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Concentration and distribution of 17 organochlorine pesticides (OCPs) in seawater from the Japan Sea northward to the Arctic Ocean

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Seventeen classic organochlorine pesticides in surface seawater were studied in terms of their composition pattern as well as their distribution pattern in the areas covering the Japan Sea, Okhotsk Sea, Bering Sea, Chukchi Sea and Arctic Ocean. Their concentrations varied, but roughly two levels were seen with one ranging between 0.1 and 1 ng L^{-1} for most HCH isomers and the other lower than 0.1 ng L^{-1} for other chemicals. Of the 17 target compounds, HCHs were dominant with a total concentration percentage generally more than 50%, and a relatively high concentration percentage of heptachlor and aldrine was also observed at scattered stations. The historical long-term trend of several target chemicals in the five sea zones considered was discussed in comparison with previous reports. Inter-sea zone comparison was carried out for individual chemicals by comparing the concentration variation in all five sea zones. A higher variation in concentration was generally found in the northern sea zones, namely the Bering Sea, Chukchi Sea and Arctic Ocean, for most target compounds. The sum concentration of the 17 target chemicals displayed a general trend of increasing northward from the Japan Sea to the Okhotsk Sea to the Bering Sea to the Arctic Ocean. Different latitudinal trends were found for α -HCH and γ -HCH, and the reason of this difference was discussed by considering their divergence of thermodynamic properties, which could contribute to a slightly different fractionation effect during their northward transport driven by atmospheric long range transport. The source of the HCHs was identified by analyzing the α -HCH/ γ -HCH ratio, which was less than 4 without exception, indicating a component characteristic featuring a mixture of technical HCHs and lindane. In addition, the vertical distribution of α -HCH, γ -HCH and their ratio at station B80 was discussed. Different patterns were found in the upper 300 m while in layers from 300 m downward to 3500 m the patterns were fairly comparable. The vertical profiles were used to correlate the water mass distribution, based on which four layers were tentatively classified at station B80.

organochlorine pesticides, Arctic Ocean, solid-phase extraction, solid-phase microextraction

1 Introduction

As typical persistent organic pollutants (POPs), most organochlorine pesticides (OCPs) are wide-spread environmental contaminants, which can occur in the atmosphere, water, soil, sediment and organisms. Due to their toxicity, persistence, bioaccumulation, being prone to long-range transport, and potential negative impacts on organisms, OCPs are of continuing public and scientific concern worldwide in recent decades [1]. OCPs have been listed as priority control pollutants by the USA EPA and among the

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so-called "dirty dozen" in the UNEP Stockholm Convention (UNEP, 2001). Some OCPs, such as dieldrin, DDT, α -HCH and β -HCH, are shown to disrupt endocrine processes even in very low concentration [2–4].

OCPs originate mainly in temperate and warmer areas of the northern hemisphere. China and nine other countries consumed the highest amount of technical HCH, accounting for almost 85% of the total global usage of 10 Mt from 1948 to 1997 [5]. The total global DDT production from the 1940s to the present is estimated at around 4.5 Mt [6], with the USA consuming the most DDT (645 kt) followed by the former Soviet Union (320 kt) [7]. Although the production and usage of most technical OCPs have been banned, their persistent properties enable them to exist in different environmental media for a relatively long time [6]. Via atmospheric long-range transport (LRT), ocean currents and runoff passing through the Arctic's large drainage basin, such semi-volatile OCPs as HCHs, DDT, toxaphene and endosulfan are transported to the Arctic region [6, 8], which is particularly vulnerable to the above pollutants and has been indicated as their ultimate repository since before the early 1990s [9-13]. However, recent declining usage and a corresponding decrease in the input of the atmospheric α -HCH isomer have caused the net exchange to reverse, and made the western Arctic Ocean a source of α -HCH to the atmosphere rather than a sink for it [14–18]. Due to global climate change in recent years, ice melting is speeding up and the ice-covered area is decreasing accordingly, which may not only press more atmospheric pollutants into the seawater by direct dry or wet deposition, but also result in more ice-born pollutants being released into the seawater.

The surface seawater is an almost unique passage where pollutants transfer from the atmosphere [6, 19, 20] or rivers [21, 22] to the lower water, and it is also a significant way to expose OCPs to the zooplankton and therefore impact on the transmission of pollutants along marine and terrestrial food webs in the Arctic region [23, 24]. However, compared to the relatively abundant data concerning OCPs in the atmosphere [1, 20, 25–27]and biota [6, 8, 24, 28–31], there is a large gap in our knowledge in terms of the characteristics of dissolved OCPs in the Arctic Ocean and this hampers a full understanding of the geochemical properties of OCPs in the Arctic zone. There are, however, a few limited reports available concerning the characteristics of OCPs in seawater from the Arctic regions, especially the Bering and Chukchi Seas [14, 18, 32–34].

In the summer of 2008, seawater samples were collected during the cruise of the 3rd Chinese Arctic Expedition. The objectives of this study were to investigate the concentration characteristics and spatial distribution of 17 trace OCPs in seawater from the Japan Sea, to the Okhotsk Sea, Bering Sea, Chukchi Sea, and the adjacent western Arctic Ocean, and further discuss the long-term historic trend of OCPs in all five sea zones by comparing the published reports. Vertical patterns (up to 3500 m) of HCH isomers at station B80 were discussed.

2 Materials and methods

2.1 Chemicals and materials

Pesticide grade organic solvents (TEDIA, USA) were used in this study. An OCP mixture standard, containing α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor, aldrin, heptachlor epoxide, α -endosulfan, dieldrin, endrin, β -endosulfan, p,p'-DDD, p,p'-DDE, endrin aldehyde, p,p'-DDT, methoxychlor and endosulfan sulfate, was purchased from the Doctor Ehrensdosfer Laboratory (Augsburg, Germany). Deionized water was produced using a Milli-Q water production machine from Millipore (Bedford, MA, USA). The original mixture standard with a concentration of 100 ng mL⁻¹ was diluted using n-Hexane to make standard solutions. All the standard solutions were preserved at 4 °C. Fresh standard was used every other day to minimize any possible systematic error originating from the standard solution.

Glass filters were wrapped in aluminum foil and baked at 450 °C for 5 h and then stored in an airtight and moisture proof container. All glassware and sample containers were washed with detergent solution, and then rinsed several times with deionized water before baking at 450 °C for 5 h. Acetone was used to rinse all glassware prior to use.

2.2 Sampling and pretreatment

The water samples were collected during the 3rd Chinese Arctic Expedition cruise from 11 July to 24 September 2008 on board the R/V "Xuelong". The cruise track covered the Japan Sea, Okhotsk Sea, Bering Sea and the zone to the north of the Bering Strait including the Chukchi Sea, Canadian Basin and Arctic Ocean. Hydrographic information (temperature and salinity) at each station in this cruise track is summarized in Table 1. Along the cruise track shown in Figure 1, 4 L surface water samples were collected at 31 stations covering areas of the Japan Sea (Z1, Z2, Z3, Z4), Okhotsk Sea (Z5, Z6, Z7), Bering Sea (BR01, BR03, BR07, BR09, NB15, NB19, NB24, NB26), Chukchi Sea (C17, C19, C10A, S13, S15) and Arctic Ocean (B79-B85, D81, D83). Vertical samples were also collected at station B80, where the sampling depth reached 3500 m, something seldom done in previous reports.

Pretreatment and analysis of the 17 OCPs in the seawater samples were based on the combination of the small-volume solid-phase extraction and the solid-phase microextraction (SPE-SPME) technique described by Qiu and Cai [35]. 4 L water samples were filtered on board over a GF/F filter (0.45 μ m pore size, 142 mm diameter) using a filtering system (Pore, German) assisted by a peristaltic pump. The filtered sample was first drawn through a C18 SPE cartridge (ENVI 18, SUPELCO, USA), which was previously conditioned by washing successively with 5 mL methanol and

Table 1	Hydrographic	information a	at each station	from the	different sea zones	sampled
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	Station	Latitude (N)	Longitude	Depth (m)	Temperature (°C)	Salinity (%)
	Z1	35.001	129.62 (E)	-	-	-
	Z2	39.841	134.76 (E)	_	-	_
Japan Sea	Z3	43.254	138.19 (E)	_	-	_
	Z4	45.006	140.02 (E)	_	_	_
	Z5	46.383	144.82 (E)	_	_	_
	Z6	47.435	147.5 (E)	_	_	_
Okhotsk Sea	Z7	49.771	155.11 (E)	_	-	_
	Z8	51.182	161.34 (E)	-	-	_
	BR01	55.945	173.13 (E)	3800	10.88	32.89
	BR03	57.985	176.21 (E)	3778	9.20	32.88
	BR07	60.081	180 (W)	2571	7.95	32.39
D	BR09	60.462	179 (W)	420	7.11	31.75
Bering Sea	NB19	61.496	168.01 (W)	23	5.40	30.39
	NB15	62.202	171.99 (W)	41	7.35	31.21
	NB26	62.427	170.1 (W)	34	7.11	31.31
	NB24	62.751	171.63 (W)	44	6.92	31.34
	R00	66.5	169 (W)	43	3.38	32.42
	C10A	71.408	157.85 (W)	107	-1.31	29.99
	C19	71.447	159.98 (W)	42	-1.01	29.98
Chukeni Sea	C17	71.486	161.98 (W)	41	-0.86	30.65
	S13	72.938	158.32 (W)	1430	0.41	27.95
	S15	73.377	157.54 (W)	3043	3.83	25.83
	B79	78.983	147.62 (W)	3863	-1.40	28.84
	B80	80.008	147.49 (W)	3854	1.29	21.59
	B81	81.009	146.25 (W)	3843	-1.40	28.01
	D81	81.034	155.29 (W)	3847	-	-
Arctic Ocean	B82	81.979	147.27 (W)	3387	-1.41	28.15
	B83	82.997	147.31 (W)	2679	-1.41	26.86
	D83	83.011	150.96 (W)	3157	-	-
	B84	83.999	144.28 (W)	2296	-1.22	28.68
	B85	85.13	147.06 (W)	2079	-1.52	28.44

-, Data not available.



Figure 1 Schematic diagram of the sampling regions.

5 mL deionized water. The SPE samples were then stored in aluminum foil in desiccators at -20 °C before further processing. The following procedures were followed in the laboratory after the cruise. Each cartridge was first eluted with 10 mL n-haxane, and then the eluent was solvent converted to an aquatic matrix, which was further enriched through SPME using PDMS fiber. After that, the target compounds enriched in PDMS fiber were thermally desorbed in the GC injection pot.

2.3 Instruments and settings

A gas chromatograph (Agilent 6890, USA), coupled with an electron capture detector (ECD, 63 Ni) was employed for the instrumental analysis. An HP-5 capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness; J&W, Agilent, USA)

was selected to separate the target compounds. The oven temperature was programmed as follows. The initial temperature 150 °C was increased to 200 °C at a rate of 2 °C /min, and then increased to 260 °C at a rate of 3 °C /min. The temperature of the injector was set to 250 °C, and the split/splitless switch was set open at 3 min with a split ratio of 50. High purity nitrogen (99.999% purity) served as the carrier gas and the makeup gas, with constant flow speeds of 2 and 60 mL/min.

2.4 Quality assurance and quality control

External calibration scheme with 5 concentrations (2, 10, 50, 100 and 150 ng/L) was employed for the quantification analysis. Method repeatability was evaluated by analyzing in situ parallel samples as well as laboratory made parallel samples. Recoveries were obtained by spiking experiments. Blank samples, made using pure deionized water, were analyzed both on deck and in the laboratory to test for any disturbance possibly introduced during sample processing. No background signals were found to be strong enough to interrupt the integration of the target chromatographic peaks, indicating a sample processing procedure free of severe systematic disturbance. The method detection limit was consistent with a concentration which would give a signal/ noise ratio of 3. The QA/QC results are summarized in Table 2, which shows that the external calibration scheme gave a good linearity with a R^2 more than 0.99, that method performance is good in terms of parallelism (less than 20%) and MDL (from 0.003 ng/L to 0.034 ng/L), and that the

recovery rate was acceptable for most target compounds, with a recovery rate exceeding 60%.

3 Results and discussion

3.1 Compositional characteristic of the target compounds in the research region

The research region was divided into five sea zones on a geographic basis for further discussion, namely the Japan Sea, Okhotsk Sea, Bering Sea, Chukchi Sea and Arctic Ocean. The concentration of each individual target compound at each station is summarized in Table 3. The basic compositional pattern at each station was fairly comparable, featuring higher concentration percentage of HCH isomers, generally more than 50% with other individual targets having a percentage seldom exceeding 5%. The HCH-dominated compositional characteristic is a general compositional pattern of OCPs in seawater [14, 18, 32, 34, 36-40]. This is probably attributable to the considerably higher historic usage of HCHs compared to other target compounds [6]. It is noteworthy that a relatively higher percentage was also seen in heptachlor and aldrine in some sea zones during this study.

Concentration variation for individual compounds within sea zones can be illustrated by the RSD of the surface water concentrations at all stations within the same sea zone. Regional results of OCPs in this study are summarized in Table 4. It was found that higher RSD generally occurred in the northern sea zones (Bering Sea, Chukchi Sea, Arctic

OCPs	Linear range (ng mL ⁻¹)	R^2	Recovery rate	RSD $(n=4)$	MDL $(ng L^{-1})$
α-HCH	0.0040–60	0.9999	102.81%	3.24%	0.004
β-НСН	0.0040-60	0.9998	128.14%	17.85%	0.027
γ-ΗCΗ	0.0040-60	0.9999	99.17%	7.58%	0.002
δ-НСН	0.0040-60	0.9999	110.71%	11.38%	0.008
Heptachlor	0.0040-60	0.9999	90.38%	5.19%	0.003
Aldrine	0.0040-60	0.9999	65.24%	10.17%	0.005
Heptachlor-epoxide	0.0040-60	0.9994	76.10%	4.92%	0.003
α -Endosulfan	0.0040-60	0.9993	65.80%	4.69%	0.004
Dieldrin	0.0040-60	0.9993	64.30%	5.53%	0.003
Endrin	0.0040-60	0.9997	44.67%	13.30%	0.008
β-Endosulfan	0.0040-60	0.9995	65.71%	3.92%	0.005
p,p'-DDD	0.0040-60	0.9997	37.38%	14.86%	0.005
p,p'-DDE	0.0040-60	0.9996	41.72%	13.67%	0.008
Endrin aldehyde	0.0040-60	0.9994	78.64%	16.33%	0.034
p,p'-DDT	0.0040-60	0.9999	38.20%	20.43%	0.015
Methoxychlor	0.0040-60	0.9988	44.39%	15.23%	0.018
Endosulfan sulfate	0.0040-60	0.9999	31.34%	19.35%	0.015

Endo. Sulf.	0.1074	0.0875	0.0875	0.0875	0.0875	0.0875	0.0875	0.0875	0.0921	0.0875	0.1250	0.0875	0.0875	0.0904	NaN	NaN	NaN	0.0875	0.0999	NaN	0.0877	0.0861	0.0941	NaN	0.0838	NaN	0.097	NaN	0.0865	0.0861	NaN	0.0875	0.0875	NaN	NaN	NaN
Meth.	NaN	0.0625	0.0525	0.0375	0.0350	0.0350	0.0325	0.0375	0.0342	0.0400	0.0350	0.0400	0.0550	0.0718	0.0504	0.0503	0.043	0.0350	0.0786	0.0396	NaN	0.0345	0.0525	0.0387	0.0414	0.0382	0.042	0.0353	0.0333	NaN	0.0399	0.0385	0.0343	NaN	0.0406	0.0478
p,p′ -DDT	0.0644	0.0525	0.0525	0.0525	0.0525	0.0500	0.0525	0.0525	0.0553	0.0500	0.0600	0.0500	0.0500	0.0656	0.0544	0.0518	0.0517	0.0525	0.0554	0.0471	NaN	0.0484	0.0535	0.0531	NaN	0.0519	NaN	0.0493	0.0500	0.0477	NaN	0.0501	0.0490	NaN	0.0478	0.0487
Endr. Alde.	NaN	NaN	NaN	NaN	NaN	0.045	NaN	NaN	NaN	0.475	NaN	0.53	NaN	NaN	NaN	0.3177	0.8346	0.6966	NaN	0.4824	NaN	0.5953	NaN	NaN	NaN	NaN	0.2934	0.4904	1.7568	NaN						
p,p' -DDE	0.0460	0.0375	0.0350	0.0350	0.0350	0.0375	0.0375	0.0375	0.0395	0.0375	0.0400	0.0375	0.0375	0.0389	0.037	0.0369	0.0408	0.0400	0.0530	0.0368	0.035	0.0348	0.0412	0.0376	0.0344	0.04	0.0382	0.0352	0.0360	0.0401	0.0348	0.0401	0.0366	0.0511	0.0347	0.037
-DDD	0.0460	0.0228	0.0400	0.0300	0.0250	0.0250	0.0300	0.0450	0.0368	0.0375	0.0400	0.0243	0.0350	0.0229	0.0407	0.0354	0.0346	0.0215	0.0264	0.021	0.0215	0.0278	0.0265	0.0276	0.0255	0.0247	0.0322	0.0216	0.0224	0.0221	0.0443	0.04	0.0314	0.0214	0.021	0.0274
β-End.	0.0255	0.0195	0.0185	0.0190	0.0218	0.0275	0.0228	0.0203	0.0226	0.0208	0.0210	0.0238	0.0275	0.0294	0.0217	0.0203	0.0226	0.0275	0.0299	0.019	0.0229	0.0242	0.0282	0.0291	0.0194	0.0258	NaN	0.0265	0.0194	0.0197	0.0184	0.0197	0.0209	0.0197	0.0257	0.03
Endr.	0.0460	0.0250	0.0300	0.0300	0.0275	0.0400	0.0300	0.0475	0.0395	0.0275	0.0275	0.0350	0.0400	0.0265	0.0259	0.0409	0.0269	0.0275	0.0343	0.0243	0.027	0.0249	0.0402	0.0316	0.0245	0.0282	0.0278	0.0267	0.0262	0.026	0.0252	0.027	0.0286	0.0256	0.0303	0.0273
Diel.	0.0552	0.0155	0.0148	0.015	0.0145	0.0182	0.045	NaN	0.0163	0.0148	NaN	NaN	0.0195	0.0183	0.0166	0.027	0.0167	0.03	0.0156	0.0157	0.0155	0.0148	0.019	0.0159	0.0193	0.0158	0.0172	0.0144	0.0094	0.0159	0.0184	0.0218	0.0151	0.0163	0.0147	0.015
α-End.	0.0307	0.0325	0.0300	0.0275	0.0375	0.0275	0.0275	0.0500	0.0868	0.0200	0.0300	0.0210	0.0213	0.0248	0.0426	0.0324	0.0418	0.0220	0.0202	0.0201	0.0193	0.0189	0.02	0.0232	0.0188	0.0212	0.0274	0.0294	0.0305	0.022	0.0296	0.0205	0.0268	0.0347	0.0991	0.0237
нері. Ерох.	0.0184	0.0183	0.0168	0.0170	0.0160	0.0168	0.0148	0.0148	0.0166	0.0170	0.0153	0.0155	0.0235	0.0276	0.0174	0.0159	0.0189	0.0153	0.0456	0.0147	0.0143	0.0217	0.0153	0.0266	0.0162	0.0154	0.0318	0.0285	0.0155	0.015	0.0147	0.0173	0.0147	0.0239	0.0285	0.0315
Aldr.	0.0399	0.0475	0.0198	0.0800	0.0238	0.0220	0.0225	0.0208	0.0842	0.0375	0.0550	0.0450	0.5900	0.3522	0.0215	0.0237	0.0215	0.6975	0.0283	0.0302	0.0219	0.2949	NaN	0.7314	0.024	0.5034	0.0224	0.5960	0.0233	0.0328	0.0228	0.0324	0.0325	0.1778	0.3308	0.0376
Hept.	0.7699	0.4200	0.4000	0.3225	1.0625	0.0825	0.0800	0.9725	0.1921	0.0575	0.0600	NaN	0.0775	0.1626	0.3922	0.1527	0.3922	0.3875	0.2367	0.147	0.1862	NaN	NaN	NaN	0.0941	0.0542	0.1206	0.0414	0.1075	0.1079	0.1079	0.1124	0.0475	NaN	0.0423	0.2023
8-HCH	0.1503	0.1250	0.1050	0.1125	0.0550	0.0600	0.0950	0.1275	0.1263	0.0550	0.1125	0.0525	0.0525	NaN	0.1	0.115	0.2	0.0525	0.0825	0.1398	0.1375	NaN	NaN	NaN	0.1165	0.0529	0.1	0.0608	0.1279	0.0769	0.1142	0.0963	0.0515	0.0505	NaN	0.0538
γ-HCH	0.2086	0.2575	0.1950	0.2350	0.3550	0.1250	0.2550	0.3025	0.1368	0.0725	0.4625	0.7175	0.2100	0.3396	0.3261	0.1658	0.2832	0.1525	NaN	0.2367	0.2135	0.0512	0.0845	0.0868	0.2935	0.1387	0.3599	0.3167	0.4625	NaN	0.7376	NaN	0.3042	0.1041	0.0893	0.3693
р-нсн	2.6687	NaN	1.6625	1.6075	1.9400	NaN	1.7975	NaN	0.3316	0.7875	0.8075	0.1000	NaN	0.1557	0.1203	NaN	0.1912	0.0775	NaN	NaN	NaN	0.1597	0.3152	0.2333	0.1308	0.5788	NaN	0.6326	0.1175	0.3559	0.1803	0.1967	0.2868	2.3241	3.2328	0.7772
α-HCH	0.1871	0.0475	0.2675	0.0475	0.3250	0.0600	0.2225	0.2500	0.3211	0.0650	0.1550	0.1275	0.0725	0.1576	0.2071	0.1315	0.2124	0.1375	0.2671	0.1421	0.181	0.0861	0.0767	0.0587	0.2053	0.1315	0.2098	0.0958	0.1942	0.2296	0.2272	0.2409	0.0583	0.3926	0.7355	0.6212
ampling :vel (m)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	10	20	30	1	1	10	30	1	10	25	30	37	40	1	1	10	20	39	1	1	10	20
Station S. Ie	Z1	Z2	Z3	Z4	Z5	Z6	ΓZ	Z8	BR01	BR03	BR07	BR09	NB19	NB15	NB15	NB15	NB15	NB26	NB24	NB24	NB24	ROO	ROO	ROO	ROO	ROO	ROO	C10A	C19	C19	C19	C19	C17	S13	S13	S13

Table 3Concentrations of 17 OCPs in Arctic water

ontinued)	Endo. Sulf.	NaN	0.0841	0.1252	0.0886	NaN	NaN	0.0898	0.0853	NaN	NaN	0.1818	0.0875	0.0867	0.0918	0.0875	NaN	0.0848	NaN	0.0894	0.0864	0.0886	0.0945	NaN	NaN	0.0939	0.1225	0.1198	0.1118	0.0859	e., Endrin						
(C	Meth.	0.0398	NaN	0.0337	0.0333	0.0489	0.0428	0.0387	NaN	0.0441	0.0337	0.0352	0.0439	0.0452	0.0601	0.0684	0.0408	NaN	0.0358	0.0342	0.0533	0.0495	0.044	0.0473	0.0424	0.0569	0.0333	0.0337	0.0343	0.0523	0.0377	NaN	0.0351	0.0342	0.0338	0.0341	Endr. Ald
	p,p' -DDT	0.0474	0.0504	0.0476	0.0475	0.0474	0.0496	0.0486	NaN	0.0492	0.053	0.0574	NaN	NaN	NaN	0.0501	NaN	NaN	0.0527	NaN	NaN	0.0472	NaN	NaN	NaN	0.0473	0.0550	0.0585	0.0483	0.0476	0.0623	0.0471	0.0501	NaN	NaN	0.0541	Indosulfan;
	Endr. Alde.	NaN	0.1991	0.2093	0.2466	0.5446	NaN	0.0175	NaN	3-End., β-E																											
	p,p' -DDE	0.0348	0.0390	0.0352	0.0367	0.0361	0.0381	0.0349	0.0378	0.0348	0.0357	0.0375	0.0351	0.0358	0.036	0.0363	0.0375	NaN	0.0429	0.0427	0.036	0.0349	0.0348	0.04	0.0421	0.0412	0.0367	0.0361	0.0356	0.0346	0.0393	0.0346	0.0391	0.0356	0.0347	0.0349	, Endrin; f
	p,p' -DDD	0.0235	0.0293	0.0263	0.0222	0.0283	0.0254	0.0320	0.024	0.0223	0.0266	0.0224	0.0218	0.0228	0.0266	NaN	0.0268	0.0506	0.0283	0.0218	0.0262	0.0239	0.023	0.0218	0.0313	0.0237	0.0380	0.0412	0.0434	0.0222	0.0570	0.0211	0.0216	0.0211	0.0224	0.0263	drin; Endr.
	β-End.	0.0234	0.0233	0.0224	0.0228	0.0362	0.0182	0.0273	0.0226	0.0202	0.0204	0.0190	0.0188	0.0197	0.0189	0.0277	0.0185	0.0421	0.0189	0.0187	0.0182	0.0191	NaN	0.0195	NaN	0.02	0.0202	0.0240	NaN	0.0398	0.0194	0.0180	0.0353	0.0201	0.0216	0.0184	Diel., Diele
	Endr.	0.0266	0.0284	0.026	0.0258	0.0327	0.027	0.0270	0.0369	0.0248	0.0366	0.0280	0.0248	0.0247	0.0253	0.0244	0.0247	0.0519	0.0255	0.0252	0.0259	0.0256	0.0256	0.027	0.0298	0.0261	0.0270	0.0267	0.0402	0.0348	0.0310	0.0246	0.0297	0.0251	0.0251	0.0284	dosulfan;]
	Diel.	0.0224	0.0165	0.0143	0.0146	0.0156	0.0155	0.0157	0.0286	0.0145	0.0143	0.0162	0.0175	0.0193	0.0257	0.0294	0.0247	0.0545	0.0284	0.0271	0.0266	0.0215	0.018	0.0182	0.0185	0.0166	0.0189	0.0294	0.0198	0.0152	0.0165	0.0163	0.016	0.02	0.0242	0.0147	End., α-En
	α-End.	0.0264	0.0980	0.0315	0.0196	0.0186	0.0213	0.0192	0.0197	0.0241	0.0302	0.0314	0.03	0.0363	0.0247	0.0191	0.0218	0.0552	NaN	0.0214	0.0257	0.0426	0.2535	0.0215	0.0595	0.021	0.0293	0.0494	0.0328	0.0255	0.0428	0.0201	0.0528	0.0189	0.0227	0.026	oxide; α -]
	Hept. Epox.	0.0208	0.0241	0.0246	0.025	0.0339	0.0327	0.0320	0.022	0.019	0.0182	0.0404	0.0143	0.0161	0.0147	0.0145	0.0148	0.0308	0.0218	0.0155	0.0155	0.0144	0.0295	0.0147	0.0301	0.015	0.0399	0.0180	0.0381	0.0406	0.0209	0.0151	0.0371	0.0181	0.0203	0.0313	ptachlor ep
	Aldr.	0.271	0.7340	0.467	0.3857	NaN	0.0409	0.5004	0.0268	0.034	0.0278	NaN	0.0264	0.0216	0.029	0.0256	0.024	0.0488	0.0271	0.0278	0.0244	0.023	0.0483	0.0215	0.0291	0.0233	0.0560	0.0326	NaN	0.7537	0.0488	0.0199	0.1014	0.0323	0.029	0.0283	Epox., He
	Hept.	0.1217	NaN	NaN	0.2138	0.0665	0.2897	0.0422	0.1931	0.0572	0.4348	0.2990	0.2552	0.3277	0.2575	0.292	0.2552	NaN	0.1447	0.3565	0.5038	0.2184	0.2253	0.3438	0.341	0.5951	0.0418	0.0436	0.3611	0.4210	0.0520	0.1332	0.4233	0.1654	0.3174	0.2736	ine; Hept.
	8-HCH	0.0622	0.0550	0.0657	0.0722	0.0531	0.0573	NaN	0.0659	0.0643	0.1422	NaN	0.1398	0.1631	0.1352	0.1025	0.1282	0.1799	0.0909	0.1258	0.0862	0.0885	0.0792	0.054	0.0914	0.0769	NaN	0.8159	0.0979	NaN	NaN	0.1049	0.1352	0.0694	0.1795	NaN	Aldr., Aldr
	ү-НСН	0.2072	0.0890	0.102	0.1798	0.224	0.1925	0.2135	0.2893	0.3335	0.1862	0.2956	0.2956	0.3314	0.1904	0.1588	0.1672	0.2232	0.1188	0.0999	0.1041	0.0883	0.0683	NaN	0.0589	0.0546	0.3651	0.2346	0.2893	0.2304	0.2009	0.2388	0.2640	0.3651	0.4345	0.3103	eptachlor; /
	β-НСН	3.4228	NaN	0.614	0.4488	0.3022	0.5252	0.5830	0.329	NaN	NaN	0.4860	0.0702	0.0718	0.1122	0.1122	0.1906	0.2051	0.088	0.1328	0.0956	0.1004	0.0812	NaN	0.1527	0.074	0.5810	3.9784	0.4054	0.5830	NaN	0.0746	2.5884	NaN	NaN	0.2629	: Hept., He
	α-HCH	0.2904	0.1184	0.3683	0.4558	0.485	0.2199	0.5531	0.8961	0.9885	0.4656	0.6431	0.699	0.9216	0.6236	0.665	0.6845	0.3934	0.1275	0.1104	0.1153	0.1275	0.1305	0.0508	0.0623	0.0501	0.7550	0.1153	0.5872	0.3950	0.1177	0.6164	0.1688	0.738	NaN	0.7064	ection limit
	Sampling level (m)	30	1	10	20	40	60	1	20	40	60	1	10	30	75	125	150	200	300	400	009	800	1500	2500	3000	3500	1	1	1	1	1	1	1	10	20	09	r method der
	Station	S13	S15	S15	S15	S15	S15	B79	B79	B79	B79	B80	B81	D81	B82	B83	D83	B84	B85	B77	B77	B77	NaN, unde														

Samp	ing	α-HCH	в-нсн	γ-HCH	8-HCH	Hept.	Aldr.	Hept.	α-End.	Diel.	Endr.	β-End.	p,p'	p,p'	Endr.	p,p'	Meth.	Endo.
Japan Sea	Min	0.0475	1.6075	0.1950	0.1050	0.3225	0.0198	0.0168	0.0275	0.0148	0.0250	0.0185	0.0228	0.0350	- Aluc.	0.0525	0.0375	0.0875
	Мах	0.2675	2.6687	0.2575	0.1503	0.7699	0.0800	0.0184	0.0325	0.0552	0.0460	0.0255	0.0460	0.0460	I	0.0644	0.0625	0.1074
	Mean	0.1374	1.9796	0.2240	0.1232	0.4781	0.0468	0.0176	0.0302	0.0251	0.0328	0.0206	0.0347	0.0384	I	0.0555	0.0508	0.0925
	RSD	79.24%	30.18%	12.42%	16.12%	41.63%	53.54%	4.81%	6.86%	79.81%	27.93%	15.79%	29.82%	13.61%	I	10.74%	24.75%	10.74%
	Rate*	4.62%	57.68%	9.98%	5.19%	18.80%	2.05%	0.76%	1.31%	0.87%	1.27%	0.85%	1.31%	1.60%	I	2.30%	2.67%	3.84%
Okhotsk Sea	Min	0.0600	1.7975	0.1250	0.0550	0.0800	0.0208	0.0148	0.0275	0.0145	0.0275	0.0203	0.0250	0.0350	0.0450	0.0500	0.0325	0.0875
3	Мах	0.3250	1.9400	0.3550	0.1275	1.0625	0.0238	0.0168	0.0500	0.0450	0.0475	0.0275	0.0450	0.0375	0.0450	0.0525	0.0375	0.0875
	Mean	0.2144	1.8688	0.2594	0.0844	0.5494	0.0223	0.0156	0.0356	0.0259	0.0363	0.0231	0.0313	0.0369	0.0450	0.0519	0.0350	0.0875
	RSD	52.09%	5.39%	37.96%	40.07%	98.62%	5.58%	6.34%	29.98%	64.26%	25.50%	13.58%	30.29%	3.39%	I	2.41%	5.83%	0.00%
	Rate*	8.93%	55.09%	12.17%	4.69%	21.64%	1.32%	0.96%	1.98%	1.44%	2.32%	1.48%	1.78%	2.23%	5.92%	3.06%	2.11%	5.24%
Bering Sea	Min	0.0650	0.0775	0.0725	0.0525	0.0575	0.0283	0.0153	0.0200	0.0148	0.0265	0.0208	0.0215	0.0375	0.4750	0.0500	0.0342	0.0875
	Мах	0.3211	0.8075	0.7175	0.1263	0.3875	0.6975	0.0456	0.0868	0.0300	0.0400	0.0299	0.0400	0.0530	0.5300	0.0656	0.0786	0.1250
	Mean	0.1629	0.3766	0.2988	0.0763	0.1677	0.2362	0.0220	0.0308	0.0191	0.0322	0.0253	0.0305	0.0405	0.5025	0.0548	0.0487	0.0947
	RSD	54.72%	89.75%	76.14%	41.48%	71.21%	116.12%	47.82%	74.45%	29.47%	17.61%	14.65%	24.59%	12.76%	7.74%	10.20%	36.44%	13.70%
	Rate*	10.71%	20.25%	18.53%	4.80%	10.25%	13.66%	1.51%	1.91%	1.17%	2.08%	1.63%	1.91%	2.60%	23.56%	3.46%	3.26%	5.95%
Chukchi Sea	Min	0.0583	0.1175	0.0512	0.0505	0.0414	0.0233	0.0147	0.0189	0.0094	0.0249	0.0194	0.0214	0.0348	0.1991	0.0484	0.0333	0.0861
3	Мах	0.3926	2.3241	0.4625	0.1279	0.1075	0.7340	0.0285	0.0980	0.0165	0.0286	0.0265	0.0314	0.0511	0.5953	0.0504	0.0353	0.0875
	Mean	0.1576	0.7041	0.2213	0.0691	0.0655	0.3098	0.0214	0.0397	0.0144	0.0267	0.0223	0.0257	0.0388	0.3792	0.0494	0.0344	0.0867
	RSD	78.70%	131.78%	74.07%	47.87%	55.80%	95.60%	25.05%	73.09%	18.00%	5.60%	12.57%	17.09%	16.02%	42.25%	1.61%	2.39%	0.83%
	Rate*	6.95%	31.07%	9.76%	3.05%	2.89%	13.67%	0.94%	1.75%	0.64%	1.18%	%66.0	1.13%	1.71%	16.73%	2.18%	1.52%	3.83%
Arctic Ocean	Min	0.1153	0.0746	0.2009	0.0979	0.0418	0.0199	0.0151	0.0192	0.0152	0.0246	0.0180	0.0211	0.0346	0.0175	0.0471	0.0333	0.0864
	Max	0.7550	3.9784	0.3651	0.8159	0.4232	0.7537	0.0406	0.0528	0.0294	0.0402	0.0398	0.0570	0.0393	0.0175	0.0623	0.0523	0.1225
	Mean	0.4391	1.1600	0.2591	0.2885	0.2019	0.2161	0.0313	0.0337	0.0182	0.0299	0.0254	0.0332	0.0365	0.0175	0.0528	0.0375	0.0972
	RSD	56.42%	118.32%	19.68%	122.02%	84.91%	134.74%	33.29%	36.07%	24.47%	16.31%	32.28%	38.05%	4.98%	I	10.67%	16.66%	14.99%
	Rate*	14.74%	38.95%	8.70%	9.69%	6.78%	7.26%	1.05%	1.13%	0.61%	1.00%	0.85%	1.12%	1.23%	0.59%	1.77%	1.26%	3.26%
Rate*, cc β-Endosulf.	ncentrat m; Endr.	ion percent Alde., End	age of each rin aldehyde	individual cl 2; Meth.: Me	hemical in e	each sea zon Endo. Sulf.	e; Hept., He	ptachlor; A 1 sulfate.	ldr., Aldrin	le; Hept. Ef	ox., Hepta	chlor epoxi	de; α-End.	α-Endosu	lfan; Diel.,	Dieldrin;]	Endr., Endr	in; β-En

Ocean) for all the target compounds, except dieldrin and endrin which had a higher concentration variation in the Japan Sea. A higher RSD may be due to a sampling area covering more diversified marine terrains where OCPs can exist and circulate in totally different ways. The biological pump has been highlighted for its influence on the removal of particle-bound POPs from the mixed layer to the deep water [26]. The coastal sea usually has a high primary productivity, which could facilitate the operation of the biological pump, while the biological pump is generally weak offshore due to the oligotrophic properties prevailing there. As shown in Figure 1, terrains within the Bering Sea consisted of coastal shallow water (NB15, NB19, NB24, and NB26), classic continental shelf water (BR07, BR09) as well as a deep water zone (BR01, BR03), while stations in the Japan Sea and Okhotsk Sea featured mainly coastal water characteristics. As for stations within the Chukchi Sea and Arctic Ocean, although no apparent variation of marine terrain was seen there, complex hydrodynamic conditions featuring water mass with divergent sources could probable spread the concentration range of OCPs there. Fairly uniform concentration distribution within all the five sea zones were observed for endrin, β -endosulfan, p,p'-DDE, p,p'-DDT, methoxychlor and endosulfan sulfate with concentration RSD less than 30%.

3.2 Temporal trend of OCPs in the oceans studied

Historic data for OCPs in Arctic water were fairly limited, associated mainly with HCHs and DDTs, and with only a few focusing on endosulfan and heptachlor. The results reported previously as well as our current results are compiled in Table 5 for temporal trend analysis.

As shown in Table 5, a typical decreasing trend was observed for α -HCH and γ -HCH in all the oceans studied, corresponding to the global ban on HCHs. However, the temporal trend of β -HCH was different in that it showed two patterns, one featuring concentrations which continually increased with time in the Japan Sea and Okhotsk Sea, and the other featuring concentrations increasing at first and decreasing later in both the Bering Sea and Chukchi Sea. Endosulfan and heptachlor exhibited a similar temporal trend as β -HCH. As for the DDT products (DDT and its metabolites), the first-increasing-then-decreasing trend was also found in the Chukchi Sea alongside the typical decreasing trend in the Okhotsk Sea, but no apparent variation was observed in the Bering Sea. The reason for this temporal trend can be geographical differences, so the locality of the temporal trends will be further discussed in the following sections.

3.2.1 Japan Sea and Okhotsk Sea

In this work, it was found that stations within the Japan Sea had concentrations of 0.0475–0.2675 ng/L for α -HCH, 1.6075–2.6687 ng/L for β -HCH, 0.1950–0.2575 ng/L for

 γ -HCH, and 0.1050–0.1503 ng/L for δ -HCH. When these were compared to the reported values of 1988 and 1992 [36], an apparent declining trend was seen for α -HCH (0.81–1.01 ng/L in 1988 and 0.84–1.64 ng/L in 1992) and γ -HCH (0.8-0.99 ng/L in 1988 and 0.34-0.83 ng/L in 1992), corresponding to the global ban on HCH usage. However, a continually increasing trend was observed for β -HCH, from 0.08-0.14 ng/L in 1988 to 0.18-0.43 ng/L in 1992 and to 1.6075-2.6687 ng/L in 2008 in this work. The temporal trend of β -HCH could probably be explained by its lower Henry's Law constant, which makes it partition in water to a greater extent than α -HCH or γ -HCH during the process of atmosphere long range transport, and hence the β-HCH carried by ocean currents showed a time lag in making up the decreasing amount of β-HCH, originating from air-water exchange at higher latitudinal sea zones, such as in the Sea of Japan. A similar temporal trend was seen in p.p'-DDE and p,p'-DDT, but this could not be explained by their thermodynamic parameters, as they do not have a Henry's Law Constant as low as α -HCH and γ -HCH. For this reason a fresh input pulse adjacent to the Japan Sea was tentatively regarded as the reason for the temporal trend of p,p'-DDE and p,p'-DDT.

In the Okhotsk Sea, α -HCH showed a concentration range of 0.0600–0.3250 ng/L, β -HCH 1.7975–1.9400 ng/L, γ -HCH 0.1250–0.3550 ng/L, p,p'-DDT 0.0500–0.0525 ng/L and p,p'-DDE 0.0350–0.0375 ng/L. Compared to values reported in 1988 [36], a similar trend to that in the Japan Sea was found, namely a decreasing trend for α -HCH and γ -HCH, with others displaying an increasing temporal trend.

3.2.2 Bering Sea and Chukchi Sea

Within the Bering Sea, eight stations were considered, consisting of BR01 and BR03 (featuring high depth of water) and other stations located on the continental shelf, as shown in Figure 1. In the Bering Sea, the surface water concentrations were found to be 0.065–0.2671 ng/L for α -HCH, 0.0775–0.8075 ng/L for β-HCH, and 0.0725–0.7175 ng/L for y-HCH. Based on the associated concentration values reported earlier [14, 18, 32, 34, 37-40], the concentration levels in 1988 and in 1990 were fairly comparable for α -HCH (as shown in Table 5), while an apparent decreasing trend was seen in γ -HCH concentration from 1988 to 1990. In 1999, the concentrations for both target chemicals dropped by about an order of magnitude from the concentration levels in 1990. Our results for γ -HCH showed a level comparable to the reported values in 1999, but a slightly decreasing trend was seen for α -HCH. As for β -HCH, although no historic data were available in 1990, an abrupt concentration drop from 1988 to 1999 was seen. Compared to the results reported in 1999, β -HCH showed a slightly higher concentration in this work. The similar temporal trend of these three HCH isomers indicated a general trend in the decreasing usage of them globally, as they were

Japan Se	ea o	-HCH	β-НСН	γ-H	СН	p,p'-DDE	p,p'-D	DT	Ref.
1988	0.8	81-1.01	0.08-0.14	0.8-	0.99	4	3		[36]
1992	0.8	84–1.64	0.18-0.43	0.34-	-0.83	2-14	2-2	1	[36]
2008	0.047	75-0.2675	1.6075-2.6687	0.1950-	-0.2575	35–46	53-6	4	this work
Okhotsk S	Sea o	-HCH	β-ΗCΗ	γ-H	СН	p,p'-DDE	p,p'-D	DT	Ref.
1988	1.0	08-1.22	0.19-0.28	1.03-	-1.07	4–5	2		[36]
2008	0.060	00-0.3250	1.7975-1.9400	0.1250-	-0.3550	35–37.5	50-52	2.5	this work
Bering Sea	α-HCH	β-ΗCΗ	ү-НСН	ΣΗCΗ	p,p'-DDD	p,p'-DDE	p,p'-DDT	ΣDDT	Ref.
1979	_	_	-	3.2-4.4	-	-	-	100-400	[37]
1988	1.764–2.44	0.39	0.57-0.937	3.091	-	5	3	8	[34, 38, 39]
1990	1.5	—	0.19	-	-	-	-	-	[32]
1993	-	_	0.371	-	-	-	-	-	[14, 40]
1999	0.165-0.683	0.028-0.058	0.063-0.196	0.256-0.937	-	13-42	40-91	-	[18]
2008	0.065-0.2671	0.0775-0.8075	0.0725-0.7175	0.215-1.7921	21.5-40	37.5–53	50-65.6	109–158.6	this work
Chukchi Sea	α-HCH	β-ΗCΗ	ү-НСН	heptachlor	α -endosulfar	n β-endosulfan	p,p'-DDE	p,p'-DDT	Ref.
1988	2.152-2.46	0.55	0.62-0.931	-	-	-	7	5	[39]
1990	1.4	_	0.18	-	-	-	-	-	[32]
1993	2.06-2.16	_	0.43-0.45	6.3	7.2	5.3	-	-	[14, 40]
1999	0.157-0.662	0.044-0.089	0.03-0.239	25-146	38-87	57	99	48-123	[18]
2008	0.0583-0.3926	0.1175-2.3241	0.089-0.4625	41.4–107.5	26.8-98	19.4–26.5	35.2–51.1	49–50.4	this work
Arctic Oce	ean o	-HCH	γ-HCH	hepta	chlor	α -endosulfan	β-endos	ulfan	Ref.
1994	2.0	07–2.63	0.33-0.70	9.6-	19.6	0.4–3.6	0.6–4	.1	[40]
2008	0.11	53-0.7550	0.2009-0.3651	42.2-	423.3	19.2-52.8	18-39	0.8	this work

Table 5 Historic data for OCPs in five sea zones (unit: ng/L for HCH isomers, and pg/L for others)

-, Data not available.

banned by most countries in the world. The concentrations of DDT products display an apparent decline from 1979 when they had sum concentrations of 0.1–0.4 ng/L to 1999 with sum concentrations of 0.053–0.133 ng/L, very close to our results (0.109–0.1586 ng/L). The temporal trend of DDT products implied that they had more or less reached equilibrium in the Bering Sea.

In this work, five stations were located on the west side of the Chukchi Sea, namely C17, C19, C10A, S13, and S15. Compared with the reported data [14, 18, 32, 39, 40], the surface concentration of α -HCH in the Chukchi Sea had dropped slightly from a value of 2.152–2.4 ng/L in 1988 to 1.4 ng/L in 1990, and then the concentration returned to the level of 1988 in 1993 (2.06–2.16 ng/L), before it dropped sharply to a level of 0.157–0.662 ng/L in 1999. Our results for α -HCH (0.0583–0.3926 ng/L) were slightly lower than the most current reports in 1999. The γ -HCH almost mimicked the α -HCH in the long-term trend from 1988 to 1990 to 1993 to 1999, suggesting a very similar source of HCH isomers in the Chukchi Sea. The γ -HCH concentration level in 2008, based on our results, was fairly comparable to that in 1999, indicating that a seemingly equilibrium state of γ -HCH was achieved recently. Historic data of β -HCH were not available in 1990 and 1993, but compared to the concentration level in 1988 (0.55 ng/L), it declined by about an order of magnitude in 1999 (0.044-0.089 ng/L). Our results for β -HCH (0.1175–2.3241ng/L) were much higher than that in 1999, and even higher than that in 1988. This abnormal case may be attributed to the extremely low sensitivity of detection, which could lead to a high error in the integration of the peak area. Apart from the HCH isomers, other OCPs in the Chukchi Sea were also reported previously (as shown in Table 5), including heptachlor, α -endosulfan, β -endosulfan, and DDT products, although the data were very sparse. An apparent increasing trend before 1999 followed by a slight decrease in 2008 was seen for each chemical. This could be explained either by the current application of some chemicals, such as endosulfan [41], or the time lag of their arrival from their emission region to the Arctic zone due to the divergence of thermodynamic parameters.

3.2.3 Western Arctic Ocean

The northern-most sea zone in this work is the western Arc-

tic Ocean, including a transect from station B79 to B85 and another two stations (D81 and D83) adjacent to this transect. The historic data of OCPs in this area are only available for 1994 [40]. The cruise track of AOS-94 covered areas from the Chukchi Sea to the western Arctic Ocean and through the North Pole to the eastern Arctic Ocean. Referring to the data associated with that cruise, we found that the section of the western Arctic Ocean had surface water concentrations of 2.07–2.63 ng/L for α -HCH, 0.33–0.70 ng/L for γ -HCH, 9.6–19.6 pg/L for heptachlor, 0.4–3.6 pg/L for α -endosulfan and 0.6–4.1 pg/L for β -endosulfan. As shown in Table 5, our results showed a much lower level for α -HCH, while a very comparable level was seen in γ -HCH. The trend in α -HCH corresponded to the application history of technical HCH, and the trend of γ -HCH was probably attributed to the usage of lindane (containing more than 90% y-HCH) as another source of y-HCH to the Arctic Ocean, which could impose on the background signal of γ -HCH originating from technical HCH, and hence magnify the total concentration level. Generally much higher concentration levels were seen for heptachlor, α -endosulfan and β -endosulfan in our study. The reasons for this could be diverse, such as a fresh input through either long range atmospheric transport or ocean current with a time lag. However, it is noteworthy that the re-volatilization from seawater to the air above was recently highlighted to explain the atmospheric pulse of some OCPs in the Arctic Ocean [14, 42, 43], so it could be expected that a pulse of those OCPs in the seawater would follow due to a local low temperature freezing effect, possibly caused by seasonal variation or climate change. Therefore, the trend in OCPs in the Arctic Ocean could be even more perplexing in the future.

3.3 Comparison of surface water concentration for individual compounds in different sea zones

The mean concentration of each individual target compound in each sea zone was calculated to represent the concentration level of the target compounds for each sea zone. As seen from Table 4, two general cases were observed with one featuring a concentration magnitude higher than 0.1 ng/L and the other featuring a concentration level higher than 0.01 ng/L but less than 0.1 ng/L. The target compounds belonging to the first case consisted of α -HCH, β -HCH, γ -HCH, δ -HCH, aldrin, heptachlor and endrin aldehyde, with the others belonging to the second case.

Three patterns of trend among different sea zones were roughly seen: the first pattern showed a trend of general increasing surface concentration northward, the second one exhibited a trend in the opposite direction, namely surface concentration generally decreasing northward, and the third one had no apparent variation among different sea zones. The northward increasing pattern was seen in α -HCH, γ -HCH, aldrin, heptachlor epoxide, and β -endosulfan, and the northward decreasing pattern was seen in β-HCH, heptachlor, dieldrin and p,p'-DDD, while the rest of the target compounds have surface concentrations featuring no apparent variation. The target compounds with no apparent geographic divergence in concentration level had probably achieved more or less equilibrium globally. These compounds generally have very low concentrations, so an even more sensitive enrichment technique is needed before tackling their distribution patterns with more certainty. The northward increasing distribution mode is explainable based on the concept of global distillation, which drives semi volatile organic compounds to enrich gradually northward. Falling into this pattern, α -HCH and γ -HCH, however, have some subtle divergence, which will be further discussed in the next section. As for the abnormal pattern, namely concentration decreasing northward, the reasons could be multiple. β-HCH, which has a very much lower sensitivity to ECD, could be disrupted to a great extent by disturbance with similar chromatographic properties but much higher sensitivity. Therefore, the distorted B-HCH data could possibly be attributed to that abnormal distribution pattern. p,p'-DDD, one product of DDT degradation, could possibly be degraded from DDT at a rate determined by temperature conditions. Considering the almost uniform distribution of DDT, the temperature gradient within the oceans studied could in some way have caused DDD to become distributed in this way. With respect to heptachlor and dieldrin, a local source adjacent to the low latitude oceans is most likely to be a factor controlling their unique distribution patterns.

3.4 Latitudinal trend of α-HCH and γ-HCH

Global distillation has been applied to explain the existence of POPs in pristine environments, even far away from their source region. Global distillation as well as the process of cold condensation driven by thermodynamic effects can lead to a unique profile in the latitudinal trend of POPs. As for α -HCH and γ -HCH in the current study, two different profiles of latitudinal trend can be seen. The surface water concentration of α -HCH showed a general increasing trend with latitude (as shown in Figure 2), and such an increasing trend was exclusively apparent in the Arctic Ocean, with the other sea zones exhibiting a more or less uniform distribution pattern. As for the γ -HCH (as shown in Figure 3), the general trend is totally different in that the increasing trend was exclusively apparent in sea zones to the south of 60°N and, in the area from 60°N northward, the general trend reversed from an increasing pattern to a decreasing pattern.

A similar latitudinal trend was reported for α -HCH and β -HCH [17], and the general latitudinal trend between β -HCH and γ -HCH is almost the same except that the division in the case of β -HCH is at about 66°N rather than 60°N. In that paper, it was highlighted that a comprehensive consideration of all possible factors affecting the long range



Figure 2 Latitudinal trend of α-HCH (Miller Projection).



Figure 3 Latitudinal trend of γ-HCH (Miller Projection).

transportation of POPs was necessary for fully understanding the geochemical property of POPs, and the interpolation of the distribution pattern of one chemical to another seemingly similar could be problematical. α -HCH is more volatile and less water soluble than β -HCH and γ -HCH, and hence less likely to deposit or be scavenged along its transport route from the emission region to the Arctic zone, so the relatively high concentration level in the Arctic Ocean is understandably attributed to the air-water exchange of α -HCH through the cold condensation effect. Different from this, the less volatile and more soluble properties of both β -HCH and γ -HCH would make them more susceptible to deposition or being scavenged during long range transport. The northward transportation is more or less a fractionation effect resulting in the target compounds being gradually partitioned in the water phase with latitude. LRT worked throughout the transport route from the emission region to the Arctic for α -HCH, while the special thermodynamic properties of γ -HCH, as mentioned above, probably

disabled the LRT before entering the Arctic Ocean once the atmospheric γ -HCH was depleted through dry and/or wet deposition. Then the ocean current would take the place of the atmosphere in transporting the chemicals northward to the Arctic Ocean, and the dilution effect thereafter would result in a declining distribution pattern.

To sum up, the global distillation theory could explain to some extent the latitudinal trends of α -HCH and γ -HCH from a macro perspective, and the reason given, based on the difference of physiochemical parameters, was also strong enough to resolve the subtle differences seen in their latitudinal trends. However, when our perspective is on an intra-station scale, no uniform profile could be seen, and a low concentration value could even be found at a station which is adjacent to a high value station. This seemed to depart from the pattern discussed above, but there is no great surprise, if we bear in mind that there are different factors in the environment, such as the chemical factors addressed here, and hydrological factors acting together to control the environmental behavior of chemicals existing in the environment.

3.5 Source analysis of α-HCH and γ-HCH

Generally, technical HCH contains approximately 60%–70% α -HCH, 5%–12% β -HCH, 10%–15% γ -HCH and 3%–4% δ -HCH, while lindane contains more than 90% γ -HCH. The α -HCH/ γ -HCH ratio of 4–7 is generally used to identify the source of technical HCH application. The α -HCH/ γ -HCH ratio profile in our current study had values less than 4 without exception, and a slightly decreasing trend with latitude within sea zones to the north of 60°N, and an apparent increasing trend from 60°N northward to the Arctic was observed, as shown in Figure 4. The α -HCH/ γ -HCH ratio pattern was consistent with the latitudinal trend of α -HCH and γ -HCH, discussed above. According to the ratio of 4–7, there must be a lindane source, and the signal imposed on that of the technical HCHs could have resulted in an α -HCH/ γ -HCH ratio less than 4.

However, Ding *et al.* [44] questioned the rationality of regarding the α -HCH/ γ -HCH ratio of 4–7 as a diagnostic tool to identify the source of technical HCHs, considering the different lifetime of these two chemicals in the air as well as their different properties, which could preferentially remove the atmospheric γ -HCH into the seawater below. Hence, mixture chemicals of technical HCHs and lindane in the emission region would exhibit an α -HCH/ γ -HCH ratio less than 4, and then the ratio could have increased to a value possibly within the range of 4–7 as the mixture of chemicals were transported to the Arctic Ocean. In this hypothesis, the ratio of 4–7 would be misleading. As the ratio in our current study was less than 4, evidence of a lindane source deduced by comparing the α -HCH/ γ -HCH ratio value to a range of 4–7 was most probably present.



Figure 4 α -HCH/ γ -HCH ratios in the surface water of each station in this study.

3.6 Vertical profile of HCH isomers in the seawater column of the Canadian Basin (station B80)

In the case of Σ HCHs (the sum of four isomers of HCH determined in this study), the characteristics of its depth profile in the upper layer of the Canadian Basin agree with some early reports from the Arctic Ocean, which show that Σ HCHs in the upper 30 m are higher, but drop rapidly to \leq 1 ng/L at 200 m [45]. Thus, Σ HCHs in the Canadian Basin are different from those in the Bering and Chukchi Seas, where Σ HCHs are distributed fairly uniformly to at least 350 m [14]. From 300 m to 3500 m, Σ HCHs changed little and remained at a very low value (averaged in 0.38 ng/L).

For individual isomers of HCH, the vertical distributions of α -HCH and γ -HCH at station B80 displayed different patterns in the upper 300 m, but were similar from 300 m to 3500 m (Figure 5). Fischer *et al.* [46] successfully used the ratio of α -/ γ -HCH to identify water masses with a small data set. Here, we also attempted to correlate the water mass distribution with the characteristics of vertical distribution of individual isomers (α - and γ -HCH) and their ratio, and found that the whole water column in B80 might be classified into four layers, with details as follows:

(1) 0–30 m layer. Concentrations of α -HCH increased slowly from 0.64 ng/L at the surface to 0.92 ng/L at 30 m, whereas γ -HCH changed little over this depth range (0.30–0.33 ng/L). The ratio of α -/ γ -HCH ranged from 2.2 to 2.8 with an average of 2.4. The observed low ratio in the surface water might imply the presence of a possible main emission source of lindane near this region. The main pathways of HCH transportation in this layer are local river-runoff and sea ice melt, but not oceanic currents, which could be supported by the much lower salinity in this layer (seen in Figure 5) and also by the results from stable isotope tracing [47].

(2) 30–150 m layer. The average concentrations for both isomers in this layer were lower than that of the surface layer, but both changed little from 30 m to 150 m (0.62-0.68 ng/L for α -HCH and 0.17–0.19 ng/L for γ -HCH). The α -/ γ -HCH ratio ranged from 3.3–4.1 ng/L (averaging 3.8 ng/L), which might imply that the isomers of HCH come from a mixture of lindane and technical HCHs, but that the former's proportion decreased. The average value of the ratio was about 60% higher than that of the 0-30 m layer. Considering that the residence time of HCHs in the upper layer is short and the hydrolytic half-life of γ -HCH (42 yr at pH 8 and 5 °C) is longer than that of α -HCH (26 yr at the same condition) [48], the ratio may not increase from the surface to the lower layer assuming that there are no other sources of HCHs in this layer, except for atmospheric precipitation.

Chen *et al.* [47] noted that the depth of the upper halocline water (UHW) in the Canada Basin is at about 150 m using the stable isotopes (18 O and 2 H) tracing method, and



Figure 5 The vertical profile of HCHs at station B80.

suggested that the water above UHW has three freshwater sources which maintain the halocline in the Arctic Ocean, namely river water, sea ice-melting water, and low salinity Pacific waters entering the Arctic Ocean through the Bering Strait. Our study showed that the temperature and the salinity at 150 m were -1.49 °C (close to ice point) and 33.01, respectively, which agreed well with the results of Chen *et al.* [47]. As a result, we deduced that the water in this layer was mainly affected by the inflow of low salinity Pacific water and was altered in the Chukchi shelf/the east Siberian shelf, which always maintained a relatively high α -/ γ -HCH ratio.

(3) 150-300 m layer. Below the 150 m layer, the concentrations of α -HCH dropped sharply to 0.13 ng/L at 300 m, which was in agreement with several earlier reports on the Arctic Ocean [15, 45, 49, 50], while concentration of γ -HCH in the 200 m layer was found to be higher than those in both the connected upper (125 m) and lower water layer (300 m), and the ratio of α -/ γ -HCH (1.76 at 200 m) differed very much from that of both layers (4.09 at 150 m and 1.07 at 300 m). The higher γ -HCH and different α -/ γ -HCH ratios in the 150-300 m layer might indicate the inflow of another kind of water mass containing high γ -HCH. Schlosser *et al.* [51] suggested that the salinity and temperature of the Barents branch of Atlantic water gradually decrease by mixing with river water and sea ice-melting water as it travels to the Canada Basin. Chen et al. [47], using stable isotopes tracing methods, found that the 300 m layer is the lower halocline water (LHW) in the Canada Basin, and the water above this is affected by the inflow of Atlantic water, which enters the Arctic Ocean mainly through the Barents Sea and the Fram Strait. Our results provided further evidence that the formation of the LHW was due to the inflow of Atlantic water and then modification in the Barents shelf. In addition, relatively higher data in the 200 m layer were found for the other two isomers of HCHs, β -HCH and δ -HCH (shown in Figure 5).

(4) 300–3500 layer. The speed of decline of both isomers slowed down from 300 m (0.13 ng/L for α -HCH and 0.12 ng/L for γ -HCH) to 3500 m (0.05 ng/L for both isomers). The average concentrations below 1500 m were 0.08 ng/L and 0.06 ng/L, respectively, which were comparable with those in the Bering Sea (0.07 ng/L and 0.02, respectively), but were much lower than those in the Alaskan Chukchi (0.66 and 0.17 ng/L in 1590 m, one sample) [14, 52]. Harner et al. [52] showed that the percentages at depths of 250–1000 m in the Nansen Basin were approximately 40% of the surface values for α -HCH and approximately 60% for γ -HCH. However, our results showed that in the same layer at station B80 they were about 20% and 30%, respectively. Considering the water masses at 250-1000 m have ages in the order of 12-20 years [16] and our cruise was 12 years later than that of the Oden cruise in 1996, our results agreed with their research results and coincided with the time of the heaviest usage of HCHs. As for the α -/ γ -HCH ratio, it changed little from 300 m to 3500 m (see Figure 5), which was somewhat similar to the α - or γ -HCHs.

4 Conclusions

Compositional pattern and spatial distribution of 17 OCPs were studied along the cruise track of the 3rd Chinese Arc-

tic Expedition. A general characteristic featuring increasing concentrations northward with concentration levels of parts per trillion for HCHs, and sub parts per trillion for other target compounds, was found in the current study. A source pattern for a mixture of technical HCHs and lindane was deduced by analyzing the α/γ -HCH ratio.

The vertical distributions of α -HCH, γ -HCH and their ratio at station B80 displayed different patterns in the upper 300 m, but were similar from 300 m to 3500 m, which were used to correlate the water mass distribution and we found that the whole water column in B80 might be classified into four layers: 0–30 m layer, 30–150 m layer, 150–300 m layer and 300–3500 m layer.

Atmospheric OCPs, especially HCHs, were reported to have declined since they were gradually phased out for agricultural use. Under these circumstances, the atmospheric long range transportation would be weakened, and ocean currents would play a relatively more significant role in transporting OCPs northward to the Arctic Ocean. The general spatial distribution determined by LRT is probably subject to change, which would be enhanced by global warming, resulting in the re-volatilization of chemicals in the Arctic water to the air above. Therefore, even more comprehensive studies are necessary in the future for fully understanding the geochemical properties of OCPs globally.

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