

1 Global Atmospheric Transport and Source-Receptor Relationships 2 for Arsenic

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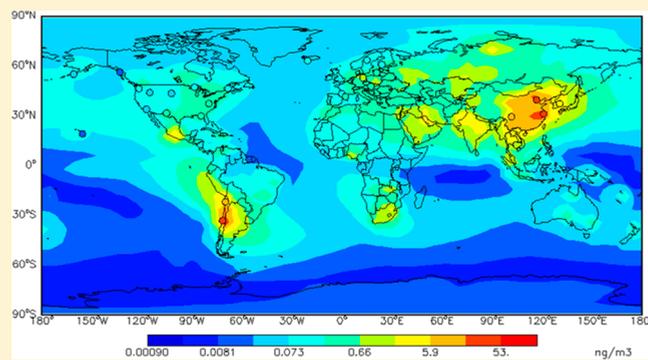
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9 **S** Supporting Information

10 **ABSTRACT:** Arsenic and many of its compounds are toxic
11 pollutants in the global environment. They can be transported
12 long distances in the atmosphere before depositing to the
13 surface, but the global source-receptor relationships between
14 various regions have not yet been assessed. We develop the
15 first global model for atmospheric arsenic to better understand
16 and quantify its intercontinental transport. Our model
17 reproduces the observed arsenic concentrations in surface air
18 over various sites around the world. Arsenic emissions from
19 Asia and South America are found to be the dominant sources
20 for atmospheric arsenic in the Northern and Southern
21 Hemispheres, respectively. Asian emissions are found to
22 contribute 39% and 38% of the total arsenic deposition over
23 the Arctic and Northern America, respectively. Another 14% of the arsenic deposition to the Arctic region is attributed to
24 European emissions. Our results indicate that the reduction of anthropogenic arsenic emissions in Asia and South America can
25 significantly reduce arsenic pollution not only locally but also globally.



26 ■ INTRODUCTION

27 Arsenic is a ubiquitous metalloid in the global environment.
28 Elemental arsenic and many of its compounds have high
29 toxicity and have been listed by the International Agency for
30 Research on Cancer (IARC) as Group 1 carcinogens.¹ There
31 have been many studies showing increased lung cancer risk for
32 people living or working near arsenic-emitting industrial plants
33 such as smelting facilities.^{2–6} These arsenic compounds, even at
34 relatively low exposure levels, can also cause many other
35 adverse health effects related to the brain and nervous system,
36 digestive system, and skin.^{7–9}

37 There have been increasing concerns about arsenic pollution
38 in the environment. In 2012, Consumer Reports¹⁰ conducted
39 tests on more than 200 samples of rice products in the United
40 States and found that many of them (including some organic
41 products and infant rice cereals) contain arsenic at “worrisome
42 levels”. Since 2013, the European Union Directive has set an air
43 quality standard for arsenic concentration in ambient air, which
44 is 6 ng m⁻³ for annual mean concentrations. Besides direct
45 inhalation, the arsenic concentration in ambient air can also
46 affect the human exposure to arsenic through atmospheric
47 deposition, which can enhance the arsenic levels in food
48 (through arsenic uptake by crops and vegetation) or drinking
49 water. Direct atmospheric deposition of arsenic was found to be
50 the dominant transport pathway for arsenic from a factory to

the leafy vegetables grown nearby, while arsenic in the root
crops originated from both the soil and the atmosphere.¹¹
Therefore, the atmospheric concentrations and deposition of
arsenic need to be accounted for to fully understand and
evaluate the human exposure risk to arsenic in the environ-
ment.^{12,13}

There are both anthropogenic and natural sources for
atmospheric arsenic. Metal (copper, zinc, and lead) smelting
and coal combustion are the major anthropogenic arsenic
sources,^{14–16} with copper smelting being the most important
single source based on arsenic emissions.^{15–17} Additional minor
anthropogenic sources include the application of herbicide,
wood preservation, and waste incineration.¹⁶ Natural sources
for arsenic in the atmosphere include volcanic emissions, wind
erosion of soil, and biological activities, with volcanic emissions
being the most important source.^{14,17,18} There are large
uncertainties associated with the estimation of arsenic
emissions to the atmosphere, but according to available
global-scale estimates of emissions, the global anthropogenic
sources are much larger than natural sources.^{14,17,19,20}

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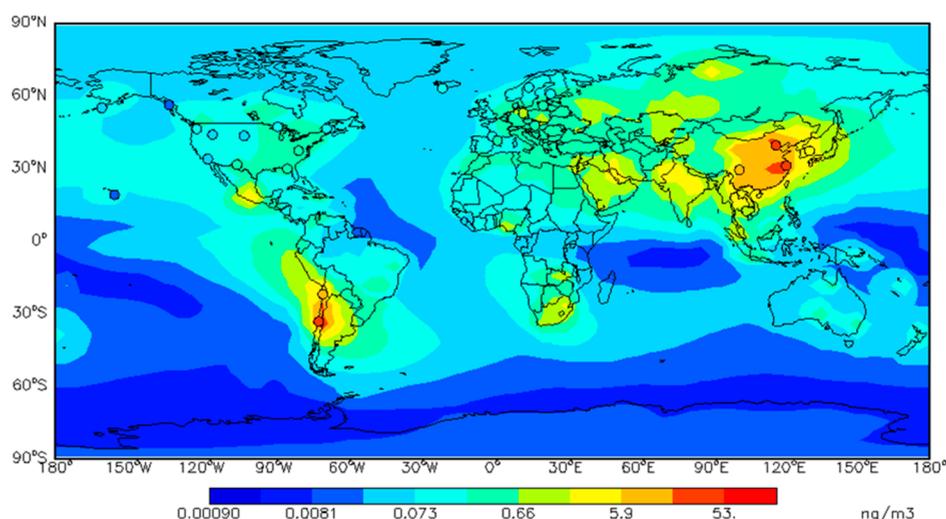


Figure 1. Arsenic concentrations in surface air. Model-simulated annual (for year 2005) mean arsenic concentrations in ambient air (background) compared with measurement data at various stations (circles) around the world. Refer to Table 1 for specific values.

71 There are large spatial variations for the atmospheric
72 concentrations of arsenic, which can vary by several orders of
73 magnitude (from less than 0.1 ng m^{-3} in remote sites to more
74 than 10 ng m^{-3} in urban and industrial areas), presumably
75 reflecting the impacts from anthropogenic activities. The
76 surface arsenic concentrations were reported to be less than
77 0.041 ng m^{-3} in the south polar atmosphere.²¹ In China and
78 Chile, the surface arsenic concentrations were found to reach
79 15 ng m^{-3} or higher.^{22,23} The typical residence time of arsenic
80 in the atmosphere is several days,^{17,24,25} making its long-range
81 transport possible. This implies that arsenic emissions from one
82 region can significantly affect other regions downwind.
83 However, the global source-receptor relationship between
84 various regions has not been quantified so far, in contrast to
85 the extensively studied source-receptor relationship for other
86 anthropogenic pollutants and dust.²⁶

87 Some previous studies have shown that the regional transport
88 of atmospheric arsenic is evident. Using a trajectory model,
89 Pacyna et al.²⁷ studied the atmospheric transport of arsenic and
90 several other trace elements from European source regions to
91 Norway and reported that the performance of the model is
92 most sensitive to changes in emissions and deposition velocities
93 of these elements. Akeredolu et al.²⁸ investigated the long-range
94 transport of arsenic and other anthropogenic heavy metals into
95 the Arctic region for the period of July 1979–June 1980 and
96 found that the model results agreed with observations within a
97 factor of 2–3. Gidhagen et al.²³ studied the regional effects
98 from smelter emissions of arsenic in Chile and demonstrated
99 that anthropogenic emissions are the dominant sources for
100 arsenic in the ambient air. A more recent study²⁹ simulating the
101 atmospheric concentrations of some heavy metals over Europe
102 pointed out that the limited data in emissions is an important
103 factor affecting the model performance. Another recent study³⁰
104 reported that the model results significantly underestimate the
105 measured atmospheric concentrations of arsenic and other
106 heavy metals in the United Kingdom, but it did not include any
107 sources outside of the European region. On the basis of the
108 significant arsenic enrichment in snowpack samples from the
109 Antarctic Plateau, Hong et al.³¹ proposed that the emissions of
110 trace elements (including arsenic) from nonferrous metal
111 smelting and fossil fuel combustion processes in South
112 America, especially in Chile, are the most likely sources. The

seemingly pristine polar regions are particularly vulnerable to
global change, and the long-range transport of air pollutants
including arsenic can have very important implications for the
polar environment.³²

In this study, we develop the first-ever global gridded
emission inventory for arsenic and implement it in a global
atmospheric chemical transport model (GEOS-Chem) to
examine the global transport and source-receptor relationships
for arsenic.

MATERIALS AND METHODS

We developed a global arsenic model based on the GEOS-
Chem chemical transport model (<http://geos-chem.org>) v9-01-
01. The GEOS-Chem model has been applied to a wide range
of research related to atmospheric trace gases, aerosols, and
mercury.^{33–35} It is driven by assimilated meteorological fields
from the NASA Global Modeling and Assimilation Office
(GMAO). The GEOS-4 meteorological data were used for all
of the model simulations except for the 2011 simulation
(specifically for comparison to measurement data from the
MBO site), which was driven by GEOS-5 data (because GEOS-
4 data is not available).

Available data on arsenic emissions for various regions
around the world were compiled, processed, and gridded to 4°
latitude by 5° longitude for the model with a base year of 2005
(unless otherwise specified). For Chile, the major arsenic
source region in the Southern Hemisphere, we followed
Gidhagen et al.²³ The Australian emissions were assessed based
on Australia's National Pollutant Inventory (NPI) ([http://
www.npi.gov.au/resource/arsenic-and-compounds-0](http://www.npi.gov.au/resource/arsenic-and-compounds-0)). Arsenic
emissions in the United States were assessed following the
U.S. EPA NATA (National-Scale Air Toxics Assessment)
inventory for 1999 ([http://archive.epa.gov/airtoxics/nata1999/
web/html/index.html](http://archive.epa.gov/airtoxics/nata1999/web/html/index.html)). The Canadian emissions assessments
were based on Environment Canada's National Pollutant
Release Inventory for 2000 (NPRI) ([http://www.ec.gc.ca/
inrp-npri](http://www.ec.gc.ca/inrp-npri)). The European emissions of arsenic were assessed
following the ESPREME inventory ([http://espreme.ier.uni-
stuttgart.de](http://espreme.ier.uni-stuttgart.de)).

There is no national emission inventory for arsenic emissions
from metal smelting available for China, so we developed a new
inventory for China in this study. It was derived using the

Table 1. Model-Simulated Annual Average Surface Atmospheric Arsenic Concentrations Compared with Observations

site	model result (ng m ⁻³)	observations (ng m ⁻³)	year of observations	source/reference for observational data ^a
Storhofdi, Iceland (63.4°N, 20.3°W)	0.07	0.18	2005	EMEP
Peyrusse Vieille, France (43.6°N, 0.2°E)	0.14	0.20	2005	EMEP
Neuglobsow, Germany (53.1°N, 13.0°E)	0.47	0.86	2005	EMEP
Topoliniky, Slovakia (48.0°N, 17.8°E)	0.84	0.44	2005	EMEP
Montseny, Spain (41.8°N, 2.4°E)	0.20	0.29	2005	EMEP
Bredkalen, Sweden (63.8°N, 15.3°E)	0.09	0.10	2002	EMEP
Pallas, Finland (61.0°N, 24.2°E)	0.27	0.15	2005	EMEP
Rucava, Latvia (56.2°N, 21.1°E)	0.27	0.38	2005	EMEP
Florida, United States (30.1°N, 84.2°W)	0.48	0.46	2005	IMPROVE
Virginia, United States (37.6°N, 79.5°W)	0.63	0.44	2005	IMPROVE
Maine, United States (46.7°N, 68.0°W)	0.25	0.16	2005	IMPROVE
Michigan, United States (47.5°N, 88.1°W)	0.19	0.15	2004	IMPROVE
South Dakota, United States (43.7°N, 101.9°W)	0.14	0.05	2005	IMPROVE
Texas, United States (31.8°N, 104.8°W)	0.23	0.23	2005	IMPROVE
Washington, United States (46.6°N, 121.4°W)	0.18	0.12	2005	IMPROVE
California, United States (34.2°N, 116.9°W)	0.18	0.07	2005	IMPROVE
Idaho, United States (44.2°N, 114.9°W)	0.19	0.03	2005	IMPROVE
Hawaii, United States (19.4°N, 155.3°W)	0.10	0.01	2005	IMPROVE
Alaska1, United States (56.5°N, 132.8°W)	0.07	0.02	2005	IMPROVE
Alaska2, United States (55.3°N, 160.5°W)	0.08	0.04	2005	IMPROVE
Beijing, China (39.8°N, 117.0°E)	22	18	2005	22
Shanghai, China (31.4°N, 121.3°E)	26	27	2004–2005	58
Sichuan, China (29.6°N, 102.0°E)	4.2	6.1	2006	59
Ulleung Island, S. Korea (37.5°N, 130.9°E)	3.6	3.0	2003–2008	60
Quillota, Chile (32.9°S, 71.2°W)	30	31	1999–2000	23
Quillagua, Chile (21.6°S, 69.5°W)	4.4	6.5	1999–2000	23

^aEMEP: European Monitoring and Evaluation Programme. IMPROVE: Interagency Monitoring of Protected Visual Environments.

154 production data of nonferrous metals from the *Yearbook of*
 155 *Nonferrous Metals Industry of China 2005*³⁶ and the correspond-
 156 ing arsenic emission factors from Chilvers and Peterson.¹⁶
 157 Arsenic emissions from coal-fired power plants in China
 158 followed Tian et al.³⁷ Initial model evaluation with our a priori
 159 arsenic emission inventory developed for China showed a
 160 systematic low bias for model-simulated arsenic concentrations
 161 over China. A likely reason for this low bias is that the arsenic
 162 emission factors¹⁶ from metal smelting used in this study might
 163 be too low for China. Thus, we scaled up the arsenic emissions
 164 due to metal smelting in China by a factor of 1.5 and then
 165 found very good agreement between model results and
 166 observational data (Figure 1 and Table 1).

167 Anthropogenic arsenic emissions from other countries
 168 around the world were estimated by taking advantage of the
 169 available SO₂ emission inventories from the Emissions
 170 Database for Global Atmospheric Research (EDGAR; [http://](http://edgar.jrc.ec.europa.eu)
 171 edgar.jrc.ec.europa.eu). We followed EDGAR version 3³⁸ for
 172 SO₂ emissions in 2005 and applied a constant value for the As/
 173 S emission ratio^{39,40} to derive the arsenic emissions from other
 174 countries not previously mentioned. The As/S emission ratio
 175 assumed the median value of 5.63×10^{-4} (standard deviation
 176 3.92×10^{-4}) g As/g S from literature studies.^{39,40} Due to the
 177 limited data available on the correlations of As/S emissions,
 178 there is significant uncertainty associated with the emission
 179 ratio we used.

180 We also estimated arsenic emissions from volcanic activities
 181 based on the As/S correlations. We followed the global volcanic
 182 SO₂ emission inventory from Andres and Kasgnoc,⁴¹ and the
 183 volcanic arsenic emissions were calculated using the ratio of
 184 1.59×10^{-4} g As/g S, which is the median value of As/S flux

185 ratios found for volcanic emissions around the world (standard
 186 deviation = 1.0×10^{-3} g As/g S).^{42–45}

187 Because most (90% or more) atmospheric arsenic sorbs onto
 188 aerosols,⁴⁶ particularly fine-mode (i.e., PM_{2.5}) aerosols,^{47,48} we
 189 treated the deposition processes of arsenic similarly as PM_{2.5}
 190 aerosols. The wet deposition of arsenic followed the scheme
 191 used by Liu et al.,⁴⁹ which considers the scavenging from
 192 convective updrafts, rainout from convective anvils, and rainout
 193 and washout from large-scale precipitation. The dry deposition
 194 followed a resistance-in-series scheme,⁵⁰ with the surface
 195 resistances following the work of Zhang et al.⁵¹ The wet
 196 deposition in GEOS-Chem with both GEOS-4 and GEOS-5
 197 meteorological fields has been previously evaluated.^{52,53}

198 For model evaluation, we focused on atmospheric arsenic
 199 measurement data from nonurban sites given the coarse spatial
 200 resolution (4° latitude × 5° longitude) of the global model. We
 201 collected available measurement data from various regions
 202 around the world in the literature and compiled them in Table
 203 1. Except for the time series data from the Mount Bachelor
 204 Observatory, data for sites in the United States and Europe
 205 were from the Interagency Monitoring of Protected Visual
 206 Environments (IMPROVE)⁵⁴ and the European Monitoring
 207 and Evaluation Programme (EMEP)⁵⁵ network, respectively.
 208 The MBO site has been used for over a decade to examine the
 209 long-range transport of aerosol- and gas-phase pollutants in
 210 baseline air arriving to North America.^{56,57} Data from the MBO
 211 were obtained using a rotating drum impactor with a 3 h time
 212 resolution and with synchrotron X-ray fluorescence analysis.⁵⁷
 213 It appears that the measurement data for atmospheric arsenic
 214 deposition are extremely limited, so we are not able to evaluate
 215 the model performance on arsenic deposition in this study.

Table 2. Sources and Average Atmospheric Lifetimes of Arsenic for Various Regions^a

	global	East Asia	Europe	North America	South America	other regions
anthropogenic sources (Gg yr ⁻¹)	28.6	15.5	0.7	0.6	4.3	7.5
natural sources (Gg yr ⁻¹)	2.1	0.3	0.2	0.04	0.1	1.5
lifetime (days) ^b	4.5	4.1	4.1	5.4	4.5	not estimated

^aThe geographical regions are defined as East Asia (20–56°N, 92.5–152.5°E); Europe (36–72°N, 12.5°W–62.5°E); North America (24–60°N, 132.5–57.5°W); and South America (40–4°S, 82.5–57.5°W). ^bAtmospheric lifetime of arsenic against deposition (dry deposition plus wet deposition).

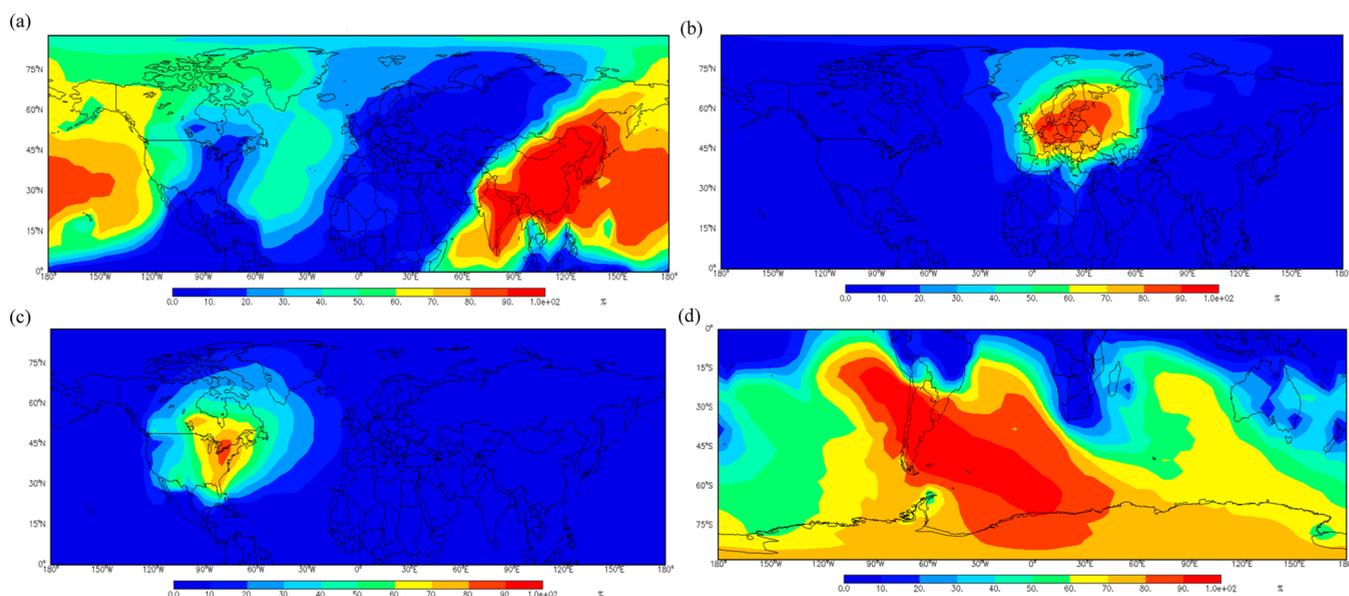


Figure 2. Source attribution for arsenic deposition. Shown as percentage of total atmospheric arsenic deposition attributable to emissions from (a) Asia; (b) Europe; (c) North America; and (d) South America. Source regions are indicated as rectangular boxes in Figure S1.

216 ■ RESULTS AND DISCUSSION

217 The global arsenic emissions are calculated to be 30.7 Gg yr⁻¹
 218 with the breakdown for major source regions (15.8 and 4.4 Gg
 219 yr⁻¹ in East Asia and South America, respectively), as
 220 summarized in Table 2. Our global total arsenic emission is
 221 comparable to that in previous studies by Walsh et al.¹⁷ and
 222 Nriagu,¹⁸ who both estimated the global total arsenic emissions
 223 to be 31 Gg yr⁻¹. In contrast, Chilvers and Peterson¹⁶ estimated
 224 a very large natural source for arsenic, leading to a much higher
 225 global total arsenic emission of 73.5 Gg yr⁻¹. The model-
 226 simulated annual mean concentrations of atmospheric arsenic
 227 are compared with available measurement data in Figure 1 and
 228 Table 1. We find very good agreement between model results
 229 and observations with a high correlation ($r^2 = 0.98$, slope of
 230 regression line = (modeled results)/(observed results) = 1.0;
 231 mean normalized bias = 89%). However, significant biases are
 232 identified for a few stations located in remote areas, such as
 233 Alaska and Hawaii, where the model strongly overestimates the
 234 atmospheric arsenic concentrations (Table 1). This likely
 235 reflects the uncertainties associated with the natural emissions
 236 of arsenic as well as the deposition parameters used in the
 237 model.

238 The global total wet and dry deposition of arsenic was
 239 calculated to be 25.4 and 5.3 Gg yr⁻¹, respectively. The global
 240 total atmospheric burden of arsenic is calculated to be 377 Mg,
 241 leading to a global average atmospheric lifetime for arsenic of
 242 4.5 days. The calculated atmospheric arsenic lifetimes against
 243 deposition range from 4.1 to 5.4 days for different regions
 244 around the world (Table 2), which are within the range (2.5–9

days) reported in the literature.^{17,24,25} The variations in arsenic
 245 lifetimes across various regions mainly reflect the differences in
 246 atmospheric deposition (in particular, wet deposition) rates.
 247 Additional factors such as atmospheric transport can also affect
 248 the regional lifetime of atmospheric arsenic.
 249

Figure 1 shows the annual average arsenic concentrations in
 250 ambient air driven by synoptic transport events. High arsenic
 251 concentrations (10 ng m⁻³ or higher) are found over large areas
 252 in eastern China and northern Chile, which are at least 1 order
 253 of magnitude higher than those in the United States and
 254 Europe. Figure 1 also illustrates the outflow of arsenic plumes
 255 from Asia, which are transported over the North Pacific and
 256 North America following the Westerlies. Similarly, the arsenic
 257 plumes from North America are transported across the North
 258 Atlantic toward Europe (Figure 1 and Figure 2c). In the
 259 Southern Hemisphere, the major arsenic source region is Chile.
 260 The arsenic plumes at lower latitudes are transported toward
 261 the tropical Pacific following the trade winds, and those at
 262 higher latitudes are transported toward the Southern Atlantic
 263 following the Westerlies. We further evaluate the model
 264 performance in simulating the daily time series of measured
 265 atmospheric arsenic concentrations at the Mount Bachelor
 266 Observatory (MBO, 44.0° N, 121.7° W), located on the west
 267 coast of the United States (Figure 3). The model reproduces
 268 the temporal variations in arsenic concentrations reasonably
 269 well ($r^2 = 0.35$, slope of regression line = modeled results/
 270 observed results = 1.15, mean normalized bias = 36%).
 271

To better examine the source-receptor relationships between
 272 various regions in terms of arsenic concentration and 273

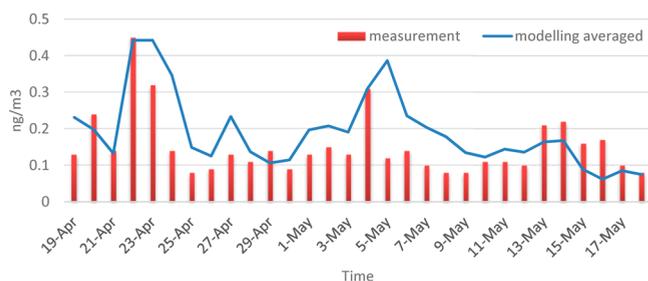


Figure 3. Daily arsenic concentrations in spring 2011. Measured daily average arsenic concentrations at the Mount Bachelor Observatory (MBO, 44.0° N, 121.7° W) compared with model results.

274 deposition, we carried out a suite of sensitivity simulations in
275 which anthropogenic arsenic emissions from a certain region
276 were turned off in the model. For example, we shut off
277 emissions from Asia in the sensitivity-model run and then
278 compared the calculated atmospheric arsenic deposition
279 ($D_{\text{no_Asia}}$) with those from the base run (D_{base}) to derive the
280 percentage contribution of Asian emissions to atmospheric
281 arsenic in the receptor region: $\text{Contribution}_{\text{Asia}} = (D_{\text{base}} -$
282 $D_{\text{no_Asia}}) / D_{\text{base}} \times 100\%$. Figure 2 shows the contribution to total
283 (wet and dry) deposition from each continental-scale source
284 region.

285 Anthropogenic arsenic emissions from Asia are found to
286 make the largest contributions to atmospheric arsenic
287 deposition over the North Pacific Ocean and western North
288 America (Figure 2a). Up to 70% of total atmospheric arsenic
289 concentration and 80% of total arsenic deposition over the
290 western part of North America are attributed to anthropogenic
291 Asian emissions. Significant contributions to the Arctic region
292 (up to 60% for atmospheric concentration and 70% for total
293 arsenic deposition; see footnote in Table 3 for the definition of
294 the Arctic) are calculated for Asian emissions (Figure 2a).

Table 3. Source-Receptor Relationships for Atmospheric Arsenic Concentration (Deposition) between Various Regions^a

		source regions		
		Asia	Europe	North America
receptor regions	Arctic	24.9 (39.2)	14.2 (13.8)	3.9 (4.3)
	Asia	56.3 (58.0)	4.3 (4.9)	0.1 (0.2)
	Europe	6.4 (10.0)	68.6 (60.1)	1.3 (2.0)
	North America	25.7 (38.2)	2.0 (1.1)	55.1 (41.4)
	Western United States	36.0 (48.3)	0.4 (0.4)	45.9 (30.0)
	Eastern United States	8.9 (16.3)	0.2 (0.2)	85.0 (67.7)

^aShown as the percentage contribution to total atmospheric arsenic concentration (deposition) in the receptor region attributable to emissions from the source region. The geographical regions are defined as Arctic (64–90°N, 180°W – 180°E); Asia (8–72°N, 57.5–147.5°E); Europe (32–72°N, 7.5°W – 62.5°E); North America (28–72°N, 127.5–62.5°W); Western United States (28–48°N, 127.5–97.5°W); and Eastern United States (28–48°N, 97.5–67.5°W).

Figure 2b shows the contribution from European anthropogenic arsenic emissions. The European contributions mainly extend northward to the Arctic and eastward over part of Russia. The European emissions are also found to contribute to arsenic deposition over the Mediterranean Sea by up to 60%. Figure 2c shows the contribution from North American anthropogenic arsenic emissions. The eastward transport of the arsenic-laden plumes from North America leads to its large contribution to the arsenic deposition over the North Atlantic Ocean (up to 80% right off the eastern coast of the United States).

The contribution of anthropogenic arsenic emissions from South America is found to dominate over the Southern Hemisphere except for Southern Africa and Australia (Figure 2d). Up to 90% of arsenic deposition over the Antarctic is attributed to emissions from South America, which confirms the hypothesis by Hong et al.³¹

The source-receptor relationships for atmospheric arsenic concentration and deposition between major regions in the Northern Hemisphere are summarized in Table 3. On average, about 39% of the total arsenic deposition over the Arctic region is attributed to Asian anthropogenic emissions, reflecting the strong arsenic emissions from Asia. The European anthropogenic emissions are calculated to contribute almost 14% of the total arsenic deposition to the Arctic. The North American contribution to arsenic in the Arctic (about 4%) is found to be much less than those from Asia or Europe, reflecting both the lower anthropogenic emission strengths and the lower latitudes of the sources. The Asian anthropogenic emissions are found to contribute to the total arsenic deposition in North America by 38%.

The intercontinental transport of arsenic, especially the significant global impacts associated with arsenic emissions from certain source regions as shown by our results, highlights the benefits of international cooperation to reduce arsenic pollution around the world. These source-receptor relationships should be considered by researchers and policymakers in the designing of mitigation strategies for arsenic pollution.

ASSOCIATED CONTENT

Supporting Information

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Figure S1, indicating the source regions used in Figure 2. (PDF)

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K.M.W. and S.W. designed the entire study and wrote the manuscript. K.M.W. developed the arsenic model based on the standard GEOS-Chem model and did all model experiments and analysis of outputs. X.L. assisted the project with literature review and database preparation at the early stage of the project. D.A.J. and K.D.P. provided data of atmospheric arsenic measurements from Mount Bachelor Observatory, Oregon.

354 **Notes**

355 The authors declare no competing financial interest.

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