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HCFOs, HBFOs, Stratospheric Ozone and Climate Change

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The HCFOs and HBFOs that have been selected for a range of applications breakdown rapidly in the atmosphere and have ultra-low GWPs, whilst maintaining a good balance of technical and safety properties. These are HCFO-1224yd(Z), HCFO-1233zd(E) and HBFO-1233xfB. All are oxidised rapidly in the lower atmosphere with atmospheric lifetimes of 21 days[i], 26 days[ii] and 7 days[iii], respectively; hence all are very short lived substance (VSLS)[iv]iv that, in view of their minimal effect on stratospheric ozone, are not listed as Ozone Depleting Substances in the Montreal Protocol.

The Montreal Protocol has a defined process for assessing new substances that the Scientific Assessment Panel has estimated to have a significant ozone-depleting potential (See Montreal Protocol Decisions on new substances, including Decision IX/24). HCFO-1233zd(E) has been reviewed and assessed by the Scientific Assessment Panel (see SAP2018). **The HCFOs do not have significant ozone depletion potentials.**

It takes several months for a substance released in northern temperate regions of the world to be transported through the lower atmosphere before it is injected into the stratosphere. Consequently, very little of these halopropenes can be transported to the ozone layer. In the case of HCFO-1233zd(E), for material emitted between 30_o and 60_oN, an average Ozone Depletion Potential (ODP) has been calculated to be 0.00034[v] and, on the same basis, that of HBFO-1233xfB is 0.0028[vi]. The ODP of HCFO-1224yd(Z) is reported as 0.00012[i]. A more recent paper reported essentially the same ODP of HCFO-1233zd(E) at 0.0003[vii]. Due to their very short atmospheric lifetimes, these substances do not accumulate in the atmosphere and the global warming potentials (GWPs) of all substances are 1 or less than 1[1,5,6] (that is less than carbon dioxide at the 100-year time horizon).
The authors of the papers which reported these data stated that, "**The short lifetime, low ODP, and low GWP indicate that [these substances] should have minimal effects on ozone and climate**."

The EU Ozone Regulation 1005/2009 defines controlled substances as ' substances listed in Annex I, including their isomers, whether alone or in a mixture, and whether they are virgin, recovered, recycled or reclaimed;" The Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures Version 5.0 – July 2017 in section 5.1 Hazardous to the Ozone Layer states that *"Any substances having an Ozone Depleting Potential (ODP) greater or equal to the lowest ODP (i.e. 0.005) of the substances currently listed in Annex I to Regulation (EC) No 1005/2009 should be classified as hazardous to the ozone layer (category 1)."* **The HCFOs have extremely low ODPs that are well below the threshold in the CLP guidance.**

Designation	Name and formula	GWP	Atmospheric lifetime (days)	Ozone Depleting Potential	Main Applications
HCFO-1224yd(Z)	2,3,3,3 Tetrafluoro-1-chloroprop-1-ene CF_3-CF=CHCl	< 1 [i]	21 [i]	0.00012 [i]	• Refrigerant for centrifugal chillers, high temperature heat pumps • working fluid for organic rankine cycle (ORC) • Blowing agent for polyurethane foams
HBFO-1233xfB	2-bromo-3,3,3-trifluoropropene $CF_3CBr=CH_2$	0.26 [vi]	7 [vi]	0.0028 [vi]	• Fire extinguishant streaming agent (also known as 2-BTP)
HCFO-1233zd(E)	Trans 1-Chloro-3,3,3-trifluoroprop-1-ene Trans-$CHCl=CHCF_3$	1 [viii]	26 [ii]	0.00034 [v]	• Refrigerant for chiller applications, high temperature heat pumps • Working fluid for organic rankine cycle (ORC) • Blowing agent for Insulation foams • Precision solvents

[i] Measured by the National Institute of Advanced Industrial Science and Technology, Japan (AIST); GWP calculated according to the IPCC AR5 method.

[ii] Myhre, G., D. Shindell, F.-M. Bréon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura and H. Zhang, 2013: Anthropogenic and Natural Radiative Forcing. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[iii] Patten, K. O., V. G. Khamaganov, V. L. Orkin, S. L. Baughcum, and D. J. Wuebbles (2011), OH reaction rate constant, IR absorption spectrum, ozone depletion potentials and global warming potentials of 2-bromo-3,3,3-trifluoropropene, J. Geophys. Res., 116, D24307, doi:10.1029/2011JD016518.

[iv] Ko M.K.W. and 32 others, Very Short-Lived Halogen and Sulphur Substances, Chapter 2 of Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project - Report No. 47, World Meteorological Organization, Geneva, 2002.

[v] Patten, K. O. and Wuebbles, D. J.: Atmospheric lifetimes and Ozone Depletion Potentials of trans-1-chloro-3,3,3-trifluoropropylene and trans-1,2-dichloroethylene in a three-dimensional model, Atmos. Chem. Phys., 10, 10867-10874, https://doi.org/10.5194/acp-10-10867-2010, 2010.

[vi] Patten, K. O., V. G. Khamaganov, V. L. Orkin, S. L. Baughcum, and D. J. Wuebbles (2012), Correction to "OH reaction rate constant, IR absorption spectrum, ozone depletion potentials and global warming potentials of 2-bromo-3,3,3-trifluoropropene," J. Geophys. Res., 117, D22301, doi:10.1029/2012JD019051.

[vii] Sulback Andersen, M.P., J.A. Schmidt, A. Volkova, and D.J. Wuebbles, A three-dimensional model of the atmospheric chemistry of *E* and *Z*-CF3CH=CHCl (HCFO-1233(zd) (E/Z)), *Atmos. Environ.*, *179*, 250−259, doi:10.1016/j.atmosenv.2018.02.018, 2018.

[viii] IPCC Working Group I – The Physical Science Basis – Chap.8 Annex 8.A.1, 5th Assessment Report