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Exploring chemical changes of the haze pollution during a recent round of COVID-19 lockdown in a megacity in Northeast China

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HIGHLIGHTS

- A recent round of lockdown in Harbin led to changes in primary emissions.
- Generally uninterruptible coal combustion resulted in relatively stable emissions.
- Stay-at-home orders considerably reduced vehicle exhaust emissions.
- Ozone and secondary aerosol were enhanced in Harbin’s frigid air during lockdown.
- Photochemistry-related aqueous-phase reactions were evident during lockdown.

GRAPHICAL ABSTRACT

ABSTRACT

COVID-19 rebounded in China in January 2021, with Heilongjiang as one of the worst-affected provinces. This resulted in a new round of lockdown in Harbin, the capital city of Heilongjiang, from 20 January to 22 February of 2021. A field campaign was conducted to explore the responses of haze pollution in Harbin to the lockdown. Levoglucosan was used to reflect biomass burning emissions, while the molar ratio of sulfur (the sum of sulfur dioxide and sulfate) to nitrogen (the sum of nitrogen dioxide and nitrate), i.e., \( R_{S/N} \), was used as an indicator for the relative importance of coal combustion and vehicle emissions. Based on a synthesis of the levoglucosan and \( R_{S/N} \) results, reference period was selected with minimal influences of non-lockdown-related emission variations. As indicated by the almost unchanged sulfur dioxide concentrations, coal combustion emissions were relatively stable throughout the lockdown and reference periods, presumably because the associated activities, e.g., heating supply, power generation, etc., were usually uninterruptible. On the other hand, as suggested by the increase of \( R_{S/N} \), vehicle emissions were considerably reduced during lockdown, likely due to the stay-at-home orders. Compared to results from the reference samples, the lockdown period exhibited higher levels of ozone and various indicators for secondary aerosol formation, pointing to an enhancement of secondary pollution. In addition, photochemistry-related reactions in aqueous phase appeared to be present during the lockdown period, which have not been reported in the frigid atmosphere over Northeast China.

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1. Introduction

The novel coronavirus discovered in Wuhan, China in December 2019, i.e., COVID-19 (Zhu et al., 2020), has become a global concern due to its world-wide dissemination. Strict measures were implemented in China during late January and late February 2020 to control the spread of the disease. These measures, e.g., stay-at-home orders, markedly reduced primary emissions of air pollutants, especially nitrogen dioxide (NO₂; Bauwens et al., 2020; Le et al., 2020). A variety of studies were conducted to investigate the responses of fine particulate matter (PM$_{2.5}$) and ozone pollution to the emission reduction. These studies most frequently relied on air quality data from the China National Environmental Monitoring Center (CNEMC) and air quality models, which typically suggested a nationwide increase of ozone during lockdown (Shi and Brasseur, 2020; Venter et al., 2020; Zhao et al., 2020; Shi et al., 2021). On the other hand, the stay-at-home orders largely limited field observation of PM$_{2.5}$ compositions, while results from a limited number of cities such as Wuhan (Zheng et al., 2020), Beijing (Lv et al., 2020; Sun et al., 2020), Shanghai (Chang et al., 2020) and Hangzhou (Liu et al., 2020) pointed to enhanced secondary aerosol formation during lockdown.

In January 2021, COVID-19 rebounded in several regions in China. During this round of outbreak, Heilongjiang was one of the worst-affected provinces, and lockdown was implemented in its capital city, Harbin, from 20 January to 22 February of 2021. Here we explored the lockdown influence on the air pollution in Harbin, based on a recent field campaign. Harbin differs from other megacities in China by its extremely cold winter (with daily average temperatures down to <−20 °C) and complex emission sources (e.g., coal and biomass burning for heating). Thus, this study helped unfold the interplay between emission and atmospheric chemistry in a frigid environment, which was unique compared to the much more intensively explored megacities such as Beijing and Shanghai.

2. Methods

2.1. Field observation

A total of 194 PM$_{2.5}$ samples (24-h integrated) were collected from 17 October 2020 to 30 April 2021 at an urban site in Harbin. The samples were measured for organic carbon (OC), elemental carbon (EC), levoglucosan (LG) and water-soluble inorganic ions. Reconstructed PM$_{2.5}$ mass was calculated as the sum of organic aerosol (determined as 1.6 × OC), EC and inorganic ions. Six samples collected during the Chinese New Year period were found to be strongly impacted by firework emissions. They were excluded in the following discussions to minimize the interference of primary sulfate and nitrate. Refer to Supporting Information for details on the field measurements.

Hourly air quality data were obtained based on measurement results from the nearest CNEMC site to the filter sampling site (~2 km apart; http://106.37.208.233:20035/). In addition, hourly meteorological data were obtained from Weather Underground (https://www.wunderground.com).

2.2. Thermodynamic and receptor models

Aerosol water content (AWC) and aerosol pH were predicted by ISORROPIA-II using an iteration approach (Liu et al., 2021). Aerosol sources were estimated using EPA’s Positive Matrix Factorization (PMF) model, with time series of OC, EC, LG, chloride, nitrate, sulfate and ammonium as inputs. A total of five factors were resolved (Fig. S1). Two of them were attributed to primary biomass burning (BB) emissions, another two factors were characteristic of secondary aerosols and the remaining one was considered primary emissions from non-BB sources. Details on the ISORROPIA-II and PMF analyses are provided in Supporting Information.

2.3. Diagnostic ratio for non-BB sources

The non-BB sources during heating season in Harbin could be generally separated into two categories, i.e., vehicle exhausts (e.g., from gasoline cars and diesel trucks) and coal combustion (heating supply, power generation, industrial production, etc.). Both categories were major contributors to NO$_2$ and thus nitrate, whereas the vast majority of sulfur dioxide (SO$_2$) and thus sulfate was from the latter (Zheng et al., 2018). Here we used the molar ratio of sulfur (the sum of SO$_2$ and sulfate) to nitrogen (the sum of NO$_2$ and nitrate), i.e., R$_{S/N}$, as an indicator for the relative importance of coal combustion and vehicle emissions. As shown in Fig. 1a, R$_{S/N}$ tended to decrease with increasing temperature, which could be mainly attributed to the fact that a less amount of coal was consumed for heating as the weather became warmer.

3. Results and discussion

3.1. Identification of the reference period

To isolate the effects of lockdown on haze pollution in Harbin, the reference samples should be selected such that any difference between the lockdown and reference periods could be primarily traced back to the COVID-19 control measures. As shown in Fig. 1a, a common feature of the lockdown period was that the daily average temperatures stayed below −6 °C, i.e., the lockdown occurred within the relatively cold segment of this study. Thus, the reference samples were selected as those collected at <−6 °C during the non-lockdown period (N = 70), with the majority of them from 63 successive days before the lockdown (starting from 19 November 2020). A benefit of this classification approach was that the influence of temperature-dependent variation of heating-induced coal combustion emissions could be largely reduced. Another benefit was that the influence of agricultural fires could also be minimized. This was because all samples characterized by elevated LG to OC ratios, which were typically associated with intensive fire hotspots (Fig. S2) and consequently pointed to open burning activities in Harbin and the surrounding regions, gathered in the “other” samples collected at temperatures >−6 °C (Fig. 1b).

3.2. Comparison of the lockdown and reference periods

The lockdown and reference periods experienced similar levels of temperature (averaging −16.1 ± 5.3 and −16.6 ± 4.8 °C, respectively; Fig. S3a) and relative humidity (RH; averaging 76 ± 7% for both cases; Fig. S3b). SO$_2$ concentrations were also comparable between the two periods, whereas R$_{S/N}$ differed substantially with higher values during lockdown (Fig. 1c and d). For example, as much as 48% of the lockdown samples showed relatively high R$_{S/N}$ values of above 0.55, compared to a corresponding fraction of only 29% for the reference samples. The most likely explanation for the almost unchanged SO$_2$ but increased R$_{S/N}$ during lockdown was that the COVID-19 control measures mainly reduced vehicle emissions, but did not impact coal combustion emissions significantly (Lian et al., 2020). The lockdown-induced reduction in vehicle emissions was within expectation, since people were required or advised to stay home, and travel (which frequently relied on gasoline cars) was largely restricted. On the other hand, coal combustion activities such as those for heating supply, power generation and some industrial processes were usually uninterruptible (Wang et al., 2020; Chu et al., 2021; Yuan et al., 2021), which should be responsible for the relative stable coal combustion emissions throughout the lockdown and reference periods.

The discussions above were supported by the different EC vs. carbon monoxide (CO) relationships derived for the two periods. Linear regression of EC on CO led to a higher slope, i.e., ΔEC/ΔCO, for the lockdown samples compared to that of the reference period (3.02 ± 0.28 vs. 2.00 ± 0.26 μg/mg; Fig. S4). Previous studies typically suggested that ΔEC/ΔCO were substantially lower for gasoline vehicle exhausts than...
that the contribution of vehicle exhausts, especially those from gasoline
lockdown-related increase in cars, was considerably reduced by the COVID-19 control measures. Thus the coal combustion emissions (Wang et al., 2011). Thus the lockdown-related increase in $\Delta EC/\Delta CO$ was in line with the inference that the contribution of vehicle exhausts, especially those from gasoline cars, was considerably reduced by the COVID-19 control measures.

Accompanied with the elevated $R_{SO2}$/OC, ozone concentrations increased by 43% during lockdown (Fig. 1e), with an average of 58.53 $\pm$ 12.89 $\mu$g/m$^3$. For the reference period, the carbonaceous aerosol became more abundant in secondary OC (Fig. S5a–S5b), i.e., SOC determined as the sum of OC masses attributed to the secondary aerosol factors. The fraction of SOC in total OC ($fSOC$) increased from 38% for the reference period to 45% during lockdown (Fig. 1f), and a similar increase was identified for the SOC to EC ratio, SOC/EC (from 2.3 to 3.1). The lockdown period also exhibited higher levels of the sulfur oxidation ratio (SOR; Fig. S5c) and the nitrogen oxidation ratio (NOR; Fig. S5d). Given the comparable RH but different ozone levels between the two periods, the higher $fSOC$, SOC/EC, SOR and NOR during lockdown should be primarily attributed to stronger photochemistry. Regarding these four ratios, in addition, their largest values were observed in the same lockdown sample (Fig. S6), which also showed the maximum ozone (87.22 $\mu$g/m$^3$) and an extremely high AWC (227 $\mu$g/m$^3$, with a pH of 5.3). This coincidence might point to the presence of photochemistry-related reactions in aqueous phase (Kuang et al., 2020), which have not been observed in the frigid atmosphere over Northeast China.

4. Conclusions

The responses of haze pollution to a new round of COVID-19 lockdown were explored in a megacity in Northeast China, based on a six-month long field campaign. Taking together an organic tracer for BB emissions and a diagnostic ratio for non-BB sources, the reference period was selected with minimal influences of non-lockdown-related emission variations, i.e., occurrences of agricultural fires and temperature-driven changes in heating-induced coal combustion. Comparisons to the reference period, $SO2$ were almost unchanged whereas $R_{SO2}$ considerably increased during lockdown, indicating relatively stable coal combustion emissions but reduced vehicle emissions. The elevated $R_{SO2}$ were accompanied with concurrent increases in ozone and various indicators for secondary aerosol formation, pointing to enhanced secondary formation, respectively (Fig. S1). As indicated by (a) and (b), the lockdown and reference samples were collected under relatively cold conditions and were insignificantly impacted by open burning. Thus the comparisons in (c)–(f) would not be complicated by temperature-dependent variation of heating-induced coal combustion or open burning, neither of which was associated with COVID-19 control measures.

Credit author contribution statement

Yuan Cheng: Conceptualization, Methodology, Writing - original draft. Xu-bing Cao, Qin-qin Yu and Ying-jie Zhong: Investigation. Jiu-meng Liu: Methodology, Writing-Review & Editing. Qiang Zhang and Ke-bin He: Validation, Writing-Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.133500.

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