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Exploring the variation of black and brown carbon during COVID-19 lockdown in megacity Wuhan and its surrounding cities, China

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HIGHLIGHTS

• BC decreased by 16–39% during lockdown compared with the same period in 2019.
• Compared with other periods, the minimum contribution (64–86%) mainly from fossil fuel to BC occurred during lockdown.
• Secondary BrC accounts for 75% to the total BrC at 370 nm during the lockdown.
• Secondary BrC absorption was promoted (decreased) under higher humidity (Ox).
• The decline of primary pollutants is more obvious than secondary due to lockdown.

ABSTRACT

Absorbing carbonaceous aerosols, i.e. black and brown carbon (BC and BrC), affected heavily on climate change, regional air quality and human health. The nationwide lockdown measures in 2020 were performed to against the COVID-19 outbreak, which could provide an important opportunity to understand their variations on light absorption, concentrations, sources and formation mechanism of carbonaceous aerosols. The BC concentration in Wuhan megacity (WH) was 1.9 μg m⁻³ during lockdown, which was 24% lower than those in the medium-sized cities and 26% higher than those in small city; in addition, 39% and 16–23% reductions occurred compared with the same periods in 2019 in WH and other cities, respectively. Fossil fuels from vehicles and industries were the major contributors to BC; and compared with other periods, minimum contribution (64–86%) mainly from fossil fuel to BC occurred during the lockdown in all cities. Secondary BrC (BrCsec) played a major role in the BrC light absorption, accounting for 65–77% in...
1. Introduction

A new type of coronavirus disease (COVID-19) has spread rapidly around the globe since late December 2019 (Zhu et al., 2020), and become a major threat to public health. China, the first country hit seriously by the COVID-19 pandemic, has released a number of measures (e.g. lockdown city, shut down commercial activities, restrict travel and stay at home and so on) to control the spread of this disease from late January 2020 (Huang et al., 2020; Wang et al., 2020a). These nationwide restrictions have led to the lowest human activities, resulting in the lowest anthropogenic pollution emissions. The Chinese government has released the Air Pollution Prevention and Control Action Plan in 2013 to reduce air pollution on a national scale (Wang et al., 2020b); however, these restrictions during the COVID-19 breakout offered an unprecedented opportunity to assess the effectiveness of the reduction in anthropogenic emissions on air quality improvement, which will be helpful for optimize future emission control strategies.

Carbonaceous aerosols have profound effects on climate, air quality and human health through their light-absorbing components, e.g. black carbon (BC) and brown carbon (BrC) (Arola et al., 2011; Bond et al., 2013). BC has been considered as secondary global warming contributor due to the most efficient light absorption in the full wavelength range (Bond et al., 2013; Moosmueller et al., 2009; Wang et al., 2019); in addition, BC plays an important role in regional or urban heavy haze events through depressing the development of planetary boundary layer (PBL) (Ding et al., 2016; Ma et al., 2020). Previous study reported that 1.0 μg m\(^{-3}\) BC increase had caused a 1.45% increase in all-cause mortality and a 1.77% increase in cardiovascular mortality (Janssen and Gelencsér, 2006; Kirchstetter and Thatcher, 2012; Saleh et al., 2013). The BC reduction trend in Wuhan was 7.79% yr\(^{-1}\) (0.11 μg m\(^{-3}\)) from 2012 to 2018 (Zheng et al., 2020b), due to emission control measures such as controlling coal consumption, energy structure adjustment and promoting clean energy. Generally, the BC in urban areas was mainly from vehicle emission (Hudda et al., 2020; Zhang et al., 2021); however, the contribution of BC from biomass burning was dominated in rural regions (Xu et al., 2020). BrC is produced not only from primary emissions, but also the secondary formation through various reaction (Gyawali et al., 2009; Zhang et al., 2013); and BrC mainly absorbs lights in both the ultraviolet (UV) and visible bands (Laskin et al., 2015; Moosmueller et al., 2009). Previous study has shown that global radiative forcing contributed by BrC accounts for 25% approximately of the total carbonaceous aerosol light absorption (Feng et al., 2013), and the importance of light absorption of BrC cannot be neglect (Chen et al., 2020a; Chen et al., 2020b; Yan et al., 2018). However, the insight of BC sources and BrC formation were still lack in nationwide reduction during the COVID-19 lockdown period.

Previous studies have reported that primary pollutants and particulate matter in Wuhan (WH) reduced dramatically, whereas O\(_3\) increased during the COVID-19 lockdown period (Lian et al., 2020; Zheng et al., 2020a). Same variation trends were shown in Fig. S1 and Table S1. In this study, one-hour resolution observation was conducted to investigate the characteristics of light absorption carbonaceous aerosol during the COVID-19 outbreak. We defined the before lockdown period as P1 (01–22 January), during lockdown period as P2 (23 January to 10 March), partial recovery phase as P3 (11 March to 07 April) and recovery stage as P4 (08–30 April), and also defined the same periods in 2019. The purposes of this study are to (1) investigate the response of variation, distribution and the source apportionment of BC; (2) determine the BrC optical properties and contribution of the secondary BrC absorption; (3) characterize the diurnal cycle of secondary BrC formation in different periods. This study could provide useful information for policymakers to improve air quality after recovering from the COVID-19 pandemic.

2. Materials and methods

2.1. Sampling sites

The BC sampling sites in this study were conducted at six cities in Hubei Province, which is located in the center of China. We classified these cities into three categories (e.g. megacity, medium-sized city and small city) based on their population (Fig. 1). The sampling site in Wuhan (WH) megacity is located in the Hubei provincial Environmental Monitoring Center (114.39° E, 30.53° N). This study covered four medium-sized cities, including Xiaoan (XG) (113.95° E, 30.91° N), Huangshi (HS) (115.02° E, 30.19° N), Huanggang (HG) (114.89° E, 30.44° N), Xianning (XN) (114.32° E, 28.84° N) and a small city of Ezhou (EZ) (114.90° E, 30.37° N). As shown in Fig. S2, these sites were all located in the urban areas.

2.2. Instruments

The light absorption coefficients of the carbonaceous aerosols were measured by a multi-wavelength aethalometer (Model AE-31, Magee
Scientific, USA) with seven-band (λ = 370, 470, 520, 590, 660, 880 and 950 nm) in six cities. The flow rate and temporal resolution were set 5 L min⁻¹ and 1 h, respectively. A detailed description of the dual-spot theory of the model AE31 aethalometer can be found in Drinovec et al. (2015). More details about the calculation of BC mass concentration and aerosol absorption coefficient are given in Zheng et al. (2019). The data were obtained in six cities in Hubei Province during the COVID-19 outbreak in 2020 and the same periods in 2019.

2.3. Data analysis

2.3.1. BC source apportionment

It is assumed that the total light absorption can be primarily due to light absorption by BC from fossil fuel combustion (BCf) and biomass burning (BCbb). The Aethalometer model was used on BC source apportionment based on the AAE value which varies significantly from different sources. The following equations are used:

\[ \frac{b_{abs}(370)_{ff}}{b_{abs}(880)_{ff}} = \left( \frac{370}{880} \right)^{\text{AAE}_f} \]  

(1)

\[ \frac{b_{abs}(370)_{bb}}{b_{abs}(880)_{bb}} = \left( \frac{370}{880} \right)^{\text{AAE}_b} \]  

(2)

\[ b_{abs}(370) = b_{abs}(370)_{ff} + b_{abs}(370)_{bb} \]  

(3)

\[ b_{abs}(880) = b_{abs}(880)_{ff} + b_{abs}(880)_{bb} \]  

(4)

where the AAEf and AAEb are set 1.0 and 2.0, respectively (Sandradewi et al., 2008). babs(370) and babs(880) are the absorption coefficients at 370 and 880 nm wavelength, respectively.

2.3.2. Separation of BrC and secondary BrC absorption

Assuming that the total babs(λ) was apportioned between BC and BrC absorption (DBCAE(λ) and DBBC(λ), respectively) in the range of near ultraviolet and visible (i.e. λ = 370, 470, 520, 590 and 660 nm). The calculation was followed Lack and Langridge (2013):

\[ b_{abs} \text{BrC}(λ) = b_{abs}(λ) – b_{abs} \text{BC}(λ) \]  

(5)

where absorption babs(λ) is the measured absorption at the short wavelength, BC absorption at λ (babs BC(λ)) can be obtained from babs(880) based on the AAE value of BC (AAEBC) via Shamjad et al. (2015):

\[ b_{abs} \text{BC}(λ) = b_{abs}(880) \times \left( \frac{λ}{880} \right)^{\text{AAE}_c} \]  

(6)

the light absorption coefficient of BrC at different wavelengths varied obviously. However, BC light absorption varies weakly with wavelength in near-UV to infrared range showing an AAE around 1.0. The AAEBC value was set 1.0, which is consistent with previous studies (Wang et al., 2019; Xie et al., 2019; Zhang et al., 2021b).

A minimum R-squared (MRS) method was developed to separate light absorption by BrCsec (babs BrCsec(λ)) versus primary BrC. The BC tracer method for calculating SOC was applied in this approach (Srivastava et al., 2018). Aerosol light absorption is due to carbonaceous particles from both primary and secondary sources. Thus, babs BrCsec(λ) can be calculated as the following equation:

\[ b_{abs} \text{BrCsec}(λ) = b_{abs}(λ) - \left( \frac{b_{abs}(λ)}{BC} \right)_{pri} \times [BC] \]  

(7)

where babs(λ) is the measured light absorption coefficient at a given wavelength (e.g., λ = 370, 470, 520, 590 and 660 nm), (babs(λ)/BC)pri is the ratio of the primary particle’s light absorption to the BC mass concentration from combustion sources, [BC] is the mass concentration of BC at 880 nm. The key step for the analyses is to find a value for babs (λ)/BC that is the representative of the primary combustion sources which affected the sampling site, but finding that value is challenging because the ratio varies among sources. More details about MRS are given in Wang et al. (2019) and Wu and Yu (2016).

3. Results and discussion

3.1. Light absorption properties of carbonaceous aerosol in Wuhan

The average light absorption coefficient of BC (babsBC) and BrC (babsBrC) with their contributions to total light absorption at different wavelengths were calculated based on Eqs. (5) and (6) during different periods in 2020 and 2019. The babs(370) and babs(880) were focused on in this study due to BrC and BC showed strongest absorption at 370 nm and 880 nm, respectively. The time series of carbonaceous aerosols light absorption coefficient at 370 nm and 880 nm were shown in Fig. 2. The babs(370) varied from 2.8 to 158.2 Mm⁻¹ and 6.0 to 217.6 Mm⁻¹ during the different periods in 2020 and 2019, respectively, and babs(880) was in the range of 0.9–60.0 Mm⁻¹ and 2.8–75.9 Mm⁻¹ (Fig. 2). As shown in Figs. 3 & S3, compared with that in P1 in 2020 (53.2 ± 26.8 Mm⁻¹) and P2 in 2019 (61.4 ± 36.0 Mm⁻¹), the babs(370) in P2 in 2020 (39.9 ± 22.0 Mm⁻¹) reduced by 25% and 35%, respectively, and the babs(880) in P2 in 2020 (14.5 ± 8.8 Mm⁻¹) decreased by 28% and 41%, respectively, compared with P1 in 2020 (20.3 ± 10.7 Mm⁻¹) and P2 in 2019 (23.6 ± 13.4 Mm⁻¹). During different periods in 2020, the contribution of BrC to total absorption (%BrC) at 370 nm was 12.3% during P1, increased up to 17.4% during P2, then decreased to below 15% during P3 and P4; however, the %BrC (370) in P1 in 2019 was only about 12%. The %BrC (370) was consistent with previous studies measured in the Guangzhou, Nanjing and Lhasa in China (about 10%) (Wang et al., 2018; Yuan et al., 2016; Zhu et al., 2017), while it was lower than those observed in northern Chinese cities in winter (about 40%) (Chen et al., 2020c; Peng et al., 2020a; Peng et al., 2020b). The results show that BC was the dominant contributor to aerosol light absorption, but BrC also cannot be neglected.

The AAE was calculated based on the aerosol light absorption coefficient at 370 and 880 nm. Previous studies reported that the AAE varied greatly at different sampling site (e.g. urban, suburban and rural) with different energy consumption structure, and the AAE from open biomass burning was highest (1.64–3.25), followed by coal combustion (1.19–1.26) and gasoline and diesel combustion (0.8–1.1) (Corbin et al., 2018; Tian et al., 2019; Zheng et al., 2019). In this study, the mean values of AAE were about 1.1 ± 0.3 during the whole observed periods, and the highest AAE occurred during P2 in 2020 (1.2 ± 0.2) in WH megacity (Table 1). Our results indicated that the air mass was influenced by intensive fossil fuel combustion emission during normal stages, whereas BC from local traffic emission decreased significantly during the lockdown due to the limitation of vehicles. In this study, the AAE in urban environment was consistent with previous studies in Nanjing (1.1) (Wang et al., 2018), Shenzhen (1.05) (Yuan et al., 2016) and Hangzhou (1.12–1.21) (Xu et al., 2020); however, it was lower than that measured in Chongqing (2.0) and Luhe (1.37) where household cooking, heating with coal and wildfires were the major source in winter (Chen et al., 2020c; Zheng et al., 2019).

3.2. Variations of concentration and source of BC in Wuhan and its surrounding cities

3.2.1. Reduction of the BC concentration

In 2020, the average BC concentration in WH was 1.9 ± 1.1 μg m⁻³ during P2, and reduced by 24% compared with that in P1 (2.5 ± 1.4 μg m⁻³) then it remained same level with P2 during the recovery stages. In addition, the BC decreased by approximately 1.2 μg m⁻³ (39%) in P2 in 2020 compared with P2 in 2019 (3.1 ± 1.7 μg m⁻³) (Table 1). These results show that vehicles control measures during P2 had significant mitigating effect on BC. Compared with that in P1, the decline of BC...
Fig. 2. Time series of carbonaceous aerosols light absorption coefficients at 370 and 880 nm and BC concentration during sampling periods in 2020 (a) and 2019 (b) in WH megacity.

Fig. 3. The light absorption coefficients of the BC and BrC at specific wavelengths during different periods in 2020 in WH. Note: we defined the before lockdown period as P1 (01–22 January), during lockdown period as P2 (23 January to 10 March), partial recovery phase as P3 (11 March to 07 April) and recovery stage as P4 (08–30 April).
during recovery stages attributed to the favorable meteorological condition, such as higher boundary layer height and larger wind speed. The BC mass concentration in WH during the strict lock measures was much lower than that (2.5 μg m⁻³) in Beijing during the APEC meeting in 2014 (Zhang et al., 2018), and close to that (1.7 μg m⁻³) during the 2016 G20 summit in Hangzhou (Li et al., 2018). However, the lower BC (1.06 μg m⁻³) was measured in Hangzhou urban areas during COVID-19 lockdown, and the BC concentration reduced by 47% from the pre-lockdown to lockdown (Xu et al., 2020), which was higher than 2 times this study because of pollution events occurred frequently during lockdown in Hubei Province (Shen et al., 2021).

In addition, the average BC concentration during P2 in 2020 for other five cities (e.g. HS, HG, XN, XG and EZ) decreased by approximately 0.6–1.2, 0.2–0.9 and 0.5–0.7 μg m⁻³ compared with that in P1, P3 in 2020 and P2 in 2019, respectively, and the corresponding decreasing percentages were 24–33%, 0.5–27% and 15–39%, respectively. The BC variation trend in different periods was decreasing at first (from P1 to P2), then increasing (from P2 to P3) and reducing in the end (from P3 to P4), and this was different from the BC variation patterns in WH. It might be that industry and transportation recovered faster than that in WH. An interesting phenomenon was observed that the BC levels in medium-sized cities (e.g. HS, HG, XN and XG) were higher, followed the WH megacity and the EZ small city during different periods (Table 1). The similar results were reported by Zheng et al. (2019): the highest BC concentration was observed at Luwu (8.48 ± 4.83 μg m⁻³), followed by Xiangyang (7.35 ± 3.45 μg m⁻³), Hong’an (5.54 ± 2.59 μg m⁻³), Suixian (4.47 ± 2.90 μg m⁻³) and WH (3.91 ± 1.86 μg m⁻³) in January 2018. Generally, the concentration of BC in urban areas of China during lockdown was still higher about 1.5–3.0 times than that measured in Somerville (0.68 μg m⁻³) in USA (Hudda et al., 2020).

3.2.2. Contribution of BC different sources

The relative contributions between fossil fuel and biomass burning to BC were apportioned using the aethalometer model. The average contribution of BCff (BCff) in WH decreased significantly from 92% during P1 to 86% during P2 but increased up to 88% during P3 and 91% during P4 (Table 1), suggesting that the variation of BC fraction attributed to gasoline and diesel combustion. The higher %BCff were observed in WH megacity during normal life (e.g. P1, P3, P4 in 2020 and P2 in 2019), which was consistent with previous results that the contribution of BC from fossil fuel was above 85% in WH (Zhang et al., 2021a; Zheng et al., 2019). As shown in Table 2, the concentration of BCff in WH decreased from 2.2 μg m⁻³ in the P1 to 1.6 μg m⁻³ in the P2. This 0.6 μg m⁻³ BCff decline in WH can be roughly attributed to the reduction in the vehicle emission, and it is consistent with the BC decline (0.6 μg m⁻³). However, the concentration variation of BCbb has small fluctuations (0.2–0.3 μg m⁻³) in WH during different periods (Table 2).

The %BCff values ranged from 93 to 91 in the other five cities during P1, and then decreased to the range of 63–86% during P2 in 2020, and this was lower than that during P2 in 2019 (79–92%). As expected, the %BCff returned to higher values gradually in P3 (range from 76 to 88%) and P4 (range from 78 to 90%). In the medium-sized cities (e.g. HS, HG, XN and XG), BCff concentration decreased by 0.8–1.1, 0.0–1.0 and 0.4–1.1 μg m⁻³ in 2020 compared to that in P1 and P3 in 2020 and P2 in 2019, respectively (Table 2). In general, the decreasing %BCff caused by the strict control measures such as the minimum level of vehicles. Another reason was that BC from biomass burning in rural areas might be transported to urban areas because people in rural areas had to stay at home for a long time than previous years, and household cooking and heating increased the fraction of wood-burning and coal combustion.

3.2.3. Diurnal variation of BC and %BCff in WH

Diurnal variation of BC concentration and the %BCff during different observed periods were shown in Fig. 4. The BC concentration during P1 and P3 in 2020 and different periods in 2019 exhibited a bimodal diurnal distribution with one peak between 8:00 and 10:00 (2.7–3.8 μg m⁻³ at 10:00 LT) and the other peak at 17:00–21:00 (3.0–4.0 μg m⁻³ at 21:00 LT). The morning BC peak value was lower than the evening peak. Meanwhile, the peak values of %BCff reached 90–95% during different periods, except P2. The morning peak could be attributed to vehicle emissions during morning rush hour, and the evening peak could be

| Urban          | 2020 Parameter | 2020 P1 | 2020 P2 | 2020 P3 | 2020 P4 | 2019 P1 | 2019 P2 |
|----------------|----------------|---------|---------|---------|---------|---------|---------|
| Wuhan(WH)      | AAE            | 1.1 ± 0.1| 1.2 ± 0.2| 1.1 ± 0.2| 1.1 ± 0.1| 1.1 ± 0.1| 1.1 ± 0.1|
|                | BC             | 2.5 ± 1.4| 1.9 ± 1.1| 1.9 ± 0.9| 1.8 ± 0.7| 3.1 ± 1.7| 3.1 ± 1.7|
|                | BCff           | 92       | 86       | 89       | 90       | 90       | 90       |
|                | BCbb           | 4.9 ± 4.6| 5.5 ± 4.5| 5.0 ± 4.5| 3.8 ± 2.4| 5.7 ± 5.0| 5.7 ± 5.0|
|                | BCff           | 65       | 75       | 71       | 69       | 77       | 77       |
| Ezhou(EZ)      | BC             | 2.0 ± 0.9| 1.4 ± 0.6| 1.6 ± 0.3| 1.2 ± 0.4| –        | –        |
|                | BCff           | 85       | 76       | 77       | 80       | –        | –        |
| Huangshi(HS)   | BC             | 3.8 ± 1.7| 2.6 ± 1.1| 2.8 ± 0.6| 2.5 ± 0.9| 3.1 ± 1.9| 3.1 ± 1.9|
|                | BCff           | 84       | 78       | 78       | 81       | 79       | 79       |
| Xianning(XN)   | BC             | 3.5 ± 1.5| 2.3 ± 1.0| 3.2 ± 0.7| 2.3 ± 0.8| 3.0 ± 1.6| 3.0 ± 1.6|
|                | BCff           | 73       | 64       | 77       | 78       | 86       | 86       |
| Xianggan(XG)   | BC             | 3.1 ± 1.5| 2.3 ± 1.2| 3.0 ± 0.8| 2.0 ± 0.7| –        | –        |
|                | BCff           | 91       | 85       | 88       | 92       | –        | –        |
| Huanggang(HG)  | BC             | 3.7 ± 1.8| 2.7 ± 1.2| 2.9 ± 0.6| 2.2 ± 0.8| 3.4 ± 1.9| 3.4 ± 1.9|
|                | BCff           | 88       | 84       | 87       | 86       | 89       | 89       |

Table 1
Variation of concentration and light absorption of BC and BrC and their contribution during 2020 and 2019.

Table 2
Average BC concentration from fossil fuel (BCff) and biomass burning (BCbb) during different periods in 2020 and 2019 (μg m⁻³).

| Urban          | 2020 P1 | 2020 P2 | 2020 P3 | 2020 P4 | 2019 P1 | 2019 P2 |
|----------------|---------|---------|---------|---------|---------|---------|
| Wuhan(WH)      | 2.2     | 2.0     | 1.6     | 0.3     | 1.7     | 1.6     | 0.2     | 2.8     | 0.3     |
| Ezhou(EZ)      | 1.7     | 1.3     | 1.0     | 0.3     | 1.2     | 1.4     | 1.0     | 0.2     | –       | –       |
| Huangshi(HS)   | 3.1     | 0.6     | 2.0     | 0.6     | 2.3     | 0.6     | 2.0     | 0.5     | 2.4     | 0.7     |
| Xianning(XN)   | 2.5     | 0.9     | 1.5     | 0.9     | 2.5     | 0.8     | 1.8     | 0.3     | 2.6     | 0.4     |
| Xianggan(XG)   | 2.8     | 0.2     | 2.0     | 0.3     | 2.5     | 0.4     | 1.8     | 0.2     | –       | –       |
| Huanggang(HG)  | 3.2     | 0.4     | 2.3     | 0.4     | 2.3     | 0.4     | 1.9     | 0.3     | 3.0     | 0.4     |
influenced by later afternoon rush hour and the emission of heavy-duty diesel trucks, in addition, the BC was easier accumulated when the mixing height decreased in the evening. However, the bimodal distribution of BC during P2 in 2020 disappeared in WH due to strict traffic control (Fig. 4b1), and the %BCff kept lower level (ranging from 81 to 85%) (Fig. 4b2). We compared the BC peak values during the lockdown in 2020 and 2019, and then roughly estimated that the decreased BC peak value of 1.2 \( \mu \text{g m}^{-3} \) (38%) in WH urban areas was attributed to the traffic reduction. During all periods, the concentration of BC at ground level decreased from 10:00 to 15:00 because of the increasing mixing height which facilitated the diffusion of air pollutants. Therefore, the diurnal variation of BC was mainly influenced by the intensity of local source and meteorological conditions (e.g. mixing height).

3.3. Formation of secondary BrC in Wuhan

The production process of BrCsec is affected by various factors such as precursors and environmental condition. The generation mechanism mainly includes the oxidation of aromatic hydrocarbon precursors to generate nitroaromatic BrC, and the reaction of carbonyl compounds with ammonium to generate nitrogen-containing heterocyclic BrC. The typical BrCsec precursors are benzene, toluene, \( \alpha \)-pinene, glyoxal and methylglyoxal (Marrero-Ortiz et al., 2019; Nakayama et al., 2013; Song et al., 2013). The difference of the BrCsec absorption spectrum is mainly due to the change in the morphology of the chromophore. The typical chromophores are nitroaromatic compounds, such as nitrophenols, imidazole-based and other N-heterocyclic compounds and quinones.

Previous studies reported that BrCsec would appear to be an important contributor to light absorption of BrC especially at 370 nm (Wang et al., 2019; Zhang et al., 2020). In this study, \( b_{\text{absBrCsec}} \) (370) values were lower during the sampling periods in 2020 (range from 3.8 to 5.5 \( \text{Mm}^{-1} \)), however, the average contribution of \( b_{\text{absBrC}} \) to \( b_{\text{absBrC}} \) at 370 nm (\( \text{C}_{\text{BrCsec}}(370) \)) was higher (range from 65 to 75%). The \( b_{\text{absBrCsec}}(370) \) and \( C_{\text{BrCsec}}(370) \) both increased from P1 to P2 in

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**Fig. 4.** Diurnal variations of BC mass concentration (a1, b1, c1) and the fraction of BCff (a2, b2, c2) during the different periods in 2019 and 2020 in WH. Note: a, b, c represent the periods of P1, P2 and P3, respectively; in addition, the variation in P4 was not shown due to the missing data in 2019.
2020, and then reduced gradually along with time. The $b_{abs}$BrCsec (370) increased significantly at P2 in 2020, and that might because of increasing atmospheric oxidizing capacity, which facilitated the formation of secondary organic aerosol during lockdown periods reported by Sun et al. (2020) and Huang et al. (2020). In addition, we also found that the $b_{abs}$BrCsec (370) and $C_{BrCsec}$ (370) during P2 in 2020 were 5.5 Mm$^{-1}$ and 75%, respectively. This results agree well with that during P2 in 2019 (5.7 Mm$^{-1}$ and 77%), and nearly consistent with $C_{BrCsec}$ in Guangzhou (72.2%), WH (69.4%) and Hong Kong (76%) during winter (Zhang et al., 2020; Zheng et al., 2020a). Our results indicated that the emission reduction measures have little effect on BrCsec.

These diurnal variation of the $b_{abs}$BrCsec (370), $b_{abs}$BrCsec (370)/ΔCO ratio, odd oxygen ($Ox = NO_2 + O_3$) and relative humidity (RH) were plotted in Fig. 5. The CO is considered as the primary emission tracer, and thus the $b_{abs}$BrCsec (370)/ΔCO ratios can minimize the planetary boundary layer (PBL) dilution (DeCarlo et al., 2010). The diurnal patterns of $b_{abs}$BrCsec (370) and $b_{abs}$BrCsec (370)/ΔCO ratio were similar and had no obvious fluctuation during P1 (Fig. 5a). This phenomenon is attributed to the higher RH because the formation of BrCsec chromophores could be produced by aqueous-phase reactions, and lower concentration of Ox in the daytime, which weakened the photobleaching of BrCsec chromophores. As shown in Fig. 5b & c, similar diurnal variation trends were found during P2 and P3 in 2020. The $b_{abs}$BrCsec (370) and $b_{abs}$BrCsec (370)/ΔCO decreased after 8:00 LT, and lower level was observed during from 12:00 to 19:00 LT in both periods. In addition, the diurnal pattern of $b_{abs}$BrCsec (370)/ΔCO ratio was opposite to Ox, which was consistent with other studies in Athens (Liakakou et al., 2020) and China (Zhang et al., 2020). This indicates that aging processes in the presence of daylight result in the degradation of the BrCsec absorption efficiency, which suggests bleaching of BrCsec chromophores through oxidative processes (Zhao et al., 2015). Strong negative correlation between $b_{abs}$BrCsec (370) and Ox in P2 in 2020 ($R^2 = 0.70$, Fig. S2b) and P3 ($R^2 = 0.24$, Fig. S4c) were measured. Increasing $b_{abs}$BrCsec (370)/ΔCO trends after 20:00 LT for extensively long times at night can be explained by the occurrences of active aqueous formation of BrCsec. Whereas, the peak of $b_{abs}$BrCsec (370) occurred in the periods of 10:00–11:00, and this can be explained by the increased solar radiation after sunrise and more gaseous precursors from emission sources (e.g. traffic and industry), which enhanced the photochemical reaction that led to the formation of BrCsec (Zhang et al., 2020). In other words, the $b_{abs}$BrCsec (370) and $b_{abs}$BrCsec (370)/ΔCO peaks appeared in a distinct time lag after the morning traffic rush hours. Then $b_{abs}$BrCsec (370)/ΔCO retained a lower level after 14:00 LT because of abundant photobleaching.

Generally, the diurnal patterns of $b_{abs}$BrCsec and RH were similar, indicating that higher levels of RH promoted the formation of BrCsec after sunset in WH. Vidovic et al. (2018) report that the aqueous-phase oxidation reactions is an important pathway for formation of BrCsec chromophores at night, especially under the high NOx and acidic particulate matter. And the reaction of carbonyl compounds with ammonium/amine is another important secondary generation pathway of BrC, which is mainly a liquid phase reaction process (Marrero-Ortiz et al., 2019). Our results also support the conclusion that photochemical oxidation and other oxidative reactions led to the bleaching of the BrCsec chromophores under high level of Ox during the daytime. The part photobleaching pathway can be explained that under direct light conditions or after being oxidized by OH radicals, BrCsec generated by the reaction of glyoxal or methylglyoxal with ammonium sulfate will undergo rapid “photobleaching” phenomenon, and the light absorption will be significantly reduced (Wong et al., 2017; Zhao et al., 2015).

4. Conclusions

In this study, in order to analyze the impact of strict city lockdown on air quality during COVID-19, the variations on light absorption, concentrations, sources and formation mechanism of BC and BrC were investigated with different periods, based on real-time measurements with the 7-wavelength Aethalometers in megacity Wuhan and its surrounding areas.
cities. The BC was the dominant light absorption contributor to the total light absorption of aerosol, while the BrC also was no-neglect in short wavelengths. The BC in the megacity WH was 2.5 and 1.9 μg m⁻³ during pre-lockdown and lockdown, respectively, which were lower by 25% and 28% than those in the medium-sized cities (e.g. HS, XN, XG and HG) and higher by 20 and 26% in small city of EZ. The BC concentrations declined by 16–39% and 24–34% during lockdown in all cities compared to the same period in 2019 and pre-lockdown in 2020, respectively; and then they increased gradually during P3, except the WH megacity. Our study indicated that the significant reduction of anthropogenic emission contributed to the decrease in the BC concentration. We found 0.6 and 0.6 emission contributed to the decrease in the BC concentration. We then they increased gradually during P3, except the WH megacity. The BC level in XG and HG increased (>80%) in other periods, which was attributed to vehicle emission reduction in the urban areas. Notably, the BC level in HG increased by 20 and 26% in small city of EZ. The BC concentrations declined by 16% in medium-sized cities (e.g. XG and HG). The values of BrCsec (370) and BrCsec (370) during the lockdown in 2020 and 2019 indicated that the variation of BrCsec was slight. We only investigated light absorption properties of secondary aerosol formation in aqueous droplets.

Generally, the lockdown measures reduced the BC concentrations significantly, however, the variation of BrCsec was slight. We only investigated light absorption properties of secondary aerosol formation in aqueous droplets.

CRediT authorship contribution statement

Qinglu Wang: Writing—original Draft, Visualization. Lili Wang: Conceptualization, Supervision, Resources and editing. Nan Chen: Data supporting, Investigation. Minghui TAO: Data supporting, Investigation. Yali LEI: Model simulation. Yang Sun: Review and Editing. Jinyuan XIN: Review and Editing. Tingting LI: Review and Editing. Jingxiang ZHOU: Sample collection, Visualization. Jingda Liu: Formal analysis, Data Curation. Dongsheng JI: Review and Editing. Yuesi Wang: Project administration.

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.scitotenv.2021.148226.

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