

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

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20 **Abstract.** While some persistent organic pollutants (POPs) have been declining globally  
21 due to their worldwide ban since the 1980s, the declining trends of many of these toxic  
22 chemicals become less significant and in some cases their ambient air concentrations,  
23 e.g., polychlorinated biphenyls (PCBs), showed observable increase during the 2000s,  
24 disagreeing with their declining global emissions and environmental degradation. As part  
25 of the efforts to assess the influences of environmental factors on long-term trend of  
26 POPs in the Arctic, step change points in the time series of ambient POPs atmospheric  
27 concentrations collected from four arctic monitoring sites were examined using various  
28 statistical techniques. Results showed that the step change points of these POPs data  
29 varied in different years and at different sites. Most step change points were found in  
30 2001-2002 and 2007-2008, respectively. In particular, the step change points of many  
31 PCBs for 2007-2008 were coincident with the lowest arctic sea ice concentration  
32 occurring in this period of time during the 2000s. The perturbations of air concentration  
33 and water-air exchange fluxes of several selected POPs averaged over the Arctic,  
34 simulated by a POPs mass balance perturbation model, switched from negative to  
35 positive from the early 2000s, indicating a tendency for reversal of POPs from deposition  
36 to volatilization which coincides with a positive to negative reversal of arctic sea ice  
37 extent anomalies from 2001. Perturbed ice-air exchange flux of PCB-28 and 153 showed  
38 an increasing trend and the negative to positive reversal in 2007, the year with the lowest  
39 arctic sea ice concentration. On the other hand, perturbed ice-air exchange flux of  
40  $\alpha$ -hexachlorocyclohexane (HCH) decreased over the period of 1995 through 2012,

41 likely owing to its lower Henry's law constant which indicates its relatively lower  
42 tendency for volatilization from ice to air.

### 43 **1. Introduction**

44 A number of studies have been carried out to examine temporal trends of POPs in the  
45 Arctic (Hung et al., 2005, 2010; Becker et al., 2008; Ma et al., 2011; Wöhrnschimmel et  
46 al., 2013). Due to worldwide ban and restrictions of these toxic chemicals, most legacy  
47 POPs have been declining in the Arctic over the last several decades. Fluctuations of  
48 many POPs on interannual or longer time scales, however, have been observed in POPs  
49 time series collected from arctic monitoring stations. The long term trends of POPs in the  
50 Arctic have been attributed to the changes in their primary emissions, use patterns,  
51 retreating sea ice, degradation, and other complex natural and anthropogenic activities  
52 (Macdonald et al., 2005; UNEP/AMAP, 2010; Armitage et al., 2011; Kallenborn et al.,  
53 2012). The fluctuations of monitored POPs atmospheric concentrations have been also  
54 associated with interannual climate change at several POPs monitoring sites where the  
55 longest atmospheric monitoring programs have been operated, notably the Great Lakes  
56 region and the Arctic (Ma et al., 2004a; MacLeod et al., 2005; Wang et al., 2010). The  
57 notable interannual climate change influencing interannual changes in elevated  
58 atmospheric level of POPs in the Northern Hemisphere are the North Atlantic Oscillation  
59 (NAO), the El Niño-Southern Oscillation (ENSO), and the Arctic Oscillation (AO) (Ma  
60 et al., 2004a,b; Ma and Li, 2006; MacLeod et al., 2005; Macdonald. 2005; Becker et al.,  
61 2008; Gao et al., 2010). These studies have revealed abundant evidence for the

62 associations between these interannual climate change and ambient atmospheric  
63 concentrations of POPs in the Great Lake and arctic regions.

64 Previous trend assessments for POPs concentration time series in the Arctic have  
65 revealed changes in these time series induced potentially by climate change. The  
66 relationship between ambient POPs air concentrations and rapid change in the arctic  
67 environment, however, has not been proven statistically. Recently, there has been  
68 ongoing debate on a climate "tipping point" (Lenton, 2011; Duarte et al., 2012; Livina  
69 and Lenton, 2013; Holland et al., 2006) in the Arctic. Such the tipping point has been  
70 connected to an abrupt increase in the amplitude of seasonal variability of sea ice area in  
71 2007 that has been persistent since then, indicating the likelihood of rapid arctic climate  
72 change (Livina and Lenton, 2013). It is worthwhile to point out that arctic climate change  
73 has a much longer time scale than POPs life time and it might not be appropriate to link  
74 short-term changes in POPs environmental level with long-term climate change.  
75 However, the rapid change in arctic environments would change the environmental fate  
76 and temporal trend of POPs, together with their primary emissions and use patterns in the  
77 globe. Yet, the response of the monitored POPs long-term time series in the Arctic to the  
78 rapid change in the arctic environment has not been investigated intensively. POPs  
79 releasing from seasonal melting snow pack and mountain glaciers has been demonstrated  
80 to alter significantly the atmospheric levels of POPs (Stocker et al., 2007; Bogdal et al.,  
81 2009; Meyer et al., 2008). Arctic sea ice as a temporal storage reservoir for POPs  
82 undergoes seasonal changes, except for permanent ice and glaciers. The sea ice melting

83 and aging may increase air concentrations of POPs. It has been observed that an abrupt  
84 increase in  $\alpha$ -HCH concentration in air occurred in accompany with the ice breakup in  
85 the central Archipelago during the Tundra Northwest 1999 (TNW-99) expedition  
86 (Jantunen et al. 2007). Increasing concentrations of hexachlorobenzene (HCB) and many  
87 PCB congeners were also observed in arctic air from the mid-2000s at the Zeppelin  
88 Mountain Air Monitoring Station, Svalbard/Norway (78° 55' N, 11° 56' E), and the Alert  
89 station, Canada (82° 30' N, 62° 19' W), resulting in the lack of statistically significant  
90 trends of these chemicals in the Arctic since the late 1990s (Hung et al., 2010). While the  
91 increasing trends of HCB and PCBs in the 2000s in the Arctic have been attributed partly  
92 to their revolatilization from their arctic repertories in ocean, ice, and snow due to arctic  
93 warming and sea ice retreat (Hung et al., 2010; Ma et al., 2011; Becker et al., 2012), this  
94 hypothesis was not supported sufficiently by statistical evidence.

95 To identify decadal or longer time scale climate change (e.g., global warming)  
96 signals, a time series of climate data should not be shorter than 30 years (the classical  
97 climate change period, Le Treut et al., 2007). This raises a question to what extent  
98 currently available POPs observational datasets are long enough to address climate change  
99 influence on their environmental fate. Several recent modeling investigations and  
100 sensitivity analysis to the long-term trend of PCBs and  $\alpha$ -HCH in the 20th and 21st  
101 centuries suggested that the long-term trends of these POPs were associated more strongly  
102 with changes in their emissions and physical-chemical properties whereas climate change

103 signals were weaker in observed POPs time series (Wöhrnschimmel et al., 2013;  
104 Armitage et al., 2011; Gouin, et al., 2013; Li, 2012).

105 Since the Arctic is warming at a rate of almost twice the global average which leads  
106 to strong sea ice melt since the 2000s (Steele et al., 2008), the measured POPs  
107 atmospheric concentrations in the Arctic might provide best datasets to discern the signals  
108 of climate change in monitored POPs data. The increasing trend of PCBs appeared to  
109 coincide to the strong sea ice melt in the Arctic, characterized by rapid decline in arctic  
110 sea ice from 2000 (Duarte et al., 2012). Since the sea ice decline took place over a short  
111 period of time, the monitored POPs air concentrations datasets in the Arctic, though short,  
112 would likely respond to rapid sea ice decline and increasing air temperature which may  
113 provide further field evidence to the association between temporal trend of POPs and  
114 climate warming. The present study examined the statistics for step changes in monitored  
115 atmospheric concentrations of POPs at several arctic monitoring stations. The association  
116 between the statistically significant step change points of POPs concentrations and arctic  
117 climate change was quantitatively assessed to identify arctic climate change signals in  
118 measured POPs time series.

## 119 **2. Materials and methods**

### 120 **2.1 Data**

121 Monitored ambient atmospheric concentrations of selected PCBs and OCPs  
122 (Organochlorine pesticides) in the present study were collected from four Arctic  
123 monitoring sites representing the longest time series of POPs across the Arctic. These are

124 the Zeppelin Mountain Air Monitoring station (Svalbard/Norway, 1992-2012), Alert  
125 (Canada, 1993-2012), Pallas (Matorova, Finland, 68° 00' N, 24° 15' E, 1996–2011), and  
126 Storhofdi (Vestmannaeyjar, Iceland, 63° 24'N, 20° 17'W, 1995–2011). The sampling  
127 frequencies vary site by site. At Zeppelin, Alert, and Pallas sites, daily air concentrations  
128 are sampled for every week and at Storhofdi site the daily concentrations are sampled for  
129 every two weeks. Detailed information in sample collection and chemical analysis are  
130 referred to Hung et al (2010). The annual mean air concentrations at each site were  
131 obtained by averaging weekly (Zeppelin, Alert, Pallas) or bi-weekly (Storhofdi) sampled  
132 data. The concentrations of selected POPs in the Arctic Oceans and ice (snow) used in  
133 subsequent perturbation modeling were collected from literature and listed on Table S1 of  
134 Supplement. These data were not routinely measured. Since the perturbation model (see  
135 section 2.3) only inputs multiple yearly averaged concentration data in air, water, and  
136 ice/snow as forcing terms to predict perturbed concentrations (Ma and Cao, 2010) and set  
137 initial concentration perturbations as zero, POPs concentration data in the Arctic Oceans  
138 and sea ice/snow collected from different years and locations were averaged over the  
139 Arctic and entire monitoring period from the 1990s to 2012. Monthly averaged arctic sea  
140 ice extent and area data were collected from National Snow and Ice Data Center (NSIDC  
141 at nsidc.org, Clark, et al., 1999). Surface air temperatures (SAT) and precipitation used in  
142 perturbation modeling were collected from the National Centers for Environmental  
143 Prediction (NCEP) reanalysis (Kalney et al. 1996). Physical-chemical properties of  
144 selected POPs in perturbation modeling are presented in Supplement Table S2,

145 respectively.

## 146 **2.2 Statistical test for POPs trend and step change**

147 Searching for a step change (also referred to abrupt change or abrupt discontinuities) in a  
148 time series is often conducted by the detection of a point year as a sign of step change in  
149 the time series. It is the process of finding step changes (or shifts) in the mean level of  
150 the time series. In the cases of POPs atmospheric concentration time series, the step  
151 changes can be considered as a statistically significant abnormal increasing or decreasing  
152 from their long-term trend, extending to a certain period of time. In climate and  
153 hydrological studies, three statistical methods have been widely used to identify abrupt  
154 climate change points. These are the Mann-Kendal (MK) test (Mann, 1945; Kendall,  
155 1948), the Moving T-Test (MMT) technique (Moraes, et al., 1998), and Yamamoto  
156 method (Yamamoto et al., 1985).

157 The MK test is a nonparametric statistical test (Kendall, 1948) which has been used  
158 to find trend and step change points of hydrological stream flows and air temperatures  
159 (Moraes et al., 1998; Gan, 1998). Under the null hypothesis (no step change point), the  
160 normally distributed statistic  $S_k$  can be calculated as:

$$161 \quad S_k = \sum_{i=1}^k r_i \quad (k = 2, 3, \dots, n) \quad (1)$$

162 where  $S_k$  is a statistic of the MK test and,



$$r_i = \begin{cases} +1, & (x_i > x_j) \\ 0, & (x_i \leq x_j) \end{cases} (j = 1, 2, \dots, i-1) \quad (2)$$

164 where  $x_i$  is  $i$ th variable in time series  $x_1, x_2, \dots, x_i$ ,  $r_i$  is the cumulative number for  
 165  $x_i > x_j$ . The expected values  $E(S_i)$  and variance  $\text{Var}(S_i)$  of  $S_k$  are given by

$$E(S_i) = \frac{i(i-1)}{4} \quad (3)$$

$$\text{Var}(S_i) = \frac{i(i-1)(2i+5)}{72} \quad (4)$$

168 From these two equations one can derive a normalized  $S_i$ , defined by

$$UF_i = \frac{S_i - E(S_i)}{\sqrt{\text{Var}(S_i)}} (i = 1, 2, \dots, n) \quad (5)$$

170 where the normalized variable statistic  $UF_i$  is the forward sequence. Likewise, the  
 171 backward sequence  $UB_i$  can be calculated using the same equation but taking a reversed  
 172 series of the data such that  $UB_i = -UF_i$ . When the null hypothesis is rejected (i.e., if any of  
 173 the points in the forward sequence are outside the confidence interval), the detection of an  
 174 increasing ( $UF_i$ ) or a decreasing ( $UB_i$ ) trend is determined. In this way the sequential  
 175 version of the test enables detection of an approximate time of occurrence of the trend by  
 176 locating the intersection of the forward and backward curves of the test. The intersection  
 177 occurring within the confidence interval indicates the beginning of a step change point  
 178 (Moraes et al., 1998; Zhang et al., 2011).

179 The idea of Moving T-Test (MTT) technique is to test the difference between two  
 180 subsamples of a random variable time series before and after the change point with

181 equivalent subsamples size under a null hypothesis of  $\mu_1 = \mu_2$  where  $\mu_1$  and  $\mu_2$  are two  
 182 subsamples. In other words, if the difference between means over two adjacent time  
 183 intervals reaches a statistical significance level, a step change is inferred to occur. For a  
 184 time series whose population is normally distributed, the  $t$ -statistics is defined as (Moraes  
 185 et al., 1998)

$$186 \quad t_0 = \frac{\bar{x}_1 - \bar{x}_2}{S_p \left( \frac{1}{n_1} + \frac{1}{n_2} \right)^{1/2}}, \quad (6)$$

$$187 \quad S_p^2 = \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2}, \quad (7)$$

188 where  $S_i^2$  and  $n_i$  are variance and sample size, respectively. In the present study, we  
 189 requested that, if  $t$ -statistics  $t_0$  at a point year beyond the control line at  $t_0 = \pm 4.6$   
 190 reaches the significant level  $\alpha=0.01$ , this point year will be identified as a step change  
 191 point year.

192 Yamamoto method is somewhat similar to the MTT approach, defined by a signal to  
 193 noise ratio (S/N, Yamamoto et al, 1985):

$$194 \quad \frac{S}{N} = \frac{|\bar{x}_1 - \bar{x}_2|}{S_1 + S_2}. \quad (8)$$

195 A step point of a concentration time series is inferred if S/N intersects with the line of  
 196  $S/N=2.66$  at the significant level  $\alpha=0.01$ . In the present study, the subset data size of both  
 197 Yamamoto and MTT methods was set to 3. Table S3 of Supplement compared the MTT  
 198 method identified step change point years for PCBs for the period of 2007-2012 at

199 Zeppelin site using the subsample size  $IH=3$  and 4, respectively. For most PCBs, the  
200 selection of the subsample size  $IH=3$  yielded the step change year 2008, and 2007 by  
201 choosing the subsample size  $IH=4$ . It should be noted that, since the subsets size  $u1 = u2$   
202 which requires the even number of data points, the data points in POPs time series used  
203 in the step change statistical test by these two methods were less than the number of  
204 measured data.

205         Since the changes in atmospheric concentrations of POPs are often driven by the  
206 first-order processes that scale multiplicatively with the concentrations (Meijer et al.,  
207 2003), in the MTT and Yamamoto statistics all concentrations are log-transformed (in  
208 natural logarithm) before they are used in the statistical analysis. Because the MK  
209 method is a rank-based test, the log-transformed time series make no difference from  
210 original time series for the step change results.

211         These methods each have their advantages and disadvantages. For example, while  
212 the MK test has been successfully used in detecting step change points (Moraes et al.,  
213 1998; Gan, 1998), it failed to discern statistically significant signals in step changes in  
214 some cases. To increase confidence of statistical test for potential step change point in the  
215 selected POPs time series, the present study applied simultaneously the MK test, MTT  
216 technique, and Yamamoto method. Although the step change points of a time series from  
217 the MK test may occur in a certain year, this year is often regarded as the onset year of  
218 the step change. The year immediate after the onset year can be also included in the  
219 period of the step change in the time series. We also applied monthly and seasonal mean

220 air concentrations data at the four arctic sites to examine the step change points for  
221 monitored POPs concentrations. The monthly and seasonal mean concentrations were  
222 compiled by averaging weekly (Zeppelin, Alert, Pallas) or bi-weekly (Storhofdi) sampled  
223 air concentrations. Using monthly or seasonally averaged time series can increase sample  
224 size. However, periodic variations in monthly and seasonal POPs concentration time  
225 series, characterized by higher concentrations in warmer months (or season) and lower  
226 concentrations in colder months (or season), overwhelmed the changes in annually  
227 averaged concentration time series. Our results showed that the monthly and seasonal  
228 averaged data could not yield step changes for most POPs data. **Figure S1** of Supplement  
229 displays the  $UF_i$  and  $UB_i$  in MK test (Eq. (5)) for monthly PCB-28 atmospheric  
230 concentration time series during the summer months in the Arctic at Zeppelin site. As  
231 seen,  $UF_i$  and  $UB_i$  fluctuate below the confidence level, and no statistically significant  
232 step changes are found. Further details in the influence of sample size, monthly and  
233 seasonal time series on step changes in POPs air concentrations are presented in  
234 Supplement.

### 235 **2.3 Perturbation Modeling**

236 The coupled air – surface perturbation model for POPs was developed by Ma and Cao and  
237 Ma et al (Ma and Cao, 2010; Ma et al., 2011) to simulate and predict perturbations of  
238 POPs concentrations in various environmental media under projected climate change  
239 scenarios. This approach defined the concentration ( $C$ ,  $\text{pg m}^{-3}$ ) of a persistent chemical  
240 (and other variables) in an environmental compartment (e.g., air, water, snow, ice,

241 sediment) to equal to the sum of its mean concentration ( $\bar{C}$ ) and perturbed concentrations  
242 ( $C'$ )  $C = \bar{C} + C'$ , or  $C' = C - \bar{C}$ . So  $C'$  can be also regarded as a concentration anomaly  
243 (or departure) from its mean. The change in this mean concentration in the Arctic was  
244 often dominated by its primary emission, degradation, and the disequilibrium or exchange  
245 of concentrations between two environmental compartments (Gioia et al., 2008). These  
246 processes control the mean state of POPs in environment. Whereas, the perturbed  
247 concentration  $C'$ , as the departure from these mean processes, might be more sensitive to  
248 other processes with weak signals in ambient POPs concentrations, such as climate  
249 change. The model was developed to quantify the response of POPs in multi  
250 environmental compartments to the long-term changes in atmospheric and ocean  
251 temperatures, and snow and sea ice. In the case of the arctic environment, the model  
252 simulates daily concentrations of POPs (with the model time step length at 1 day) in  
253 different environmental compartments forced mostly by the change in temperatures,  
254 ice/snow melting, and the mean concentrations (Supplement Table S1). The model can be  
255 applied either in a single spatial site or entire arctic region. Details in the perturbation  
256 model were referred to Ma and Cao (2010) and Ma et al (2011). To interpret the  
257 occurrence of step change point years of POPs concentration data detected by the  
258 statistical analysis, the perturbation modeling for PCB-28, 153, and  $\alpha$ -HCH was  
259 performed using their mean and perturbed emissions. To examine the response of the  
260 exchange of POPs in multi-media environments to their step changes, perturbed water-air  
261 and ice-air exchange flux were also calculated. It is arguable that the most processes that

262 control the concentration in air are first-order processes that scale multiplicatively with  
 263 concentrations whereas the perturbation model treats concentrations in air as a linear sum  
 264 of their mean and perturbed concentrations (Ma and Cao, 2010). It must be noted, as  
 265 aforementioned, that the sole external forcing term in the perturbation model was mean  
 266 concentrations in different environmental compartments and initial perturbed  
 267 concentrations were set zero in the model (Ma and Cao, 2010). Those nonlinear processes  
 268 related to the chemical-physical properties of a chemical and their associations with  
 269 temperature have been also taking into consideration through the calculation of their mean  
 270 and perturbation.

271 The global emission inventory of selected POPs employed in the perturbation  
 272 modeling  $\alpha$ -HCH and PCBs used the results from Li et al (2000) and Breivik et al. (2007).  
 273 We implemented mean and perturbed air emissions, subjected to mean temperatures and  
 274 temperature anomalies, into the model, expressed as (Lamon et al., 2009; Ma and Cao,  
 275 2010; Gouin et al., 2013)

$$276 \quad \bar{E}_{OHC} = E_{OHC-ref} \exp\left[\Delta U_A \left(1/T_{ref} - 1/\bar{T}\right) / R\right] \quad (9)$$

$$277 \quad E'_{OHC} = \frac{\Delta U_A}{R} \bar{E}_{OHC} \frac{T'}{\bar{T}^2} \quad (10)$$

278 where  $T_{ref}$  is reference temperatures (K),  $E_{OHC-ref}$  is the emission at the reference  
 279 temperature, obtained from an emission inventory.  $\Delta U_A$  is the internal energy of  
 280 vaporization (Lamon et al., 2009). Since  $\bar{E}_{OHC}$  does not change with temperature and time,  
 281 it can be linked with the mean air concentration in our model.

282 The instantaneous water-air exchange flux is calculated by the Whitman two-film  
 283 model (Bidleman and McConnell, 1995),

$$284 \quad F_w = K_{OL} (C_w - C_a RT / H) \quad (11)$$

285 where  $F_w$  is the water-air exchange flux,  $K_{OL}$  is the air-water exchange velocity,  $C_w$  is  
 286 dissolved concentration in water,  $C_a$  is air concentration,  $H$  is the Henry's law constant,  
 287 and  $R$  is the ideal gas constant. Equation (11) suggests that, at the interface between water  
 288 and air, POPs concentration in air and water is in equilibrium through the Henry's law  
 289 constant, defined as  $C_a/C_w = H/RT$ . Following the rules in perturbation theory (Ma and  
 290 Cao, 2010) one can derive the perturbed water-air exchange flux as

$$291 \quad F'_w = \bar{K}_{OL} \left[ \frac{R}{H} \left( \frac{\bar{T}\bar{C}_a}{H} H' - \bar{T}C'_a - \bar{C}_a T' \right) + C'_w \right] + K'_{OL} \left( \bar{C}_w - \frac{R\bar{T}}{H} \bar{C}_a \right). \quad (12)$$

293 Calculations of mean and perturbed  $K_{OL}$  and  $H$  followed Ma and Cao (2010). Likewise,  
 294 the ice-air exchange flux can be defined as, assuming that the ice-air exchange process is  
 295 the same as the snow-air exchange,

$$296 \quad F'_i = v_a (C_i / K_{sa} - C_a), \quad (13)$$

297 where  $C_i$  is the concentration in ice.  $v_a$  is the exchange velocity of a chemical between air  
 298 and ice ( $m s^{-1}$ ),  $K_{sa}$  is the ice – air partition coefficient. The expressions of these mean and  
 299 perturbed parameters were referred to Ma et al (2011). The perturbed ice-air exchange  
 300 flux is given by

$$301 \quad F'_i = \bar{v}_a \left[ \frac{1}{K_{sa}} \left( C'_i - \frac{K'_{sa}}{K_{sa}} \bar{C}_i \right) - C'_a \right] + v'_a \left( \frac{\bar{C}_i}{K_{sa}} - \bar{C}_a \right). \quad (14)$$

### 302 3. Results

#### 303 3.1 Step change points by MK test

304 The number of PCBs congeners and OCPs measured at different sites differs from  
305 each other. We have calculated the step change points for all monitored PCBs and OCPs  
306 at each monitoring site. The presence of these points in the monitored PCBs and OCPs  
307 was not identical but varied with different chemicals at different monitoring sites. It is  
308 impossible to illustrate the step change points for all POPs time series at all monitoring  
309 sites. In the present study, only those chemicals whose forward and backward sequences  
310 ( $UF_i$  and  $UB_i$ ) lay partly within the confidence interval (-1.96 – 1.96) in the MK test were  
311 selected for step change analysis.

##### 312 3.1.1 Alert

313 **Figure 1** displays  $UF_i$  and  $UB_i$  for 16 PCBs and 9 OCPs derived by the MK test (Eq .  
314 (5)) at Alert monitoring station. As defined, the intersections between the forward and  
315 backward sequences  $UF_i$  (curved blue line) and  $UB_i$  (curved red line) within the  
316 confidence levels of -1.96 (straight purple line) to 1.96 (straight green line) denote step  
317 change points for these POPs time series. As shown,  $UF_i$  and  $UB_i$  intersected at least once  
318 over the period of 1993 through 2012. Most intersections were well within the confidence  
319 levels between -1.96 and 1.96 at the statistical significance  $\alpha = 0.01$ , except for  $\alpha$ - and  
320  $\gamma$ -HCH whose intersections were outside the confidence level. Hence, there were no step  
321 change points of these two HCH isomers. The two step change points in 1997 and 2004  
322 were detected for  $\beta$ -HCH.  $\beta$ -HCH partitions much more strongly into cold water than



323  $\alpha$ -HCH. Ocean currents and river currents were thought to dominate the entry of  $\beta$ -HCH  
324 into the western Arctic Ocean (Li et al., 2002). Elevated concentrations of  $\beta$ -HCH in air  
325 over the Canadian Arctic might be partly explained by its outgassing from the nearby  
326 ocean. It is not clear if the two step change years of this HCH isomer were attributable to  
327 its revolatilization following its increasing oceanic transport. The increasing trend of  $UF_i$   
328 for  $\beta$ -HCH from 2002 at Alert, suggesting its increasing air concentration, was not  
329 observed at other monitoring sites which are far from the western Arctic Ocean as  
330 compared with Alert site.

331 For tri-PCBs, three step change points were found between 2000 and 2005 (PCB-16,  
332 25, and 26) and two found in 1998 (PCB-18 and 25), respectively. The step change points  
333 in PCB-44, 49, 105, 106, and 209 were also found after 2000 but more step change points  
334 in tetra-, penta-, hexa-, and deca-PCBs were detected before 2000. On the other hand, the  
335 step change points in all 6 DDT (dichlorodiphenyldichloroethane) isomers were found  
336 after 2000 and the four of these six DDT isomers showed step change points before 2000.  
337 It can be also observed that, though  $UF_i$  and  $UB_i$  were intersected over 2001 – 2002, the  
338 point of the intersection was outside of the confidence level. Hence, this point was not  
339 regarded as a step change point. The number of chemicals with statistically significant  
340 step change points for different periods is presented in **Table 1**.

### 341 **3.1.2 Zeppelin**

342 **Figure 2** illustrates  $UF_i$  and  $UB_i$  for 13 PCBs, HCB, and p,p'-DDT from 1994-2012  
343 at Zeppelin site, derived by the MK test. The intersections between  $UF_i$  and  $UB_i$  were

344 identified for these PCBs except for PCB-189. The first intersection occurred between  
345 2001 and 2003, and the second one took place mostly in 2007. **Table 1** also presents the  
346 MK test derived step change point years of 20 PCBs congeners and 3 DDTs isomers at  
347 Zeppelin and other arctic sites during the 2000s. The step change points for other OCPs  
348 were below the confidence level and hence not accounted here. Although the  $UF_i$  and  
349  $UB_i$  sequences lay between the positive and negative confidence levels (1.96 and -1.96)  
350 before 2000 and after 2008, no intersections between the two sequences were detected  
351 within the confidence levels. Overall, the MK test detected the most step change points  
352 of these chemicals for the two periods, spanning from 2001 to 2003 and from 2007 to  
353 2008, respectively. Both step changes span approximately a 3-year time period. Eighteen  
354 chemicals were found to exhibit step change points for the period of 2001 through 2003  
355 and twenty one chemicals were identified to have step change points for the period of  
356 2006 through 2008. Since most PCBs data were only available from 1998, their trends  
357 and step change points could not be identified in the 1990s. Nevertheless, while the  
358 ambient air concentrations of three DDTs isomers are available from 1994, the only step  
359 change point year 1997 for *p,p'*-DDD was found during the 1990s by the MK test (**Table**  
360 **1**).

### 361 **3.1.3 Storhofdi and Pallas**

362 There are only 10 coeluting PCB congeners reported by Storhofdi station (Hung et al.,  
363 2010). The  $UF_i$  and  $UB_i$  sequences of 9 PCBs out of 10, together with  $\alpha$ -,  $\gamma$ -HCH, and  
364 HCB which fall into the confidence levels from 1995 to 2011 are shown in **Fig. S2**. The

365 most intersections between the  $UF_i$  and  $UB_i$  sequences of the 9 PCBs can be found  
366 between 2006 and 2008, except for PCB-105 and 180. Other step change points for these  
367 PCBs were found in the 1990s and the early 2000s (PCB-28, 31, 105, 138, 153, 180, and  
368 HCB), as is also shown in **Table 1**. No step change year for  $\alpha$ -HCH was detected during  
369 this period of time but there was the step change year for  $\gamma$ -HCH in 2007. HCB exhibited  
370 a step change point in 1999. Further details are shown on **Table 1**.

371 There are 7 coeluting PCB congeners reported by Pallas station. The  $UF_i$  and  $UB_i$  of  
372 all these 7 PCBs fall into the confidence level. The MK statistics of these 7 PCB  
373 congeners and  $\alpha$ - and  $\gamma$ -HCH is illustrated in **Fig. S3**. Analogous to Zeppelin and  
374 Storhofdi stations, the most intersections between  $UF_i$  and  $UB_i$  of the reported PCBs  
375 were found in 2007, except for PCB-180 which showed the step change year in 2003.  
376 Other statistically significant step change years were detected between 2001 and 2003  
377 (PCB-101, 118, 138, and 180), and in 2005 (PCB-52, 101, and 153), as is also shown in  
378 **Table 1**. Again, although the  $UF_i$  and  $UB_i$  of  $\alpha$ - and  $\gamma$ -HCH were intersected in 2003 and  
379 2004, these two intersections were below the confidence level and therefore no step  
380 change points for HCHs were accounted for.

### 381 **3.2 Step change points identified by MTT and Yamamoto methods**

382 Considering that in some cases the MK test failed to yield step change point for a  
383 time series (Yamamoto et al., 1985), the MTT and Yamamoto methods were further  
384 employed in the same datasets of PCBs and OCPs at the four arctic monitoring sites to  
385 verify the MK test results and to increase the confidence of detected step change points

386 by the MK test. **Figures S4** and **S5** in the Supplement show the MTT and Yamamoto  
387 statistics for PCBs and OCPs time series at Storhofdi and Pallas monitoring stations,  
388 respectively. Compared with the results from the MK statistics, both the MTT and  
389 Yamamoto methods did not detected statistically significant step change points in 2007  
390 for most PCBs and OCPs at Pallas. The MTT method detected the step change point  
391 around 2000 for penta-PCB (PCB-101 and 118) and hexa-PCB (PCB-138 and 153), and  
392 for penta-PCB from 2007 to 2008. Step changes in  $\alpha$ - and  $\gamma$ -HCH were found between  
393 2000 and 2002, and in 2005. Yamamoto method only detected a step change year around  
394 2000 for PCB-138, but, analogous to the MTT method, found the step change between  
395 2000 and 2002 for the two HCH isomers. Both MTT and Yamamoto methods detected  
396 the step change in 2001 for PCB-101 and 2003 for PCB-105, but only found the 2007 as  
397 the step change year for PCB-52 and  $\alpha$ -HCH, respectively (Supplement **Fig. S5**).

398 **Figure 3** shows the MTT statistics for 30 PCBs at Zeppelin station. The MTT  
399 statistics for these PCBs illustrate a “V” pattern except for several heavier PCBs. All  
400 tri-PCBs exhibited the step change year in 2008. The same step change year was also  
401 found for PCB-52, 74, 101, 138, 149, 170, and 180. The step change year 2008 for these  
402 PCBs derived from the MTT method lagged one year behind the step change year (2007)  
403 detected by the MK test (**Fig. 1** and **Table 1**). However, this step change year (2008) can  
404 be regarded as an extension of the step change year 2007 because the step change year  
405 2007 by the MK test is an onset year of step change. Other step change years were  
406 detected in 2000, 2002, and 2005, but for only several PCBs out of 30 PCB congeners.

407 The MTT statistics for OCPs did not show any well-organized pattern like PCBs (figures  
408 not shown). The step change points of OCPs varied with different chemicals but 1999  
409 and 2003 appeared to be mostly detected step change years among these OCPs. The  
410 Yamamoto statistics also displayed peak values and step changes in 2008 for many PCBs,  
411 followed by 2000 and 2002 (results not shown). Supplement Tables S4 and S5 present  
412 the step change years for PCBs and OCPs at Zeppelin site computed by the MTT and  
413 Yamamoto method.

414 The results from the MTT and Yamamoto statistics for 20 PCBs at Alert are  
415 illustrated in **Fig. 4** and also presented on Supplement Tables S4 and S5. The both MTT  
416 and Yamamoto methods yielded a step change point in 2006 for several PCBs, notably  
417 PCB-16A, 25, 44, 118, 174, and 209. The MTT method detected the step change year in  
418 2005 for both  $\alpha$ - and  $\gamma$ -HCH but the Yamamoto method only found this step change year  
419 for  $\alpha$ -HCH (Tables S4 and S5). Nevertheless, this step change year for HCHs was not  
420 discerned by the MK test, as illustrated previously. The two methods also detected the  
421 step change year for *p,p'*-DDE in 2000 which was consistent with the step change year  
422 detected by the MK test, and in 2001 for *p,p'*-DDD, leading the MK test result (2002) by  
423 one year.

#### 424 **4. Discussions**

425 To summarize the step change points for selected chemicals at the 4 arctic atmospheric  
426 monitoring sites, we firstly selected those PCBs and OCPs whose step point years were  
427 identified by the MK test and confirmed by one of the other two methods. Results show

428 that, for Alert, the statistically significant step change year detected by the MK test and  
429 the MTT or Yamamoto method was only found in 2005-2006 for PCB-16 and 44,  
430 respectively. While the MK test also identified the same step change in PCB-49, 105, and  
431 110 during this period of time (**Fig. 1**), this step change was not detected by the other two  
432 methods (**Fig. 4**). The step change years in OCPs detected by the MK test were not  
433 confirmed by the MTT and Yamamoto method either. In the MK test,  $UF_i$  (the forward  
434 sequence, Eq. (5)) was often used to represent the trend of a time series. At Alert, the  $UF_i$   
435 values of lighter PCBs (tri-PCBs and PCB-44) showed an increasing trend and a negative  
436 to positive reversal since 2005. In fact, almost all intersections between  $UF_i$  and  $UB_i$  of  
437 these lighter PCBs, indicating the step change, took place when  $UF_i$  became positive,  
438 confirming the increasing trend of these lower molecular PCBs measured at Alert during  
439 the mid-2000s whereas heavier PCBs did not show significant increasing trend for the  
440 same period of time.

441 The step change years detected by the MK test and the MTT or Yamamoto method  
442 at Storhofdi include 2007 for PCB-52 and 2003 for PCB-105, respectively (**Fig. S2** and  
443 **Fig. S4**). Among the measured PCBs, the  $UF_i$  values of PCB-52, 101, and 118 exhibited  
444 an increasing trend since 1998-2000. Such an increasing trend was not observed in  $UF_i$   
445 values in other PCBs and OCPs.

446 At Pallas site, the MK test and MTT or Yamamoto method found the step change  
447 year 2001 for PCB-118 and 138, and 2007 for PCB-101 and 108, respectively (**Fig. S3**  
448 and **Fig. S5**). The  $UF_i$  did not show significant increasing trend for all PCBs and OCPs.

449 The MTT method confirmed the step change year in most PCBs in 2007 at Zeppelin  
450 calculated by the MK test, except for PCB-47, 153, and 180 (**Figs. 2 and 3**). Another step  
451 change year in 2002 – 2003 for several PCBs detected by the MTT method was also  
452 consistent, to some extent, with that derived from the MK test. As shown by **Fig. 2**, the  
453  $UF_i$  values of many PCBs showed an increasing trend from the early and mid-2000s and  
454 reached the maximum for 2007 – 2008, again agreeing with the measured trend of  
455 ambient atmospheric concentrations of these PCBs.

456 **Table 2** summarized the step change years for PCBs and OCPs at the 4 arctic  
457 atmospheric monitoring sites discerned simultaneously by the MK test and the MTT or  
458 Yamamoto method. Overall, although the step changes years varied with different  
459 chemicals and monitoring sites, these step change points all took place in the 2000s.  
460 Further, although individual statistical method did identify the step changes in OCPs,  
461 these changes were not detected simultaneously by 2 out of the 3 statistical methods used  
462 in the present study. Among the three periods of 2001-2003, 2005-2006, and 2007-2008  
463 listed in **Table 2**, the step change point was found in the highest number of monitored  
464 chemicals for the period of 2007-2008, followed by 2001-2003 and 2005-2006,  
465 respectively. Although 2005-2006 and 2007-2008 are two adjacent periods, the step  
466 changes in POPs concentrations during these two periods might show their distinct  
467 response to marked decline of sea ice concentrations in 2005 and 2007, respectively, as  
468 shown in **Fig. 5**. Another common feature from the MK test was that the forward  
469 sequence  $UF_i$  for many PCBs showed increasing trend from 2000, as illustrated by **Figs.**

470 **1, 2, S2, and S3.**

471 The causes for the existence of those step change points in monitored POPs time  
472 series at the different arctic sites are complex. They depend on locations of the monitoring  
473 sites, chemical-physical properties of individual chemical, changes in arctic sea ices and  
474 air temperatures which are non-uniform across the Arctic, and others. Our statistical tests  
475 showed that the step change points were mostly detected in PCBs. This is likely related to  
476 their relatively higher Henry's law constants, ranging from  $4.4 \text{ Pa m}^3 \text{ mol}^{-1}$  for PCB-194  
477 to  $33.9 \text{ Pa m}^3 \text{ mol}^{-1}$  for PCB-31 (Li et al., 2003), as compared with other chemicals (e.g.,  
478 DDTs and HCHs), indicating higher tendencies for volatilization from water/ice to air.  
479 The ambient atmospheric concentrations of HCB at Zeppelin, which has higher Henry's  
480 law constant ( $= 65 \text{ Pa m}^3 \text{ mol}^{-1}$ , Shen and Wania, 2005), also showed an increasing trend  
481 from 2003 (**Fig. 2**). This increasing trend has been attributed to changes in source types  
482 and the presence of impurities in current use pesticides as well as sea ice retreat (Hung et  
483 al., 2010; Becker et al., 2012). However, no step change point for HCB in our statistical  
484 analysis was detected, though this substance exhibited a clear increasing trend in the  
485 mid-2000s at Zeppelin site. This might be attributed to strong persistence of HCB in air  
486 which leads to less significant declining in the Arctic over the last two decades (Hung et  
487 al., 2010). The increasing HCB concentrations in the mid-2000s were not significant  
488 enough to yield a "step change" from its weak decreasing trend before the mid-2000s.

489 Results presented on **Tables 1 and 2** also show more PCBs congeners with  
490 statistically significant step change points at Zeppelin than that detected at Alert.



491 Compared with Zeppelin monitoring site which is located in the western coast of  
492 Spitsbergen (Svalbard, Norway), the Alert station is under lower temperature, surrounded  
493 by rugged hills and valleys, and hence less affected by sea ice retreat and open waters. In  
494 addition, as shown by **Fig. 1** and **Table 1**, the step change points in several PCBs and  
495 DDTs were detected in 2001 – 2003 by the MK test. Due to laboratory switching in 2002  
496 which led to increasing air concentrations of monitored POPs after 2002 (Hung et al.,  
497 2010), the step changes in POPs from 2001 to 2003 at Alert might be also subject to  
498 laboratory switching.

499 The both temporal and spatial patterns of POPs in arctic air have been attributed to  
500 various processes driven by climate induced changes in the arctic environment, such as  
501 reduced ice cover, increasing air and seawater temperatures, and biomass burning in  
502 boreal regions (Hung et al., 2010; Ma et al., 2010; Becker et al., 2012). Since the step  
503 changes in POPs are unlikely associated with interannual climate variability (e.g., the  
504 NAO, ENSO) and biomass burning which should affect primarily the seasonal or  
505 interannual alteration in POPs, these step changes were anticipated to be fluctuations in  
506 long-term trend in POPs time series. The statistically significant step change point years  
507 for PCBs in the present study appeared to coincide with those years during which arctic  
508 sea ice exhibited marked decline. **Figure 5** shows the mean summer temperature and sea  
509 ice extent anomalies from 1981 to 2012 averaged over the Arctic as the departures from  
510 their means over 1950 to 2010 and 1979 to 2010, respectively. It can be seen that the  
511 mean sea ice extent declined in the summer of 2002, 2005, and 2007. In particular, the

512 mean summer sea ice extent exhibited a decreasing trend and become negative since 2001.  
513 This result agreed with a previous report which showed that, during the 2000s, the arctic  
514 sea ice September minimum extent (i.e., area with at least 15% sea ice coverage,  $10^7 \text{ km}^2$ )  
515 reached new record lows in 2002, 2005, and 2007 ([http://earthobservatory.nasa.gov/  
516 Features/WorldOfChange/sea\\_ice.php](http://earthobservatory.nasa.gov/Features/WorldOfChange/sea_ice.php)). Accordingly, a negative to positive transition of  
517 the mean air temperature anomalies averaged over the Arctic took place since 2001, as  
518 also shown in **Fig. 5**. In particular, summer ice extent in 2007 was about 33% below the  
519 1979-2013 average, broking all previous low ice extent records. Our calculated step  
520 change points of 2007 through 2008 for many PCBs matched well with this strong decline  
521 of the sea ice extent for this period of time.

522 Since sea-ice melting is a crucial factor for controlling environmental fate of POPs  
523 in the Arctic under a warming climate (Becker et al., 2012; Grannas et al., 2013) and the  
524 associations between the step changes in ambient atmospheric concentrations and sea ice  
525 concentrations, it is worthwhile to elucidate the response of POPs to arctic warming and  
526 sea ice fluctuation and melting. We simulated perturbed air concentration ( $\text{pg m}^{-3}$ ) of  
527 PCB-28, 153, and  $\alpha$ -HCH from 1995 to 2012 subject to water-air and ice-air exchange  
528 processes using the perturbation model (Ma and Cao, 2010, Ma et al., 2011). Considering  
529 that the most prominent arctic sea ice melting occurs from July to September, in the  
530 simulation we employed mean sea ice volume and area during this season averaged over  
531 the Arctic. Air temperature (K) and precipitation ( $\text{mm yr}^{-1}$ ) anomalies used in the  
532 perturbation modeling for the same period were also adopted in the modeling. The mean

533 concentrations in air, water, and sea ice used in perturbation modeling are presented in  
534 Supplement Table S1. The perturbed concentrations of the three chemicals averaged over  
535 the Arctic are displayed in **Fig. 6**. As shown, perturbed concentrations of all three  
536 chemicals correlated inversely with the mean sea ice anomaly. It is evident that the  
537 perturbed concentrations of PCB-28 and 153 illustrated a statistically significant  
538 increasing trend during the period of 1995 through 2012. While there was also an  
539 increasing trend of  $\alpha$ -HCH, this trend was not statistically significant. Opposite to the sea  
540 ice extent whose anomalies become negative from 2001, perturbed concentrations of  
541 PCB-28 turned to positive from 2003, after the first step change point year (2001) of this  
542 PCB congener (**Table 1**), whereas the negative to positive reversal of perturbed  
543 concentration of the other two chemicals (PCB-153 and  $\alpha$ -HCH) took place in  
544 2007-2008, during which the Arctic recorded lowest sea ice extent. The concentration  
545 perturbations trend of PCB-28 exhibited a much steep slope at 0.031 ( $R^2=0.809$ ) as  
546 compared with that of PCB-153 (slope=0.008,  $R^2=0.626$ ), suggesting that lighter PCBs  
547 respond more strongly to arctic sea ice melting. Since perturbation model simulated  
548 concentration perturbations via ice-air exchange process were about one order of  
549 magnitude lower than that through water-air exchange in the present study (results not  
550 shown), the integrated perturbed concentrations were mostly driven by the water-air  
551 exchange. As aforementioned, the monitored atmospheric concentrations of many PCBs  
552 across the Arctic have already shown an increasing trend around 2007, potentially the  
553 result of outgassing from the Arctic Oceans due to sea ice retreat (Hung et al., 2010;

554 Becker et al., 2012). Since the perturbed concentrations discern largely the climate  
555 change signals in POPs time series, associated with temperatures and sea ice, it might not  
556 be appropriate to compare the step change points in the time series of perturbed  
557 concentrations with measured annual mean air concentrations. The latter are driven  
558 primarily by emissions and degradation. Nevertheless, the perturbed air concentrations of  
559 many PCBs examined in the present study showed the step change in 2001 (**Fig. S6**), the  
560 first step change point of monitored PCBs atmospheric concentrations (Tables 1 and 2)  
561 and the year when the mean summer temperature and sea ice extent anomalies over the  
562 Arctic change their signs (**Fig. 5**).

563 Compared with the measured ice concentration used in the present study ( $0.1 \text{ ng L}^{-1}$ ,  
564 Table S1), higher levels of  $\alpha$ -HCH ( $0.31 \text{ ng L}^{-1}$ ) in sea ice at a high Canadian Arctic site  
565 in Beaufort Sea during 2007-2008 was reported by Pućko et al (2010). They also  
566 measured  $\alpha$ -HCH in sea ice brine and expected that arctic sea-ice changes associated with  
567 climate change would make the brine concentration pathway more widespread in the  
568 future Arctic Ocean. To test potential influence of higher  $\alpha$ -HCH concentrations in sea ice  
569 and sea ice brine on the fluctuation and temporal trend of this chemical over the Arctic air,  
570 we adopted the measured  $\alpha$ -HCH concentrations in sea ice and sea ice brine by Pućko et  
571 al (2010) as the mean concentrations in the perturbation model and integrated the model  
572 from 1995 to 2012. **Figure S7** compared the perturbed  $\alpha$ -HCH concentrations in air and  
573 ice due to air-ice exchange from 1995 – 2012 using the data in Table S1 and Pućko et al  
574 (2010). As expected, the model input higher mean concentrations of  $\alpha$ -HCH in sea ice and

575 ice brine increase the magnitude of perturbed annual concentrations in air and ice but does  
576 not alter their fluctuations and long-term trend. This suggests again that the changes in  
577 temperature dominate the fluctuations of perturbed  $\alpha$ -HCH concentrations over the  
578 Arctic.

579         The rapid decline of arctic sea ice in 2007 has triggered the debate on abrupt climate  
580 change in the Arctic and low summer sea ice area was likely persistent on a decadal  
581 (climate change) time scale. Given that the environmental fate of the selected POPs in the  
582 Arctic have been dominated by their primary emission and outgassing from their  
583 reservoirs accumulated from past use, deposition, and long-range transport from  
584 atmosphere and oceanic currents (Macdonald et al., 2005; Gioia et al., 2008; Hung et al.,  
585 2010; Kallenborn et al., 2012; Wöhrnschimmel et al., 2013), atmospheric levels of many  
586 POPs in the Arctic have been declining during last decades after their regulation and  
587 phase out. Previous modeling investigations (Lamon et al., 2009; Wöhrnschimmel, et al.,  
588 2013) have revealed that the maximum changes in POPs atmospheric concentrations  
589 induced by climate change were driven mostly by climate warming forced potential  
590 changes in primary emission. This appeared to suggest that the POPs outgassing from  
591 their arctic repositories associated with arctic warming and sea ice retreat would not  
592 change their long-term declining trend because the emission and degradation  
593 overwhelmed the POPs long-term declining trend. However, as aforementioned, the  
594 measured ambient POPs air concentrations in the mid-2000s did not follow the declining  
595 trend driven by primary emissions and degradations. The perturbation modeling was

596 aimed at assessing major processes contributing to concentration anomalies as the  
597 departure from the mean POPs concentrations driven mostly by their primary emission  
598 and degradation. We have demonstrated that the temperature-dependent emission (Eqs. (8)  
599 and (9)) could alter the magnitude of modeled concentration perturbations but not change  
600 long-term trend and interannual variation of the perturbed concentrations (Ma and Hung,  
601 2012). The perturbed (rather than measured) POPs air concentrations were, therefore,  
602 forced largely by the outgassing from their reservoirs in melting ice (snow) and the Arctic  
603 Oceans. In this context, a reversal of many POPs from deposition to volatilization  
604 associated potentially with arctic warming and sea ice retreat would likely take place. To  
605 examine this argument, we estimated perturbed water-air and ice-air exchange flux ( $\text{ng}$   
606  $\text{m}^{-2} \text{s}^{-1}$ ) of the three selected chemicals (PCBs-28, 153, and  $\alpha$ -HCH). Results show that the  
607 modeled water-air exchange flux perturbations of the three selected chemicals exhibited  
608 similar trend and interannual variability. So in **Fig 7** we only present perturbed water-air  
609 exchange flux of PCB-28 and  $\alpha$ -HCH. As shown, the modeled exchange flux  
610 perturbations of PCB-28 were negative over the 1990s except for 1998, indicating  
611 deposition of perturbed PCB-28. From 2001 onward, the perturbed flux turned to positive  
612 and exhibited a clear increasing trend with greater values in 2007 and after 2010, implying  
613 climate change forced revolatilization of this PCB congener. The perturbed water-air  
614 exchange fluxes of  $\alpha$ -HCH were positive throughout the modeling period of 1995 through  
615 2012, except for 1996. This agrees with previous modeling results which predicted  
616 reversal of  $\alpha$ -HCH for its exchange direction from deposition to volatilization in the

617 Arctic Ocean in the early 1990s (Wania and Mackay 1999a, Wania et al. 1999b).  
618 Comparing with the mean air concentration of PCB-28 at  $3 \text{ pg m}^{-3}$ , the modeled maximum  
619 perturbed concentration of PCB-28 due to water-air and ice-air exchange was  $0.25 \text{ pg m}^{-3}$ ,  
620 about 8% of the mean. For PCB-153, the modeled maximum perturbed concentration was  
621 almost 30% of the mean (Supplement Table S1), showing stronger response of this PCB  
622 congener to the change in the arctic environment. On the other hand, the modeled  
623 maximum perturbed  $\alpha$ -HCH concentration was only 5% of its mean concentration  
624 (Supplement Table S1). The perturbation of POPs air concentrations at this magnitude  
625 induced by sea ice retreat and snow melting should not be overlooked. If there was indeed  
626 the onset of arctic abrupt climate change “tipping” point, continuous decline of arctic sea  
627 ice in the forthcoming years may lead to stronger release of POPs into arctic air. As  
628 shown in **Fig. 7**, both perturbed air concentrations and water-air exchange fluxes of  
629 PCB-28 become positive after 2001 with relatively large values in 2007, coincident with  
630 these two years during which many PCBs showed the onset of step changes and the arctic  
631 sea ice extents reduced considerably (**Figs.1, 2, S2, S3** and **Table 2**).

632 The modeled annual ice-air exchange flux perturbations of two PCBs averaged over  
633 the Arctic also showed similar trend and interannual variation. The exchange fluxes of  
634 PCB-28 were positive throughout the modeling period (1995-2012), indicating outgassing.  
635 The fluxes of the other two chemicals were negative. To illustrate ice-air exchange,  
636 **Figure 8** displays perturbed ice-water exchange fluxes ( $\text{ng m}^{-2} \text{ s}^{-1}$ ) of three chemicals. The  
637 flux perturbations of PCB-28 and 153 show an increasing trend and the negative to

638 positive reversal in 2007, the year for the potential onset of arctic abrupt climate change  
639 “tipping” point (Livina and Lenton, 2013). Differing from its water-air exchange flux, the  
640 annual mean ice-air exchange flux perturbation of  $\alpha$ -HCH averaged over the Arctic  
641 decreased from the 1990s. It is not clear if the stronger response of PCB-28 to sea ice  
642 retreat characterized by its step changes in 2001 and 2007 at the Zeppelin station (**Table 2,**  
643 **Figs. 2 and 3**) could be attributed to its outgassing from melting sea ice and glaciers as  
644 compared with PCB-153 and  $\alpha$ -HCH. The latter two chemicals showed negative  
645 exchange fluxes, indicating deposition. Accordingly, there were no step change points for  
646 these two chemicals in 2001 and 2007 (Table 2). While the releasing from melting ice  
647 may increase air concentrations, it would also lead to increased potential for air to sea  
648 transfer (Gioia et al., 2008), characterized by the negative flux. Overall, our results  
649 showed that the perturbed ice-air exchange fluxes were lower than the water-air fluxes in  
650 arctic environment. Since the modeled water-air exchange flux perturbations were positive  
651 which might increase air concentrations, these increasing air concentrations from the  
652 water-air exchange may lead to deposition in the ice-air exchange, as interpreted by Gioia  
653 et al (2008). POPs releasing from seasonal melting snow pack and mountain glaciers has  
654 been demonstrated to change significantly the environmental fate of POPs (Stocker et al.,  
655 2007; Bogdal et al., 2009; Meyer et al., 2008). Previous studies in this aspect almost  
656 entirely focused on the effect of seasonal changes in sea ice melting on POPs  
657 environmental fate (Daly and Wania, 2004; Gioia et al., 2008; Jantunen et al. 2007, Wong  
658 et al. 2010). Little is known about the change in long-term environmental fate of POPs in



659 the Arctic induced by interannual or decadal scale sea ice variation. It should be noted that,  
660 due to very sparse POPs measurements in sea ice and glaciers across the Arctic, the mean  
661 ice concentrations we input to the perturbation model may have large errors which could  
662 even alter the exchange direction in modeled fluxes. Using the sampled  $\alpha$ -HCH  
663 concentrations in air, water, and brine from Pućko et al (2010) collected in the Canadian  
664 High Arctic we have simulated the perturbed air-brine gas phase exchange flux of  $\alpha$ -HCH  
665 and compared the result with the perturbed air-ice exchange fluxes using the data  
666 presented in Table S1. It was found that, though the two time series of the perturbed fluxes  
667 exhibited the same fluctuation and trend driven by temperatures and sea ice extents, the  
668 air-brine exchange fluxes were several orders of magnitude greater than the air-ice fluxes  
669 and did not switch from positive to negative as shown in perturbed air-ice flux which  
670 turned from positive to negative from 2008 (**Fig. 8**).

## 671 **5. Conclusions**

672 After their phase out, many legacy POPs have been and will be still declining in the  
673 Arctic environment in forthcoming years. An increasing trend of POPs atmospheric  
674 concentrations under strong warming and sea ice melt across the Arctic is unlikely to take  
675 place as comparing with continuously increasing trend of arctic temperature. However,  
676 there is likely a "turning point" for these POPs in the context of climate change. From  
677 this point of year onward arctic warming influence on POPs trend may become relatively  
678 stronger. In other words, there would be stronger arctic climate change "signals" in  
679 monitored ambient POPs concentrations data after this turning point. Our statistical test

680 identified two major step change points in the measured PCB time series, coincident with  
681 the onset of rapid arctic sea ice melting after 2001. Our perturbation modeling suggested  
682 that the periods of 2001-2002 and 2007-2008 were likely the "turning points" for PCBs  
683 in arctic air, as demonstrated by the reversal of deposition to outgassing of the perturbed  
684 water-air exchange flux and negative to positive transition in the modeled air  
685 concentration perturbations of the selected chemicals. In particular, from the second step  
686 change point year (2007-2008) onward identified in the present study, we would expect  
687 that the effect of arctic climate change on POPs environmental fate would become more  
688 detectable. This is supported partly by the increasing air concentrations of many PCBs  
689 measured at the Zeppelin and Alert sites (Hung et al., 2010). The finding from the present  
690 study discerned not only the abrupt climate change signatures in measured time series of  
691 POPs atmospheric concentrations, but also provided additional evidence for the response  
692 of arctic environment and ecosystem to arctic climate change.

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698

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861  
 862 **Table list:**

863  
 864 **Table 1.** PCBs congeners and OCPs isomers having step change points at four arctic  
 865 monitoring stations detected by the MK test.

	<b>Step change point years</b>		
	2001-2003	2005-2006	2007-2008
<b>Zeppelin</b>	CB-28,31,33,37,47,99,14 4,156,167,170,180,183,1 87,189,194,206,209, p,p'-DDE	CB-180	CB-18,28,31,33,37,47,52 ,99,101,153, 156,167,170,183,p,p'-D DD, p,p'-DDE,
<b>Alert</b>	CB-25,26,44, p,p'-DDE, o,p'-DDD, p,p'-DDD, p,p'-DDT	CB-16,49,p,p'-DDE	CB-44,49,105,110, o,p'-DDE, o,p'-DDT
<b>Storhofdi</b>	CB-28,31,105,138,180	CB-138, $\gamma$ -HCH	CB-28,31,52,101,118, 138,153,
<b>Pallas</b>	CB,101,118,138,180	CB-52,101,153	CB-28,52,101,118,153

866  
 867  
 868 **Table 2.** PCBs congeners having step change points at four arctic monitoring stations  
 869 detected by the MK test and Moving T-Test (MTT) or Yamamoto methods.

	<b>Step change point years</b>		
	2001-2003	2005-2006	2007-2008
<b>Zeppelin</b>	CB-18,28,33,37,170,189		CB-18,28,31,33,37,52, 101,149,170,180
<b>Alert</b>		CB-16A, 44	
<b>Storhofdi</b>	CB-28,31		CB-52
<b>Pallas</b>	CB-118,138		CB-101,108

870  
 871 **Figure list and captions:**

872

873 **Figure 1.** Mann–Kendall’s testing statistics for PCBs and OCPs collected from the Alert  
874 station (1993–2012). Blue solid line is the forward sequence  $UF_i$  and red solid line is  
875 backward sequence  $UB_i$ , defined by Eq. (5). Two straight solid lines stand for confidence  
876 interval between -1.96 (straight purple line) and 1.96 (straight green line) in the MK test.  
877 Intersection of  $UF_i$  and  $UB_i$  sequences within interval between two confidence levels  
878 indicates a step change point.

879 **Figure 2.** Same as Fig. 1 but for Zeppelin station (1992-2012).

880 **Figure 3.** Moving T-Test statistics for ambient annual mean air concentrations of 30  
881 PCBs collected at Zeppelin station (1992–2012).

882 **Figure 4.** Moving T-Test (left panel) and Yamamoto (right panel) statistics for annual  
883 mean ambient air concentrations of 20 PCBs collected at Alert station (1993–2012).

884 **Figure 5.** Mean summer temperature (July – September, K, 1981-2012) averaged over the  
885 Arctic as the departures from 1950 to 2010 mean (NCEP reanalysis, Kalney et al., 1996)  
886 and sea ice extent (July –September,  $10^7$  km<sup>2</sup>) anomalies from 1981-2012 averaged over  
887 the Arctic as the departures from 1979 to 2010 mean, manipulated from NSIDC data  
888 (Clark, et al., 1999) .

889 **Figure 6.** Modeled perturbed air concentration ( $C_a'$ , pg m<sup>-3</sup>) of PCB-28, 153, and  $\alpha$ -HCH  
890 from 1995 to 2012.  $C_a'$  of PCB-28 and 153 is scaled on the right Y axis and perturbed air  
891 concentration of  $\alpha$ -HCH is scaled on the left Y axis. The mean concentrations in air, water,  
892 and sea ice of the three chemicals used in perturbation are presented in Table S1 and their  
893 physical-chemical properties are presented in Table S2, respectively.

894 **Figure 7.** Simulated water-air exchange flux perturbations (ng m<sup>-2</sup> s<sup>-1</sup>) of PCB-28 and  
895  $\alpha$ -HCH from 1995 to 2012.

896 **Figure 8.** Simulated ice-air exchange flux perturbation (ng m<sup>-2</sup> s<sup>-1</sup>) of three selected  
897 chemicals from 1995 to 2012. Perturbed fluxes of PCB-28 and 153 are scaled on the left  
898 Y axis and  $\alpha$ -HCH flux perturbation is scaled on the right Y axis. Blue dished line stands  
899 for the case for  $\alpha$ -HCH flux perturbation = 0 and pink dashed line stands for the case for  
900 PCB-28 and 153 flux perturbation = 0.

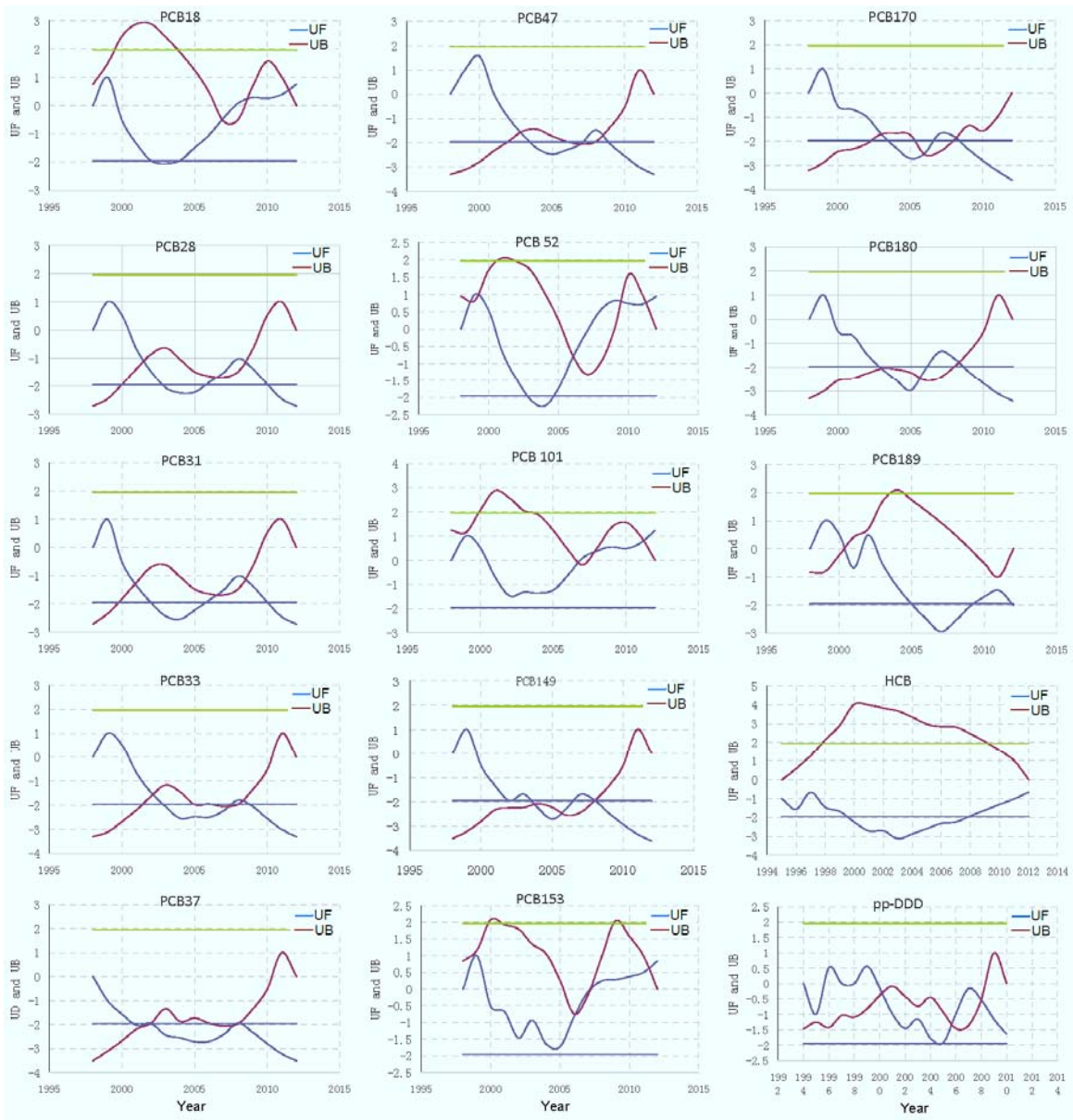
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902 **Figures**



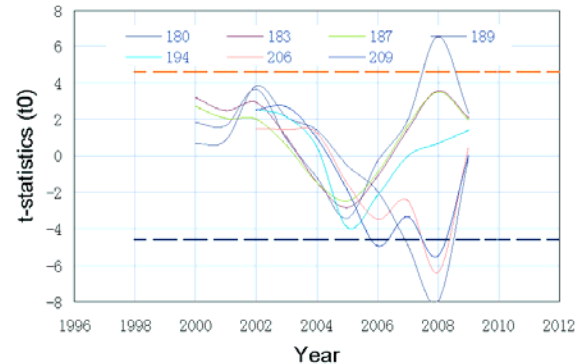
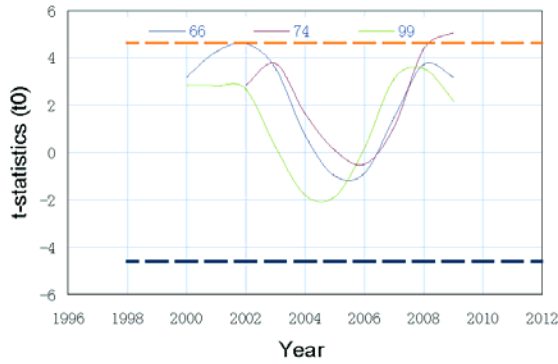
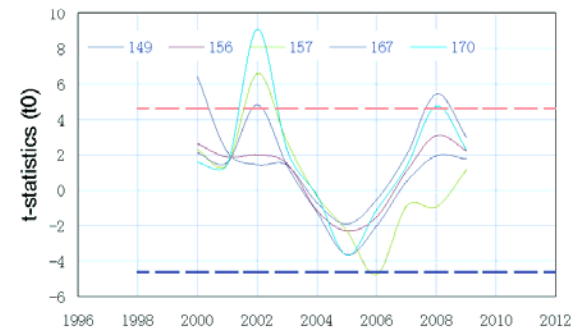
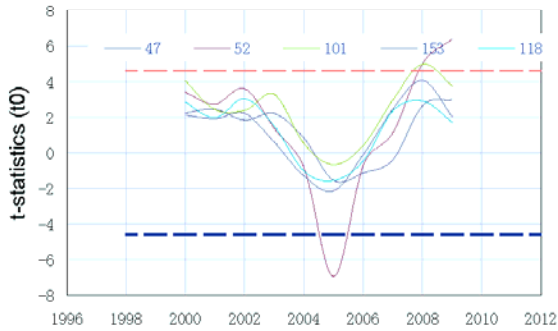
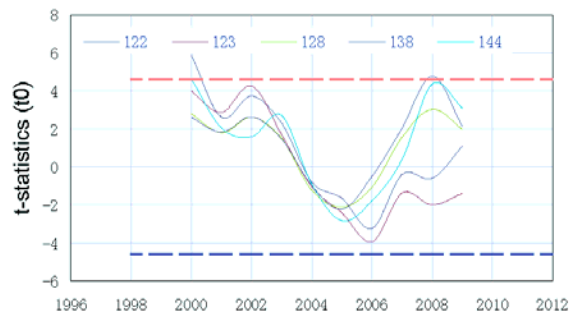
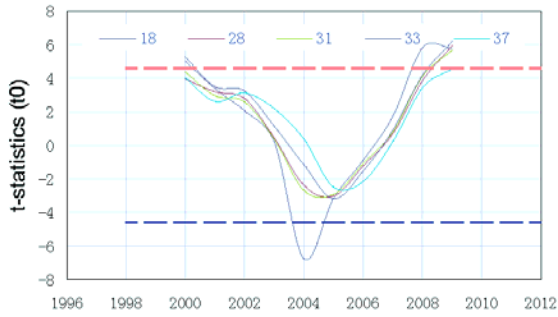
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904 Figure 1



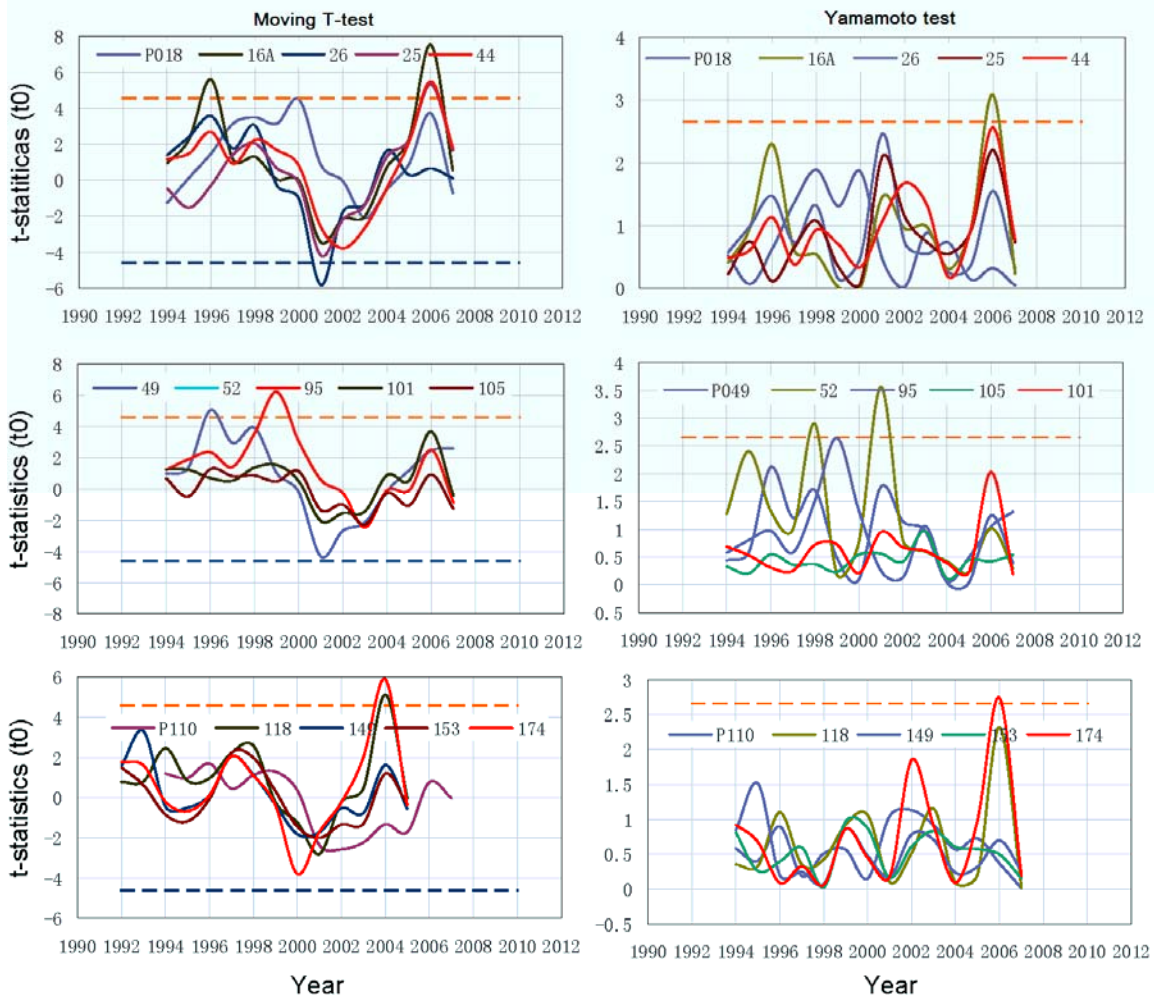
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906 Figure 2



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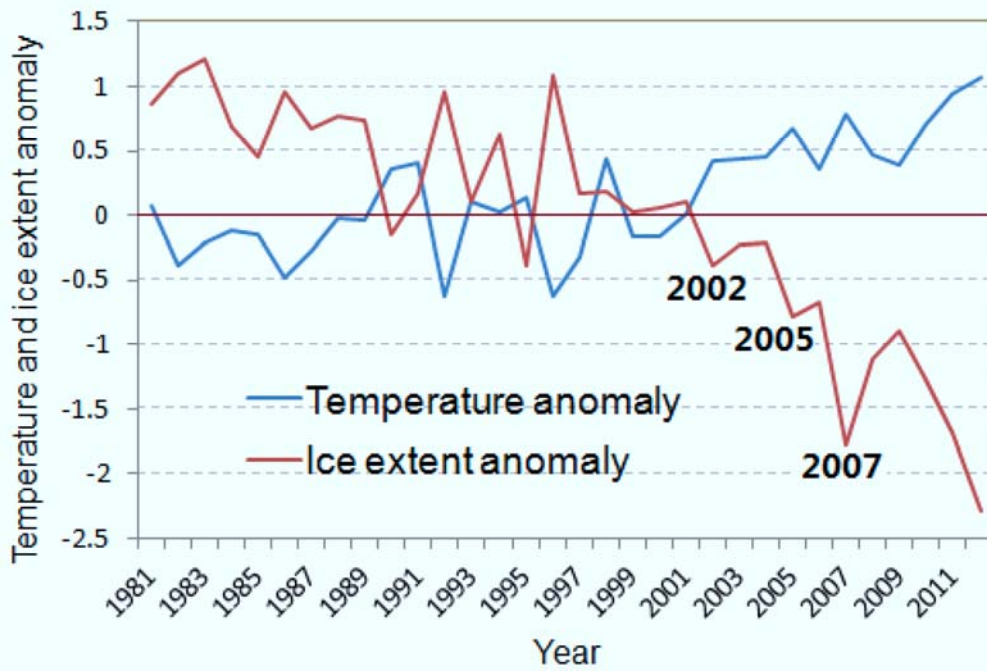
Figure 3



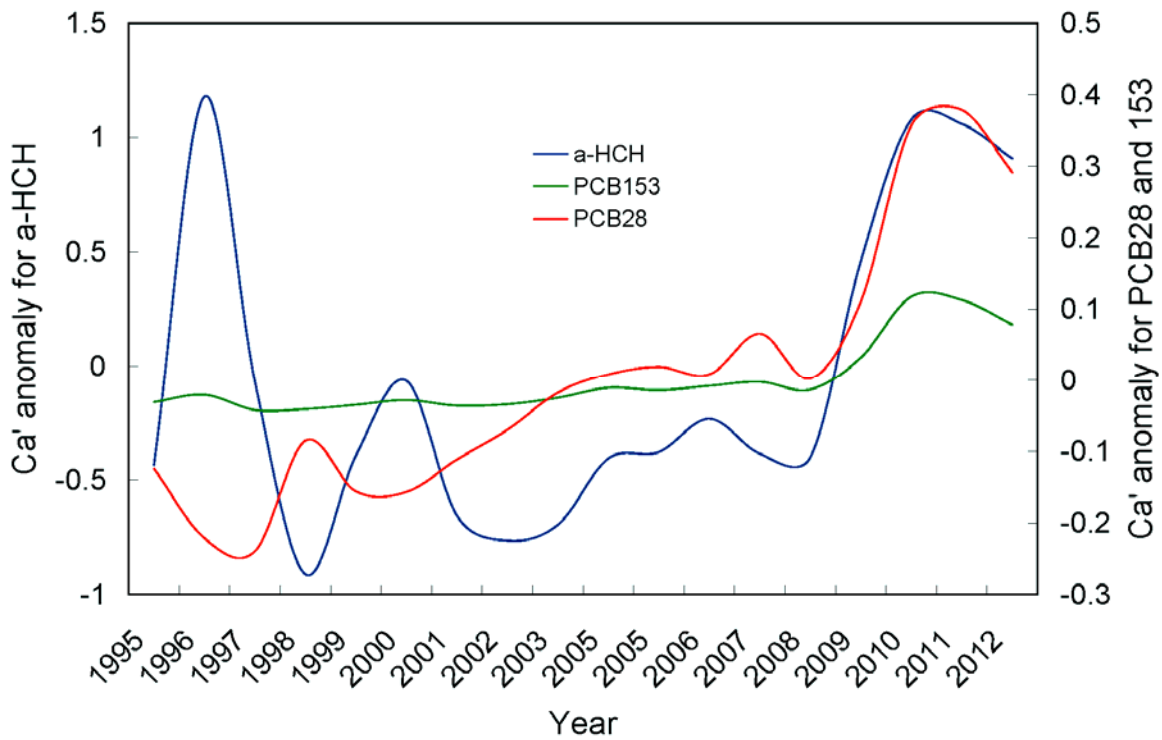
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911 Figure 4

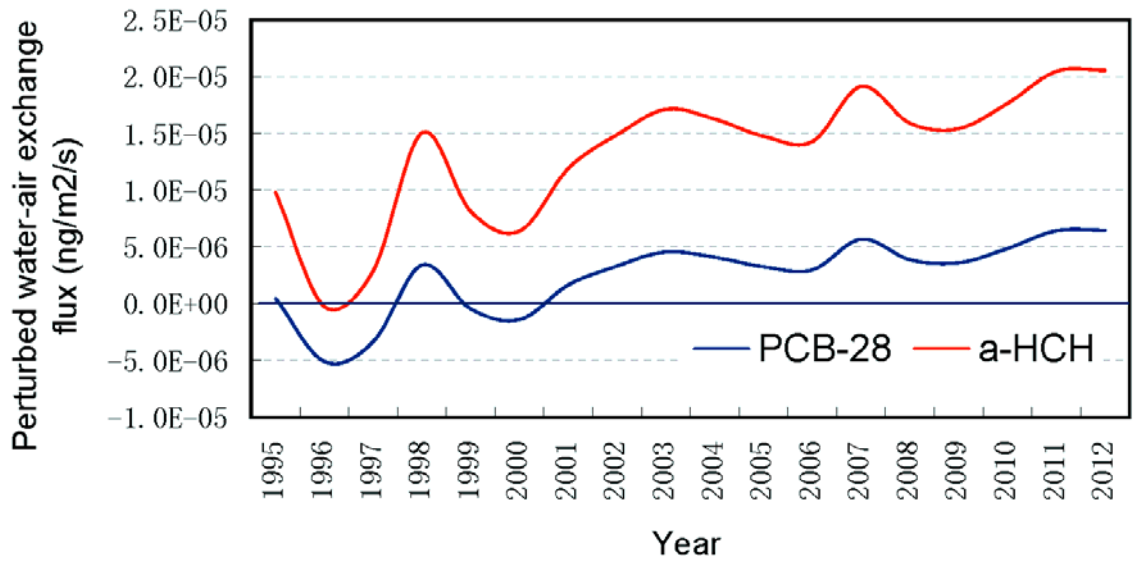
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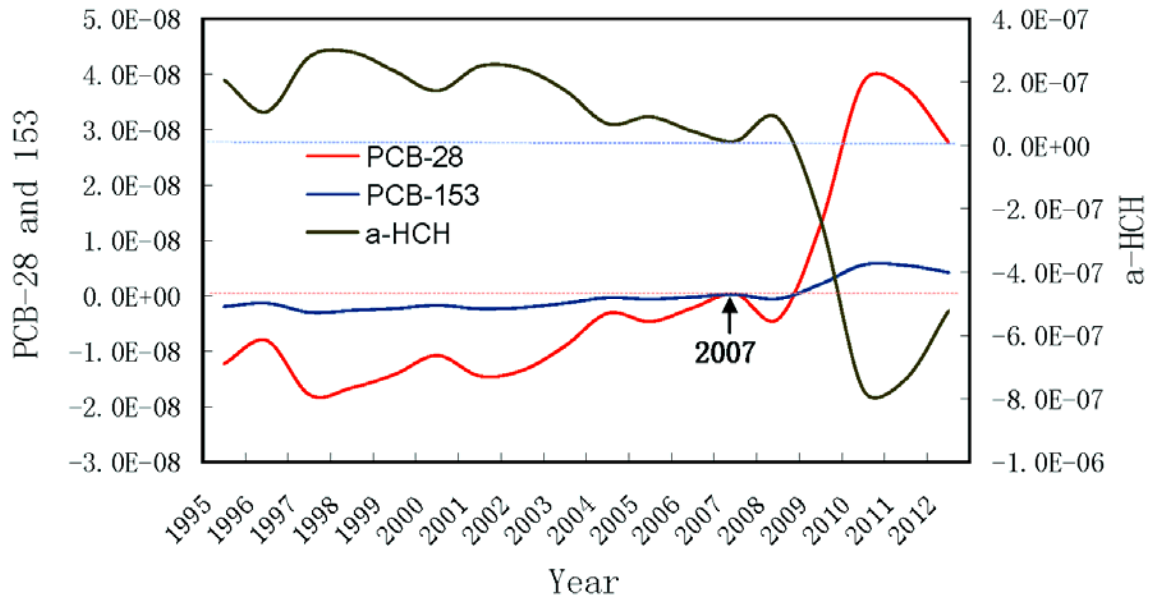
913  
914 Figure 5  
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917 Figure 6



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