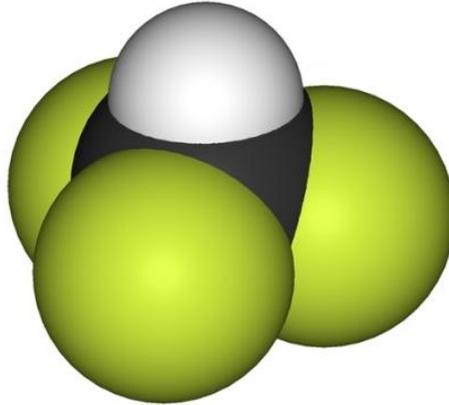


Halocarbon



Model of the fluorocarbon molecule (carbon trifluoride), a potent greenhouse gas. Source: Creative Commons

A **halocarbon** is an organic chemical molecule composed of at least one carbon atom bound covalently with one or more halogen atoms; the most common halogens in these molecules are fluorine, chlorine, bromine and iodine. Naturally occurring halocarbons are created by certain volcanic eruptions, forest fires, fungal decay, certain marine organism metabolism and are found in tissues of diverse organisms ranging from marine snails to various plants.

Many halocarbons become air pollutants, water pollutants in surface and groundwater resources and as soil contaminants. In the atmosphere, some of these chemicals produce significant impacts of upper atmosphere ozone depletion and also as radiative forcing gases implicated in climate change. In fact, many scientists have suggested that effective regulation of halocarbons may be a more cost effective approach to mitigating global warming than extensive regulation of the much weaker greenhouse gas, carbon dioxide.

Natural occurrence

The most commonly occurring halocarbon is methyl chloride (CH_3Cl), which is produced variously through fungal decay, marine organism metabolism and burning of biomass (e.g. forest fires). Due to spatial variations in these processes, the lower atmospheric concentration of methyl chloride varies from 500 to 2000 parts per trillion by volume (pptv); however, mean tropospheric wide levels are around an estimated 600 pptv.

Man-made sources



Slash-and-burn practice, Morondava, Madagascar. Source: Frank Vassen

Principal anthropogenic sources of halocarbons are: (a) release of refrigerants into the atmosphere; (b) accidental release of tetrachloroethylene, carbon tetrachloride and other industrial solvents into the environment; and (c) slash-and-burn agriculture, whereby indigenous people burn forests for quick yields of charcoal and first year crops.

Natural sinks

Halocarbons find their way into the atmosphere from both natural occurrence and through escape from manufactured products. However, there are natural sinks at work, whose potency is difficult to compute, due to the low concentrations of halocarbons, and due to the infinite variety of halocarbon compounds, microbial agents and environmental variables. Sinks include bacterial dehalogenation in air, water and soil media.

In the troposphere dehalogenation by the hydroxyl ion is an important sink, whereas stratospheric dehalogenation involves important contributions from excited oxygen and chlorine ions.

The reductive dehalogenation capability of certain microbes such as *Methanosarcina barkerii* has been known to act on numerous chlorinated halocarbons for some time. Soil sinks have been studied sufficiently to determine that they are robust removal agents. The upper two meters of aerobic soils have been extrapolated to be responsible for removal of about forty percent of all atmospheric carbon tetrachloride.

Since man-made halocarbons have been emitted in large quantities into the environment for many decades, and natural sources for hundreds of thousands of years, oceanic concentrations of many of these chemicals are in quasi-equilibrium, particularly in the Epipelagic zone, where mixing is robust. For example, concentrations of carbon tetrachloride is found to be approximately 0.25 of saturation at a depth of 95 meters in the sub-oxic zone of Saanich Inlet, British Columbia, while CFC-12 is at virtually saturation at the same depth.

To demonstrate the efficacy of bacterial dehalogenation, in the Gotland Basin of the Baltic Sea, carbon tetrachloride and CFC-11 are severely depleted in the shallow anoxic zone compared to surface concentrations, due to robust anoxic bacterial attack.

Methyl chloride and methyl bromide are also subject to natural process anaerobic bacterial dehalogenation. As a more specialized example, methyl chloride was found to undergo efficient dehalogenation within an anaerobic cyanobacterial mat on the shoreline of Mono Lake, where anoxic conditions were present within three millimeters of the mat surface.

History and uses

The first synthesis of a chlorocarbon was carried out by Michael Faraday in 1821, with creation of tetrachloroethene. In the late 1890s Belgian chemist Frederic Swarts was the first to synthesize a fluorocarbon in the laboratory. Not until 1928 did halogens realize commercial importance, when DuPont chemist Thomas Midgely Jr. created a fully halogenated compound for use as a refrigerant. By the 1970s chlorofluorocarbons were in broad industrial use as the main working fluid for refrigerant systems, air conditioning gases, as aerosol propellants, foam producing agents, solvents, dry cleaning chemicals, and paint strippers.

Environmental contamination and toxicity



Tetrachloroethylene tankage used in dry-cleaning

Source: Montana DEQ

Many halocarbons are fundamentally troublesome, due to the volatility of many of these compound to escape into the atmosphere, and due to relatively high solubility and persistence in groundwater and soil, when they are released into surface waters or rupture of underground storage tanks. As air pollutants, many of the halocarbons are both toxic and carcinogenic.

The most prevalent origin of major groundwater contamination is from rupture or spillage of tetrachloroethylene storage tanks, since these have been used broadly throughout the industrialized world for dry cleaning solvents. Prior to the 1980s the common standards, even in Western countries, did not require double-containment, so that there accumulated thousands of subsurface plumes of tetrachloroethylene, rendering groundwater supplies both carcinogenic as well as toxic; many of these plumes extend more than one kilometer from the point of release.

Greenhouse gases

Since most halocarbons absorb radiant reflected sunlight, they contribute to the heating of the troposphere, and thus function as a greenhouse gas. Residence times of a given halocarbon vary significantly. In particular, some are relatively unstable with tropospheric residence times on the order of hours or a few days; iodomethane, for example, is one of these reactive gas molecules. Initially most of the refrigerants used were freon and related chlorofluorocarbons; however, the long residence times of such compounds in the atmosphere led to replacement of preferred refrigerant gases to the more reactive hydrochlorofluorocarbons, whose atmospheric residence time is a lesser ten to fifteen years half-life.

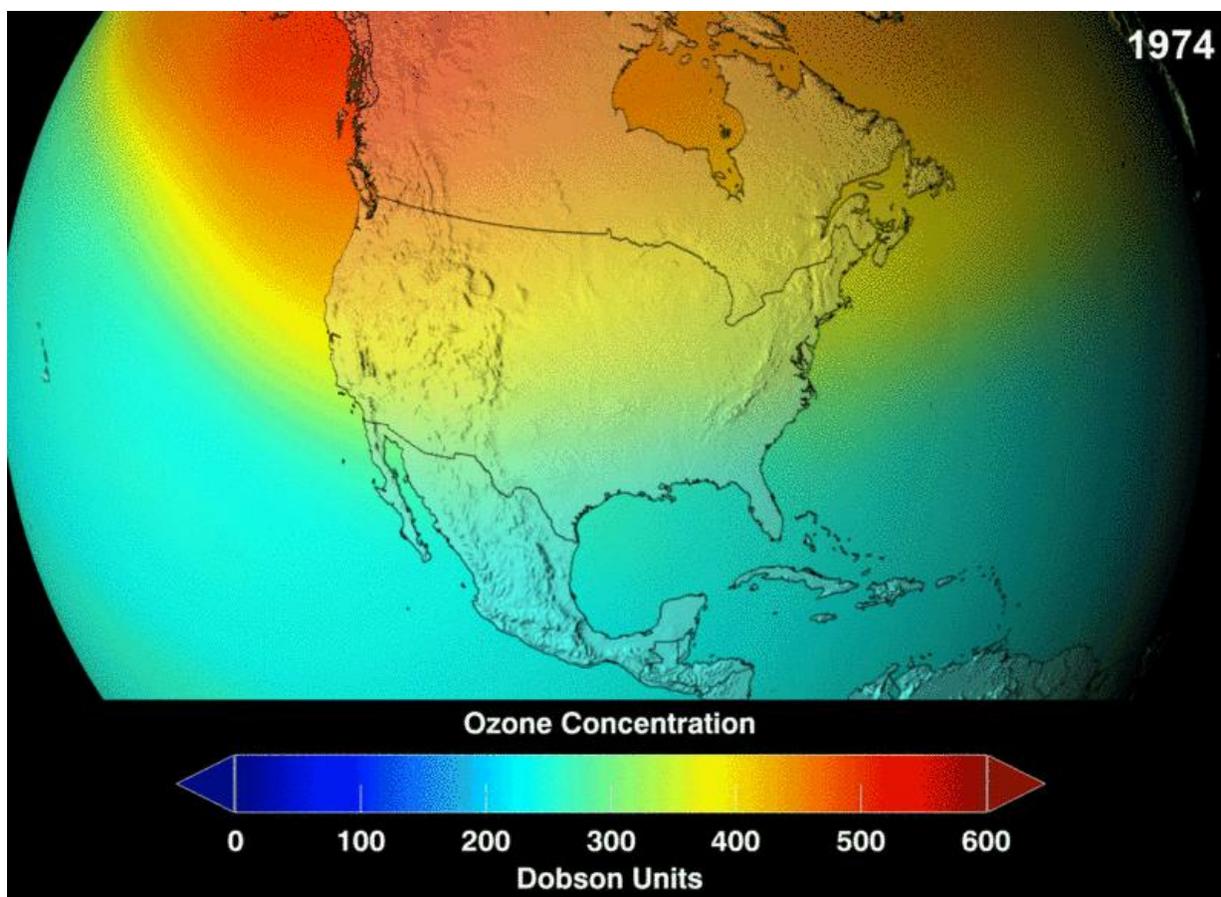
Although there is a wide variation in the Global Warming Potential (GWP) among the halocarbons, these chemicals generally have a much greater GWP than either methane or carbon dioxide. For example, HFC-23 (CF₃H) has an atmospheric half-life of 264 years and GWP of 9200; HFC-125 has an atmospheric half-life of 33 years and GWP of 4800; HFC-124a has an atmospheric half-life of 15 years and a GWP of 3300; HFC-152a (CF₂HCH₃) has an atmospheric half-life of two years and a GWP of 460 years; HFC-227ea has an atmospheric half-life of 37 years and a GWP of 4300; perfluoromethane has an atmospheric residence time of 50,000 years and a GWP of 4400; perfluoroethane has an atmospheric half-life of 10,000 years and a GWP of 6200.

In terms of time trends, some halocarbons such as carbon tetrachloride are in atmospheric decline, whereas other molecular species such as HFC-23 and HCFC-22 are steadily rising as of the early 21st century.

Ozone depletion

Halocarbons which reach the stratosphere have significant effects of destroying the ozone layer. The efficacy of ozone destruction is often measured by a comparative unit termed Ozone depletion potential (ODP), which is based upon the ODP of trichlorofluoromethane (CFC-11) being assigned a value of unity.

The international agreement known as the Montreal Protocol has been responsible for reduction of most chlorofluorocarbons, especially in Western countries.



Time lapse view of atmospheric ozone over North America, assuming absence of Montreal Protocol. Source: NASA Goddard

The Dobson Unit is a common term for reporting atmospheric ozone concentrations. The Dobson Unit is defined as the number of molecules of ozone required to create a layer of pure ozone ten microns s thick at a temperature of zero degrees Celsius and a pressure of one atmosphere (the air pressure at the surface of the Earth). Expressed alternatively, a column of air with an ozone concentration of one Dobson Unit contains approximately 2.69×10^{16} ozone molecules for every square centimeter of area at the base of the column. As a mean level throughout the Earth's atmosphere, the ozone layer's average thickness is about 300 Dobson Units or a layer that is effectively around three millimeters thick.

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6