0.016
HG-02	29	−1.785	0.026
HG-21	17	−3.041	0.003
HG′-00	4403[d,e]	0.067[f]	0.662
HG′-01	248	−0.667	0.183
HG′-02	19	−1.401	0.051
HG′-03	7	−2.134	0.014

[a] Vapor pressure was calculated by using three-parameter corresponding-states equation (i.e., Pitzer expansion) [13].

[b] Octanol/water partition coefficient (K_{ow}), estimated by the Meylan and Howard method [42].

[c] Bioconcentration factor (BCF) was obtained from the regression equation correlating BCF with K_{ow} [18].

[d] The experimental values (see Table 2) were used in the estimation calculation.

[e] The reported data in the literature [19]: vapor pressure = 4450 mmHg.

[f] The reported data in the literature [20]: $\log K_{ow} = 0.1$.

partitioning between gas- and liquid-phases because the property indicates its vapor phase being equilibrium with the corresponding liquid phase. Generally, a chemical with a high vapor pressure has the potential to be easily transported into the atmospheric air, resulting in a relatively environmental hazard and/or health risk in the case of inhaling and/or exposing to the polluted air. Therefore, a reliable method for estimating the vapor pressure of organic materials will be important in screening environmentally risky chemicals.

Although there are many approaches to estimating vapor pressure in terms of temperature [13], most of them are based on the reduced temperature (T_r) and reduced pressure (P_r) if the critical temperature (T_c) and critical pressure (P_c) are given or known. It is noted that the values of T_c and P_c for HFPEs have been estimated by using the Marrero–Pardillo method as shown in Table 2. In the present work, a three-parameter corresponding-states equation was used for estimating vapor pressure because it is more accurate than other methods [13]

$$\ln P_{vpr} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + \omega^2 f^{(2)}(T_r) \tag{8}$$

where P_{vpr} is the reduced vapor pressure. The functions $f^{(0)}$, $f^{(1)}$ and $f^{(2)}$ have been defined and given in the reference [16,17]. Table 5 lists the estimated vapor pressure of HFPEs at 25 °C. As also listed in Table 5, the estimated value (i.e., 4403 mmHg) of model compound, HG′-00, has been predicted to validate the accuracy of the estimation method. It showed that the error is only 1% compared to the measured value (i.e., 4450 mmHg) [19]. From the results in Table 5, the vapor pressures of HFPEs discussed in the present study are significantly lower than the corresponding ethers (e.g., HG′-00) and hydrofluoroethers (e.g., HG-00), showing that HFPEs are not easy to leave its liquid phase as organic vapor, via evaporation. Further, it is obvious that the molecular polarities of HFPEs increase with the increase in ether group (–O–) and molecular weight, resulting in their vapor pressures on the decreasing trend.

3.4. Partition coefficient

Partition coefficient is an empirically dimensionless property that describes how a chemical substance distributes itself between two phases. Hence, it is useful to describe and model the environmental fate of an organic compound. Because the octanol–water partition coefficient (K_{ow}) is characterized by partitioning between aqueous and organic, lipid-like phases, it provides a significant indication of how much of an organic compound will be taken up by aquatic organisms. Because of K_{ow} ranging from 10^{-3} to 10^7, values for K_{ow} are often reported as $\log K_{ow}$ [18]. Generally, organic compounds with high values of K_{ow} tend to be hydrophobic and hence partition to organic matter, lipids (fat) and soil, indicating that they are less mobile in the environment.

It is well known that several methods are available for the estimation of K_{ow} for organic chemicals [18]. However, these approaches are somewhat complicated and not easy to use them. In the present paper, a simple group contribution method, or Meylan and Howard method was used for estimating the partition coefficient of HFPEs as follows [42]:

$$\log K_{ow} = 0.229 + \sum n_i f_i \tag{9}$$

where $\log K_{ow}$ is the base 10 logarithm of the ratio the chemical's concentration in octanol to the chemical's concentration in water, n_i is the number of groups of type i in the molecule, f_i is the contribution of each group to the partition coefficient, and the summation is taken over all groups. To validate the accuracy of the method in the estimation of partition coefficients for HFPEs, four common ethers (i.e., dimethoxymethane, dimethoxyethane, diethyleneglycoldimethylether, and bis(2-chloromethyl)ether) that are similar in chemical structure to these HFPEs were estimated to obtain their partition coefficients, which were then compared to those reported or measured in the literatures [20]. According to their molecular structures, the predicted values of $\log K_{ow}$ are given by:

- Dimethoxymethane ($CH_3OCH_2OCH_3$):

  $K_{ow} = 0.229 + 0.5473 \times 2 + 0.4911 \times 1 + (-1.2566)$
  $\times 2 \fallingdotseq -0.699$

- Dimethoxymethane ($CH_3OCH_2CH_2OCH_3$):

  $K_{ow} = 0.229 + 0.5473 \times 2 + 0.4911 \times 2 + (-1.2566)$
  $\times 2 \fallingdotseq -0.207$

- Diethyleneglycoldimethylether ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$):

  $K_{ow} = 0.229 + 0.5473 \times 2 + 0.4911 \times 4 + (-1.2566)$
  $\times 3 \fallingdotseq -0.482$

- Bis(2-chloromethyl)ether $ClCH_2OCH_2Cl$:

  $K_{ow} = 0.229 + 0.3102 \times 2 + 0.4911 \times 2 + (-1.2566)$
  $\times 1 \fallingdotseq 0.575$

As illustrated with the experimental or reported values (i.e., 0.0, −0.21, −0.36, and 0.57, respectively) of dimethoxymethane, dimethoxyethane, diethyleneglycoldimethylether, and bis(2-chloromethyl)ether, it showed that the Meylan and Howard method should be a practically useful approach to predicating the octanol–water partition coefficient of HFPEs.

Table 5 lists the estimated values of $\log K_{ow}$ for selected HFPEs. For example, HG′-00 has the molecular structure $H_3C–O–CH_3$. Referring to the contribution groups in the method, this compound can be represented by two –CH$_3$ (methyl) group, and one –O– (aliphatic attachment) group. The estimated value of $\log K_{ow}$ is thus given by

$$\log K_{ow} = 0.229 + 0.5473 \times 2 + (-1.2566) \times 1 \fallingdotseq 0.067$$

However, the reported $\log K_{ow}$ value for HG′-00 is 0.1 [20], which is very close to the calculated value (i.e., 0.067) from the Meylan and Howard method. From the predicted data in Table 5, it can be summarized that the values of $\log K_{ow}$ for selected HFPEs are significantly below zero, showing that these fluoroethers have very low potential bioaccumulation in the environment [43].

Table 6
Exposure standards/guidelines of primary and secondary products from the degradation of HFPEs

Photodegradation products	TLV[a] (ppm)	PEL[b] (ppm)	MAK[c] (ppm)	IDLH[d] (ppm)	REL[e] (ppm)	PCS[f] (ppm)
Carbonyl fluoride (COF_2)	2	–		–	2	–
Hydrogen fluoride (HF, as F)	3 (ceiling)	3	2	30	3	3
Carbon dioxide (CO_2)	5000	5000	5000	40,000	5000	5000
Hydrogen chloride (HCl)	5 (ceiling)	5 (ceiling)	2	50	5 (ceiling)	5 (ceiling)
Formaldehyde (HCHO)	0.3 (ceiling)	0.75	0.3	20	0.016 (cancer)	1 (cancer)
Carbon monoxide (CO)	25	50	30	1,200	35	35
Formic acid (HCOOH)	5	5	5	30	5	5
Acetic acid (CH_3COOH)	10	10	–	50	10	10

[a] Threshold limit value, American Conference of Governmental Industrial Hygienists [47].
[b] Permissible exposure limit, Occupational Safety and Health Administration [48].
[c] Maximum allowable concentration, Deutsche Forschungsgemeinschaft (DFG, Germany) [49].
[d] Immediately dangerous to life or health, National Institute for Occupational Safety and Health [50].
[e] Recommended exposure limit, National Institute for Occupational Safety and Health [51].
[f] Permissible Concentration Standard, Council of Labor Affairs (COLA, Taiwan).

Based on the estimated values of HFPEs, the bioconcentration factor (BCF), which is generally used as an essential component in risk assessments for the purpose of determining the tendency of an organic chemical to bioconcentrate on the lipid tissues (e.g., fat), can be further predicted by using the well-developed correlation between BCF and K_{ow} [18]

$$\log \text{BCF} = 0.76 \log K_{ow} - 0.23 \qquad (10)$$

As listed in Table 5, the estimated values of BCF for selected HFPEs are below unity, indicating that they should be a very low potential for bioaccumulation.

3.5. Toxicological profile of HFPEs

Due to their physiochemical properties similar to those of ethers, HFPEs would be expected to have no significant health risk because of the low potential for human toxicity by aliphatic ethers and glycol ethers from the viewpoints of a wide variety of industrial and commercial uses [44,45]. With respect to the toxicological profiles for selected HFPEs, there are no detailed data in the literature. According to the limited references [11,12] and material safety data sheet from the manufacturers, available toxicological data strongly support conclusion that HFPEs do not pose any risk in the field of carcinogenicity, mutagenicity and reprotoxicity. As observed in the literature [11], commercial grades of HFPEs consist of polydispersed components with a limited molecular weight range from fractional distillation, exhibit relatively low toxicity from the results of acute and long term toxicity tests.

Although less extreme maximum atmospheric concentrations of HFPEs were employed, their degradation products derived from the photochemical reactions and thermal decompositions may generate toxic vapors possibly containing COF_2, F^-, or HF. The human exposure limits to possible degradation products from HFPEs established or recommended by the governmental or non-profit organizations were compiled for a comparative use and listed in Table 6. Among them, carbonyl fluoride (COF_2) is a powerful irritating gas. The carbonyl fluoride is easily hydrolyzed to form hydrogen fluoride, which is moderately toxic to human by inhalation due to the release of fluoride ions in contact with moist body tissues [46]. Unfortunately, the data on the atmospheric concentrations of the degradation products are not available.

4. Conclusions

Hydrofluoropolyethers (HFPEs) are a family of linear oligomeric fluorinated fluid having repeated units (i.e., $-CF_2O-$ and $-CF_2CF_2O-$) and two terminal groups (i.e., $-OCF_2H$ and $-OCH_3$). Due to their unique properties, they may be used as fire suppression agent, heat transfer fluid, and cleaning solvent. Though HFPEs discussed in this paper have been exempted from the blanket of ozone depleting substances (ODS) and should possess very low potential for bioaccumulation in the environment based on their estimated values of octanol-water partition coefficient (K_{ow}), these chemicals inevitably pose some risks to the environment in terms of global warming potential and photochemical potential. Therefore, the emission of organic vapors from the manufacturing and filling processes may contain HFPEs, suggesting that it still needs to be mitigated and even prevented to reduce the overexposure risk even if their acceptable exposure limits have been set at 1000 ppm over eight working hours by US Environmental Protection Agency (USEPA).

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