HALOCARBONS

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Keywords: Ozone depletion, Montreal Protocol, alternative compounds, concentration, trend, lifetime.

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Summary

This article contains the inventory of primary uses of basic halocarbons and their classification. The majority of these halocarbons have mainly a anthropogenic origin and, therefore, their emission is evaluated exactly enough. The annual production of some halocarbons during 1980-1995 period is presented. The photochemical sinks of halocarbons and the chlorine ozone depleting catalytic cycle are described briefly. Due to the Montreal Protocol and its amendments, the new alternative halocarbons substitute the ones of first generation. The ability of both new and old halocarbons to destroy the ozone layer is compared. Climatic impact of halocarbons is considered also. The measurements of basic halocarbons content and their trends are presented.

1. Introduction

Unlike methane whose emission has a large uncertainty, the intensity of halocarbons flux into the atmosphere is relatively well known. It is due to an anthropogenic origin of overwhelming majority of halocarbons. Thus, the total pollution of the atmosphere by halocarbons is determined through their production and emission and it is reasonable to judge the regional pollution level in accordance with the sales volume of halocarbon-containing products there. There is some uncertainty in estimates of the time period between the halocarbons production and their use.

The halocarbons are produced with different trade marks by various producers. For the uniformity, the code consisting of characters and two- or three-digit number is used for designation of each halocarbon. The characters show what atoms are in its molecule. As a result, halocarbons are designated as chlorofluorocarbon CFC-kmn, hydrochlorofluorocarbon HCFC-kmn or hydrofluorocarbon HFC-kmn, where k=C-1,

m=H+1, n=F (where C, H and F are the numbers of carbon, hydrogen and fluorine atoms in the molecule respectively). For example, $CClF_3$ is CFC-13, CF_3CHCl_2 is HCFC-123, CHF_3 is HFC-23 and so on. If the molecule contains bromine atoms this compound is called as halon with four-digit number corresponding consequently to number of atoms of carbon, fluorine, chlorine and bromine in its molecule, e.g. $C_2F_4Br_2$ is halon-2402.

The halocarbons persistence, their noncombustibility and low toxicity lead to the world-wide use of halocarbons in various industrial sectors and in everyday life. The key branches of the most popular halocarbons usage are given in Table 1. It is necessary to specify that the field of halocarbons use is wider. For example, CFC-12 may be used as sterilant in medicine and medical industry, CFC-113 - as refrigerant and so on. Some chlorine- and bromine-containing species as presented in Table 1 have a natural part of their emission. Specifically, the principal sources of methyl bromide CH_3Br are in oceans; carbon tetrachloride emission has a significant share from natural source.. And methyl chloride CH_3Cl has a natural origin completely. But both natural and anthropogenic sources of halocarbons are located at the Earth's surface and any atmospheric ones are absent.

	Compound	**Formula**	**Primary uses**
Basic	CFC-11	CCl_3F	Insulating foams, refrigeration, air conditioning
	CFC-12	CCl_2F_2	Refrigeration, air conditioning, insulating foams
	CFC-113	CCl_2FCClF_2	Solvents
	CFC-114	$CClF_2CClF_2$	Foam packing, aerosols
	CFC-115	$CClF_2CF_3$	Refrigeration
Replacements	HCFC-22	CHF_2Cl	Air conditioning, refrigeration, foam packing
	HCFC-123	CF_3CHCl_2	Refrigeration, insulating foams, solvents
	HCFC-124	CF_3CHFCl	Air conditioning, insulating foams
	HCFC-141b	$CFCl_2CH_3$	Insulating foams, solvents
	HCFC-142b	CF_2ClCH_3	Insulating foams, solvents
	HFC-125	CHF_2CF_3	Refrigeration
	HFC-134a	CH_2FCF_3	Refrigeration, air conditioning
	HFC-152a	CH_3CHF_2	Insulating foams, aerosols
Halons	Halon-1211	CF_2ClBr	Fire-extinguishers
	Halon-1301	CF_3Br	Fire-extinguishers
Others	Carbon tetrachloride	CCl_4	CFC-11 and CFC-12 production, solvents, fumigation
	Methyl chloroform	CH_3CCl_3	Solvents
	Methyl bromide	CH_3Br	Agriculture, biomass burning, automobiles

Table 1. Primary uses of some halocarbons.

2. Halocarbon sources

The production of first halocarbons, CFC-11 and CFC-12, began in the early 1930s. Since then their production has increased, up to the 1980s. The large-scale production of other basic halocarbons started significantly later. Therefore, the atmospheric

concentrations of CFC-11 and CFC-12 exceeded all others and continue to do so.

Following the international restrictions introduced by the known Montreal Protocol (1987) and its London (1991) and Copenhagen (1992) Amendments, the basic halocarbons denoted in Table 1 were substituted by some new less ozone depleting species called as replacements. According to the above agreements, the halons production was to be cut down in 1994 and the production of basic CFCs, CCl_4 and methyl chloroform was to be totally stopped by 1996. The restrictions for the production of CH_3Br and HCFCs began from 1995 and 1996, respectively. The necessity of such substitution is due to the unfavorable influence of CFCs on the ozone layer and climate of our planet (see below for a more detailed discussion of this aspect).

The evolution of annual production of CFCs and some of their replacements by eleven leading chemical companies- halocarbon producers in the Western Europe, North America and Japan during 1980-1995 is shown in Figure 1. It is clear from Figure 1, that the annual production of CFC-11 and CFC-12 decreased from the late 1980s up to 1995 by about twelve and five times, respectively. Their production in 1995 corresponded to one of around 1958 approximately. The CFC-113 production shows the same behavior; it dropped eleven-fold during 1988-1995. On the contrary, e.g., the relatively new compounds, CFCs replacements HCFC-141b and HFC-134a, grew sharply, their annual increase in 1995 was 39 and 46%, respectively.

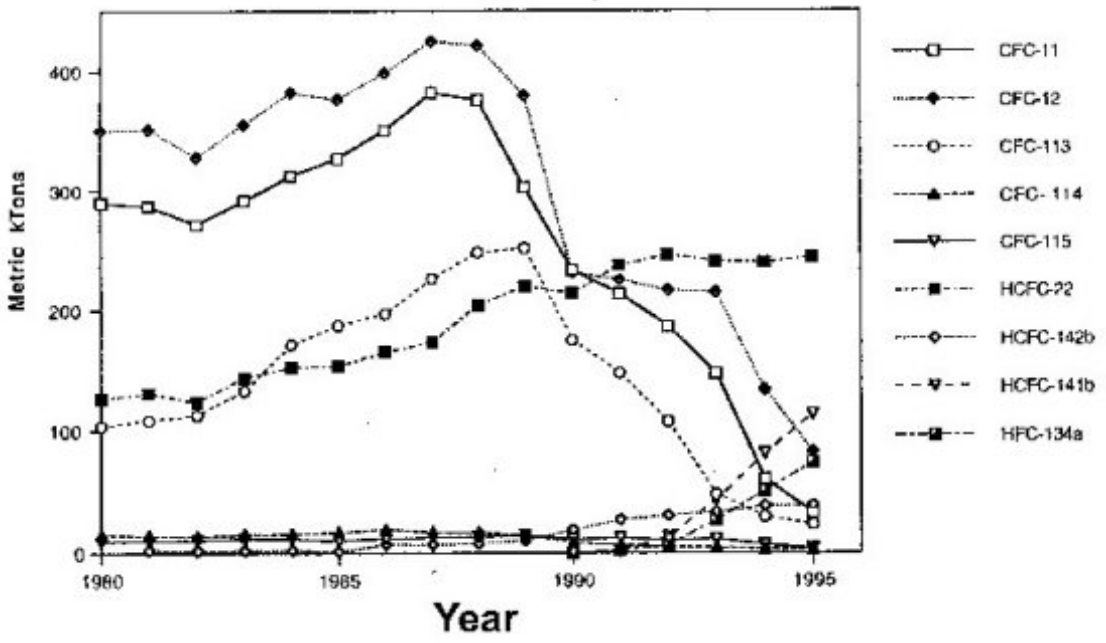

Figure 1. Annual production of fluorocarbons reported to Alternative Fluorocarbons Environmental Acceptability Study during 1980-1995. From: Production, Sales and Atmospheric Release of Fluorocarbons through 1995 (1995). Alternative Fluorocarbons Environmental Acceptability Study, SPS-AFEAS, Inc., Washington, D.C., USA. "Production" (as defined in the Montreal Protocol) does not include feedstock uses.

According to available statistics, after 1980 only 5-10% of the total annually produced

CFC-11 and CFC-12 was sold in the southern hemisphere, the same share for CFC-113, CFC-114 and CFC-115 is 1-1.5, 2-3 and 2-6% respectively. The maximum share of new generation halocarbon sales, in the southern hemisphere, fell during the last few years by 4-6% for HCFC-22, 1-2% for HCFC-141b and HFC-134a, and a few tenths of a percent for HCFC-142b. Thus, mainly the atmospheric pollution by halocarbons takes place in the northern hemisphere, namely, in the most inhabited northern mid-latitudes.

It is important to know how long the halocarbons exist before they reach the atmosphere. For instance, CFC-11 was released from spray cans within about one year after production, but from refrigerators it may be a few decades before its release. Therefore, in spite of CFCs production stopping (not globally in all countries) they will be released into the atmosphere in the future and accurate evaluation of this delay is difficult enough. The delay during a decade is typical for CFC-115, HCFC-22 and for two-thirds of CFC-114 amount. But for four-fifths of HCFC-142b the delay is more than 10 years. Thus, the above cause of uncertainty for halocarbons emission inventories will remain for many years. The other cause of uncertainty is due to the absence of reliable and full information about halocarbons production and use in Russia, India and China.

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HCFC-22, halons and their analysis.]

Biographical Sketches

I.L. Karol was born on 27 July 1927 in Leningrad, USSR. In 1944 he entered the Hydrodynamics Dept. of Leningrad State University, Mathematics and Mechanics Faculty, graduating in 1949. He passed postgraduate studies from 1949 to 1952, when he received a scientific degree of Candidate in Maths & Physics. After three years of lecturing in mathematics at the Ural University in Sverdlovsk, in 1956 he entered the Institute of applied Geophysics USSR Academy of Sciences in Moscow as a senior scientist. In 1959 he was transferred to Institute of Experimental Meteorology of USSR Hydrometeorological Service in Obninsk, near Moscow, where he was nominated as chief of laboratory in 1970. Since 1972 he has been with Main Geophysical Observatory of USSR Hydrometeorological Service in Leningrad (now St. Petersburg) after receiving the USSR scientific degree of Doctor of Math & Physics, presenting in 1970 his theses, which was published in 1972 as a book by Gidrometeoizdat Publishing House "Radioactive isotopes and global transport in the atmosphere". This book was translated into English and published in 1974. Since 1953 I.L. Karol has published 10 scientific monographs and more than 140 papers individually or with co-authors. The original papers are dealing with modeling of global atmospheric composition and climate changes due to natural and anthropogenic causes. During several periods he served as a member of various international commissions and committees of the International Association of Meteorology and Atmospheric Physics, of the World Meteorological Organization, of the World Climate Research Program Joint Scientific Committee. Since 1974 he has been the USSR (now Russian) co-leader of the joint project: "Composition of the atmosphere and climate changes" of the US-Russian Cooperation in Environmental Protection. He was the author or co-author of numerous scientific reports, which he presented at international and national scientific meetings throughout his scientific career.

A.A. Kiselev was born on 26 April 1953 in Leningrad, USSR. In 1970 he entered and in 1975 he graduated from the Hydrodynamics Dept. of Leningrad State University. From 1977 to 1981 he passed postgraduate studies at the Mathematics and Mechanics Faculty. In 1986 he received scientific degree of Candidate in Maths & Physics after presenting the candidate theses in geophysics. In 1975 he entered in the Main Geophysical Observatory of USSR Hydrometeorological Service in Leningrad as a junior scientist. Since 1990 he took position of senior research scientist in Main Geophysical Observatory. Since 1975 A.A. Kiselev has published about 30 papers individually and with coauthors. He is a contributor to the Intergovernmental Panel on Climate Change Reports of 1990 and 1999. The original papers are dealing with modeling of photochemical processes in the atmosphere, of global atmospheric composition change due to natural and anthropogenic causes.