

1 **Atmospheric deposition exposes pandas to toxic pollutants**

2 Yi-ping Chen^{1*}, Ying-juan Zheng^{1,2}, Qiang Liu¹, Yi Song¹, Zhi-sheng An¹, Qing-yi Ma³, and
3 Aaron M. Ellison⁴

4 ¹ SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, 710075,
5 China

6 ² University of Chinese Academy of Sciences, Beijing 100049, China

7 ³ Shaanxi Wild Animal Research Center, Zhouzhi Xi'an, 710402, China

8 ⁴ Harvard University, Harvard Forest, Petersham, Massachusetts, USA

9 *Correspondence to: Yi-ping Chen, Institute of Earth Environment, CAS, No. 97, Yan-Xiang
10 Road, Xi'an, 710061, China; Tel: +86-29-88324766; Fax: +86-29a -88320456; E-mail:
11 Chenyp@ieecas.cn

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13 *Abstract.* The giant panda (*Ailuropoda melanoleuca*) is one of the most endangered
14 animals in the world, and it is recognized worldwide as a symbol for conservation. A
15 previous study showed that wild and captive pandas were exposed to toxins in their diet of
16 bamboo, but the ultimate origin of these toxins is unknown. Here we show that atmospheric
17 deposition is the origin of heavy metals and persistent organic pollutants (POPs) in the diets
18 of captive and wild Qinling giant pandas. Atmospheric deposition averaged 115 and 49
19 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ at China's Shaanxi Wild Animal Research Center (SWARC) and Foping National
20 Nature Reserve (FNNR), respectively. Atmospheric deposition of heavy metals (As, Cd, Cr,
21 Pb, Hg, Co, Cu, Zn, Mn and Ni) and POPs at SWARC was higher than at FNNR. Soil
22 concentrations of the aforementioned heavy metals other than As and Zn also were

23 significantly higher at SWARC than at FNNR. We conclude that efforts to conserve the
24 Qinling subspecies of panda may be compromised by air pollution attendant to China's
25 economic development. Improvement of air quality and reductions of toxic emissions are
26 urgently required to protect China's iconic species.

27 **Keywords:** *Air pollution; atmospheric deposition; heavy metals; Qingling panda,*

28 **Introduction**

29 The giant panda (*Ailuropoda melanoleuca* (David, 1869)) is one of the most endangered
30 animals in the world and a worldwide symbol for conservation. Two strategies, developed in
31 the last several decades, are now used to protect this flagship endangered species. One
32 strategy uses *ex-situ* breeding in, for example, the zoos of Beijing and the seven breeding
33 centers, established since the 1950s, of Wolong and Chengdu. The other strategy has been to
34 establish natural conservation zones that preserve panda habitat: 50 conservation zones, with
35 a total area > 20,000 km², have been delimited (Zhang and Wei 2006). In these conservation
36 zones, efforts are ongoing to reduce habitat destruction, logging, resource exploitation, and
37 tourism, all of which threaten wild panda populations.

38 As China's economy has developed rapidly, environmental problems have emerged.
39 This trade-off of environmental quality for economic development was common in the
40 developed nations (Seinfeld 2004), and in China has had predictable effects of particulate
41 pollution influencing air quality, regional and global climates, and human health (Cao et al.
42 2012, Wang et al. 2014). For example, in 2013, China experienced extremely severe and
43 persistent haze pollution: measurements of average daily concentrations of PM_{2.5} (particulate
44 matter with an aerodynamic < 2.5- μ m diameter) in 74 major cities exceeded the Chinese

45 pollution standard of $75 \mu\text{g}/\text{m}^3$. During the same year, a maximum daily concentration of
46 $772 \mu\text{g}/\text{m}^3$ was observed over 1.3 million km^2 , affecting at the health of at least 800 million
47 people (China National Environmental Monitoring Centre 2013).

48 Xi'an, one of the largest cities in China, is situated on the Guanzhong Plain at the
49 Northern edge of the Qinling Mountains. This city has a resident population of eight million
50 people and receives at least two million visitors annually. Between 2005 and 2010, the 24-hr
51 $\text{PM}_{2.5}$ in Xi'an ranged from 130–351 $\mu\text{g}/\text{m}^3$ (Han et al. 2010, Shen et al. 2011), exceeding
52 Chinese government standards 2–5-fold. Intense “haze-fog” events occur regularly, making
53 air pollution one of the most important environmental issues in Xi'an (Cao et al. 2011).

54 Xi'an also is home to the Shaanxi Wild Animal Research Center (SWARC: $34^\circ 06' \text{N}$,
55 $108^\circ 32' \text{E}$). Established in 1987, SWARC is on the north slope of the Qinling Mountains and
56 is dedicated to the conservation of the golden monkey (*Rhinopithecus roxellana*
57 Milne-Edwards, 1870), golden takin (*Budorcas taxicolor* Hodgson, 1850), crested ibis
58 (*Nipponia nippon* (Temminck, 1835)), and the Qinling subspecies of giant panda, of which
59 only 345 individuals remain (Sun et al. 2005, SFA 2015). Captive pandas at SWARC and
60 wild pandas elsewhere in the region are exposed to heavy metals and persistent organic
61 pollutants (POPs), including PCBs (polychlorinated biphenyls), PCDDs (polychlorinated
62 dibenzo-p-dioxins), and PCDFs (polychlorinated dibenzofurans) through their diet of bamboo
63 (Chen et al. *in press*). However, the ultimate origin of these pollutants is not known. Here we
64 test the hypothesis that these pollutants are derived from atmospheric deposition.

65 **Methods and materials**

66 *Sample collection*

67 Atmospheric deposition samples were collected from November 8, 2013 to November 8,
68 2014 at the Foping National Nature Reserve (FNNR: Qinling Mountain, 33° 33′ – 33° 46′ N,
69 107° 40′ – 107° 55′ E), Shaanxi Wild Animal Research Center (SWARC: Louguantai,
70 Zhouzhi County, Xi'an city, 34° 06′ N, 108° 32′ E), and Xi'an City (34° 23′ N, 108° 89′ E).
71 Samples of dry deposition and precipitation were collected continuously for one year into
72 66×40×12-cm plastic containers located at four sites at FNNR, three at SWARC, and four in
73 Xi'an city. During the sampling period, purified water was added to the containers to avoid
74 the collected deposition being blown out of the containers. After collection, the containers
75 were rinsed with purified water to release particles deposited or sorbed onto the container
76 walls. At the same time, soils samples also were collected from FNNR and at SWARC where
77 bamboos are planted to feed captive pandas. Both the suspensions and the soil samples were
78 dried to a constant weight at 60 °C before being homogenized with a ball mill.

79 *Heavy metal analysis*

80 Five hundred mg of each sample was placed into a Teflon digestion vessel to which was
81 added 11 mL GR-grade acid digestion mixture (1mL HNO₃, 3mL HCl, 5mL HF, 2mL
82 HClO₄) for digestion with an electric hot plate. After digestion, samples were diluted to 50
83 mL with ultrapure water (18.2 MΩ/cm² Milli-Q water, Millipore). Heavy metal
84 concentrations were analyzed using atomic absorption spectroscopy (AAS, ZEEnit 700P,
85 Analytik Jena, Germany). Concentrations of Cu, Zn, Mn and Cr were measured using the
86 air-acetylene flame method with electrically modulated deuterium-HCl background
87 correction. The hydride-forming elements As and Hg were measured using the HS55 Hydride
88 System. Concentrations of Cd, Ni and Pb were measured using a graphite furnace AAS

89 coupled to a MPE 60 graphite autosampler with 2-field mode Zeeman effect background
90 correction. Heavy metal concentrations are expressed as $\mu\text{g/g}^1$ dry weight.

91 *Analysis of persistent organic pollutants*

92 Sample extraction, cleanup, and chemical analysis of POPs followed established methods
93 with some modifications (Liu et al. 2006, Chen et al. 2016, Li et al. 2008). Samples from
94 atmospheric deposition were freeze-dried before being spiked with ^{13}C -labeled surrogate
95 standards (Environmental Protection Agency (EPA) methods 1613B and 1668A) and
96 undergoing accelerated solvent extraction with dichloromethane: hexane (1:1). Each sample
97 extract was adjusted to 50 ml with hexane; 15 g of acid silica (30% w/w) was added to
98 remove lipids. The acid silica was stirred for 2 h and the extract was poured through ≈ 5 g of
99 anhydrous sodium sulfate. All extracts were concentrated to 2 ml by rotary evaporation
100 before cleanup. All solvents were purchased from Fisher (Fair Lawn, New Jersey, USA).
101 Silica gel was obtained from Merck (silica gel 60, Darmstadt, Germany). Basic alumina was
102 obtained from Aldrich (Brockmann I, standard grade, Milwaukee, Wisconsin, USA). Florisil
103 was obtained from Riedel-de Haën (60–100 mesh ASTM, Seelze, Germany).

104 PCBs, PCDDs, and PCDFs were analyzed by the POP laboratory of the Research Center
105 for Eco-environmental Sciences, Chinese Academy of Sciences; all concentrations were
106 corrected for lipid weight. Twenty-five PCB congeners, including 12 dioxin-like congeners,
107 were quantified with an isotope dilution method using high-resolution gas chromatography
108 coupled with high-resolution mass spectrometry (HRGC/HRMS). Total organic carbon (TOC)
109 concentration was analyzed on a TOC Analyzer (O.I Analyzer, College Station, Texas, USA).
110 A 0.1 g sample was weighed and loaded into the combustion cup, which was packed with

111 quartz wool. Prior to combustion, the samples were wetted with 5% phosphoric acid and
112 heated to 250°C for 1 min to purge inorganic carbon. The signal was detected by
113 non-dispersed infrared (NDIR) detection when flashed at 900 °C for 6 min in the combustion
114 chamber. Calibration standard solutions, ¹³C₁₂-labeled surrogate standards, and ¹³C₁₂-labeled
115 injection standards were purchased from Wellington Laboratories (Guelph, Canada).

116 Quantification of 17 PCDD and PCDF homologues was done by HRGC/HRMS on an
117 Agilent 6890 gas chromatograph coupled with an Autospec Ultima mass spectrometer
118 (Waters Micromass, Manchester, UK) operating in EI mode at 35 eV; the trap current was
119 600 Å. The GC was equipped with a CTC PAL autosampler. One or two microlitre samples
120 were injected in splitless mode (splitless time, 2 min for PCDD/Fs) in a DB-5MS fused silica
121 capillary column (60 m for PCDD/Fs and PCBs) with helium as carrier gas at a constant flow
122 rate of 1.2 ml/min. The oven temperature programs were as follows: for PCDD/Fs, start
123 150 °C held for 3 min, 150-230 °C at 20 °C min⁻¹ held for 18 min, 230-235 °C at 5 °C min⁻¹
124 held for 10 min, 235-320 °C at 4°C min⁻¹ held for 3 min; for PCBs, start 120 °C held for 1
125 min, 120-150 °C at 30 °C min⁻¹, 150-300 °C at 2.5°C min⁻¹ held for 1 min.

126 *Statistical Analysis*

127 All statistical analyses were done using the SPSS 20.0 software (IBM SPSS Statistics,
128 IBM Corp.,USA Inc.); the significance level was set at $P < \alpha = 0.05$. Amounts of atmospheric
129 heavy metals deposition from FNNR, SWARC, and Xi'an City were compared using
130 one-way ANOVA followed by Tukey post-hoc tests. Comparisons of heavy metals
131 concentrations in soils were done using *t*-tests. Because PCCD, PCDF, and PCB congeners

132 differ in toxicity, toxic equivalency factors (set by the World Health Organization), were used
133 to calculate a single toxic equivalent (WHO-TEQ) for each sample (Van et al. 2006).

134 **Results**

135 The annual average rate (2013-2014) of atmospheric deposition of dust was 199 ± 6.50
136 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in Xi'an city, $115 \pm 9.84 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ at SWARC, but only $49 \pm 6.79 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ at
137 FNNR. Deposition rates of all assayed heavy metals were significantly lower at FNNR than
138 at SWARC (Fig. 1), and all but As were significant lower at SWARC than at Xi'an. In
139 parallel, concentrations of all assayed heavy metals except for As and Zn in soils around
140 SWARC were significantly higher than in soils around FNNR (Fig. 2). Concentrations of Cd,
141 Pb, Zn and Mn at both SWARC and FNNR exceeded their soil background criteria (CNEMC
142 2000), whereas concentrations of Hg exceeded its soil background criterion only at SWARC
143 (Fig. 2). There were significant positive correlations in the concentrations of these metals in
144 deposited dust between Xi'an and SWARC ($r = 0.98$), and between Xi'an and FNNR (r
145 $=0.87$).

146 Deposition rates of dioxin and dioxin-like compounds (PCDDs and PCDFs) and PCBs
147 were highest in Xi'an, intermediate at SWARC, and lowest at FNNR (Fig. 3). Seventeen
148 congeners of PCDD/Fs and 12 of PCBs were detected in atmospheric deposition of PM
149 (Table 1). The most prevalent PCDD/Fs were 1,2,3,4,6,7,8-HeptoCDF, OctaCDF and
150 1,2,3,4,6,7,8-HeptaCDD, whereas the most prevalent PCBs were 3,3',4,4'-TetraCB,
151 2,3,3',4,4'-PentaCB, 2,3',4,4',5-PentaCB. The WHO-TEQ for PCDD/Fs and PCBs (Fig. 3c, 3d)
152 paralleled trends in atmospheric deposition rates of total PCDD/Fs and PCBs (Figs. 3a, 3b).

153 **Discussion**

154 The Qinling Mountain region is home to a number of threatened and endangered species,
155 including the golden monkey, golden takin, crested ibis, and the Qinling subspecies of the
156 giant panda. The Shaanxi Wild Animal Research Center, which focuses on *ex situ*
157 conservation of these species, is on the north slope of the Qinling Mountains and near Xi'an
158 city. Intense "haze-fog" events have taken place in this region many times in recent years,
159 and air pollution has become one of the important environmental issues in Xi'an. We
160 explored possible relationships between atmospheric deposition of heavy metals and POPs in
161 light of the previously documented exposure to all of these toxins in the diet of pandas (Chen
162 et al. *in press*) and to some heavy metals in captive monkeys at SWARC (Liu et al. 2015).

163 The high annual deposition rate of metal- and pollutant-laden dust at Xi'an and SWARC
164 originates from coal combustion; the transport of sand from deserts during droughts and from
165 bare soil surfaces in the surrounding areas; heavy traffic; and a large number of on-going
166 construction sites in the cities. The elevated levels of metals in deposition parallels that found
167 in bamboo fed to captive pandas at SWARC (Chen et al. *in press*) and far exceeds that found
168 in both deposition (Fig. 1–2) at and bamboo eaten by pandas in the wild (at FNNR) (Chen et
169 al. *in press*). Correlations in the concentrations of metals between Xi'an city and either
170 SWARC or FNNR suggest a source for these metals in the industrial activity and traffic in
171 Xi'an (Dun and Tan 2013, Ha et al. 2014), upwind from both SWARC and FNNR. At high
172 concentrations, these metals all have serious health effects (e.g., Rodier 1955, Friberg et al.
173 1985, Buchet and Lauwerys 1989, Winge and Mehra 1990, Rowbotham et al. 2000, Falcón et
174 al. 2003, Doreswamy et al. 2004), and ten serious events of heavy metal (Hg, Cr, Cd, Pb and

175 As) contamination in China have taken place in the past decade with significant public health
176 impacts (Lu et al. 2015).

177 In parallel, deposition rates of dioxin and dioxin-like compounds (PCDDs and PCDFs)
178 and polychlorinated biphenyls (PCBs) were highest in Xi'an, intermediate at SWARC, and
179 lowest at FNNR (Fig. 3). Like heavy metals, PCDDs and PCDFs are by-products of
180 combustion and industrial processes (Fiedler et al. 2007); these persistent organic pollutants
181 are known human carcinogens and endocrine disruptors (Mai et al. 2005, van den Berg et al.
182 2006, Imamura et al. 2007). In contrast, PCBs were once used widely as non-flammable
183 insulators and heat-exchange fluids (De Voogt et al. 1990), but their production ceased in
184 1974. Nonetheless, their long-term and continuing persistence in the environment and in
185 tissues of living organisms has been associated with reduction in reproductive success, birth
186 defects, and behavioral changes (Mai et al. 2005, Imamura et al. 2007).

187 The most prevalent congeners of PCDD/Fs recovered in samples of atmospheric
188 deposition were 1,2,3,4,6,7,8-HeptoCDF, OctaCDF and 1,2,3,4,6,7,8-HeptaCDD, whereas the
189 most prevalent PCBs were 3,3',4,4'-TetraCB, 2,3,3',4,4'-PentaCB, 2,3',4,4',5-PentaCB (Table
190 1). Total Concentrations of PCDD/Fs were higher at Xi'an than SWARC. Together, these data
191 indicated that the main toxic organic chemicals deposition at SWARC originated from Xi'an.

192 Atmospheric deposition of pollutants in China, including in and around Xi'an, has been
193 increasing rapidly (Cao et al. 2011). Deposition of heavy metals and POPs has resulted in
194 high concentrations of these toxins in soils, well in excess of established soil background
195 criteria. POPs and heavy metals can be inhaled directly by pandas or taken up by bamboo and
196 subsequently bioaccumulate in pandas. Our results suggest that urban and industrial areas are

197 the main sources of these environmental toxins, and pandas in captive breeding centers near
198 cities are at greater risk than pandas in natural reserves further from urban areas and
199 industrial centers. Rapid action to improve atmospheric conditions, including efforts to
200 decrease automobile emissions, reduce coal usage, and improve urban efficiency should
201 parallel efforts to relocate pandas from urban-based captive breeding centers to
202 environmentally cleaner areas.

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205 **Author's contributions**

206 Yi-ping Chen conceived the study and wrote the initial draft. Qiang Liu and Ying-juan Zheng
207 performed the experiments, Yi Song performed statistical analysis, Zhi-sheng An contributed
208 significantly to discussion, Qing-yi Ma performed sample collection, Aaron M. Ellison
209 discussed results and their interpretation, and edited the manuscript.

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295 Table 1. Concentrations of PCDD/F and PCB congeners in atmospheric deposition at the
 296 different sites (FNNR, SWARC and Xi'an City). Data are from four pooled samples
 297 from FNNR and Xi'an city, and three pooled samples from SWARC.

POP	Congeners (ng·m ⁻² ·y ⁻¹)	FNNR	SWARC	Xi'an city
	2,3,7,8-TetraCDF	0.04	0.23	0.71
	1,2,3,7,8-PentaCDF;	0.07	0.37	0.66
	2,3,4,7,8-PentaCDF;	0.05	0.40	0.64
	1,2,3,4,7,8-HexaCDF	0.11	0.70	1.21
	1,2,3,6,7,8-HexaCDF	0.10	0.71	1.06
	2,3,4,6,7,8-HexaCDF;	0.13	0.73	1.21
	1,2,3,7,8,9-HexaCDF	0.03	0.13	0.26
PCDD/Fs	1,2,3,4,6,7,8-HeptoCDF	0.46	3.32	3.95
	1,2,3,4,7,8,9-HeptaCDF	0.10	0.37	0.45
	OctaCDF	0.39	3.48	4.32
	2,3,7,8-TetraCDD	0.01	0.03	0.05
	1,2,3,7,8-PentaCDD;	0.03	0.05	0.08
	1,2,3,4,7,8-HexaCDD	0.02	0.14	0.26
	1,2,3,6,7,8-HexaCDD	0.05	0.18	0.22
	1,2,3,7,8,9-HexaCDD	0.05	0.15	0.27

	1,2,3,4,6,7,8-HeptaCDD	0.80	1.38	2.51
	OctaCDD	0.48	5.68	10.30
	3,3',4,4'-TetraCB	0.24	1.13	6.38
	3,4,4',5-TetraCB	0.04	0.15	0.72
	3,3',4,4',5-PentaCB	0.06	0.27	1.26
	3,3',4,4',5,5'-HexaCB	0.03	0.08	0.27
	2,3,3',4,4'-PentaCB	0.21	0.75	5.32
	2,3,4,4',5-PentaCB	0.08	0.17	0.73
PCBs	2,3',4,4',5-PentaCB	0.05	1.79	9.31
	2',3,4,4',5-PentaCB	0.16	0.11	0.29
	2,3,3',4,4',5-HexaCB	0.17	0.32	1.30
	2,3,3',4,4',5'-HexaCB	0.03	0.15	0.39
	2,3',4,4',5,5'-HexaCB	0.06	0.07	0.66
	2,3,3',4,4',5,5'-HeptaCB	0.07	0.14	0.50

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301 **Figure legends**

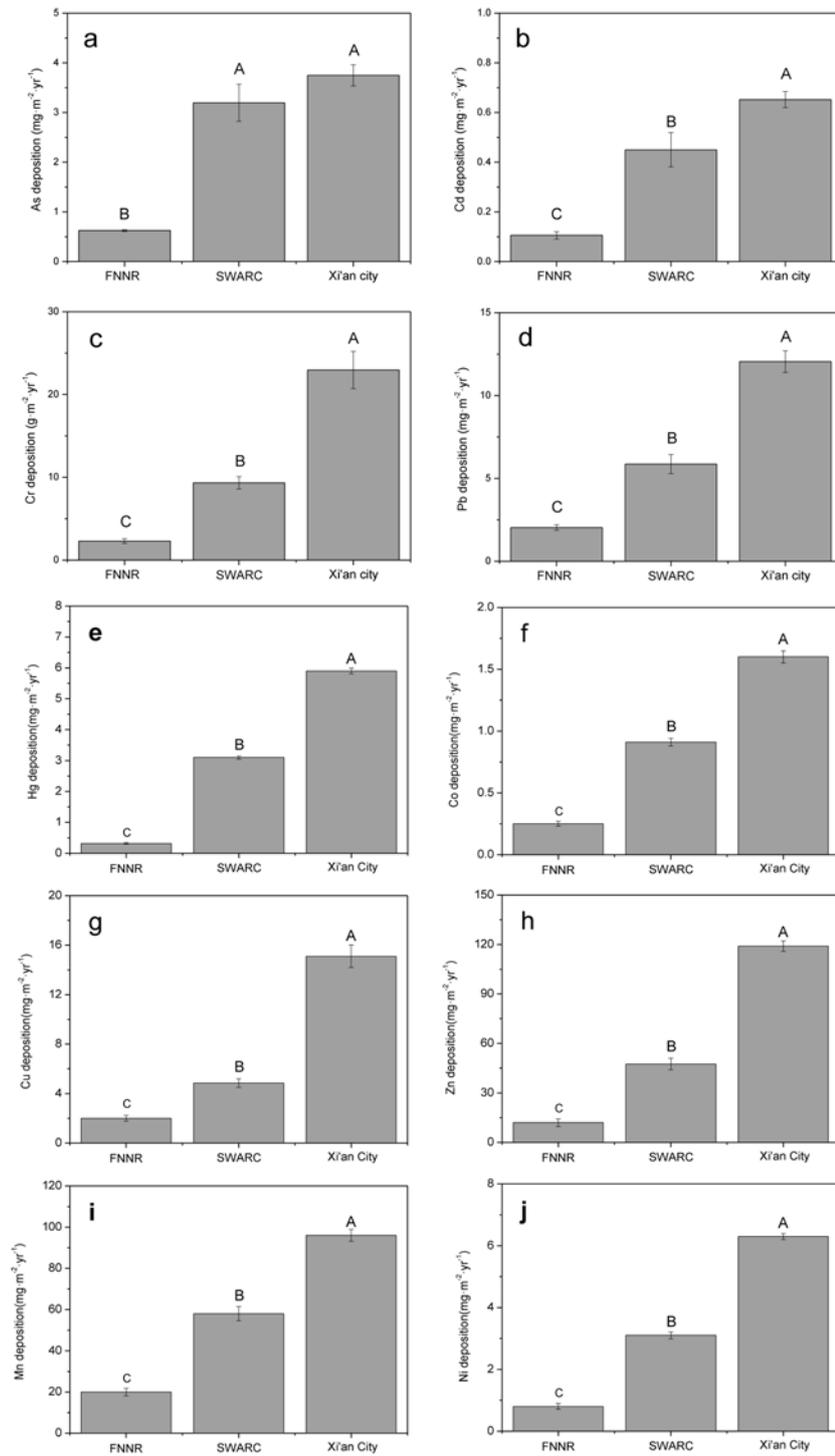
302 Figure 1. Mean (± 1 SE of the mean) amounts of atmospheric deposition of heavy metals: As (a), Cd
303 (b), Cr (c), Pb (d), Hg (e), Co (f), Cu (g), Zn (h), Mn (i) and Ni (j) at the three studied sites [FNNR (n=4),
304 SWARC (n=3) and Xi'an city (n=4)] over a one-year period. Differences among means at the three sites
305 were compared using one-way ANOVA; different letters denote significant differences ($P < 0.05$; Tukey
306 post-hoc test).

307 Figure 2. Comparison of toxic metals concentrations in soils at the southern (FNNR) and northern
308 (SWARC) slopes of the Qinling Mountains. Bars illustrate mean (± 1 SE of the mean) amounts of soil As
309 (a), Cd (b), Cr (c), Pb (d), Hg (e), Co (f), Cu (g), Zn (h), Mn (i) and Ni (j) at FNNR (n=4) and SWARC
310 (n=3)]. A dashed red line in each panel indicates the soil background criteria value for polluted soils
311 (CNEMC, 1990). Different letters denote significant differences ($P < 0.05$; *t*-test).

312 Figure 3. Total atmospheric deposition of PCDD/Fs (a) and PCBs (b), and the WHO-TEQs of
313 PCDD/Fs (c) and PCBs (d) at the three different sites (FNNR, SWARC and Xi'an city) over a one-year
314 period. Values are from four pooled samples for FNNR and Xi'an city, and three pooled samples for
315 SWARC. Data for individual congeners of PCBs, PCDDs, and PCDFs are given in Table 1.

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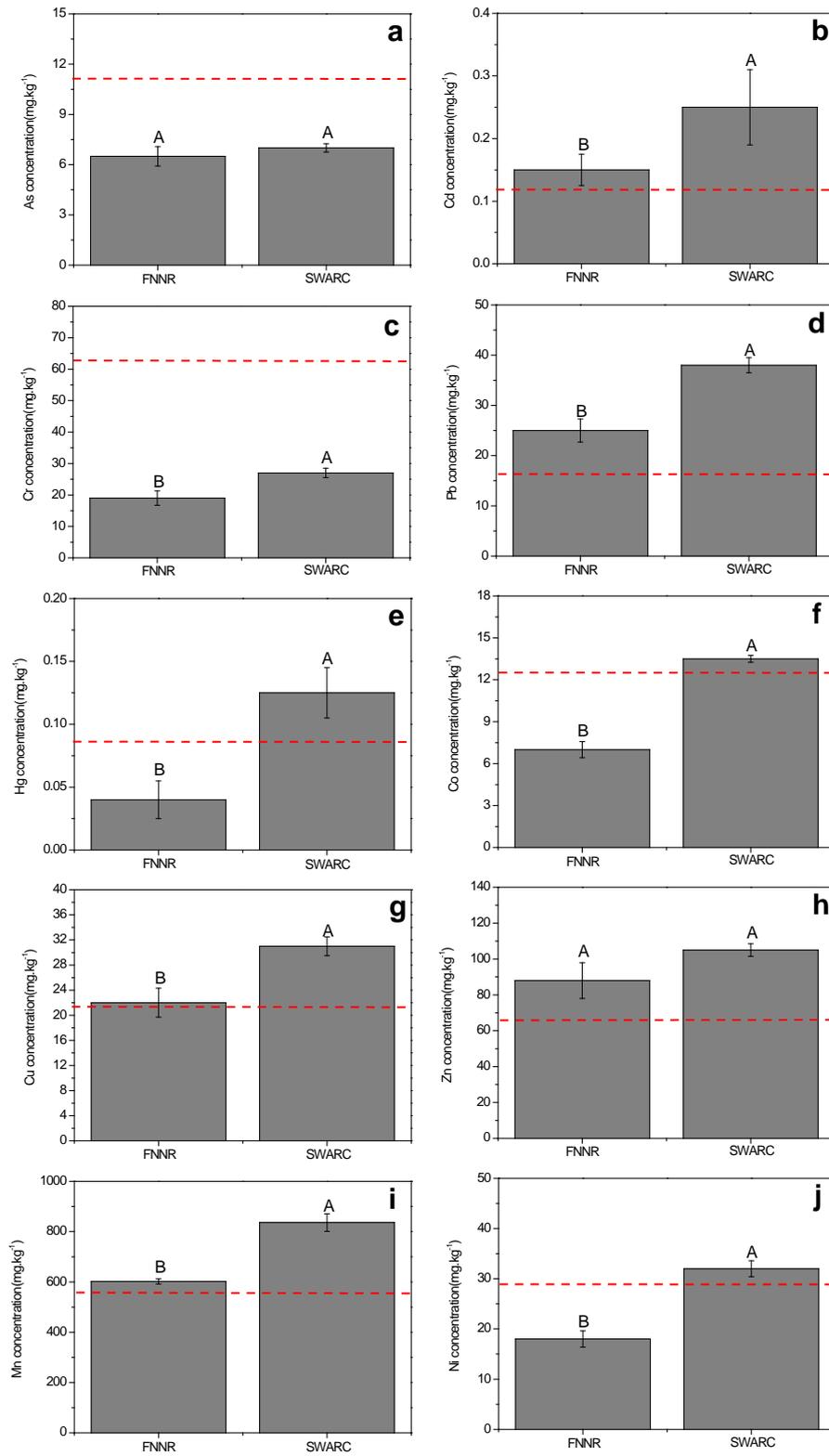
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Figure 1

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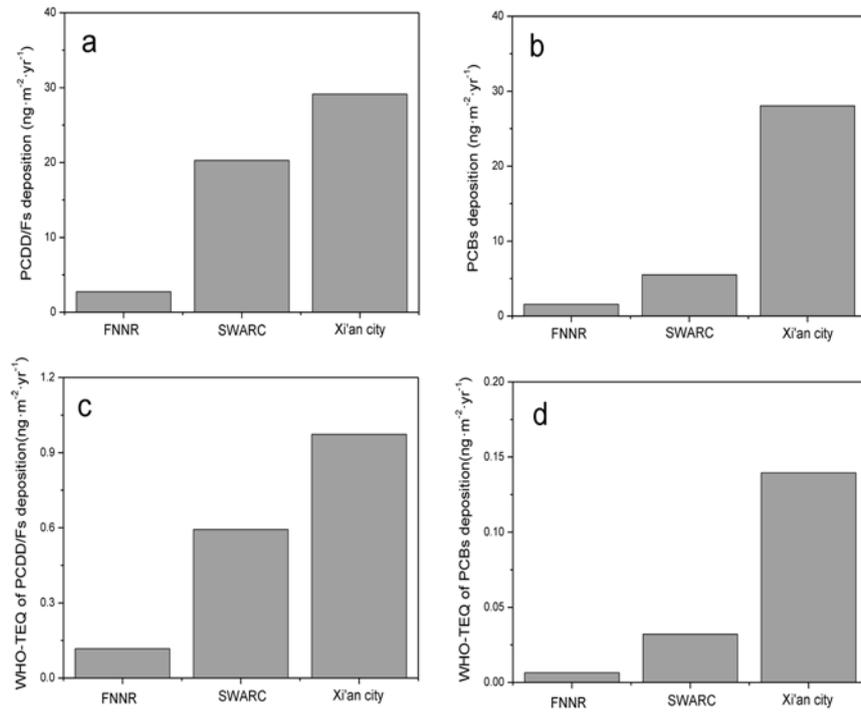
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Figure 2

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Figure 3