



HFO-1234yf in the environment

by Félix Dalang, Dr in Chemistry EPF-Z, 8-6-2010

• Introduction

Through out history, we have seen an important evolution of the substances utilized in refrigeration machines. Ammoniac and carbon dioxide were initially used. Chlorofluorocarbons (CFCs) then rapidly replaced these fluids, since they were more simple to employ and apparently non-hazardous. However, due to their ability to deplete the ozone layer in the stratosphere, they were in turn substituted by Hydrochlorofluorocarbons (HCFC), which had an inferior ozone depletion index (ODI). Today, HFC is widely utilized, a substance that is inoffensive for the ozone layer but with a considerable global warming potential (GWP). The research is currently going in two directions:

1. return to the inoffensive ammoniac, carbon dioxide and hydrocarbons.
2. towards products similar to HFC, but with no ODI or GWP.

A promising product for the second option is HFO-1234yf. Its chemical name (IUPAC) is 2,3,3,3-tetrafluoroprop-1-ene, its formula is $\text{CH}_2=\text{CFCF}_3$. This molecule contains a double bond between two carbon atoms. These substances are called olefines. The term HFO is an abbreviation for hydrofluoroolefine.

According to its producers, this substance is the ideal replacement for HFC134a, which has an estimated GWP 1300 times higher than that of carbon dioxide (over a time span of 100 years)¹. The chemical and physiochemical properties of these two substances are very similar. HFO-1234yf has a low toxicity level and is non-ozone depleting. It has a short life cycle in the atmosphere, thus a low GWP.

For what reasons is it then being criticized? HFO-1234yf (here after HFO) decomposes in the environment to form trifluoroacetic acid (TFA). In turn, TFA is an extremely persistent substance that accumulates in nature without decomposing. It is water-soluble, thus rapidly migrating from the atmosphere into natural water sources. Within this environment, it is suspected to accumulate locally and attain harmful concentrations. The estimated average concentration levels that are expected, do not seem to initially be catastrophic. However, there is currently insufficient knowledge to make such an assessment. The effects of ecotoxicity, induced gene mutation, and the effects on fertility etc., remain unknown. Besides some technical issues, it is this formation of TFA and the major environmental hazard that it entails, which is the main obstacle to the use of HFO.

• Properties of HFO

The HFO has a low toxicity level, but is flammable (only slightly flammable in the USA). However, the fumes from fires contains hydrofluoric acid, an extremely toxic gas ^{2,3}.

Since HFC-134a is less expensive to produce than HFO and that these products have very similar physio-chemical properties, there is a risk for fraudulent replacements with HFC-134a during maintenance procedures. The utilisation of HFC-134a is in this manner prolonged without restraint ⁴.

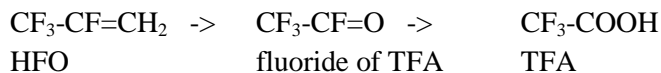
HFO is largely responsible for the formation of ozone in the troposphere (this being the detrimental ozone which creates the summer smog, not to be confused with the useful ozone in the stratosphere). According to Luecken et al. this impact can be compensated by a slight improvement in the efficiency of refrigeration machines ⁵.

The above-mentioned inconveniences of HFO are simply technical, and in our opinion, are not too significant. They are comparable to the inconveniences of other technical solutions.

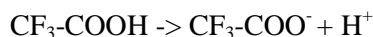
The major ecological risk presented by HFO is the property it has of transforming into trifluoroacetic acid (TFA) within nature, an extremely preoccupying substance to find in the environment. Since this product is rapidly leached out of the atmosphere and into the hydrosphere, the implied risks cannot be detected by superficial research.

• Trifluoroacetic acid (TFA)

The life cycle of HFO in the atmosphere is very short, only approximately 11 days. Therefore, the product very rapidly disappears from the atmosphere, for this reason the calculated GWP over 100 years is only of 4 ⁶. The HFO decomposes in two stages, in order to form almost 100% trifluoroacetic acid (TFA) ⁷.



Like all the strong acids, trifluoroacetic acid is present in nature in its neutralised ionic form, trifluoroacetate: $\text{CF}_3\text{-COO}^-$. This ion is formed by deprotonation of the trifluoroacetic acid.



TFA is not very toxic. The most sensitive organism known to this day, the algae *Selenastrum capricornutum*, shows alterations at a concentration of 120 microgram/litre. The current concentrations in natural surface waters are almost 1000 times inferior. However, the level of increase of this concentration over time is yet unidentified. Some authors suspect the existence of a preindustrial source of TFA ⁸.

It is true that the other HFC also transform into TFA. According to Luecken et al. this transformation only occurs at a level of 20 to 30 %, whereas HFO-1234yf transforms to 100% ⁹.

TFA is non-biodegradable, except eventually in very particular anaerobic situations ¹⁰. Consequently, all TFA introduced into nature remains there unchanged, for centuries and centuries.

Even the industry (AFEAS) supports this fact ¹¹. Yet, according to the AFEAS, all signs indicate that TFA is not harmful for the environment.

TFA is soluble in water. It does not accumulate in the fatty tissues like PCB or DDT. Still, we ignore if there are other mechanisms of accumulation elsewhere in nature.

• Origins of TFA

Luecken estimates that it is impossible for the sum of TFA currently present in the hydrosphere to stem from the decomposition of the F-gases produced by the industry to this day¹². The authors therefore suspect a natural presence of TFA. This paper is an attempt to present the pollution of the atmosphere with TFA, as well as of rainwater, as something safe.

According to the European Fluorocarbon Technical Committee (EFCTC)¹³, TFA is a natural substance that has accumulated in the oceans over millions of years. It has probably been formed around the eruption of deep-sea volcanoes^{14,15}.

There is currently proof that TFA is to be found everywhere within the hydrosphere. In the ocean, it is detected at concentrations of approximately 0.2 µg/l.¹⁶

Another source of TFA is the thermodecomposition of fluoropolymers – for example through the incineration of Teflon at a waste incineration plant. This could also explain the important quantities of TFA present in the hydrosphere¹⁷.

However, no traces of TFA have been found in the deep ice layers of Greenland. This indicates that there exists no natural source of TFA in fresh water or in the atmosphere¹⁸.

In conclusion there seems to be no natural source of TFA in the atmosphere or fresh water. In their natural state, fresh water and the atmosphere, contain no TFA. Within the latter environments this substance is anthropogenic. However, in its natural state, the ocean contains TFA most probably formed during the eruption of deep-sea volcanoes.

The anthropogenic sources are mainly from the decomposition of fluorinated products, such as HFO but also HFC, probably also, due to the thermodecomposition of fluoropolymer materials (eg. Teflon in waste incineration).

Currently we discover more and more processes that lead to the formation of TFA from anthropogenic substances, such as fluoracetates¹⁹.

• The concentration of TFA in nature

Luecken et al.²⁰ give an estimation of the accumulation of TFA during one summer, assuming that the air-conditioning systems of all cars function using HFO1234yf. The results are concentrations in the summer rainwater of 0.5 µg/l, on average, in eastern USA and superior to 1 µg/l in the south of Los Angeles. These concentrations yield an accumulation of 160 to 240 g/km² for the USA, with peaks going up to 800 g/km². The fact that this substance accumulates over years in the hydrosphere is unfortunately not taken into account. One can fear that the harmful effects will only manifest themselves in the decades to come, and in an irreversible manner.

A similar research has made estimates for Japan. It estimates the concentrations of HFO, CF₃-CF=O and TFA in the air and the surface water, assuming that all the cars are equipped with an air conditioning system that uses R1234-yf. The results are similar: the maximum concentrations vary between 0.45 and 1.3 µg/l, the average in the study area is between 0.04 and 0.08 µg/l. This result is

not seen as preoccupying. The maximal concentration in the water is according to the study 80 times inferior to the "no observed adverse effect level" (NOAEL) on the algae ²¹.

It should be highlighted here that these estimates match the current level of concentration in the ocean's depth, accumulated over thousands of years. Furthermore, the estimates are rough and the factor of 80 between the expected concentration and the "no-effect level" could reveal itself to be insufficient.

An environmental report of the United Nations expresses its concern for example, about the assimilation by the roots of plants, and an accumulation in leaves, caused by the solubility of this substance ²². According to the same study, there is insufficient information to evaluate the impacts on development, reproduction and chronic effects ²³.

The Society of Automotive Engineers (SAE) has carried out a Life Cycle Climate Performance (LCCP) analysis of HFO, which is supposedly significantly better than R134a ²⁴.

In conclusion: TFA is presently found everywhere in the hydrosphere apart from in the deep ice of Greenland. Its average concentration in fresh water is approximately 0.15 µg/l, with important local variations. The concentration in the oceans is uniformly approximately 0.2 µg/l. The promoters of TFA argue that if there would be a generalized utilisation of HFO, it would only lead to a negligible increase of TFA in the rainwater. Yet, this would be a concentration equal to that currently present in the deep ocean. To this date, there has been no study to measure the effects of the accumulation of this substance in fresh water and on land.

• The precautionary principle

There is no scientific disagreement on the degradation of F-gases into TFA and on the persistence of this substance in nature. The disagreement is at a political level: how to evaluate the environmental risk of the production of products that are precursors to TFA?

The proof of TFA in the environment is quite recent. Its chemical behaviour in nature is still poorly understood. For example, we ignore whether there exists a mechanism of accumulation in nature that could cause negative side effects.

At one point in time, humanity was in a similar situation with PCB or DDT. These two substances, which were at first reputed to be inoffensive, are also quasi imperishable in nature. They were produced in mass and released into nature, with serious ecological consequences caused by unsuspected mechanisms. Today we are behaving with the same irresponsible manner with the nanoparticles. Will TFA be the next candidate in a sad series of human errors?

What value do we give to the precautionary principle? The fact remains that this non-natural substance is highly persistent and accumulates infinitely in the hydrosphere – but is *apparently* non-toxic. Is this, together with the knowledge that harmless alternative technologies exist, not enough reason to prohibit it? The USA and Europe disagree on this matter.

The literature on this issue is abundant but not very precise. Following are some citations:

The precautionary principle is well established in people's minds, but has not been given much legal recognition, neither in the USA nor in Europe ²⁵: "Very little of this is enshrined in law, though the European Union has enclosed the principle in a legally untested (as yet) manner in its Fifth

Environmental Action Plan for the period 1992 – 1999. In United States legislation, the principle is particularly applied to potentially bioaccumulative, persistent and toxic chemicals. However, a strict legal interpretation could be too prohibitive of technological advance so the courts loathe pronouncing upon it; nor are the regulatory authorities willing to push it to its commercial limits (Bodansky);"

A book ²⁶ offers a historical overview of the notion of the precautionary principle in different countries and different settings.

Here is also a text from the EPA on the precautionary principle, enclosing the definition of the 1992 Rio Conference: “[w]here there are threats of serious or irreversible damage, lack of scientific certainty shall not be used as a reason for postponing cost effective measures to prevent environmental degradation.” ²⁷.

• Political appreciation

The Federal Office for the Environment (FOEN) in Switzerland establishes that: "... it is particularly troublesome to note that the degradation of R134a produces trifluoroacetic acid, basically non-biodegradable in nature. The increasing utilisation of R134a, with the high concentrations of trifluoroacetic acid that this implies, could pose a grave long-term threat to the environment the extent of which is still unknown, since the eco-toxicological potential of TFA has only been evaluated to a small extent" ²⁸. This observation is even more applicable to HFO.

FOEN warns against the use of all substances that are non-biodegradable in the environment ²⁹.

According to this same office, a good example of an alternative for supermarkets would be the use of ammonia refrigerating machines, together with a distribution network system throughout the store that uses liquid CO₂ at room temperature. The FOEN also deplores the fact that manufacturers of fluorinated products disregard the use of “natural” fluids, and attempt to complicate their application through the promotion of biased security regulations ³⁰.

The following tract presupposes for example that HFO-1234yf is better than CO₂ ³¹.

Kriebler et al. establish that the precautionary principle is of European origin. The principle is better accepted in Europe. They provide a definition and a certain number of examples. The most telling example is plasticisers in PVC toys. They are prohibited due to the simple suspicion that they may be harmful to our health and because there exists economical alternative techniques. The authors offer a reflection on how to rationalise and apply the precautionary principle. They criticize the customary scientific methods and affirm that these methods are inadequate for a dangerous situation that presents too many uncertainties. This paper calls for policies that properly take into consideration the uncertainties still existing in scientific results ³².

• Conclusion

It is not easy to find a clear-cut opinion on the generalized use of HFO-1234yf, because the industry floods the web with information that trivialises this substance and disclaims “natural” refrigerants.

Taking into account the existing knowledge, many specialists judge the mass production of precursors to trifluoroacetic acid as irresponsible!

The precautionary principle forbids the mass production of HFO-1234yf until completion of studies on the environmental impact of this substance.

To allow the accumulation of synthetic products in nature is inadmissible! This is the case for TFA – it seems to accumulate ad infinitum. The ecotoxicological potential of TFA is still highly uncertain and its release could trigger serious ecological problems. In the past, certain persistent substances have provoked several catastrophes (DDT, PCB, CFC, SF6). Presently, we are facing similar predicaments with, for example PFOS (perfluorooctane sulfonate) or nanoparticles. Is it really necessary to add TFA to the list?

¹ UNFCCC: Climate Change 1995, The Science of Climate Change: Summary for Policymakers and Technical Summary of the Working Group I Report, page 22
http://unfccc.int/ghg_data/items/3825.php

² <http://www.r744.com/articles/2010-02-15-tests-confirm-hfc-1234yf-explosive-at-low-concentration.php>

³ http://www.alliance-co2-solutions.org/docs/press_release_2008_06_04_en.pdf

⁴ <http://www.r744.com/articles/2009-10-28-new-greenpeace-position-paper-four-reasons-against-hfos.php>

⁵ D.J. Luecken et al., "Ozone and TFA Impacts in North America from Degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf): A Potential Greenhouse Gas Replacement" Environ. Sci. Technol. 2010, 44, 343–348 <http://pubs.acs.org/doi/pdf/10.1021/es902481f>

⁶ Nielsen ; Javadi ; Sulbaek Andersen, "Atmospheric chemistry of CF₃CF=CH₂: Kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and O₃", Chemical physics letters 2007, 439, 18 – 22. Article disponible sous:
www.cogci.dk/network/OJN_174_CF3CF=CH2.pdf

⁷ Luecken et al., loc. cit.

⁸ Jean Charles Boutonnet; Pauline Bingham; Davide Calamari; Christ de Rooij; James Franklin; Toshihiko Kawano; Jean-Marie Libre; Archie McCulloch; Giuseppe Malinverno; J. Martin Odom; George M. Rusch; Katie Smythe; Igor Sobolev; Roy Thompson; James M. Tiedje, "Environmental Risk Assessment of Trifluoroacetic Acid", Human and Ecological Risk Assessment: An International Journal, 1549-7860, Volume 5, Issue 1, 1999, Pages 59 – 124

⁹ Luecken et al., loc.cit.

¹⁰ B.R. Kim, M.T. Suidan, T.J. Wallington, X. Du, "Biodegradability of Trifluoroacetic Acid", *Environmental Engineering Science*. NOVEMBER/DECEMBER 2000, 17(6): 337-342

¹¹ <http://www.afeas.org/environ.html>

¹² Luecken et al., loc. cit.

¹³

http://www.fluorocarbons.org/documents/Regulatory/Position%20Papers/15.03.2010_P.P.%20HFOs.pdf

¹⁴ cité d'après Frank H., E.H. Christoph, O. Holm-Hansen and J.L. Bullister, "Trifluoroacetate in Ocean Waters", *Environ. Sci. Technol.*, 36, 12-15, 2002 abstract: <http://pubs.acs.org/doi/abs/10.1021/es0101532>

¹⁵ Scott B.F., R.W. Macdonald, K. Kannan, A. Fisk, A. Witter, N. Yamashita, L. Durham, C. Spencer and D.C.G. Muir, "Trifluoroacetate (TFA) Profiles in the Arctic, Atlantic and Pacific Oceans", *Environ. Sci. Technol.*, 39, 6555-6560, 2005 abstract: <http://pubs.acs.org/doi/abs/10.1021/es047975u>

¹⁶ Frank, H et al.: loc cit.

¹⁷ David A. Ellis, Scott A. Mabury, Jonathan W. Martin & Derek C. G. Muir, "Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment", *Nature* 412, 321-324

¹⁸ Ole John Nielsen, Brian F. Scott, Christine Spencer, Timothy J. Wallington and James C. Ball, "Trifluoroacetic acid in ancient freshwater", *Atmospheric Environment*, Volume 35, Issue 16, June 2001, Pages 2799-2801 abstract http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6VH3-42YF8W4-1&_user=10&_coverDate=06%2F30%2F2001&_rdoc=1&_fmt=high&_orig=search&_sort=d&_docanchor=&_view=c&_searchStrId=1351201926&_rerunOrigin=scholar.google&_acct=C000050221&_version=1&_urlVersion=0&_userid=10&md5=b175f7effb536a54554bc914e9a773bf

¹⁹ Blanco M.B. et al., "Atmospheric photooxidation of fluoroacetates as a source of fluorocarboxylic acids", *Environ. Sci. Technol* 2010, 2354-59 (2010)

²⁰ Luecken et al., op.cit.

²¹ Hideo Kajihara, Kazuya Inoue, Kikuo Yoshida, Ryuichi Nagaosa, "Estimation of environmental concentrations and deposition fluxes of R-1234-YF and its decomposition products emitted from air conditioning equipment to atmosphere", 2010 International Symposium on Next-generation Air Conditioning and Refrigeration Technology, 17 – 19 February 2010, Tokyo, Japan. www.nedo.go.jp/english/publications/reports/reitou/ns/ns24.pdf

²² United Nations environmental programme, "Environmental effects of ozone depletion", 1998 <http://sedac.ciesin.columbia.edu/ozone/docs/UNEP98/UNEP98p57.html>

²³ <http://sedac.ciesin.columbia.edu/ozone/docs/UNEP98/UNEP98p2.html>

²⁴ <http://www.sae.org/technical/papers/2009-01-0179>

²⁵ Tim O'Riordan, "The politics of the precautionary principle" in Ronnie Harding and E. Fisher ed. "Perspectives on the precautionary principle", p. 285, Federation Press, Annadale (Australia) 1999

²⁶ Tim O'Riordan, James Cameron ed: "Interpreting the precautionary principle", London 1994.

²⁷ <http://www.epa.gov/environmentaljustice/resources/publications/nejac/p2-recommend-report-0703.pdf>

²⁸ Federal Office for the Environment, E. Furrer,
<http://www.bafu.admin.ch/chemikalien/01389/01404/index.html?lang=fr> , url:
http://www.bafu.admin.ch/chemikalien/01389/01404/index.html?lang=fr&download=NHZLpZeg7t,lnp6I0NTU042I2Z6ln1ae2IZn4Z2qZpnO2Yuq2Z6gpJCDeoR5fmym162epYbg2c_JjKbNoKSn6A--

²⁹
<http://www.bafu.admin.ch/publikationen/publikation/00317/index.html?lang=fr&download=NHZLpZig7t,lnp6I0NTU042I2Z6ln1ae2IZn4Z2qZpnO2Yuq2Z6gpJCGd398fWym162dpYbUzd,Gpd6emK2Oz9aGodetmqaN19XI2IdvoaCVZ,s-.pdf>

³⁰ (<http://www.bafu.admin.ch/chemikalien/01389/01404/index.html> chapitre 2 ou
http://www.bafu.admin.ch/chemikalien/01389/01404/index.html?download=NHZLpZeg7t,lnp6I0NTU042I2Z6ln1acy4Zn4Z2qZpnO2Yuq2Z6gpJCDeoR5fmym162epYbg2c_JjKbNoKSn6A--&lang=de

³¹ www.1234facts.com/pdf/Honeywell_1234yf_chart.pdf

³² D Kriebel, J Tickner, P Epstein, J Lemons, R Levins, E L Loechler, M Quinn, R Rudel, T Schettler, and M Stoto, "The precautionary principle in environmental science"; Environ Health Perspect. 2001 September; 109(9): 871–876