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Views & Comments

Coordinated Control of Fine-Particle and Ozone Pollution by the Substantial Reduction of Nitrogen Oxides

Biwu Chu [a,b,c], Yan Ding [b,d], Xiang Gao [e], Junhua Li [f], Tingyu Zhu [b,g], Yunbo Yu [a,b,c], Hong He [a,b,c]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[c] University of the Chinese Academy of Sciences, Beijing 100049, China
[d] Chinese Research Academy of Environmental Sciences, Beijing 100012, China
[e] State Environmental Protection Engineering Center for Coal-Fired Air Pollution Control, Zhejiang University, Hangzhou 310027, China
[f] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China
[g] National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

1. Introduction

In recent years, the air quality in China has improved significantly. In many cities, however, the concentration of fine particulate matter ($PM_{2.5}$) remains higher than the secondary-level national ambient air quality standard (NAAQS level-2, 35 $\mu g\cdot m^{-3}$, GB3095–2012 [1]) and much higher than the first-level NAAQS (15 $\mu g\cdot m^{-3}$, GB3095–2012 [1]) and the World Health Organization (WHO) air quality guidelines (5 $\mu g\cdot m^{-3}$). In addition, heavy haze pollution still occurs, especially in wintertime. The concentration of ozone (O_3) has increased in many regions of China. Indeed, O_3 has become the major air pollutant after $PM_{2.5}$, especially in summertime. Thus, the coordinated control of $PM_{2.5}$ and O_3, as part of the 14th Five-Year Plan for Economy and Social Development of the People's Republic of China, remains a considerable challenge.

2. Substantial reduction of nitrogen oxides for the effective coordinated control of $PM_{2.5}$ and O_3

2.1. Negative correlation between $PM_{2.5}$ and O_3

Highly complex interactions occur under elevated concentrations of both $PM_{2.5}$ and O_3, which affect radiation flux, quench free radicals, and drive oxidation, among other examples. In most regions of China with high $PM_{2.5}$ levels, especially in northern China, the temporal variations of $PM_{2.5}$ and O_3 (i.e., the hourly average concentrations) are negatively correlated in both wintertime and summertime. The same thing has occurred in the interannual variations of $PM_{2.5}$ and O_3 in recent years [2]. This relationship has only disappeared in a few regions of southern China, such as the Pearl River Delta, where the concentration of $PM_{2.5}$ is close to NAAQS level-2, which is also the WHO first-stage interim target. In every city of China, $PM_{2.5}$ and O_3 vary in opposite directions, unless the concentration of $PM_{2.5}$ falls below a certain threshold (e.g., 50 $\mu g\cdot m^{-3}$) [2], as indicated by the correlation coefficients of $PM_{2.5}$ and O_3 in Fig. 1. Therefore, reducing the concentration of $PM_{2.5}$ to the threshold value in order to disrupt the negative correlation is an essential precondition for the coordinated control of $PM_{2.5}$ and O_3.

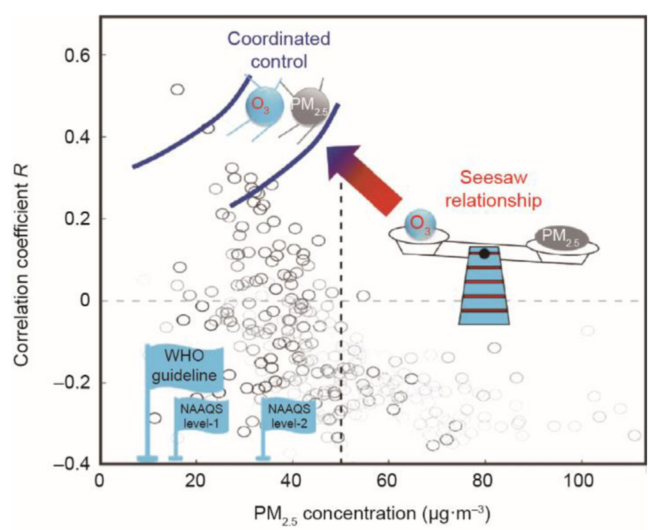

Fig. 1. Disrupting the negative correlation (a "seesaw relationship") between $PM_{2.5}$ and O_3 to achieve coordinated control of both pollutants. Circles mark the $PM_{2.5}$ concentration and the correlation coefficient between $PM_{2.5}$ and O_3 in individual cities in China. In the right region of the figure, where the concentration of $PM_{2.5}$ is high (e.g., > 50 $\mu g\cdot m^{-3}$), the correlation coefficient between $PM_{2.5}$ and O_3 is always negative in these cities. In comparison, in the upper left region of the figure, where the concentration of $PM_{2.5}$ is low (e.g., < 50 $\mu g\cdot m^{-3}$), the correlation coefficient between $PM_{2.5}$ and O_3 can be positive, so coordinated control of both pollutants is possible in these cities. Detailed information on the methods and data sources used to calculate the correlation coefficients can be found in our previous study [2]. Reproduced from Ref. [2] with permission of American Chemical Society, © 2020.

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2.2. Reduction of nitrogen oxides for the effective control of $PM_{2.5}$

From 2013 to 2019, the concentrations of $PM_{2.5}$ and sulfur dioxide (SO_2) in 74 key Chinese cities decreased by 47% and 75%, respectively, while the concentration of nitrogen dioxide (NO_2) only decreased by 23% [3]. Thus, nitrogen oxides (NO_x) emissions remain poorly controlled, which limits further decreases in $PM_{2.5}$. NO_x convert to nitrate, which is the most abundant chemical component of $PM_{2.5}$ in many cities [4]. Furthermore, high concentrations of NO_x result in a high atmospheric oxidation capacity for heterogeneous and aqueous phase reactions [5–7], which is an important driving force for the growth of $PM_{2.5}$. According to the analysis of the observational data from the China National Environmental Monitoring Center (CNEMC), the sensitivity of $PM_{2.5}$ to NO_2 is much higher than its sensitivity to SO_2 (Fig. 2). For example, in China, research has indicated that a reduction of 1 $\mu g{\cdot}m^{-3}$ NO_2 will reduce $PM_{2.5}$ much more than a reduction of 1 $\mu g{\cdot}m^{-3}$ SO_2 [2]. In 2020, the concentration of NO_2 decreased significantly during the coronavirus disease 2019 (COVID-19) lockdown [8]. Although the concentrations of SO_2 and carbon monoxide (CO) did not markedly decrease, the concentration of $PM_{2.5}$ decreased significantly and showed highly similar spatial and temporal distribution characteristics with the decrease in NO_2 [8]. This finding indicates the high effectiveness of NO_x reduction in $PM_{2.5}$ control.

2.3. The feasibility of substantial NO_x reduction for the coordinated control of O_3

From 2013 to 2019, the concentration of O_3 in 74 key Chinese cities increased by 29% [3]. Atmospheric O_3 is mainly generated via photochemical reactions between NO_x and volatile organic compounds (VOCs) and is mainly a problem during summer conditions. As a result, controlling O_3 requires the control of these two main precursors. There is a significant nonlinear relationship between O_3 and the emissions of NO_x and VOCs [3,9]. Although O_3 formation is usually controlled by NO_x concentration on a regional scale, it is sensitive to VOCs in most urban areas of China. However, it is usually very difficult to achieve a substantial emission reduction of VOCs in a short time. VOCs emitted by biogenic sources are natural processes and are difficult to regulate. Moreover, anthropogenic emissions of VOCs are highly complex and dispersed, so their effective control remains a great challenge. In a VOC-controlled O_3 formation regime, a slight reduction in NO_x emissions may cause an increase in O_3, whereas a substantial reduction in NO_x will change the VOC-controlled regime to a NO_x-controlled regime and thus effectively reduce O_3. In the United States, the historical control of O_3 supports the reduction of NO_x emissions: In the early stages, the California Government initially attempted to control VOCs, but the effect on O_3 was limited; after increasing NO_x emission control efforts, however, O_3 pollution gradually decreased [10], indicating the key role of reducing NO_x in O_3 pollution control [9]. The change in air quality during the COVID-19 lockdown in early 2020 in China also provides solid evidence. During the initial lockdown, the slight decrease in NO_2 and $PM_{2.5}$ concentrations resulted in an obvious increase in O_3 concentrations. However, under the strictest lockdown conditions, the NO_2 concentration decreased by about 70% in some regions of China, which resulted in a significant reduction in $PM_{2.5}$ and a cessation of the increase in O_3 [8]. These results indicate that strengthening the reduction of NO_x emissions is an effective and feasible measure for the coordinated control of $PM_{2.5}$ and O_3 in China. This conclusion is also supported by modeling studies. For example, in a case study in the Beijing–Tianjin–Hebei (BTH) region, a reduction in NO_x emissions of greater than 60% was proposed in order to ensure the effectiveness of $PM_{2.5}$ and O_3 control [11]. Recently, WHO updated the global air quality guidelines. The new guidelines recommend a much lower level (10 $\mu g{\cdot}m^{-3}$) for NO_2 concentration than 2005 guidelines (40 $\mu g{\cdot}m^{-3}$). The updates indicate an international consensus on substantial NO_x reduction for further improvement of air quality and protection of human health.

3. Nitrogen oxides: Key pollution precursors with high reduction potential

NO_x are the key precursors of $PM_{2.5}$ and O_3 pollution and demonstrate high reduction potential in China. They are mainly emitted from stationary combustion plants and internal combustion engines of transportation vehicles. Therefore, reducing NO_x emissions is also highly consistent with the current carbon peaking

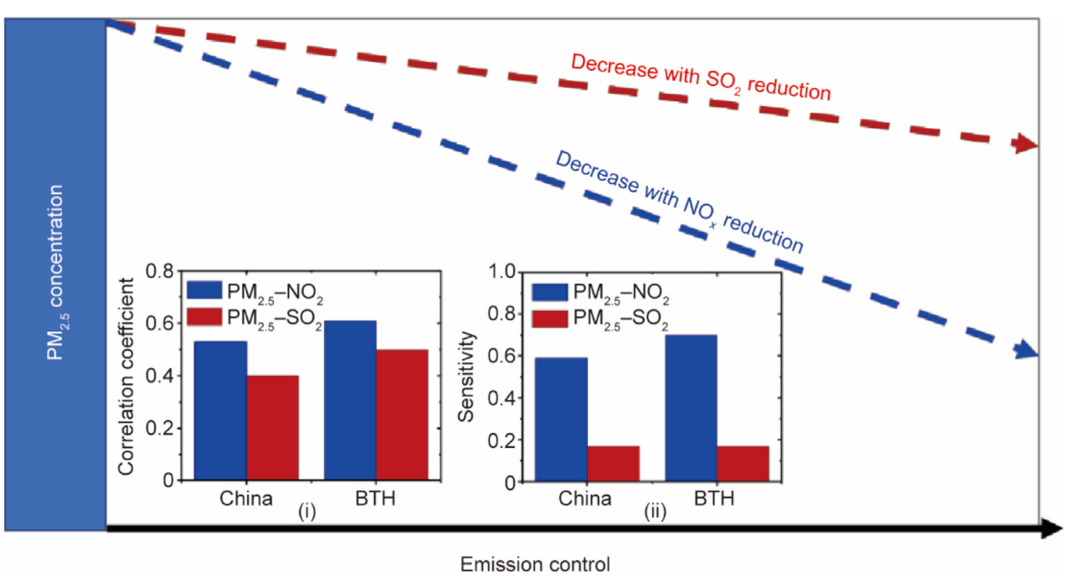

Fig. 2. The emission control strategy in China and Beijing–Tianjin–Hebei (BTH) region. (i) Correlations between $PM_{2.5}$ and NO_2 and SO_2; (ii) sensitivity of $PM_{2.5}$ to NO_2 and SO_2. The sensitivity of $PM_{2.5}$ to NO_2 and SO_2 is the increase or decrease of $PM_{2.5}$ ($\mu g{\cdot}m^{-3}$) with NO_2 and SO_2 concentration changes of 1 $\mu g{\cdot}m^{-3}$, respectively.

and carbon neutralization policies. At present, the selective catalytic reduction (SCR) of NO_x by NH_3 (NH_3-SCR) technique is widely applied in coal-fired power plants, satisfying the ultra-low NO_x emission limit [12]. However, for NO_x reduction in non-electric industries, such as the steel, nonferrous metal, cement, glass, and ceramic industries, the NH_3-SCR technique requires improvement, such as low-temperature activity and a tolerance to sulfur. Thus, different denitrification technologies need to be developed.

Meanwhile, remarkable progress has been made in NO_x reduction from automotive exhausts [13]. For example, using a three-way catalytic technique, NO_x, hydrocarbons, and CO can be efficiently removed from gasoline vehicle exhausts. The SCR of NO_x by urea (urea-SCR) has also been successfully developed for diesel vehicle NO_x emission control [14]. Under real driving conditions, however, NO_x emissions from diesel vehicles equipped with the urea-SCR system often exceed the standard limits. Firstly, the messages of on-board diagnostic (OBD) systems regarding NO_x emissions could be artificially shielded. Of course, this illegal situation is being corrected through the technical means of online monitoring. Secondly, certain diesel vehicles (e.g., buses and garbage trucks) often run at low speed. In this case, the urea-SCR system cannot operate efficiently. At present, urea-SCR catalyst with wide temperature window is being developed to solve this technical problem. Finally, if an unqualified urea solution (commonly known as AdBlue) is used in the SCR system to reduce cost—for example, urea solution with a low concentration of urea and/or containing impurities—it results in NO_x emissions that exceed the standard limits. In addition, the domestic technologies for engine control systems and high-pressure common rail injection systems are still relatively undeveloped, which further impedes the implementation of China VI emission standards for diesel heavy-duty vehicles and the formulation of the next stage of emission standards. Thus, the actual effectiveness of NO_x reducing technology is still far from perfect, leaving considerable room for improvement. Furthermore, China's targets are to achieve peak carbon dioxide emissions before 2030 and carbon neutrality by 2060. These targets require a great change in the energy structure, which will fundamentally solve the NO_x emission problem in the future. For example, the number of electric vehicles is increasing rapidly in China. With electricity being generated from sustainable energy, a significant reduction in both NO_x and VOC emissions from vehicles can be expected [9].

4. Suggestions for substantial reductions in NO_x

4.1. Accelerating research and development of high-efficiency NO_x control technologies for various industrial furnaces

To achieve ultra-low NO_x emissions in industries other than thermal power plants, great effort should be devoted to the development of high-efficiency denitrification technologies with low cost and the promotion of large-scale application. These technologies include low-/intermediate-temperature SCR technologies with high efficiency and stability [15] and selective non-catalytic reduction (SNCR) combined with SCR and oxidative denitrification [16]. Moreover, to achieve impactful abatement of NO_x and the simultaneous reduction of carbon dioxide (CO_2) emissions, embedded denitrification technologies that suit the temperature distribution inside furnaces should be developed, which would help to reduce energy input (e.g., coal, gas, and electricity). In addition, for the simultaneous reduction of NO_x and CO_2 emissions in industries with long and multiple manufacturing processes, such as the steel and nonferrous metal industries, the industrial structure should be upgraded by developing clean and short-process smelting, as well as by conducting comprehensive process optimization.

4.2. Formulating ultra-low emission limits and strengthening assessment and supervision for key industries

The formulation of ultra-low emission limits and the development of technological guidelines for NO_x control are urgently needed for non-electric industries such as building materials and nonferrous metals, according to their flue gas characteristics. Comprehensive evaluation after the implementation of ultra-low emission technologies in the iron and steel industry also needs to be strengthened, and techno-economic analysis of different ultra-low NO_x emission technologies in such industries should be emphasized [17,18]. In addition, clarifying the benefits and shortcomings of such technologies should provide an important reference for proposing and improving ultra-low NO_x emission technologies and schemes suitable for different industries. Finally, in combination with China's economic development and energy consumption trends, it is necessary to predict total NO_x emissions and their distribution by industry in the future, and to evaluate the reduction potential of NO_x emissions in various industries and the environmental impacts induced by NO_x reduction.

4.3. Promoting the research and development of key technologies for diesel engine emission control, and enhancing joint management and control of vehicle fuel

Firstly, efforts must be made to advance engine control systems, high-pressure common rail injection systems, turbocharger systems, and after-treatment catalysts and to establish independent and controllable diesel engine emission control technology chains [19]. Secondly, the next stage of national emission standards for diesel heavy-duty vehicles, off-road diesel engines, and vessels should be formulated as soon as possible. The implementation of these standards should encourage the adoption of new technologies to further reduce diesel engine exhaust emissions. Furthermore, more stringent standards for diesel, additives, AdBlue, and lubricating oil should be formulated and implemented to ensure the efficient and stable operation of diesel engines. Thirdly, the research and development of remote online diagnostic systems, remote sensing, and portable emission measurement technologies should be promoted. By integrating these advanced technologies, an intelligent digitized system can be developed for the supervision and management of in-use vehicle emission control. With this complete system, the closed-loop control of remote real-time vehicle emission monitoring, inspection, and maintenance can be achieved.

Acknowledgments

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References

[1] Ministry of Environmental Protection of the People's Republic of China, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China. GB3095–2012: Ambient air quality standards. Chinese standard. Beijing: China Environmental Science Press; 2012.

[2] Chu B, Ma Q, Liu J, Ma J, Zhang P, Chen T, et al. Air pollutant correlations in China: secondary air pollutant responses to NO_x and SO_2 control. Environ Sci Technol Lett 2020;7(10):695–700.

[3] Professional Committee on Ozone Pollution Control of Chinese Society for Environmental Science. [Blue book on Ozone Pollution Control in China (2020)]. Nanjing: Professional Committee on Ozone Pollution Control of Chinese Society for Environmental Science; 2020. Chinese.

[4] Li H, Cheng J, Zhang Q, Zheng B, Zhang Y, Zheng G, et al. Rapid transition in winter aerosol composition in Beijing from 2014 to 2017: response to clean air actions. Atmos Chem Phys 2019;19(17):11485–99.

[5] Liu C, Ma Q, Liu Y, Ma J, He H. Synergistic reaction between SO_2 and NO_2 on mineral oxides: a potential formation pathway of sulfate aerosol. Phys Chem Chem Phys 2012;14(5):1668–76.

[6] He H, Wang Y, Ma Q, Ma J, Chu B, Ji D, et al. Mineral dust and NO_x promote the conversion of SO_2 to sulfate in heavy pollution days. Sci Rep 2014;4(1):4172.

[7] Cheng Y, Zheng G, Wei C, Mu Q, Zheng B, Wang Z, et al. Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. Sci Adv 2016;2(12):1601530.

[8] Chu B, Zhang S, Liu J, Ma Q, He H. Significant concurrent decrease in $PM_{2.5}$ and NO_2 concentrations in China during COVID-19 epidemic. J Environ Sci 2021;99:346–53.

[9] Erickson LE, Newmark GL, Higgins MJ, Wang Z. Nitrogen oxides and ozone in urban air: a review of 50 plus years of progress. Environ Prog Sustain Energy 2020;39(6):e13484.

[10] Reactivity Research Work Group Policy Team. VOCs reactivity policy white paper. Report. Washington, DC: US Environmental Protection Agency; 1999 Oct 1.

[11] Xing J, Ding D, Wang S, Zhao B, Jang C, Wu W, et al. Quantification of the enhanced effectiveness of NO_x control from simultaneous reductions of VOC and NH_3 for reducing air pollution in the Beijing–Tianjin–Hebei region. China, Atmos Chem Phys 2018;18(11):7799–814.

[12] Dai H, Ma D, Zhu R, Sun B, He J. Impact of control measures on nitrogen oxides, sulfur dioxide and particulate matter emissions from coal-fired power plants in Anhui Province, China. Atmosphere 2019;10(1):35.

[13] Liu Y, Tan J. Green traffic-oriented heavy-duty vehicle emission characteristics of China VI based on portable emission measurement systems. IEEE Access 2020;8:106639–47.

[14] Granger P, Parvulescu VI. Catalytic NO_x abatement systems for mobile sources: from three-way to lean burn after-treatment technologies. Chem Rev 2011;111(5):3155–207.

[15] Wang D, Luo J, Yang Q, Yan J, Zhang K, Zhang W, et al. Deactivation mechanism of multipoisons in cement furnace flue gas on selective catalytic reduction catalysts. Environ Sci Technol 2019;53(12):6937–44.

[16] Wang D, Chen Q, Zhang X, Gao C, Wang B, Huang X, et al. Multipollutant control (MPC) of flue gas from stationary sources using SCR technology: a critical review. Environ Sci Technol 2021;55(5):2743–66.

[17] Li Q, Hou Y, Han X, Wang J, Liu Y, Xiang N, et al. Promotional effect of cyclic desulfurization and regeneration for selective catalytic reduction of NO by NH_3 over activated carbon. J Clean Prod 2020;249:119392.

[18] Cai M, Liu X, Zhu T, Zou Y, Tao W, Tian M. Simultaneous removal of SO_2 and NO using a spray dryer absorption (SDA) method combined with O_3 oxidation for sintering/pelleting flue gas. J Environ Sci 2020;96:64–71.

[19] Shan Y, Du J, Zhang Y, Shan W, Shi X, Yu Y, et al. Selective catalytic reduction of NO_x with NH_3: opportunities and challenges of Cu-based small-pore zeolites. Natl Sci Rev 2021;8:nwa010.