

1 **Response to the Anonymous Referee #1**

2

3 We would like to thank the Anonymous Referee #1 for his/her comments. Listed below
4 are point-by-point replies to the reviewer's comments. The original comments are shown
5 in italics and responses are given in normal fonts.

6

7 *I think the authors have taken into consideration previous comments by this reviewer.*

8 *The paper studies important data and applies carefully several tools to explore them. This*

9 *approach is very useful, and detailed study of valuable data is central for science and*

10 *policy. For future work it might be positive to relate these data to other types of data*

11 *such as emissions or meteorology to advance in the understanding of the possible*

12 *attribution of observed features in the time series to processes driving them.*

13

We appreciate the reviewer's suggestions to extend present study to further elucidate other processes from emission and meteorology contributing to the step changes in ambient POPs time series. Related studies are underway and planned.

14 **Response to the Anonymous Referee #2**

15

16 We would like to thank the reviewer for his/her comments. Listed below are changes
17 made to the manuscript according to the reviewer's comments, and a point-by-point reply
18 to the reviewer's comments. The original comments are shown in italics and responses
19 are given in normal fonts.

20

21 *This paper examines the step point of the atmospheric concentration of POPs in the Arctic*
22 *using three statistical analysis. The authors modeled the relative contribution of*
23 *secondary emission from sea-ice/water on the atmospheric concentration of POPs, to*
24 *primary emission and degradation. The authors employed long-term monitoring air data*
25 *from four Arctic stations for their analysis. The paper is well-written but requires*
26 *improvement on the figures. The paper is suitable for publication pending on the*
27 *response to the following comments.*

28

29 *General comments:*

30

31 *I think the authors should only show the highlights of the results in the figures instead of*
32 *everything. For example, Figure 1, 2, 3 and 4 are showing the same results from the step*
33 *change statistical analysis for the 4 Arctic stations. There are too much information here.*
34 *Perhaps the authors can just show the significant results and put the rest into the*
35 *Supplement. The authors should also simplify Figures 5 and 6.*

36

37 Following the reviewer's suggestion, we have moved Figures 3 and 4 to Supplement
38 (Figs S2 and S3) and combined two subsections 3.1.3 and 3.1.4 to one subsection 3.1.3
39 Storhofdi and Pallas (line 361 in the revised paper). Further efforts were made to
40 simplify Figs 5 and 6, now Figs 3 and 4 in the revised manuscript by removing the figures
41 for those chemicals showing no statistical significant step changes from Moving T-test
42 and Yamamoto method.

43

44 *There are very limited data on the concentration of POPs in ice and they may be of high*
45 *uncertainty. Have you tried running the model with different ice concentration? I see that*
46 *you have used the measurements from Hansen et al., for α -HCH in ice and snow*
47 *concentration. Have you considered using recent measurements from Pucko et al.*
48 *Environ. Sci. Technol., 2010, 44, 9258-9264?*

49

50 Thanks to the reviewer for providing us Pucko et al's work. Pucko et al's data of
51 monitored α -HCH concentrations in air, ice, and ice brine have been input to the
52 perturbation model to examine potential influence of higher α -HCH concentrations in
53 sea ice and sea ice brine on the fluctuation and temporal trend of this chemical over the
54 Arctic air. Results show that the input higher mean concentrations of α -HCH in sea ice

55 and ice brine (Pucko et al., (2010), compared with the data we used in the present study
56 as presented in Table S1, increases the magnitude of perturbed annual concentrations in
57 air and ice but do not alter their fluctuations and long-term trend (see new Fig. S7). This
58 suggests again that the changes in temperature dominate the fluctuations of perturbed
59 α -HCH concentrations over the Arctic. Likewise, the perturbed gas-phase air-brine
60 exchange fluxes using Pucko et al.'s data (2010) also exhibited the similar trend and
61 inter-annual fluctuations as the air-ice exchange fluxes, though two time series of the
62 perturbed fluxes differed in magnitude. We have added a new paragraph and discussions
63 for the new result in the revised paper (line 563-578) and a figure (Fig. S7) in the
64 Supplement. Pucko et al's manuscript (2010) has been also included in the references of
65 revised paper and Supplement.

66

67 *Have the authors considered air-brine gas exchange and how would that be affected by*
68 *climate change?*

69

70 The reviewer raised an interesting question but we feel that investigation into the
71 association between air-brine gas exchange and climate change is beyond scope of this
72 study. Nevertheless, following the reviewer's comment, we have run the perturbation
73 model using the sampled α -HCH concentrations in air, water, and brine collected by
74 Pucko et al (2010) and compared the results with modeled air-ice exchange fluxes using
75 the data presented in Table S1 of Supplement. It was found that, though the two time
76 series of the perturbed fluxes exhibited the same fluctuation and trend driven by
77 temperatures and sea ice extents, the air-brine exchange fluxes were several orders of
78 magnitude greater than the air-ice fluxes and did not switch from positive to negative as
79 shown in perturbed air-ice flux which turned from positive to negative from 2008 (**Fig. 8**)
80 (line 662-670).

81

82 *The authors have identified the step points for a number of POPs with the hypothesis that*
83 *rapid melting of sea ice and rising of temperature is the cause. Does the observed step*
84 *change coincide with the model results? It is not clearly state in the paper. Maybe the*
85 *authors can elaborate on this point.*

86

87 Since the perturbed concentrations discern largely the climate change signals in POPs
88 time series, associated with temperatures and sea ice, it might not be appropriate to
89 compare the step change points in the time series of measured annual mean air
90 concentrations. The latter are driven primarily by emissions and degradation.
91 Nevertheless, the perturbed air concentrations of many PCBs examined in the present
92 study showed the step change in 2001. New Figure S6 in Supplement illustrates the
93 MK-test for perturbed concentration of PCB-28, showing the step change in 2001 which
94 is also the first step change point of monitored PCBs atmospheric concentrations (Tables
95 1 and 2) and the year when the mean summer temperature and sea ice extent

96 anomalies over the Arctic change their signs (**Fig. 5**). These statements have been added
97 to the revised manuscript (line 554-562) and a new figure (figure S6) has been added to
98 the revised Supplement.

99

100 *The authors often described the model concentration as "perturbation concentration",*
101 *which seems awkward. I think it should be called "perturbed concentration" or just*
102 *"modeled concentration". It does not sound right when you put two nouns together.*

103

104 All these were corrected in the revised paper.

105

106 *Specific comments: p. 1249, line 14, "duo" should be "due"*

107

108 Thanks for the correction of this typo error.

109

110 *Supplement, Reference Hansen et al., "r-HCH" should be "α-HCH"? or "g-HCH"?*

111 *Please double check.*

112

Yes the reviewer is right. It is α -HCH and we have corrected this typo error.

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

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132 **Abstract.** While some persistent organic pollutants (POPs) have been declining globally
133 due to their worldwide ban since the 1980s, the declining trends of many of these toxic
134 chemicals become less significant and in some cases their ambient air concentrations,
135 e.g., polychlorinated biphenyls (PCBs), showed observable increase during the 2000s,
136 disagreeing with their declining global emissions and environmental degradation. As part
137 of the efforts to assess the influences of environmental factors on long-term trend of
138 POPs in the Arctic, step change points in the time series of ambient POPs atmospheric
139 concentrations collected from four arctic monitoring sites were examined using various
140 statistical techniques. Results showed that the step change points of these POPs data
141 varied in different years and at different sites. Most step change points were found in
142 2001-2002 and 2007-2008, respectively. In particular, the step change points of many
143 PCBs for 2007-2008 were coincident with the lowest arctic sea ice concentration
144 occurring in this period of time during the 2000s. The perturbations of air concentration
145 and water-air exchange fluxes of several selected POPs averaged over the Arctic,
146 simulated by a POPs mass balance perturbation model, switched from negative to
147 positive from the early 2000s, indicating a tendency for reversal of POPs from deposition
148 to volatilization which coincides with a positive to negative reversal of arctic sea ice
149 extent anomalies from 2001. Perturbed ice-air exchange flux of PCB-28 and 153 showed
150 an increasing trend and the negative to positive reversal in 2007, the year with the lowest
151 arctic sea ice concentration. On the other hand, perturbed ice-air exchange flux of
152 α -hexachlorocyclohexane (HCH) decreased over the period of 1995 through 2012,

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

155 **1. Introduction**

156 A number of studies have been carried out to examine temporal trends of POPs in the
157 Arctic (Hung et al., 2005, 2010; Becker et al., 2008; Ma et al., 2011; Wöhrnschimmel et
158 al., 2013). Due to worldwide ban and restrictions of these toxic chemicals, most legacy
159 POPs have been declining in the Arctic over the last several decades. Fluctuations of
160 many POPs on interannual or longer time scales, however, have been observed in POPs
161 time series collected from arctic monitoring stations. The long term trends of POPs in the
162 Arctic have been attributed to the changes in their primary emissions, use patterns,
163 retreating sea ice, degradation, and other complex natural and anthropogenic activities
164 (Macdonald et al., 2005; UNEP/AMAP, 2010; Armitage et al., 2011; Kallenborn et al.,
165 2012). The fluctuations of monitored POPs atmospheric concentrations have been also
166 associated with interannual climate change at several POPs monitoring sites where the
167 longest atmospheric monitoring programs have been operated, notably the Great Lakes
168 region and the Arctic (Ma et al., 2004a; MacLeod et al., 2005; Wang et al., 2010). The
169 notable interannual climate change influencing interannual changes in elevated
170 atmospheric level of POPs in the Northern Hemisphere are the North Atlantic Oscillation
171 (NAO), the El Niño-Southern Oscillation (ENSO), and the Arctic Oscillation (AO) (Ma
172 et al., 2004a,b; Ma and Li, 2006; MacLeod et al., 2005; Macdonald. 2005; Becker et al.,
173 2008; Gao et al., 2010). These studies have revealed abundant evidence for the

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

176 Previous trend assessments for POPs concentration time series in the Arctic have
177 revealed changes in these time series induced potentially by climate change. The
178 relationship between ambient POPs air concentrations and rapid change in the arctic
179 environment, however, has not been proven statistically. Recently, there has been
180 ongoing debate on a climate "tipping point" (Lenton, 2011; Duarte et al., 2012; Livina
181 and Lenton, 2013; Holland et al., 2006) in the Arctic. Such the tipping point has been
182 connected to an abrupt increase in the amplitude of seasonal variability of sea ice area in
183 2007 that has been persistent since then, indicating the likelihood of rapid arctic climate
184 change (Livina and Lenton, 2013). It is worthwhile to point out that arctic climate change
185 has a much longer time scale than POPs life time and it might not be appropriate to link
186 short-term changes in POPs environmental level with long-term climate change.
187 However, the rapid change in arctic environments would change the environmental fate
188 and temporal trend of POPs, together with their primary emissions and use patterns in the
189 globe. Yet, the response of the monitored POPs long-term time series in the Arctic to the
190 rapid change in the arctic environment has not been investigated intensively. POPs
191 releasing from seasonal melting snow pack and mountain glaciers has been demonstrated
192 to alter significantly the atmospheric levels of POPs (Stocker et al., 2007; Bogdal et al.,
193 2009; Meyer et al., 2008). Arctic sea ice as a temporal storage reservoir for POPs
194 undergoes seasonal changes, except for permanent ice and glaciers. The sea ice melting

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

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

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

217 Since the Arctic is warming at a rate of almost twice the global average which leads
218 to strong sea ice melt since the 2000s (Steele et al., 2008), the measured POPs
219 atmospheric concentrations in the Arctic might provide best datasets to discern the signals
220 of climate change in monitored POPs data. The increasing trend of PCBs appeared to
221 coincide to the strong sea ice melt in the Arctic, characterized by rapid decline in arctic
222 sea ice from 2000 (Duarte et al., 2012). Since the sea ice decline took place over a short
223 period of time, the monitored POPs air concentrations datasets in the Arctic, though short,
224 would likely respond to rapid sea ice decline and increasing air temperature which may
225 provide further field evidence to the association between temporal trend of POPs and
226 climate warming. The present study examined the statistics for step changes in monitored
227 atmospheric concentrations of POPs at several arctic monitoring stations. The association
228 between the statistically significant step change points of POPs concentrations and arctic
229 climate change was quantitatively assessed to identify arctic climate change signals in
230 measured POPs time series.

231 **2. Materials and methods**

232 **2.1 Data**

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

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

257 respectively.

258 **2.2 Statistical test for POPs trend and step change**

259 Searching for a step change (also referred to abrupt change or abrupt discontinuities) in a
260 time series is often conducted by the detection of a point year as a sign of step change in
261 the time series. It is the process of finding step changes (or shifts) in the mean level of
262 the time series. In the cases of POPs atmospheric concentration time series, the step
263 changes can be considered as a statistically significant abnormal increasing or decreasing
264 from their long-term trend, extending to a certain period of time. In climate and
265 hydrological studies, three statistical methods have been widely used to identify abrupt
266 climate change points. These are the Mann-Kendal (MK) test (Mann, 1945; Kendall,
267 1948), the Moving T-Test (MMT) technique (Moraes, et al., 1998), and Yamamoto
268 method (Yamamoto et al., 1985).

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

$$273 \quad S_k = \sum_{i=1}^k r_i \quad (k = 2, 3, \dots, n) \quad (1)$$

274 where S_k is a statistic of the MK test and,

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

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

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

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

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

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

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

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

293 equivalent subsamples size under a null hypothesis of $\mu_1 = \mu_2$ where μ_1 and μ_2 are two
 294 subsamples. In other words, if the difference between means over two adjacent time
 295 intervals reaches a statistical significance level, a step change is inferred to occur. For a
 296 time series whose population is normally distributed, the t -statistics is defined as (Moraes
 297 et al., 1998)

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

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

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

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

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

307 A step point of a concentration time series is inferred if S/N intersects with the line of
 308 $S/N=2.66$ at the significant level $\alpha=0.01$. In the present study, the subset data size of both
 309 Yamamoto and MTT methods was set to 3. Table S3 of Supplement compared the MTT
 310 method identified step change point years for PCBs for the period of 2007-2012 at

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

317 Since the changes in atmospheric concentrations of POPs are often driven by the
318 first-order processes that scale multiplicatively with the concentrations (Meijer et al.,
319 2003), in the MTT and Yamamoto statistics all concentrations are log-transformed (in
320 natural logarithm) before they are used in the statistical analysis. Because the MK
321 method is a rank-based test, the log-transformed time series make no difference from
322 original time series for the step change results.

323 These methods each have their advantages and disadvantages. For example, while
324 the MK test has been successfully used in detecting step change points (Moraes et al.,
325 1998; Gan, 1998), it failed to discern statistically significant signals in step changes in
326 some cases. To increase confidence of statistical test for potential step change point in the
327 selected POPs time series, the present study applied simultaneously the MK test, MTT
328 technique, and Yamamoto method. Although the step change points of a time series from
329 the MK test may occur in a certain year, this year is often regarded as the onset year of
330 the step change. The year immediate after the onset year can be also included in the
331 period of the step change in the time series. We also applied monthly and seasonal mean

332 air concentrations data at the four arctic sites to examine the step change points for
333 monitored POPs concentrations. The monthly and seasonal mean concentrations were
334 compiled by averaging weekly (Zeppelin, Alert, Pallas) or bi-weekly (Storhofdi) sampled
335 air concentrations. Using monthly or seasonally averaged time series can increase sample
336 size. However, periodic variations in monthly and seasonal POPs concentration time
337 series, characterized by higher concentrations in warmer months (or season) and lower
338 concentrations in colder months (or season), overwhelmed the changes in annually
339 averaged concentration time series. Our results showed that the monthly and seasonal
340 averaged data could not yield step changes for most POPs data. **Figure S1** of Supplement
341 displays the UF_i and UB_i in MK test (Eq. (5)) for monthly PCB-28 atmospheric
342 concentration time series during the summer months in the Arctic at Zeppelin site. As
343 seen, UF_i and UB_i fluctuate below the confidence level, and no statistically significant
344 step changes are found. Further details in the influence of sample size, monthly and
345 seasonal time series on step changes in POPs air concentrations are presented in
346 Supplement.

347 **2.3 Perturbation Modeling**

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

353 sediment) to equal to the sum of its mean concentration (\bar{C}) and perturbed concentrations
354 (C') $C = \bar{C} + C'$, or $C' = C - \bar{C}$. So C' can be also regarded as a concentration anomaly
355 (or departure) from its mean. The change in this mean concentration in the Arctic was
356 often dominated by its primary emission, degradation, and the disequilibrium or exchange
357 of concentrations between two environmental compartments (Gioia et al., 2008). These
358 processes control the mean state of POPs in environment. Whereas, the perturbed
359 concentration C' , as the departure from these mean processes, might be more sensitive to
360 other processes with weak signals in ambient POPs concentrations, such as climate
361 change. The model was developed to quantify the response of POPs in multi
362 environmental compartments to the long-term changes in atmospheric and ocean
363 temperatures, and snow and sea ice. In the case of the arctic environment, the model
364 simulates daily concentrations of POPs (with the model time step length at 1 day) in
365 different environmental compartments forced mostly by the change in temperatures,
366 ice/snow melting, and the mean concentrations (Supplement Table S1). The model can be
367 applied either in a single spatial site or entire arctic region. Details in the perturbation
368 model were referred to Ma and Cao (2010) and Ma et al (2011). To interpret the
369 occurrence of step change point years of POPs concentration data detected by the
370 statistical analysis, the perturbation modeling for PCB-28, 153, and α -HCH was
371 performed using their mean and perturbed emissions. To examine the response of the
372 exchange of POPs in multi-media environments to their step changes, perturbed water-air
373 and ice-air exchange flux were also calculated. It is arguable that the most processes that

374 control the concentration in air are first-order processes that scale multiplicatively with
 375 concentrations whereas the perturbation model treats concentrations in air as a linear sum
 376 of their mean and perturbed concentrations (Ma and Cao, 2010). It must be noted, as
 377 aforementioned, that the sole external forcing term in the perturbation model was mean
 378 concentrations in different environmental compartments and initial perturbed
 379 concentrations were set zero in the model (Ma and Cao, 2010). Those nonlinear processes
 380 related to the chemical-physical properties of a chemical and their associations with
 381 temperature have been also taking into consideration through the calculation of their mean
 382 and perturbation.

383 The global emission inventory of selected POPs employed in the perturbation
 384 modeling α -HCH and PCBs used the results from Li et al (2000) and Breivik et al. (2007).
 385 We implemented mean and perturbed air emissions, subjected to mean temperatures and
 386 temperature anomalies, into the model, expressed as (Lamon et al., 2009; Ma and Cao,
 387 2010; Gouin et al., 2013)

$$388 \quad \bar{E}_{OHC} = E_{OHC-ref} \exp\left[\Delta U_A \left(\frac{1}{T_{ref}} - \frac{1}{\bar{T}}\right) / R\right] \quad (9)$$

$$389 \quad E'_{OHC} = \frac{\Delta U_A}{R} \bar{E}_{OHC} \frac{T'}{\bar{T}^2} \quad (10)$$

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

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

$$396 \quad F_w = K_{OL}(C_w - C_a RT / H) \quad (11)$$

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

$$403 \quad F'_w = \bar{K}_{OL} \left[\frac{R}{H} \left(\frac{\bar{T}\bar{C}_a}{H} H' - \bar{T}C'_a - \bar{C}_a T' \right) + C'_w \right] + K'_{OL} \left(\bar{C}_w - \frac{R\bar{T}}{H} \bar{C}_a \right). \quad (12)$$

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

$$408 \quad F'_i = v_a (C_i / K_{sa} - C_a), \quad (13)$$

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

$$413 \quad F'_i = \bar{v}_a \left[\frac{1}{K_{sa}} \left(C'_i - \frac{K'_{sa}}{K_{sa}} \bar{C}_i \right) - C'_a \right] + v'_a \left(\frac{\bar{C}_i}{K_{sa}} - \bar{C}_a \right). \quad (14)$$

414 3. Results

415 3.1 Step change points by MK test

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

424 3.1.1 Alert

425 **Figure 1** displays UF_i and UB_i for 16 PCBs and 9 OCPs derived by the MK test (Eq .
426 (5)) at Alert monitoring station. As defined, the intersections between the forward and
427 backward sequences UF_i (curved blue line) and UB_i (curved red line) within the
428 confidence levels of -1.96 (straight purple line) to 1.96 (straight green line) denote step
429 change points for these POPs time series. As shown, UF_i and UB_i intersected at least once
430 over the period of 1993 through 2012. Most intersections were well within the confidence
431 levels between -1.96 and 1.96 at the statistical significance $\alpha = 0.01$, except for α - and
432 γ -HCH whose intersections were outside the confidence level. Hence, there were no step
433 change points of these two HCH isomers. The two step change points in 1997 and 2004
434 were detected for β -HCH. β -HCH partitions much more strongly into cold water than

435 α -HCH. Ocean currents and river currents were thought to dominate the entry of β -HCH
436 into the western Arctic Ocean (Li et al., 2002). Elevated concentrations of β -HCH in air
437 over the Canadian Arctic might be partly explained by its outgassing from the nearby
438 ocean. It is not clear if the two step change years of this HCH isomer were attributable to
439 its revolatilization following its increasing oceanic transport. The increasing trend of UF_i
440 for β -HCH from 2002 at Alert, suggesting its increasing air concentration, was not
441 observed at other monitoring sites which are far from the western Arctic Ocean as
442 compared with Alert site.

443 For tri-PCBs, three step change points were found between 2000 and 2005 (PCB-16,
444 25, and 26) and two found in 1998 (PCB-18 and 25), respectively. The step change points
445 in PCB-44, 49, 105, 106, and 209 were also found after 2000 but more step change points
446 in tetra-, penta-, hexa-, and deca-PCBs were detected before 2000. On the other hand, the
447 step change points in all 6 DDT (dichlorodiphenyldichloroethane) isomers were found
448 after 2000 and the four of these six DDT isomers showed step change points before 2000.
449 It can be also observed that, though UF_i and UB_i were intersected over 2001 – 2002, the
450 point of the intersection was outside of the confidence level. Hence, this point was not
451 regarded as a step change point. The number of chemicals with statistically significant
452 step change points for different periods is presented in **Table 1**.

453 **3.1.2 Zeppelin**

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

456 identified for these PCBs except for PCB-189. The first intersection occurred between
457 2001 and 2003, and the second one took place mostly in 2007. **Table 1** also presents the
458 MK test derived step change point years of 20 PCBs congeners and 3 DDTs isomers at
459 Zeppelin and other arctic sites during the 2000s. The step change points for other OCPs
460 were below the confidence level and hence not accounted here. Although the UF_i and
461 UB_i sequences lay between the positive and negative confidence levels (1.96 and -1.96)
462 before 2000 and after 2008, no intersections between the two sequences were detected
463 within the confidence levels. Overall, the MK test detected the most step change points
464 of these chemicals for the two periods, spanning from 2001 to 2003 and from 2007 to
465 2008, respectively. Both step changes span approximately a 3-year time period. Eighteen
466 chemicals were found to exhibit step change points for the period of 2001 through 2003
467 and twenty one chemicals were identified to have step change points for the period of
468 2006 through 2008. Since most PCBs data were only available from 1998, their trends
469 and step change points could not be identified in the 1990s. Nevertheless, while the
470 ambient air concentrations of three DDTs isomers are available from 1994, the only step
471 change point year 1997 for *p,p'*-DDD was found during the 1990s by the MK test (**Table**
472 **1**).

473 **3.1.3 Storhofdi and Pallas**

474 There are only 10 coeluting PCB congeners reported by Storhofdi station (Hung et al.,
475 2010). The UF_i and UB_i sequences of 9 PCBs out of 10, together with α -, γ -HCH, and
476 HCB which fall into the confidence levels from 1995 to 2011 are shown in **Fig. S2**. The

477 most intersections between the UF_i and UB_i sequences of the 9 PCBs can be found
478 between 2006 and 2008, except for PCB-105 and 180. Other step change points for these
479 PCBs were found in the 1990s and the early 2000s (PCB-28, 31, 105, 138, 153, 180, and
480 HCB), as is also shown in **Table 1**. No step change year for α -HCH was detected during
481 this period of time but there was the step change year for γ -HCH in 2007. HCB exhibited
482 a step change point in 1999. Further details are shown on **Table 1**.

483 There are 7 coeluting PCB congeners reported by Pallas station. The UF_i and UB_i of
484 all these 7 PCBs fall into the confidence level. The MK statistics of these 7 PCB
485 congeners and α - and γ -HCH is illustrated in **Fig. S3**. Analogous to Zeppelin and
486 Storhofdi stations, the most intersections between UF_i and UB_i of the reported PCBs
487 were found in 2007, except for PCB-180 which showed the step change year in 2003.
488 Other statistically significant step change years were detected between 2001 and 2003
489 (PCB-101, 118, 138, and 180), and in 2005 (PCB-52, 101, and 153), as is also shown in
490 **Table 1**. Again, although the UF_i and UB_i of α - and γ -HCH were intersected in 2003 and
491 2004, these two intersections were below the confidence level and therefore no step
492 change points for HCHs were accounted for.

493 **3.2 Step change points identified by MTT and Yamamoto methods**

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

498 by the MK test. **Figures S4** and **S5** in the Supplement show the MTT and Yamamoto
499 statistics for PCBs and OCPs time series at Storhofdi and Pallas monitoring stations,
500 respectively. Compared with the results from the MK statistics, both the MTT and
501 Yamamoto methods did not detected statistically significant step change points in 2007
502 for most PCBs and OCPs at Pallas. The MTT method detected the step change point
503 around 2000 for penta-PCB (PCB-101 and 118) and hexa-PCB (PCB-138 and 153), and
504 for penta-PCB from 2007 to 2008. Step changes in α - and γ -HCH were found between
505 2000 and 2002, and in 2005. Yamamoto method only detected a step change year around
506 2000 for PCB-138, but, analogous to the MTT method, found the step change between
507 2000 and 2002 for the two HCH isomers. Both MTT and Yamamoto methods detected
508 the step change in 2001 for PCB-101 and 2003 for PCB-105, but only found the 2007 as
509 the step change year for PCB-52 and α -HCH, respectively (Supplement **Fig. S5**).

510 **Figure 3** shows the MTT statistics for 30 PCBs at Zeppelin station. The MTT
511 statistics for these PCBs illustrate a “V” pattern except for several heavier PCBs. All
512 tri-PCBs exhibited the step change year in 2008. The same step change year was also
513 found for PCB-52, 74, 101, 138, 149, 170, and 180. The step change year 2008 for these
514 PCBs derived from the MTT method lagged one year behind the step change year (2007)
515 detected by the MK test (**Fig. 1** and **Table 1**). However, this step change year (2008) can
516 be regarded as an extension of the step change year 2007 because the step change year
517 2007 by the MK test is an onset year of step change. Other step change years were
518 detected in 2000, 2002, and 2005, but for only several PCBs out of 30 PCB congeners.

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

526 The results from the MTT and Yamamoto statistics for 20 PCBs at Alert are
527 illustrated in **Fig. 4** and also presented on Supplement Tables S4 and S5. The both MTT
528 and Yamamoto methods yielded a step change point in 2006 for several PCBs, notably
529 PCB-16A, 25, 44, 118, 174, and 209. The MTT method detected the step change year in
530 2005 for both α - and γ -HCH but the Yamamoto method only found this step change year
531 for α -HCH (Tables S4 and S5). Nevertheless, this step change year for HCHs was not
532 discerned by the MK test, as illustrated previously. The two methods also detected the
533 step change year for *p,p'*-DDE in 2000 which was consistent with the step change year
534 detected by the MK test, and in 2001 for *p,p'*-DDD, leading the MK test result (2002) by
535 one year.

536 **4. Discussions**

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

540 that, for Alert, the statistically significant step change year detected by the MK test and
541 the MTT or Yamamoto method was only found in 2005-2006 for PCB-16 and 44,
542 respectively. While the MK test also identified the same step change in PCB-49, 105, and
543 110 during this period of time (**Fig. 1**), this step change was not detected by the other two
544 methods (**Fig. 4**). The step change years in OCPs detected by the MK test were not
545 confirmed by the MTT and Yamamoto method either. In the MK test, UF_i (the forward
546 sequence, Eq. (5)) was often used to represent the trend of a time series. At Alert, the UF_i
547 values of lighter PCBs (tri-PCBs and PCB-44) showed an increasing trend and a negative
548 to positive reversal since 2005. In fact, almost all intersections between UF_i and UB_i of
549 these lighter PCBs, indicating the step change, took place when UF_i became positive,
550 confirming the increasing trend of these lower molecular PCBs measured at Alert during
551 the mid-2000s whereas heavier PCBs did not show significant increasing trend for the
552 same period of time.

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

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

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

568 **Table 2** summarized the step change years for PCBs and OCPs at the 4 arctic
569 atmospheric monitoring sites discerned simultaneously by the MK test and the MTT or
570 Yamamoto method. Overall, although the step changes years varied with different
571 chemicals and monitoring sites, these step change points all took place in the 2000s.
572 Further, although individual statistical method did identify the step changes in OCPs,
573 these changes were not detected simultaneously by 2 out of the 3 statistical methods used
574 in the present study. Among the three periods of 2001-2003, 2005-2006, and 2007-2008
575 listed in **Table 2**, the step change point was found in the highest number of monitored
576 chemicals for the period of 2007-2008, followed by 2001-2003 and 2005-2006,
577 respectively. Although 2005-2006 and 2007-2008 are two adjacent periods, the step
578 changes in POPs concentrations during these two periods might show their distinct
579 response to marked decline of sea ice concentrations in 2005 and 2007, respectively, as
580 shown in **Fig. 5**. Another common feature from the MK test was that the forward
581 sequence UF_i for many PCBs showed increasing trend from 2000, as illustrated by **Figs.**

582 **1, 2, S2, and S3.**

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

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

603 Compared with Zeppelin monitoring site which is located in the western coast of
604 Spitsbergen (Svalbard, Norway), the Alert station is under lower temperature, surrounded
605 by rugged hills and valleys, and hence less affected by sea ice retreat and open waters. In
606 addition, as shown by **Fig. 1** and **Table 1**, the step change points in several PCBs and
607 DDTs were detected in 2001 – 2003 by the MK test. Due to laboratory switching in 2002
608 which led to increasing air concentrations of monitored POPs after 2002 (Hung et al.,
609 2010), the step changes in POPs from 2001 to 2003 at Alert might be also subject to
610 laboratory switching.

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

624 mean summer sea ice extent exhibited a decreasing trend and become negative since 2001.
625 This result agreed with a previous report which showed that, during the 2000s, the arctic
626 sea ice September minimum extent (i.e., area with at least 15% sea ice coverage, 10^7 km^2)
627 reached new record lows in 2002, 2005, and 2007 ([http://earthobservatory.nasa.gov/
628 Features/WorldOfChange/sea_ice.php](http://earthobservatory.nasa.gov/Features/WorldOfChange/sea_ice.php)). Accordingly, a negative to positive transition of
629 the mean air temperature anomalies averaged over the Arctic took place since 2001, as
630 also shown in **Fig. 5**. In particular, summer ice extent in 2007 was about 33% below the
631 1979-2013 average, broking all previous low ice extent records. Our calculated step
632 change points of 2007 through 2008 for many PCBs matched well with this strong decline
633 of the sea ice extent for this period of time.

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

645 concentrations in air, water, and sea ice used in perturbation modeling are presented in
646 Supplement Table S1. The perturbed concentrations of the three chemicals averaged over
647 the Arctic are displayed in **Fig. 6**. As shown, perturbed concentrations of all three
648 chemicals correlated inversely with the mean sea ice anomaly. It is evident that the
649 perturbed concentrations of PCB-28 and 153 illustrated a statistically significant
650 increasing trend during the period of 1995 through 2012. While there was also an
651 increasing trend of α -HCH, this trend was not statistically significant. Opposite to the sea
652 ice extent whose anomalies become negative from 2001, perturbed concentrations of
653 PCB-28 turned to positive from 2003, after the first step change point year (2001) of this
654 PCB congener (**Table 1**), whereas the negative to positive reversal of perturbed
655 concentration of the other two chemicals (PCB-153 and α -HCH) took place in
656 2007-2008, during which the Arctic recorded lowest sea ice extent. The concentration
657 perturbations trend of PCB-28 exhibited a much steep slope at 0.031 ($R^2=0.809$) as
658 compared with that of PCB-153 (slope=0.008, $R^2=0.626$), suggesting that lighter PCBs
659 respond more strongly to arctic sea ice melting. Since perturbation model simulated
660 concentration perturbations via ice-air exchange process were about one order of
661 magnitude lower than that through water-air exchange in the present study (results not
662 shown), the integrated perturbed concentrations were mostly driven by the water-air
663 exchange. As aforementioned, the monitored atmospheric concentrations of many PCBs
664 across the Arctic have already shown an increasing trend around 2007, potentially the
665 result of outgassing from the Arctic Oceans due to sea ice retreat (Hung et al., 2010;

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

675 Compared with the measured ice concentration used in the present study (0.1 ng L^{-1} ,
676 Table S1), higher levels of α -HCH (0.31 ng L^{-1}) in sea ice at a high Canadian Arctic site
677 in Beaufort Sea during 2007-2008 was reported by Pućko et al (2010). They also
678 measured α -HCH in sea ice brine and expected that arctic sea-ice changes associated with
679 climate change would make the brine concentration pathway more widespread in the
680 future Arctic Ocean. To test potential influence of higher α -HCH concentrations in sea ice
681 and sea ice brine on the fluctuation and temporal trend of this chemical over the Arctic air,
682 we adopted the measured α -HCH concentrations in sea ice and sea ice brine by Pućko et
683 al (2010) as the mean concentrations in the perturbation model and integrated the model
684 from 1995 to 2012. **Figure S7** compared the perturbed α -HCH concentrations in air and
685 ice due to air-ice exchange from 1995 – 2012 using the data in Table S1 and Pućko et al
686 (2010). As expected, the model input higher mean concentrations of α -HCH in sea ice and

687 ice brine increase the magnitude of perturbed annual concentrations in air and ice but does
688 not alter their fluctuations and long-term trend. This suggests again that the changes in
689 temperature dominate the fluctuations of perturbed α -HCH concentrations over the
690 Arctic.

691 The rapid decline of arctic sea ice in 2007 has triggered the debate on abrupt climate
692 change in the Arctic and low summer sea ice area was likely persistent on a decadal
693 (climate change) time scale. Given that the environmental fate of the selected POPs in the
694 Arctic have been dominated by their primary emission and outgassing from their
695 reservoirs accumulated from past use, deposition, and long-range transport from
696 atmosphere and oceanic currents (Macdonald et al., 2005; Gioia et al., 2008; Hung et al.,
697 2010; Kallenborn et al., 2012; Wöhrnschimmel et al., 2013), atmospheric levels of many
698 POPs in the Arctic have been declining during last decades after their regulation and
699 phase out. Previous modeling investigations (Lamon et al., 2009; Wöhrnschimmel, et al.,
700 2013) have revealed that the maximum changes in POPs atmospheric concentrations
701 induced by climate change were driven mostly by climate warming forced potential
702 changes in primary emission. This appeared to suggest that the POPs outgassing from
703 their arctic repositories associated with arctic warming and sea ice retreat would not
704 change their long-term declining trend because the emission and degradation
705 overwhelmed the POPs long-term declining trend. However, as aforementioned, the
706 measured ambient POPs air concentrations in the mid-2000s did not follow the declining
707 trend driven by primary emissions and degradations. The perturbation modeling was

708 aimed at assessing major processes contributing to concentration anomalies as the
709 departure from the mean POPs concentrations driven mostly by their primary emission
710 and degradation. We have demonstrated that the temperature-dependent emission (Eqs. (8)
711 and (9)) could alter the magnitude of modeled concentration perturbations but not change
712 long-term trend and interannual variation of the perturbed concentrations (Ma and Hung,
713 2012). The perturbed (rather than measured) POPs air concentrations were, therefore,
714 forced largely by the outgassing from their reservoirs in melting ice (snow) and the Arctic
715 Oceans. In this context, a reversal of many POPs from deposition to volatilization
716 associated potentially with arctic warming and sea ice retreat would likely take place. To
717 examine this argument, we estimated perturbed water-air and ice-air exchange flux (ng
718 $\text{m}^{-2} \text{s}^{-1}$) of the three selected chemicals (PCBs-28, 153, and α -HCH). Results show that the
719 modeled water-air exchange flux perturbations of the three selected chemicals exhibited
720 similar trend and interannual variability. So in **Fig 7** we only present perturbed water-air
721 exchange flux of PCB-28 and α -HCH. As shown, the modeled exchange flux
722 perturbations of PCB-28 were negative over the 1990s except for 1998, indicating
723 deposition of perturbed PCB-28. From 2001 onward, the perturbed flux turned to positive
724 and exhibited a clear increasing trend with greater values in 2007 and after 2010, implying
725 climate change forced revolatilization of this PCB congener. The perturbed water-air
726 exchange fluxes of α -HCH were positive throughout the modeling period of 1995 through
727 2012, except for 1996. This agrees with previous modeling results which predicted
728 reversal of α -HCH for its exchange direction from deposition to volatilization in the

729 Arctic Ocean in the early 1990s (Wania and Mackay 1999a, Wania et al. 1999b).
730 Comparing with the mean air concentration of PCB-28 at 3 pg m^{-3} , the modeled maximum
731 perturbed concentration of PCB-28 due to water-air and ice-air exchange was 0.25 pg m^{-3} ,
732 about 8% of the mean. For PCB-153, the modeled maximum perturbed concentration was
733 almost 30% of the mean (Supplement Table S1), showing stronger response of this PCB
734 congener to the change in the arctic environment. On the other hand, the modeled
735 maximum perturbed α -HCH concentration was only 5% of its mean concentration
736 (Supplement Table S1). The perturbation of POPs air concentrations at this magnitude
737 induced by sea ice retreat and snow melting should not be overlooked. If there was indeed
738 the onset of arctic abrupt climate change “tipping” point, continuous decline of arctic sea
739 ice in the forthcoming years may lead to stronger release of POPs into arctic air. As
740 shown in **Fig. 7**, both perturbed air concentrations and water-air exchange fluxes of
741 PCB-28 become positive after 2001 with relatively large values in 2007, coincident with
742 these two years during which many PCBs showed the onset of step changes and the arctic
743 sea ice extents reduced considerably (**Figs.1, 2, S2, S3** and **Table 2**).

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

750 positive reversal in 2007, the year for the potential onset of arctic abrupt climate change
751 “tipping” point (Livina and Lenton, 2013). Differing from its water-air exchange flux, the
752 annual mean ice-air exchange flux perturbation of α -HCH averaged over the Arctic
753 decreased from the 1990s. It is not clear if the stronger response of PCB-28 to sea ice
754 retreat characterized by its step changes in 2001 and 2007 at the Zeppelin station (**Table 2,**
755 **Figs. 2 and 3**) could be attributed to its outgassing from melting sea ice and glaciers as
756 compared with PCB-153 and α -HCH. The latter two chemicals showed negative
757 exchange fluxes, indicating deposition. Accordingly, there were no step change points for
758 these two chemicals in 2001 and 2007 (Table 2). While the releasing from melting ice
759 may increase air concentrations, it would also lead to increased potential for air to sea
760 transfer (Gioia et al., 2008), characterized by the negative flux. Overall, our results
761 showed that the perturbed ice-air exchange fluxes were lower than the water-air fluxes in
762 arctic environment. Since the modeled water-air exchange flux perturbations were positive
763 which might increase air concentrations, these increasing air concentrations from the
764 water-air exchange may lead to deposition in the ice-air exchange, as interpreted by Gioia
765 et al (2008). POPs releasing from seasonal melting snow pack and mountain glaciers has
766 been demonstrated to change significantly the environmental fate of POPs (Stocker et al.,
767 2007; Bogdal et al., 2009; Meyer et al., 2008). Previous studies in this aspect almost
768 entirely focused on the effect of seasonal changes in sea ice melting on POPs
769 environmental fate (Daly and Wania, 2004; Gioia et al., 2008; Jantunen et al. 2007, Wong
770 et al. 2010). Little is known about the change in long-term environmental fate of POPs in

771 the Arctic induced by interannual or decadal scale sea ice variation. It should be noted that,
772 due to very sparse POPs measurements in sea ice and glaciers across the Arctic, the mean
773 ice concentrations we input to the perturbation model may have large errors which could
774 even alter the exchange direction in modeled fluxes. Using the sampled α -HCH
775 concentrations in air, water, and brine from Pućko et al (2010) collected in the Canadian
776 High Arctic we have simulated the perturbed air-brine gas phase exchange flux of α -HCH
777 and compared the result with the perturbed air-ice exchange fluxes using the data
778 presented in Table S1. It was found that, though the two time series of the perturbed fluxes
779 exhibited the same fluctuation and trend driven by temperatures and sea ice extents, the
780 air-brine exchange fluxes were several orders of magnitude greater than the air-ice fluxes
781 and did not switch from positive to negative as shown in perturbed air-ice flux which
782 turned from positive to negative from 2008 (Fig. 8).

783 5. Conclusions

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

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

805 **The Supplement related to this article is available online at**

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810

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973
 974 **Table list:**

975
 976 **Table 1.** PCBs congeners and OCPs isomers having step change points at four arctic
 977 monitoring stations detected by the MK test.

	Step change point years		
	2001-2003	2005-2006	2007-2008
Zeppelin	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,
Alert	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
Storhofdi	CB-28,31,105,138,180	CB-138, γ -HCH	CB-28,31,52,101,118, 138,153,
Pallas	CB,101,118,138,180	CB-52,101,153	CB-28,52,101,118,153

978
 979
 980 **Table 2.** PCBs congeners having step change points at four arctic monitoring stations
 981 detected by the MK test and Moving T-Test (MTT) or Yamamoto methods.

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

982
 983 **Figure list and captions:**

984

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

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

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

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

996 **Figure 5.** Mean summer temperature (July – September, K, 1981-2012) averaged over the
997 Arctic as the departures from 1950 to 2010 mean (NCEP reanalysis, Kalney et al., 1996)
998 and sea ice extent (July –September, 10^7 km²) anomalies from 1981-2012 averaged over
999 the Arctic as the departures from 1979 to 2010 mean, manipulated from NSIDC data
1000 (Clark, et al., 1999) .

1001 **Figure 6.** Modeled perturbed air concentration (C_a' , pg m⁻³) of PCB-28, 153, and α -HCH
1002 from 1995 to 2012. C_a' of PCB-28 and 153 is scaled on the right Y axis and perturbed air
1003 concentration of α -HCH is scaled on the left Y axis. The mean concentrations in air, water,
1004 and sea ice of the three chemicals used in perturbation are presented in Table S1 and their
1005 physical-chemical properties are presented in Table S2, respectively.

1006 **Figure 7.** Simulated water-air exchange flux perturbations (ng m⁻² s⁻¹) of PCB-28 and
1007 α -HCH from 1995 to 2012.

1008 **Figure 8.** Simulated ice-air exchange flux perturbation (ng m⁻² s⁻¹) of three selected
1009 chemicals from 1995 to 2012. Perturbed fluxes of PCB-28 and 153 are scaled on the left
1010 Y axis and α -HCH flux perturbation is scaled on the right Y axis. Blue dished line stands
1011 for the case for α -HCH flux perturbation = 0 and pink dashed line stands for the case for
1012 PCB-28 and 153 flux perturbation = 0.