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Supplement of

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

¹Mean 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.

	logK _{oa} (25°C)	H (25°C) Pa m ⁻³ mol ⁻¹	k _a h ⁻¹	k _w h ⁻¹	ΔH _{1A} 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

¹Xiao et al. (2004); ²Brubaker and Hites (1998), ³Beyer et al. (2000), ⁴Stocker et al (2007),

⁵Li et al. (2003), ⁶Anderson 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	<i>p,p'</i> -DDD	CB-16A, 174, α -HCH	

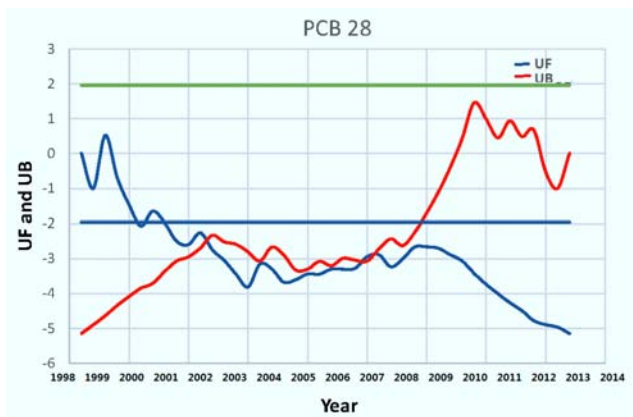


Figure S1. Mann–Kendall’s testing statistics for monthly PCB-28 concentrations in July, August, and September averaged from weekly measured concentrations at Zeppelin station (1993–2012). Curved blue line is UF_i and curved red line is UB_i . Two straight solid lines stand for confidence interval of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

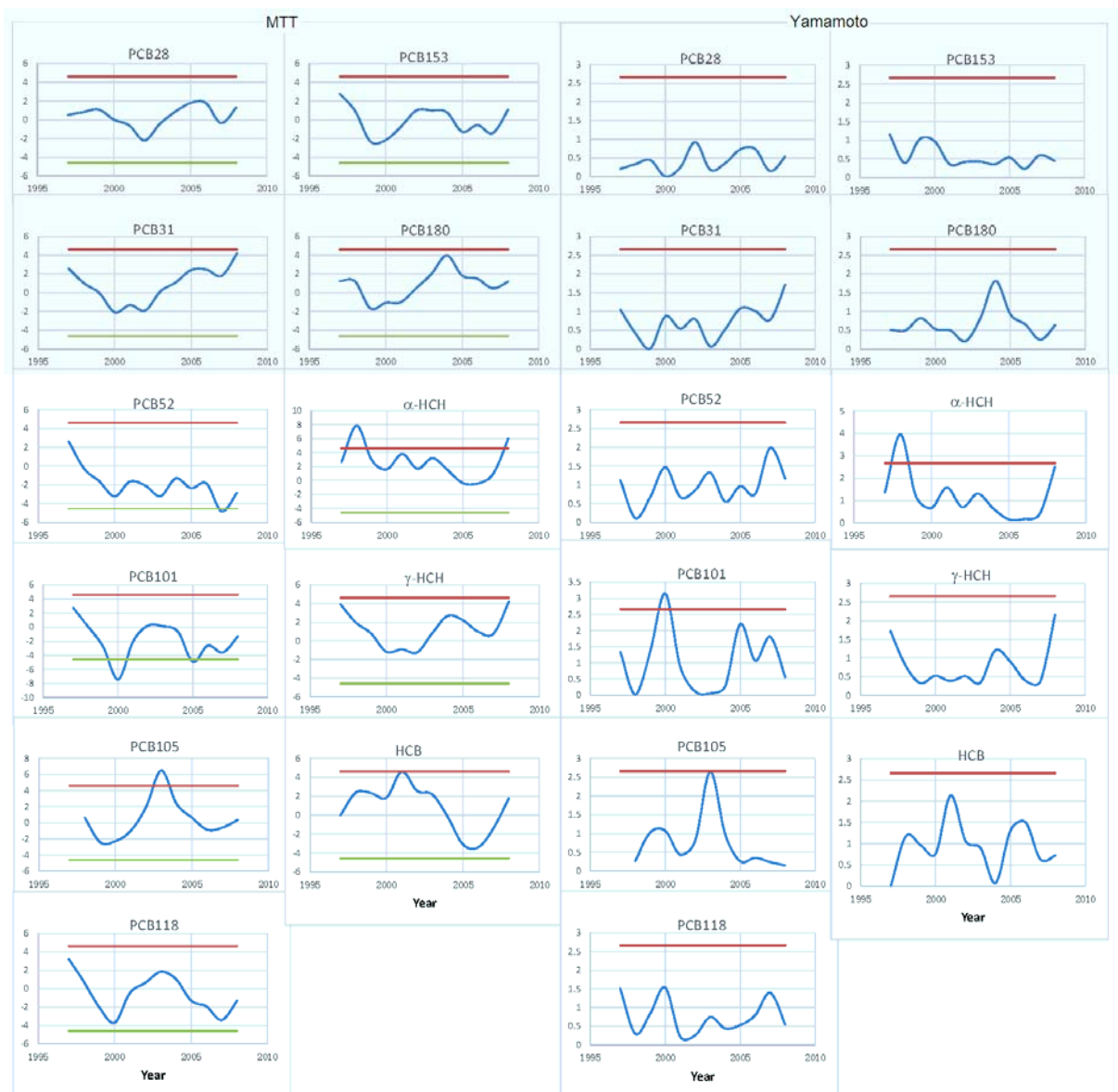


Figure S2. Step changes in monitored time series of POPs at Storhofdi monitoring station by the Moving T-Test (MTT, Eqs. (6) and (7), shown in left two panels) and Yamamoto method (Eq. (8), shown in right two panels).



Figure S3. Same as Fig. S2 but for Pallas monitoring station.

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