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Interactive comment on "Transport and fate of hexachlorocyclohexanes in the oceanic air and surface seawater" *by* Z. Xie et al.

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We are pleased that all three reviewers agree that the manuscript is sound and delivers new and significant data set of various HCH isomers along Atlantic transect from Germany to the Antarctic. The positive and insightful comments on the methodology applied, the scientific discussion and the conclusions on regional and temporal trends of this important class of legacy pollutants, encourage us to improve the manuscript according to all suggestions. All the comments and suggestions from Dr. Lohmann

(R1), Dr. Dachs (R2) and the anonymous referee (R3) will be taken into account in the final revised version of the manuscript. Below we have compiled our responses, and we hope the revised version will be considered as responsive to the concerns of three reviewers and suitable for publication in Biogeosciences. Comment 1 R1: "I disagree that b-HCH displays a multi-hopper transport behaviour just because it displays air-water exchange gradients that are either favoring deposition or volatilization" this conclusion was removed from the abstract to avoid any misunderstanding. Comment 2 R1: "G-HCH in the gas-phase showed declining concentrations compared to other studies – this is not apparent from the range of concentrations reported here. Refer to a figure or table with exact data or better argue by focusing on specific regions where data can be compared!" A Table for the data of α-, γ- and β-HCH in air and water in the ocean environment was added into the manuscript to support the discussion (Table 3). Comment 3 R1 and R2: "Not sure how the wide range of data can be used to support a 'homogenous distribution' of atmospheric HCHs." We actually want to highlight the similar distribution patterns of HCHs in both Atlantic and Pacific Ocean in the Northern Hemisphere, which may be resulted from historical application of technical HCHs and lindane. Anyway the sentence is deleted from the manuscript. comment 4 R1: "the concept of cold condensation is used here again to explain increasing concentrations of α- and γ-HCH with increasing latitude N and S. yet later in the manuscript (p.5546), the authors argue, probably correctly, that increasing concentrations of HCHs in the SH are linked to Ocean currents from the Indian Ocean, hence not global distillation! Also note that the r2 value for a-HCH is strong, but rather weak for g-HCH, suggesting that latitude is not a sufficient proxy to explain trends!" R2: "Even though the term "Cold condensation" has been used in the literature, it is false that HCHs, and other POPs, undergo cold condensation and we understand condensation as a term from thermodynamics. Condensation occurs when the gas phase concentrations are higher than their vapor pressures, and this never happens in environmental conditions. It is better to use the "cold trapping" term, when referring to the fact that at low temperatures partitioning to water is favored." As the R2 suggested we changed from cold

condensation to cold trapping in the context of this manuscript. The cold trapping of HCHs towards to high latitudes have been clearly illustrated both in this present work and in the ref. (Lohmann et al. 2009). However, with the global warming processes, especially in the retreat of sea ice and melting of snow pack in the Polar Regions, the globe fate of some kind of POPs may change. The retreat of sea ice and melting of snow pack would lead to the enhanced release of HCHs trapped in ice sheets to the Southern Ocean. Moreover, technical HCH, has been used as insecticides since 1943. Usage of technical HCH was banned in most western countries and Japan in the 1970s but continued in China and Russia until 1983 and 1990. In 1990, India also banned technical HCH for agricultural use but kept it for public health uses (Li, 1998, Wu et al., 2010). It is assumed that release of HCH from India, China and other developing Asian and African countries may distribute into the Pacific and Indian Ocean and be transported with Ocean current. Therefore, we assumed that the elevated HCH level in the Southern Ocean should be resulted from both global distillation and the additions of Antarctic release and ocean current from Indian Ocean. However the contributions of HCHs from different ocean currents should be further demonstrated by the vertical profile in the Southern Ocean. Comment 5 R1: "There is no temporal trend for b-HCH available?" as data of β-HCH are very limited, the temporal trend of β-HCH is not discussed in this manuscript. Comment 6 R1: "Is there really sufficient biomass present in the tropical Atlantic to significantly deplete HCHs in the water column via particle settling? I suggest you retrieve average TOC values, and using a BCF approach estimate what fraction of HCHs can be removed. I assume this fraction is rather small." In this cruise we have achieved good data to support deplete HCHs in water column via biomass blooming. Unfortunately, we could not detect HCHs in the particle phase (water filter sample). We though that the extraction might be insufficient when the water filter is wet. We are going to test other extraction method for the determination of HCHs in water filters. Hopefully we can address this open question with another expedition cruise carried out in winter 2010. Comment 6 R1: "an uncertainty of 0.2 is used here for H, while in the section above, Bruhn et al is cited, and used, who suggest

that overall uncertainty of air-water exchange is closer to a factor of 3, mostly driven by uncertainty of H values" the uncertainty of 0.2 for H adopted in this work is an estimated from an experimental value determined by Sahsuvar et al. (Sahsuvar et al., 2003). We used this uncertainty to calculate the propagation uncertainty of air-water exchange flux. While Bruhn et al. (2003) suggested that an overall uncertainty for air-water direction estimation is closer to a factor of 3, which is a good value even for those compounds with unknown H values. We often refer the factor of 3 for evaluate the air-water exchange directions (Xie et al., 2011, Lohmann et al., 2009). Comment 7 R1: "maybe better reference either a textbook or early papers as part of the two-film model calculations here." R2: No information is given on the estimation methods of Kol. For example there are several correlations used to estimate the influence of wind speed, or for example, averaging wind speeds introduce an error in the final estimates. The exact correlations used for Kol estimation should be shown in the supplementary material; it is not enough to cite a couple of references." Add ional information has been added into the manuscript for the terms and the references. Comment 8 R2: "Please, be explicit when discussing the trends. It is not clear when you are discussing trends of gas-phase concentrations and when you are referring to dissolved phase concentrations. Improve the sentence in lines 18-21. I agree that the biological pump (sorption to particles and settling) could explain, in part, the decrease of concentrations in regions with high primary productivity. To estimate this is difficult because the particle-water and plankton-water partitioning coefficients are poorly constrained for the marine environment. However, in addition to settling, degradation (bacterial, photodegradation, by zooplankton) may play an important role. Recently, Berrojalbiz et al. (Environ. Sci. Technol. 45, 4315-4322, 2011) has found strong evidence that degradation plays a role explaining the lower concentrations of HCH in regions with higher biomass, Even though Berrojalbiz et al. (2011) focus on concentrations in plankton, it may also be true for water column dissolved concentrations. In fact, I think that the conclusions of Berrojalbiz et al. concerning HCH are consistent with the results and discussion shown here." The sentence is revised and the literature is cited in the manuscript. Indeed, the

study just conducted by Berrojalbiz et al. (Environ. Sci. Technol. 45, 4315-4322, 2011) has shown a good evidence for biogeochemical process of POPs in the marine environment. It is a good example for our current studies on HCHs and other emerging organic contaminants in global Ocean. Comment 9 R2: “last sentence. Again, I don’t agree that there is evidence of river influence. Of course rivers influence the dissolved concentrations very close to the coast, but usually their influence is not relevant at open sea waters for semivolatile compounds. This is due to dilution, but also due to strong volatilization fluxes of POPs from coastal waters. The authors need to support further their sentence or delete it. As there are no data available for input source of HCHs from rivers to the open Atlantic, river influence was phased out from this manuscript. Comment 10 R3, R2, R1: “The author should use consistent significant figure in the manuscript. e.g. P5538 Line9,11,18;P5542 Line13,18,21,22;....and Table1. I suggest the author use 2 significant figures all over the paper.” We revised the numbers with 2 significant figures through over the paper. Technical comments R1, R2, R3: We addressed all smaller concerns of three reviewers as well as technical comments, e.g. rephrasing, references, figure adaptions and English editing in the final revised version.

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