# Global hexachlorocyclohexane use trends and their impact on the arctic atmospheric environment

Y.F. Li, T.F. Bidleman and L.A. Barrie

Atmospheric Environment Service, Downsview, Ontario, Canada

#### L.L. McConnell

Environmental Chemistry Laboratory, Beltsville, Maryland, U.S.A

The relationship between the global technical HCH use trends and their impact on the arctic atmospheric environment has been studied. Two significant drops in global technical HCH usage were identified. In 1983, China banned the use of technical HCH. This represented the largest drop ever in global use rates. In 1990 India stopped technical HCH usage in agriculture and the former Soviet Union banned the use of technical HCH. Since 1990, India has been the biggest user of technical HCH in the world. Significant drops in atmospheric α-HCH in the arctic were observed between 1982 and 1983, and again between 1990 and 1992. The rapid response in atmospheric concentrations to usage is encouraging; however, since α-HCH concentrations in the arctic waters have remained relatively unchanged, the decline in atmospheric  $\alpha$ -HCH has reversed the net direction of airsea gas flux. The accumulated mass in oceans and large lakes may represent a new source of HCH to the arctic atmosphere.

## Introduction

Hexachlorocyclohexane (HCH) is an organochlorine insecticide that is available in two formulations: technical HCH which is dominated by the  $\alpha$ -HCH and  $\gamma$ -HCH with traces of the  $\beta$ -,  $\delta$ -, and  $\epsilon$ -HCH [Metcalf, 1955], and lindane (> 90%  $\gamma$ -HCH). Because of its low cost and high effectiveness, HCH was one of the most widely used insecticides in the world. Technical HCH usage began in 1943, and the total global consumption was estimated to be as high as 6.0 million tonnes [Huang, 1989] with maximum annual usage at 334,400 tonnes in 1981.

HCH compounds volatilize soon after application in source regions [Glotfelty et al., 1984] and migrate through the atmosphere to the polar regions [Gregor and Gummer, 1989]. Since the low Henry's law constants of HCHs favour partitioning from air into water [Kucklick et al., 1991], especially at low temperatures, HCHs condense into the lakes and oceans of northern ecosystems [McConnell et al., 1993, Hinckley et al., 1991]. This is sometimes referred to as the "cold condensation" phenomenon [Wania, and Mackay, 1993, 1996]. In fact, HCHs have been found to be the most abundant organic compounds in the arctic atmosphere and surface waters [Iwata et al., 1993; Hargrave et al., 1988; Bidleman et al., 1995]. A compilation of measurements made

Copyright 1998 by the American Geophysical Union.

Paper number 97GL03441. 0094-8534/98/97GL-03441\$05.00 between 1979-93 from stations in the Canadian and Norwegian arctic and from cruises in the Bering and Chukchi seas indicates that atmospheric concentrations of  $\alpha$ -HCH have declined significantly [Bidleman et al., 1995, Jantunen and Bidleman, 1995, 1996]. This decline was not linear but rather occurred in steps, decreasing after 1982 and again between 1990 and 1992.

This letter summarizes global usage of  $\alpha$ -HCH from 1979 to 1994, and compares the usage trends with concentration of  $\alpha$ -HCH in arctic air during the same time period.

## Global Usage of Technical HCH

Many countries, especially developed countries, banned technical HCH usage in 1970s [Voldner and Li, 1995]. In 1979 there were around 70 countries still using technical HCH, but half of these countries banned the product between 1979 to 1992 [Voldner and Li, 1995]. Since 1979 China, India and the former Soviet Union have been the top technical HCH consuming countries. In 1980, the annual consumption of technical HCH in these three countries accounted for more than 90% of the total technical HCH usage in the world.

Technical HCH production and usage data for China, India and the former Soviet Union are summarized in Table 1. China was the largest producer and user of technical HCH from the1970s until April 1, 1983 when China banned both production and usage of technical HCH [Chinese Ministry of Agriculture, 1989, Li et al., 1997]. The total amount of technical HCH produced from 1952 to 1983 in China was around 4.5 million tonnes. This represents three times the total usage for rest of the world [Huang, 1989]. We should point out that data published earlier by Li et al., 1996 were lower by almost 20 times than those listed in Table 1. The discrepancy between this and the earlier report is due to improved accuracy and reliability of sources.

India is another country with large technical HCH consumption in both the agriculture and public health sectors. Maximum annual usage reached 57,000t in the latter 1980s. On October 30,1990 the government of India banned technical HCH usage on vegetable, fruit, and oilseed crops and for preservation of grains, but continued to allow its use for public health protection [Parmar, 1993] and on certain food crops [David et al., 1993] at around 20,000t annually. It was reported that the India Government has taken a decision to phase out a production of 30,000 tonnes of HCH per annum (Sugavanam and Kim, 1996).

In the former Soviet Union, technical HCH was one of the most widely used insecticides from 1940s to 1980s [Kundiev and Kagan, 1993a]. The most extended areas of the arable

Table 1. Technical HCH Production (t·a-1) in China and
Usage (t·a-1) in India and in the Former Soviet Union*.

Year	China	India	Form.
		111414	USSRa
1979	246,000	26,065	N.A.
1980	286,000	25,070	11,160
1981	264,000	37,113	N.A.
1982	210,000	42,541	N.A.
1983	Banned	42,603	N.A.
1984		40,210	N.A.
1985		37,860	16,693
1986		38,600	N.A.
1987		38,830	N.A.
1988		56,010	N.A.
1989		57,510	N.A.
1990		52,570	Banned
1991		24,100	

\* Chinese data are from Li et al., 1997, Indian data are from Food and Agriculture Organization, 1980-90; Government of India, 1990; Parmar, 1993; Battelle Europe, and data for the former Soviet Union are from Kundiev and Kagan, 1993a.

a. The data were tonnage of technical HCH used in agriculture only, and calculated from  $\gamma$ -HCH (active ingredient) usage by assuming that technical HCH contains 15%  $\gamma$ -HCH.

N.A.: Data not available.

lands on the territory of the former Soviet Union were in Russia and Ukraine. In Russia, pesticides were intensively used in the Northern Caucasus, Central chernozem (black soil) zones (Voronezh, Kursk, Rostov, Belgorod, Tambov regions), and in the areas adjacent to the river Volga (Saratov, Volgograd, Astrakhan regions) [Kundiev and Kagan, 1993b].

Historical usage of technical HCH in the former Soviet Union is listed in Table 1. The use of technical HCH was banned at the end of the 1980's for the major agricultural crops, however, use of remaining stockpiles was allowed even after 1991. [Kundiev et al., 1993a].

Estimated global technical HCH usage from 1979 to 1994 are depicted in Figure 1. In the estimation, we assume that total technical HCH produced each year in China was used in the same year. This figure also reflects the assumption that technical HCH stockpiles were used in countries for two years after a ban. For example, although China banned technical HCH in 1983, we assumed that technical HCH was still used in this country in 1983 and 1984 but at a declining level, reaching zero usage in 1985. In the former Soviet Union, we assumed the usage of technical HCH was 16,693t in 1989, same as the amount consumed in 1985, and 0 in 1992. For those years when the data were not available, a linear interpolation was used to fill the gap.

# The Impact of Global HCH Usage on the arctic Atmosphere

As  $\alpha$ -HCH is the dominant isomer in the formulation of technical HCH, tracking the atmospheric concentration of this

compound should directly reflect current use rates. In Figure 1, global use rates of technical HCH can be compared with historical measurements of  $\alpha$ -HCH concentration (from June to November) in the atmosphere of arctic regions [Bidleman et al. 1995, Jantunen and Bidléman, 1995, 1996, Patton et al., 1989, 1991, Hargrave et al., 1988, Falconer et al., 1995, Oehme & Ottar, 1984, Pacyna & Oehme, 1988, Oehme, 1991, Oehme et al., 1995, Tanabe & Tatsukawa, 1980, Hinckley et al., 1991, Iwata et al., 1993]. These air concentration data were measured from different stations in different years by several research groups. The variability for these data can be found in [Bidleman et al. 1995].

Two significant drops of global technical HCH usage are identified in Fig. 1. One started in 1983 when China banned the use of technical HCH, and another occurred around 1990 when India banned technical HCH usage in agriculture and the former Soviet Union banned the usage of technical HCH. Air concentrations of  $\alpha$ -HCH appear to respond within a few years to changes of usage. The long-term trends also show two significant decreases, one between 1982 and 1983, and another between 1990 and 1992. The consistency between global technical HCH usage and air concentrations of  $\alpha$ -HCH in arctic regions illustrates a relationship between usage and air concentrations on a global level.

The net direction of the air-sea gas flux is controlled by the dissolved and gaseous HCH concentrations in water and air, the Henry's law constant, and the air temperature. The drop in atmospheric  $\alpha$ -HCH concentrations since 1991 in arctic regions has actually caused a shift in the direction of the air-water flux of  $\alpha$ -HCH from deposition to volatilization [Jautunen and Bidleman, 1995, Bidleman et al., 1995]. Up until 1991, measurements of HCH air-water flux in the arctic as well as in other large, cold water bodies such as the Great Lakes and Lake Baikal, Russia resulted in an air-to-water flux direction for both  $\alpha$ - and  $\gamma$ -HCH except for the warmest months of the year [Bidleman and McConnell, 1995, McConnell et al., 1996].

Atmospheric concentrations of  $\alpha$ -HCH seem to be responding rapidly to reductions in global use rates. A continuation in the trend in declining air concentrations is expected as more and more countries phase out the use of this compound. However, as the air  $\alpha$ -HCH concentration drops, the net direction of air-sea gas flux has been reversed since  $\alpha$ -HCH concentrations in the arctic waters have remained

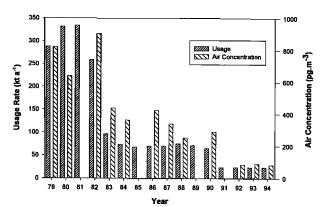


Figure 1: Long-term trends of global Technical HCH usage and mean air concentrations of  $\alpha$ -HCH in the arctic regions from 1979 to 1994.

relatively unchanged. Thus, soils and surface waters containing HCH will be a diffuse, non-point source to the atmosphere that will likely maintain detectable atmospheric concentrations for some time in the future.

Acknowledgments. This work was financially supported by Environment Canada and Indian and Northern Affairs Canada. This research is a contribution of the Global Emissions Inventory Activities (GEIA), a component of the International Global Atmospheric Chemistry (IGAC) core project of the International Geosphere - Biosphere Program (IGBP).

#### References

- Battelle Europe, World agrochemical data bank, Battelle world pesticides programme, Geneva Research Centres, Geneva, Switzerland, Undated.
- Bidleman, T.F., L.M. Jantunen, R.L. Falconer, L.A. Barrie, and P. Fellin, Decline of hexachlorocyclohexane in the arctic atmospheric and reversal of air-sea gas exchange, *Geophys. Res. Lett.* 22, 219-222, 1995.
- Bidleman, T.F., and L.L. McConnell, A review of field experiments to determine air-water gas exchange of persistent organic pollutants, Sci. Total Environ. 159, 101-117, 1995.
- Chinese Ministry of Agriculture, A new pesticide manual, Agriculture Publisher, Beijing, 1989.
- David, B., Pest Management and Pesticides: Indian Scenario. Namrutha Publications, Madras, 1992.
- Food and Agriculture Organization, FAO Production Yearbook, Rome, Italy, 1980-90.
- Falconer, R.L., T.F. Bidleman and D.J. Gregor, 1995. Air-water gas exchange and evidence for metabolism of hexachlorocyclohexanes in Resolute Bay, N.W.T. Sci. Total Environ., 160/161: 65-74.
- Glotfelty, D.E., A.W. Taylor, B.C. Turrer, and W.H. Zoller, Volatilization of surface-applied pesticides from fallow soil, *J. Agric. Food Chem.* 32, 638-643, 1984.
- Government of India, Department of Chemicals and Petrochemicals, India Chemicals Statistics 1986-87, 1990.
- Gregor, D.J. and W.D. Gummer, Evidence of atmospheric transport and deposition of organochlorine pesticides and polychlorinated biphenyls in Canadian arctic snow, *Environ. Sci. Technol.* 23, 561-565, 1989.
- Hargrave, B.T., W.P. Vass, P.E. Erickson, and B.T. Fowler, Atmospheric transport of organochlorines to the arctic Ocean, *Tellus* 40B, 480-493, 1988.
- Hinckley, D.A., T.F. Bidleman, and C.P. Rice, Atmospheric organochlorine pollutants and air-sea exchange of hexachlorocyclohexane in the Bering and Chukchi seas, J. Geophys. Res. 76, 7201-7213, 1991.
- Huang, Hexin, Discussion on environmental contaminant and related problems caused by organochlorine pesticides, Science and Management of Pesticides (in Chinese) 2, 26-29, 1989.
- Iwata, H., S. Tanabe, N. Sakai, and R. Tatsukawa, Distribution of persistent organochlorine pollutants in the oceanic air and surface seawater and the role of ocean on their global transport and fate, *Environ. Sci. Technol.* 27, 1080-1098, 1993.
- Jantunen, L.J., and T.F. Bidleman, Reversal of the air-water gas exchange of hexachlorocyclohexanes in the Bering and Chukchi seas: 1993 vs. 1988. Environ. Sei. Technol. 29, 1081-1089, 1995.
- Jantunen, L.J., and T.F. Bidleman, Air-water gas exchange of hexachlorocyclohexanes (HCHs) and the enantiomers of α-HCH in arctic regions\_J. Geophys. Res. 101, 28837-28845, 1996.
- Kucklick, J.R., D.A. Hinckley, and T.F. Bidleman, Determination of Henry's law constants for hexachlorocyclohexanes in distilled water and artificial seawater as a function of temperature, *Mar. Chem.* 34, 197-209, 1991.

- Kundiev, Y.I. and Y.S. Kagan, Pesticide usage in the U.S.S.R., Report prepared for Environment Canada, Downsview, Ontario, Canada, 1993a.
- Canada, 1993a.

  Kundiev, Y.I. and Y.S. Kagan, Pesticide usage in the Russian Federation, Report prepared for Environment Canada, Downsview, Ontario, Canada, 1993b.
- Li, Y. F., McMillan, A., and Scholtz, M. T., Global HCH usage with 1°X1° longitude/latitude resolution, *Environ. Sci. Technol.* 30, 3525-3533, 1996.
- Li, Y. F., D. Cai, and A. Singh, Technical HCH use trends in China and their impact on the environment, in preparation for publication, 1997.
- McConnell, L.L., W.E. Cotham, and T.F. Bidleman, Gas exchange of hexachlorocyclohexanes in the Great Lakes, *Environ. Sci. Technol.* 27, 1304-1311, 1993.
- McConnell, L.L., Kuckliek, J.R., T.F. Bidleman, Ivenor, G.P., and Chernyak, S.M., Air-water gas exchange of organochlorine compounds in Lake Baikal, Russia, *Environ. Sci. Technol.* 30, 2975-2983, 1996.
- Metcalf, R. L., Organic Insecticides, Their Chemistry and Mode of Action, Interscience, New York, 1955.
- Oehme, M., and B. Ottar, The long-range transport of polychlorinated hydrocarbons to the arctic, *Geophys. Res. Lett.* 11, 1133-1136, 1984.
- Oehme, M., Further evidence for long-range air transport of polychlorinated aromates and pesticides, North America and Eurasia to the arctic. *Ambio* 20, 293-297, 1991.
- Oehme, M., J.-E. Haugen, and M. Schlabach, Ambient levels of persistent organochlorines in spring, 1992 at Spitzbergen and the Norwegian mainland, comparison with 1984 results and quality control measures, Sci. Total Environ., 160/161, 139-152, 1995.
- Pacyna, J.M., and M. Oehme, Long-range transport of some organic compounds to the Norwegian arctic, Atmos. Environ. 22, 243-257, 1988.
- Parmar B. C., India Agricultural Research Institute, New Delhi, India, personal communication. 1993.
- Patton, G.W., D.A. Hinckley, M.D. Walla, T.F. Bidleman, and B.T. Hargrave, Airborne organochlorines in the Canadian high arctic, Tellus 41B, 243-255, 1989.
- Sugavanam, B., and Kim, Y.-H. 1996, UNIDO activities related to a global plan of action for reducing or eliminating risks associated with persistent organic pollutants (POPs). Presented at IFCS meetings on POPs, Manila, Philippines, 17-22 June 1996.
- Tanabe, S., and R. Tatsukawa, Chlorinated hydrocarbons in the North Pacific and Indian Oceans, J. Oceanog. Soc. Japan 36, 217-226, 1980.
- Voldner, E.C. and Y.F. Li, Global usage of selected persistent organochlorines, Sci. Total Environ. 160/161, 201-210, 1995.
- Wania, F., and D. Mackay, Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions, Ambio. 22, 10-18, 1993.
- Wania, F., and D. Mackay, Tracking the distribution of persistent organic pollutants, Environ. Sci. Technol. 30, A390-A396, 1996.

(Received August 26, 1997; revised November 20, 1997; accepted November 24, 1997.)

Y.F. Li, T.F. Bidleman and L.A. Barrie, Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario, M3H 5T4, Canada. (e-mail: yi-fan.li@ec.gc.ca; len.barrie@ec.gc.ca; terry.bidleman@ec.gc.ca)

L.L. McConnell, Environmental Chemistry Laboratory, Agricultural Research Service, Beltsville, Maryland 20705. (e-mail: mcconnel@asrr.arsusda.gov)