Emission of Polycyclic Aromatic Hydrocarbons in China by County

YANXU ZHANG,[†] SHU TAO,[*,†,‡]
JUN CAO,[†] AND
RAYMOND M. COVENEY, JR.[‡]

Laboratory for Earth Surface Processes, College of Environmental Sciences, Peking University, Beijing 100871, China, Department of Geosciences, and Center for Applied Environmental Research, University of Missouri, Kansas City, Missouri 64110-2499

Quantitative relationships among social, economic, and climate parameters, and energy consumption for Chinese provinces, provide data for regression models' estimated rates of energy consumption and emission of polycyclic aromatic hydrocarbons (PAHs) by county. A nonlinear model was used for domestic coal combustion with total population and annual mean temperature as independent variables. Linear regression models were utilized for all other types of fuel consumption. Monte Carlo simulation demonstrated that emission factors, rather than the regression modeling, constitute the main source of uncertainty in prediction. Models were validated using available energy data of several northern and southern counties of China from the literature. The total PAHs produced by each county is approximately equivalent to the sum of the total emission from energy, coke, and aluminum production.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the most persistent organic pollutants detected in environmental media of China (*1, 2*) and adjacent countries whose emissions affect the environment on a global scale (*3*).

Xu et al. have estimated the emission of 16 PAHs listed as United Sates Environmental Protection Agency (USEPA) priority pollutants from major sources in China have increased substantially from around 18 000 tons in 1980 to >25 000 tons in 2003 (*4*). As a consequence of recent economic expansion and population growth, it is reasonable to expect that PAH emissions in other developing countries would follow a similar trend. Such an increase would tend to compensate for any emission decreases in developed countries, and a sustained rate of PAH emission dating from the start of the modern industrial era (*5*). Geographical coverage of emission has been limited to provincial resolution in China as a result of data availability (*4*). Nevertheless, published data suggest relatively high emission densities in southeast provinces and high emission intensity in western and northern China (*4*). Since 70% of the provinces in China have areas exceeding 100 000 km^2, higher resolution emission information is desirable for regional fate modeling, ecological studies, health risk assessment, and control strategy development.

High-resolution data on emission and energy consumption are not readily available for China. With energy as a prime driving force in social and economic development, quantitative relationships are to be expected among population, economic activity, and energy consumption. The relationship between energy consumption and the gross domestic product (GDP) has been extensively investigated. Nathwani et al. revealed a strong relationship between the availability of energy, economic activity, improvement in living standards, and total social welfare of OECD (Organisation for Economic Co-operation and Development) countries (*6*). Similar results have been reported for developing countries (*7*). Energy is also widely used in human daily life and depends on population. Mazur indicated that population growth led to increased energy consumption in the U.S. between 1947 and 1991 (*8*). Differences in atmospheric PAHs concentrations can be largely attributed to population (*9, 10*). Energy consumption can be strongly influenced by local climate. For example, firewood is more commonly used for heating at high altitude than at lower elevations in India (*11*).

If the dependence of energy consumption on the above parameters can be quantified, county level energy use, and subsequently, PAH emission can be compiled provided that social and economical data are available. The objectives of this study were (1) to model the quantitative relationships between the consumption of fossil fuels and biomass in various sectors and social-economic parameters based on provincial data in China and (2) to estimate PAHs emission and address the spatial distribution of the emission at the county level in China.

Materials and Methods

Major PAH Emission Sources. The major emission sources of PAHs in China are burning of biomass including straw and firewood, combustion for heating in homes and businesses, industrial combustion of fossil fuels, petroleum used for transportation, and production of coke and aluminum (*4*). Each of these PAHs sources were adopted in this study with straw and firewood combined as biomass.

Modeling the Energy Consumption. For coal and aluminum production, location and energy consumption PAH of each major manufacturer and emission could be tallied for specific counties. For all other PAH emission activities, nationwide county level data are not available, and regression models were developed for estimating their magnitudes. A range of parameters including total and rural populations, GDPs of various combinations, annual mean temperature, local coal production, forest coverage, duration of indoor heating period, and efficiency of energy utilization were examined for their quantitative relationships with various types of energy consumption. Most parameters were not employed in the final models either because of an absence of quantitative relationships or the lack of full data sets by county.

Both linear and nonlinear regression models were tested for quantitative relationships. For the most part, a univariate linear model was preferred for simplicity. However, a good regression could not be determined for heating without including introduction of a second nonlinear independent variable. Although regression models were developed by trial-and-error, the final format could be interpreted reasonably well. Regressions and statistical analysis were conducted using MATLAB (*12*).

* Corresponding author phone: 0086-10-62751938; fax: 0086-10-62751938; e-mail: taos@urban.pku.edu.cn.
[†] Peking University.
[‡] University of Missouri.

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Data Collection. China has a total of 2352 counties located in 23 provinces, five autonomous districts, and six municipalities and special administrative regions under the jurisdiction of the central government. Data, including total and rural populations (P_{total}, P_{rural}), secondary plus tertiary GDPs (GDP_{23}), and annual mean temperature (T_{mean}, for the capital city of a given province as an approximation), were assembled at county and provincial levels (*13*, *14*). For 282 counties, rural populations of 2003 were not available necessitating the use of data from 2000 (*15*). County boundaries of 2003 (at a scale of 1:400 0000) were used for mapping (*16*). County GDPs of Taiwan were not available and are assumed to be proportional to population. The consumption rates of fossil fuels and biomass at provincial level and the emission factors were taken from Xu et al. Values for straw and firewood were averaged to provide the overall biomass emission (*4*).

Emission Estimation at County Level. Emission rates were calculated from consumption data for all counties in China for 16 PAH compounds: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]-fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz-[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene. Emissions were quantifiable for major manufacturers of coke and aluminum. The total emission of each county was presented as a sum of PAHs from all major emission sources. Taking the random error of the regression models into consideration, a directly calculated county emission value from a given source was adjusted for mapping by multiplying a rectification factor (the ratio of the directly calculated provincial emission and the sum of the calculated emissions of all counties within the province).

Model Validation. Since energy consumption models were derived from provincial data as applied to counties, the rationality of the interpolation had to be justified. Energy consumption data for industrial coal, industrial petroleum, and biomass of a number of counties were collected (See Supporting Information) and compared with model estimates for validation. Models were also evaluated by comparing provincial PAHs emission to the sums of the county estimates before rectification.

Uncertainty Analysis. Xu et al. have characterized the uncertainty of the provincial level emission estimation by generating probability distributions of the emissions from various sources (*4*). The same procedure of uncertainty analysis was adopted for coke and aluminum production. For the other sources, the distributions of activity rates were generated from normal distributions with a fixed coefficient of variation (5%) of a number of independent variables including T_{mean}, P_{total}, P_{rural}, and GDP_{23}. Actual distribution statistics of emission factors were derived from the dataset (*4*). A total of 2000 runs were conducted for the Monte Carlo simulation.

Results and Discussion

Prediction of Domestic Coal Consumption. Wang et al. compiled a SO_2 emission inventory for eastern China and allocated the residential fuel consumption based on population (*17*). Domestic coal is mainly used for cooking, heating, and commercial purposes depending on population. Reddy et al. estimated the domestic coal consumption of India using local population as a proxy (*18*). In our study, a positive correlation ($p < 0.001$) between the log-transformed domestic coal consumption and population was revealed at a provincial level. However, if a linear regression model were fitted to the data, large residues resulted with $r^2 = 0.328$, insufficient for prediction.

It appears that population is not the sole major factor affecting domestic coal consumption, which could also under the influences of a number of other underlying factors, e.g., local climate, type of coal combustion facilities, economic status, availability of coal and other fuels, and even habitats of local residents. After a through examination of these factors, it was found that the residuals of the domestic coal-population model are significantly correlated to T_{mean} with only a few exceptions (Figure 1, left). The territory of China extends from cool temperature to tropical zone with T_{mean} values vary from 5.4 °C (Heilongjiang) to 25.0 °C (Hainan) (*19*). Indoor heating in north China lasts for 4−7 months depending on local climate. Since the residuals of the domestic coal-population model were calculated by subtracting the recorded domestic coal consumption from the predicted ones, it is not surprising to see a general trend from underestimation of domestic coal consumption in northern provinces to overestimation of coal use in southern provinces.

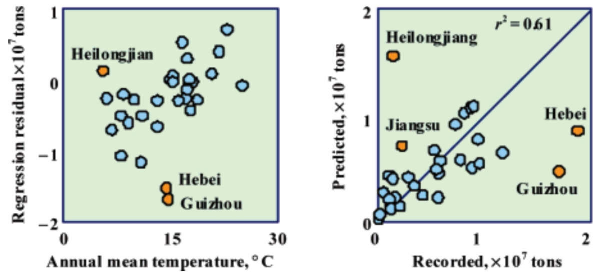

FIGURE 1. Dependence of domestic coal-population regression residuals on T_{mean} (left) and comparison between the real and the model calculated domestic coal consumption using the bivariate regression model (right).

Taking the influence of T_{mean} into account, bivariate regression models of various forms were tested and compared, and a reasonable degree of fit could be achieved with the following equation: $C_{DC} = aP_{total}/(b + T_{mean})^d$, where C_{DC} represents domestic coal consumption and a, b, and d are empirical constants of the model. Figure 1 (right) presents the relationship between the model calculated and the real domestic coal consumption. If the four outliers (Heilongjiang, Jiangsu, Hebei, and Guizhou) are removed from consideration, the r^2 value is 0.610. Forests cover a large portion (38.7%) of Heilongjiang, where firewood is plentiful (*20*). Firewood, instead of coal, is widely used for residential cooking and heating, resulting in an overestimation of domestic coal consumption. On the other hand, Guizhou produced 78 million tons of coal in 2003, and a large amount was used in stoves for cooking and heating by more than 80% of the local population (*19*, *21*), which may explain the underestimation of coal consumption for the province.

Prediction of Fossil Fuel Consumption. The use of fossil fuel is strongly influenced by GDP_{23}. When GDP_{23} is used as the independent variable in simple linear models, industrial coal, industrial petroleum, and traffic petroleum consumption could be predicted with only a few exceptional outliers (Figure 2). Unlike the other provinces in China, the economy of Hong Kong and Taiwan rely very much on high-tech, trading, logistics, finance, and commerce sectors, leading to significantly lower energy consumption in industry per GDP output. In fact, the energy intensities of China's mainland, Hong Kong, and Taiwan were 7590, 870, and 2480 tons of oil equivalent per 100 million RMB in 2003, respectively (*14*, *22*, *23*). The predicted industrial petroleum consumption of Guangdong was also significantly lower than the actual value. During the past decade, many new petroleum-driven power stations have been put into operation in this area, partly due to limited capacity and the high cost of coal transportation from coal-rich north provinces (*23*, *24*). This resulted not only in the underestimation of industrial petroleum consumption, but also overestimation of industrial coal consumption (Figure 2, left). With the outliers (marked yellow

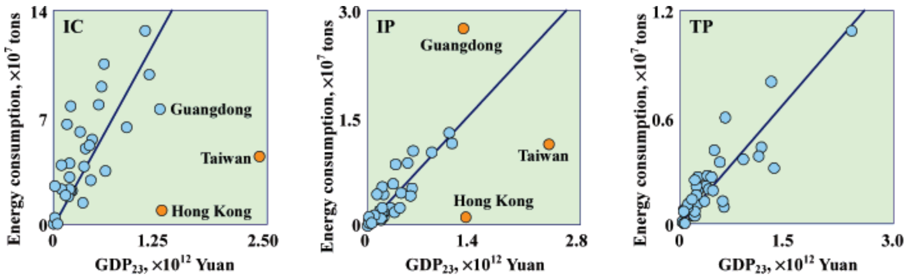

FIGURE 2. Industrial coal (IC), industrial petroleum (IP) and traffic petroleum (TP) consumptions as functions of GDP_{23}.

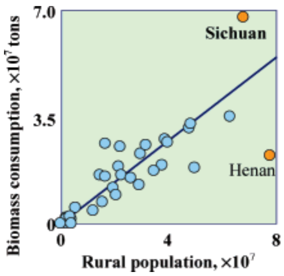

FIGURE 3. Biomass consumption as a function of P_{rural}.

in Figure 2) removed, the r^2 values of the regression equations were 0.46, 0.77, and 0.72 for industrial coal, industrial petroleum, and traffic petroleum consumption, respectively.

Biomass burning is a common practice in rural China where both straw and firewood are widely used for cooking and heating (*25*). Although a number of parameters were tested against biomass consumption at the provincial level, it was found that a simple linear regression with P_{rural} as the independent variable would predict the biomass consumption well (Figure 3). Two outliers were Henan and Sichuan. According to Xu et al., the total PAH emission in Sichuan ranked first in China in 2003, with 79% from biomass burning (*4*). Sichuan is one of the largest agricultural provinces in China and production of straw exceeded the needs for cooking in rural areas, and open fire burning was a way of getting rid of the straw, leading to underestimation. Henan is the most populated province in China with a total population over 100 million and more than 80% of which live in rural area (*19*). The overestimation of biomass in Henan could be partly caused by the nonlinear dependence of biomass on P_{rural} within high population range. In fact, if Sichuan was removed as an outlier, biomass seems to increase linearly first then level off (Figure 3). Since the residuals of a linear model and a power function model are not significantly different for our data, a linear function was used for simplification. Without the two outliers, the r^2 value of the model was as high as 0.78. The energy consumption prediction models developed for domestic coal, industrial coal, industrial petrleum, traffic petroleum, and biomass are summarized in the Supporting Information.

Model Validation and Uncertainty Analysis. With a sample size of 34, it was unrealistic to divide the database randomly into modeling and validation subsets in the regression model. Other means of model validation had to be applied. In this study, industrial coal, industrial petroleum, and biomass consumption data of 72, 46, and 120 counties were collected for this purpose. Figure 4 presents the results by plotting the predicted fuel consumption against the real values. Among the three fuel categories, the modeled data for biomass consumption fit the actual data well. For industrial coal and industrial petroleum consumption, although the data points deviate notably from the 1:1 line, they are scattered around the line showing no systematic error.

The results of the uncertainty analysis on fuel consumption model predictions are presented in Figure 5 using the three major emission sources as examples. The uncertainties were characterized using semi-interquartile ranges (SR, the difference between the 75th and the 25th percentiles). It was found that the SR values varied from 5.00% (biomass) to 18.9% (coke production) of the medians for the estimated total PAHs emission from these sources, while the calculated SR values for the activity rates ranged from 0.38% (biomass) to 1.46% (industrial coal) of their media values. It appears that the variation in emission factors contributed to the major portion of the uncertainties for the estimation.

Estimation of PAH Emissions at the County Level. Based on the regression models for various types of fuel consumption, as well as the information on the point sources of coking and aluminum industries, emissions of 16 individual PAHs were calculated for all counties in China. The overall prediction is further evaluated by plotting the predictions directly at provincial level against those calculated at county level and summed for each province (Figure 6). All data points fall around the 1:1 line on a log−log plot, showing no systematic error in the results. The total PAH emission calculated for all counties in China was 28 800 tons, which was very close to the provincial-level estimation of 28 250 tons. Similar estimation at provincial level based on the separated straw and firewood sources was 25 300 ton in 2003 (*4*). The final estimates of PAHs emission for individual counties were rectified based on the provincial level estimation, bring all data points in Figure 6 right on the 1:1 line and making the total emission of 28 250 tons.

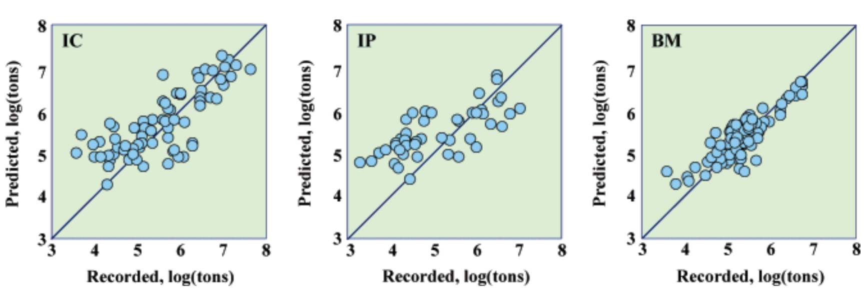

FIGURE 4. Comparison between the model predicted and the real consumptions of Industrial coal (IC), industrial petroleum (IP) and biomass (BM) in a number of counties in China.

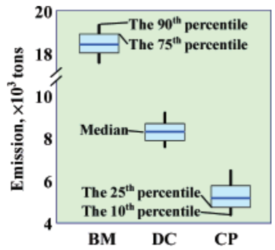

FIGURE 5. Means, 10th, 25th, 75th, and 90th percentiles of PAH16 emissions from biomass (BM), domestic coal (DC), and coke production (CP) derived from the Monte Carlo simulation.

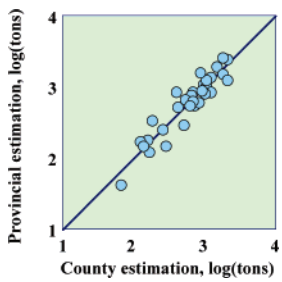

FIGURE 6. Comparison of the total PAH emissions derived from provincial level and county level estimations.

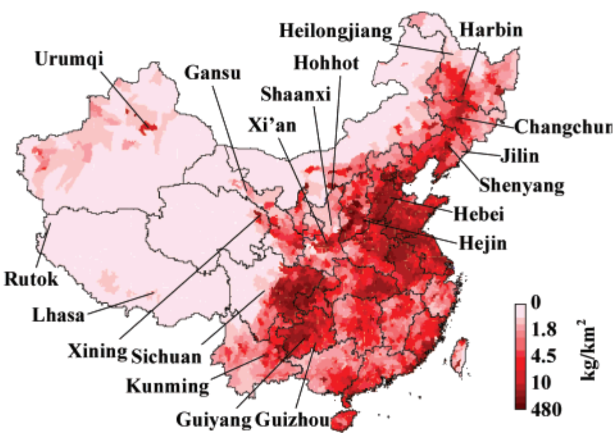

FIGURE 7. Geographical distribution of PAH emission density (area normalized) in China.

Geographical Distribution of PAH Emission in China. Xu et al. have discussed the spatial distribution of PAH emission in Chinese provinces (*4*). Because of great differences in local social-economical conditions, total PAHs emissions differed considerably from one county to the next in many provinces (Figure 7). As indicated by Xu et al., PAH emission densities of the southeastern provinces were generally higher than those of the other provinces (*4*). When the emission is presented at county resolution, detailed differences within various provinces are revealed. For all provinces, major cities stand out as the emission centers, even for the lower emission provinces in the west. Capital cities such as Harbin, Changchun, and Shenyang in the northeast; Hohhot, Urumqi, and Xining in the north and the west; and Guiyang and Kunming in the southwest, even Lhasa in Tibet can be clearly pinpointed with notably higher emissions than those of surrounding areas. For the 76 largest cities with a population greater than 1 million in China, the average emission density was 158 kg/km^2 in 2003, more than 55 times higher than the national mean of 2.85 kg/km^2. Although these cities occupy only 0.15% of the total territory, they contributed to 7.8% of the total emission.

For rural areas with all major cities excluded, the highest emission density was found in Hejin of Shanxi province with an emission density of 479 kg/km^2. The lowest value recorded was 0.0000017 kg/km^2 for Rutok of Tibet (population density, 0.095 cap/km^2). A full 79% of the emission from Hejin is from large coke and aluminum manufacturing plants.

Geographical variations within individual provinces are noteworthy. For example, emissions average 5.35 kg/km^2 in Sichuan close to the average for all provinces (*4*). Emissions are high, 12.7 kg/km^2, for the 105 counties of the Sichuan Basin, but only 0.624 kg/km^2 for the 47 counties of the Chuanxi Mountain area. Although the average PAH emission density in Shaanxi was only 0.314 kg/km^2, falling in a category of western provinces, the emission density of Xi'an and surrounding counties (Guanzhong Plain) was as high as 7.31 kg/km^2. Such high intraprovince variations are also remarkable in Heilongjiang, Gansu, Jilin, Hebei, and some other provinces.

Contributions of Major Sources. Major PAH emission sources in China are biomass (59%), domestic coal combustion (23%), and coke production (15%), while all other emission sources contributed to only 3% of the total. These results are slightly different from those reported by Xu et al. (56, 24, and 16% for biomass, domestic coal combustion, and coking production, respectively) due to combination of straw and firewood consumption data in the current study (*4*). If the contributions of various sources were calculated only for major cities with populations larger than 1 million, then the source profile would be very different following an order of coke production (49%), domestic coal combustion (34%), vehicular fuel (8%), and aluminum production (6%). It is important to note that 14.2% of the total population lives in these cities.

Emissions from each source were calculated individually, plotted after normalization by area (Figure 8). The total emission map (Figure 7) is approximately equivalent to the total of biomass and domestic coal combustion emissions, which together account for more than 80% of the total. It can be seen that Sichuan, Fujian, Guangxi, and Hainan were dominated by biomass emission, while more PAH from domestic coal was found in Guizhou and Xinjiang. Although emission sources from coking industries spread over the eastern China, a cluster of strong sources can be found in Shanxi where many large coal mines are located.

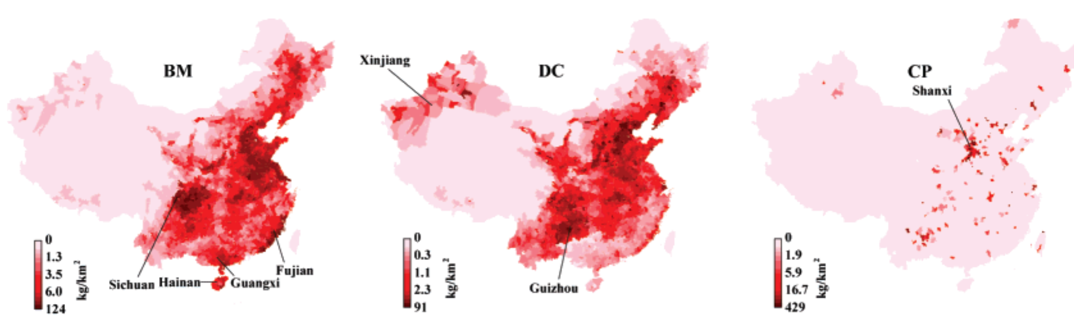

FIGURE 8. Distributions of PAH emission densities from biomass (BM), domestic coal (DC), and coke production (CP).

Acknowledgments

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Supporting Information Available

The regression models as well as the source literatures of county energy consumption data are summarized. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Zhu, L. Z.; Cai, X. F.; Wang, J. PAHs in aquatic sediment in Hangzhou, China: Analytical methods, pollution pattern, risk assessment and sources. *J. Environ. Sci. (China)* **2005**, *17*, 748–755.

(2) Mai, B. X.; Fu, J. M.; Sheng, G. Y.; Kang, Y. H.; Lin, Z.; Zhang, G.; Min, Y. S.; Zeng, E. Y. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. *Environ. Pollut.* **2002**, *117*, 457–474.

(3) UNEP Chemicals. *Global Report 2003: Regionally Based Assessment of Toxic Substances*; GEF, UNEP Chemicals: Châtelaine, GE, Switzerland. 2003.

(4) Xu, S. S.; Liu, W. X.; Tao, S. Emission of polycyclic aromatic hydrocarbons in China. *Environ. Sci. Technol.* **2006**, *40*, 702–708.

(5) Masclet, P.; Hoyau, V.; Jaffrezo, J. L.; Legrand, M. Evidence for the presence of polycyclic aromatic hydrocarbons in the polar atmosphere and in the polar ice of Greenland. *Analusis* **1995**, *23*, 250–252.

(6) Nathwani, J. S.; Siddall, E.; Lind, N. C. *Energy for 300 Years*; Institute for Risk Research, University of Waterloo: Waterloo, ON, Canada, 1992.

(7) Lee, C. C. Energy consumption and GDP in developing countries: a cointegrated panel analysis. *Energy Econ.* **2005**, *27*, 415–427.

(8) Mazur, A. How does population-growth contribute to rising energy-consumption in America? *Popul. Environ.* **1994**, *15*, 371–378.

(9) Hafner, W. D.; Carlson, D. L.; Hites, R. A. Influence of local human population on atmospheric polycyclic aromatic hydrocarbon concentrations. *Environ. Sci. Technol.* **2005**, *39*, 7374–7379.

(10) Garban, B.; Blanchoud, H.; Motelay-Massei, A.; Chevreuil, M.; Ollivon, D. Atmospheric bulk deposition of PAHs onto France: trends from urban and remote Sites. *Atmos. Environ.* **2002**, *36*, 354A-359A.

(11) Bhatt, B. P.; Sachan, M. S. Firewood consumption along an altitudinal gradient in mountain villages of India. *Biomass Bioenergy* **2004**, *27*, 69–75.

(12) MathWorks. *Using MATLAB Ver. 6*; The MathWorks Inc.: Natick, MA, 2002.

(13) National Bureau of Statistics of China. *China Statistical Yearbook for Regional Economy 2004*; China Financial and Economic Publishing House: Beijing, 2005.

(14) Bureau of Statistics of Taiwan. http://www.stat.gov.tw.

(15) Population Census Office of State Council. *China 2000 County Population Census*; China Statistic Press: Beijing, 2003.

(16) Institute of Geographical Sciences and Natural Resources Research, Chinese Academy of Sciences. http://www.naturalresources.csdb.cn.

(17) Wang, X. P.; Mauzerall, D. L.; Hu, Y. T.; Russell, A. G.; Larson, E. D.; Woo, J. H.; Streets, D. G.; Guenther, A. A high-resolution emission inventory for eastern China in 2000 and three scenarios for 2020. *Atmos. Environ.* **2005**, *39*, 5917–5933.

(18) Reddy, M. S.; Venkataraman, C. Inventory of aerosol and sulphur dioxide emissions from India. *Atmos. Environ.* **2002**, *36*, 677–697.

(19) National Bureau of Statistics of China. *China Statistical Yearbook 2004*; China Statistics Press: Beijing, 2004.

(20) State Forestry Administration of China. *China Forestry Statistical Yearbook 2003*; China Forestry Press: Beijing, 2004.

(21) Feng, X. B.; Sommar, J.; Lindqvist, O.; Hong, Y. T. Occurrence, emissions and deposition of mercury during coal combustion in the province Guizhou, China. *Water, Air, Soil Pollut.* **2002**, *139*, 311–324.

(22) Census and Statistics Department of Hong Kong. http://censtatd.gov.hk.

(23) International Energy Agency. *Energy Balances of non-OECD countries, 2002~2003*; Organisation for Economic Co-operation and Development: Paris, 2005.

(24) National Bureau of Statistics of China. *China Energy Statistical Yearbook 2004*; China Statistics Press: Beijing, 2005.

(25) Catania, P. China's rural energy system and management. *Appl. Energy* **1999**, *64*, 229–240.

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