# Hexachlorocyclohexanes in Air in Southern Norway. Temporal Variation, Source Allocation, and Temperature Dependence

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Concentrations of  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH) were measured in ambient air samples on a weekly basis between 1991 and 1995 at Lista, a coastal station in southern Norway. The levels averaged at 66 pg/m<sup>3</sup>  $\alpha$ -HCH and 48 pg/m<sup>3</sup>  $\gamma$ -HCH. A 50% decline of  $\alpha$ -HCH concentrations in air could be observed during the 5 year period, while no such trend was found for  $\gamma$ -HCH. The time profile of concentrations in air was characterized by a generally low base line level with a few spring-time episodes of highly elevated concentrations. Under this pattern of episodic concentration spikes lies a background with seasonally variable  $\gamma$ -HCH levels, showing higher concentrations at higher temperatures.  $\alpha$ -HCH concentrations in air are far less temperature sensitive. Episodes with air concentrations of  $\gamma$ -HCH up to 1000 pg/m<sup>3</sup> coincided with air transport from Western Central Europe, whereas episodes with elevated  $\alpha$ -HCH levels up to 300 pg/m<sup>3</sup> tended to correlate with air transport from easterly directions, but did no longer occur in 1994 and 1995. This is in agreement with the usage pattern of HCH pesticides in different regions of Europe and points toward regional atmospheric transport as the major source of these chemicals, especially  $\gamma$ -HCH. Short episodes of elevated concentrations proved to be very important when trying to quantify the atmospheric input of  $\gamma$ -HCH into southern Norway, whereas  $\alpha$ -HCH levels are more strongly influenced by the global background situation. Air concentrations and  $\alpha/\gamma$  concentration ratios were clearly correlated with air mass origin.

#### Introduction

Hexachlorocyclohexane (HCH) is one of the major persistent organochlorine compounds found in the environment worldwide. Both a technical HCH mixture (65–70%  $\alpha$ -HCH, 14–15%  $\gamma$ -HCH and other compounds) and lindane (>99%  $\gamma$ -HCH) have been used as broad-spectrum insecticides since the early 1950s for a variety of purposes in agriculture, forestry, and public health. The total world production has been estimated to several million tons (1). Whereas lindane is still used in some European and North American countries,

the use of technical grade HCH has been banned there since the 1970s. In eastern Europe and in parts of Asia and Africa, the technical mixture was in widespread use for much longer (2).

This paper presents results of 5 years of weekly measurements of  $\alpha$ - and  $\gamma$ -HCH in air at a coastal site in southern Norway. The concentration data are analyzed to identify source areas, to reveal temporal trends, both on a seasonal and longer time scale, and to study temperature relationships.

#### **Materials and Methods**

Sampling Site and Sampling Method. Lista, located at the southernmost end of Norway (58°06′N, 6°34′E, Figure 1), is a rural coastal site 14 m above sea level. The prevailing wind direction at the station is from east-southeast and northwest, the annual precipitation during the five years of sampling varied from 886 to 1419 mm, and the yearly mean temperature was approximately 8 °C. From the beginning of 1991 to the end of 1995, air samples of approximately 500 m³ were collected over a period of 24 h once every week, using a previously described high-volume sampler (3) at a flow of approximately 20 m³/h. Particles were collected on glass fiber filters, which had been pretreated at 450 °C for 8 h. Compounds in the vapor phase were adsorbed on two sequential polyurethane foam (PUF) plugs.

Sample Extraction and Cleanup. Prior to sample extraction,  $\epsilon$ -HCH and <sup>13</sup>C-isotope-labeled standards of  $\hat{\alpha}$ -HCH and  $\gamma$ -HCH were added to the first PUF plug. Glass fiber filter and PUF plugs were Soxhlet extracted separately for 8 h with 150 and 300 mL of n-hexane/diethyl ether 9:1. The extracts were combined since earlier studies had shown that at the temperatures prevalent at Lista only a very minor fraction of HCHs (<3%) is present in the particle phase. Nonane was added to the extracts to prevent losses during volume reduction to 1 mL using a evaporator. The concentrated extracts were treated with concentrated sulfuric acid. The organic phase was dried with sodium sulfate, placed on a silica column and eluted with *n*-hexane/diethyl ether. After volume reduction to approximately 0.5 mL, 2 ng of tetrachloronaphtalene and 10 ng of octachloronaphtalene were added as recovery standards. Then the sample was further concentrated to 100  $\mu$ L by applying a gentle stream of purified nitrogen. Further details about sampling and cleanup are given in Oehme et al. (4).

Quantification by Low-Resolution Mass Spectrometry. HCHs were quantified using high-resolution gas chromatography combined with low-resolution negative ion chemical ionization mass spectrometry. Methane was used in the ion source, which was at 200 °C and 0.6 hPa and which was tuned for optimum performance with perfluorotributylamine at m/z312, 414, and 464. The energy of the primary electrons was about 170 eV, and the dynode voltage was set to 10 kV. The M $^{\bullet-}$  and (M + 2) $^{\bullet-}$  ions of (M - Cl) $^{-}$  were recorded for each compound in the selected ion mode employing a dwell time of 50 ms/ion. For quantification, the most abundant ions were used. The HRGC conditions were as follows: separation on a 25 m  $\times$  0.2 mm i.d. fused silica capillary coated with 0.11  $\mu$ m of HP Ultra 2; carrier gas, He, at a flow of 35–40 cm/s (180 °C); splitless injection of 1  $\mu$ L; splitless time 2 min; injector temperature 250 °C; temperature program 60 °C for 2 min, then 20 °C/min to 150, and 4 °C/ min to 280 °C (10 min isothermal). Crystalline  $\alpha$ - and  $\gamma$ -HCH of officially certified purity >99% were used as reference

**Quality Control.** A rigorous quality control concept for the determination of organic compounds in air based on the

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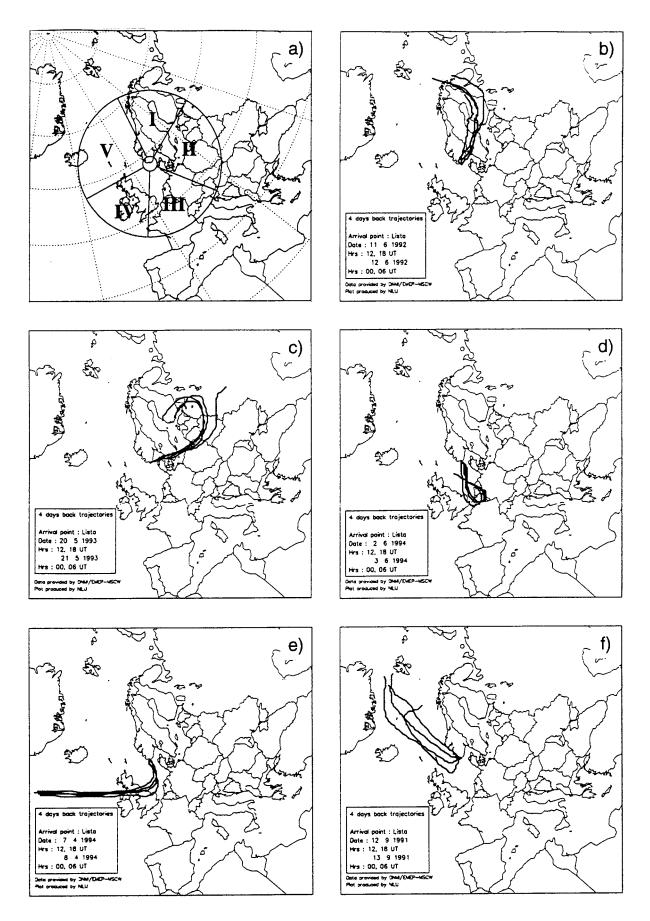


FIGURE 1. (a) Map of Europe showing the location of the sampling station Lista in southern Norway and the five sectors of trajectory origin. (b—f) Trajectory maps with typical long range and regional air transport episodes within a sector. (b) June 11, 1992, (c) May 20, 1993, (d) June 2, 1994, (e) April 7, 1994, (f) September 12, 1991.

TABLE 1. Range and Mean Concentrations of  $\alpha$ - and  $\gamma$ -HCHs in Air Sampled at Various European Locations during 1990—1995 in Units of Picograms per Cubic Meter

		α-HC	Н	$\gamma$ -HCH		
sample location	time period	range	mean	range	mean	ref
Lista, South Norway	1991	18-429	84	6.0-533	48	
•	1992	22-279	82	8.3-501	60	
	1993	28-297	67	12-283	43	
	1994	6.4 - 142	59	2.8-1004	59	
	1995	4.0-100	47	2.0 - 593	37	
Karvatn, Central Norway	Mar-May 92	55-129	88	13-487	77	4
Svanvik, North Norway	Mar-May 92	39-205	97	10-194	46	4
Ny-Ålesund, Spitsbergen	Mar-May 92	62-338	144	13-99	32	4
, , ,	Apr-Dec 93	7-203	77	3-38	14	6
Rörvik, South Sweden	Feb 90	64-88	76	87-182	134	10
	May 90	190-550	370	287-1100	693	10
Rörvik, Nidingen, S-Swe.	Mar-Apr 91	10-150	43	10-520	98	11
· ·	Nov-Dec 91	32-106	75	42-90	61	12
	May-Jun 92	62-93	77	124-132	128	12
	Nov-Dec 92	24-45	36	19-26	22	12
North Atlantic	Oct 90	47-143	105	22-331	79	13
	Apr-May 91	36-109	63	8.9-215	66	13
Paris, Central France	Jan-Dec 89-90			300-3500	1500	14

requirements in the European quality norm EN 45001 was applied (5). Blank and control samples were run through the complete cleanup procedure frequently and parallel with the samples. As blank values were always very low compared to the samples, no blank correction was performed. Further quality assurance measures and criteria are discussed in detail in Oehme *et al.* (4, 6). Selected samples were analyzed separately for filter and PUF plug I and II. The particle bound fraction of HCHs made up less than 1%. The detection limits for  $\alpha$ - and  $\gamma$ -HCH were 0.1 and 0.3 pg/m³.

Meteorological Data and Trajectory Calculations. Meteorological data for Lista station were provided from the Norwegian Meteorological Institute (DNMI). The trajectories calculations, which are based on meteorological data, were provided by the Meteorological Synthesizing Centre West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP) located at DNMI. For all air sampling occasions, four days' back trajectory was calculated every 6 h using winds on the  $\sigma = 0.925$  level ( $\sigma = P/Ps = pressure/$ surface pressure, approx. 600 m above ground) on the EMEP grid, using the EMEP trajectory model described by Eliassen and Saltbones (7). The horizontal components of the wind are given every 6 h on 150 km × 150 km grid squares. No vertical (i.e.  $cross-\sigma$ ) motion is calculated. The trajectories arriving at 12 and 18 the actual day and at 0 and 6 the following day were grouped together, consistent with the air sampling times. The calculated trajectories may extend to a distance of 3000 km from Lista.

Sector allocation analysis based on trajectories was employed to correlate air transport with the HCH concentration data. A circle with its center at Lista was divided into five sectors (I to V) as shown in Figure 1a. An atmospheric sample was allocated to a sector, if at least 50 percent of the four trajectories arriving during the 24 h sampling time were inside one of the sectors. Otherwise, the sample was characterized as of undefined origin (designated by VI). Only the part of the trajectory between 150 km and 1500 km from the arrival point was used in this calculation. Additionally, trajectories up to 3000 km distance from Lista (within the EMEP grid) were used. Even though air trajectories have been employed previously for studying long range air transport (4, 6, 8, 9), trajectories should be interpreted with care and may only give an indication of air transport from a source region.

#### **Results and Discussion**

Mean Levels and Interannual Trends. Annually averaged air concentrations for  $\alpha$ - and  $\gamma$ -HCH are listed in Table 1. Because arithmetic means are skewed by a few very high levels, geometric mean concentration is presented. The annual mean air concentrations at Lista between 1991 and 1995 varied from 47 to 84 pg/m³ for  $\alpha$ -HCH and from 37 to 60 pg/m³ for  $\gamma$ -HCH. These levels are similar to levels found in European air in recent years (Table 1), in particular to those reported from the Swedish west coast (10–12). The highest measured concentrations of  $\gamma$ -HCH approach the concentration levels measured in areas of lindane usage during the periods of application (14).

The atmospheric  $\alpha$ -HCH concentrations (annual geometric means) decreased from 1991 to 1995 by approximately 50% (linear slope = 10 pg/m³ per year, p < 0.1,  $r^2 = 0.97$ , n = 5). This is in excellent agreement with recent data from the Arctic (15) where a 50% decline in  $\alpha$ -HCH over a four year period from 1992 to 1995 was observed. Our own data from the Norwegian Arctic show a similar decrease in  $\alpha$ -HCH in the atmosphere. No clear interannual trend ( $r^2 = 0.13$ , n = 5) can be seen for  $\gamma$ -HCH in air. There is a hint of decreasing  $\gamma$ -HCH concentrations during the 5 years. However, the high annual mean concentration observed in 1994 deviates from this decreasing trend.

Confirming earlier statements by Oehme *et al.* (4) based on fewer measurements,  $\alpha$ -HCH concentrations in southern Norway in the 1990s are by a factor of 3–5 lower than in the early 1980s (16, 17) (Figure 2). Compared with data from USA and Canada from the early 1980s (18, 19), the  $\alpha$ -HCH levels are a factor of 5–10 lower.  $\gamma$ -HCH concentrations measured during March were about twice as high as the levels found at the same time in southern Norway in 1984, but summer concentrations were approximately 75% lower than measured in 1984 (Figure 2). The observed time trends may reflect a steady reduction in the use of technical grade HCH in Europe, whereas the use of lindane continues on a more or less steady level. This is also indicated by the detailed analysis of the episodes with elevated concentrations (see below).

**Episodes of Elevated Concentrations.** The time profiles of the HCH concentrations at Lista (Figure 3) are characterized by fairly steady baseline levels around 60 pg/m³  $\alpha$ -HCH and 40 pg/m³  $\gamma$ -HCH with short episodes of clearly elevated concentrations of up to several hundred picograms per cubic

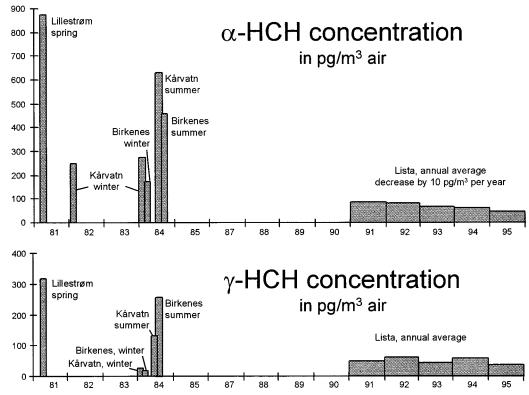


FIGURE 2. Time trend of the atmospheric concentrations of  $\alpha$ - and  $\gamma$ -HCH in southern and central Norway from 1981 to 1995. Data for the 1990s are geometric annual means, data for the 1980s are for shorter campaigns (16, 17).

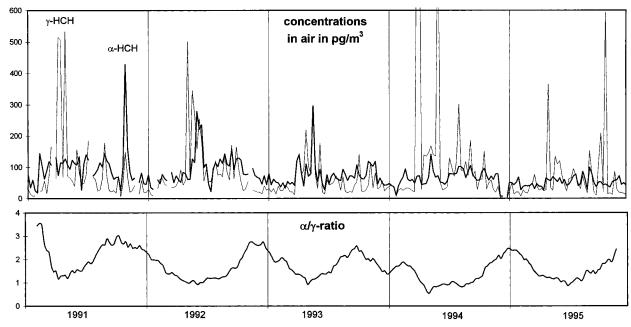


FIGURE 3. The measured concentrations of  $\alpha$ - and  $\gamma$ -HCH in air at Lista and the gliding 2-month average of the  $\alpha/\gamma$ -ratio.

meter. For  $\gamma$ -HCH, these episodes are more frequent and the increase tends to be more pronounced. Whereas quite common in 1991 and 1992, periods with significantly increased  $\alpha$ -HCH levels were no longer observed during the second half of the measurement campaign. Episodes with elevated air concentrations typically occurred in spring. In the years 1991 and 1995, episodes with increased HCH concentrations occurred also in autumn. Similar seasonal variations with peaks during spring and autumn have been observed during shorter measurement campaigns (9, 20, 21).

For further analysis, it was desirable to separate the data with clearly elevated levels from the base line data. As a

criterion for what constitutes an elevated concentration, we used the geometric mean plus 1 standard deviation. For  $\alpha\text{-HCH}$ , this critical concentration was 130 pg/m³ (based on the 1991 mean) and for  $\gamma\text{-HCH}$  180 pg/m³ (based on the 1991–1995 mean). To pinpoint the origin of the HCH-polluted air masses, we investigated the meteorological situations prevailing during some of the more conspicuous episodes using calculated trajectories (Figure 1).

There were 15 measurements with elevated  $\alpha\text{-HCH}$  levels (Table 2), but 10 of these were in the range  $140-161~pg/m^3$  and thus only slightly higher than the critical concentration. Of the 15 episodes, 12 occurred in 1991 and 1992, none in

TABLE 2. Sampling Date, Concentration in Picograms per Cubic Meter and Sector of Trajectory Origin of Atmospheric Samples with Elevated Levels<sup>a</sup>

$\alpha$ -HCH (levels exceeding 130 pg/m³)			$\gamma$ -HCH (levels exceeding 180 pg/m³)				
date	level	sector	date	level	sector		
Feb 7, 91	145	II	April 4, 91	515	Ш		
March 28, 91	133	VI	April 11, 91	507	III		
June 6, 91	134	VI	April 25, 91	533	II		
June 27, 91	140	V	July 4, 91	186	V		
Aug 22, 91	145	Ш	April 30, 92	501	IV		
Oct 24, 91	429	V	May 15, 92	346	Ш		
Oct 31, 91	161	II	May 21, 92	270	II		
May 28, 92	279	II	June 4, 92	255	II		
June 4, 92	221	II	June 11, 92	188	1		
June 11, 92	236	1	April 29, 93	219	II		
Aug 20, 92	143	VI	May 20, 93	283	II		
Sept 10, 92	157	Ш	March 31, 94	979	III		
April 8, 93	140	1	April 7, 94	1004	IV		
May 20, 93	297	II	June 2, 94	922	III		
May 12, 94	142	1	Aug 4, 94	302	III		
			Sept 9, 94	186	III		
			May 4, 95	365	Ш		
			Oct 12, 95	210	Ш		
			Oct 26, 95	594	Ш		

<sup>&</sup>lt;sup>a</sup> Dates in bold had elevated levels of both HCH-isomers.

1995. Four of the five highest  $\alpha$ -HCH levels, all in the range 220-300 pg/m<sup>3</sup>, occurred during late spring 1992 and 1993. During three of these four occasions (June 4 and 11, 92 and May 20, 93), the  $\gamma$ -HCH levels were also elevated. Indeed these were the only 3 days when increased concentrations of both quantified isomers were observed. The trajectories show that air transport occurred from easterly directions during the four sampling occasions with highest α-HCH levels. On June 11, 92, air masses originating in NW Russia had passed over Finland, the northern Baltic Sea, and Sweden before arriving at Lista (Figure 1b, sector I). On May 20, 93, air from Russia had passed over the Baltic states, Northern Poland, the southern Baltic Sea, and southern Scandinavia (Figure 1c, sector II). The trajectories indicate an identical situation for June 4, 92. According to Li et al. (2), in 1990 (East) Germany and the Ukraine were the only European countries using technical HCH to any significant extent. The Soviet Union banned the technical mixture in 1990 (1). The high spring levels of  $\alpha$ -HCH during air mass movement from the east provide strong evidence that technical HCH was nevertheless still used in eastern Europe in 1992 and 1993. The highest  $\alpha$ -HCH concentration of 429 pg/m<sup>3</sup> during the 5 years of monitoring was observed on Oct 24, 91, when the trajectory calculations indicate air mass movement to Lista from the North Atlantic across Iceland, the Norwegian Sea and southern Norway (sector V). It is hard to find a reasonable explanation for this extraordinarily high value, because similar meteorological situations generally led to below-average levels of α-HCH.

There were 19 occasions with elevated  $\gamma$ -HCH levels (Table 2). All but four of these occurred between the last week of March and the first week of July, and most of these during April and May, which is the main application period for lindane in Central Europe. Four samples had high  $\gamma$ -HCH levels in late summer 1994 or fall 1995, indicating that lindane may also be used during other times of the year. During 10 of the 19 episodes, air masses arrived in Lista from western central Europe (sector III), and during another five occasions from eastern central Europe (sector II). An example for transport from western Europe causing a high  $\gamma$ -HCH concentration is June 2, 94, when air masses originated in the southern part of the North Sea and the surrounding

coastal states (Figure 1d, sector III). The same meteorological situation prevailed during the episode of August 4, 94. The highest  $\gamma$ -HCH concentration of 1004 pg/m<sup>3</sup> was measured during the first week of April 1994, when air masses arrived in Lista straight from the West after crossing the U.K. (Figure 1e, sector IV). The week before (March 31, 94), elevated concentrations of  $\gamma$ -HCH were also observed when air arrived from the U.K. and France. A similar meteorological situation prevailed in late October 95 when  $\gamma$ -HCH reached a concentration of 594 pg/m³. These findings are in agreement with what is known about the use of lindane in Europe with respect to the time of application and the countries of origin. France has been the major consumer of lindane in Europe in recent years with an annual consumption of 1600 tons (22). Other West European countries where lindane is still in use are Italy, Germany, the U.K., and Benelux (2). HCH usage in Scandinavia is very limited, although lindane was still in use in Denmark until the summer of 1994 when it was totally banned (23).

As an example of a weather situation which caused no elevated concentrations of HCHs, Figure 1f depicts the trajectories calculated for September 12, 91, when concentrations of 82 pg/m³  $\alpha$ -HCH and 22 pg/m³  $\gamma$ -HCH were recorded. Such a situation with low levels of HCH and relatively high  $\alpha/\gamma$ -ratios were typical for transport of air from the polar region (sector V). During summer, the  $\gamma$ -HCH levels would often be slightly higher. Since HCH is believed to have minor or no use in polar areas, this ratio probably reflects the global background composition of HCHs.

Given the compositon of the two main HCH pesticide formulations, a high  $\alpha/\gamma$ -ratio of HCHs in air should indicate the input of technical HCH and a low ratio the use of lindane. Such an interpretation is confounded by the potential conversion of  $\gamma$ -HCH into a-HCH in the atmosphere. However, estimated rates for atmospheric degradation (*9*, *24*) and photochemical isomerization (*25*) tend to be slow compared to regional atmospheric transport, suggesting that the  $\alpha/\gamma$ -ratio of HCH in air is a useful source indicator on the regional scale.

Figure 3 shows the seasonal fluctuation of the  $\alpha/\gamma$ -ratio in air. High ratios >2 occur in winter (October to March) and low ratios <2 in spring and summer (April to September). A similar temporal pattern has also been observed in southern Ontario (8), Québec (9) and in the Canadian and Norwegian Arctic (26). The periods with low  $\alpha$  to  $\gamma$ -ratios coincide with the HCH application period in central Europe which is dominated by use of lindane. During summer the synoptic systems also favor air mass transport from central Europe, whereas midlatitudal exchange of Arctic air is restricted.  $\alpha/\gamma$ -Ratios of around 3 during winter reflect global background composition, and are indeed similar to what has been observed in the Arctic atmosphere in recent years (4, 6, 15, 26). The winter weather situation at Lista is characterized by inflow of air masses from the North Atlantic and the Arctic region.

The highest  $\alpha/\gamma$ -ratio of 7.5 was observed on January 16, 91, when air originating from the North Sea passed over Denmark, northern Germany, and Poland before arriving at Lista. Heavy rainfall during this period may have resulted in preferential scavenging of  $\gamma$ -HCH resulting in the high  $\alpha/\gamma$ -ratio. The lowest ratios of 0.1 were observed during April and May when air masses with elevated  $\gamma$ -HCH concentration arrived from the U.K., France, and Denmark.

Only 15 out of 238  $\alpha$ -HCH (6%) and 19 out 233  $\gamma$ -HCH (7.5%) measurements had elevated concentration according to the above definition. The data should allow to evaluate the importance of such short episodes of high levels to the overall import of HCH to Norway: if it is assumed that the air concentration is a measure of the atmospheric inflow into a region, the sum of the concentrations during episodes

TABLE 3. Assignments of All Atmospheric Samples and of the Sum of  $\alpha$ -HCH and  $\gamma$ -HCH Concentrations to the Five Sectors of Air Mass Origin<sup>a</sup>

sector	I	II	Ш	IV	V	VI
% of samples with air mass origin from a sector	5.1	13.8	10.7	21.7	35.6	13.0
% of $\Sigma$ $\alpha$ -HCH concentrations assigned to a sector	6.4	18.8	11.9	18.2	32.5	12.2
% of $\sum \gamma$ -HCH concentrations assigned to a sector	3.7	17.0	30.9	19.7	16.9	11.8

<sup>&</sup>lt;sup>a</sup> Sector VI denominates the percentage of samples which could not be assigned to one of the sectors due to uncertainty of air mass origin.

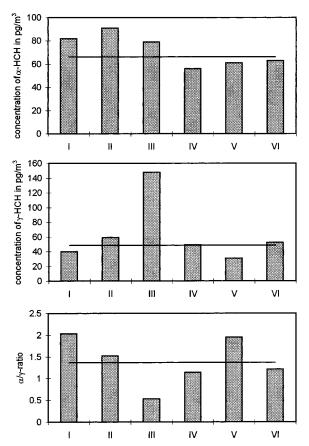


FIGURE 4. Geometric mean of the concentration of  $\alpha$ - and  $\gamma$ -HCH and of the  $\omega / \gamma$ -ratio in air for the samples originating in a particular sector as defined in Figure 1. The line indicates the geometric mean of all samples.

with elevated levels of HCH divided by the sum of all measured concentrations should be an approximate measure of the relative importance of episodes vs baseline concentration inflow. Using this approach, we can estimate that 7.5% of the sampling events account for almost 40% of the  $\gamma$ -HCH measured at Lista, and 6% of the sampling days account for the inflow of 15% of the  $\alpha$ -HCH. Obviously, episodes of elevated concentrations are very important when trying to quantify the atmospheric inflow of  $\gamma$ -HCH into southern Norway.

**Source Allocation.** Trajectories were calculated for all samples and assigned to the five sectors of air mass origin (Table 3). During more than a third of the sampling occasions, the air had Arctic origin (sector V), another third could be assigned to air mass transport from western Europe (sector III and IV), whereas less than a fifth originated in northern and eastern Europe (sector I and II). Only 13% of the occasions could not be assigned to one of the five sectors.

Figure 4 shows the geometric mean of the  $\alpha$ -HCH and  $\gamma$ -HCH concentrations and of the  $\alpha/\gamma$ -ratio for all the samples assigned to a sector. Samples originating in sectors I, III, and especially II have higher-than-average levels; samples

originating in sectors IV and V have below-average  $\alpha\text{-HCH}$  levels. However, the differences between the sectors are not very pronounced for  $\alpha\text{-HCH}$ . A clearer pattern is emerging for  $\gamma\text{-HCH}$ . The average  $\gamma\text{-HCH}$  concentrations in samples originating in sector III is three times higher than the mean of all samples. Correspondingly,  $\gamma\text{-HCH}$  levels in air from the north (sectors I and V) are on average considerably lower. Samples with air originating from the north (sectors I and V) are thus characterized by rather high  $\alpha/\gamma\text{-ratio}$ , while samples with air transport from western Europe (sector III) have on average very low  $\alpha/\gamma\text{-ratio}$ . Interestingly, the mean  $\alpha/\gamma\text{-ratio}$  of samples with origin in eastern Europe (sector II) is only slightly higher-than-average, because not only  $\alpha\text{-HCH}$  levels, but also  $\gamma\text{-HCH}$  concentrations tend to be higher than average in these samples.

Following a similar reasoning as above, the sum of the concentrations measured during air mass transport from one sector divided by the sum of all measured concentrations should be an approximate measure of the relative importance of atmospheric inflow from that sector. The results of the respective calculations are listed in Table 3. Although only 12% of the assigned trajectories originated in western central Europe (sector III), transport from that region accounts for more than a third (35%) of the (assigned)  $\gamma$ -HCH inflow to southern Norway. Conversely, even though air arrived from the Norwegian Sea (sector V) during two out of five sampling days, this accounts for less than one-fifth of the  $\gamma$ -HCH measured in the air in Lista. Transport of  $\alpha$ -HCH to southern Norway, on the other hand, occurs from all directions, and sector V accounts for a large part of the inflow simply because air is often advected to southern Norway from that region.

Usage of  $\alpha$ -HCH within the area of potential regional air transport to southern Norway seems to be very limited, particularly during the latter half of the sampling period. The atmospheric levels of  $\alpha$ -HCH at Lista in 1991 through 1995 are rather influenced by global background values, which decreased steadily throughout the measurement period.  $\gamma$ -HCH, on the other hand, still seems to have substantial usage in western and central Europe, and air mass transport to southern Scandinavia during favorable weather situations can be fast and efficient. Then, concentrations can for brief periods reach levels similar to those in areas of application, exceeding background values by more than 1 order of magnitude. These short episodes are quantitatively significant for the overall atmospheric import of  $\gamma$ -HCH into southern Norway.

**Temperature Dependence of Atmospheric Concentrations.** If the amount of HCHs present in the atmosphere is partly controlled by temperature-dependent revolatilization from soils, vegetation, and water bodies, the measured concentrations should be related to ambient temperature. The clearly elevated air concentrations (see definition above) were excluded from the investigation of the relationship between temperature and atmospheric HCH concentrations, because these concentration spikes are obviously not related to temperature-driven air-surface partitioning, but caused by recent applications. The remaining atmospheric concentration values were converted into partial pressures p (in units of pascal) and the logarithm  $\ln p$  was regressed against reciprocal mean temperature during the day of sampling (in

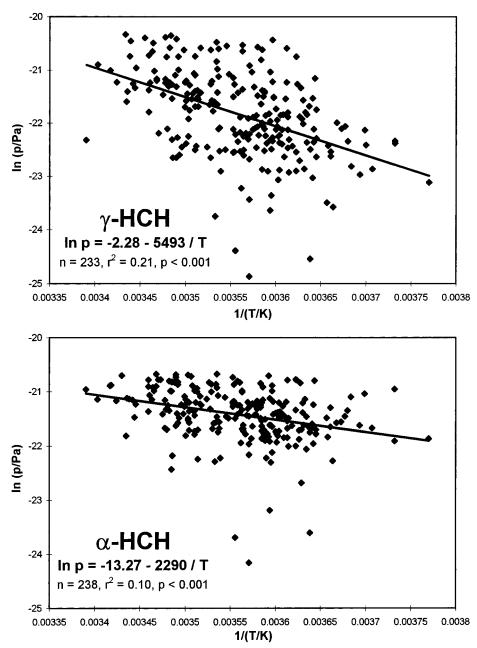


FIGURE 5. Logarithm of the partial pressure of  $\alpha$ -HCH and  $\gamma$ -HCH in air plotted against the reciprocal of the temperature on the sampling day.

kelvin). Figure 5 plots the data and gives the regression results.

Although the temperature dependence of the  $\alpha$ -HCH levels in air is significant, it is very weak, and the low correlation coefficient indicates that only a very small part of the variability can be explained by temperature fluctuations. The  $\gamma$ -HCH levels shows a stronger dependence on temperature, but again only a small part of the variation in air concentrations is due to temperature changes. Considering the large importance of regional air mass transport for the air concentrations in Lista, it is not surprising that temperature is accounting for only a small fraction of the variability.

Also in some previous studies of the temperature dependence of atmospheric HCH concentrations in Ontario (8), Quebec (9), and Minnesota (27), temperature could explain no or only a very minor fraction of the variability in the air concentrations of  $\alpha$ -HCH, i.e., correlation coefficients  $r^2$ , and slopes of the ln p vs 1/T relationships were small.

Atmospheric  $\gamma$ -HCH concentrations, on the other hand, tended to be much stronger correlated with temperature ( $r^2 > 0.4$ ), showing  $\ln p$  vs 1/T slopes greater than 7000. The  $\gamma$ -HCH data from Lista are unique in that the slope is shallower (5500) and the  $r^2$  is only around 0.2.

We suggest that a steep slope indicates that air concentrations are controlled by re-evaporation from surfaces in the local surroundings of the sampling site, whereas a shallow slope indicates that advection of air is governing atmospheric concentration levels. The lack of a temperature relationship for  $\alpha\text{-HCH}$  may be due to the fact that all studies were relatively far from regions which had experienced technical HCH usage in the recent past, so re-evaporation of  $\alpha\text{-HCH}$  close to sampling sites should be very limited. It is rather likely that most of the measured  $\alpha\text{-HCH}$  has been advected into the sampling area. In Lista, the same should apply for  $\gamma\text{-HCH}$ , but its use areas are closer and a temperature signal may be preserved to some extent during the relatively short transport form central Europe to the south of Norway.

Merit of Long-Term Measurements. Multiannual measurements of the concentrations of semivolatile organic compounds in the atmosphere provide information concerning the extent of variability of measured concentrations, temporal trends on a seasonal and longer time scale, and an approximate identification of the origin of the contaminants in an area. As a side product, a better mechanistic understanding of the processes semivolatile organic chemicals undergo in the environment may be obtained, such as the temperature-dependent cycling between the Earth's surface and the atmosphere.

Because some parameters show substantial interannual variability, single year measurements may give erroneous estimates of long-term average conditions. Long-term trends can only be detected in measurements campaigns covering several years. To account for the seasonal variability and episodicity of air mass transport, air monitoring for semi-volatile organics should be performed throughout the entire year, or at least during every season. This study in particular highlighted the potentially large impact of singular events.

A comparison of the levels of HCHs measured in Lista with those from the Swedish West Coast suggest that differences on a small spatial scale are likely to be minor. In atmospheric measurements of semivolatile organic contaminants, a high temporal resolution may thus be more crucial than high spatial resolution. A few stations running for a longer period of time and with a high sampling frequency might be more sensible and economic than many stations running for a short time.

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