Vapor isotopic evidence for the worsening of winter air quality by anthropogenic combustion-derived water

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Supplementary Information
SI Materials and Methods

Study site
Xi’an is located in the south-central part of Guanzhong Basin (GZB), a horn-shaped basin, of Shaanxi province (Fig. S1). Many studies have been conducted on the causes and mechanisms of haze formation in the region (1–3).

Isotope measurement of water vapor
We used a Cavity Ring Down Spectroscopy (CRDS) analyzer (model Picarro-
L2130i, Picarro, Inc.) to measure near surface air water vapor hydrogen and oxygen isotope compositions in Xi’an during heating seasons starting from January 1, 2016 to March 15, 2018. In general, heating season in Xi’an starts from 15th November to 15th March of the following year. We placed the analyzer in a room at a constant temperature of 25°C, connected one end of a 2-m long stainless-steel tube with a diameter of 1/8 inch to a vaporizer, extended the other end out of a building, and covered the stainless-steel tube with a heating tape maintained at 60°C to prevent water vapor from condensing in the stainless-steel tube.

We followed a recommended dual mode (4) for measuring water vapor isotope composition. A CTC Analytics autosampler (model HTC-PAL; Leap Technologies, Carrboro, NC, USA) was applied to inject liquid standard samples at different volumes to correct the influence from RH variations and instrumental drifts. The raw measurements were collected at ~1 Hz and were averaged to 1 hour before data filtering and calibration described in detail below in Data Correction. Experiments with the inlet system showed that the transfer time from the inlet to analyzer was less than 30 s and that measurements stabilized within 5 min of a switch in vapor isotope values imposed at the inlet. Thus, after each calibration, we discarded the first 5 minutes of ambient air measurements to ensure that any remaining water vapor was purged out of the system (5).

Isotope compositions of samples are reported using the δ-notion:

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{vsmow}}} - 1 \right) \times 1000 \quad (1)$$

where $R_{\text{sample}}$ and $R_{\text{vsmow}}$ are the isotopic ratios of the sample and of the Vienna Standard Mean Ocean Water (VSMOW), respectively, and the ratios for $HH^{18}O/HH^{16}O$ and $H^{2}H^{16}O/HH^{16}O$ are for $\delta^{18}O$ and $\delta^{2}H$, respectively. The deuterium excess values are computed based on the commonly used definition:
\[ d\text{-excess} = \delta^2H - 8 \times \delta^{18}O \] (2).

Data measured on rain and snow days were excluded.

**Isotope Data Correction**

*Humidity effect:* Humidity-concentration dependence in CRDS-based isotope measurements has been indicated by previous studies (4-6). We therefore determined the humidity-isotope calibration response function (6). The analyzer was programmed to perform self-calibrations by measuring standard using an autosampler to inject liquid standards at different levels of humidity. This was done every 12 hours prior to 1st Oct 2016 (after 10 months measurement, we found that the drift of the standards in 12-hour interval was low, and thus we extended the standards measuring interval) and every 24 hours afterward. Injections were arranged at absolute humidity levels of 2500, 3000, 5000, 8000, 10000, 15000, 20000, 25000, 30000 and 35000 ppmv. Each reference sample was measured continuously for 8 times at one humidity level, and the last 3 times results were used to calculate the average to be recognized as the $\delta$-value at the measured humidity. The humidity correction is the difference between the $\delta$-value at the measurement humidity and the $\delta$-value at a reference value taken at 20000 ppmv humidity. A best fit was obtained with an exponential function for $\delta^{18}O$ and $\delta^2H$ (Fig. S10a and S10b). After each humidity calibration, the first 5 min of ambient air measurements were discarded to ensure that any water vapor used for calibration was purged out of the system. Humidity effects were corrected using:

\[
\delta^{18}O_{\text{humidity corrected}} = \delta^{18}O_{\text{measured}} - (-17.65 \times \exp (-7.89 \times 10^{-4} \times \text{Measured humidity})) \] (3)

\[
\delta^2H_{\text{humidity corrected}} = \delta^2H_{\text{measured}} - \exp (0.91 - 5.73 \times 10^{-5} \times \text{Measured humidity}) \] (4)
where $\delta_{\text{humidity corrected}}$ is the humidity-corrected data for water vapor stable isotope composition; $\delta_{\text{measured}}$ is the measured data before correction; and measured humidity was the corresponding humidity at the time of measurement.

Isotope measurement and calibration used six different liquid water standards that had been calibrated to the VSMOW–GISP scale, two international standards ($\delta^{18}\text{O}=0\%$, $\delta^2\text{H}=0\%$ for VSMOW and $\delta^{18}\text{O}= -24.8\%$, $\delta^2\text{H}= -189.5\%$ for GISP) (Table S5). Protocols (7, 8) for known-standard calibration for CRDS water vapor isotope analyzers were followed. Instrument drifts were corrected by repetitively measuring known standard at regular intervals (9).

**Air Quality and Meteorological Data**

Hourly atmospheric chemical concentration data, such as SO$_2$, NO$_2$, CO, O$_3$, and PM$_{2.5}$, and the meteorological data, such as temperature, RH, and precipitation amount in Xi’an are reported by the China’s Ministry of Ecology and Environment (10, 11) and China Meteorological Administration, respectively, and can be downloaded from the websites of http://www.aqistudy.cn/ and http://www.weather.com.cn/.

**Water vapor sources analyzing**

During our studying period, back trajectory statistical results showed that the air masses in Xi’an mainly transported from the west, which excluded a vapor source from the Pacific Ocean (Fig. S11, 32-34).

**Determination of the weighted isotope compositions of fossil fuel combustion**

To measure the isotope compositions of CDW derived from natural gas, we set up a gas stove in a largely enclosed shipping container (6.1m$\times$2.4m$\times$2.6m) and connected
the stove using an 8-m special hose for natural gas to a tank of liquified natural gas. We then linked an 8m stainless-steel tube from the container to our Picarro-L2130i. We covered outside of the stainless-steel tube with heating tapes. Isotope measurement started after we lighted the gas stove and closed the container’s door (Fig. S12, Table S6b). To measure the isotope compositions of CDW derived from coal, we used a smaller chamber with a volume of ~8 m³. Detailed information about the chamber can be found in Tian et al. (12). Different types of coals such as anthracite and bituminous were tested in a stove. We connected our Picarro instrumental pipeline to the exhaust outlet of the chamber and measured the water vapor isotope compositions (Fig. S12, Table S6b). The isotope compositions of CDW from vehicles that burn gasoline, diesel, natural gas, and methanol were determined using a transmission device at Xi’an Automobile Testing Center. The cars or trucks were placed onto the transmission device and ran at a normal speed (40-50 km h⁻¹). A 1/8-inch stainless-steel tubing was inserted into the exhaust pipe for measurement (Fig. S12, Table S6b).

The consumption data of Coal, natural gas, and crude oil were obtained from Xi’an Statistical Yearbook (2018) (13). Xi’an’s weighted CDW isotope composition δₓi’an was then calculated by:

\[ \delta_{\text{xi’an}} = \delta_{\text{natural gas}} \times F_{\text{natural gas}} + \delta_{\text{coal}} \times F_{\text{coal}} + \delta_{\text{car}} \times F_{\text{crude oil}} \]  

(5)

where \( \delta_{\text{natural gas}}, \delta_{\text{coal}}, \) and \( \delta_{\text{car}} \) represent respectively the measured CDW isotope composition for natural gas, coal, gasoline, and diesel cars (Table S6b). \( F_{\text{natural gas}}, F_{\text{coal}}, \) and \( F_{\text{crude oil}} \) stand for the respective fractions of fossil fuels usage calculated from data in Yearbook (Table S6a). Because the usage of bituminous was much higher than that of anthracite, the \( \delta_{\text{coal}} \) only considered the isotope composition from bituminous combustion. In addition, since the number of cars used methane and natural gas as fuel was negligible, the \( \delta_{\text{car}} \) represents the arithmetic mean value of CDW from gasoline-
cars and diesel-cars. As the Yearbook data provided only annual usage without monthly data, we used the annual data to calculate Xi’an’s weighted CDW isotope compositions during 4 months’ heating seasons. The difference should be small.

**WRF-Chem model, configurations, and evaluation**

The version of the WRF-Chem model (14, 15) used in this study has been modified by Li et al. (16–19) at the Molina Center for Energy and the Environment, La Jolla, CA, USA, including a new flexible gas phase chemical module and the CMAQ aerosol module developed by US Environmental Protection Agency (20). Wet deposition of aerosols followed the method used in the CMAQ module and dry deposition of chemical species was parameterized following Wesely (21). Photolysis rates were calculated using the fast radiation transfer model (FTUV), considering both the aerosol and cloud effects on photolysis (16, 22, 23). Inorganic aerosols were calculated using ISORROPIA Version 1.7 (24). Besides the SO$_2$ gas-phase oxidations by OH and sCl, we adopt a SO$_2$ heterogeneous reaction parameterization, in which the SO$_2$ oxidation in aerosol water by O$_2$ catalyzed by Fe$^{3+}$ is limited by mass transfer resistances in the gas-phase and gas-particle interface (19). Secondary organic aerosol (SOA) was predicted using the volatility basis-set (VBS) modeling method, with contributions from glyoxal and methylglyoxal (25, 26).

A persistent and heavy haze episode in late December 2015 to January 2016 was simulated using WRF-Chem model (Table S4, 35-40). The WRF-Chem model adopts one grid with horizontal resolution of 6 km centered at (34.25°N, 109.0°E) (Fig. S6), and 35 sigma vertical levels with a stretched vertical grid with spacing ranging from 30 m near the surface, to 500 m at 2.5 km and 1 km above 14 km, and the grid cells used for the domain are $150 \times 150$. The physical parameterizations employed in the model
were listed in Table S4. Initial and boundary meteorological conditions were from the National Centers for Environmental Prediction (NCEP) 1° × 1° reanalysis data, and initial and boundary chemical conditions were interpolated from the 6 h output of MOZART (27). Spin-up time of the WRF-Chem model was 28 h. The SAPRC-99 (Statewide Air Pollution Research Center, version 1999) chemical mechanism was used in the study. Anthropogenic emissions were from the MEIC (Multi-resolution Emission Inventory for China) model developed by Zhang et al. (28), mainly including contributions from agriculture, industry, power generation, residential, and transportation sources. There were no water vapor emissions from fossil fuel combustion in the current emission inventory. The CO₂ emissions were used to evaluate the emission of water of combustion. We assumed that 1~2 moles of H₂O molecule were produced with 1 mole of CO₂ molecule emitted. The biogenic emissions were calculated online using MEGAN (Model of Emissions of Gases and Aerosol from Nature) developed by Guenther et al. (29). Detailed information can be found in Li et al. (17, 18).

Mean bias (MB), root mean square error (RMSE), and index of agreement (IOA) were used to validate the WRF-Chem model performance in simulating air pollutants and aerosol species against observations and measurements. IOA describes the relative difference between the model predictions and observations, ranging from 0 to 1, with 1 indicating perfect agreement of predictions and observations.

\[
MB = \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i), \quad (6)
\]

\[
RMSE = \left[ \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i)^2 \right]^{\frac{1}{2}}, \quad (7)
\]

\[
IOA = 1 - \frac{\sum_{i=1}^{N} (P_i - O_i)^2}{\sum_{i=1}^{N} (|P_i - \overline{O}| + |O_i - \overline{P}|)^2}, \quad (8)
\]

where \(P_i\) and \(O_i\) are the predicted and observed mass concentrations of pollutants,
respectively. $N$ is the total number of the predictions used for comparisons, and $\bar{O}$ represents the average of observations.

WRF-Chem Model evaluation: Figure S7 presents the distributions of predicted and observed near-surface mass concentrations of PM$_{2.5}$, O$_3$, NO$_2$, and SO$_2$ along with the simulated wind fields averaged from 27th December 2015 to 15th January 2016 in the GZB. Generally, the predicted spatial pattern of PM$_{2.5}$ is consistent with observations at ambient monitoring sites in the basin. WRF-Chem model reasonably reproduced the high PM$_{2.5}$ concentrations exceeding 150 $\mu$g m$^{-3}$ in the central GZB. Apparently, during the simulation period, weak winds in the GZB facilitated the accumulation of PM$_{2.5}$, resulting in persistent and heavy air pollution. The observed and simulated O$_3$ concentrations were rather low in the GZB, varying from 10 to 50 $\mu$g m$^{-3}$.

The simulated and observed diurnal profiles of near-surface PM$_{2.5}$, O$_3$, NO$_2$, SO$_2$, and CO mass concentrations averaged over all monitoring sites in the GZB and Xi’an from 27th December 2015 to 15th January 2016 are showed in Figure S9. The WRF-Chem model reproduced well the diurnal variations in PM$_{2.5}$ mass concentrations when compared with observations in the basin during the simulation period. The $MB$ and $RMSE$ is -1.9 and 46.6 $\mu$g m$^{-3}$, respectively, and the $IOA$ is 0.79. During persistent haze episodes in the GZB, the model generally replicates the haze developing stages, but tends to underestimate the PM$_{2.5}$ concentrations against observations during the haze dissipation stages. One of the most likely reasons is the uncertainty of the simulated meteorological fields, which determine the formation, transformation, diffusion, transport, and removal of air pollutants in the atmosphere (30, 31). The WRF-Chem model also reasonably well simulated the diurnal variations of air pollutants in Xi’an against the observations, with considerable model biases (Fig. S9b). The good
agreements of the simulated mass concentrations of air pollutants with observations at adjacent monitoring sites in the GZB and Xi’an city suggest that the simulated wind fields and emission inventory used in the present study are reasonable, providing a reliable base for further evaluations.

Water emission from burning coal or natural gas

Water vapor produced from natural gas combustion follows

$$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} \quad (9)$$

Since the density of CH$_4$ is 0.7174 kg m$^{-3}$, 1.61 kg water will be produced by combusting 1 m$^3$ natural gas based on equation (9). We consider that the coal does not contain crystallization water, and the water vapor mainly comes from the product of the H atoms combining with O$_2$ atoms during combustion as simplified in eq. (10).

$$2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \quad (10)$$

Since the H mass concentration in the coal from China is less than 5%, ranging from 2%-5% (12, 41–43), and we pick 3% to calculate the water vapor production from coal burning. 1 kg coal can produce 0.27 kg water.

Since the mean calorific capacities of coal and natural gas are 20908 kJ kg$^{-1}$ and 38931 kJ m$^{-3}$, respectively (44), and 1 megawatt-hour equals to $3.6 \times 10^6$ kJ, we calculate that to generate 1 megawatt-hour equivalent energy, burning coal and natural gas will produce 46 kg and 149.4 kg water respectively. Thus, natural gas combustion produces 3-time more water vapor than coal combustion.

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Figure S1 Geography, topography, and the location of our monitoring/sampling site at IEECAS Building, the city of Xi’an and the Guanzhong Basin, central China.
Figure S2 Cross-plots of PM$_{2.5}$ concentrations with $\delta^{18}$O$_{vap}$ (A) and with d-excess$_{vap}$ (B) in Xi’an during the 2016-2018 heating seasons. The inserted figures represent these relationships for individual years, respectively. Color bar on the right represents the range of relative humidity.
Figure S3 Method for calculating CDW fraction

Background line: $\delta^2H = 7.65 \times \delta^{18}O + 29.21$ (d-excess$_{vap} \geq 32.8$)

CDW fraction (%) = \frac{AC}{AB}
Figure S4 CDW fractions calculated using three different methods (see Materials and Methods). The CDW fractions lower than 0 imply nonphysical negative proportions.
Figure S5 Positive correlations between CDW fraction and PM$_{2.5}$ concentration as well as relative humidity (RH) of the air in 12 selected episodes when PM$_{2.5}$ concentration was rising during the three-heating seasons from the beginning of 2016 to March 2018. Correlation coefficients are marked on individual panels and RH is color-coded. Uncertainty for CDW fraction is 0.4%. The blue shadows represent the selected episodes, and the cyan dash line stands for the PM$_{2.5}$ concentration at 200 μg m$^{-3}$ level.
Figure S6 (a) Map showing the location of the simulation domain with blue rectangle showing the location of the Guanzhong Basin and (b) The topography of the Guanzhong Basin with filled black circles representing adjacent monitoring sites in the basin, filled red triangles denoting center of the nearby cities, and outer black line outlines the location of the Guanzhong Basin, and the inner black line outlines the urban area of the city Xi’an.
Figure S7 Pattern comparisons of simulated (color counters) vs. observed (colored circles) near-surface mass concentrations of (a) PM$_{2.5}$, (b) O$_3$, (c) NO$_2$, and (d) SO$_2$ averaged from 27 December 2015 to 15 January 2016. Small black arrows indicate simulated surface winds. The size of the colored circles represents the number of monitoring sites. The outer black line outlines the location of the Guanzhong Basin, and the inner black line outlines the urban area of the city Xi’an.
Figure S8 Effects of combustion-derived water on near-surface PM$_{2.5}$ concentration in Xi’an. a/b: diurnal profiles of average PM$_{2.5}$ increase in Xi’an from 00:00 (Beijing Time, BJT) Dec. 27, 2015 to 00:00 BJT Jan. 15, 2016 in μg/m$^3$ or in %; c/d: spatial distribution of average PM$_{2.5}$ increase during the simulation period in μg/m$^3$ or in %. The outer black line outlines the location of the Guanzhong Basin, and the inner black line outlines the urban area of the city Xi’an.
Figure S9

(a) Guanzhong Basin

PM$_{10}$ ($\mu$g m$^{-3}$)

$MB = -1.9 \mu$g m$^{-3}$  $RMSE = 46.6 \mu$g m$^{-3}$  $IOA = 0.79$

Date & Time (BJT)

$O_3$ ($\mu$g m$^{-3}$)

$MB = -2.2 \mu$g m$^{-3}$  $RMSE = 9.8 \mu$g m$^{-3}$  $IOA = 0.87$

$NO_x$ ($\mu$g m$^{-3}$)

$MB = 1.7 \mu$g m$^{-3}$  $RMSE = 11.1 \mu$g m$^{-3}$  $IOA = 0.88$

$SO_2$ ($\mu$g m$^{-3}$)

$MB = 3.2 \mu$g m$^{-3}$  $RMSE = 12.4 \mu$g m$^{-3}$  $IOA = 0.88$

CO (mg m$^{-3}$)

$MB = -0.1$ mg m$^{-3}$  $RMSE = 0.7$ mg m$^{-3}$  $IOA = 0.79$
Figure S9 Comparisons of observed (black dots) and simulated (solid red lines) diurnal profiles of near-surface hourly mass concentrations of PM$_{2.5}$, O$_3$, NO$_2$, SO$_2$, and CO averaged over all ambient monitoring sites in the (a) The Guanzhong Basin and (b) Xi’an from 27 December 2015 to 15 January 2016. See supplemental text for the explanation of Mean bias (MB), root mean square error (RMSE), and index of agreement (IOA).
Figure S10

Figure S10 a) Six standards humidity-isotope response functions measured by CRDS; b) Time series of absolute humidity, $\delta^{18}O$, and $\delta^2H$ of the measured six standards.
Figure S11 Air mass back trajectories for 2016-2018 heating seasons at our sampling site computed based on NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, version 4) interactive model (32,33). The trajectories identify the moisture transport paths and moisture sources variability. A software TrajStat was used for air mass trajectory visualization and statistical analysis (34). We utilized HYSPLIT to determine 120-hours (5-day) back trajectories of the air mass at 500 m above ground level every 6 hours. We chose 500 m above ground level as the trajectory endpoint since the water vapor isotope data were collected at the surface level.
Figure S12 The $\delta^{18}$O$_{vap}$, $\delta^{2}H_{vap}$, and humidity variations for experiments with different fossil fuel combustion. (a) natural gas combustion measured at the first time and (b) at the second time; (c) bituminous combustion measured at the first time and (d) at the second time; (e) anthracite combustion measured at first time and (f) at the second time; (g) vehicle exhaust emitted by gasoline-powered car at first time and (h) at the second time; (i) vehicle exhaust emitted by diesel-powered car at first time and (j) at the second time; (k) vehicle exhaust emitted by natural-gas-powered car; and (l) vehicle exhaust emitted by diesel-powered car.
Table S1. The mean of PM$_{2.5}$ concentrations at different combinations of RH bins, (a) SO$_2$ bins, and (b) NO$_2$ bins. Bold black letters represent PM$_{2.5}$ concentrations less than 35 μg m$^{-3}$, bold red letters represent PM$_{2.5}$ concentrations more than 150 μg m$^{-3}$, and SD represents standard deviation.

| RH Range (%) | 0-20 (Mean ±SD) | 20-40 (Mean ±SD) | 40-60 (Mean ±SD) | 60-80 (Mean ±SD) | 80-100 (Mean ±SD) |
|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0-10 SO$_2$ Range (μg m$^{-3}$) | 24.5±13.5 (n=44) | 22.3±11.9 (n=18) | 25.8±10.5 (n=15) | 35.2±18.5 (n=20) | 39.9±27.7 (n=134) |
| 10-15       | 27.3±13.0 (n=92) | 31.2±16.2 (n=173)| 32.7±20.7 (n=79) | 59.7±39.9 (n=74) | 72.9±41.7 (n=194) |
| 15-20       | 32.5±12.0 (n=49) | 37.5±21.3 (n=263)| 51.9±34.3 (n=211)| 72.6±40.0 (n=147)| 110.4±46.3 (n=194) |
| 20-30       | 43.3±24.1 (n=63) | 56.1±22.7 (n=474)| 78.9±36.6 (n=584)| 112.2±49.5 (n=636)| 165.6±70.2 (n=448) |
| 30-40       | 45.9±16.5 (n=8)  | 78.6±35.7 (n=295)| 120.4±54.3 (n=563)| 163.9±74.1 (n=569)| 231.1±92.6 (n=247) |
| >40         | 77.0±40.8 (n=3)  | 104.5±42.1 (n=278)| 168.7±66.9 (n=668)| 235.7±97.1 (n=503)| 295.2±128.1 (n=123) |

| RH Range (%) | 0-20 (Mean ±SD) | 20-40 (Mean ±SD) | 40-60 (Mean ±SD) | 60-80 (Mean ±SD) | 80-100 (Mean ±SD) |
|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0-20 NO$_2$ Range (μg m$^{-3}$) | 23.0±10.8 (n=87) | 19.5±5.4 (n=65) | 22.2±9.4 (n=39)  | 37.3±58.1 (n=20) | 31.0±10.6 (n=24) |
| 20-30       | 32.1±15.9 (n=61) | 35.9±19.2 (n=152)| 37.9±32.7 (n=44) | 52.9±37.8 (n=28) | 35.8±15.1 (n=56) |
| 30-40       | 32.1±9.5 (n=44)  | 43.5±21.6 (n=225)| 70.2±47.9 (n=126)| 72.0±36.5 (n=58) | 60.7±33.4 (n=136) |
| 40-60       | 44.1±24.9 (n=50) | 58.6±31.5 (n=478)| 85.7±46.5 (n=441)| 108.5±59.4 (n=412)| 106.2±58.3 (n=399) |
| 60-80       | 52.0±16.4 (n=14) | 75.5±35.4 (n=339)| 106.4±50.2 (n=672)| 135.4±65.7 (n=610)| 178.1±78.2 (n=309) |
| >80         | 65.0±51.1 (n=3)  | 100.5±42.7 (n=242)| 150.2±76.5 (n=798)| 201.4±99.3 (n=821)| 245.3±102.1 (n=416) |
Table-S2 Model sensitivity test of precursors reduction for the Guanzhong basin (a) and Xi’an (b).

### Case (Guanzhong Basin)

|                  | SO₂ (μg m⁻³) | NO₂ (μg m⁻³) | RH (%) | PM₂.₅ (μg m⁻³) |
|------------------|--------------|--------------|--------|----------------|
| Base             | 47.9         | 70.8         | 58.9   | 164.1          |
| RH-Reduction     | 48.3         | 71.2         | 53.1   | 159.5          |
| NO₂, RH-Reduction| 46.1         | 19.7         | 53.1   | 160.4          |
| SO₂, RH-Reduction| 10.3         | 72.3         | 53.1   | 156.1          |
| SO₂, NO₂ and RH-Reduction | 8.9         | 19.6         | 53.1   | 143.9          |

### Case (Xi’an)

|                  | SO₂ (μg m⁻³) | NO₂ (μg m⁻³) | RH (%) | PM₂.₅ (μg m⁻³) |
|------------------|--------------|--------------|--------|----------------|
| Base             | 57.0         | 81.9         | 60.3   | 177.3          |
| RH-Reduction     | 57.7         | 82.6         | 54.3   | 171.3          |
| NO₂, RH-Reduction| 54.8         | 23.0         | 54.3   | 171.8          |
| SO₂, RH-Reduction| 11.8         | 84.3         | 54.3   | 168.6          |
| SO₂, NO₂ and RH-Reduction | 10.0         | 22.8         | 54.3   | 152.7          |
Table-S3. One-way ANOVA statistical analysis results at p = 0.01 level. The number in the table represents the differences of means between the two RH ranges at the same (a) SO\textsubscript{2} range and (b) NO\textsubscript{2} range, and the number in parentheses represent the p-value. The number with asterisk denotes the p-value lower than 0.01.

| SO\textsubscript{2} Range (μg m\textsuperscript{-3}) | RH Range (%) | 0-20-40 | 20-40-60 | 40-60-80 |
|---------------------------------|--------------|--------|----------|---------|
| 0-10                            | 20-40        | 2.2 (0.736) |
|                                 | 40-60        | -1.3 (0.846) -3.5 (0.663) |
|                                 | 60-80        | -10.7 (0.086) -12.9 (0.086) -9.4 (0.234) |
|                                 | 80-100       | -15.4 (0.000) -17.6 (0.003) -14.1 (0.026) -4.7 (0.398) |
| 10-15                           | 20-40        | -3.9 (0.309) |
|                                 | 40-60        | -5.4 (0.237) -1.5 (0.000) |
|                                 | 60-80        | -32.4 (0.000) -28.5 (0.000) -27.0 (0.000) |
|                                 | 80-100       | -45.6 (0.000) -41.7 (0.000) -40.2 (0.000) -13.2 (0.001) |
| 15-20                           | 20-40        | -5.0 (0.349) |
|                                 | 40-60        | -19.4 (0.000) -14.4 (0.000) |
|                                 | 60-80        | -40.1 (0.000) -35.1 (0.000) -20.7 (0.000) |
|                                 | 80-100       | -77.9 (0.000) -72.9 (0.000) -58.5 (0.000) -37.8 (0.000) |
| 20-30                           | 20-40        | -12.8 (0.042) |
|                                 | 40-60        | -35.6 (0.000) -22.8 (0.000) |
|                                 | 60-80        | -69.0 (0.000) -56.2 (0.000) -33.4 (0.000) |
|                                 | 80-100       | -122.4 (0.000) -109.6 (0.000) -86.8 (0.000) -53.4 (0.000) |
| 30-40                           | 20-40        | -32.7 (0.166) |
|                                 | 40-60        | -74.5 (0.002) -41.8 (0.000) |
|                                 | 60-80        | -118.0 (0.000) -85.4 (0.000) -43.5 (0.000) |
|                                 | 80-100       | -185.3 (0.000) -152.6 (0.000) -110.7 (0.000) -67.2 (0.000) |
| >40                             | 20-40        | -27.5 (0.558) |
|                                 | 40-60        | -91.7 (0.050) -64.3 (0.000) |
|                                 | 60-80        | -158.7 (0.001) -131.3 (0.000) -67.0 (0.000) |
|                                 | 80-100       | -218.2 (0.000) -190.7 (0.000) -126.4 (0.000) -59.4 (0.000) |

| NO\textsubscript{2} Range (μg m\textsuperscript{-3}) | RH Range (%) | 0-20-40 | 20-40-60 | 40-60-80 |
|---------------------------------------------------|--------------|--------|----------|---------|
| 0-20                                             | 20-40        | 3.5 (0.260) |
|                                                 | 40-60        | 0.8 (0.824) -2.7 (0.483) |
|                                                 | 60-80        | -14.3 (0.003) -17.8 (0.000) -15.1 (0.004) |
|                                                 | 80-100       | -8.1 (0.065) -11.5 (0.011) -8.9 (0.072) 6.2 (0.278) |
| 20-30                                            | 20-40        | -3.8 (0.267) |
|                                                 | 40-60        | -5.8 (0.192) -2.0 (0.600) |
|                                                 | 60-80        | -20.8 (0.000) -17.0 (0.000) -15.0 (0.006) |
|                                                 | 80-100       | -3.7 (0.373) -0.1 (0.981) 2.1 (0.643) 17.1 (0.001) |
| 30-40                                            | 20-40        | -11.5 (0.033) |
|                                                 | 40-60        | -36.1 (0.000) -26.7 (0.000) |
|                                                 | 60-80        | -40.0 (0.000) -28.5 (0.000) -1.9 (0.721) |
|                                                 | 80-100       | -28.6 (0.000) -17.2 (0.000) 9.5 (0.019) 11.3 (0.027) |
| 40-60                                            | 20-40        | -14.5 (0.047) |
|                                                 | 40-60        | -41.6 (0.000) -27.1 (0.000) |
|                                                 | 60-80        | -64.4 (0.000) -49.9 (0.000) -22.8 (0.000) |
|                                                 | 80-100       | -62.1 (0.000) -47.7 (0.000) -20.5 (0.000) 2.2 (0.514) |
| 60-80                                            | 20-40        | -23.5 (0.140) |
|                                                 | 40-60        | -54.4 (0.001) -30.9 (0.000) |
|                                                 | 60-80        | -83.4 (0.000) -59.9 (0.000) -29.0 (0.000) |
|                                                 | 80-100       | -119.8 (0.000) -96.3 (0.000) -65.4 (0.000) -36.4 (0.000) |
| >80                                             | 20-40        | -35.5 (0.486) |
|                                                 | 40-60        | -85.2 (0.094) -49.6 (0.000) |
|                                                 | 60-80        | -136.4 (0.000) -100.8 (0.000) -51.2 (0.000) |
|                                                 | 80-100       | -180.3 (0.000) -144.7 (0.000) -95.1 (0.000) -43.9 (0.000) |
Table-S4. WRF-Chem model configurations.

| Region                      | The Guanzhong Basin |
|-----------------------------|---------------------|
| Simulation period           | 12:00 UTC, 25 December 2015 to 00:00 UTC, 15 January 2016 |
| Domain size                 | 150 × 150           |
| Domain center               | 34.25°N, 109°E     |
| Horizontal resolution       | 6 km × 6 km         |
| Vertical resolution         | 35 vertical levels with a stretched vertical grid with spacing ranging from 30 m near the surface, to 500 m at 2.5 km and 1 km above 14 km |
| Microphysics scheme        | WSM 6-class graupel scheme (35) |
| Cumulus scheme              | Grell-Devenyi ensemble scheme (36) |
| Boundary layer scheme       | MYJ TKE scheme (37) |
| Surface layer scheme        | MYJ surface scheme (37) |
| Land-surface scheme         | Unified Noah land-surface model (38) |
| Longwave radiation scheme   | Goddard longwave scheme (39) |
| Shortwave radiation scheme  | Goddard shortwave scheme (40) |
| Meteorological boundary and initial conditions | NCEP 1°×1° reanalysis data |
| Chemical initial and boundary conditions | MOZART 6-hour output (27) |
| Anthropogenic emission inventory | Developed by Zhang et al. (28), 2013 base year, and SAPRC-99 chemical mechanism |
| Biogenic emission inventory | Online MEGAN model developed by Guenther et al. (29) |
| Spin-up                     | 28 hours            |
Table-S5. Isotope compositions of our six water standards

| Lab-label | Light standard | Heavy standard |
|-----------|----------------|---------------|
|           | $\delta^{18}$O/‰ | $\delta^{2}$H/‰ | $\delta^{18}$O/‰ | $\delta^{2}$H/‰ |
| LS2       | -17.68         | -134.0        | LS3           | -10.2         | -72.4 |
| GB3       | -24.5          | -189.1        | GB2           | -8.8          | -64.8 |
| LA3       | -19.1          | -143.2        | LA2           | -10.0         | -69.5 |
Table-S6a. 2017 Xi’an energy consumption inventory

| Fossil Fuel Type | Consumption/year | Unit | Factor | Unit | Amount of Water | Unit | Contribution Proportion/% |
|-----------------|-----------------|------|--------|------|-----------------|------|---------------------------|
| Coal            | 1.19×10^7       | ton  | 0.27   | kg/kg| 5.38×10^6       | ton  | 45.8                      |
| Natural Gas     | 2.31×10^9       | m^3  | 1.6    | kg/m^3| 3.70×10^6       | ton  | 52.5                      |
| Gasoline&Kerosen&Diesel | 8.57×10^4 | ton  | 1.42   | kg/kg| 1.22×10^5       | ton  | 1.7                       |

Table-S6b. Measured fossil fuel combustion-derived water vapor isotope compositions and weighted mean isotope compositions in the city of Xi’an

| Type                | δ^18O/%o Mean | Standard deviation | δ^2H/%o Mean | Standard deviation | D-excess/%o Mean | Standard deviation |
|---------------------|--------------|--------------------|--------------|--------------------|----------------|--------------------|
| Natural gas         | 13.2         | 0.7                | -160.8       | 2.8                | -266.5         | 3.8                |
| Coal:Bituminous     | 4.2          | 1.3                | -102.2       | 16.3               | -135.5         | 26.4               |
| Coal:Anthracite     | -0.2         | 0.2                | -103.7       | 7.7                | -102.2         | 9.2                |
| Car:Gasoline-1      | 6.6          | 0.5                | -175.6       | 4.1                | -180.4         | 4.0                |
| Car:Gasoline-2      | 17.4         | 0.3                | -187.8       | 1.3                | -327.0         | 2.5                |
| Car:Diesel-1        | 13.8         | 0.3                | -167.4       | 2.6                | -278.0         | 3.9                |
| Car:Diesel-2        | 9.8          | 0.5                | -207.5       | 2.4                | -286.0         | 1.7                |
| Car:Natural Gas     | 11.8         | 0.6                | -227.6       | 3.3                | -321.7         | 4.6                |
| Car:Methane         | 9.2          | 2.5                | -237.0       | 9.8                | -311.0         | 10.2               |
| Xi’an Weighted value| 9.0          | -134.4             | -206.7       |                   |                |                    |