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α-HCH enantiomer fraction (EF): A novel approach to calculate the ventilation age of water in the Arctic Ocean?

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[1] α-HCH (hexachlorocyclohexane) and the enantiomeric fraction (EF) of its mirror-image isomers have been determined for water column profiles in the southern Beaufort Sea in 2004 and 2007. Using estimated rates of metabolic degradation, we have applied a simple kinetic model to convert the observed EFs to apparent ventilation ages of the water masses in the study region. We found an age of 1.7 ± 0.1 years for the Polar Mixed Layer (PML), 6.6 ± 0.6 for the core of the Pacific Layer centered at salinity 33.1, and 21.7 ± 0.5 years for the core of the Atlantic Layer identified by a Tmax of ~0.5°C. These ages are in reasonable accord with other methods used to date water masses in the Arctic Ocean suggesting that α-HCH has an unexploited potential as a dating tool.

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1. Introduction

[2] In a manner and quantity closely paralleling CFC-11, ~10 Mt of α-hexachlorocyclohexane (α-HCH) was released to the environment between 1948 and 1997 as a constituent of technical HCH, a broad-spectrum pesticide [*Li and Macdonald*, 2005]. When produced, α-HCH consists of two mirror-image enantiomers, (+) and (−), in equal proportion (i.e., racemic). An enantiomer ratio [ER = (+) α-HCH/(−) α-HCH] differing from 1, or an enantiomer fraction [EF = ER/(ER + 1)] differing from 0.5 indicates bacterial degradation [*Hühnerfuss et al.*, 1992]. Bacterial degradation has been shown to be a major removal route of α-HCH within the Arctic Ocean [*Harner et al.*, 2000; *Macdonald et al.*, 2000], and the sum of bacterial and hydrolytic degradation rates established for the eastern Arctic Ocean [*Harner et al.*, 1999] predict decreases in inventories in different water masses in the western Arctic Ocean between 1993 and 2010 very well, within 10% error from the measured values [*Pućko et al.*, 2012]. In general, a relatively small fraction of α-HCH present in seawater will be adsorbed to suspended particulate matter, making this transfer route negligible. *Tanabe and Tatsukawa* [1983] report this fraction to be <3% for the western Pacific, Eastern Indian and Antarctic Oceans. In the Arctic, α-HCH is present in particulate phases of air, snow, ice and seawater in trace amounts which usually means below limits of quantification defined as 10 Standard Deviations of the blank [*Hargrave et al.*, 1988; *Jantunen and Bidleman*, 1996].

[3] The Arctic Ocean is strongly stratified by ~3300 km^3/year of freshwater runoff, and in the western Arctic Ocean by the additional density contrast between Pacific water (salinity of ~33) and Atlantic water (~35) [*McClelland et al.*, 2012]. Stratification during winter in the Beaufort Sea is evident as Polar Mixed Layer (PML) in the top 30–50 m, waters of predominantly Pacific origin between 50 and 230 m (a mode water centered at salinity 33.1), and waters of predominantly Atlantic origin deeper than 230 m (Atlantic Layer (AL)) [*Macdonald et al.*, 1989; *Lansard et al.*, 2012].

[4] Given the distances of transport to the Beaufort Sea and the means by which different tracers enter the Arctic Ocean, the transport times indicated by ventilation tracers, e.g., CFCs [*Wallace and Moore*, 1985; *Smethie et al.*, 2000], fallout products, e.g., ^{3}H/^{3}He [*Ekwurzel et al.*, 2001] and nuclear reprocessing plant radionuclides, ^{129}I, ^{137}Cs [*Smith et al.*, 1998], differ. Here, we evaluate the potential for α-HCH to provide another means to estimate transport timescales within the Arctic Ocean.

2. Material and Methods

2.1. α-HCH EF: Field Sampling and Laboratory Analysis

[5] Water column samples were collected from CCGS *Amundsen* in the southern Beaufort Sea and the Amundsen Gulf as part of the Canadian Arctic Shelf Exchange Study

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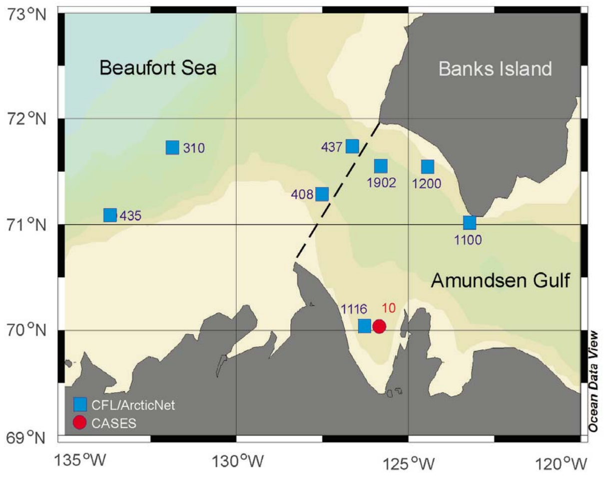

Figure 1. Location of sampling stations during CASES 2004 and CFL/ArcticNet 2007. Dashed line shows the border between the Beaufort Sea and the Amundsen Gulf defined by International Hydrographic Organization (IHO). Ocean Data View software from http://odv.awi.de.

(CASES; 2003–04) and the Circumpolar Flaw Lead system study/ArcticNet (CFL/ArcticNet; 2007–08) (Figure 1). Field sampling and laboratory procedures have been described in detail elsewhere [*Pućko et al.*, 2012]. Details of α-HCH EF determination have been previously presented by *Pućko et al.* [2010]. The average ± standard deviation (SD) of EFs for a racemic α-HCH standard was 0.501 ± 0.005, n = 20.

2.2. Water Salinity and Temperature Profiles

[6] Water temperature and salinity measurements were obtained from the SBE 911*plus* CTD profiler (Sea-Bird Electronics, Bellevue, USA) attached to a Rosette sampler. The accuracy of the conductivity, temperature, and depth measurements were 0.0003 S/m, 0.001°C, and 0.015 m, respectively.

2.3. Calculations

[7] The degradation rate constants for (+) and (−) α-HCH, based on ventilation ages of surface and deep waters in the Nansen Basin, were taken from *Harner et al.* [1999]:

$$(+)\ \alpha\text{-HCH}_1 = (+)\ \alpha\text{-HCH}_0 \cdot \exp^{-(kd1)t} \tag{1}$$

$$(-)\ \alpha\text{-HCH}_1 = (-)\ \alpha\text{-HCH}_0 \cdot \exp^{-(kd2)t}, \tag{2}$$

where (+) α-HCH$_1$ and (−) α-HCH$_1$ is the (+) and (−) α-HCH concentration after *t* years of degradation, (+) α-HCH$_0$ and (−) α-HCH$_0$ are the initial (+) and (−) α-HCH concentrations, *kd*1 and *kd*2 are degradation rate constants for (+) and (−) α-HCH, respectively (0.128 ± 0.006 and 0.041 ± 0.041) [*Harner et al.*, 1999], and *t* is time of degradation [years].

[8] Transforming equations (1) and (2) into

$$\begin{aligned}(+)\ \alpha\text{-HCH}_1/(-)\ \alpha\text{-HCH}_1 = {} & (+)\ \alpha\text{-HCH}_0 \cdot \exp^{-(kd1)t} \\ & /(-)\ \alpha\text{-HCH}_0 \cdot \exp^{-(kd2)t}\end{aligned} \tag{3}$$

and using the following equation [*Hühnerfuss et al.*, 1992]:

$$(+)\ \alpha\text{-HCH}/(-)\ \alpha\text{-HCH} = ER \tag{4}$$

we obtain

$$ER_1 = ER_0 \cdot \exp^{-(kd1-kd2)t} \tag{5}$$

thus

$$t = \ln(ER_1/ER_0)/-(kd1-kd2), \tag{6}$$

where ER_1 is the α-HCH enantiomer ratio after *t* years of degradation, ER_0 is the initial α-HCH enantiomer ratio, and ER = EF/(1 − EF).

3. Results and Discussion

3.1. α-HCH EF Vertical Profiles

[9] Following water mass designations given for the southern Beaufort Sea by *Macdonald et al.* [1989] and *Lansard et al.* [2012], we find a shallow PML (<50 m) at all stations, underneath which the 33.1 core depth varies from ~75 m to ~150 m (Figure 2). Beneath that, the AL core depths were at ~250–300 m (Figure 2b).

[10] Vertical profiles of α-HCH EFs are similar to one another and consistent between the CASES and CFL time periods (Figure 3 and Table 1). Even though α-HCH concentrations have declined in the PML by a factor of two between 2004 and 2007, the EF values have remained almost constant at ~0.45 (Figure 3a). Likewise, the deep EF values at ~200 m have remained at ~0.13. The offset between profiles, apparent at water depths between 50 and 150 m, can be assigned largely to the upward shift in the 33.1 core at this station from 150 m in 2004 to 75 m in 2007 (Figure 3a).

[11] The α-HCH EF values show a consistent decline going from surface water to depth, suggesting progressive degradation. Water in the PML has the opportunity to ventilate annually driving it toward the racemic EFs observed in Arctic air over ice-covered ocean [*Wong et al.*, 2011]. The average α-HCH EF for the water near the 33.1 core for both the CASES and CFL data was 0.361 ± 0.011 (SE), and at depths dominated by Atlantic water, the EFs declined from 0.132 ± 0.005 at the AL core (~280 m) to 0.085 at 340 m. Rapid decrease of EFs with depth below the PML reflects the limited capacity for mixing to occur between the stratified surface layer and the water below, and likewise limited mixing of 33.1 water with AL water due to the cold haloclines [*Macdonald and Bewers*, 1996].

3.2. α-HCH EF Tracer Age in the Beaufort Sea

[12] Using equation (6), the EF profiles imply an apparent ventilation age of 1.7 ± 0.1 years for the PML, 6.6 ± 0.6 years for the 33.1 core, and 21.7 ± 0.5 years for the AL core (Figure 4). For the PML, our value is in reasonable agreement with the ^{3}H/^{3}He estimates of 5 years for the eastern and <4 years for western Arctic Oceans made respectively by *Schlosser et al.* [1995] and *Ekwurzel et al.* [2001] (Figure 4). Over the Alpha Ridge, *Wallace and Moore* [1985] used CFC-11 and CFC-12 to estimate the ventilation age of PML water at <4 years. The nonzero age for PML water reflects restricted atmospheric exchange during winter when

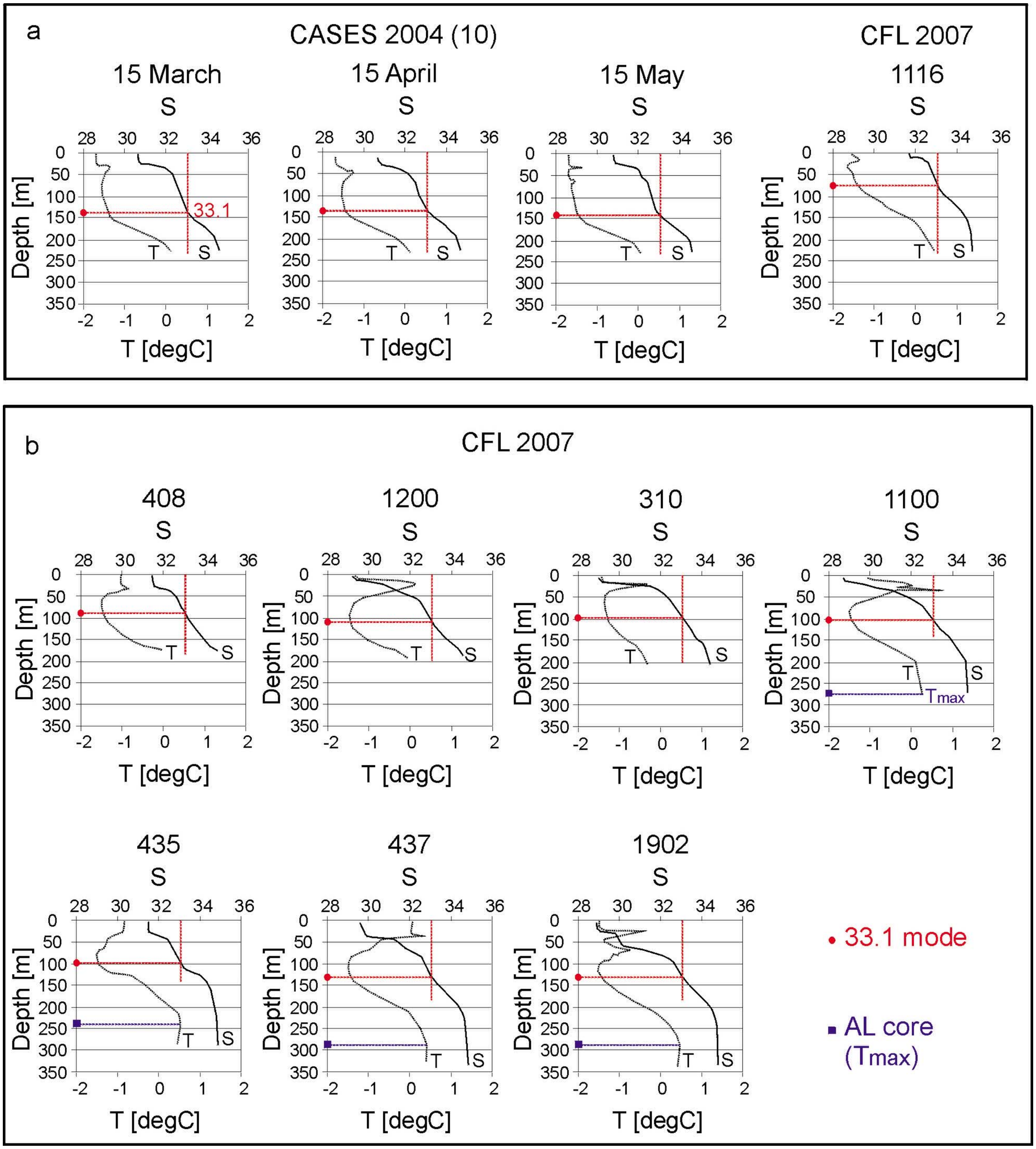

Figure 2. Vertical profiles of salinity (S) and temperature (T) with the 33.1 mode and AL core marked: (a) at two stations sampled in close geographic proximity in 2004 (St. 10, CASES) and 2007 (St. 1116, CFL) and (b) at other stations of increasing depth sampled in October–November 2007 (CFL).

the PML is forming. Likewise, stratification by sea-ice melt and runoff inhibits exchange with deeper portions of the PML in summer, as proposed by *Schlosser et al.* [1995].

[13] The 33.1 mode water has a residence time of approximately 10 years based on inventories and supply of runoff [*Macdonald et al.*, 2005], although it is becoming clear that that residence time is strongly affected by atmospheric forcing, which varies on the decadal scale [*Morison et al.*, 2012]. The HCH EF data yield a range of ages from 2 to about 20 years old (Figure 4), probably reflecting a central value near 10–15 years mixing with more recently ventilated water above and aged water below. *Ekwurzel et al.* [2001] provide $^{3}H/^{3}He$ tracer ages for the Pacific layer ranging from 2 to about 10–14 years at 230 m

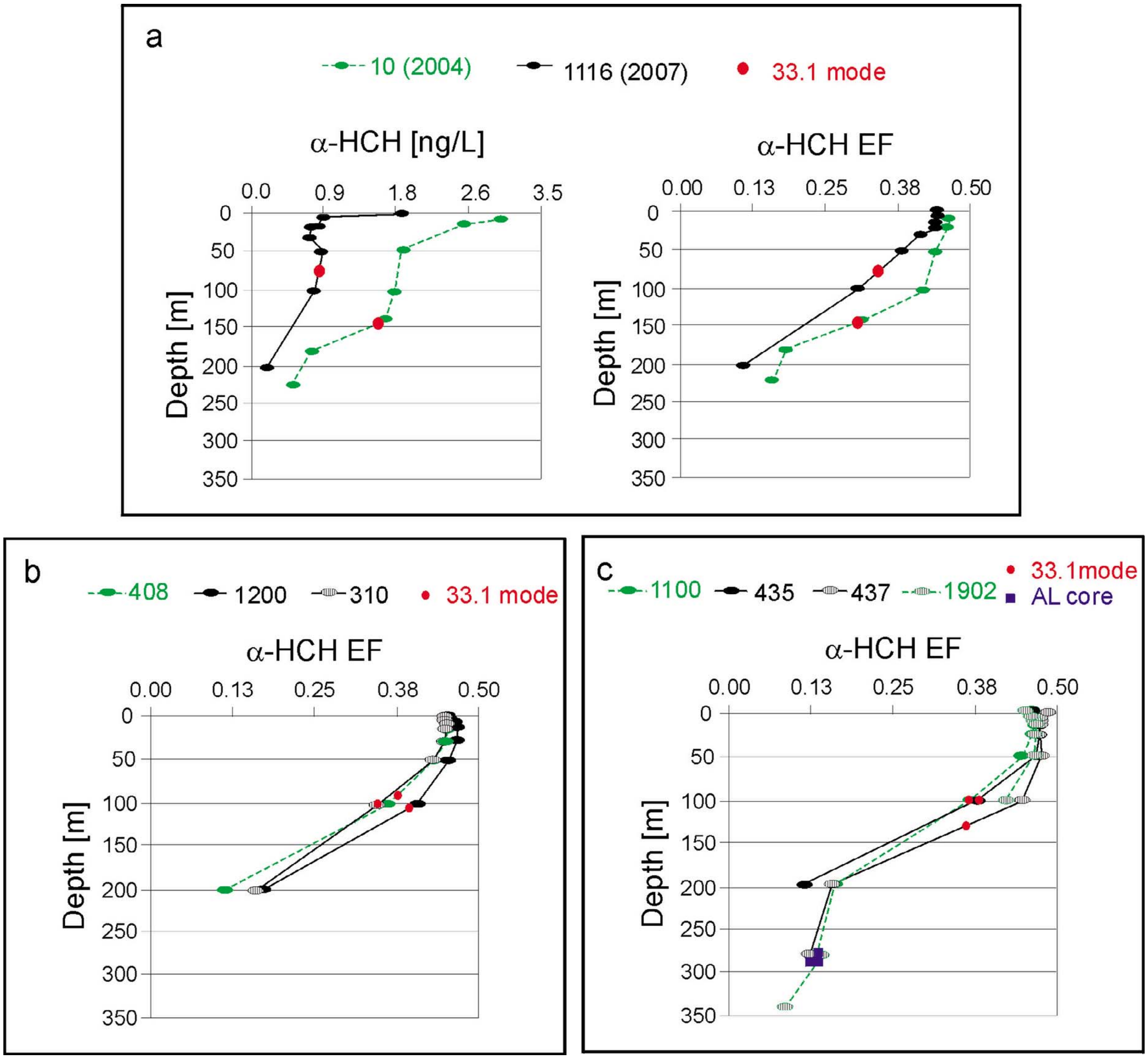

Figure 3. (a) Vertical profiles of α-HCH concentration and EF at two stations sampled in close geographic proximity in 2004 (St. 10, CASES) and 2007 (St. 1116, CFL). Vertical profiles of α-HCH EF (b) at shallower stations sampled in October–November 2007 (CFL) with only 33.1 mode water defined and (c) at deeper stations with both 33.1 mode and AL core present. α-HCH concentration in Figure 3a after *Pućko et al.* [2012].

in the western Arctic Ocean, which agrees with the CFC ages of 4 to 14 years over the Alpha Ridge [*Wallace and Moore*, 1985].

[14] The estimated transit time of AL water to the Beaufort Sea from where it last was in contact with the atmosphere in the Barents and Greenland Seas, is 15 years or longer [*Smith et al.*, 1998; *Macdonald et al.*, 2005]. The HCH EF data imply a similar AL core age of ~22 years. In contrast, water in the AL over the Alpha Ridge had an apparent age of >30 years based on CFC measurements [*Wallace and Moore*, 1985]. It seems likely that the AL at the southern margin of the Beaufort Sea is supplied by boundary currents that follow a pathway along the slopes of the Eurasian margin. This transport pathway, illuminated by reprocessing-plant ^{129}I-^{137}Cs [*Smith et al.*, 2011], takes less time (~20 years) to arrive at our location than at the CESAR camp site over the Alpha Ridge.

3.3. Using α-HCH EF as a Tracer of the Water Ventilation Age

[15] As shown here, a reliable estimate for metabolic rate of selective degradation of HCH presents an opportunity to use EFs to determine the length of time that has elapsed since the HCH freely exchanged with a racemic atmosphere. The benefit of using EF as a dating tool is that this term responds to degradation kinetics in a way that is insensitive to initial α-HCH concentration (Figure 5). However, two assumptions are necessary: (1) ventilated water assumes a racemic EF before it subducts and (2) subducted HCH is subject to constant metabolic rate. The first assumption appears reasonable given that atmospheric α-HCH EFs were observed to be uniformly racemic spatially and temporally prior mid-1990s, and the net exchange of HCH in the polar ocean was strongly into the surface water due to high use

Table 1. Vertical Profiles of α-HCH Enantiomer Fraction (EF) Measured in 2004 (CASES) and 2007 (CFL) in the Beaufort Sea and the Amundsen Gulf[a]

	α-HCH EF														
	CASES 2004 (Station 10)					CFL 2007									
Depth (m)	15–31 Mar	1–30 Apr	1–15 May	Mean	SE	11 Oct St.310	16 Oct St.435	20 Oct St.437	22 Oct St.408	26 Oct St.1100	28 Oct St.1116	31 Oct St.1200	3 Nov St.1902	Mean	SE
PML															
0	n/a	n/a	n/a	n/a	n/a	0.468	0.465	0.488	0.454	0.458	0.446	0.452	0.452	0.460	0.005
5	0.462	0.465	n/a	0.464	0.002	0.470	0.473	0.474	0.456	0.475	0.448	0.466	0.471	0.467	0.003
7.5	n/a	n/a	n/a	n/a	n/a	0.472	0.460	0.466	0.452	0.466	0.453	0.465	0.459	0.462	0.002
10	n/a	n/a	n/a	n/a	n/a	0.482	0.466	0.471	0.460	0.474	0.441	0.468	0.469	0.466	0.004
15	n/a	0.464	0.463	0.464	0.001	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
25	n/a	n/a	n/a	n/a	n/a	0.468	0.471	0.466	0.451	0.465	0.418	0.467	0.464	0.459	0.006
PL															
50	0.449	n/a	0.437	0.443	0.006	0.451	0.467	0.478	0.433	0.447	0.385	0.454	0.468	0.448	0.010
100	0.421	0.421	0.430	0.424	0.003	0.345	0.378	0.446	0.362	0.369	0.307	0.409	0.422	0.380	0.016
140	n/a	0.316	n/a	0.316	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
180	0.183	n/a	n/a	0.183	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
200	n/a	n/a	n/a	n/a	n/a	0.161	0.114	0.154	0.113	0.159	0.110	0.172	n/a	0.140	0.010
220	n/a	0.174	0.143	0.158	0.015		n/a	n/a		n/a			n/a	n/a	n/a
AL															
280								0.124		0.131			0.141	0.132	0.005
340													0.085	0.085	n/a

[a] Here n/a, not available; SE, standard error of the mean; PML, Polar Mixed Layer; PL, Pacific Mode Layer; AL, Atlantic Layer.

[e.g., *Li and Macdonald*, 2005]. Following curtailment of use, the atmosphere has begun to reflect surface water values (0.476 ± 0.010 in the Beaufort Sea) in the spring and summer months signaling net evasion of α-HCH back to the atmosphere [*Wong et al.*, 2011]. For the second assumption, we know the Arctic Ocean provides a unique setting where water is cold and practically isothermal (~0 ± 2°C), although temperatures as high as 4–5°C may be found at the core of the West Spitsbergen Current [*Swift et al.*, 1997]; this, we speculate, results in a nearly constant metabolic rate.

3.4. Uncertainties of the α-HCH EF Tracer Age Estimate

[16] The EF measurements can be made to ±1%, and kd1 and kd2 are reported to be within ±5% and ±100%, respectively [*Harner et al.*, 1999]. Uncertainty in the α-HCH EF water ventilation age is due almost entirely to uncertainty in kd2, and was determined to propagate a 48% error to age determined using equation (6). This error is comparable with the 40–50% error determined for the ^{3}H/^{3}He method [*Schlosser et al.*, 1994; *Ekwurzel et al.*, 2001]. Comparing it to ages estimated using other tracers (CFCs, ^{129}I, ^{137}Cs) is not possible as they involve visual estimation techniques and only uncertainties of the tracer measurements are available in the literature [e.g., *Smith et al.*, 1998].

[17] The insensitivity to α-HCH starting concentrations makes this method appealing. However, the EF will introduce error where there is exceptional mixing between water masses. For example, at 80 m (~50% mixture of PML and 33.1 water) or 220 m (~15% of PML and ~42% of 33.1 and AL water) [*Macdonald et al.*, 1989], a different age will be

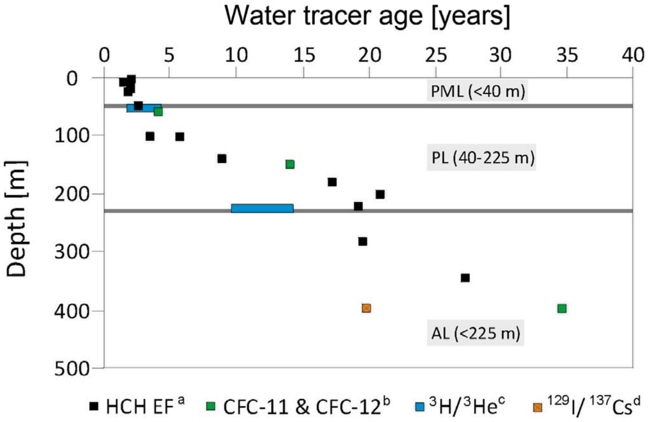

Figure 4. Tracer age of water in the Beaufort Sea and the western Arctic Ocean estimated in this study based on α-HCH EF profiles and in previous studies using CFC-11 and CFC-12 [*Wallace and Moore*, 1985], ^{3}H/^{3}He [*Ekwurzel et al.*, 2001], and ^{129}I/^{137}Cs [*Smith et al.*, 2011]. Footnotes: a, this study; b, *Wallace and Moore* [1985]; c, *Ekwurzel et al.* [2001]; d, *Smith et al.* [2011].

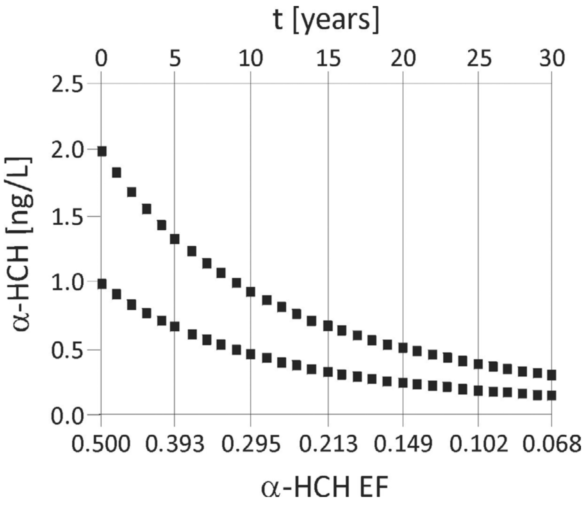

Figure 5. The influence of α-HCH starting concentration on α-HCH EF reached after 1–30 years of degradation.

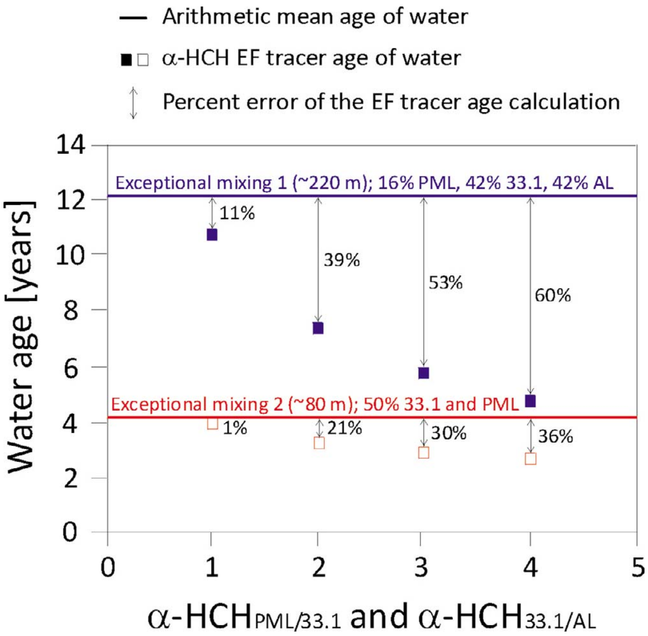

Figure 6. Arithmetic mean age and α-HCH EF tracer age of water at exceptional mixing depths in the Beaufort Sea (~80 and ~220 m) as a function of increasing α-HCH concentration ratio in the PML to 33.1 mode water (α-HCH$_{PML/33.1}$) and 33.1 water to AL (α-HCH$_{33.1/AL}$).

determined depending on whether it is calculated as the arithmetic mean of ages of input core layers or estimated by applying equation (6) to the mixed EF value (Figure 6). The offset between these two methods depends on the contrast between α-HCH concentrations and is greater for the 220 m depth than for the 80 m depth (Figure 6).

3.5. Constraints of the α-HCH EF Tracer Age Estimate Application

[18] Conceptually, chiral signatures of many chemicals exhibiting 'handedness' have the potential to provide an estimation of ventilation age as illustrated here using the example of α-HCH. In the case of α-HCH, we are fortunate in possessing a substantial data set for the Arctic Ocean, sufficient to propose a budget where known major sources and sinks plausibly account for inventories of α-HCH over time, together with age estimates for water masses based on several different tracers applied over the past two decades. Furthermore, the Arctic Ocean has the substantial advantage of almost isothermal water masses below the PML, and exceptionally weak export fluxes of labile carbon from the euphotic zone. Here, we have applied α-HCH as a 'chiral clock' by implementing bacterial degradation rates established by *Harner et al.* [1999] who used α-HCH data together with ventilation age estimates for a profile collected in the eastern Arctic. Bacterial degradation rates for α-HCH by *Harner et al.* [1999] are, to our knowledge, the only appropriate estimates in the literature; that is, they most closely match the circumstances of our data. Using degradation rates based on tracer ventilation age of water at different depths scales the α-HCH 'chiral clock' so as to show ages similar to the ones established by those tracers; another factor limiting application of this method in its current form to the Arctic Ocean. A refinement to using α-HCH EF as an independent tracer of ventilation age would require development of accurate, independent α-HCH bacterial degradation rate constants. Future research will hopefully expand on the concept presented herein by measuring a number of age tracers simultaneously with target chiral compounds, thereby providing the means to validate modeled results based on enantiomer fractions.

[19] **Acknowledgments.** We thank the crew of CCGS *Amundsen* for the field work assistance. We also thank Joanne DeLaronde, Allison MacHutchon, Paul Helm, and Debbie Armstrong for collecting the samples. We acknowledge the Canadian program office of the International Polar Year, the Natural Sciences and Engineering Research Council (NSERC), Canada Foundation for Innovation (CFI), Canada Research Chairs (CRC), Canada Excellence Research Chairs (CERC), the Department of Fisheries and Oceans Canada, ArcticNet, Centre for Earth Observation Science, and the University of Manitoba for funding.

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