

# Organochlorine compounds pose health risks to the Qinling Giant Panda (*Ailuropoda melanoleuca qinlingensis*)

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**Abstract:** To assess organochlorine compound (OC) contamination, its possible sources, and adverse health impacts on giant pandas, we collected soil, bamboo, and panda fecal samples from the habitat and research center of the Qinling panda (*Ailuropoda melanoleuca qinlingensis*)—the rarest recognized panda subspecies. The polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) concentrations were comparatively low which suggests that moderate sources of OC pollution currently. OC levels were lower in samples from nature reserve than in those collected from pandas held in captivity, and OC levels within the reserve increased between functional areas in the order: core, buffer and experimental. The distribution patterns, and correlation analyses, combined with congener distributions suggested PCBs and OCPs originated from similar sources, were dispersed by similar processes, being transported through atmosphere and characterized by historical residues. Backward trajectory analyses results, and detected DRINs (aldrin, dieldrin, endrin and isodrin) both suggest long-range atmospheric transport of pollution source. PCBs pose potential cancer risk, and PCB 126 was the most notable toxicant as assessed by the high carcinogenic risk index. We provide data for health risk assessment that can guide the identification of priority congeners, and recommend a long-term monitoring plan. This study proposes an approach to ecotoxicological threats whereby giant pandas may be used as sentinel species for other threatened or endangered mammals. By highlighting the risks of long-distance transmission of pollutants, the study emphasizes the importance of transboundary cooperation to safeguard biodiversity.

POPs pollution caused by human activities pose potential health risk to giant pandas, and the global cooperation for biodiversity conservation should be considered.

**Keywords:** Health risk assessment, Long-range atmospheric transport, Organochlorine pesticides (OCPs), Polychlorinated biphenyls (PCBs), Biodiversity conservation

## 1. Introduction

Organochlorine compounds (OCs), such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), are well-known persistent organic pollutants (POPs). They were banned by the Stockholm Convention since 2001 and have been listed as primary pollutant concerns (UNEP, 2009) because of their persistence, toxicity, long-range atmospheric transport, bioaccumulation via food chains, and adverse effects on environmental and biological health (De Souza et al., 2018; Jones and de Voogt, 1999). Production and use of OCs have a long history worldwide. PCBs were produced and used for industrial and commercial applications, such as transformers, flame retardants, plasticizers, and capacitors since the 1930s (Arfaeina et al., 2017; Dumanoglu et al., 2017; Saeedi et al., 2017). OCPs, such as dichlorodiphenyltrichloroethane and metabolites (DDTs) and hexachlorocyclohexanes (HCHs), were once extensively used in agriculture (Zhang et al., 2018). As of 1993, the global production of PCBs exceeded 1.32 million tons (Breivik et al., 2007). China produced approximately 4.9 million tons of HCHs and 0.4 million tons of DDT (Hua and Shan, 1996), accounting for 33% and 20% of total global production (Fu et al., 2003). These pollutants are globally distributed because their distributions are mediated by repeated evaporation,

atmospheric transport, and deposition (Wang et al., 2016). OCs can even be detected in polar regions and remote areas protected for nature (Chen et al., 2016; Wang et al., 2019).

In wildlife, OCs can be associated with neurotoxicity, immunosuppression, endocrine system damage, reproductive dysfunction and carcinogenicity (FR.1982; Ontiveros-Cuadras et al., 2019). Considering publicity associated with impacts of PCBs, e.g., on otters in the 1970s (Mason et al., 1986), this is not just a recent concern. However, since the days of *Silent Spring* (Carson, 1962), it has been largely neglected until recent years, especially with respect to endangered mammals. Recently, Monclús et al., (2018) detected PCBs (1.30–6.16 ng g<sup>-1</sup> dw (dry weight)), polybrominated diphenyl ethers (PBDEs) (0.23–1.35 ng g<sup>-1</sup> dw) and lindane (0.25–3.12 ng g<sup>-1</sup> dw) via non-invasive feather sampling of the endangered cinereous vulture (*Aegypius monachus*). In addition, POP levels in endangered marine animals are of great concern, and there is consequently a focus on methods to detect them. For example, there is a risk that the elevated tissue concentrations of organohalogen contaminants in the St. Lawrence Estuary might hinder the recovery of the endangered beluga whale population (Simond et al., 2020). Due to the difficulty of acquiring fresh tissue from protected marine wildlife, some studies have examined toxicity mechanisms by using “omics” to investigate contaminant exposure-related effects – this technology can yield substantial bio-information from only a small amount of tissue (Mancia, 2018; Godard-Coding and Fossi, 2018). This approach may have utility for the conservation of terrestrial

animals.

Being the highest mountains in central-western China, the Qinling Mountains are the geographic barrier and climatic boundary between North and South China. Sources of OCs in this region are numerous, and transport patterns complex. At a large scale, three air masses are important: the East Asian Winter Monsoon (EAWM), moving from west to east and pluming over countries in Europe and Central Asia; the East Asian Summer Monsoon (EASM), consisting of maritime air from the Pacific Ocean moving from southeast to west; and a third from the Indian Ocean (Cheng et al. 2017). In addition to their persistence and semi-volatility, most OCs are capable of long-range atmospheric transport (LRAT), leading to their accumulation in remote regions (Blais et al., 1998; Tatton and Ruzicka, 1967). Under the influence of regional climate, the Qinling Mountains are affected by northeast prevailing winds that have passed through large industrial cities (Zhao et al., 2019). In addition, geography (e.g., elevation) (Calamari et al., 1991; Liu et al., 2014), terrain, and ecological factors can affect the transmission and distribution of OCs.

The Qinling giant panda (*Ailuropoda melanoleuca qinlingensis*) is regarded as the most endangered subspecies of panda (Chen et al., 2016), with an estimate of only 345 individuals distributed in the Qinling Mountains of Shaanxi Province, China (Zhao et al., 2019). The habitat extends over 360,587 ha and is shrinking (Zhou 2017). The subspecies' survival is threatened by habitat fragmentation, epidemics, bamboo

flowering, human activities (such as road network construction, solid waste, industrial activities, etc.) and harmful pollutants (Chen et al., 2016; Chen et al., 2017; Zhao et al., 2019). The contamination of water, soil, and vegetation (especially bamboo) by OCs is of great concern because of the possible risk to giant pandas and other wildlife. However, little is known of contamination levels and distribution of OCs, either in bamboo—the panda’s staple food— or in the environment more generally. Even less is known of the sources of OCs in panda habitat, so this is a clear risk to the giant panda that has not been evaluated.

The objectives of this present study were: (1) to measure concentrations of OCs in different functional areas within and around the Qinling Nature Reserve (within the protected area: core area-CA, buffer area-BA, experimental area-EA; outside the protected areas: anthropogenically-dominated area-AA, and the research center-RC); (2) to identify the distribution of OCs in soil, bamboo and feces within the nature reserve; (3) to analyze the composition and sources through congener profiles of OCs in Qinling panda habitat; and (4) to develop a health risk assessment model for the giant panda. In addition to the relevance of our findings to giant panda conservation, we offer it as a model for a wider assessment of pollutants on other threatened animals.

## **2. Materials and Methods**

### **2.1 Study area and sampling**

The Foping National Nature Reserve (FNNR, 33°33′–33°46′ N, 107°40′–107°55′ E) is

the world's highest density panda nature reserve, with up to 0.23 individual per km<sup>2</sup> dispersed through 29,240 ha of bamboo habitat. Guangtoushan mountain (GTS, 30°–33°8' N, 108°7'–108°8' E, 2960m) is located at the junction of the Foping National Nature Reserve and Laoxiancheng National Nature Reserve, part of the buffer area (Fig. S1). The description and availability of three functional areas (core, buffer and experimental) in nature reserve were listed in Table S4. The Shaanxi Wild Animal Research Center (RC, Louguantai, Zhouzhi County, Xi'an City, 34°06' N, 108°32' E) was established in 1987 and is the only ex-situ conservation center for the Qinling Giant Panda (Fig. S1).

In this study, 21 soil, 21 bamboo, and 18 fecal samples were collected in November 2017. In the nature reserve, soil samples were collected along a 50 m altitudinal gradient, and the samples of two adjacent sampling sites were combined. The details of the collection method were described in a previous study (Zhao et al., 2020). At each soil collection site, samples of bamboo were also collected and separated into two species: *Bashania fargesii* and *Fargesia qinlingensis*. Fecal samples were difficult to find, and widely scattered in the study area, but were found at approximately the same altitude near the corresponding bamboo sampling sites. Bamboo and soil samples were also collected at three sites outside the nature reserves in places dominated by anthropogenic use (anthropogenically-dominated area, AA). Also, at the Research Center, samples from nine panda sheds were collected at the same time and sorted into three soil samples, three bamboo samples, and three feces samples. Each sample was wrapped in aluminum

foil, pre-baked at 450 °C, packed in a sample bag, and then stored at –20 °C until analysis. Samples were then freeze-dried in the lab and homogenized before analysis for different organic contaminants.

## **2.2 Chemical analysis**

Sample extraction and instrumental analysis followed the methodology detailed in Qiu et al. (2019). About 10 g soil, bamboo and fecal samples were separately spiked with 20 ng TCmX (2,4,5,6-tetrachloro-m-xylene), PCB 30 and PCB 209 as surrogate recovery standards and extracted using dichloromethane (DCM) for 36 h. Activated copper granules were added to the soil samples to remove elemental sulfur. Each sample extract was concentrated by a rotary evaporator and solvent-exchanged into hexane. Then, those extracts were cleaned-up through a multilayer acidic silica gel column and followed with gel permeation chromatography (GPC) for final clean-up step. The concentrated samples were loaded and eluted with 40ml of mixture hexane: dichloromethane (1:1, V/V), and 30µL of isooctane containing a known amount of <sup>13</sup>C-PCB 141 (internal standard) were added as “keeper”. Samples were concentrated to the final volume of 30 µL under a gentle nitrogen stream and then stored at –20 °C until injection. The concentrations of PCBs and OCPs were measured by an Agilent 7890/7000 GC-MS/MS equipped with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm, Agilent, CA, USA). Thirty-two PCB congeners were quantified: Di-CBs: CB 8; Tri-CBs: CB 28, 37; Tetra-CBs: CB 44, 52, 54, 60, 66, 70, 74, 77; Penta-CBs: CB 82, 87, 99, 101, 105, 114, 118, 126; Hexa-CBs: CB 128, 138, 153, 156, 158, 166,

169; Hepta-CBs: CB 170, 179, 180, 183, 187, 189. Twenty-two OCP compounds were measured: HCHs ( $\alpha$ -HCH,  $\beta$ -HCH,  $\delta$ -HCH and  $\gamma$ -HCH), DDTs (*o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDE, *p,p'*-DDE), cis-Chlordane (CC), trans-Chlordane (TC), Isodrin,  $\alpha$ -Endosulfan,  $\beta$ - Endosulfan, Methoxychlor, Aldrin, Dieldrin, Endrin, Heptachlor, Mirex, and HCB. The methods for instrumental analysis, quality assurance, and quality control are described in detail in the supplementary materials.

### 2.3 Risk assessment

Health risks to giant pandas posed by exposure to contaminated soil and dietary intake of bamboo were evaluated, based on the Regional Screening Levels (RSL) proposed by the US Environmental Protection Agency (EPA) (USEPA, 2015). The total lifetime span carcinogenic risk (TLCR) and total non-carcinogenic hazard quotient (TnHQ), were calculated, including the exposure routes of incidental ingestion of soil and daily intake of bamboo, as well as inhalation of dust particulates from soil. In this study, health risks through ingestion and inhalation pathways posed by OCs were calculated by the following equations:

$$LCR_{Ingestion} = \frac{C_s \times IRS_0 \times EF \times ED \times CSF}{BW \times AT \times LT} \quad (1)$$

$$LCR_{Inhalation} = \frac{C_s \times IUR \times ET \times EF \times ED}{AT \times PEF \times LT} \quad (2)$$

$$TLCR = LCR_{Ingestion} + LCR_{Inhalation} \quad (3)$$

where  $C_s$  was the concentration of OCs in soil and bamboo ( $\text{mg kg}^{-1}$  dw); CSF was the

carcinogenic slope factor ( $\text{mg kg}^{-1} \text{d}^{-1}$ )<sup>-1</sup>; AT was the averaging time (365 days); LT was the average lifetime of the giant panda, 25 years (Zhang and Wei. 2006); EF was an assumed exposure frequency, 350 days  $\text{y}^{-1}$ ; ED was the exposure duration, 10.36 years (Zhang and Wei. 2006); IUR was the chronic inhalation unit risk ( $\text{mg m}^{-3}$ )<sup>-1</sup>; ET was the exposure time, 24 h  $\text{d}^{-1}$ ; PEF was the particulate emission factor ( $1.36 \times 10^9 \text{ m}^3 \text{ kg}^{-1}$ ); IRS<sub>o</sub> was an estimated ingestion rate, 100  $\text{mg d}^{-1}$  for soil, 7  $\text{kg d}^{-1}$  dw for bamboo (Zhang and Wei. 2006); and BW was average body weight, 115 kg (Zhang and Wei. 2006).

Also, the following were calculated:

$$nHQ_{\text{Ingestion}} = \frac{C_s \times \text{IRS}_o \times \text{EF}}{\text{BW} \times \text{AT} \times \text{RfD}} \quad (4)$$

$$nHQ_{\text{Inhalation}} = \frac{C_s \times \text{ET} \times \text{EF}}{\text{AT} \times \text{PEF} \times \text{RfC}} \quad (5)$$

$$\text{TnHQ} = nHQ_{\text{Ingestion}} + nHQ_{\text{Inhalation}} \quad (6)$$

where RfD refers to the chronic oral reference dose ( $\text{mg kg}^{-1} \text{d}^{-1}$ ); and RfC was the chronic inhalation reference concentration ( $\text{mg m}^{-3}$ ). The parameters are provided in Table S1 in the Supplementary Material. Using the risk criterion of  $1 \times 10^{-6}$  (based on the 2007 International Commission on Radiological Protection), if  $\text{TLCR} > 1 \times 10^{-6}$ , there may be a potential cancer risk. The target level of TnHQ is 1 (Man et al., 2010).

## 2.4 Statistical analysis

Statistical analysis was performed in SPSS 22.0 (IBM SPSS Statistics, IBM Corp., USA) and Origin 8.0 (OriginLab Corporation, USA). Correlation analysis was used to explore

associations between concentrations of OCs in soil, bamboo, and feces. Multivariate analysis was conducted to examine potential differences in concentrations of OCs between data groups, including among sample types, functional areas, bamboo species, and tissues. The significance level was set at  $P < \alpha = 0.05$ .

### **3. Results and Discussion**

#### **3.1 OCs levels in giant panda habitat**

##### *3.1.1 Concentrations in soil, bamboo, and feces*

A summary of the range and mean values of PCB (sum of the 32 congeners listed above) concentrations and detection frequencies, is shown in Table S2. Across all samples, total PCB concentrations ranged between 28.2–448 pg g<sup>-1</sup> dw (average 121 pg g<sup>-1</sup> dw) in soil, 102–727 pg g<sup>-1</sup> dw (average 301 pg g<sup>-1</sup> dw) in bamboo, and 69.1–579 pg g<sup>-1</sup> dw (average 204 pg g<sup>-1</sup> dw) in feces. Low-chlorinated PCBs dominated. Tetra-CBs had the highest concentration ratio, accounting for 38%, 43%, and 38%, in soil, bamboo, and feces, respectively; Di+Tri-CBs ratio was second highest, with concentrations in the three sample types 23%, 30%, and 34%. PCB concentrations in soil samples were only ~25% background levels of surface soils sampled throughout China (average 424 pg g<sup>-1</sup> dw) (Ren et al., 2007), but are comparable to levels recorded in soils from the Tibetan Plateau (average 163 pg g<sup>-1</sup> dw), i.e., in areas comparably remote from human activity (Zheng et al., 2012). Global soil background level (5410 pg g<sup>-1</sup>) (Meijer et al., 2003) is much higher than those presented in our study. There are few published levels of PCBs in bamboo; although the PCB levels we recorded in bamboo were double that in soil,

they still reflect background values when compared to PCB concentrations in Antarctic  
mats ( $<0.003\text{--}0.699\text{ ng g}^{-1}\text{ dw}$ ) and vegetation in the Alps ( $1.1 \pm 0.50\text{ ng g}^{-1}$ ) (Corsolini  
et al., 2019; Tato et al., 2011). Ma et al. (2008) reported PCB concentrations in Arctic  
deer droppings of  $1.26 (\pm 0.51)\text{ ng g}^{-1}\text{ dw}$ , higher than our recordings in panda feces.  
Seven indicator PCBs (including CB-28, 52, 101, 118, 153, 138, and 180) were detected  
in all samples, with concentration ranges of  $18.7\text{--}231$ ,  $56.6\text{--}321$ , and  $38.0\text{--}145\text{ pg g}^{-1}$   
 $\text{dw}$  in soil, bamboo, and feces, respectively, which accounted for 41–49% of all PCBs.  
Although these levels are low, and generally comparable to those in other remote,  
uninhabited parts of the globe, the threat is real and therefore further study of the  
environmental fates of PCBs in panda habitat is warranted (Zheng et al., 2012).

Concentrations of total OCPs (sum of 22 congeners) were much higher than those of  
PCBs (Table S3). The highest OCP concentrations were again observed in bamboo, and  
ranged  $1300\text{--}9230\text{ pg g}^{-1}\text{ dw}$ , with a mean value of  $3350\text{ pg g}^{-1}\text{ dw}$ . OCP concentrations  
in fecal samples ranged from  $1390\text{--}6070\text{ pg g}^{-1}\text{ dw}$ , with a mean value of  $2770\text{ pg g}^{-1}$   
 $\text{dw}$ . The lowest OCPs concentrations were found in soil, and were  $952\text{--}3930\text{ pg g}^{-1}\text{ dw}$   
(average  $1590\text{ pg g}^{-1}\text{ dw}$ ). Concentrations of OCP groups ranked as DDTs > HCHs >  
HCB > SULPHs, and their total concentrations accounted for more than 85%, 79%, and  
77% of OCPs in soil, bamboo and feces, respectively, indicating that these should be  
given priority in future studies. The study area is a remote region, and human activity  
there is minimal. DDT concentrations were far lower than those in mountain soil in  
Europe, such as Pic de Teide ( $8.75\text{ ng g}^{-1}$ ) and the Pyrenees ( $2.55\text{ ng g}^{-1}$ ) (Grimalt et al.,

2004; Ribes et al., 2002). HCH levels were comparable to those in European mountain soil ( $0.38 \text{ ng g}^{-1}$ ) but less than Tibetan soil in China ( $1.08 \text{ ng g}^{-1}$ ) (Fu et al., 2001; Grimalt et al., 2004). In the absence of data on bamboo elsewhere, we compared our results for bamboo with OCP levels in other plants from regions with minimal human disturbance. For example, total concentrations of DDT ( $1.08\text{--}6.99 \text{ ng g}^{-1}$ ) and HCB ( $0.016\text{--}1.25 \text{ ng g}^{-1}$ ) in grasses from Mt. Qomolangma are at the same level or slightly higher than those in panda habitat (Wang et al., 2007). DDT concentrations in bamboo and panda feces in this study are slightly higher than those in Arctic mosses ( $0.7 \text{ ng g}^{-1} \text{ dw}$ ) and deer feces ( $0.6 \text{ ng g}^{-1} \text{ dw}$ ), whereas levels of HCHs in panda habitat are ~50% of those in Arctic areas ( $2.9 \text{ ng g}^{-1} \text{ dw}$  for moss,  $1.46 \text{ ng g}^{-1} \text{ dw}$  for deer feces) (Ma et al. 2008).

Overall, levels of pollutants we report for Qinling panda habitat are low. Most OCPs we tested for have been banned in China since 2009, except for emergency exemptions (MEP 2009). However, residues of these pollutants are persistent, even in regions where they have evidently never been used (Wania and Mackay, 1995). Among all the transportation media, soil has a large retention capacity for POPs from atmospheric deposition, which can be re-emitted as a secondary source (Barra et al., 2005). Vegetation can collect pollutants from soil through its roots, and leaves can also absorb pollutants from air via stomata (McLachlan and Horstmann, 1998), mechanisms that may account for high concentrations of OCs in bamboo. Giant pandas ingest a large amount of bamboo every day, yet concentrations of OCs in their feces was were slightly

lower than that of bamboo (Table S2 & Table S3). One hypothesis is therefore that these pollutants are accumulating in panda tissues, and are thus potential risks to their health, especially low-chlorinated PCBs, DDTs and HCHs.

### *3.1.2 Spatial distribution*

OCs were distributed similarly in the three functional areas from which we gathered samples (Fig. 1). Concentrations of PCBs and OCPs were highest in RC, then decreased in order from AA, EA, BA, to CA. OC concentrations of RC were significantly higher than at the nature reserve ( $p<0.05$ ), especially in soil and bamboo, where OC levels in RC were threefold those in CA, indicating the captive giant pandas were exposed to more OC pollution than were wild pandas. This is consistent with our previous studies on dl-PCBs and PCDD/Fs. (Chen et al., 2016). The RC is located on the northern slope of the Qinling Mountains and is closer to Xi'an City (with intensive human activities) than the other four areas (on the southern slope) with the mountains a natural barrier for diffusing of pollution. In support of the hypothesis of bio-accumulation, we found that feces of the captive giant pandas (at RC) had significantly lower concentrations of OCs than did the bamboo on which they were fed ( $p<0.05$ , Fig. 1). Further indicative, although not statistically significant, evidence in support of the bio-accumulation hypothesis is that OC levels were lower in panda feces than in bamboo in the nature reserve (Fig. 1), implying a higher possible OC absorption in captive panda. This may be due to either or both higher pollutant levels and captive lifestyle. In soil and bamboo, OCs levels were significantly higher in AA than in the nature reserve, except for OCPs

in bamboo. The CA is a clearly defined area of well-preserved natural ecosystems, rare and endangered wildlife, and natural relics; human activity is forbidden there; in contrast, in BA and EA human activities, although restricted, nonetheless still occur (Wang, 1987). For example, a small number of farmers still reside in EA, and there are small-scale road construction and ecotourism activities, increasing the likelihood of pollutant input into the nature reserves (Zhu et al. 2019). The frequency of human activities increases in AA around the reserve.

We extracted data from Guangtoushan to study the geo-distribution of OCs levels, and results suggested that both in soil and bamboo, there was a tendency for higher OC concentrations at high latitudes (Fig. 2a, 2b, 2d and 2e) closer to large cities, which may not be the case for fecal samples (Fig. 2c and 2f). In the nature reserve, low-chlorinated PCBs with high volatility and long atmospheric residence time are the main components, while the proportion of stable high-chlorinated PCB near large cities increases in RC (Fig. 1). Further, taking Foping meteorological station (33°31' N, 107°59' E) as the observation site, we analyzed the backward trajectory at three elevations (500m, 1000m and 3000m) during November 2016 – November 2017, and found the combined influence of atmospheric short-distance and long-distance transmission (Fig. 3). We conclude, in agreement with Dragović et al., (2014) that pollutants are transported via the atmosphere from areas associated with intense human activities, conveyed by the short-distance local wind (mediated by local topography), as well as affected by worldwide long-range atmospheric transport.

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### 327 3.1.3 Tissue and species comparison and BCF of bamboo

328 Concentrations of OCs in bamboo leaves were significantly higher than those in stems  
329 (Fig. S2a). Qiu et al. (2019) reported a similar pattern in mangrove leaves and branches.  
330 In addition to the uptake of OCs from soil, atmospheric deposition and air-leaf exchange  
331 may both (or also) contribute to the relatively higher OC levels in bamboo leaves. Plants  
332 play an important role in trapping semi-volatile organic compounds from the  
333 atmosphere to the biosphere (Nizzetto et al., 2008; Salamova and Hites, 2013).  
334 Herbivorous animals further accumulate pollutants (Bertazzi et al., 1998). In Qinling  
335 habitat, there are two main staple bamboo species for pandas and they have comparable  
336 lipid content (Li et al. 2016). OCs tend to accumulate more in *F. qinlingensis* (Fig. S2b)  
337 which is usually distributed in the EA higher than 2200m, whereas *B. fargesii* grows  
338 commonly in the BA that is less polluted; the distinction between the accumulation in  
339 the two species of bamboo is therefore more likely attributable to their different  
340 altitudinal ranges, rather than to any intrinsic differences in their physiologies.

341

342 We also analyzed the enrichment ability of bamboo through bioconcentration factor  
343 (BCF), which is useful in providing an overview of the potential accumulation of  
344 compounds. BCF was defined as the ratio of pollutant concentrations in bamboo and  
345 soil. The BCF values of PCBs were generally higher than OCPs (Fig. S3). The most  
346 enriched congeners were Tetra-CBs (4-cl), Penta-CBs (5-cl), HCHs, and CHLs. This is  
347 consistent with the general concentration distribution of PCBs, and lower chlorinated

CB congeners can be more easily bioaccumulated by plants (Qiu et al., 2019). However, DDTs, the predominant component of OCPs, showed a relatively low BCF, indicating DDTs were not bioaccumulating as much as some other OCPs in bamboo. Some homologues with both high concentrations and enrichment capacity are noteworthy, such as Tetra-CBs (4-cl) and HCHs, and should be a focus of attention in formulating plans to manage staple supplies of bamboo for panda conservation.

#### *3.1.4 Correlation among OCs*

Correlations among OCs are shown in Fig. S4. Positive correlations were observed between total OCPs and PCBs ( $r = 0.751$ ,  $P < 0.01$ ), as well as OCPs and PCBs in soil ( $r = 0.870$ ,  $P < 0.01$ ), bamboo ( $r = 0.679$ ,  $P < 0.01$ ), and feces ( $r = 0.539$ ,  $P < 0.05$ ), suggesting similar processes and sources associated with these two kinds of contaminants. This result is similar to our previous study on the strong positive correlation between heavy metal concentration in bamboo and feces in giant panda habitat (Zhao et al., 2019). Significant correlations of OC concentrations between soil and bamboo, and feces and bamboo, perhaps indicate similar bioaccumulation patterns and pathways of pollutants in panda habitat. Bamboo falls to the soil surface and is then buried during decomposition. Pandas feed on bamboo, but can digest only 12.5%–23.3% of it, with whole leaves and branches often found in droppings (Zhang and Wei, 2006), such low digestibility may explain, in part, positive contaminant correlations between feces and bamboo.

### 3.2 Congener distributions and sources

The most abundant homologues of PCBs in the nature reserve are Tetra-CBs and Di+Tri - CBs (Fig. 1). These lower-chlorinated congeners move through the atmosphere and are more readily bioaccumulated than highly chlorinated PCBs, and are the major contributor to total PCBs concentrations in remote regions (Ren et al., 2007). There are no other direct sources of pollutants in the Qinling Mountains, except for small construction projects. We conclude that the main input of PCBs is via atmospheric transmission from industrial areas. The increasing trend of Hepta+Hexa+Penta - CBs concentrations in RC (Fig. 1), for soil, bamboo, and fecal samples, is very likely due to human activities, such as agriculture, industry and associated traffic outside the conservation areas. For example, though the production and use of PCBs were banned in the 1980s in China (Breivik et al., 2002), there are still some electronic manufacturing and recycling activities, as well as waste incineration, which may be potential fresh sources of PCBs in China.

OCPs in panda habitat also derive from atmospheric deposition. Several isomeric ratios of compounds were applied to distinguish specific sources. In China, the application of technical DDT and dicofol in agriculture generally caused pollution of DDTs (Yang et al., 2013). DDE and DDD are the degradation products of DDT through biotic/abiotic decomposition in natural environments (Fries, 1972). The average ratios of (DDE + DDD) / DDT in soil, bamboo, and feces were  $1.09 \pm 0.14$ ,  $1.02 \pm 0.05$ , and  $1.10 \pm 0.03$ , respectively, indicating their sources from historical residues ( $> 1$ ), since significant

degradation would have occurred since the banning of DDTs in 1983 (Sun et al., 2010) (values < 1 would imply more recent inputs (Jiang et al., 2009). The ratios of o,p'-DDT / p,p'-DDT in the present study ranged 0.15–0.35, indicative of technical DDT (0.2–0.3) in panda habitat (Qiu et al., 2005); values of 1.3–9.3 or greater are assumed to indicate a dicofol source. Although technical HCHs were prohibited, the application of technical lindane and endosulfan continued until March 2019 (Tao et al., 2008; MEE, 2019). In technical HCHs, the ratios of  $\alpha/\beta$ -HCH and  $\alpha/\gamma$ -HCH are 11.8 and 4.6–5.8, respectively (Niu et al., 2013), and the input of lindane ( $\gamma$ -HCH) reduces the value of the  $\alpha/\gamma$ -HCH ratio (Li et al., 2001). Average ratios of  $\alpha/\beta$ -HCH in this study were  $0.62 \pm 1.36$ ,  $0.68 \pm 0.03$ , and  $0.60 \pm 0.14$  in soil, bamboo, and feces, suggesting historical sources of technical HCHs. Because  $\beta$ -HCH is the most stable isomer of HCH,  $\alpha$ -HCH and  $\gamma$ -HCH are found to isomerize to it (Ya et al., 2017). The average ratios of  $\alpha/\gamma$ -HCH in soil, bamboo and feces were  $4.30 \pm 8.96$ ,  $1.08 \pm 0.27$  and  $1.19 \pm 0.09$  respectively, which were also lower than the typical ratio (4.6), indicating the possibility of recent usage of lindane. Also, we observed ratios of TC (trans-Chlordane)/CC (cis-Chlordane) to be  $0.98 \pm 1.87$ ,  $0.81 \pm 0.72$ , and  $0.66 \pm 0.26$  in soil, bamboo, and feces, respectively, suggesting use of Chlordane from previous decades (Bidleman et al., 2002). Our results are consistent with the historical residue sources provided by most studies on PCBs and OCPs (De Souza et al., 2018; Qiu et al., 2009; Zhang et al., 2018). Although aldrin, dieldrin, and endrin were never produced or used for agriculture in China (Niu et al., 2013), our observation of them in panda habitat is further evidence in support of the conclusion that these chemical compounds are brought to China by long-range

atmospheric transport through the East Asian Winter Monsoon (Table S3) (Jiang et al., 2009).

### **3.3 Risk assessment and food safety**

The total lifetime carcinogenic risk (TLCR) of PCBs and OCPs in panda habitat was calculated via ingestion (soil and bamboo) and inhalation (soil) (Fig. 4). Some congeners, such as endosulfan and endrin, were not included because we lacked the requisite slope factors. The overall TLCR of 32 PCB congeners exceeded the target risk level of  $10^{-6}$  in five areas (BA, EA, GTS, AA and RC); the main contributor was PCB126 due to its highest toxicity, and cancer risks of PCB169 were close to the critical value (Fig. 4a). In CA of panda habitat TLCRs were below  $10^{-6}$  and acceptable (Fig. 4a). For OCPs, the overall TLCRs, and carcinogenic risks of all individual congeners, were within the acceptable range and posed no potential cancer risk for pandas (Fig. 4b). However,  $\alpha$ -HCH, with the highest value, should be evaluated over longer periods. The non-carcinogenic risk of OCs for giant panda was quantified in the form of the total non-carcinogenic hazard quotient (TnHQ), as illustrated in Fig. 5. Both PCBs and OCPs were under the non-carcinogenic value of 1 (Man et al., 2010), thus the potential risk from OCs is acceptable for pandas. However, we cannot rule out the possibility that PCB 126, PCB 52, p,p' -DDT, and p,p' -DDE may lead to non-carcinogenic risks in the future. However, higher concentrations of pollutants do not necessarily correspond to higher health risks, and the foregoing assessment is only a guideline. Overall, health risks to pandas from pollutants were higher in captivity than in the wild.

436

437 Bioaccessible concentrations of pollutants were suitable proxies in portraying actual  
438 risk, because bioavailable pollutant concentrations exceed ethical acceptability (Wragg  
439 and Cave, 2002). The use of biological tissue, blood and organ for scientific  
440 experiments is forbidden for rare animals. The non-invasive sampling method we used  
441 neither endangers rare animal populations nor interferes with their reproduction. The  
442 giant panda has a prodigious appetite for bamboo but digests it inefficiently,  
443 consequently health risks from OCs may be overestimated based on bioaccessible  
444 concentrations: this hypothesis merits further study, including more refined assessments  
445 of daily intake and of potential health risks and this might involve the use of exposure  
446 parameters as modified by non-invasive and omics toxicity testing models mentioned  
447 in the introduction. Despite uncertainties in the absolute risk assessments we provide,  
448 our findings can be used to frame future research to determination health risks to giant  
449 panda associated with OCs and specifically regarding OC congener distributions,  
450 composition, and sources.

451 The most significant exposure pathway of health risk assessment for giant pandas  
452 is ingestion, in which bamboo intake (7 kg) is much larger than that of soil (100 mg),  
453 so assessment of carcinogenic and non-carcinogenic risks caused by ingestion should  
454 reflect pandas' food safety. According to the results discussed above, PCB 126 poses  
455 threat to Qinling pandas, and is at a level that exceeds the acceptable carcinogenic risk  
456 threshold. This finding makes it imperative that bamboo is monitored for PCB 126 as  
457 an immediate priority with respect to the giant panda's food safety.

458

#### 459 **4. Conclusion**

460 We determined OC levels, their spatial distribution patterns and possible sources, and  
461 the health risk they pose to the Qinling panda. The comparatively low OCs levels  
462 suggest that only moderate sources of OC pollution currently impact Qinling panda  
463 habitat. Sampling sites differed in their pollution, and RC was more heavily polluted  
464 than the nature reserve, and captive pandas absorbed relatively more pollutants. Within  
465 the nature reserve, OC concentration decreased successively from EA, BA, to CA.  
466 Moreover, regions at high latitude tended to accumulate higher OCs in the same  
467 functional area, which we interpret as the result of regional meteorological conditions  
468 and topography. Tetra-CBs and HCHs, with higher BCF in bamboo leaves and *F.*  
469 *qinlingensis* should be a focus of attention. PCBs and OCPs are affected by similar  
470 processes and sources, both being transported through the atmosphere and deposited in  
471 panda habitat, and nowadays mainly originate from historical residues. The results of  
472 backward trajectory analyses and traces of DRINs—compounds thought never to have  
473 been used in China—suggest the possibility of long-range atmospheric transport of OCs.  
474 PCBs occurred at levels that pose potential cancer risk, to which PCB126 was the  
475 biggest contributor.

476

477 Overall, the accumulation of OCs in Qinling panda habitat is influenced by a  
478 combination of long-range atmospheric transport, local climate, topography and human  
479 activity, and is also related to the distance of high latitude industrial areas in large cities.

The diversity of factors that we demonstrate must be taken into account to understand modern biodiversity conservation (Macdonald, 2019). We demonstrated that health risk assessments are important for prioritizing congeners of pollutants in Qinling, as high concentrations of pollutants may not necessarily translate to significant health risks for pandas or other species. However, further studies should focus on more refined assessments of daily intake and improvements of exposure parameters. Hence, regular monitoring is needed to ensure that dangerous increases in these pollutants do not go unnoticed. In light of the long-distance transport of pollutants, our study provides an additional strand of evidence for the necessity of trans-boundary, and indeed global, actions to deliver conservation of biodiversity: such coordinated and cooperative approaches to conservation are urgent, and raise important questions as to how people can achieve the necessary cooperation (Curry et al., 2019).

### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- Arfaeinia, H., Asadgol, Z., Ahmadi, E., Seifi, M., Moradi, M., Dobaradaran, S., 2017. Characteristics, distribution and sources of polychlorinated biphenyls (PCBs) in coastal sediments from heavily industrialized area of Asalouyeh, Iran. *Water Sci. Technol.* 76, 3340-3350.
- Barra, R., Popp, P., Quiroz, R., Bauer, C., Cid, H., von Tumpling, W., 2005. Persistent toxic substances in soils and waters along an altitudinal gradient in the Laja River Basin, Central Southern Chile. *Chemosphere* 58, 905-915.
- Bertazzi, P., Bernucci, I., Brambilla, G., Consonni, D., Pesatori, A., 1998. The Seveso Studies on Early and Long-Term Effects of Dioxin Exposure: A Review. *Environ. Health Perspect.* 106, 625-633.
- Bidleman, T. F., Jantunen, L. M., Helm, P. A., Brorström-Lundén, E., Juntto, S., 2002. Chlordane enantiomers and temporal trends of chlordane isomers in arctic air. *Environ. Sci. Technol.* 36, 539-544.
- Blais, J. M., Schindler, D. W., Muir, D. C. G., Kimpe, L. E., Donald, D. B., Rosenberg, B., 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. *Nature* 395, 585-588.
- Breivik, K., Sweetman, A., Pacyna, J. M., Jones, K. C., 2002. Towards a global historical emission inventory for selected PCB congeners — a mass balance approach: 1. Global production and consumption. *Sci. Total Environ.* 290, 181-198.
- Breivik, K., Sweetman, A., Pacyna, J. M., Jones, K. C., 2007. Towards a global historical emission inventory for selected PCB congeners—a mass balance approach 3. An update. *Sci. Total*

524 Environ. 377, 296-307.

525 Calamari, D., Bacci, E., Focardi, S., Gaggi, C., Morosini, M., Vighi, M., 1991. Role of plant biomass

526 in the global environmental partitioning of chlorinated hydrocarbons. Environ. Sci. Technol.

527 25, 1489-1495.

528 Carson, R., 1962. Silent Spring. Houghton Mifflin Company. Boston.

529 Chen, Y. P., Maltby, L., Liu, Q., Song, Y., Zheng, Y. J., Ellison, A. M., Ma, Q. Y., Wu, X. M., 2016.

530 Captive pandas are at risk from environmental toxins. Front. Ecol. Environ. 14, 363-367.

531 Chen, Y. P., Zheng, Y. J., Liu, Q., Ellison, A. M., Zhao, Y., Ma, Q. Y., 2017. PBDEs (polybrominated

532 diphenyl ethers) pose a risk to captive giant pandas. Environ. Pollut. 226, 174–181.

533 Cheng, Y., Liu, H., Wang, H., Piao, S., Yin, Y., Ciais, P., Wu, X. C., Luo, Y., Zhang, C. N., Song, Y.

534 Q., Gao, Y. S., Qiu, A. A., 2017. Contrasting effects of winter and summer climate on alpine

535 timberline evolution in monsoon-dominated East Asia. Quat. Sci. Rev. 169, 278-287.

536 Corsolini, S., Baroni, D., Martellini, T., Pala, N., Cincinelli, A., 2019. PBDEs and PCBs in terrestrial

537 ecosystems of the Victoria Land, Antarctica. Chemosphere 231, 233-239.

538 Curry, O. S., Hare, D., Hepburn, C., Johnson, D. D., Buhrmester, M. D., Whitehouse, H., Macdonald,

539 D. W., 2019. Cooperative conservation: Seven ways to save the world. Conserv. Sci. Prac.

540 2(1), c123.

541 De Souza, A. C., Taniguchi, S., Lopes Figueira, R. C., Montone, R. C., Caruso Bícago, M., Martins,

542 C. C., 2018. Historical records and spatial distribution of high hazard PCBs levels in

543 sediments around a large South American industrial coastal area (Santos Estuary, Brazil).

544 J. Hazard. Mater. 360, 428-435.

545 Dragović, R., Gajić, B., Dragović, S., Đorđević, M., Đorđević, M., Mihailović, N., Onjia, A., 2014.

546           Assessment of the impact of geographical factors on the spatial distribution of heavy metals  
 547           in soils around the steel production facility in Smederevo (Serbia). *J. Clean. Prod.* 84, 550-  
 548           562.

549   Dumanoglu, Y., Gaga, E. O., Gungormus, E., Sofuoglu, S. C., Odabasi, M., 2017. Spatial and  
 550           seasonal variations, sources, air-soil exchange, and carcinogenic risk assessment for PAHs  
 551           and PCBs in air and soil of Kutahya, Turkey, the province of thermal power plants. *Sci.*  
 552           *Total Environ.* 580, 920-935.

553   FR., Priority pollutants. U.S. Environmental Protection Agency. *Federal Register* 47, 1982, pp.  
 554           52290-52309.

555   Fries, G. F., Degradation of Chlorinated Hydrocarbons under Anaerobic Conditions. *Fate of Organic*  
 556           *Pesticides in the Aquatic Environment.* American Chemical Society, 1972, pp. 256-270.

557   Fu, J., Mai, B., Sheng, G., Zhang, G., Wang, X., Peng, P. A., Xiao, X., Ran, R., Cheng, F. Z., Peng,  
 558           X. Z., Wang, Z. S., Wa, T. U., 2003. Persistent organic pollutants in environment of the  
 559           Pearl River Delta, China: an overview. *Chemosphere* 52, 1411-1422.

560   Fu, S., Chu, S., Xu, X., 2001. Organochlorine Pesticide Residue in Soils from Tibet, China. *Bull.*  
 561           *Environ. Contam. Toxicol.* 66, 171-177.

562   Godard-Coddig, C. A. J., Fossi, M. C., Chapter 9 Field Sampling Techniques and Ecotoxicologic  
 563           Biomarkers in Cetaceans. In: M. C. Fossi, C. Panti (Eds.), *Marine Mammal Ecotoxicology.*  
 564           Academic Press, 2018, pp. 237-259.

565   Grimalt, J. O., Van Drooge, B. L., Ribes, A., Vilanova, R. M., Fernandez, P., Appleby, P., 2004.  
 566           Persistent organochlorine compounds in soils and sediments of European high altitude  
 567           mountain lakes. *Chemosphere* 54, 1549-1561.

568 Hua, X., Shan, Z., 1996. The production and application of pesticides and factor analysis of their  
569 pollution in environment in China. *Adv. in Environ. Sci. (Chinese Journal)* 4(2), 33–45.

570 Jiang, Y. F., Wang, X. T., Jia, Y., Wang, F., Wu, M. H., Sheng, G. Y., Fu, J. M., 2009. Occurrence,  
571 distribution and possible sources of organochlorine pesticides in agricultural soil of  
572 Shanghai, China. *J. Hazard. Mater.* 170, 989-997.

573 Jones, K. C., De Voogt, P., 1999. Persistent organic pollutants (POPs): state of the science. *Environ.*  
574 *Pollut.* 100, 209-221.

575 Li, Y. F., Cai, D. J., Shan, Z. J., Zhu, Z. L., 2001. Gridded usage inventories of technical  
576 hexachlorocyclohexane and lindane for China with 1/6 degrees latitude by 1/4 degrees  
577 longitude resolution. *Arch. Environ. Contam. Toxicol.* 41, 261-266.

578 Li, Y. J., Cai, Q., Liu, X. H., Melissa, S., Wu, P. F., Jia, X. D., He, X. B., 2016. The effect of elevation  
579 on structure and nutrition of staple food bamboo and seasonal distribution of giant pandas.  
580 *Acta Theriol. Sinica* 36, 24-35.

581 Liu, X., Li, J., Zheng, Q., Bing, H., Zhang, R., Wang, Y., Luo, C., Liu, X., Wu, Y., Pan, S., Zhang,  
582 G., 2014. Forest filter effect versus cold trapping effect on the altitudinal distribution of  
583 PCBs: a case study of Mt. Gongga, eastern Tibetan Plateau. *Environ. Sci. Technol.* 48,  
584 14377-14385.

585 Ma, X. D., Wang Y. J., Na, G. S., Lin, Z. S., Zhou, C. G., Wang, Z., Yao, Z. W., 2008. Organochlorine  
586 pesticides and polychlorinated biphenyls concentrations and characteristics in the Arctic  
587 New Orson region in different environmental samples. *Chin. J. Polar Res.* 20(4), 329-337

588 Man, Y. B., Sun, X. L., Zhao, Y. G., Lopez, B. N., Chung, S. S., Wu, S. C., Cheung, K. C., Wong,  
589 M. H., 2010. Health risk assessment of abandoned agricultural soils based on heavy metal

590 contents in Hong Kong, the world's most populated city. *Environ. Int.* 36, 570-576.

591 Mancina, A., 2018. New technologies for monitoring marine mammal health M.C. Fossi, C. Panti  
 592 (Eds.), *Marine Mammal Ecotoxicology*, Academic Press, pp. 291-320.

593 Mason, C. F., Ford, T. C., Last, N. I., 1986. Organochlorine residues in British otters. *Bull. Environ.*  
 594 *Contam. Toxicol.* 36, 656-661.

595 Macdonald, D. W., 2019. Mammal Conservation: Old Problems, New Perspectives,  
 596 Transdisciplinarity, and the Coming of Age of Conservation Geopolitics. *Annu. Rev. Env.*  
 597 *Resour.* 44(1), 61-88.

598 McLachlan, M. S., Horstmann, M., 1998. Forests as Filters of Airborne Organic Pollutants: A  
 599 Model. *Environ. Sci. Technol.* 32, 413-420.

600 MEE, 2019. Ministry of Ecology and Environment of the People's Republic of China.  
 601 [http://www.mee.gov.cn/xxgk2018/xxgk/xxgk01/201903/t20190312\\_695462.html](http://www.mee.gov.cn/xxgk2018/xxgk/xxgk01/201903/t20190312_695462.html)  
 602 (accessed September 2020).

603 Meijer, S. N., Ockenden, W. A., Sweetman, A., Breivik, K., Grimalt, J. O., Jones, K. C., 2003.  
 604 Global Distribution and Budget of PCBs and HCB in Background Surface Soils:  
 605 Implications for Sources and Environmental Processes. *Environ. Sci. Technol.* 37, 667-672.

606 MEP, 2009. Announcement of Ministry of Environment Protection of the People's Republic of  
 607 China [2009] No.23.  
 608 [http://www.zhb.gov.cn/gkml/hbb/bgg/200910/t20091022\\_174552.htm](http://www.zhb.gov.cn/gkml/hbb/bgg/200910/t20091022_174552.htm) (accessed  
 609 September 2020).

610 Monclus, L., Lopez-Bejar, M., De la Puente, J., Covaci, A., Jaspers, V. L. B., 2018. First evaluation  
 611 of the use of down feathers for monitoring persistent organic pollutants and

organophosphate ester flame retardants: A pilot study using nestlings of the endangered cinereous vulture (*Aegypius monachus*). *Environ. Pollut.* 238, 413-420.

Niu, L., Xu, C., Yao, Y., Liu, K., Yang, F., Tang, M., Liu, W., 2013. Status, influences and risk assessment of hexachlorocyclohexanes in agricultural soils across china. *Environ. Sci. Technol.* 47, 12140-12147.

Nizzetto, L., Pastore, C., Liu, X., Camporini, P., Stroppiana, D., Herbert, B., Boschetti, M., Zhang, G., Brivio, P. A., Jones, K. C., Di Guardo, A., 2008. Accumulation Parameters and Seasonal Trends for PCBs in Temperate and Boreal Forest Plant Species. *Environ. Sci. Technol.* 42, 5911-5916.

Ontiveros-Cuadras, J. F., Ruiz-Fernandez, A. C., Sanchez-Cabeza, J. A., Sericano, J., Perez-Bernal, L. H., Paez-Osuna, F., Dunbar, R. B., Mucciarone, D. A., 2019. Recent history of persistent organic pollutants (PAHs, PCBs, PBDEs) in sediments from a large tropical lake. *J. Hazard. Mater.* 368, 264-273.

Qiu, X., Zhu, T., Yao, B., Hu, J., Hu, S., 2005. Contribution of Dicofol to the Current DDT Pollution in China. *Environ. Sci. Technol.* 39, 4385-4390.

Qiu, Y. W., Qiu, H. L., Zhang, G., Li, J., 2019. Bioaccumulation and cycling of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in three mangrove reserves of south China. *Chemosphere* 217, 195-203.

Ren, N., Que, M. X., Li, Y. F., Liu, Y., Wan, X., Sverko, E., Ma, J., 2007. Polychlorinated Biphenyls in Chinese Surface Soils. *Environ. Sci. Technol.* 41, 3871-3876.

Ribes, A., Grimalt, J. O., Torres García, C. J., Cuevas, E., 2002. Temperature and Organic Matter Dependence of the Distribution of Organochlorine Compounds in Mountain Soils from the

634 Subtropical Atlantic (Teide, Tenerife Island). *Environ. Sci. Technol.* 36, 1879-1885.

635 Saeedi, R., Khakzad, S., Koolivand, A., Dobaradaran, S., Khaloo, S., Jorfi, S., Abtahi, M., 2017.

636 Transformer oils as a potential source of environmental exposure to polychlorinated

637 biphenyls (PCBs): an assessment in three central provinces of Iran. *Environ. Sci. Pollut.*

638 *Res. Int.* 24, 19098-19103.

639 Salamova, A., Hites, R. A., 2013. Brominated and chlorinated flame retardants in tree bark from

640 around the globe. *Environ. Sci. Technol.* 47, 349-354.

641 Simond, A. E., Houde, M., Lesage, V., Michaud, R., Verreault, J., 2020. Metabolomic profiles of

642 the endangered St. Lawrence Estuary beluga population and associations with

643 organohalogen contaminants. *Sci. Total Environ.* 717, 137204.

644 Sun, J., Feng, J., Liu, Q., Li, Q., 2010. Distribution and sources of organochlorine pesticides (OCPs)

645 in sediments from upper reach of Huaihe River, East China. *J. Hazard. Mater.* 184, 141-

646 146.

647 Tao, S., Liu, W., Li, Y., Yang, Y., Zuo, Q., Li, B., Cao, J., 2008. Organochlorine Pesticides

648 Contaminated Surface Soil As Reemission Source in the Haihe Plain, China. *Environ. Sci.*

649 *Technol.* 42, 8395-8400.

650 Tato, L., Tremolada, P., Ballabio, C., Guazzoni, N., Parolini, M., Caccianiga, M., Binelli, A., 2011.

651 Seasonal and spatial variability of polychlorinated biphenyls (PCBs) in vegetation and cow

652 milk from a high altitude pasture in the Italian Alps. *Environ. Pollut.* 159, 2656-2664.

653 Tatton, J. O. G., Ruzicka, J. H. A., 1967. Organochlorine Pesticides in Antarctica. *Nature* 215, 346-

654 348.

655 UNEP, 2009. Stockholm Convention on persistent organic pollutants. United Nations Environment

656 Programme. <http://www.pops.int/> (accessed September 2020).

657 USEPA, 2015. Regional Screening Levels (RSL) for Chemical Contaminants. United States  
 658 Environmental Protection Agency. <http://www.epa.gov/region9/superfund/prg/> (accessed  
 659 September 2020).

660 Wang, X., Gong, P., Wang, C., Ren, J., Yao, T., 2016. A review of current knowledge and future  
 661 prospects regarding persistent organic pollutants over the Tibetan Plateau. *Sci. Total*  
 662 *Environ.* 573, 139-154.

663 Wang, X., Wang, C., Zhu, T., Gong, P., Fu, J., Cong, Z., 2019. Persistent organic pollutants in the  
 664 polar regions and the Tibetan Plateau: A review of current knowledge and future prospects.  
 665 *Environ. Pollut.* 248, 191-208.

666 Wang, X. B., 1989. Theory and Practice of nature reserves. China Environmental Science Press.  
 667 Beijing.

668 Wang, X. P., Yao, T. D., Cong, Z. Y., Yan, X. L., Kang, S. C., Zhang, Y., 2007. Distribution of  
 669 persistent organic pollutants in soil and grasses around Mt. Qomolangma, China. *Arch.*  
 670 *Environ. Contam. Toxicol.* 52, 153-162.

671 Wania, F., Mackay, D., 1995. A global distribution model for persistent organic chemicals. *Sci. Total*  
 672 *Environ.* 160-161, 211-232.

673 Wragg, J., Cave, M. R., 2002. UK In-vitro Methods for the Measurement of the Oral Bioaccessibility  
 674 of Selected Metals and Metalloids in Soils: A Critical Review. Environment Agency.  
 675 [https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/290321/sp5-062-tr-1-e-e.pdf)  
 676 [data/file/290321/sp5-062-tr-1-e-e.pdf](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/290321/sp5-062-tr-1-e-e.pdf) (accessed September 2020).

677 Ya, M., Wu, Y., Li, Y., Wang, X., 2017. Anthropogenic organochlorine compounds as potential

678 tracers for regional water masses: A case study of estuarine plume, coastal eddy, wind-  
679 driven upwelling and long-range warm current. *Chemosphere* 170, 75-82.

680 Yang, D., Qi, S., Zhang, J., Wu, C., Xing, X., 2013. Organochlorine pesticides in soil, water and  
681 sediment along the Jinjiang River mainstream to Quanzhou Bay, southeast China.  
682 *Ecotoxicol. Environ. Saf.* 89, 59-65.

683 Zhang, Y., Qi, S., Xing, X., Yang, D., Devi, N. L., Qu, C., Liu, H.-X., Zhang, J.Q., Zeng, F.M.,  
684 Chapter 21 - Legacies of Organochlorine Pesticides (OCPs) in Soil of China—A Review,  
685 and Cases in Southwest and Southeast China. In: B. De Vivo, et al. (Eds.), *Environmental*  
686 *Geochemistry* (Second Edition). Elsevier, 2018, pp. 543-565.

687 Zhang Z. H., Wei F. W., 2006. Giant panda ex-situ Conservation Theory and Practice. Science Press.  
688 Beijing, China.

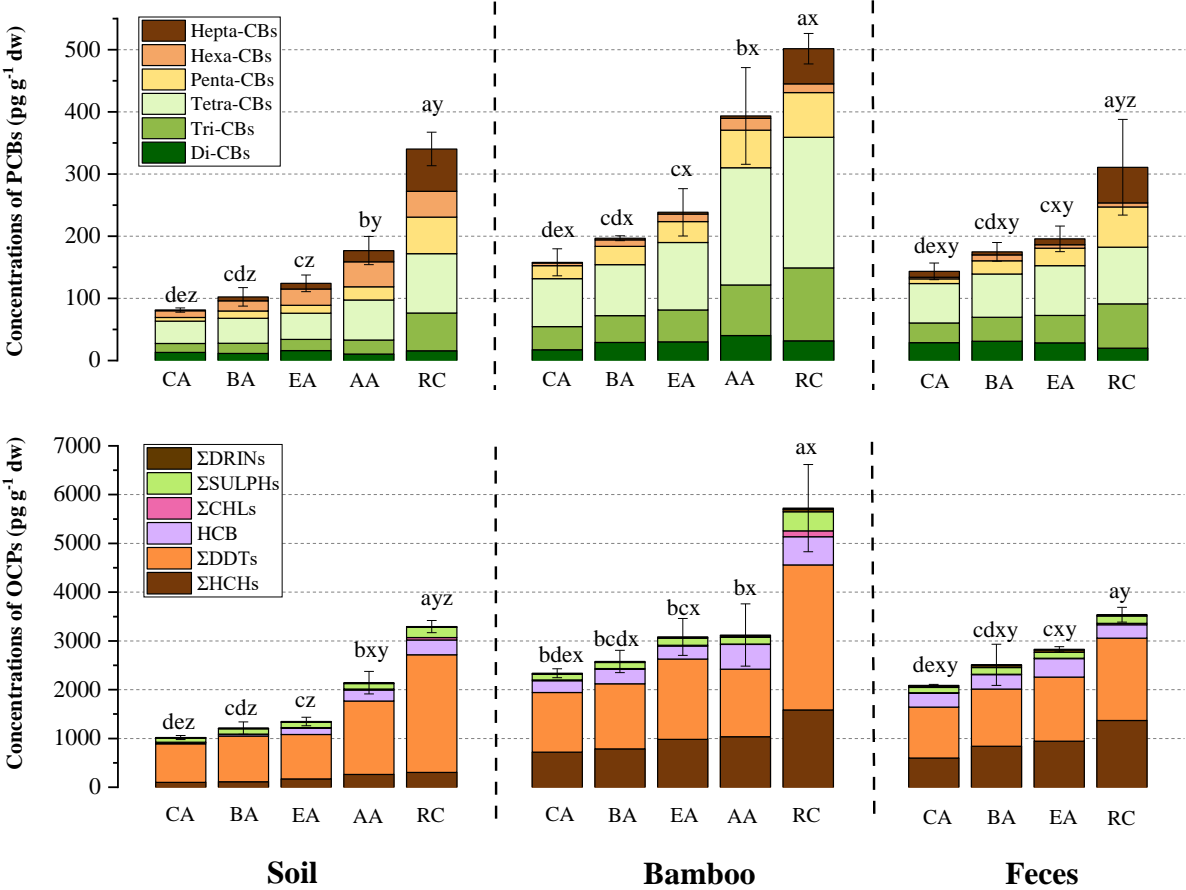
689 Zhao, Y., Chen, Y. P., Zheng, Y. J., Ma, Q. Y., Jiang, Y., 2020. Quantifying the heavy metal risks from  
690 anthropogenic contributions in Sichuan panda (*Ailuropoda melanoleuca melanoleuca*) habitat.  
691 *Sci. Total Environ.* 745, 140941.

692 Zhao, Y., Chen, Y. P., Ellison, A. M., Liu, W. G., Chen, D., 2019. Establish an environmentally  
693 sustainable Giant Panda National Park in the Qinling Mountains. *Sci. Total Environ.* 668,  
694 979-987.

695 Zheng, X., Liu, X., Jiang, G., Wang, Y., Zhang, Q., Cai, Y., Cong, Z., 2012. Distribution of PCBs  
696 and PBDEs in soils along the altitudinal gradients of Balang Mountain, the east edge of the  
697 Tibetan Plateau. *Environ. Pollut.* 161, 101-106.

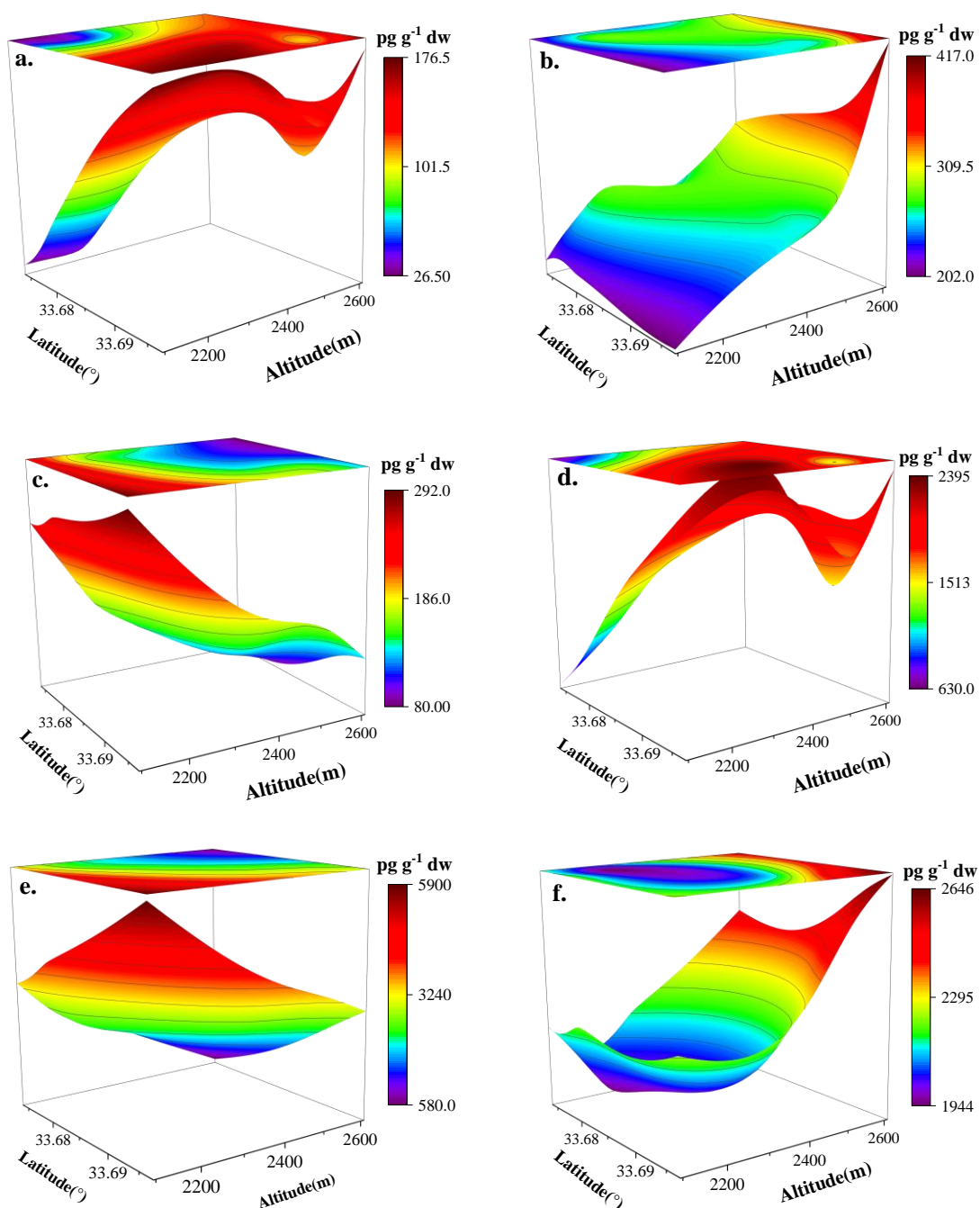
698 Zhou, L. G., 2017. Qingling panda-the forth giant panda survey report of Shaanxi province. Shaanxi  
699 Science and Technology Press. Xian.

700     Zhu, J, Lu, C. T., Shi, J. L., Zhang, L. R., Pan, Z., 2019. Diachronic study on the residents' well-  
701             being in natural reserves: a case study of Foping National Nature Reserve, China. Acta  
702             Ecol. Sinica 39(22), 8299-8309.  
703

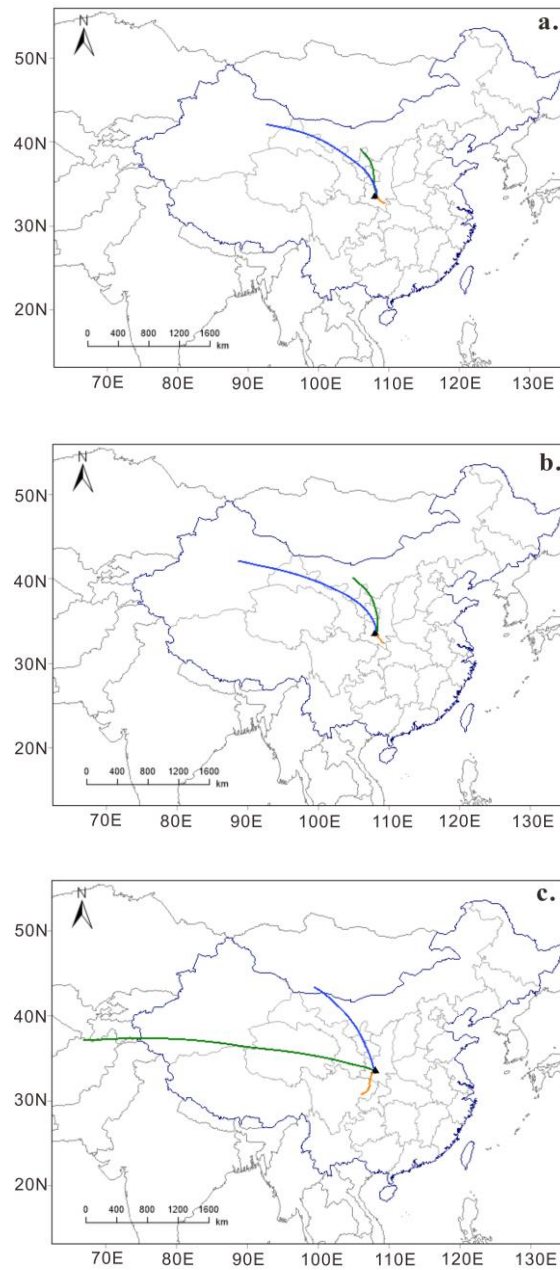


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706 **Figure 1.** PCBs and OCPs concentrations in different areas. The five different functional areas are:  
707 core area (CA), buffer area (BA), experimental area (EA) anthropogenically-dominated area (AA)  
708 and Shaanxi Wild Animal Research Center (RC), respectively. Different letters indicate significant  
709 differences for CA, BA, EA, AA and RC (a, b, c, d, e), and soil, bamboo and feces (x, y, z) ( $p<0.05$ ).  
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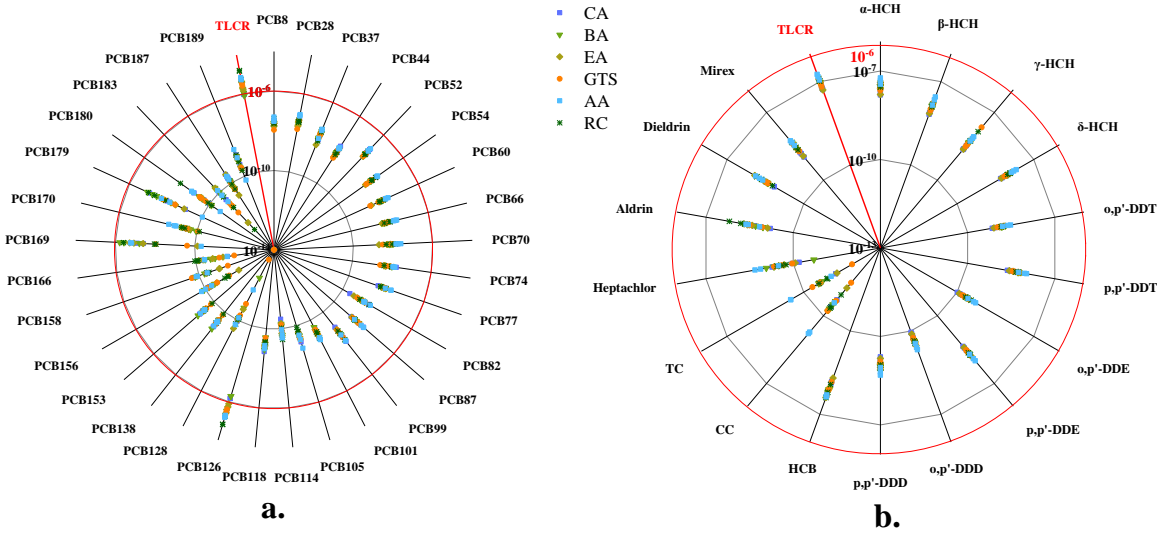


**Figure 2.** Variation of PCBs concentrations with latitude and elevation in soil (a), bamboo (b) and feces (c); Variation of OCPs concentrations with latitude and elevation in soil (d), bamboo (e) and feces (f).



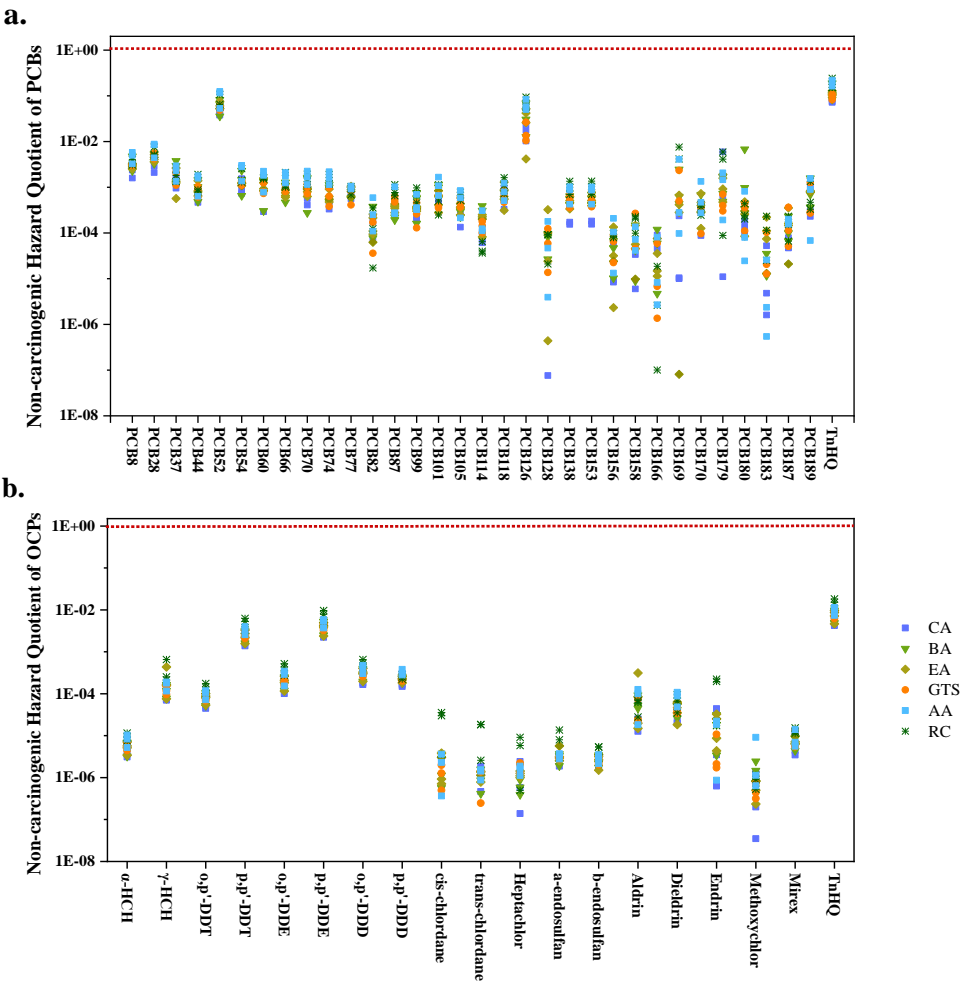
**Figure 3.** The results of backward trajectory analyses at three different ground elevations: 500m (a), 1000m (b) and 3000m (c). All air mass data (November 2016 to November 2017) is grouped into three colors using clustering method: blue, green and orange.

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**Figure 4.** The carcinogenic risk of PCB (a) and OCP (b). TLCR is the total lifetime span carcinogenic risk, GTS stands for Guangtoushan.



**Figure 5.** The non-carcinogenic risk of PCB (a) and OCP (b). TnHQ is the total non-carcinogenic hazard quotient.