

6. HALOCARBONS AND OTHER HALOGENATED SPECIES

Basic information on halocarbons with regard to environmental issues

Halocarbons are carbon compounds containing one or more halogens, *i.e.*, fluorine, chlorine, bromine or iodine, with most being industrial products. Halocarbons are classified into chlorofluorocarbons (CFCs), which contain fluorine and chlorine; the hydrochlorofluorocarbons (HCFCs), which contain hydrogen in addition to fluorine and chlorine; and the halons, which contain bromine and other halogens. Perfluorocarbons (PFCs) are carbon compounds in which all hydrogen atoms are replaced by fluorine atoms, and hydrofluorocarbons (HFCs) are halocarbons that contain hydrogen and fluorine but no chlorine. Sulphur hexafluoride (SF_6), although not a halocarbon, behaves similarly to halocarbons and it is a potent long-lived greenhouse gas. Carbon tetrachloride (CCl_4) and methyl chloroform (CH_3CCl_3) are produced industrially, whereas methyl chloride (CH_3Cl) has natural sources. Although the mole fractions of the halocarbons are relatively low in the atmosphere, they have high global warming potentials. The halocarbons have been shown to account for about 12% of the total increase in radiative forcing due to long-lived greenhouse gases from 1750 to 2010 (WMO, 2011c).

The halocarbons are colourless, odourless and innocuous substances that can be readily gasified and liquefied and have low surface tension. Thus, they were commonly used as refrigerants, propellants and detergents for semiconductors, resulting in a rapid increase in their mole fractions in the atmosphere until the mid-1980s. Halocarbons containing chlorine and bromine led to the depletion of the ozone layer. Since the mid-1990s, the Montreal Protocol on Substances that Deplete the Ozone Layer and its subsequent Adjustments and Amendments have progressively increased the regulation of the production, consumption and trade of ozone-depleting compounds.

The CFCs are destroyed mainly by ultraviolet radiation in the stratosphere, and their lifetimes are generally long (*e.g.*, about 50 years for CFC-11). However, the HCFCs and CH_3CCl_3 , which contain hydrogen, react with hydroxyl radicals (OH) in the troposphere and have relatively short lifetimes (*e.g.*, about 5 years for CH_3CCl_3). As the reaction with OH in the troposphere is a major sink for CH_3CCl_3 , global measurements of CH_3CCl_3 provide an accurate estimate of the global mole fraction of OH (Prinn *et al.*, 2001). Due to substantial decrease of CH_3CCl_3 in the atmosphere the other compounds are considered now to trace OH mole fraction changes.

The Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC), which entered into force on 16 February

2005, specifies HFCs, PFCs and SF_6 as targets for quantified emission limitation and reduction commitments.

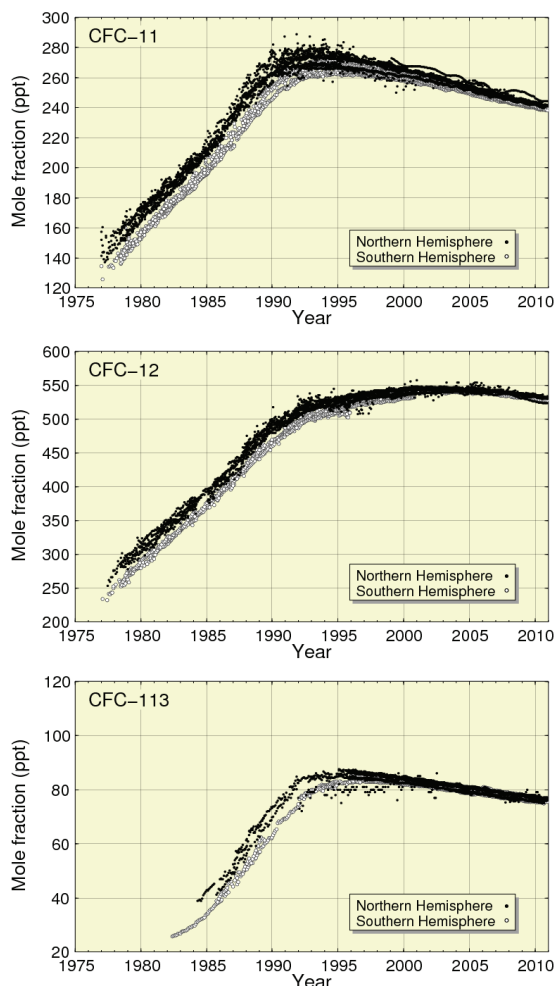


Fig. 6.1 Time series of the monthly mean mole fractions of CFC-11, CFC-12 and CFC-113. Solid circles show mole fractions measured in the Northern Hemisphere and open circles show mole fractions in the Southern Hemisphere.

Annual changes in the levels of halocarbons in the atmosphere

The map at the beginning of this chapter shows observational sites that have submitted data on halocarbons and other halogenated species to the WDCGG. Plates 6.1 and 6.2 show all the monthly mean mole fractions of these gases submitted to the WDCGG. The figures (6.1 – 6.7) in this chapter plot the monthly mean data reported to the WDCGG without spatial averaging. Some discrepancies in the absolute mole fractions were observed for several stations, suggesting that these stations may have

adopted different standard scales. Observational data based on identical standard scales revealed that the differences in the mole fractions between the two hemispheres were large in the 1980s for CFCs, CCl_4 and CH_3CCl_3 but have since narrowed as the emissions have been suppressed and the existing constituents have been mixed across the hemispheres.

Figure 6.1 shows monthly mean mole fractions of CFC-11 (CCl_3F), CFC-12 (CCl_2F_2) and CFC-113 ($\text{CCl}_2\text{FCClF}_2$) over time. The mole fractions of CFC-11 were maximal around 1992 in the Northern Hemisphere, followed by a maximum about one year later in the Southern Hemisphere. The mole fractions of CFC-113 were maximal around 1992 in the Northern Hemisphere and around 1997 in the Southern Hemisphere. The mole fractions of these gases have since been decreasing slowly in both hemispheres. The mole fraction of CFC-12 increased until around 2005 and then started decreasing gradually.

Figure 6.2 shows time series of the monthly mean mole fractions of Halon-1211 (CBrClF_2) and Halon-1301 (CBrF_3). The mole fraction of Halon-1211 has not increased since 2005, whereas the mole fraction of Halon-1301 is increasing.

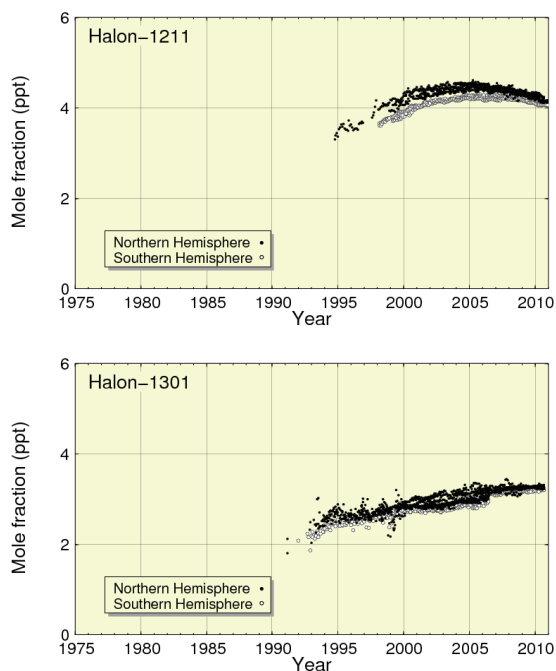


Fig. 6.2 Time series of the monthly mean mole fractions of Halon-1211 and Halon-1301. Solid circles show mole fractions measured in the Northern Hemisphere and open circles show mole fractions in the Southern Hemisphere.

Figure 6.3 shows time series of the mole fractions of HCFC-22 (CHClF_2), HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$) and HCFC-142b (CH_3CClF_2). The mole fractions of these gases increased significantly during the last

decade as a result of their continued use as substitutes for CFCs. However, the growth of HCFC-141b decelerated rapidly in the second half of the decade.

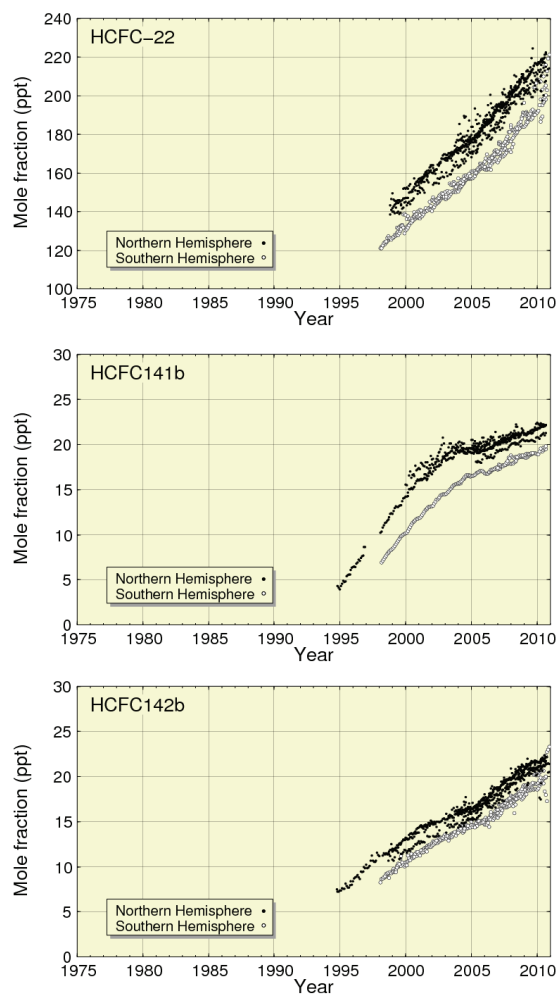


Fig. 6.3 Time series of the monthly mean mole fractions of HCFC-22, HCFC-141b, and HCFC-142b. Solid circles show mole fractions measured in the Northern Hemisphere and open circles show mole fractions in the Southern Hemisphere.

Figure 6.4 shows time series of the mole fractions of CCl_4 and CH_3CCl_3 . The mole fractions of CCl_4 in both hemispheres were at a maximum around 1991. The mole fractions of CH_3CCl_3 were at a maximum around 1992 in the Northern Hemisphere and around 1993 in the Southern Hemisphere. The mole fractions of these gases have since been decreasing.

Figure 6.5 shows time series of the monthly mean mole fractions of HFC-134a (CH_2FCF_3) and HFC-152a (CH_3CHF_2). The mole fractions of HFC-134a and HFC-152a have increased by 4 to 5-fold over the last 10 years. These increases have been larger in the Northern than in the Southern Hemisphere, suggesting that their predominant sources are located in the Northern Hemisphere.

Figure 6.6 shows a time series of the monthly mean mole fractions of methyl chloride (CH_3Cl). The mole fraction of CH_3Cl has remained steady although the signs of the seasonal variation can be noticed in the dataset.

Figure 6.7 shows a time series of the monthly mean mole fractions of SF_6 . The mole fraction of SF_6 in 2010 was double that in the mid-1990s increasing nearly linearly with a rate of 0.24 ppt/year (WMO, 2011c).

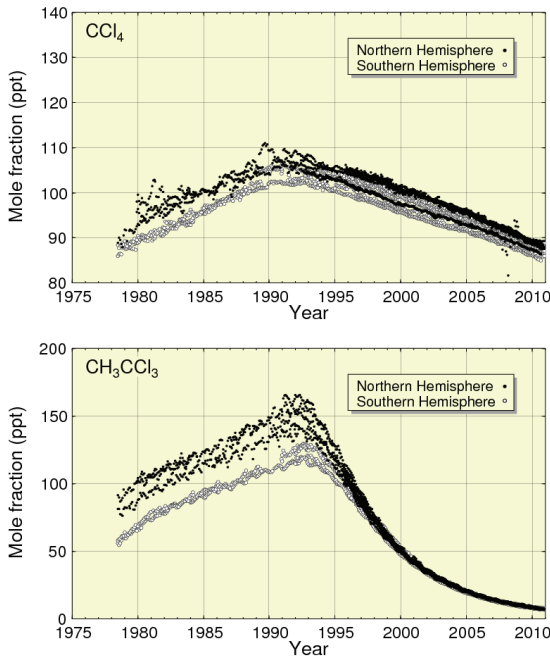


Fig. 6.4 Time series of the monthly mean mole fractions of CCl_4 and CH_3CCl_3 . Solid circles show mole fractions measured in the Northern Hemisphere and open circles show mole fractions in the Southern Hemisphere.

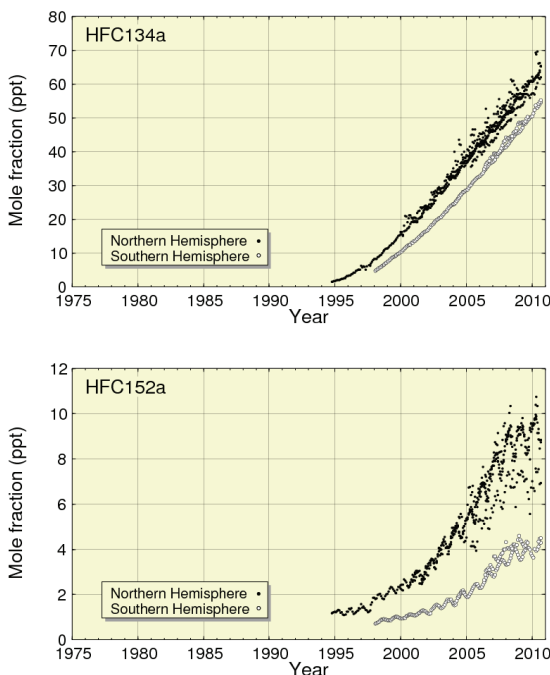


Fig. 6.5 Time series of the monthly mean mole fractions of HFC-134a and HFC-152a. Solid circles show mole fractions measured in the Northern Hemisphere and open circles show mole fractions in the Southern Hemisphere.

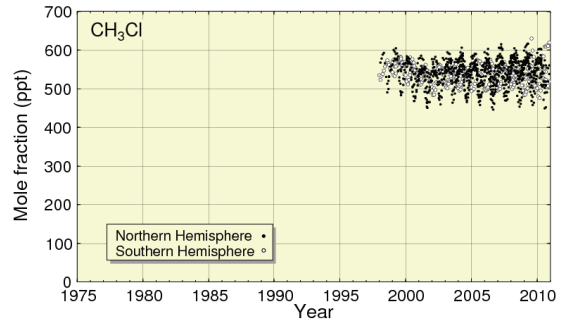


Fig. 6.6 Time series of the monthly mean mole fractions of CH_3Cl . Solid circles show mole fractions measured in the Northern Hemisphere and open circles show mole fractions in the Southern Hemisphere.

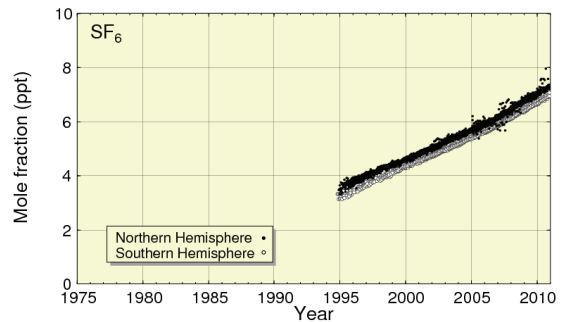


Fig. 6.7 Time series of the monthly mean mole fractions of SF_6 . Solid circles show mole fractions measured in the Northern Hemisphere and open circles show mole fractions in the Southern Hemisphere.