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Step changes in persistent organic pollutants over the Arctic and their implications

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Sample size

To examine sample size and subsample size in MTT and Yamamoto method on the step changes in POPs time series, monthly, seasonal, and annual mean concentrations were applied in the three statistical tests. Results show that, since short-term periodic variation in monthly and seasonal mean concentrations overwhelmed the step changes, monthly and seasonal mean data could not detect step change points in long-term time series of POPs air concentrations. While the statistical tests used in the present study detected some statistical significant step changes (e.g., in August and September), these short-term change points were almost entirely induced by seasonal (periodic) variations in POPs air concentration. The true integrated step change points in a certain year in the long-term POPs air concentrations time series were not detectable using monthly and seasonal mean data.

As a non-parametric statistical test, there appeared no restriction on sample size in the MK test. The step changes in the MTT and Yamamoto methods are detected by examining the difference between two subseries. The MTT adopts T-test which is applicable for small sample time series ($n < 30$) and hence can be effectively employed in the POPs time series examined in the present study.

We have also compared the effect of the subseries length (IH) in the MTT and Yamamoto methods on the detection of step change points. We set IH from 2-6 and carried out these two statistical tests. Results show that IH<3 and IH>4 could not detect clearly step change points. Hence, IH=3 was selected in the MTT and Yamamoto tests in the present study.

Table S1. Mean concentrations of selected POPs in air, water, and ice (dissolved + particle phase) used in perturbation modeling.

	Air (pg m^{-3})[1]	Water (ng L^{-1})[2]	ice (pg L^{-1})[3]
α-HCH	30	3.0	100.0
PCB 28	3	0.04	1.8
PCB 153	0.4	0.03	1.6

[1]Mean air concentrations are derived from measured time series of POPs at Zeppelin Mountain Air Monitoring Station, Ny-Ålesund

[2] Water concentrations for OCPs in the Arctic were collected from Jantunen and Bidleman (2006) and Canadian Arctic Contamination Report II (2003). PCBs data were collected from Carrizo and Gustafsson (2011). Water concentrations in the Arctic Oceans were assumed not to be altered significantly during the 1990s and 2000s.

[3] Concentrations of selected chemicals in ice/snow were collected from Gustafsson et al., (2005) and Hansen et al (2008).

Table S2 Physical-chemical properties of selected POPs in perturbation modeling.

	logKoa (25°C)	H (25°C) Pa m^{-3} mol^{-1}	k_a h^{-1}	k_w h^{-1}	ΔH_{IA} kJ mol^{-1}
α-HCH	[1]7.46	[1]0.74	[2]4.88×10^{-4}	[3]2.06×10^{-4}	[4]-96.5
PCB-28	[5]7.85	[5]30.2	[6]4.3×10^{-3}	[6]1.26×10^{-4}	[4]-79.99
PCB-153	[5]9.44	[5]1.30	[6]9.40×10^{-4}	[6]1.26×10^{-5}	[4]-92.5

[1]Xiao et al. (2004); [2]Brubaker and Hites (1998),[3] Beyer et al. (2000), [4] Stocker et al (2007), [5]Li et al. (2003), [6]Anderson and Hites (1996)

Table S3. Step change years for PCBs from 2007-2012 at Zeppelin station computed by the MTT method using subsample size IH=3 and 4, respectively.

PCBs	IH=3	IH=4
18	2007	2007
28	2008	2007
31	2008	2007
33	2008	
52	2008	2007
74	2008	2009
101	2008	2007
138	2008	
149	2008	2007
170	2008	
180	2008	
189		2007
206		2007
209		2007

Table S4 Step change point years in PCBs congeners and OCPs isomers at Zeppelin and Alert monitoring stations detected by the Moving T-test (MTT).

	Step change point years		
	2001-2003	2005-2006	2007-2008
Zeppelin	CB-18,33,122,149,157, 167,170,189, o,p'-DDE	CB-52	CB-18,28,31,33,52,74, 101,138,149,170,180
Alert	CB-52, *p,p'*-DDD	CB-16A,25,44,118,174, 209,α-HCH,γ-HCH	

Table S5 Step change point years in PCBs congeners and OCPs isomers at Zeppelin and Alert monitoring stations computed by the Yamamoto method.

	Step change point years		
	2001-2003	2005-2006	2007-2008
Zeppelin	CB-149,157,170,α-HCH	CB-52,α-HCH	CB-18,180,187,206, o,p'-DDE
Alert	*p,p'*-DDD	CB-16A, 174,α-HCH	

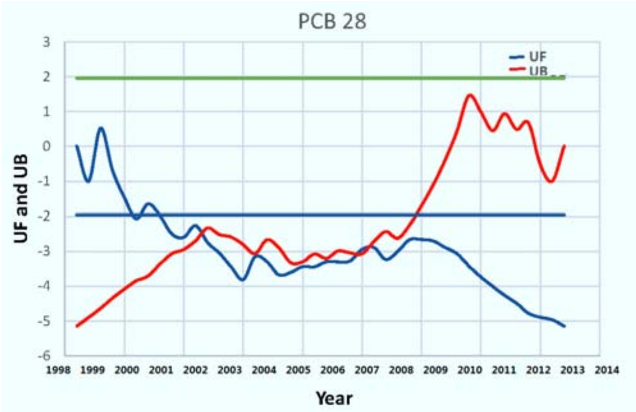

Figure S1. Mann–Kendall's testing statistics for monthly PCB-28 concentrations in July, August, and September averaged from weekly measured concentrations at Zeppelin station (1993–2012). Curved blue line is UF_i and curved red line is UB_i. Two straight solid lines stand for confidence interval of -1.96 (straight blue line) and 1.96 (straight green line).

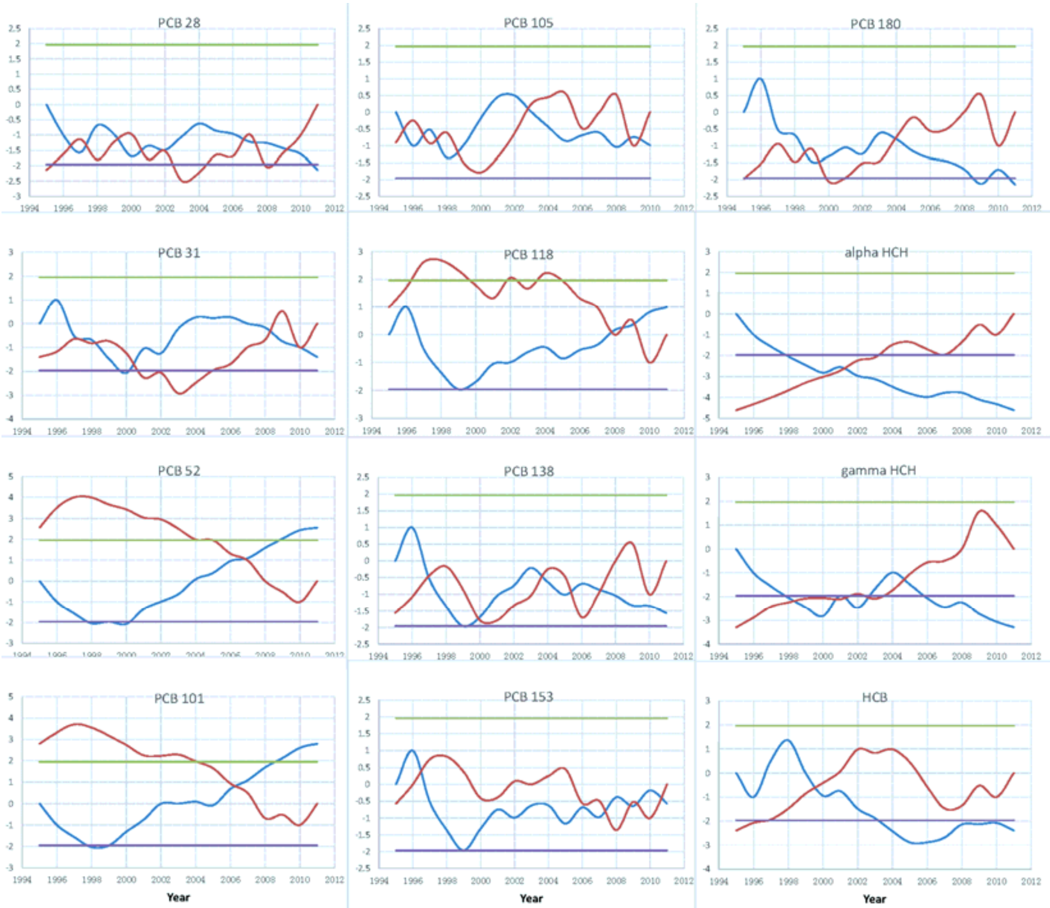

Figure S2. Mann–Kendall's testing statistics for PCBs and OCPs collected from the Storhofdi station (1995–2011). Blue solid line is the forward sequence UF_i and red solid line is backward sequence UB_i, defined by Eq. (5). Two straight solid lines stand for confidence interval between -

1.96 (straight purple line) and 1.96 (straight green line) in the MK test. Intersection of UF_i and UB_i sequences within interval between two confidence levels indicates a step change point.

Figure S3 Same as Fig. S2but for Pallas station (1996-2011).

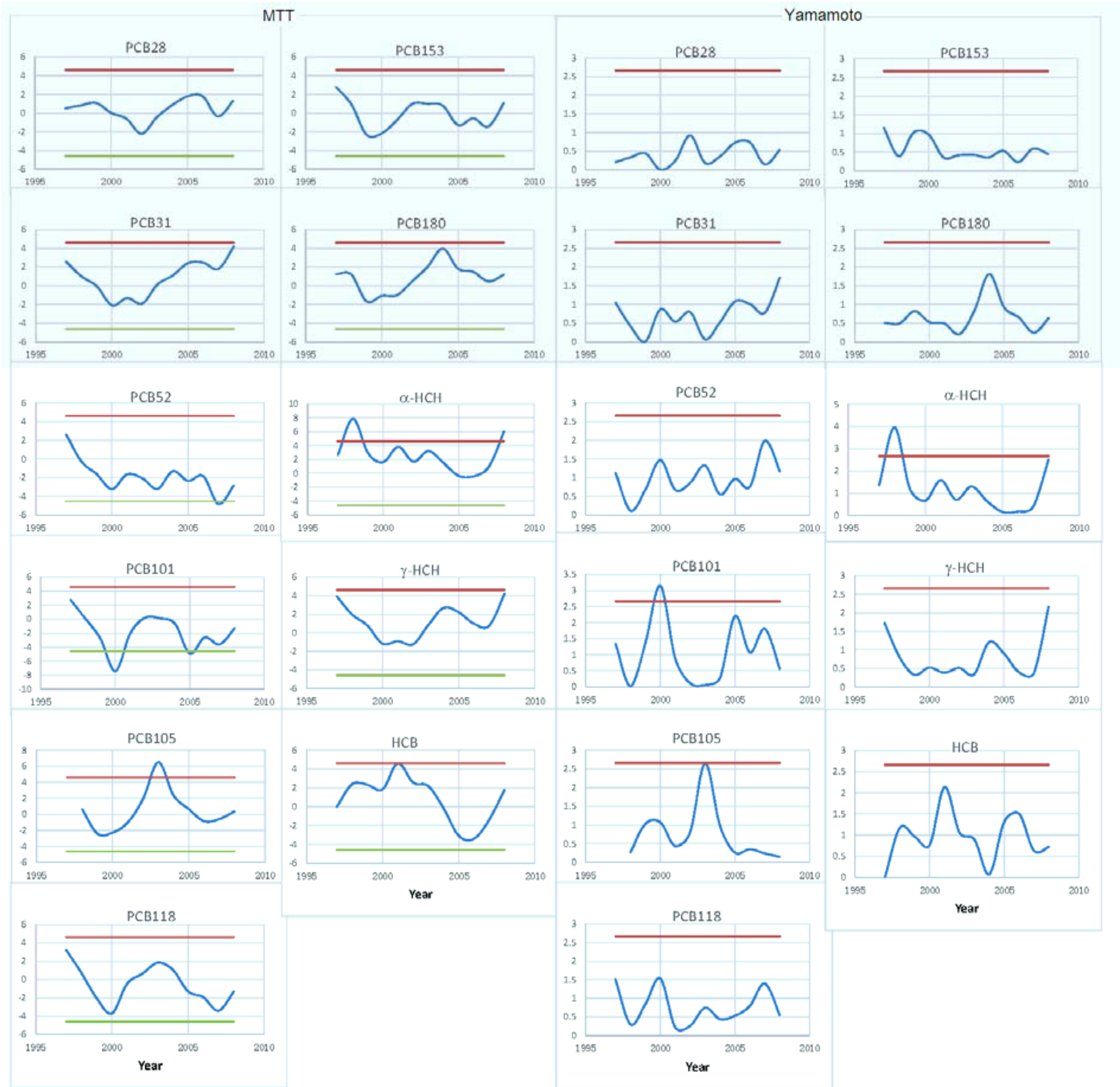

Figure S4. Step changes in monitored time series of POPs at Storhofdi monitoring station by the Moving T-Test (MTT, Eqs. (6) and (7), shown in left two panels) and Yamamoto method (Eq. (8), shown in right two panels).

Figure S5. Same as Fig. S4 but for Pallas monitoring station.

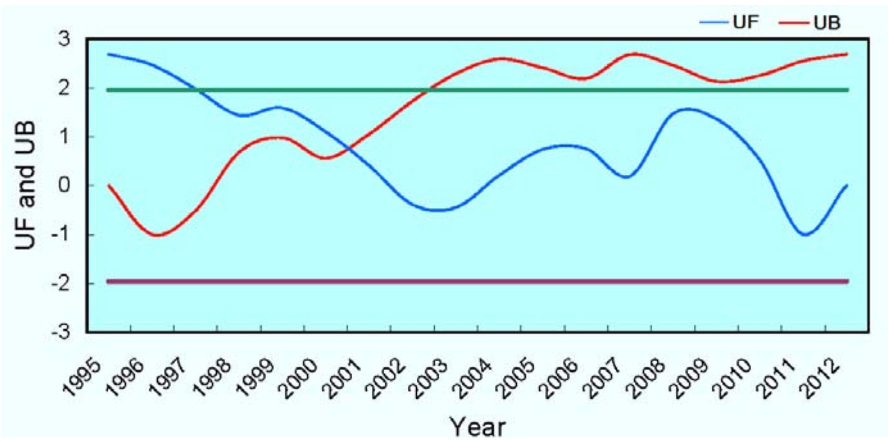

Figure S6. Mann–Kendall's testing statistics for perturbed air concentration of PCB-28. Blue solid line is the forward sequence UF and red solid line is backward sequence UB_i, defined by Eq. (5) in main test. Two straight solid lines stand for confidence interval between -1.96 (straight purple line) and 1.96 (straight green line) in the MK test. Intersection of UF and UB sequences within interval between two confidence levels indicates a step change point in 2001.

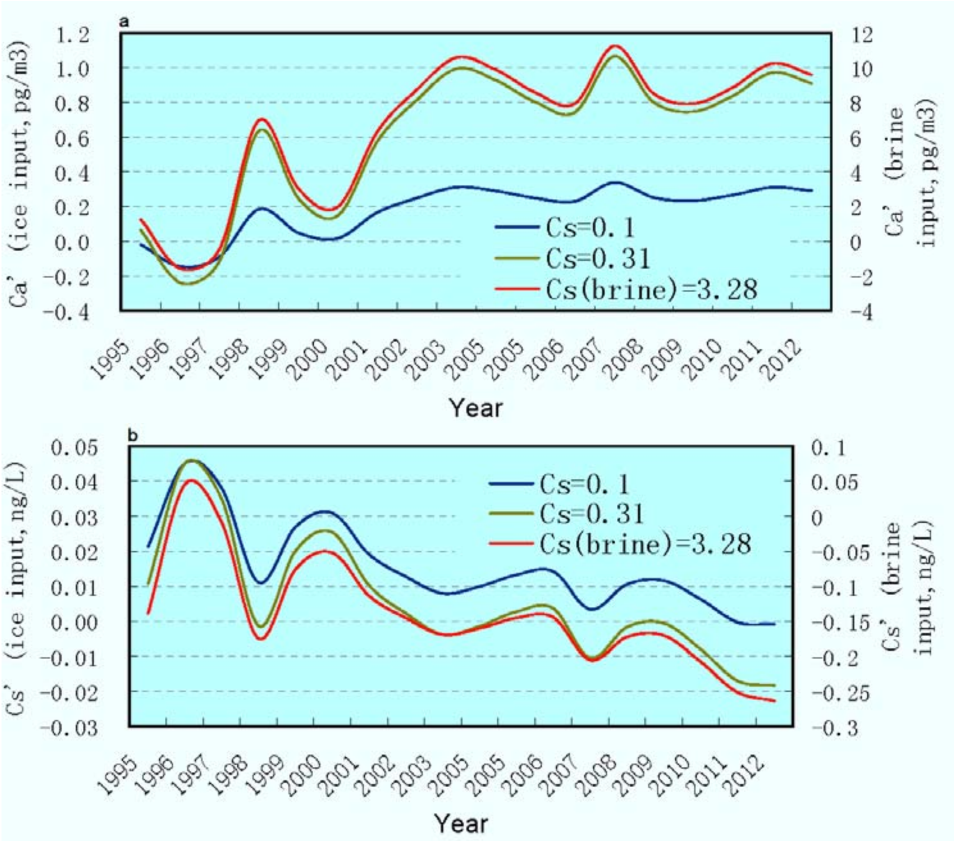

Figure S7. Modeled perturbations of α-HCH concentrations due to air-ice exchange from 1995 – 2012 in air and ice over the Arctic. Mean concentration in air used C_a = 30 pg m^{-1} (Table 1). Mean concentrations in ice were collected from Hansen et al (C_s=0.1 ng L^{-1}, Table 1), Pućko et al (2010, C_s=0.31 ng L^{-1}) over 90 and 5 cm depth, and in sea ice brine (Pućko et al, 2010, $C_{s\text{-}brine}$=3.28 ng L^{-1}) averaged over 90 and 5 cm depth and over the winter 2007-2008 and spring 2008, respectively. **a**. perturbed air concentration (pg m^{-3}); **b.** perturbed ice concentration (ng L^{-1}). In the figure, perturbed concentrations using C_s=0.1 and 0.31 ng L^{-1} (ice input) are scaled on left-hand-side Y-axis and C_s=3.28 (brine input) is scaled on right-hand-side Y-axis.

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