Distribution and Air−Sea Exchange of Current-Use Pesticides (CUPs) from East Asia to the High Arctic Ocean

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S Supporting Information

ABSTRACT: Surface seawater and marine boundary layer air samples were collected on the ice-breaker R/V *Xuelong* (*Snow Dragon*) from the East China Sea to the high Arctic (33.23−84.5° N) in July to September 2010 and have been analyzed for six current-use pesticides (CUPs): trifluralin, endosulfan, chlorothalonil, chlorpyrifos, dacthal, and dicofol. In all oceanic air samples, the six CUPs were detected, showing highest level (>100 pg/m^3) in the Sea of Japan. Gaseous CUPs basically decreased from East Asia (between 36.6 and 45.1° N) toward Bering and Chukchi Seas. The dissolved CUPs in ocean water ranged widely from <MDL to 111 pg/L. Latitudinal trends of α-endosulfan, chlorpyrifos, and dicofol in seawater were roughly consistent with their latitudinal trends in air. Trifluralin in seawater was relatively high in the Sea of Japan (35.2° N) and evenly distributed between 36.9 and 72.5° N, but it remained below the detection limit at the highest northern latitudes in Chukchi Sea. In contrast with other CUPs, concentrations of chlorothalonil and dacthal were more abundant in Chukchi Sea and in East Asia. The air−sea gas exchange of CUPs was generally dominated by net deposition. Latitudinal trends of fugacity ratios of α-endosulfan, chlorothalonil, and dacthal showed stronger deposition of these compounds in East Asia than in Chukchi Sea, while trifluralin showed stronger deposition in Chukchi Sea (−455 ± 245 pg/m^2/day) than in the North Pacific (−241 ± 158 pg/m^2/day). Air−sea gas exchange of chlorpyrifos varied from net volatilizaiton in East Asia (<40° N) to equilibrium or net deposition in the North Pacific and the Arctic.

■ INTRODUCTION

Organochlorine pesticides (e.g., chlordane, DDTs, and lindane) were defined as persistent organic pollutants (POPs) by the Stockholm Convention because of their persistence, bioaccumulation and potential for long-range transport (LRT) (www.pops.int). As these legacy pesticides were phased out or underwent significant reduction of usage, some current-use pesticides (CUPs) are, or have been, high production volume chemicals.[1] Although most CUPs were designed to have reduced environmental persistence in comparison with the older organochlorine pesticides,[1,2] some of them have been detected in air and the aquatic environment in agricultural or urban areas.[3−8] CUPs also occurred in areas where no pesticides are or ever have been used, such as high mountains.[9−11] They were even found in Arctic media, i.e., the ice caps on Svalbard, Norway,[12,13] fog in the Bering and Chukchi Seas,[14] and snow collected over northwest Alaskan sea ice.[15]

The occurrence of CUPs in high mountain regions and the Arctic indicates that they can undergo LRT. In 1999, van Dijk and Guicherit reviewed the monitoring studies of atmospheric CUPs throughout the world, summarizing CUPs concentrations in air usually ranged from a few pg/m^3 to many ng/m^3 and concentrations in rain generally ranged from a few ng/L to several μg/L.[2] Some important knowledge gaps are also mentioned in this overview, e.g., only a few studies were conducted outside Europe and North America, and most results of monitoring studies were published in "gray literature", reducing their availability to the international scientific community. In recent years, most data on CUPs in atmospheric and aquatic environment published in international journals were from North America.[4,6,8,9,11,16] That indicates most current studies are not more than nationwide, but actually sampling sites in the majority of studies even covered only a small geographical area (a small

part of a country). Thus the global CUPs distribution is not well understood.

The legacy pesticides, e.g., hexachlorobenzene (HCB) and hexachlorocyclohexane (HCH), can move through the atmosphere from warmer source regions and accumulate at colder and higher latitudes.[17,18] Although CUPs have been observed in the Arctic, there is little evidence to identify whether the occurrence of CUPs in the Arctic implies global distribution mechanisms similar to those for legacy pesticides. Oceanic water bodies have been believed to be a final sink of the persistent organochlorines after undergoing some processes such as long-range atmospheric transport from emission sources, mass transfer between air and water, and scavenging to deep sea layers with particles.[19,20] However, data on CUPs in oceanic air and water are extremely limited.

To improve the knowledge of global CUPs distribution and the role of oceans on CUPs long-range transport and fate, marine boundary layer air samples and seawater samples were taken during an Arctic expedition of the Chinese research vessel *Xuelong* from East China Sea to the high Arctic in 2010. The samples were analyzed for six CUPs (trifluralin, endosulfan, chlorothalonil, chlorpyrifos, dacthal, and dicofol), whose environmental impact has attacted much attention in recent years. In the present study, levels of CUPs in the gaseous, dissolved, and particulate phases are given. Distribution and air–water gas exchange of CUPs will be discussed. To our knowledge, this is the first paper on occurrence and environmental fate of chlorothalonil, chlorpyrifos, dacthal, and dicofol on a trans-ocean scale.

■ MATERIALS AND METHODS

Sample Collection. Air and seawater samples were taken from the East China Sea to the high Arctic (33.23–84.5° N) onboard the Arctic expedition of the research ice-breaker R/V *Xuelong* (*Snow Dragon*) from June to September 2010. Seventeen air samples (~500 m³) were collected in front of the ship's most upper deck using a high-volume air sampler equipped with a glass fiber filter ([GFF], GF/F, pore size: 0.7 μm) to trap airborne particles and a self-packed PUF/Amberlite XAD-2 glass column (air column) for the gas phase. Air samples were collected within 1–2 days during the cruise. Both air column and filters were stored at −20 °C until analysis. Seawater samples were taken by the ship's intake system operated for 12–24 h to obtain a volume of 176–1120 L. Seawater samples were passed through a GFF (GF/C, pore size: 1.2 μm) for the particulate phase, followed by a self-packed Serdolit PAD-3 glass column for the dissolved phase. Seawater filters and columns were stored at −20 and 4 °C, respectively. A total of 17 air samples and 18 water samples were taken. Sampling parameters including date, position, temperature, and wind speed are included in Tables S1 and S2 in the Supporting Information (SI).

Chemicals. All solvents were residue grade and additionally distilled in a full glass unit prior to use. Individual standards of chlorothalonil, trifluralin, chlorpyrifos, dacthal, dicofol, and a pesticide-mix 163 containing α-endosulfan and β-endosulfan were purchased from Dr. Ehrenstorfer GmbH, Germany. Trifluralin-d_{14} (surrogate) and ^{13}C-HCB were purchased from Cambridge Isotope Laboratories. PCB-207 was also obtained from Dr. Ehrenstorfer GmbH. Both ^{13}C–HCB and PCB-207 were used as injection standards (see details below).

Extraction, Cleanup, and Analysis. Extraction and cleanup of the samples were done in a clean laboratory (class 10000).

Samples were spiked with 500 pg of trifluralin-d_{14} as surrogate standard prior to extraction. Air columns, water columns, and filters were extracted in a modified Soxhlet apparatus for 16 h using dichloromethane. Extracts were evaporated to 0.2 mL using hexane as keeper and further cleaned on a silica-gel (mesh size 60) column (10% water deactivated) topped on 3 g of anhydrous granulated sodium sulfate. The extracts were purified by eluting with 20 mL of hexane (fraction 1), followed by 30 mL of dichloromethane/acetone (1:1) (fraction 2), and evaporated to a final volume of 30 μL. One ng of ^{13}C–HCB and 0.5 ng PCB207 were added to fraction 1 and 2 as recovery standard, respectively. Both fractions were measured with a GC/MS system (Agilent 6890N GC/5975 MSD) in electron capture negative chemical ionization mode (ECNCI) with methane as ionization gas fitted with a HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific). The injector was operated in pulsed-splitless mode (injection pulse 20 psi for 2 min) with the following inlet temperature program: 60 °C for 0.1 min, 500 °C/min until 280 °C, and held for a final 20 min. The GC oven program was as follows: initial 60 °C for 2 min, 30 °C/min until 150 °C, 2 °C/min until 240 °C, 20 °C/min until 300 °C, and held for 5 min. The MS transfer line was held at 280 °C and the ion source and quadrupole temperature was 150 °C. The m/z values monitored for quantification and quality control are shown in Table S3 in the SI. Total amounts of individual CUPs in the samples are the sum of fraction 1 and 2.

QA/QC. The air columns were protected against UV–sunlight during sampling using aluminum foil in order to avoid degradation of the target compounds on the column. All air columns were precleaned with solvents of different polarity and GFFs were baked at 450 °C for 12 h prior to their usage. Silica gel was cleaned with acetone for 12 h and baked at 450 °C for 12 h prior to usage. All glassware was baked at 250 °C for 10 h and rinsed with solvent. Field air, water, and filter blanks were prepared on board, and stored together with other samples. Three field blanks were run for each sample type. Due to coelution of chlorothalonil with an unknown compound in air filters and water filters, particulate chlorothalonil will not be considered below. Mean absolute blank values of other CUPs ranged from <0.1 to 60 pg (see Table S4 in the SI). Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation (σ) (for compounds showing no blanks the instrumental limits at a signal-to-noise ratio of three were used). Atmospheric MDLs ranged from 0.002 to 0.15 pg/m³ and seawater MDLs ranged from 0.001 to 0.06 pg/L (see Table S5 for details). The mean recoveries of trifluralin-d_{14} for air samples, water samples, air filter samples, and water filter samples were 88 ± 18%, 100 ± 11%, 101 ± 6%, and 106 ± 16%, respectively. The method recovery was examined by spike tests resulting in mean recoveries around 80% to 110% for trifluralin-d_{14}, trifluralin, chlorpyrifos, dacthal, α-endosulfan, and β-endosulfan. But recoveries of spike tests of air columns were relatively low (48 ± 13%) for dicofol and high for chlorothalonil (222 ± 18%). After careful scrutiny, the high recovery values for chlorothalonil are considered to be signal enhancement caused by certain material eluted from air columns (see more details of recoveries of spike tests in Table S3). It is noted the gaseous concentrations of chlorothalonil reported in this study might be with relatively high uncertainty.

Air Mass Back Trajectories. Air mass origins along the cruise segments of the individual air samples were calculated using NOAA's HYSPLIT model.[21] Air mass back trajectories (BTs) were calculated in 6-h steps tracing back the air masses for 5 days

using the sampling height as arrival height (see Figure S1 for individual BTs).

■ RESULTS AND DISCUSSION

CUPs in Air. Details of CUPs concentrations in air are shown in Table S6. We will not discuss the particulate phase below because of its minor proportion (generally <0.001%). Gaseous CUPs were ubiquitous in oceanic air with 100% detection frequencies for individual target compounds (except 41% for β-endosulfan) and showed highest level (>100 pg/m^3) in the Sea of Japan (Figure 1A). The insecticides α-endosulfan, chlorpyrifos, and dicofol were the most abundant CUPs ($\sim$14 pg/m^3 on average), in contrast to lower concentrations (0.14−2 pg/m^3 on average) of those used as herbicides (trifluralin and dacthal), and fungicides (chlorothalonil) (Table S6). Actually, these herbicides and fungicide have higher vapor pressures (0.006−0.013 Pa) compared to insecticides (<0.005 Pa) (Table S7), which should favor volatilization from surfaces. So higher concentrations of insecticides may result from their larger cumulative global use, while the lower level of herbicides and fungicide might be due to higher tendencies of removal during atmospheric transport, e.g., trifluralin is readily degraded under sunlight in air and water.[22] Significant correlations ($p < 0.001$, $r = 0.77−0.99$, Table S8) were observed for atmospheric chlorothalonil, dacthal, and chlorpyrifos indicating similar source regions and comparable LRT behavior. Airborne α-endosulfan is the only CUP which exhibited a significant positive correlation ($r = 0.77$, $p < 0.001$, Table S9) with air temperature, which reflects that volatilization from surfaces owing to elevated air temperature is an important process for this pesticide.

CUPs in Seawater. CUPs remained below their detection limits for almost all water filters (suspended particulate matters) indicating that sedimentation is relatively less important removal process of these CUPs from seawater. The dissolved CUPs ranged widely from <MDL to 111 pg/L (Figure 1B and Table S10). The insecticides α-endosulfan, chlorpyrifos, and dicofol were also the most abundant, but their mean concentrations in seawater were not as similar as they were in the air. Dicofol in seawater was just slightly higher than chlorpyrifos, although dicofol's Henry's law constant is much lower than chlorpyrifos. That indicates greater degradation tendency of dicofol in seawater, since sedimentation is not an important removal process for CUPs in seawater as discussed above.

Latitudinal Trends. The spatial distribution of CUPs in air along the sampling transect and the latitudinal trends for individual CUPs are shown in Figure 1A and Figure SI2, respectively. Gaseous CUPs basically decreased from East Asia (36.6 and 45.1°N) toward Bering and Chukchi Seas. The highest CUPs concentrations were generally observed in the Korean Straight and the Sea of Japan, but air masses BTs showed only a slight influence of the air samples in Korean Straight and the Sea of Japan by (Asian) continent-derived air masses. To better identify the continental source regions, station-based monitoring for a longer period (>5 days) would be necessary. A global survey of endosulfan in tree barks showed that endosulfan tends to remain in the region of use because of its low volatility.[17] A similar effect can be also expected for chlorpyrifos, dacthal, and dicofol, which have similar or lower volatility (see vapor pressure in Table S7). Moreover, in a study of airborne CUPs along the Mississippi River, the most important factor controlling the atmospheric concentration of trifluralin was the proximity to use regions.[23]
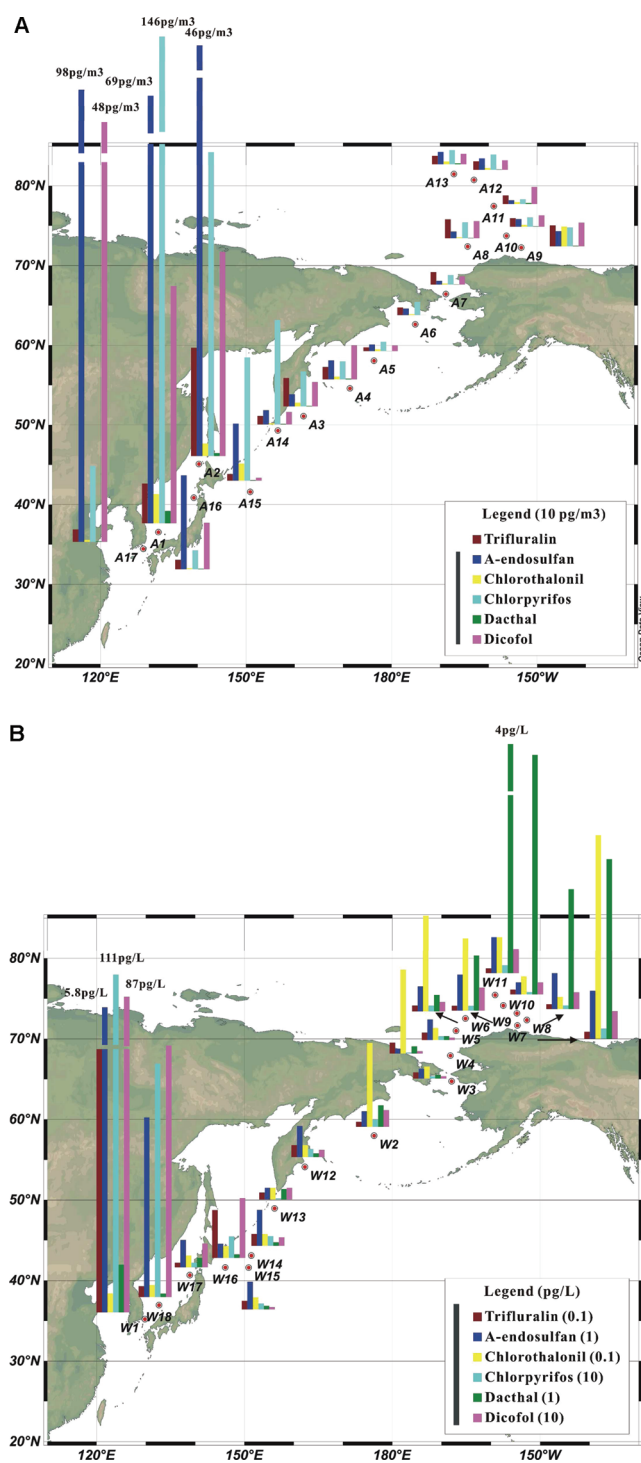
Figure 1. Concentrations of CUPs (chlorothalonil, trifluralin, chlorpyrifos, dacthal, dicofol, α-endosulfan, and β-endosulfan) in the atmosphere (A) and seawater (B) from East Asia to the Arctic.

Therefore, the adjacent Asian continent is more possibly the source region of airborne CUPs in Korean Straight and the Sea of Japan. One of the reasons for the decline from East Asia toward Bering Sea was the dilution during atmospheric transport caused by oceanic air masses (Figure S1). In addition, organic pollutants also undergo some removal processes during atmospheric transport, e.g., chemical transformation in the atmosphere and exchange

between the atmosphere and the Earth's surface which involves dry deposition of particles, gas exchange, and precipitation scavenging.[24]

Latitudinal trends of α-endosulfan, chlorpyrifos, and dicofol in seawater were roughly consistent with their latitudinal trends in oceanic air (Figure 1B and Figure SI3). Trifluralin in seawater was relatively high at 35.2° N following a sharp decrease northwards. Trifluralin was evenly distributed from 36.9 to 72.5° N, whereas it was below the detection limit in the highest northern latitudes from 73.2 to 75.5° N (Figure SI3). In contrast to other CUPs, chlorothalonil and dacthal in seawater were much more abundant in Chukchi Sea than in East Asia (Figure SI3), although the highest air concentrations of chlorothalonil and dacthal were observed in East Asia. This observation could be an evidence of "cold trapping" of these compounds into the Arctic region as it was described for the legacy pesticides, e.g., α-HCH.[18] Another possible reason for the occurrence of CUPs in Chukchi Sea is dispersion from the adjacent Bering Sea. It is more likely that CUPs in Chukchi Sea originate from circumpolar countries, since air masses in Chukchi Sea were mainly originating from the Arctic Ocean, Russia, and North America (Figure S1). The north Eurasia (>60° N) seems to deserve more attention, since it is a region of likely high pesticide use for the much higher cropland density (e.g., in Russia) compared with other circumpolar regions (>60° N).[13]

Trifluralin. Trifluralin is a commonly used pre-emergence herbicide. European Union (EU) banned trifluralin since 2009. Trifluralin is registered to be used in India, Japan, and China,[25,26] but annual use of trifluralin in East Asian countries is unavailable. Our study shows that mean gaseous trifluralin in Chukchi Sea (1.3 pg/m^3) is ~10 times of those in South-West Greenland[27] and Canadian Arctic.[28] Levels of atmospheric trifluralin in these regions are similar, which approximately coincide with the fact small difference exists between the annual usage of trifluralin in EU and North America. In the Global Atmospheric Passive Sampling (GAPS) study during 2005−2008, levels of trifluralin in Europe and North America were higher than those in Asia and the southern hemisphere.[29] Although we know of the existence of trifluralin in the environment of these regions, more research is needed to understand the attribution of different regions on the occurrence and distribution of trifluralin in the Arctic. Trifluralin can undergo rapid photochemical conversion, e.g., dealkylation and cyclization with a half-life of approximately 15 min under sunlight condition and reaction with HO radicals and O$_3$,[30] which implies atmospheric degradation of trifluralin is mostly controlled by photolysis with HO radicals during transport from source region to remote ocean. In this study, concentrations of trifluralin in seawater were generally much lower than those of other CUPs, although air concentrations of trifluralin were comparable with other CUPs. This result might be attributed to the relatively high vapor pressure (0.01 Pa, 25 °C) and low solubility (0.21 mg/L, 25 °C) of trifluralin (Table S7).

Endosulfan. Endosulfan is an insecticide applied to a wide number of crop types including cotton, cereals, fruit trees, and plantation crops such as tea and coffee.[31] Only recently, about six months after our sampling campaign, endosulfan was added into Annex A to the Stockholm Convention, with specific exemptions.[32] Endosulfan has not been manufactured in Japan, but it has been imported for manufacturing the formulation products, which have been used as agricultural insecticide since 1960.[33] The total shipping volume of endosulfan into Japan from 2003 to 2007 was about 80 t.[33] Widespread environmental contamination by

this chemical also has been reported in South Korea[34] and urban Seoul.[35] Although mainland China is relatively far away from the sampling sites in Korean Straight and Japan Sea, it still deserves attention caused by its high endosulfan consumption (4100 t/a)[36] and high concentrations of atmospheric endosulfan in the provinces along the coast of Chinese Bohai Sea, Yellow Sea, and East Sea owing to high cotton production reported.[37] In our study, mean gaseous α-endosulfan in Chukchi Sea (1 pg/m^3) is slightly lower than the result from six circumpolar monitoring stations in Canada, the United States, Norway, and Russia in 2000−2003 (4.2 pg/m^3)[38] and the result from South-West Greenland in 2004−2005 (4.8 pg/m^3).[27] That indicates that gaseous α-endosulfan changed only a little on a large scale within the polar region in the past ten years. α-Endosulfan in Chukchi Sea water averaged 0.5 pg/L, which is several times lower than results from different regions in the Arctic Ocean in 1990s.[39] Less annual use in North America (200 t/a),[36] ban of use in EU from 2007,[36] and decreasing use in the northern hemisphere in the period 1996−2004[40] may have contributed to the lower and stable endosulfan levels in the Arctic air and seawater in recent years. Technical grade endosulfan contains two isomers, known as α-endosulfan and β-endosulfan, in ratios from 2:1 to 7:3 depending on the technical mixture.[41] In our study, β-endosulfan in the air was <MDL at latitudes >60° N, whereas α/β-endosulfan ratios varied a lot (ranging from 15 to 545) at latitudes <60° N. In the Global Atmospheric Passive Sampling (GAPS) study on POPs in 2004−2005, β-endosulfan accounted for 16% of total endosulfans (α-, β-endosulfan, and endosulfan sulfate).[42] Henry's law constant of β-endosulfan (0.045 Pa m^3/mol)[43] is lower than α-endosulfan's (0.82 Pa m^3/mol, Table S7). β-endosulfan is more likely to be scavenged from the atmosphere by precipitation than the α-isomer and likely to be more susceptible to dissolve to surface waters. Significant conversion of the β-endosulfan to the α-endosulfan has also been reported in many studies.[44−46] These might be the main reasons that there are much larger α/β-endosulfan ratios in the air in our study than in the GAPS study.

Chlorpyrifos. In this study, concentrations of gaseous chlorpyrifos were high in the Sea of Japan, but consumption data or data about air concentrations of chlorpyrifos in East Asian countries are sparse. To our knowledge, data of environmental chlorpyrifos in Asian continent were limited. Li et al. reported sediment-associated chlorpyrifos in urban waterways in Pearl River Delta, China up to 100 ng/g dry weight.[47] Chlorpyrifos was reported from 0.3 to 1.89 ng/L in Beijing Guanting reservoir in 2005[48] and it was detected in river water in Okinawa, Japan.[49] Chlorpyrifos is a persistent residue when it is used as termiticide in soil.[50] Yoshida et al. reported that summertime levels of chlorpyrifos in indoor air did not decrease over a period of seven years after initial application of the termiticide.[51] However, degradation may also significantly contribute to the sharp decrease of chlorpyrifos northward of the Sea of Japan, since Kales et al. demonstrated that ^{14}C-chlorpyrifos degrades rapidly in the marine ecosystem.[52] Moreover, the phaseout of chlorpyrifos used in outdoor urban settings has resulted in a rapid decline in concentrations of this insecticide in urban streams and rivers in the northeastern and midwestern United States.[53] This study showed concentrations of chlorpyrifos in seawater in Bering and Chukchi Sea were less than 1 pg/L. In the summer of 1993, CUPs in air, ice, fog, seawater, and surface microlayer in the Bering and Chukchi Seas were measured.[54] Chlopyrifos was one of the most frequently identified contaminants in seawater; it was highest (170 ng/L) in marine ice and higher in seawater (19−67 ng/L)

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at locations closest to the ice edge. Chlorpyrifos was detected at concentrations several times higher in Arctic marine fog than in adjacent waters or ice.[54] High chlorpyrifos concentrations (70−80 ng/L) in sea ice also were estimated at three sites in four northwest Alaskan Arctic estuaries.[15] Chlorpyrifos concentrations measured in this study were 2−3 orders of magnitude lower than those of previous studies. The decline of chlorpyrifos in the Bering and Chukchi Seas can reflect the fact that chlorpyrifos was phased out for residential and termite uses in North America.[55]

Chlorothalonil and Dacthal. In 2001, production of chlorothalonil (3600−5000 t/a) in the United States is comparable with that of chlorpyrifos (5000−7300 t/a).[1] Dacthal was first registered as a pesticide in the United States in 1958 as a selective pre-emergence herbicide for weed control on turf grasses. The annual sales/use quantity of dacthal in Canada is less than 1% of U.S. use, which is approximately 271 t/a.[56] Chlorothalonil and dacthal have been reported to be one of the most abundant CUPs in the air of Centre Region (France)[57] and North America.[3,16,58] Dacthal has been detected even in the snowpack samples in Alaskan parks.[9] Similar to trifluralin, in the GAPS study during 2005−2008, levels of chlorothalonil in Europe and North America were higher than those in Asia and the southern hemisphere.[29] Extemely low chlorothalonil and dacthal in seawater at lower latitudes may result from low chlorothalonil and dachtal levels in the air, whereas high concentrations in Chukchi Sea are possibly due to long-term deposition from circumpolar countries.

Dicofol. Global production of dicofol was estimated to be 5500 t/a.[1] In EU countries, the use of dicofol for plant protection products was restricted by March 30, 2009. Historic use was estimated by OSPAR to be 290 t/a in Europe for the year 2000. Use in North America was also estimated to be 290 t/a.[59] In spite of dicofol's high production volume, Hoferkamp et al. found dicofol had not been reported in the Arctic when they reviewed the occurrence of CUPs in Arctic media.[1] In our study, observation of dicofol in the Artic is possibly not only due to atmospheric deposition, but also due to input from riverine freshwater, since high levels of dicofol-related DDT have been reported in river water samples from the Russian Arctic in 2003 and 2005.[60] In Japan, dicofol was used as a pesticide from 1956, and then banned in 2004.[61] China is suspected of being one of the major sources of dicofol in the air over Japan Sea, since dicofol has been widely used in agricultural practices in China until the present time.[62,63]

Air−Sea Gas Exchange. To estimate the direction (or equilibrium status) of the gas exchange, the fugacity ratio (FR) f_a/f_w was calculated. A FR >1, =1, and <1, respectively, indicates deposition, air−water equilibrium, and volatilization. The air−sea gas exchange flux (F_{aw}) was calculated with the modified version of the Whitman two-film resistance model.[64−66] Due to uncertainties of knowing air−water transfer coefficient and Henry's law constant of CUPs, a significant deviation from equilibrium cannot be assessed within a factor of 3 around a fugacity ratio of 1,[67,68] therefore, an equilibrium window was set up as $0.3 < f_a/f_w < 3$ for the CUPs. The uncertainty of the flux can be estimated by propagation of the uncertainties in C_W (20%), C_A (20%), K_{OL} (40%), and H (30% for chlorpyrifos and α-endosulfan, and 300% for chlarathalonil, dacthal, and dicofol). The flux uncertainty was estimated to be ±57% for chlorpyrifos and α-endosulfan and ±300% for chlorathalonil, dacthal, dicofol, and trifluralin (see SI for details of fugacity ratio, air−sea gas exchange flux, and uncertainty calculation).

Details of FR values and air−sea gas exchange fluxes at different latitudes are shown in Table S11. The air−sea gas exchange
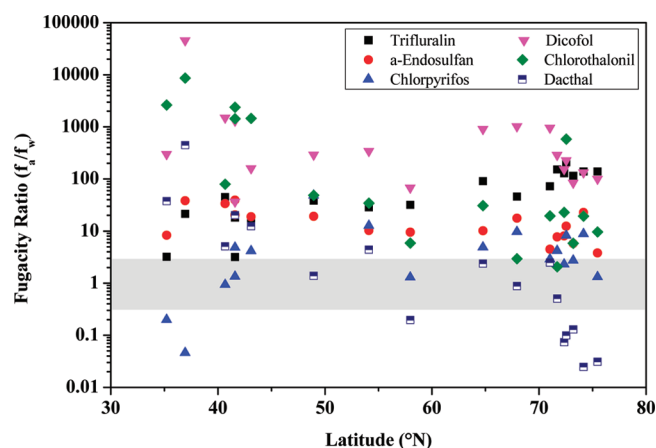
Figure 2. Latitudinal trends of fugacity ratio along the sampling transect for chlorothalonil, trifluralin, chlorpyrifos, dacthal, dicofol, and α-endosulfan. The equilibrium state ($0.3 < f_a/f_w < 3$) is highlighted in gray.

was generally dominated by net deposition. Comparison of the latitudinal trends of FR values and CUPs in air and seawater (Figure SI2, Figure SI3 and Figure 2) indicates the strong net deposition is basically driven by the relatively high atmospheric concentrations or extremely low concentrations in water. For instance, large FR values of α-endosulfan in East Asia and large FR values of dicofol in East Asia and Bering Sea were consistent with highest atmospheric concentrations in these areas, whereas large FR values of chlorothalonil and dacthal in East Asia were due to extremely low concentrations in seawater. Latitudinal trends of FR values of α-endosulfan, chlorothalonil, and dacthal showed stronger deposition of these compounds in East Asia than in Chukchi Sea. Interestingly trifluralin showed stronger deposition in Chukchi Sea than in East Asia where higher atmospheric concentrations were observed. The mean deposition flux of trifluralin was about two times higher in Chukchi Sea (-455 ± 245 pg/m²/day) than the mean deposition flux in North Pacific (-241 ± 158 pg/m²/day) (Table S11). As trifluralin is relatively volatile and less soluble in water, it is more favorable to atmospheric transport rather than ocean current. Moreover input sources of trifluralin from the North America and Russia can also contribute to the elevated deposition flux. Based on trifluralin concentrations measured from a joint U.S.−Russian expedition in the Chukchi Sea in 1993, deposition fluxes were estimated to be 104−109 pg/m²/day, which were 2−4 times lower than this study, suggesting atmospheric deposition dominated air−sea gas exchange process in the Arctic in past decades.[69] FR values of chlorpyrifos were lower, averaging 8 ± 14 and 4 ± 3, respectively, in North Pacific and Chukchi Sea. In 1997, McConnell et al. reported a volatilization flux of 4000 to 40 000 pg/m²/day for chlorpyrifos in Chesapeake Bay in March and July, which was driven by high surface water concentrations and low air concentrations.[70] Rawn et al. also reported a volatilization flux (July and August, 1994−1996) in the South Tobacco Creek Watershed in Manitoba, Canada.[71] In this study, chlorpyrifos also showed relatively high volatilization flux (31 552 and 93 455 pg/m²/day) in Japan Sea (Figure 3), which was due to high chlorpyrifos concentration in seawater (111 pg/L). α-Endosulfan deposited into the southern Japan Sea ($-21 627$ and $-38 413$ pg/m²/day), whereas the deposition of α-endosulfan in Chukchi Sea was relatively low (mean of -374 ± 200 pg/m²/day) (Figure 3).
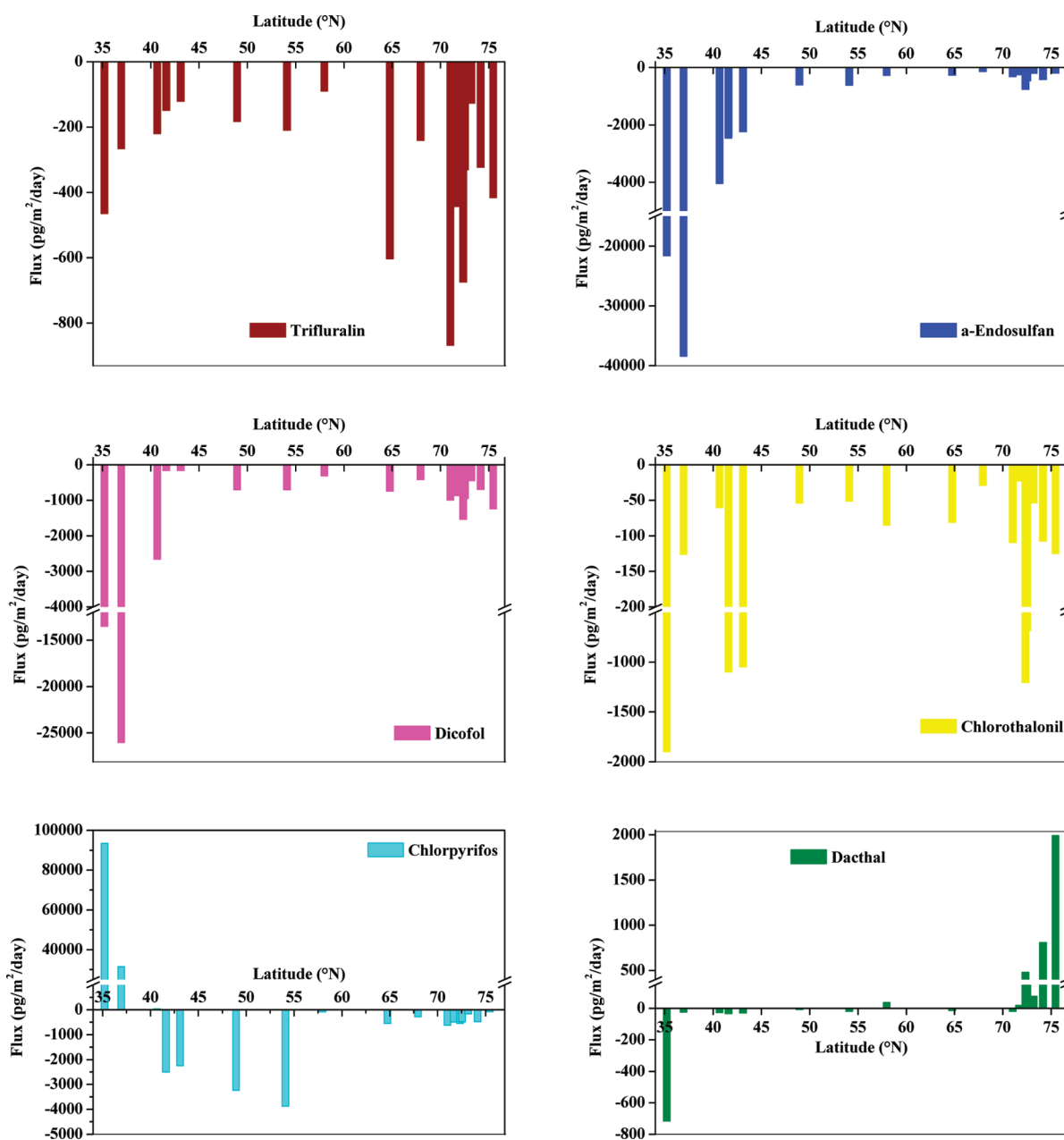
Figure 3. Air—sea gas exchange fluxes for chlorothalonil, trifluralin, chlorpyrifos, dacthal, dicofol, and α-endosulfan from East Asia to the Arctic; minus value means net deposition, and plus value means volatilization.

■ IMPLICATIONS

Concentrations of α-endosulfan, chlorpyrifos, and dicofol in East Asia and the North Pacific Ocean were 1—2 orders of magnitude higher than those in the Arctic, both in the atmosphere and seawater, indicating Asian countries as sources for their long-range transport to the Arctic. Interestingly, spatial distribution of chlorothalonil, dacthal, and dicofol showed increasing concentrations from the North Pacific toward the Arctic, which might be due to direct input from Russia and North America into the Arctic or caused by ocean current transport like the story of beta-hexachlorobenzene.[72] Elevated concentrations of trifluralin occurred in the area close to application region such as China (for East Asia) and Russia and North America (for the Arctic). Air—sea gas exchange

data suggest that there was net deposition of α-endosulfan, chlorpyrifos, dicofol, and trifluralin into the North Pacific and the Arctic, while chlorothalonil and dacthal varied between net volatilization and net deposition. Climate change may significantly accelerate the releasing process of CUPs and drive long-range transport from sources to deposition in the open ocean and the Arctic. However, the CUP trapped in the Arctic snow and ice in the past decades may be released again into ocean water due to global warming process, and thus interfering with the air—water exchange process. Consequently, further investigation is necessary to determine discharge sources of CUPs into the Arctic and to reveal the long-term trends and the biogeochemical processes of CUPs in the oceanic environment.

■ ASSOCIATED CONTENT

ⓢ Supporting Information.   Tables and figures on the sampling sites, results of spike tests, blanks, MDLs, BTs, individual concentrations, physical—chemical properties, correlations, and the calculation of fugacity ratio and air—seawater exchange flux. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Hoferkamp, L.; Hermanson, M. H.; Muir, D. C. G. Current use pesticides in Arctic media; 2000—2007. *Sci. Total Environ.* **2010**, *408*, 2985–2994.

(2) van Dijk, H. F. G.; Guicherit, R. Atmospheric dispersion of current-use pesticides: A review of the evidence from monitoring studies. *Water, Air Soil Pollut.* **1999**, *115*, 21–70.

(3) Kuang, Z. H.; McConnell, L. L.; Torrents, A.; Meritt, D.; Tobash, S. Atmospheric deposition of pesticides to an agricultural watershed of the Chesapeake Bay. *J. Environ. Qual.* **2003**, *32*, 1611–1622.

(4) Raina, R.; Hall, P.; Sun, L. N. Occurence and relationship of organophosphorus insecticides and their degradation products in the atmosphere in Western Canada agricultural regions. *Environ. Sci. Technol.* **2010**, *44*, 8541–8546.

(5) Harnly, M. E.; Bradman, A.; Nishioka, M.; McKone, T. E.; Smith, D.; McLaughlin, R.; Kavanagh-Baird, G.; Castorina, R.; Eskenazi, B. Pesticides in Dust from Homes in an Agricultural Area. *Environ. Sci. Technol.* **2009**, *43*, 8767–8774.

(6) Yao, Y.; Harner, T.; Blanchard, P.; Tuduri, L.; Waite, D.; Poissant, L.; Murphy, C.; Belzer, W.; Aulagnier, F.; Sverko, E. Pesticides in the atmosphere across Canadian agricultural regions. *Environ. Sci. Technol.* **2008**, *42*, 5931–5937.

(7) Lehotay, S. J.; Harman-Fetcho, J. A.; McConnell, L. L. Agricultural pesticide residues in oysters and water from two chesapeake bay tributaries. *Mar. Pollut. Bull.* **1998**, *37*, 32–44.

(8) Gouin, T.; Shoeib, M.; Harner, T. Atmospheric concentrations of current-use pesticides across south-central Ontario using monthly-resolved passive air samplers. *Atmos. Environ.* **2008**, *42*, 8096–8104.

(9) Hageman, K. J.; Simonich, S. L.; Campbell, D. H.; Wilson, G. R.; Landers, D. H. Atmospheric deposition of current-use and historic-use pesticides in snow at national parks in the Western United States. *Environ. Sci. Technol.* **2006**, *40*, 3174–3180.

(10) Daly, G. L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Castillo, L. E.; Wania, F. Accumulation of Current-Use Pesticides in Neotropical Montane Forests. *Environ. Sci. Technol.* **2007**, *41*, 1118–1123.

(11) Bradford, D. F.; Heithmar, E. M.; Tallent-Halsell, N. G.; Momplaisir, G. M.; Rosal, C. G.; Varner, K. E.; Nash, M. S.; Riddick, L. A. Temporal Patterns and Sources of Atmospherically Deposited Pesticides in Alpine Lakes of the Sierra Nevada, California, USA. *Environ. Sci. Technol.* **2010**, *44*, 4609–4614.

(12) Ruggirello, R. M.; Hermanson, M. H.; Isaksson, E.; Teixeira, C.; Forsström, S.; Muir, D. C. G.; Pohjola, V.; van de Wal, R.; Meijer, H. A. J. Current use and legacy pesticide deposition to ice caps on Svalbard, Norway. *J. Geophys. Res.* **2010**, *115*, D18308.

(13) Hermanson, M. H.; Isaksson, E.; Teixeira, C.; Muir, D. C. G.; Compher, K. M.; Li, Y. F.; Igarashi, M.; Kamiyama, K. Current-Use and Legacy Pesticide History in the Austfonna Ice Cap, Svalbard, Norway. *Environ. Sci. Technol.* **2005**, *39*, 8163–8169.

(14) Rice, C. P.; Chernyak, S. M. Marine arctic fog: An accumulator of currently used pesticide. *Chemosphere* **1997**, *35*, 867–878.

(15) Garbarino, J. R.; Snyder-Conn, E.; Leiker, T. J.; Hoffman, G. L. Contaminants in Arctic Snow Collected over Northwest Alaskan Sea Ice. *Water, Air Soil Pollut.* **2002**, *139*, 183–214.

(16) Peck, A. M.; Hornbuckle, K. C. Gas-phase concentrations of current-use pesticides in Iowa. *Environ. Sci. Technol.* **2005**, *39*, 2952–2959.

(17) Simonich, S. L.; Hites, R. A. Global distribution of persistent organochlorine compounds. *Science* **1995**, *269*, 1851–1854.

(18) Li, Y. F.; Macdonald, R. W. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: A review. *Sci. Total Environ.* **2005**, *342*, 87–106.

(19) Knap, A. H.; Binkley, K. S.; Deuser, W. G. Synthetic organic chemicals in the deep Sargasso Sea. *Nature* **1986**, *319*, 572–574.

(20) Tanabe, S.; Tatsukawa, R. Vertical transport and residence time of chlorinated hydrocarbons in the open ocean water column. *J. Oceanogr.* **1983**, *39*, 53–62.

(21) Draxler, R. R.; Hess, G. D. *Description of the HYSPLIT_4 Modeling System*; NOAA Tech. Memo ERL ARL-224, NOAA Air Resources Laboratory: Silver Spring, MD, 1997; 24 pp.

(22) Grover, R.; Wolt, J. D.; Cessna, A. J.; Schiefer, H. B. Environmental fate of trifluralin. *Rev. Environ. Contam. Toxicol.* **1997**, *153*, 1–64.

(23) Majewski, M. S.; Foreman, W. T.; Goolsby, D. A.; Nakagaki, N. Airborne Pesticide Residues along the Mississippi River. *Environ. Sci. Technol.* **1998**, *32*, 3689–3698.

(24) Macdonald, R. W.; Barrie, L. A.; Bidleman, T. F.; Diamond, M. L.; Gregor, D. J.; Semkin, R. G.; Strachan, W. M. J.; Li, Y. F.; Wania, F.; Alaee, M.; Alexeeva, L. B.; Backus, S. M.; Bailey, R.; Bewers, J. M.; Gobeil, C.; Halsall, C. J.; Harner, T.; Hoff, J. T.; Jantunen, L. M. M.; Lockhart, W. L.; Mackay, D.; Muir, D. C. G.; Pudykiewicz, J.; Reimer, K. J.; Smith, J. N.; Stern, G. A.; Schroeder, W. H.; Wagemann, R.; Yunker, M. B. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. *Sci. Total Environ.* **2000**, *254*, 93–234.

(25) BiPRO. *Exploration of management options for Trifluralin*; 2010.

(26) China Ministry of Agriculture. China Pesticide Information Network. http://www.chinapesticide.gov.cn/service/aspx/e2.aspx (April 12th, 2011).

(27) Bossi, R.; Skov, H.; Vorkamp, K.; Christensen, J.; Rastogi, S. C.; Egelov, A.; Petersen, D. Atmospheric concentrations of organochlorine pesticides, polybrominated diphenyl ethers and polychloronaphthalenes in Nuuk, South-West Greenland. *Atmos. Environ.* **2008**, *42*, 7293–7303.

(28) Hung, H.; Halsall, C. J.; Blanchard, P.; Li, H. H.; Fellin, P.; Stern, G.; Rosenberg, B. Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere. *Environ. Sci. Technol.* **2002**, *36*, 862–868.

(29) Shunthirasingham, C.; Oyiliagu, C. E.; Cao, X.; Gouin, T.; Wania, F.; Lee, S.-C.; Pozo, K.; Harner, T.; Muir, D. C. G. Spatial and temporal pattern of pesticides in the global atmosphere. *J. Environ. Monit.* **2010**, *12*, 1650–1657.

(30) Le Person, A.; Mellouki, A.; Muñoz, A.; Borras, E.; Martin-Reviejo, M.; Wirtz, K. Trifluralin: Photolysis under sunlight conditions and reaction with HO radicals. *Chemosphere* **2007**, *67*, 376–383.

(31) Weber, J.; Halsall, C. J.; Muir, D.; Teixeira, C.; Small, J.; Solomon, K.; Hermanson, M.; Hung, H.; Bidleman, T. Endosulfan, a global pesticide: A review of its fate in the environment and occurrence in the Arctic. *Sci. Total Environ.* **2010**, *408*, 2966–2984.

(32) Stockholm Convention Secretariat. United Nations targets widely-used pesticide endosulfan for phase out. http://chm.pops.int/Convention/ThePOPs/tabid/673/Default.aspx (Accessed July 28th, 2011).

(33) Stockholm Convention Secretariat *Consideration of a newly proposed chemical, endosulfan, for inclusion in Annexes A, B or C of the Convention*; Stockholm Convention on Persistent Organic Pollutants: Geneva, 2007.

(34) Yeo, H.-G.; Choi, M.; Chun, M.-Y.; Sunwoo, Y. Concentration distribution of polychlorinated biphenyls and organochlorine pesticides and their relationship with temperature in rural air of Korea. *Atmos. Environ.* **2003**, *37*, 3831–3839.

(35) Yeo, H. G.; Choi, M.; Sunwoo, Y. Seasonal variations in atmospheric concentrations of organochlorine pesticides in urban and rural areas of Korea. *Atmos. Environ.* **2004**, *38*, 4779–4788.

(36) Stockholm Convention. *Secretariat Draft risk management evaluation on endosulfan*-Supporting Information 1; 2010.

(37) Liu, X.; Zhang, G.; Li, J.; Yu, L. L.; Xu, Y.; Li, X. D.; Kobara, Y.; Jones, K. C. Seasonal Patterns and Current Sources of DDTs, Chlordanes, Hexachlorobenzene, and Endosulfan in the Atmosphere of 37 Chinese Cities. *Environ. Sci. Technol.* **2009**, *43*, 1316–1321.

(38) Su, Y. S.; Hung, H. L.; Blanchard, P.; Patton, G. W.; Kallenborn, R.; Konoplev, A.; Fellin, P.; Li, H.; Geen, C.; Stern, G.; Rosenberg, B.; Barrie, L. A. A circumpolar perspective of atmospheric organochlorine pesticides (OCPs): Results from six Arctic monitoring stations in 2000−2003. *Atmos. Environ.* **2008**, *42*, 4682–4698.

(39) Weber, J.; Halsall, C. J.; Muir, D. C. G.; Teixeira, C.; Burniston, D. A.; Strachan, W. M. J.; Hung, H.; Mackay, N.; Arnold, D.; Kylin, H. Endosulfan and gamma-HCH in the Arctic: An assessment of surface seawater concentrations and air-sea exchange. *Environ. Sci. Technol.* **2006**, *40*, 7570–7576.

(40) Mackay, N.; Arnold, D. *Evaluation and interpretation of environmental data on endosulfan in Arctic regions. Report for Bayer CropScience*; Cambridge Environmental Assessments (CEA), Report number 107: Cambridge, U.K., 2005.

(41) Herrman, M. *Preliminary Risk Profile of Endosulfan*; Umweltbundesamt: Berlin, Germany, 2002.

(42) Pozo, K.; Harner, T.; Lee, S. C.; Wania, F.; Muir, D. C. G.; Jones, K. C. Seasonally Resolved Concentrations of Persistent Organic Pollutants in the Global Atmosphere from the First Year of the GAPS Study. *Environ. Sci. Technol.* **2009**, *43*, 796–803.

(43) Shen, L.; Wania, F. Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. *J. Chem. Eng. Data* **2005**, *50*, 742–768.

(44) Rice, C. P.; Chernyak, S. M.; Hapeman, C. J.; Biboulian, S. Air-water distribution of the endosulfan isomers. *J. Environ. Qual.* **1997**, *26*, 1101–1106.

(45) Schmidt, W. F.; Bilboulian, S.; Rice, C. P.; Fettinger, J. C.; McConnell, L. L.; Hapeman, C. J. Thermodynamic, spectroscopic, and computational evidence for the irreversible conversion of beta- to alpha-endosulfan. *J. Agric. Food Chem.* **2001**, *49*, 5372–5376.

(46) Walse, S. S.; Shimizu, K. D.; Ferry, J. L. Surface-Catalyzed Transformations of Aqueous Endosulfan. *Environ. Sci. Technol.* **2002**, *36*, 4846–4853.

(47) Li, H.; Tyler Mehler, W.; Lydy, M. J.; You, J. Occurrence and distribution of sediment-associated insecticides in urban waterways in the Pearl River Delta, China. *Chemosphere* **2011**, *82*, 1373–1379.

(48) Xue, N.; Xu, X.; Jin, Z. Screening 31 endocrine-disrupting pesticides in water and surface sediment samples from Beijing Guanting reservoir. *Chemosphere* **2005**, *61*, 1594–1606.

(49) Kitada, Y.; Kawahata, H.; Suzuki, A.; Oomori, T. Distribution of pesticides and bisphenol A in sediments collected from rivers adjacent to coral reefs. *Chemosphere* **2008**, *71*, 2082–2090.

(50) Racke, K. D.; Lubinski, R. N.; Fontaine, D. D.; Miller, J. R.; McCall, P. J.; Oliver, G. R. Comparative Fate of Chlorpyrifos Insecticide in Urban and Agricultural Environments. In *Pesticides in Urban Environments*; American Chemical Society: Washington, DC, 1993; Vol. 522, pp 70−85.

(51) Yoshida, S.; Taguchi, S.; Hori, S. Chlorpyrifos and S-421 residues in indoor air and polished rice around nine years after application for termite control. *J. Soc. Indoor Environ. Japan* **2004**, *7*, 7–15.

(52) Kale, S. P.; Carvalho, F. P.; Raghu, K.; Sherkhane, P. D.; Pandit, G. G.; Mohan Rao, A.; Mukherjee, P. K.; Murthy, N. B. K. Studies on degradation of ^{14}C-chlorpyrifos in the marine environment. *Chemosphere* **1999**, *39*, 969–976.

(53) Phillips, P. J.; Ator, S. W.; Nystrom, E. A. Temporal Changes in Surface-Water Insecticide Concentrations after the Phaseout of Diazinon and Chlorpyrifos. *Environ. Sci. Technol.* **2007**, *41*, 4246–4251.

(54) Chernyak, S. M.; Rice, C. P.; McConnell, L. L. Evidence of currently used pesticides in air, ice, fog, seawater and surface microlayer in the Bering and Chukchi seas. *Mar. Pollut. Bull.* **1996**, *32*, 410–419.

(55) USEPA. *Interim Reregistration Eligibility Decision for Chlorpyrifos*; Office of Prevention, Pesticides Protection and Toxic Substances, United States Environmental Agency: Washington DC, 2006; 260 pp.

(56) Yao, Y.; Ma, J.; Tuduri, L.; Blanchard, P. Sources and Occurrence of Dacthal in the Canadian Atmosphere. *Environ. Sci. Technol.* **2006**, *41*, 688–694.

(57) Coscollà, C.; Colin, P.; Yahyaoui, A.; Petrique, O.; Yusà, V.; Mellouki, A.; Pastor, A. Occurrence of currently used pesticides in ambient air of Centre Region (France). *Atmos. Environ.* **2010**, *44*, 3915–3925.

(58) Brun, G. L.; MacDonald, R. M.; Verge, J.; Aube, J. Long-term atmospheric deposition of current-use and banned pesticides in Atlantic Canada; 1980−2000. *Chemosphere* **2008**, *71*, 314–327.

(59) OSPAR. *Background Document on Dicofol*; OPSAR Comission, 2002.

(60) Carroll, J.; Savinov, V.; Savinova, T.; Dahle, S.; McCrea, R.; Muir, D. C. G. PCBs, PBDEs and pesticides released to the Arctic ocean by the Russian rivers Ob and Yenisei. *Environ. Sci. Technol.* **2008**, *42*, 69–74.

(61) Fujii, Y.; Haraguchi, K.; Harada, K. H.; Hitomi, T.; Inoue, K.; Itoh, Y.; Watanabe, T.; Takenaka, K.; Uehara, S.; Yang, H.-R.; Kim, M.-Y.; Moon, C.-S.; Kim, H.-S.; Wang, P.; Liu, A.; Hung, N. N.; Koizumi, A. Detection of dicofol and related pesticides in human breast milk from China, Korea and Japan. *Chemosphere* **2011**, *82*, 25–31.

(62) Yang, X.; Wang, S.; Bian, Y.; Chen, F.; Yu, G.; Gu, C.; Jiang, X. Dicofol application resulted in high DDTs residue in cotton fields from northern Jiangsu province, China. *J. Hazard. Mater.* **2008**, *150*, 92–98.

(63) Qiu, X.; Zhu, T.; Yao, B.; Hu, J.; Hu, S. Contribution of Dicofol to the Current DDT Pollution in China. *Environ. Sci. Technol.* **2005**, *39*, 4385–4390.

(64) Bidleman, T. F.; McConnell, L. L. A review of field experiments to determine air-water gas exchange of persistent organic pollutants. *Sci. Total Environ.* **1995**, *159*, 101–117.

(65) Liss, P. S.; Slater, P. G. Flux of gases across air-sea interface. *Nature* **1974**, *247*, 181–184.

(66) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley and Sons: Hoboken, NJ, 2003.

(67) Bruhn, R.; Lakaschus, S.; McLachlan, M. S. Air/sea gas exchange of PCBs in the southern Baltic Sea. *Atmos. Environ.* **2003**, *37*, 3445–3454.

(68) Lohmann, R.; Gioia, R.; Jones, K. C.; Nizzetto, L.; Temme, C.; Xie, Z.; Schulz-Bull, D.; Hand, I.; Morgan, E.; Jantunen, L. Organochlorine Pesticides and PAHs in the Surface Water and Atmosphere of the North Atlantic and Arctic Ocean. *Environ. Sci. Technol.* **2009**, *43*, 5633–5639.

(69) Kohl, S.; Rice, C.; Grebmeier, J.; Chernyak, S.; Sauer, J. *Results of the fourth Joint U.S.- Russian Bering and Chukchi Seas Expedition (BERPAC): summer 1993*; U.S. Fish and Wildlife Service, 2010.

(70) McConnell, L. L.; Nelson, E.; Rice, C. P.; Baker, J. E.; Johnson, W. E.; Harman, J. A.; Bialek, K. Chlorpyrifos in the Air and Surface Water of Chesapeake Bay: Predictions of Atmospheric Deposition Fluxes. *Environ. Sci. Technol.* **1997**, *31*, 1390–1398.

(71) Rawn, D. F. K.; Muir, D. C. G. Sources of Chlorpyrifos and Dacthal to a Small Canadian Prairie Watershed. *Environ. Sci. Technol.* **1999**, *33*, 3317–3323.

(72) Li, Y. F.; Macdonald, R. W.; Jantunen, L. M. M.; Harner, T.; Bidleman, T. F.; Strachan, W. M. J. The transport of β-hexachlorocyclohexane to the western Arctic Ocean: a contrast to α-HCH. *Sci. Total Environ.* **2002**, *291*, 229–246.

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