

Global Distribution and Atmospheric Transport of Chlorinated Hydrocarbons: HCH (BHC) Isomers and DDT Compounds in the Western Pacific, Eastern Indian and Antarctic Oceans*

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Abstract: Concentrations of chlorinated hydrocarbons such as HCH isomers and DDT compounds were determined in air and surface water samples taken from the Western Pacific, Eastern Indian and Antarctic Oceans. The most interesting finding was their presence in measurable concentrations in the Antarctic Ocean. Chlorinated hydrocarbon pesticides are widely distributed in the open ocean environment over both the northern and southern hemispheres, and some characteristic distribution patterns of pesticide species in different oceanic regions were observed both in air and water samples. HCH residues found in the northern hemisphere were much higher in concentration than those in the southern hemisphere. On the other hand, higher concentrations of DDT residues were found in the tropical regions, but their levels were not so different between both the northern and southern hemispheres. HCH isomers found in the northern hemisphere had the following order of concentrations: α -HCH > γ -HCH > β -HCH, while in the southern hemisphere γ -HCH was apparently dominant. DDT compound compositions were rather uniform in all the oceans surveyed, and more than 50 % was *p,p'*-DDT. These facts can be explained by the world wide situation regarding pesticide use and the physicochemical properties of the pesticides such as their vapor pressures and water solubilities. In addition, the meridional circulation of the atmosphere, particularly the mass flows of the Hadley and Ferrel cells in the troposphere, also contributes to the atmospheric transport and global distribution of these pesticides.

1. Introduction

It had been predicted early in the last decade that the open ocean environment will have served as the final sink for persistent man-made organics such as PCBs and chlorinated hydrocarbon pesticides (NAS, 1971; WOODWELL *et al.*, 1971). Recently, the National Academy of Sciences (1979) reported that 80 to 90 % of PCB residues in the environment of the United States were present in the Atlantic Ocean, which confirmed the above prediction.

The occurrence and distribution of chlorinated hydrocarbon residues in the open ocean environment have been reported by many authors (HARVEY *et al.*, 1973, 1974; BIDLAMAN and OLNEY, 1974; HARVEY and STEINHAUER, 1976a, 1976b; JONAS and PFAENDER, 1976; DAWSON

and RILEY, 1977; TANABE and TATSUKAWA, 1980; ATLAS and GIAM, 1981; BIDLAMAN *et al.*, 1981). Some of these reports provide strong evidence that atmospheric transport is a dominant pathway that determines the fate and distribution of chlorinated hydrocarbons on the global scale. Recent studies have focused on modeling of chlorinated hydrocarbon fluxes across the air/water interface and their global atmospheric transport (MCCLURE, 1976; JUNGE, 1977; NAS, 1978, 1979; DOSKEY and ANDREN, 1981). However, a refined model does not yet seem to be established, because most measurement data published are confined to the northern hemisphere and little information is available on the global distribution of pesticides, particularly in the southern hemisphere.

For the last decade, many of the industrialized countries have banned or restricted the use of persistent chlorinated hydrocarbons because of their accumulative characteristics and harmful

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biological effects. However, in the developing countries especially in the southern hemisphere and tropical regions, the use of chlorinated hydrocarbon pesticides such as DDT and HCH (BHC) is considered to be unavoidable for agriculture and public health in order to sustain a food supply and to prevent the propagation of malaria (SNELSON, 1977). Judging from the world trends in pesticide use, the application of several chlorinated hydrocarbon pesticides in the tropical zone and southern hemisphere is expected to continue for at least the next decade, and the global transport of these pesticides does not appear to be decreasing. The National Academy of Sciences (1978) recommended that the most urgent need is measurements of DDT in the marine environment of the southern hemisphere, because the major areas of DDT use in the future lie there.

For this reason an attempt was made to investigate the worldwide distributions of PCBs and chlorinated hydrocarbon pesticides in the Western Pacific and Eastern Indian Oceans as well as the Antarctic Ocean from November 1980 to March 1981 on board two Japanese vessels mentioned below (Fig. 1). The details

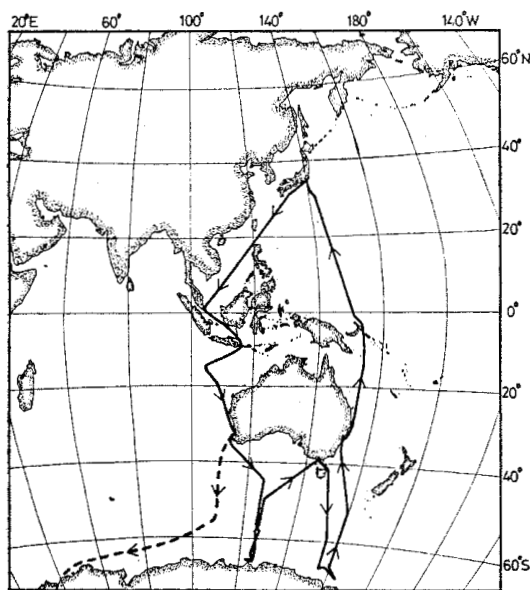


Fig. 1. Survey cruise routes. The solid and broken lines show the cruise routes of the T/S Umitaka Maru and the Icebraker Fuji, respectively. Air and water samples were collected along the cruise routes.

of PCB measurements were reported elsewhere (TANABE *et al.*, 1982). In this paper, we describe the distribution of chlorinated hydrocarbon pesticides such as HCH isomers (Hexachlorocyclohexane, including α , β and γ isomers) and DDT compounds (including *p*, *p'*-DDT, *p*, *p'*-DDE and *o*, *p'*-DDT) in the open ocean air and surface water over both hemispheres, and also discuss their atmospheric transport.

This study was supported as part of the BIOMASS program (Biological Investigations of Marine Antarctic Systems and Stocks) carried out on a cruise of the T/S Umitaka Maru, Tokyo University of Fisheries and partly through the JARE-22 program (22nd Japanese Antarctic Research Expedition) of the Ministry of Education, Science and Culture on a cruise of the Icebreaker Fuji.

2. Sample Collection

DDT compounds in air were collected by a high-volume air sampler (Staplex Co.) attached to an aluminum cylinder packed with four polyurethane foam plugs (85 mm diameter \times 50 mm thick). HCH isomers were sampled by a low-volume air sampler (Iwaki : Model AP-220) attached to a glass column also packed with four polyurethane foam plugs (32 mm diameter \times 50 mm thick). About 1,000 m³ of air was drawn at flow rates of 550 to 650 l/min. for DDT compounds, and about 200 m³ at 25 to 27 l/min. for HCH isomers. The collection of air samples followed basically the method described by SIMON and BIDDLEMAN (1979), but a glass fiber filter was not used in either sampler—polyurethane foam retained the pesticides in both vapor-phase and aerosol. The collection efficiencies by the method employed in this study were preliminarily examined and found to be satisfactory. The percentages lost by breakthrough for the air volumes mentioned above were less than 10% in all chlorinated hydrocarbon pesticides determined.

About 300 to 500 l of sea water was collected and then passed through Amberlite XAD-2 resin columns. The details of the collection method were given in previous papers (TATSUKAWA *et al.*, 1979; TANABE and TATSUKAWA, 1980). Absorption efficiencies for this resin for 500 l samples of water were 86% for α -HCH, 88% for γ -HCH and more than 90% for the others.

3. Chemical Analysis

Chlorinated hydrocarbons trapped on polyurethane foam and Amberlite XAD-2 resin were eluted with acetone and ethanol, respectively. The crude extracts from air and water samples were transferred to hexane and then concentrated to 10 ml. The concentrated hexane was cleaned by shaking with 5% fuming sulfuric acid. The final hexane extract was further concentrated to 100 μ l with a microconcentrator under a stream of purified nitrogen gas (TATSUKAWA *et al.*, 1979).

The determination of chlorinated hydrocarbons was mainly performed on a gas chromatograph-mass spectrometer equipped with a multi-ion detector (Shimadzu: Model LKB 9000) but was occasionally carried out on an electron capture gas chromatograph (Shimadzu: Model GC-4BM). The chromatograph column was 2 mm i.d. \times 1.8 m long and packed with 2% QF-1+1.5% OV-17 on 100 to 120 mesh Chromosorb W AW HMDS. The details of the determination procedures and measurement conditions are the same as those previously reported (TATSUKAWA *et al.*, 1979).

4. Results

HCH isomers and DDT compounds were detected in air (Tables 1 and 2) and water

samples (Table 3) in all locations surveyed. The most interesting finding was the presence of these pesticides in measurable concentrations in the Antarctic Ocean. According to a review on chlorinated hydrocarbon residues in the Antarctic (HIDAKA and TATSUKAWA, 1981), eighteen papers were published during 1966 to 1979. All papers, however, were concerned with wildlife and snow, and no quantitative data for these pesticides in the Antarctic air and sea water seem to have been published to date. The data presented here clearly indicate that the influence of human activities is spreading all over the world, even over the Antarctic Ocean.

The distributions of HCH residues in air and surface water are shown in Fig. 2. Levels of Σ HCH (sum of α , β and γ isomers) in the northern hemisphere were higher than those in the southern hemisphere, and in the former, the seas bordering the Asian Continent were found to have much higher concentrations within the range of 1.1 to 2.0 ng m^{-3} in air and 3.1 to 7.3 ng l^{-1} in water. HCH residues were also detected in the Antarctic air (0.09 to 0.17 ng m^{-3}) and water (0.26 to 0.92 ng l^{-1}), although these are much lower levels compared with the other oceans. Recently, ATLAS and GIAM (1981) reported the presence of HCH residues in air taken from Enewetak (Eniwetok) Atoll in the

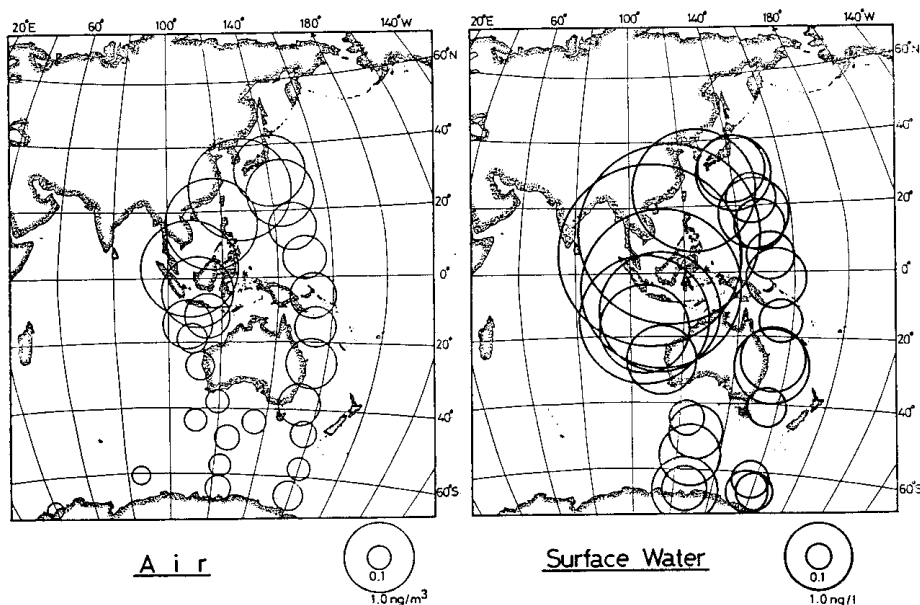


Fig. 2. Σ HCH distributions in air and surface water

Table 1. HCH isomer concentrations (ng m^{-3}) in air over the Western Pacific, Eastern Indian and Antarctic Oceans. Samples numbered 25-27 were collected during the cruise of the Fuji. ΣHCH shows the sum of α , β and γ isomers.

Sample No.	Date (yr. month/day)		Start location		End location		α -HCH	β -HCH	γ -HCH	ΣHCH
	start	end	lat.	long.	lat.	long.				
1	'80 11/13	'80 11/16	33°11'N	134°05'E	22°08'N	122°05'E	1.4	0.026	0.55	2.0
2	11/16	11/19	22°08'N	122°05'E	11°36'N	111°52'E	1.0	0.13	0.60	1.7
3	11/19	11/21	11°36'N	111°52'E	2°43'N	105°09'E	1.2	0.098	0.68	2.0
4	11/27	11/30	0°59'N	105°12'E	8°44'S	115°41'E	0.51	0.064	0.48	1.1
5	11/30	12/ 3	9°28'S	114°51'E	13°16'S	109°39'E	0.098	0.040	0.26	0.40
6	12/ 4	12/ 7	14°07'S	107°58'E	15°39'S	105°10'E	0.089	0.038	0.37	0.50
7	12/11	12/13	15°12'S	105°56'E	23°17'S	111°56'E	0.060	0.009	0.10	0.17
8	12/13	12/15	23°17'S	111°56'E	31°32'S	115°19'E	0.050	0.008	0.094	0.15
9	12/20	12/23	32°39'S	115°10'E	44°43'S	124°43'E	0.042	0.009	0.052	0.10
10	12/23	12/26	44°43'S	124°43'E	54°52'S	125°02'E	0.043	0.005	0.068	0.12
11	12/26	12/30	54°52'S	125°02'E	61°30'S	121°05'E	0.041	0.006	0.039	0.086
12	12/30	'81 1/ 3	61°30'S	121°05'E	65°03'S	124°28'E	0.023	0.008	0.092	0.12
13	'81 1/10	1/15	48°58'S	127°03'E	39°36'S	143°29'E	0.022	0.009	0.082	0.11
14	1/26	1/30	60°03'S	154°56'E	67°26'S	164°18'E	0.036	0.011	0.12	0.17
15	2/ 4	2/ 8	62°59'S	160°01'E	52°01'S	160°01'E	0.030	0.004	0.059	0.093
16	2/ 8	2/11	51°48'S	160°02'E	42°53'S	156°06'E	0.045	0.009	0.074	0.13
17	2/11	2/13	42°57'S	156°06'E	34°46'S	151°49'E	0.13	0.023	0.18	0.33
18	2/20	2/23	32°28'S	152°51'E	20°59'S	154°31'E	0.16	0.067	0.28	0.51
19	2/23	2/26	20°59'S	154°31'E	10°09'S	154°20'E	0.091	0.037	0.20	0.33
20	2/26	2/28	10°08'S	154°20'E	0°41'S	152°10'E	0.15	0.045	0.22	0.42
21	3/ 1	3/ 3	1°33'N	151°57'E	11°21'N	149°27'E	0.17	0.020	0.19	0.38
22	3/ 3	3/ 5	11°21'N	149°27'E	21°11'N	145°21'E	0.29	0.011	0.14	0.44
23	3/ 5	3/ 7	21°12'N	145°21'E	29°54'N	141°22'E	0.66	0.019	0.26	0.94
24	3/ 7	3/ 9	29°54'N	141°22'E	35°33'N	140°01'E	0.65	0.028	0.36	1.0
25	'80 12/17	'80 12/21	35°58'S	112°11'E	51°32'S	109°59'E	0.032	0.006	0.050	0.088
26	12/23	12/27	57°48'S	102°26'E	63°47'S	69°40'E	0.014	0.004	0.038	0.056
27	'81 1/23	'81 1/27	Syōwa Station (69°00'S, 39°35'E)				0.011	0.004	0.033	0.048

Table 2. DDT compound concentrations (ng m^{-3}) in air over the Western Pacific, Eastern Indian and Antarctic Oceans. ΣDDT shows the sum of p , p' -DDE, p , p' -DDT and o , p' -DDT.

Sample No.	Date (yr. month/day)		Start location		End location		p , p' -DDE	p , p' -DDT	o , p' -DDT	ΣDDT
	start	end	lat.	long.	lat.	long.				
1	'80 11/13	'80 11/14	33°11'N	134°05'E	29°13'N	130°24'E	0.015	0.098	0.034	0.15
2	11/16	11/17	22°08'N	122°05'E	17°41'N	118°55'E	0.060	0.27	0.13	0.46
3	11/20	11/21	7°33'N	108°40'E	3°32'N	105°37'E	0.11	0.49	0.26	0.86
4	11/28	11/29	1°23'S	108°00'E	5°38'S	112°53'E	0.081	0.34	0.18	0.60
5	11/30	12/ 1	9°28'S	114°51'E	12°18'S	110°38'E	0.062	0.33	0.15	0.54
6	12/ 5	12/ 6	15°02'S	106°13'E	14°12'S	106°04'E	0.059	0.27	0.074	0.40
7	12/11	12/12	15°12'S	104°56'E	18°53'S	108°45'E	0.016	0.097	0.042	0.16
8	12/12	12/13	19°23'S	109°12'E	24°27'S	112°10'E	0.041	0.13	0.051	0.22
9	12/14	12/15	26°36'S	112°51'E	31°32'S	115°19'E	0.027	0.15	0.065	0.24
10	12/22	12/23	39°24'S	119°24'E	44°20'S	124°21'E	0.013	0.093	0.027	0.13
11	12/25	12/26	52°20'S	125°04'E	54°59'S	125°01'E	0.015	0.066	0.029	0.11
12	12/29	12/30	59°03'S	125°20'E	63°01'S	125°07'E	0.015	0.083	0.035	0.13

Table 2. (Continued)

Sample No.	Date (yr. month/day)		Start location		End location		<i>p</i> , <i>p</i> '-DDE	<i>p</i> , <i>p</i> '-DDT	<i>o</i> , <i>p</i> '-DDT	Σ DDT
	start	end	lat.	long.	lat.	long.				
13	'81 1/ 1	'81 1/ 2	64°52'S	124°37'E	64°56'S	124°41'E	0.027	0.15	0.059	0.24
14	1/13	1/14	46°10'S	133°00'E	42°28'S	139°16'E	0.016	0.085	0.046	0.15
15	1/28	1/29	65°48'S	155°12'E	64°56'S	160°39'E	0.030	0.12	0.038	0.19
16	2/ 7	2/ 8	55°00'S	159°57'E	51°59'S	160°05'E	0.034	0.062	0.024	0.12
17	2/10	2/11	46°06'S	157°25'E	41°55'S	155°40'E	0.022	0.11	0.047	0.18
18	2/12	2/13	38°47'S	153°53'E	34°33'S	151°42'E	0.046	0.24	0.096	0.38
19	2/21	2/22	29°27'S	153°45'E	23°50'S	153°57'E	0.045	0.20	0.10	0.35
20	2/24	2/25	15°44'S	154°39'E	14°00'S	154°42'E	0.037	0.14	0.068	0.25
21	2/27	2/28	6°30'S	153°43'E	1°38'S	152°15'E	0.038	0.20	0.084	0.32
22	3/ 1	3/ 2	2°58'N	151°43'E	8°44'N	150°38'E	0.034	0.12	0.050	0.20
23	3/ 3	3/ 4	12°17'N	149°07'E	17°51'N	146°54'E	0.026	0.11	0.049	0.19
24	3/ 5	3/ 6	21°41'N	145°07'E	27°04'N	142°40'E	0.033	0.13	0.068	0.23
25	3/ 7	3/ 8	30°38'N	141°04'E	34°59'N	139°07'E	0.017	0.093	0.043	0.15

Table 3. HCH isomer and DDT compound concentrations (ng l^{-1}) in surface water samples from the Western Pacific, Eastern Indian and Antarctic Oceans. Σ HCH shows the sum of α , β and γ isomers. Σ DDT shows the sum of *p*, *p*'-DDE, *p*, *p*'-DDT and *o*, *p*'-DDT.

Sample No.	Date (yr. month/day)	Location		α -HCH	β -HCH	γ -HCH	Σ HCH	<i>p</i> , <i>p</i> '-DDE	<i>p</i> , <i>p</i> '-DDT	<i>o</i> , <i>p</i> '-DDT	Σ DDT
		lat.	long.								
1	'80 11/15	24°52'N	125°55'E	1.8	0.11	1.4	3.3	0.007	0.035	0.007	0.049
2	11/18	16°01'N	116°44'E	2.9	0.80	3.3	7.0	0.011	0.091	0.018	0.12
3	11/20	5°38'N	107°10'E	3.4	1.0	2.9	7.3	0.006	0.028	0.014	0.048
4	11/29	4°03'S	111°03'E	1.3	0.54	3.7	5.5	0.013	0.030	0.014	0.057
5	12/ 2	12°22'S	110°40'E	0.48	0.14	2.5	3.1	0.007	0.086	0.032	0.13
6	12/ 8	15°04'S	104°49'E	0.56	0.16	2.9	3.6	0.003	0.022	0.006	0.031
7	12/13	18°03'S	104°49'E	0.12	0.11	1.5	1.7	0.001	0.005	0.001	0.007
8	12/15	27°25'S	113°37'E	0.021	0.066	0.93	1.0	0.001	0.011	0.002	0.014
9	12/24	44°40'S	122°14'E	0.027	0.039	0.20	0.27	0.002	0.053	0.003	0.058
10	12/29	56°19'S	125°05'E	0.065	0.064	0.67	0.80	0.001	0.003	0.001	0.005
11	12/31	64°42'S	124°15'E	0.037	0.026	0.35	0.41	0.001	0.006	0.001	0.008
12	'81 1/ 2	64°55'S	124°40'E	0.074	0.043	0.81	0.93	0.001	0.003	0.001	0.005
13	1/10	48°59'S	127°31'E	0.10	0.026	0.49	0.62	0.003	0.014	0.003	0.020
14	1/30	62°37'S	157°38'E	0.072	0.010	0.21	0.29	0.002	0.009	0.004	0.015
15	2/ 2	64°42'S	162°11'E	0.065	0.021	0.30	0.39	0.004	0.019	0.004	0.027
16	2/ 7	62°00'S	160°06'E	0.086	0.005	0.20	0.29	0.002	0.013	0.006	0.021
17	2/11	41°44'S	155°16'E	0.12	0.008	0.19	0.32	0.003	0.012	0.005	0.020
18	2/21	28°16'S	153°35'E	0.27	0.009	0.94	1.2	0.005	0.011	0.005	0.021
19	2/22	24°19'S	153°54'E	0.16	0.022	0.72	0.90	0.002	0.013	0.005	0.020
20	2/24	15°49'S	154°53'E	0.15	0.024	0.24	0.41	0.002	0.011	0.006	0.019
21	2/27	2°58'S	152°49'E	0.26	0.060	0.45	0.77	0.003	0.021	0.010	0.034
22	3/ 1	5°37'N	151°10'E	0.22	0.028	0.27	0.52	0.002	0.019	0.007	0.028
23	3/ 3	14°15'N	148°16'E	0.24	0.078	0.21	0.53	0.001	0.008	0.003	0.012
24	3/ 4	18°09'N	146°33'E	0.32	0.15	0.59	1.1	0.001	0.005	0.002	0.008
25	3/ 5	22°05'N	145°02'E	0.33	0.034	0.16	0.52	0.001	0.022	0.005	0.029
26	3/ 6	30°50'N	141°05'E	0.64	0.30	0.25	1.2	0.001	0.008	0.003	0.012
27	3/ 7	30°57'N	140°51'E	0.71	0.17	0.11	0.99	0.002	0.010	0.004	0.016

Central Pacific. Average concentration of Σ HCH (0.27 ng m^{-3} , sum of α and γ isomers) in their report was fairly close to our measurements at locations near Enewetak Atoll (0.37 and 0.45 ng m^{-3} for sample Nos. 21 and 22 in Table 1). The large scale distribution of HCH residues has been clarified in recent publications which reported their presence over the North Pacific and Indian Oceans (TANABE and TATSUKAWA, 1980) and over the North Atlantic (BIDLEMAN *et al.*, 1981).

An apparent difference of HCH isomer compositions between the northern and southern hemispheres was found in the present survey. As shown in Fig. 3, a higher proportion of α -HCH to γ -HCH was observed in the north, whereas their relative abundances were reversed in the tropical regions, and the proportion of γ -HCH exceeded that of α -HCH in the south. This tendency was observed in both air and water samples. High proportions of α -HCH have recently been reported in the open ocean air and water over the northern hemisphere (TANABE and TATSUKAWA, 1980; ATLAS and GIAM, 1981; BIDLEMAN *et al.*, 1981). However, there are no reports on the higher proportion of γ -HCH to α -HCH in the marine environment of the southern hemisphere. It is an interesting question as to whether the predomi-

nance of γ -HCH extends all over the oceans in the southern hemisphere.

Besides HCH isomers, DDT residues are widely distributed in the open ocean environment (Fig. 4). High concentrations of Σ DDT (sum of p, p' -DDT, p, p' -DDE and o, p' -DDT) were found in the regions near the Asian Continent (0.15 to 0.85 ng m^{-3} in air, 0.05 to 0.12 ng l^{-1} in water), but Σ DDT levels between the northern and southern hemispheres were not so different. Moreover, it is noteworthy that similar levels of concentration were found in the Central Pacific between 20°N and 20°S (0.19 to 0.32 ng m^{-3} in air, 0.008 to 0.034 ng l^{-1} in water) and the Antarctic Ocean (0.11 to 0.23 ng m^{-3} in air, 0.005 to 0.058 ng l^{-1} in water). DDT

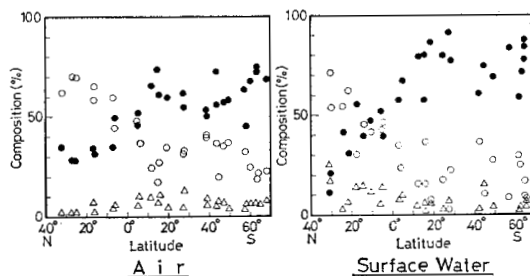


Fig. 3. HCH isomer compositions in air and surface water.

○ α -HCH, △ β -HCH, ● γ -HCH.

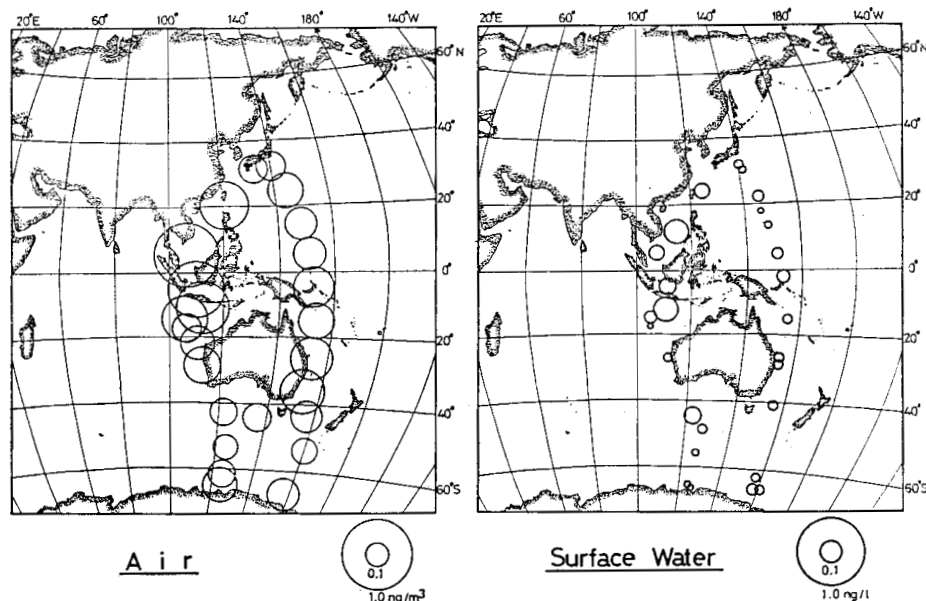


Fig. 4. Σ DDT distributions in air and surface water.

residues in open ocean air and water have also been measured by several researchers. BIDLÉMAN and OLNEY (1974) reported the presence of DDT residues in air over the North Atlantic with a range of values from 0.02 to 0.09 ng m⁻³ (sum of *p*, *p'*-DDT and *o*, *p'*-DDT). DAWSON and RILEY (1977) also found 0.02 and 0.04 ng l⁻¹ of DDT residues (sum of *p*, *p'*-DDT, *p*, *p'*-DDE and *p*, *p'*-DDD) in the North Sea surface water. According to a previous survey (TANABE and TATSUKAWA, 1980), ΣDDT concentrations (sum of *p*, *p'*-DDE and *p*, *p'*-DDT) in the air over the Bay of Bengal, Arabian Sea and the mid-latitudinal zone of the North Pacific between Tokyo and Los Angeles were found to be in the ranges of 0.15 to 0.27, 0.09 to 0.40 and <0.01 to 0.12 ng m⁻³, respectively. In that study, DDT residues in surface waters from the Bay of Bengal, Arabian Sea and Bering Sea were also reported, and ΣDDT concentrations (sum of *p*, *p'*-DDE and *p*, *p'*-DDT) were in the ranges of 0.08 to 0.09, 0.06 to 0.16 and 0.01 to 0.04 ng l⁻¹. The results reported previously by TANABE and TATSUKAWA (1980) and those from the Central Pacific and Antarctic Oceans in the present study indicate that DDT residue levels in the air are not so different among the oceans, but those in surface waters are somewhat higher in the Bay of Bengal and Arabian Sea than in the other seas. The variations of DDT residue levels in surface waters may be due to the different amounts of particulate matter in the oceans.

DDT compound compositions were found to have make-ups with concentrations in the order *p*, *p'*-DDT > *o*, *p'*-DDT > *p*, *p'*-DDE in both air and water, and this trend was rather uniform

in all the oceans surveyed (Fig. 5). In a previous survey (TANABE and TATSUKAWA, 1980), a high proportion of *p*, *p'*-DDT (normally more than 50% of ΣDDT) was found all over the North Pacific and Indian Oceans. Recently, BIDLÉMAN and LEONARD (1982) found 0.005 to 0.041 ng m⁻³ of *p*, *p'*-DDT and 0.004 to 0.085 ng m⁻³ of *o*, *p'*-DDT in air over the equatorial regions in the Indian Ocean. Their DDT residue levels, particularly *p*, *p'*-DDT, were approximately one order of magnitude lower than ours, and their DDT compound compositions, in which *o*, *p'*-DDT comprised about 50%, also differed with ours. Some discrepancies regarding DDT residue levels and compositions in the open ocean environment remain to be solved.

5. Discussion

It is apparent that HCH isomers and DDT compounds are widely transported not only in the northern hemisphere but also in the southern hemisphere. In this survey, we found some characteristic distribution patterns of pesticide species in different oceanic regions in both air and water samples. These patterns seem to result from the world situation regarding pesticide use, the physicochemical properties of the pesticides and the global circulation of the atmosphere.

FAO statistics (1979) indicated that a large amount of HCH has been used in many countries for the last decade, amongst which India consumed about 77,000 metric tons of technical HCH during 1975 to 1977—this figure is extraordinarily high in comparison with that for other countries. In China, HCH has also been produced and used for a long time (WANG, 1981), and recent annual production of technical HCH amounts to about 20,000 metric tons in Shenyang Chemical Plant alone (ANONYMOUS, 1981). Japan used 400,000 metric tons of technical HCH during 1948 to 1970 (TATSUKAWA *et al.*, 1972). Although reliable statistics on the world production and use of HCH are not yet available, it is safe to assume that the major consumption areas of HCH are still concentrated in the northern hemisphere, especially in the Asian Continent. From our survey and those of other workers' (TANABE and TATSUKAWA, 1980; ATLAS and GIAM, 1981; BIDLÉ-

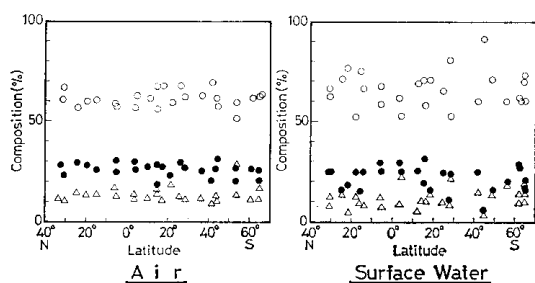


Fig. 5. DDT compound compositions in air and surface water.

○ *p*, *p'*-DDT, △ *p*, *p'*-DDE. ● *o*, *p'*-DDT.

MAN *et al.*, 1981; BIDDLEMAN and LEONARD, 1982), high concentrations of HCH residues were found in the Northwest Pacific and off the western coast of India, but have not yet been observed in other oceans. The fact that higher HCH levels were found in the northern hemisphere as compared with the southern hemisphere (Fig. 2) depends largely on its extensive use in the Asian Continent.

Though HCH are used the world over, it is assumed that HCH formulations applied in the northern and southern hemispheres are different, because the HCH isomer compositions found in the open ocean air and water differed greatly between both hemispheres (Fig. 3). There are two pesticide formulations of HCH supplied in the world, known as technical HCH and lindane. Technical HCH consists roughly of 70% α -HCH, 7% β -HCH, 13% γ -HCH, 5% δ -HCH and 5% of other impurities, and lindane is the purified γ -HCH isomer (TATSUKAWA *et al.*, 1972; BAUMANN *et al.*, 1980). While, α -HCH and γ -HCH have similar vapor pressures and water solubilities, β -HCH has smaller ones compared with those of α -HCH and γ -HCH (TANABE and TATSUKAWA, 1981). Therefore, the proportional relationship of α -HCH and γ -HCH found in open ocean air and water is thought to reflect the isomer composition of HCH formulation applied on the land. We found a higher proportion of α -HCH to γ -HCH in the northern hemisphere, which can be explained by the major use of technical HCH in the Asian Continent, as mentioned above. On the other hand, the relative abundance of γ -HCH in the southern hemisphere strongly suggests the extensive use of lindane in tropical and southern countries. In fact, much higher concentrations of γ -HCH were observed in the urban air in Australia (Table 4). OLAFSON (1978) reported that a large amount of lindane, as compared with other organochlorine insecticides, have been applied in the sugar cane growing regions adjacent to the Great Barrier

Reef in eastern Australia, and significantly high concentrations of γ -HCH were detected in many marine organisms there. Although only a little information is available for the status quo of HCH use in the southern hemisphere, lindane has been used, at least in Australia, which serves as a γ -HCH source for the surrounding ocean environment.

GOLDBERG (1975) predicted that the areas of DDT use would shift from the north to the south, the so-called "southward tilt", and he also estimated that about one million tons of DDT would be consumed in the world during 1971 to 1981. Actually in India, 140,000 metric tons of DDT were used for agriculture between 1975 and 1977 (FAO, 1979) and 7,500 metric tons were required for public health in 1978 to 1979 (JALEES and VEMURI, 1980). In recent years, fairly large amounts of DDT were also used in tropical and southern countries such as Mexico, Guatemala, El Salvador, Nicaragua, Argentina (FAO, 1979; CHAPIN and WASSERSTRÖM, 1981). Reflecting this worldwide use of DDT, high concentrations of DDT residues in marine air have been measured off the coast of the Arabian Sea (TANABE and TATSUKAWA, 1980; BIDDLEMAN and LEONARD, 1982), Gulf of Mexico (GIAM *et al.*, 1980) and off the western coast of Central America (TANABE and TATSUKAWA, 1980). In this survey, a marked difference in DDT residue levels between the northern and southern hemispheres was not observed (Fig. 4). Recently, GIAM and ATLAS (1981) found approximately the same concentrations of DDT residues in air taken from Samoa (Central Pacific in the southern hemisphere) and Enewetak (Central Pacific in the northern hemisphere). A similar DDT level was also recognized in fish samples collected from both hemispheres (TANABE *et al.*, 1980). These observations imply the continuous use of DDT in many countries in the tropics and the southern hemisphere, and a decrease in its discharge into the open ocean environment from

Table 4. HCH isomer concentrations (ng m^{-3}) in the urban air in Australia.

Location	Date (yr. month/day)		α -HCH	β -HCH	γ -HCH	Σ HCH
	start	end				
Fremantle	'80 12/19	'80 12/20	0.14	0.16	0.74	1.0
Melbourne	'81 1/18	'81 1/21	0.17	0.23	1.0	1.4

developed countries in the northern hemisphere.

The DDT formulation used for agriculture and malaria control consists roughly of 70 to 80 % *p,p'*-DDT and 15 to 20 % *o,p'*-DDT (HALLER *et al.*, 1945; MUTO, 1970), and vapor pressure of *o,p'*-DDT is greater than that of *p,p'*-DDT (SPENCER and CLIATH, 1972). Thus, it might be expected that a comparatively larger portion of *o,p'*-DDT is transported into the open ocean environment through the atmosphere. PERFECT (1980), however, pointed out that 98 % of DDT applied to a crop of cowpea in Ibadan, Nigeria, rapidly volatilized into the atmosphere. During tropical agricultural use, a large amount of pesticides is expected to volatilize rapidly into atmosphere due to the high temperature climate. Under these circumstances, DDT compound compositions in air appear to be close to the composition of the DDT formulation regardless of their different vapor pressures. Therefore, the higher proportion of *p,p'*-DDT to *o,p'*-DDT found in open ocean air and water (Fig. 5) may reflect the extensive use and active vaporization of DDT in tropical countries.

In addition to the situation of pesticide use in the world and their physicochemical properties, atmospheric circulation should be considered in the fate and transport of pesticides in the open ocean environment. Fig. 6 shows the meridional circulation of the atmosphere described by LOUIS (1975). There are three meridional cells in the troposphere called the Hadley cell existing over the tropical zone, the Ferrel cell over the mid-latitude zone and the polar direct cell over the high latitude zone in both northern and

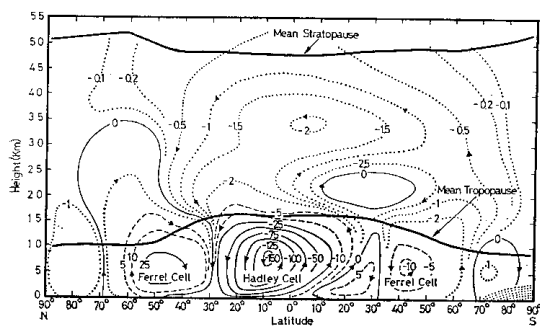


Fig. 6. Mean meridional circulation of the atmosphere during December to February reported by LOUIS (1975). The figures in this diagram indicate the mass flow in units of 10^9 kg sec^{-1} .

southern hemispheres. Atmospheric mixing in each cell is rather slow due to the inactive diffusion of its mass flow. In order to understand the global distribution and transport of pesticides, ΣHCH and ΣDDT concentrations in open ocean air determined in a previous survey (TANABE and TATSUKAWA, 1980) and this study are plotted against the latitude and given in Figs. 7 and 8, respectively. Higher concentrations of both pesticides were found in the mid-latitude zone of the northern hemisphere. Furthermore, relatively high concentrations of DDT residues were also measured in the tropical region and in the mid-latitudes of the southern hemisphere. The regions with high concentrations of pesticides approximately correspond to the areas of the Hadley cell and Ferrel cell. These facts indicate that the general circulation of the atmosphere also contributes to the global transport of chlorinated hydrocarbons, besides their usage as pesticides in the world. This may give further insight into the different

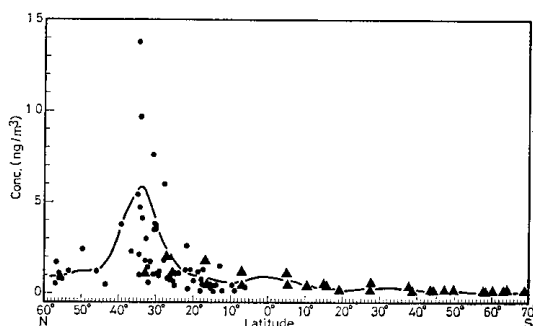


Fig. 7. Latitudinal distribution of ΣHCH in air surveyed from 1975 to 1979 (●) and from 1980 to 1981 (▲).

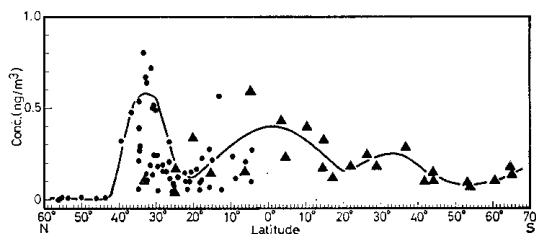


Fig. 8. Latitudinal distribution of ΣDDT in air surveyed from 1975 to 1979 (●) and from 1980 to 1981 (▲). ΣDDT presented in this figure includes only *p,p'*-DDT and *p,p'*-DDE because of the lack of *o,p'*-DDT data from 1975 to 1979.

residence times of pesticides in the atmosphere according to oceanic region.

CZEPLAK and JUNGE (1974) indicated that interhemispheric exchange of the atmosphere was fairly slow because of the impeding action of the Hadley cell which exists over tropical regions. We found apparent differences in HCH isomer compositions and their concentration levels in air between both hemispheres (Figs. 3 and 7). These differences seem to be enhanced by the slow interhemispheric exchange of the atmosphere.

The data obtained in this study will be useful for the estimation of the fluxes of persistent chlorinated hydrocarbons into the marine environment and for the construction of more refined mathematical models of their global atmospheric transport.

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References

- ANONYMOUS (1981): Pesticides in China. *Kongetsu no Nōyaku* (Monthly Review of Pesticide), Kagaku Kōgyō Nippōsha, Tokyo, April, pp. 114-116 (in Japanese).
- ATLAS, E. and C. S. GIAM (1981): Global transport of organic pollutants: Ambient concentrations in the remote marine atmosphere. *Science*, **211**, 163-165.
- BAUMANN, K., J. ANGERER, R. HEINRICH and G. LEHNERT (1980): Occupational exposure of hexachlorocyclohexane. 1. Body burden of HCH isomers. *Int. Arch. Occup. Environ. Health*, **47**, 119-127.
- BIDLEMAN, T. F. and C. E. OLNEY (1974): Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. *Science*, **183**, 516-518.
- BIDLEMAN, T. F., E. J. CHRISTENSEN, W. N. BILLINGS and R. LEONARD (1981): Atmospheric transport of organochlorines in the North Atlantic Gyre. *J. Mar. Res.*, **39**, 443-469.
- BIDLEMAN, T. F. and R. LEONARD (1982): Aerial transport of pesticides over the Northern Indian Ocean and adjacent seas. *Atmos. Environ.*, **16**, 1099-1107.
- CHAPIN, G. and R. WASSERSTRÖM (1981): Agricultural production and malaria resurgence in Central America and India. *Nature*, **293**, 181-185.
- CZEPLAK, G. and C. JUNGE (1974): Studies of interhemispheric exchange in the troposphere by a diffusion model. *Adv. Geophys.*, **18B**, 57-72.
- DAWSON, R. and J. P. RILEY (1977): Chlorine-containing pesticides and polychlorinated biphenyls in British coastal waters. *Est. Coast. Mar. Sci.*, **4**, 55-69.
- DOSKEY, P. V. and A. W. ANDREN (1981): Modeling the flux of atmospheric polychlorinated biphenyls across the air/water interface. *Environ. Sci. Technol.*, **15**, 705-711.
- FOOD AND AGRICULTURE ORGANIZATION (1979): 1978 FAO Production Year Book, FAO, Rome, **32**, 245 pp.
- GIAM, C. S., E. ATLAS, H. S. CHAN and G. S. NEFF (1980): Phthalate esters, PCB and DDT residues in the Gulf of Mexico atmosphere. *Atmos. Environ.*, **14**, 65-69.
- GIAM, C. S. and E. ATLAS (1981): Concentrations of chlorinated hydrocarbons are found to be 2 to 10 times lower at Samoa in the southern hemisphere than at Enewetak in the northern hemisphere. *SEAREX Newsletter*, **4**, 7-9.
- GOLDBERG, E. D. (1975): Synthetic organohalides in the sea. *In*, A Discussion on Organic Pollutants in the Sea, organized by H. A. COLE and J. E. SMITH, *Proc. Roy. Soc. London, Ser. B*, **189**, pp. 277-289.
- HALLER, H. L., P. B. BARTLETT, N. L. DRAKE, M. S. NEWMAN, S. J. CRISTOL, C. M. EAKER, R. A. HAYES, G. W. KILMER, B. MAGERLEIN, G. P. MUELLER, A. SCHNEIDER and W. WHEATLEY (1945): The chemical composition of technical DDT. *J. Americ. Chem. Soc.*, **67**, 1591-1602.
- HARVEY, G. R., W. G. STEINHAEUER and J. M. TEAL (1973): Polychlorinated biphenyls in North Atlantic Ocean water. *Science*, **180**, 643-644.
- HARVEY, G. R., W. G. STEINHAEUER and H. P. MIKILAS (1974): Decline of polychlorinated biphenyl concentrations in North Atlantic surface water. *Nature*, **252**, 387-388.
- HARVEY, G. R. and W. G. STEINHAEUER (1976a): Biochemistry of PCB and DDT in the North Atlantic. *In*, *Environmental Biochemistry*, ed. by J. O. NRIAGU, **1**, Ann Arbor Sci., Michigan, pp. 203-221.
- HARVEY, G. R. and W. G. STEINHAEUER (1976b): Transport pathways of polychlorinated biphenyls in Atlantic water. *J. Mar. Res.*, **34**, 561-575.
- HIDAKA, H. and R. TATSUKAWA (1981): Review:

- Environmental pollution by chlorinated hydrocarbons in the Antarctic. *The Antarctic Record*, No. 71, 151-164 (in Japanese).
- JALEES, K. and R. VEMURI (1980): Pesticides pollution in India. *Int. Environ. Stud.*, **15**, 49-54.
- JONAS, R. B. and F. K. PFAENDER (1976): Chlorinated hydrocarbon pesticides in Western North Atlantic Ocean. *Environ. Sci. Technol.*, **10**, 770-773.
- JUNGE, C. E. (1977): Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants. *In*, *Fate of Pollutants in the Air and Water Environments*, ed. by I.H. SUFFET, Part 1, Wiley-Interscience, New York, pp. 7-25.
- LOUIS, J. F. (1975): Mean meridional circulation. The natural stratosphere of 1974. CIAP Monograph 1, Dept. of Transportation, Washington, D. C., pp. 6-23-6-31.
- MCCLURE, V. E. (1976): Transport of heavy chlorinated hydrocarbons in the atmosphere. *Environ. Sci. Technol.*, **10**, 1223-1229.
- MUTO, T. (1970): DDT. *Nōyaku Gaisetsu* (Outline of Pesticides), Gihōdō, Tokyo, pp. 721-726 (in Japanese).
- NATIONAL ACADEMY OF SCIENCES (1971): Chlorinated Hydrocarbons in the Marine Environment. Washington, D. C., 42 pp.
- NATIONAL ACADEMY OF SCIENCES (1978): Halogenated hydrocarbons. *In*, *The Tropospheric Transport of Pollutants and Other Substances to the Oceans*, Washington, D. C., pp. 146-168.
- NATIONAL ACADEMY OF SCIENCES (1979): PCB transport throughout the environment. *In*, *Polychlorinated Biphenyls*, Washington, D. C., pp. 11-76.
- OLAFSON, R. W. (1978): Effect of agricultural activity on levels of organochlorine pesticides in hard corals, fish and molluscs from the Great Barrier Reef. *Mar. Environ. Res.*, **1**, 87-107.
- PERFECT, J. (1980): The environmental impact of DDT in a tropical agro-ecosystem. *AMBIO*, **9**, 16-21.
- SIMON, C. G. and T. F. BIDLEMAN (1979): Sampling airborne polychlorinated biphenyls with polyurethane foam—chromatographic approach to determining retention efficiencies. *Anal. Chem.*, **51**, 1110-1113.
- SNELSON, J. T. (1977): The importance of chlorinated hydrocarbons in the world agriculture. *Ecotoxicol. Environ. Safety*, **1**, 17-30.
- SPENCER, W. F. and M. M. CLIATH (1972): Volatility of DDT and related compounds. *J. Agric. Food Chem.*, **20**, 645-649.
- TANABE, S. and R. TATSUKAWA (1980): Chlorinated hydrocarbons in the North Pacific and Indian Oceans. *J. Oceanogr. Soc. Japan*, **36**, 217-226.
- TANABE, S., H. TANAKA, R. TATSUKAWA and I. NAKAMURA (1980): Organochlorine compound residues in several species of fishes caught off Chile. *Bull. Japanese Soc. Fisher.*, **46**, 763-769 (in Japanese).
- TANABE, S. and R. TATSUKAWA (1981): Behavior of man-made organics in the coastal and estuarine environment. *Bull. Coastal. Oceanogr.*, **19**, 9-19 (in Japanese).
- TANABE, S., M. KAWANO and R. TATSUKAWA (1982): Chlorinated hydrocarbons in the Antarctic, Western Pacific and Eastern Indian Oceans. *Trans. Tokyo Univ. Fisher.*, (5), 97-109.
- TATSUKAWA, R., T. WAKIMOTO and T. OGAWA (1972): BHC residues in the environment. *In*, *Environmental Toxicology of Pesticides*, ed. by F. MATSUMURA, C. M. BOUSH and T. MISATO, Academic Press, New York, pp. 229-238.
- TATSUKAWA, R., S. TANABE and T. YOSHIDA (1979): Man-made organics. *In*, *Kaiyō Kankyō Chōsahō*, ed. by The Oceanogr. Soc. Japan, Kōseisha Kōseikaku, Tokyo, pp. 232-269 (in Japanese).
- WANG, D. (1981): The status of pesticides in China and their future. *J. Pest. Sci.*, **6**, 397-399.
- WOODWELL, G. M., P. P. CRAIG and H. A. JOHNSON (1971): DDT in the biosphere: Where does it go? *Science*, **174**, 1101-1107.

有機塩素化合物の地球規模での分布と大気による輸送過程：
西部太平洋，東部インド洋，南極海における HCH (BHC)
異性体および DDT 化合物

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要旨：西部太平洋，東部インド洋および南極海の大気と表層海水に残留する HCH 異性体と DDT 化合物を測定した。世界的に広く使用されている HCH (BHC) や DDT などの有機塩素系農薬が，南極周辺の大気や海水にも検出可能な濃度で存在するすが今回見出されたが，その他南北両半球の外洋環境からも検出され，地球規模で汚染の進行していることが明らかとなった。

大気および表層海水に残留する HCH 異性体は，南半球に比べて北半球の濃度が高い。一方，DDT 化合物は，熱帯域で高濃度分布が認められたものの，南北両半球間

の濃度差は少く，HCH の分布とは明らかな違いが認められた。さらに DDT 化合物組成は *p,p'*-DDT が 50% 以上を占め，海域間の差はほとんど認められなかったが，HCH 異性体の組成は，北半球では α -HCH > γ -HCH > β -HCH，南半球では γ -HCH > α -HCH > β -HCH であった。

海域間で物質の分布に差が見られ，あるいは物質の種類間でも分布に特徴が認められることは，世界における農薬の使用状況および物質の物理化学性に加え，地球規模での大気の大循環，とくにハドレーセルやフェレルセルなどの空気塊の存在も関与していることが示唆された。

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