



Residential coal combustion as a source of primary sulfate in Xi'an, China

Qili Dai^a, Xiaohui Bi^{a,*}, Wenbin Song^b, Tingkun Li^a, Baoshuang Liu^a, Jing Ding^a, Jiao Xu^a, Congbo Song^a, Naiwang Yang^b, Benjamin C. Schulze^c, Yufen Zhang^a, Yinchang Feng^a, Philip K. Hopke^{d,e}

^a State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control & Center for Urban Transport Emission Research, College of Environmental Science and Engineering, Nankai University, Tianjin, 300350, China

^b Xi'an Environmental Monitoring Station, Xi'an, Shaanxi, 710054, China

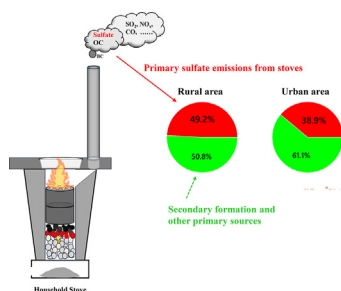
^c Department of Civil and Environmental Engineering, Rice University, Houston, TX, 77005, USA

^d Center for Air Resources Energy and Science, Clarkson University, Potsdam, NY, 13699, USA

^e Department of Public Health Sciences, University of Rochester School of Medicine and Dentistry, Rochester, NY, 14642, USA



GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Residential coal combustion
Sulfate
OC
Particulate matter
Source apportionment
Rural area

ABSTRACT

Sulfate is a major component of atmospheric fine particulate matter in the troposphere. Globally, observed sulfate concentrations are generally high in summer and low in winter. Current air quality models fail to reproduce high winter sulfate concentrations observed during substantial pollution episodes in northern China. From ambient measurement data, it was reported that contrary to current belief, sulfate, that is normally considered as a secondary species, was actually largely primary. The present study presents direct evidence of primary sulfate emissions from residential coal combustion (RCC) by testing particulate matter (PM) emissions from briquettes and chunk coal burned in a household stove. Sulfate accounted for $16.6 \pm 7.7\%$ and $29.2 \pm 8.7\%$ of $PM_{2.5}$ mass emissions from this stove burning coal briquettes and chunk coal, respectively. Using the 2014 emissions inventory, 1215 tons of PM_{10} sulfate were estimated to have been emitted from RCC in Xi'an, a megacity that continually experiences severe PM pollution in northern China. The RCC contribution was also estimated using a constrained positive matrix factorization in which RCC accounted for averages of 26% and 32% of ambient $PM_{2.5}$ mass during the heating season at urban and rural sites in Xi'an, respectively. The winter contributions were higher than that during non-heating season. $PM_{2.5}$ emissions from RCC during heating season were 1.5–4.0 times those during non-heating season for the urban sites, and 2.5 to 6.8 times those for the rural sites. Thus, severe PM pollution in rural areas resulted from intense household coal combustion for space heating. Primary sulfate from RCC was responsible for a large fraction of ambient sulfate during heating season, on average contributing 38.9% and 49.2% of ambient sulfate mass in $PM_{2.5}$ at urban sites and rural sites, respectively. These results highlight the fact that RCC is an important primary source of atmospheric sulfate

* Corresponding author.

E-mail address: bixh@nankai.edu.cn (X. Bi).

<https://doi.org/10.1016/j.atmosenv.2018.10.002>

Received 12 July 2018; Received in revised form 10 September 2018; Accepted 4 October 2018

Available online 05 October 2018

1352-2310/© 2018 Elsevier Ltd. All rights reserved.

during the heating season, and provides information that will improve air quality models and support development of more effective abatement strategies for atmospheric particles.

1. Introduction

Sulfate is a major component of atmospheric fine particulate matter typically with aerodynamic diameters less than 1.0 μm (PM_{10}) and imposing significant impacts on the environment, human health, and climate change (Seinfeld and Pandis, 2006; Zhang et al., 2015). Previous measurements indicated that sulfate in China, Europe, and North America was generally the second/third largest component of $\text{PM}_{2.5}$ at urban areas, and contributed more at regional and background areas (Huang et al., 2014; Putaud et al., 2010; Zhang et al., 2012c; Zheng et al., 2016). On average, sulfate accounted for $15 \pm 6\%$ and $20 \pm 5\%$ of the observed $\text{PM}_{2.5}$ mass in north and south China during 2005–2014, respectively (Zhang et al., 2017a). Thus, understanding the sources and formation mechanisms of sulfate is critical for reducing particulate pollution and its impacts.

Air quality models, including the Comprehensive Air quality Model with extensions (CAMx), the Community Multiscale Air Quality (CMAQ), and the GEOS-Chem model, etc. fail to capture the high $\text{PM}_{2.5}$ and sulfate concentrations in winter high pollution periods. The models underestimate sulfate concentrations compared to observed sulfate values (Astitha et al., 2008; Cheng et al., 2016; Luo et al., 2011; Wang et al., 2014b, 2016; Zhang et al., 2012b; Zheng et al., 2015). The performance of these models is affected by many factors including biased emissions estimates due to different base years for the emissions and the simulation, bias in meteorological predictions, or lack of sufficient chemical production mechanisms. The origin of the differences between the modeled and observed sulfate is still unclear and calls for critical examination and explanation.

To improve model performance, focus has been placed on the sulfate formation mechanisms in the model. The standard model simulation assumes that sulfate is formed through gas phase oxidation of SO_2 by hydroxyl radicals (OH), and several aqueous phase chemical pathways primarily involving hydrogen peroxide (H_2O_2) and ozone (O_3) in cloud or fog water (Cheng et al., 2016; Sarwar et al., 2013; Wang et al., 2014b), and heterogeneous reactions of SO_2 catalyzed by iron and manganese on the surface of dust particles (Wang et al., 2014b; Zheng et al., 2015). Given the low levels of photochemical activity during winter with low temperatures and reduced actinic fluxes, gas phase oxidation of SO_2 by photochemical oxidants cannot fully reproduce the observed sulfate concentrations. New sulfate formation hypotheses have been intensively investigated to reduce the model discrepancies. For example, the heterogeneous uptake of SO_2 on deliquesced aerosols associated with high relative humidity conditions during haze period was found to be an important sulfate formation pathway compared to simulations with combined adjustments in emissions and meteorology only (Wang et al., 2014b). Recent studies have suggested that reactive nitrogen chemistry during the haze periods in the presence of high relative humidity and sufficient neutralizing NH_3 may be responsible for the missing sulfate (Cheng et al., 2016; He et al., 2014; Ma et al., 2018; Wang et al., 2016). Gas phase oxidation of SO_2 by Stabilized Criegee Intermediates has also been reported as another potential sulfate formation pathway (Sarwar et al., 2013).

These studies have improved our understanding of urban sulfate formation during haze episodes. However, it should be noted that the gap between simulations and observations not only exists during haze periods, but in clean periods though the bias is comparatively much smaller (Wang et al., 2014b). Thus, it is likely there are missing sources of winter sulfate. Additionally, modeled PM concentrations in rural areas are generally more substantially underestimated compared to urban sites (Wang et al., 2014a), again suggesting there are important

missing sulfate sources in rural areas.

In addition to forming in the atmosphere via gas or aqueous phase oxidation (secondary formation), particulate sulfate can be emitted directly from emission sources (primary emissions) that are often overlooked. The objective of this study was to further investigate a generally unrecognized source of primary sulfate previously found in our ambient measurements and to assess RCC as a possibly important primary source of winter sulfate in Xi'an, China (Dai et al., 2018). Recently, Liu et al. (2016) found that combustion of household fuels was a major and underappreciated source of air pollutants during the heating season in China (typically November 15 to the following March 15). Similar results were reported in several other studies (Liao et al., 2017; Xue et al., 2016; Zhang et al., 2017b). Many studies have focused on SO_2 , NO_x , CO, CO_2 , PM, organic carbon (OC), black carbon (EC), polyaromatic hydrocarbons (PAHs), and volatile organic compounds (VOCs), non-methane hydrocarbons (NMHCs), and carbonyls emissions from household stoves (Chen et al., 2004, 2005; Li et al., 2017; Liu et al., 2017; Shen et al., 2010; Xue et al., 2016). However, despite their importance (Hopke, 2016), source compositional profiles for residential coal combustion have not been routinely measured. Measured source profiles for RCC have rarely been reported in China (Zhang et al., 2012a). The present study presents evidence from source testing and ambient measurements that demonstrates that primary particulate sulfate from RCC is a major and overlooked source of ambient sulfate. Air quality and human health in developing areas would benefit substantially from reductions in residential coal combustion emissions, especially in rural areas and for low-income families.

2. Background of particulate sulfate formation in household stoves

Sulfur (S) in coal exists as organic and inorganic (principally pyrite) components that can be oxidized to gaseous SO_2 and SO_3 during coal combustion. SO_3 can be produced through chemical reactions in the fuel bed due to the decomposition of mineral matter in coal, or by the reaction in the flame between SO_2 and atomic oxygen (Srivastava et al., 2004).

The thermal decomposition of iron pyrites in coal leads to:



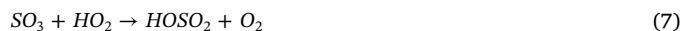
In flames, the primary reaction that causes SO_3 formation is (Coykendall, 1962):



Atomic oxygen is derived from reactions as following (Coykendall, 1962):



Reaction (4) proceeds rapidly near the combustion zone in the presence of super-equilibrium concentrations of oxygen atoms (Srivastava et al., 2004). The depletion of SO_3 near flames occurs primarily via:



Other reactions result in the formation and consumption of SO_3 near

Download English Version:

<https://daneshyari.com/en/article/11262737>

Download Persian Version:

<https://daneshyari.com/article/11262737>

[Daneshyari.com](https://daneshyari.com)