Supporting Information

Spatial Distributions of DDTs in the Water Masses of the Arctic Ocean

Daniel Carrizo[‡*], Anna Sobek[†], Joan A. Salvadó[†], Örjan Gustafsson[†]

[‡] Astrobiology Centre (INTA-CSIC), Dept. of Planetology and Habitability, Torrejón de Ardóz 28850, Madrid, Spain

[†]Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, 10691 Sweden

***Corresponding Author**

Tel: +34 915206433, Fax +34 915201074, E-mail: dcarrizo@cab.inta-csic.es, carrizodan@gmail.com

Oceanographic Setting

The oceanic surface water in the Arctic Ocean is characterized by a large clockwise Beaufort Gyre, (around 80ºN 150ºW) over the Canadian Basin, and the Transpolar Drift beginning in the East Siberian Sea/Laptev Sea, which moves across the CAOB and the North Pole area (Figure 1) (1). Pacific waters coming through the Bering Strait and moves across the Eurasian Basin of the CAOB, follow the Transpolar Drift, while the North Atlantic water enters through the Fram Strait (NW Spitsbergen current) and Barents Sea (St. Anna Trough). The Beaufort Gyre can trap large quantities of water and freshwater (2). The AtWL follow the movement along the continental margins and the ridges with a cyclonic circulation around the Arctic Ocean; although, the ArDWL has no direct contact with the surrounding oceans and its movement and replacement could take several hundred years (1).

Sample Analysis.

Samples were spiked with a surrogate standard (^{13}C-labeled PCB-180) and extracted by Soxhlet for 24 h with toluene (glass-distilled quality; Burdick&Jackson, Fluka Chemie AG, Buchs, Switzerland) using a Dean-Stark trap for collection of water. The use of PCB-180 as internal standard of OCPs was previously tested and used in other studies (3-5). The extracts were eluted on an open silica column prior to further cleanup and HPLC separation on an amino column (µBondapak NH_2, 7.8x300mm; Waters Corporation, Milford, MA). The OCP fraction was thereafter eluted on an open column containing three layers of modified silica (SiO_2/H_2-SO_4 10mm, SiO_2/KOH 10mm, and SiO_2/H_2O 10mm).

The instrumental analytical conditions for OCP analyses are described elsewhere (3,4). Briefly, sample aliquots (1 µL) were injected into a gas chromatograph coupled to a mass spectrometer (Trace DSQ instrument from Thermo Scientific, TX, USA)

operating in negative ion chemical ionization mode (NICI). Samples were injected in splitless mode onto a 60 m x 0.25 mm I.D. DB-5 column (J&W Scientific, Folsom, CA, USA) coated with 5% diphenyl-polydimethylsiloxane (film thickness 0.25 µm). Helium was used as carrier gas at a flow of 1.5 mL min^{-1} during GC-NICI-MS analyses. Ammonia was used as buffer gas at a flow of 1.75 mL min^{-1}. The temperature programme ranged from 90°C (held for 2 min) to 140°C at 20°C min^{-1}, then to 200°C (held for 13 min) at 4°C min^{-1} and finally to 310°C (held for 10 min) at 4°C min^{-1}. Injection temperature was 250°C. Ion source and transfer line temperatures in GC-NICI-MS were 176°C and 280°C, respectively.

References

1. Stein, R.; Macdonald, R. W. *The Organic Carbon Cycle in the Arctic Ocean*. Springer Berlin Heidelberg. Germany., 2004.

2. Proshutinsky, A.; Krishfield, R.; Timmermans, M.-L.; Toole, J.; Carmack, E.; McLaughlin, F.; Williams, W. J.; Zimmermann, S.; Itoh, M.; Shimada, K., Beaufort Gyre freshwater reservoir: State and variability from observations. *Journal of Geophysical Research-Oceans* **2009,** *114*.

3. Grimalt, J.O.; Howsam, M.; Carrizo, D.; Otero, R.; Rodrigues de Marchi, M.R.; Vizcaino, E. Integrated analysis of halogenated organic pollutants in sub-millilitre volumes of venous and umbilical cord blood sera. *Analitical and Bioanalytical Chemistry* **2010**, *396*, 2265–2272.

4. Carrizo, D.; Grimalt, J.O. Physical-chemical and Maternal Determinants of the Accumulation of Organochlorine Compounds in Four-Year-Old Children. *Environmental Science & Technology* **2006**, *40*, 1420-1426.

5. Salvadó, J.A.; Grimalt, J.O.; López, J.F. Rapid and simplified method for the quantitative analysis of polycyclic aromatic hydrocarbons, lipid biomarkers and organochlorine compounds in marine settling particles. *Microchimica Acta*, **2012**, 179, pp 131-139.

Table S1. General characteristiscs of sampling stations at the expeditions AO-01, Beringia-05 and ISSS-08

Sample ID	Position start		Position end		Volume	Salinity	Temp	HS
	Lat	Long	Lat	Long	(L)	(‰)	(ºC)	(µg/QSe L^{-1})
AO-01-1	62.1	4.6	63.5	6.6	1079	33.2	10.8	1.3
AO-01-2	66.4	10.3	68.6	14.0	972	33.8	10.3	0.9
AO-01-4	77.5	29.5	77.5	29.7	1137	33.5	-1.6	0.3
AO-01-5	78.2	27.2	78.2	27.3	701	33.2	-1.5	0.4
AO-01-6	78.4	33.1	78.4	33.8	1136	33.0	0.1	0.4
AO-01-7	80.3	15.5	80.3	15.3	628	34.2	3.4	0.3
AO-01-8	80.3	11.6	80.6	20.2	335	34.6	3.6	nd
AO-01-9	81.2	24.2	-	-	1476	32.9	-1.2	0.1
AO-01-10	82.3	25.6	81.6	26.2	2645	34.3	-1.5	0.5
AO-01-11	84.2	33.4	84.2	34.9	823	34.3	-1.3	nd
AO-01-12	85.1	38.3	87.3	31.5	1270	34.5	-1.7	0.1
AO-01-13	88.6	-1.1	88.5	-2.5	5103	31.4	-1.6	3.6-5.6
AO-01-14	87.6	69.5	88.2	95.1	999	34.0	-1.6	2.6
AO-01-15	87.6	154.2	87.5	154.4	2814	31.0	-1.7	6.4
OC-05-3	61.4	-22.4	61.2	-30.3	1391	35.2	11.2	0.6
OC-05-8	59.8	-46.5	63.4	-53.2	1404	32.5	2.8	0.8
OC-05-10	70.1	-62.1	-	-	1019	33.2	3.8	0.9
OC-05-14	70.2	-123.6	70.9	-127	964	28.7	3.8	1.0
OC-05-15	70.5	-133.4	70.4	-135.2	750	17.4	3.8	3.3
OC-05-17	65.5	-169.1	64.5	-171.0	694	32.8	2.5	1.6
OC-05-18	65.9	-170.7	66.6	-171.5	578	32.8	2.1	1.7
OC-05-19	67.9	-174.4	71.5	-176.4	1555	31.1	8.1	1.9
OC-05-20	71.7	-176.2	73.5	-179.6	1080	29.1	1.3	1.4
OC-05-21	77.2	-179.9	76.5	-180.0	895	27.3	-1.4	0.9
ISSS-08-1	77.1	117.5	76.1	119.0	870	28.8	0.2	3.8
ISSS-08-2	75.3	124.4	75.5	128.3	932	17.5	6.0	23.0
ISSS-08-3	73.0	135.1	73.2	139.4	784	2.1	12.1	26.4
ISSS-08-4	72.4	149.4	71.4	157.4	828	17.6	8.4	7.7
ISSS-08-5	72.0	174.3	72.4	173.5	965	30.2	2.9	1.1
ISSS-08-6	74.3	170.5	74.3	148.1	1106	28.3	1.1	9.6
ISSS-08-7	74.0	148.1	73.2	155.1	788	18.8	3.4	-
ISSS-08-8	76.2	94.2	75.3	87.5	1278	27.8	-	4.2

Table S2. General characteristiscs of sampled water masses in the Central Arctic Ocean Basin (CAOB)

Station ID	Depth (m)	Water mass	Volume (L)	Salinity (‰)	T (°C)
AO-01-6	8	PML	1136	32.8	-0.3
	50	halocline	1098	34.4	-1.7
	250	AtWL	807	34.9	1.2
AO-01-7	8	PML	628	33.9	3.5
	40	halocline	451	34.8	3.6
AO-01-10	8	PML	2645	33.9	-1.6
	40	halocline	762	34.4	-1.7
	250	AtWL	958	34.9	2.1
	1000	ArDWL	1195	34.9	-0.3
AO-01-13	8	PML	5103	31.4	-1.6
	300	AtWL	1202	34.9	1.4
	2500	ArDWL	2038	34.9	-0.9
	2500	ArDWL	960	34.9	-0.9
AO-01-15	8	PML	2814	31.2	-1.6
	650	AtWL	754	34.9	0.2
	2500	ArDWL	1895	35.0	-0.5

PML, Polar Mixed Layer; AtWL, Atlantic Water Layer; ArDWL, Arctic deep water layer.
AO-01-10, Nansen Basin; AO-01-13, Amundsen Basin; AO-01-15, Makarov Basin.

Table S3. List of analyzed DDTs compunds, ions used for quantification (m/z) and limits of detection (LOD; pg)

Abbreviation	Compound	Ions	LOD
2,4'-DDE	2,2-(2-Chlorophenyl-4'-chlorophenyl)-1,1-dichloroethene	246, 281	25
4,4'-DDE	2,2-Bis(4-chlorophenyl)-1,1 dichloroethylene	281, 317	122
2,4'-DDD	1-chloro-**2**-[**2**,**2**-dichloro-1-(4-chlorophenyl) ethyl]benzene	225, 246	10
4,4'-DDD	1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl) ethyl]benzene	71, 249	65
2,4'-DDT	1-chloro-2-[2,2,2-trichloro-1-(4-chlorophenylethyl]benzene	255, 246	6
4,4'-DDT	1-chloro-4-[**2**,**2**,**2**-trichloro-1-(4-chlorophenylethyl]benzene	71, 281	101

Table S4. DDTs concentrations (pg·L^{-1}) in seawater (dissolved+particulate) of the Arctic polar mixed layer.

Sample ID	2,4'-DDE	4,4'-DDE	2,4'-DDD	4,4'-DDD	2,4'-DDT	4,4'-DDT
AO-01-1	nd	11.8	nd	nd	0.1	nd
AO-01-2	nd	11.7	nd	nd	0.1	nd
AO-01-4	nd	61.8	nd	0.3	0.1	4.0
AO-01-5	nd	27.5	nd	0.1	nd	4.3
AO-01-6	nd	22.9	nd	0.2	nd	0.5
AO-01-7	nd	3.1	nd	nd	nd	nd
AO-01-8	nd	3.2	nd	nd	nd	nd
AO-01-9	nd	3.4	nd	nd	0.1	0.1
AO-01-10	0.1	1.9	nd	0.3	0.1	2.1
AO-01-11	nd	0.2	nd	nd	0.1	0.2
AO-01-12	nd	0.5	nd	nd	0.1	0.1
AO-01-13	0.1	0.1	nd	nd	0.6	nd
AO-01-14	nd	nd	nd	nd	0.1	nd
AO-01-15	nd	0.1	nd	nd	nd	nd
OCO-05-3	nd	21.4	0.1	0.3	nd	nd
OCO-05-8	0.1	6.6	0.1	0.2	nd	nd
OCO-05-10	0.1	12.7	nd	nd	nd	nd
OCO-05-14	nd	2.3	nd	0.1	0.1	nd
OCO-05-15	nd	0.6	nd	0.3	0.1	nd
OCO-05-17	0.1	10.9	nd	nd	nd	0.3
OCO-05-18	nd	1.3	nd	nd	nd	nd
OCO-05-19	0.1	1.3	nd	nd	nd	nd
OCO-05-20	nd	0.6	nd	nd	nd	0.1
OCO-05-21	nd	nd	nd	0.1	nd	nd
ISSS-08-1	0.1	0.8	nd	1.5	nd	nd
ISSS-08-2	0.1	1.8	nd	0.1	nd	0.1
ISSS-08-3	nd	nd	nd	0.1	nd	0.1
ISSS-08-4	nd	0.2	0.1	nd	nd	nd
ISSS-08-5	nd	0.1	nd	nd	nd	nd
ISSS-08-6	nd	nd	nd	nd	nd	nd
ISSS-08-7	nd	0.4	nd	nd	nd	nd
ISSS-08-8	nd	3.4	nd	nd	nd	nd

nd= not detected.

Table S5. Concentrations of detected DDTs (pg·L^{-1}) in seawater (dissolved+particulate) of deep water masses of the Arctic Ocean

Station ID	Depth (m)	2,4'-DDE	4,4'-DDE	4,4'-DDD	2,4'-DDT	4,4'-DDT
AO-01-6	8	nd	23.0	0.2	nd	0.5
	50	0.1	0.2	nd	nd	0.3
	250	0.1	0.6	nd	nd	nd
AO-01-7	8	nd	3.1	nd	nd	nd
	40	bd	0.5	nd	nd	nd
AO-01-10	8	0.1	1.9	0.3	0.1	2.1
	40	0.1	0.5	nd	nd	nd
	250	nd	nd	nd	nd	nd
	1000	0.3	1.3	nd	nd	0.2
AO-01-13	8	0.1	0.1	nd	0.1	nd
	300	0.1	0.5	nd	nd	nd
	2500	0.1	0.5	nd	nd	0.1
AO-01-15	8	0.1	nd	nd	nd	nd
	650	0.1	0.4	nd	nd	nd
	2500	0.1	0.3	nd	nd	nd

nd= not detected.

Table S6. Inventories of DDTs (kg), PBDEs (kg) and PCBs (kg) in the water masses of the Arctic Ocean.

Compartment	$\sum_6$DDTs[a]	$\sum_{14}$PBDEs[b]	$\sum_{13}$PCBs[c]
Polar Mixed Layer			
Chukchi Sea	27±7	17±3	24.5±8
East Siberian Sea	3±0.5	16±1	33±4
Laptev Sea	12±2	32±11	37±5
Kara Sea	48±9	18±9	35±9
Barents Sea	402±169	67±28	46±9
Beaufort Sea	4±1	13±6	7±1
SNCAA[d]	28±7	11±5	11±4
Central Arctic Ocean Basin	31±8	158±77	104±24
Total Arctic PML	555±145	470±108	527±130
Deep Water Masses			
AtWL	1649±424	6320±235	7930±1340
ArDWL	6620±298	30800±3100	48800±7900

[a]Sum of 6 DDTs (2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, 4,4'-DDT).

[b]Sum of 14 BDE congeners analyzed (IUPAC numbers 17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, 209). (Salvado et al, 2016)

[c]Sum of 13 most abundant PCB congeners (IUPAC numbers 18, 28, 52, 70, 101, 110, 118, 105, 149, 153, 138, 180, 199) (Carrizo and Gustafsson, 2011; Sobek and Gustafsson, 2014).

[d]Shelf of Northern Canadian Arctic Archipelago.

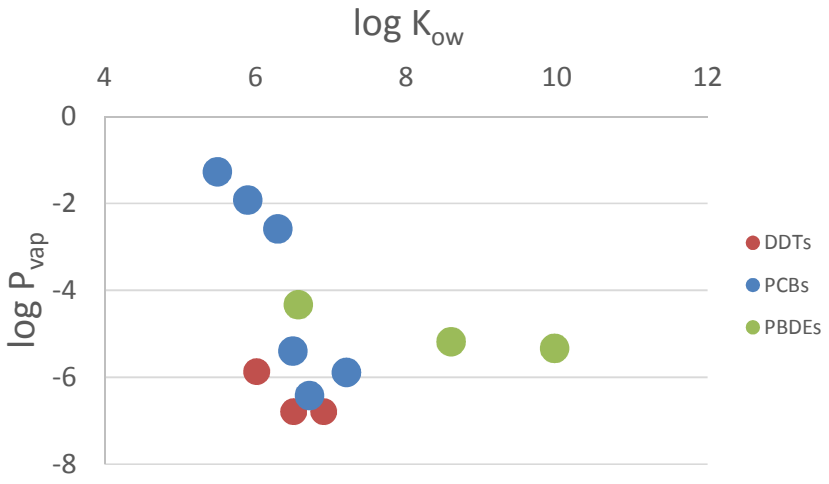

Figure S1. Chemical space plot with log vapur pressure (P_{vap}) versus log K_{ow} for DDTs in red (4,4'-DDE; 4,4'-DDD; 4,4'-DDT), PCBs in blue (CBs #28; #52; #101; #138; #153; #180) and PBDEs in green (BDEs #47; #99; #209).

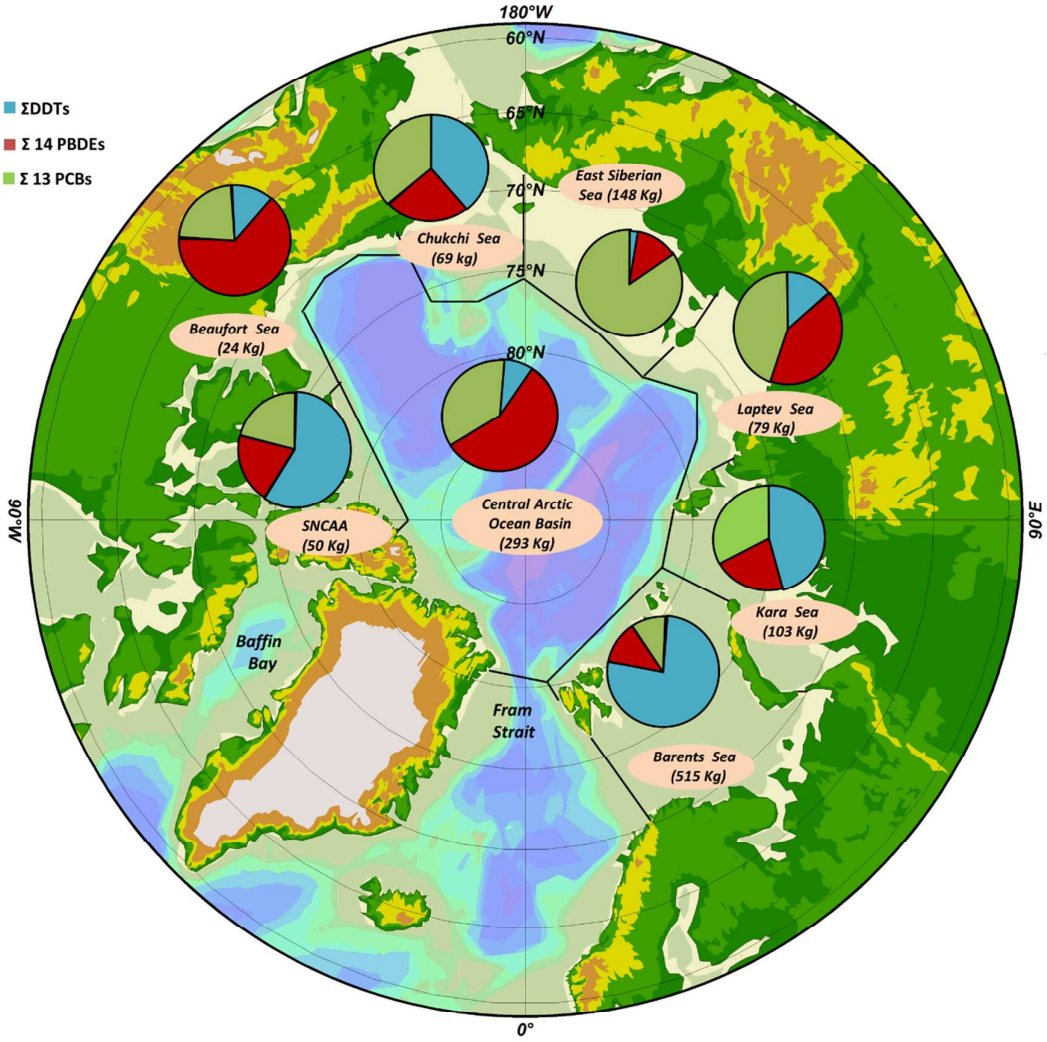

Figure S2. Comparison of $\sum_6$DDTs, $\sum_{14}$PBDEs and $\sum_{13}$PCBs inventories (kg) in the polar mixed layer of the different pan-Arctic shelf seas. SNCAA; Shelf of Northern Canadian Arctic Archipelago.

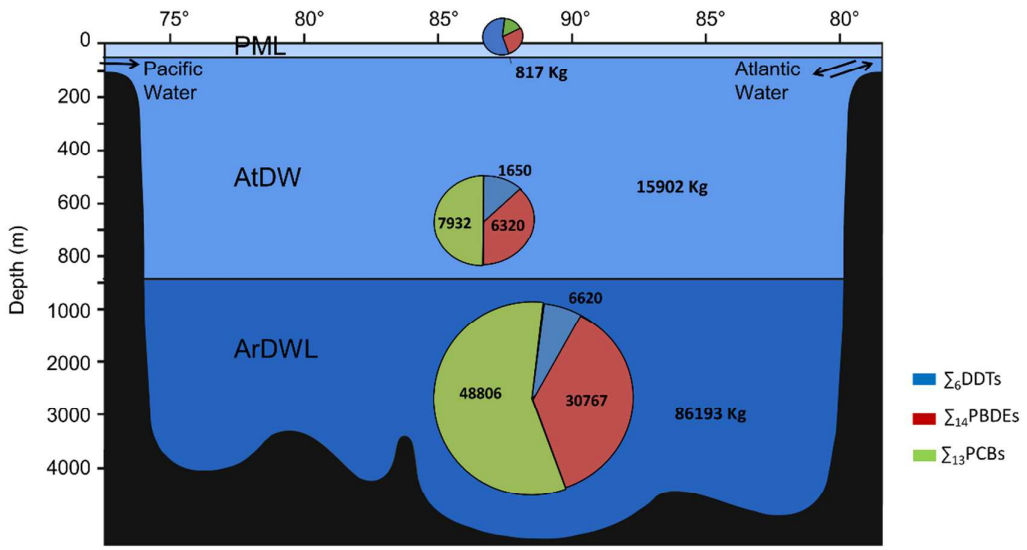

Figure S3. Comparison of $\sum_6$DDTs inventories with $\sum_{14}$PBDEs and $\sum_{13}$PCBs inventories (kg) in the water masses of the Central Arctic Ocean Basin. PML, Polar Mixed Layer; AtWL; intermediate Atlantic water layer; ArDWL; Arctic deep water layer.