# Oxidative potential and water-soluble heavy metals of size-segregated airborne particles in haze and non-haze episodes: Impact of the “Comprehensive Action Plan” in China

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**Highlights:**

1. The highest level of particle-induced DNA damage decreased after the enactment of the CAP
2. The DNA damage was concentrated in the 'fine' particle size range (0.43-1.1μm) following the CAP
3. The DNA damage was predominantly caused by the heavy metals Pb, Cr, Cd, and Zn following the CAP
4. The heavy metals Pb, Cr, Cd, and Zn were concentrated in particles smaller than 2μm

**Abstract**

Air pollution is a major environmental health challenge in megacities, and as such a Comprehensive Action Plan (CAP) was issued in 2017 for Beijing, the capital city of China. Here we investigated the size-segregated airborne particles collected after the implementation of the CAP, intending to understand the change of oxidative potential and water-soluble heavy metal (WSHM) levels in 'haze' and 'non-haze' days. The DNA damage and the levels of WSHM were analyzed by Plasmid Scission Assay (PSA) and High-Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) techniques. The PM mass concentration was higher in the fine particle size (0.43-2.1 μm) during haze days, except for the samples affected by mineral dust. The particle-induced DNA damage caused by fine sized particles (0.43-2.1 μm) exceeded that caused by the coarse sized particles (4.7-10 μm). The DNA damage from haze day particles significantly exceeded those collected on non-haze days. Prior to the instigation of the CAP, the highest value of DNA damage decreased, and DNA damage was seen in the finer size (0.43-1.1μm). The Pearson correlation coefficient between the concentrations of water-soluble Pb, Cr, Cd and Zn were positively correlated with DNA damage, suggesting that these WSHM had significant oxidative potential. The mass concentrations of water-soluble trace elements (WSTE) and individual heavy metals were enriched in the finer particles between 0.43 μm to 1.1 μm, implying that smaller sized particles posed higher health risks. In contrast, the significant reduction in the mass concentration of water-soluble Cd and Zn, and the decrease of the maximum and average values of DNA damage after the CAP, demonstrated its effectiveness in restricting coal-burning emissions. These results have demonstrated that the Beijing CAP policy has been successful in reducing the toxicity of 'respirable' ambient particles.

Keywords: health risk, respirable particles, Plasmid Scission Assay, size-segregated particulate matter, The Comprehensive Action Plan, water-soluble heavy metals

## 1. Introduction

As the capital of China and one of the World's major megacity, Beijing suffers from life-threating air pollution, which has been a monumental environmental challenge over the past two decades (Fu and Chen, 2017; Li et al., 2020b; Xing et al., 2020). To reduce the air pollution in Beijing, the "Air Pollution Prevention and Control Action Plan" (the Clean Air Action Plan) and the "Action Plan for Comprehensive Control of Atmospheric Pollution in Autumn and Winter of Beijing-Tianjin-Hebei region in 2017–2018" (the Comprehensive Action Plan, abbreviated as "CAP") were carried out (Li et al., 2020a; Liu et al., 2019; MEP, 2017; The State Council of China, 2013; Zhong et al., 2019). The air quality improvement after the implementation of the two action plans, when demonstrated by the annual mean concentration of $PM_{2.5}$ (airborne particulate matter with an aerodynamic diameter less than 2.5μm), revealed a reduction in the 'fine-sized' particle fraction (Beijing Ecology and Environment Statement, 2019). The particulate matter emissions from industry and coal combustion decreased after the implementation of the two action plans (Barrington-Leigh et al., 2019; Geng et al., 2019; Wang et al., 2020). In addition, the decreasing 'risk of death' brought on by reducing the levels of air pollution was a positive signal of improving air quality (Bi et al., 2019; Maji et al., 2020; Zhou et al., 2021). However, there are still annual incidences in Beijing when the air quality reaches unhealthy levels (Li et al., 2020a), e.g., when $PM_{2.5}$ values significantly exceeded the II Grade standard of the National Ambient Air Quality Standards (GB3095–2012) (MEP, 2012). These high values may be caused by regional transport, e.g., when $PM_{2.5}$ values changed from 4.40 $\mu g/m^3$ to 855.10 $\mu g/m^3$ (Wang et al., 2019; Zheng et al., 2015a). The regional transport of air masses and local emissions both affect air quality and may have an influence on PM components. A study on the mass concentration of trace elements in the rural mountainous site of Xinglong, a typical background site of northern China, determined that long-range transport caused an increase in trace elements (Pan et al., 2013).

Airborne particles, as important atmospheric pollutants, have a significant influence on morbidity and mortality (Apte et al., 2018; Silva et al., 2021; Ren et al.,

2021; Xue et al., 2019). Epidemiological investigations have shown that airborne PM has adverse health effects in Beijing (Chen et al., 2020; Huang et al., 2018a; Sheehan et al., 2016). Exposure to high levels of $PM_{2.5}$ can lead to premature death (Liu et al., 2016; Maji et al., 2018; Zheng et al., 2015b), cardiovascular diseases (Lin et al., 2019; Ma et al., 2019), chronic obstructive pulmonary disease (Guo et al., 2020; Song et al., 2017), respiratory disease (Crabbe, 2012; Han et al., 2020) and lung cancer (Chen et al., 2016; Cohen et al., 2017; Pirozzi et al, 2018). However, the toxic mechanisms underlying the adverse health effects following inhalation exposure to particles remains unclear. An extensively accepted hypothesis is that PM-induced oxidative stress causes toxic effects (Shao et al., 2017). The studies of physicochemical characteristics and toxicology of particles have revealed that the heavy metals in the particulate matter can cause oxidative damage in humans (Conibear et al., 2018; Gao and Ji, 2018; Rohra et al., 2018; Silva et al., 2021; Wu et al., 2021). Moreover, the heavy metals bound to particulate matter differ with particle size and mass concentration (Lyu et al., 2017). Therefore, it is important to study the components of size-segregated airborne particles, especially heavy metals, to understand the particle-induced damage and resulting human health risk.

Many methods are being employed to assess the oxidative potential of atmospheric particles, such as the Ames test (Du et al., 2019), dithiothreitol (DTT) -driven assay (Carville et al., 2013), hemolysis assay (Zhang et al., 2019; Mesdaghinia et al., 2019), comet assay (Bahadori et al., 2018), and plasmid scission assay (PSA) (Shao et al., 2017). The PSA is an *in vitro* method to evaluate PM oxidative capacity and then semi-quantify particulate bioreactivity (Lawson et al., 2020; Bandowe et al., 2021; Niu et al., 2021). PSA has been used due to the simplicity, rapid high-throughput, high sensitivity, and reproducibility of the assay (Feng et al., 2020; Shao et al., 2006, 2013, 2016; Sun et al., 2014).

In this study, ambient PM were collected in 2018 after the instigation of the CAP program in Beijing, and the oxidative capacities and heavy metal compositions of size-segregated particles were determined. The relationships between the levels of WSHM

and DNA damage were analyzed. Finally, a comparison between the WSHM compositions of size-segregated haze particles, both before and after the CAP, was made to elucidate the CAP's effect on harmful elements in airborne particles.

## 2. Sampling and Methods

### 2.1 Sampling

The sampling site was situated at the China University of Mining and Technology (Beijing) in Haidian District, Beijing. The sampling site was on the North Fourth Ring Road 1km to the south, with Xueyuan Road (one of the main roads in Beijing) 100 m to the east. The sampler was installed outside on the top of the fourth floor of the Comprehensive Building, approximately 18m above the ground. This collection site was part of a typical campus and residential area in Beijing, with no large heavy industrial pollution sources in the immediate area.

An eight-stage Anderson cascade impact sampler (TE-20-800 TISCH, Germany) was used, with a collection height of 1.5 m higher than the floor on which it was located. The sampling flow rate utilized was 28.3 L/min. The sampler effectively separated the PM into 8 equivalent cut-off diameters (μm): 0.43-0.65, 0.65-1.1, 1.1-2.1, 2.1-3.3, 3.3-4.7, 4.7-5.8, 5.8-9.0, 9.0-10. Quartz fiber filters (80 mm diameter, Millipore, China) were used to collect the different sized particles. The sampling period was conducted from November 30th to December 4th in 2018, and the sampling time was 23.5 hours from 9:00 to 8:30 the next day. The meteorological data were obtained from a portable meteorological instrument (Kestrel 5500 Weather LiNK, USA: Supplementary Table S1 during sampling period). The quartz fiber filters were heated at 450℃ for 4 hours by a muffle furnace (ZK-6XY-1400, Beijing ZHONGKEBEIYIKEJI, China), and placed in a constant temperature and humidity chamber (Hitachi, Japan; temperature: 20℃±5℃, relative humidity: 45% ± 5%) for 48 hours before sampling and weighing.

The mass concentrations of size-segregated particles were obtained using the gravimetric method. The fiber filters were weighed using an electronic balance (Sartorius CP225D, Switzerland) with an accuracy of 0.01 mg. The formula calculating

147 the mass concentration, as defined by Feng et al. (2020), was employed.
148
149 **2.2 Plasmid scission assay**
150 The PSA is an *in vitro* method to determine the oxidative potential. The principle
151 of the assay is that free radicals induced by heavy metals occurring on the surfaces of
152 the particles can damage the supercoiled plasmid DNA. The initial oxidative damage
153 causes the supercoiled DNA to relax, and the maximum extent of damage results in
154 linearization. The relative electrophoretic mobility of supercoiled, relaxed, and
155 linearized DNA in the gel analysis system (Synoptics Ltd., Cambridge, UK) was used
156 to calculate the percentages of the three forms of plasmid DNA. The total percentages
157 of the relaxed and linearized DNA were taken as the level of oxidative damage.
158 Ultra-pure water (conductivity 18.2 MΩ, Millipore, China) was used as the blank
159 sample for each group of pollution samples. The value of the blank oxidative damage
160 was subtracted from the sample DNA damage. Four parallel samples were run in each
161 group. The details on the methodology were as follows:
162 (1) Preparation of water-soluble sample: the filters and blank filter were cut into 5mm
163 squares and put into a 15 ml centrifuge tube (Corning, USA). A measured amount
164 of ultra-pure water was added to the centrifuge tube to make the particle dosage of
165 100 μg/ml. Each sample solution was mixed for 20 hours using a platform shaker
166 (VORTEX-GENIE2, Scientific Industries, USA). The solution was transferred to a
167 1.5 ml centrifuge tube by pipette (Eppendorf, Germany). A Kendro centrifuge (D-
168 37520 Osterode, Germany) centrifuged the solution for 80 s and the supernatant
169 was extracted.
170 (2) DNA sample and gel preparation: 82 μl of the sample supernatant and 4 μl of the
171 plasmid X174-RF DNA (Promega, USA) was added to a 1.5 ml centrifuge tube.
172 This was oscillated horizontally for 6 hours to ensure a good mixing (HX-3000,
173 YOUNING, China). Agarose (molecular biology grade; Sigma-Aldrich, China) was
174 dissolved in 100 *X* Tris/Borate/EDTA (TBE) buffer solution (Thermo Scientific,
175 China) and the solution was heated to transparency. Ten millilitres of ethidium

bromide (EB; Sigma-Aldrich, China) was added to the agarose solution when cooled to 78℃, and this forms a gel on the electrophoresis plate (DYCP34C; LIUYI, China).

(3) Fourteen microliters of bromophenol blue stain (Sigma- Aldrich, China) was added to the mixture of the sample supernatant, and DNA was injected into the solidified gel wells. Each gel well was injected with 20 μl of the final solution. The electrophoresis apparatus (DYY-6C, LIUYI, China) was operated at 30 volts for 16 hours at room temperature.

(4) Analysis of DNA damage: the variation of DNA morphologies was observed and quantified by the UV gel imaging system (ChemiDoc, Bio-red, China) and the Syngene Genetools software (version 4.0; Syngene, USA).

### 2.3 High-Resolution Inductively Coupled Plasma Mass Spectrometry

Each PM sample was immersed in a measured amount of ultra-pure water to make the soluble concentration of 100 μg/ml and was shaken for 20 hours. The water-soluble sample was obtained from the centrifuged supernatant (D-37520 Osterode, Germany), after spinning at 13000 rpm for 80 minutes. The WSTE compositions of the samples were analyzed in a High-Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS; ThermoFisher; Element XR). Forty-three WSTE were examined. Seven typical heavy metals within the detection limit were analyzed, namely, Zn, Cu, Pb, Ni, Cd, Cr, and Co (values shown in Table S2). The mass concentration of the WSHM elements (ng/m$^3$) was calculated using the formula:

$$C = \frac{c \times Vt}{Vs}$$

Where: $C$ represents the mass concentration of the water-soluble element (ng/m$^3$); $c$ represents the trace element level in the water-soluble sample (μg/ml); $Vt$ represents the total solution volume (ml), $Vs$ represents standard sample volume (m$^3$)

## 3. Results

### 3.1 The mass concentration of $PM_{2.5}$ during the haze episode

In this study, the specific $PM_{2.5}$, $SO_2$, $NO_2$, and $O_3$ mass concentration data were obtained from data published by the Wanliu State-Control Air Monitoring Station (https://github.com/tuanvvu) during the sampling period (Fig.S1.). The $PM_{2.5}$ accumulation stage began at 13:00 on November 30th. At 02:00 on December 3rd, the $PM_{2.5}$ mass concentration began to decrease, from 154 μg/m$^3$ to 121 μg/m$^3$ at 03:00. At 05:00 on December 3rd, the $PM_{2.5}$ mass concentration significantly decreased, from 112 μg/m$^3$ at 04:00 to 93 μg/m$^3$ (Fig.S1.). Based on the data, sample A represented moderate pollution, samples B and C indicated heavy pollution, and sample D denoted a non-haze day.

### 3.2 Mass concentration of size-segregated particles in haze and non-haze days

The mass concentrations of size-segregated particles in haze days were higher than those on non-haze days, although the size distributions appeared similar (Fig.2). The levels were also higher in heavy pollution days of samples B and C when compared to those in the moderate pollution of sample A.

The mass concentrations of different sized particles were different in haze days. For the moderate pollution of sample A and heavy pollution of sample B, the mass concentration of size-segregated particles in the fine size scale of 0.43-2.1 μm was higher than that in the coarser sized PM (i.e., 4.7-10 μm). The level of sample C increased in the large particle size fraction of 4.7-10 μm, which is believed to be due to mineral dust that would be expected in the larger size fractions of 5.8-10 μm. The PM mass concentration increased with increased particle size in the non-haze day of sample D.

### 3.3 Oxidative potential of water-soluble components in size-segregated airborne particles

Previous studies have demonstrated that the DNA damage caused by the whole sample was like that caused by water-soluble components, indicating that the DNA damage was mainly induced by the water-soluble components in particles (Lv et al.,

2006; Shao et al., 2006, 2007, 2017; Song et al., 2015). It is confirmed in many prior studies that the DNA damage of each sample increases with the increased particle dosage (Shao et al., 2006, 2007, 2017; Xiao et al., 2014), and for the expediency of comparison between different samples, we took the DNA damage percentage at the particle dosage of 100 μg/ml (Table 1). The particulate mass within the 0.43-1.1 μm size zone in the non-haze day sample was too low to perform the PSA at the selected comparative particle dosage of 100 μg/ml.

When comparing the DNA damage induced by the water-soluble fractions of the size-segregated particles, the DNA damage in the 0.43-2.1 μm size exceeded that in the 4.7-10 μm size fraction. In addition, the DNA damage in the smaller size range of 0.43-1.1 μm was significantly higher than that in the 1.1-2.1 μm range. In haze days, the DNA damage decreased first in the PM fraction ranging from 0.43 μm to 2.1 μm (aerodynamic diameter) and then increased in the size range of 5.8 μm to 10 μm with increased particle size. In the 0.43-1.1μm size limit, the DNA damage of sample A was higher than that of samples B and C. In the 1.1-2.1μm size span, the DNA damage of sample B was higher than that of samples A and C. DNA damages induced by samples B and C were higher than that induced by sample A in 2.1-10 size limit. In conclusion, the DNA damage was highest in the smaller sized PM, i.e., 0.43 μm to 1.1 μm (aerodynamic diameter).

The DNA damage caused by size-segregated particles in haze days was higher than that on the non-haze days. The variability of DNA damage was not significant with increased particle size on non-haze days.

### 3.4 The mass concentration of WSHM in size-segregated particles

The mass concentrations of the total WSTE and individual WSHM could present a health risk above certain levels of PM exposure (Fig.3). The mass concentration of the total WSTE, which represented the sum of the contents of the total 43 trace elements in size-segregated particles detected, is shown in Fig.3. The mass concentration of total WSTE in haze days was higher than that on the non-haze days. Over the course of the

haze days, the mass concentration of total WSTE had a normal distribution over the particle size range, with the peak value at 1.1-2.1 μm. In the 0.43-1.1 μm size range, the mass concentration of total WSTE of sample A was higher than that of sample B and sample C, which corresponded to the level of DNA damage (Table 1). In the 1.1-2.1 μm size range, the mass concentration of total WSTE within sample B was higher than that of samples A and C, again corresponding to the level of the DNA damage (Table 1). These results indicated that the particles below 2.1 μm would present a higher health risk than those above this size.

The mass concentrations of Pb and Cr were noticeably higher during haze days when compared to non-haze days. There was no significant variation and very low levels with increased particle size on the non-haze days. However, the mass concentration of Cr decreased with the increased particle sizes on the non-haze day (Fig.3). During haze days, the mass-size distribution of Pb and Cr was highest in the fine PM (i.e., 0.43-2.1 μm). For Pb and Cr, the highest value of mass concentration in the moderate pollution of sample A appeared in the 0.65-1.1 μm fraction, whereas in the heavy pollution of samples B and C the highest values appeared in the PM limited between 1.1 μm to 2.1 μm (aerodynamic diameter). Interestingly, the mass concentration in the moderate pollution of sample A was significantly higher than that in the heavy pollution of samples B and C.

The mass concentrations of Cd and Zn in both the haze and the non-haze days demonstrated a remarkable similarity. The haze day samples were enriched in both metals in the small size range (i.e., 0.43-2.1 μm; Fig.3). The mass-size distribution of Cd and Zn in the heavy pollution of samples B and C was most significant in the 1.1 μm to 2.1 μm size range (aerodynamic diameter). For the moderate pollution of sample A, the mass-size distribution of Cd was greatest in the 0.56 μm to 1.1 μm range, and that of Zn was highest in the 1.1 μm to 2.1 μm PM distribution. The mass concentrations of Cd and Zn revealed no significant variation with increased particle size on the non-haze days.

For Co, Ni, and Cu, the mass-size distribution was highest in PM larger than 1.1

μm (aerodynamic diameter) in haze days (Fig.3). The mass of Cu was concentrated in particles within the respirable size range (i.e., 1.1-3.3 μm), and that of Co enriched in PM capable of 'thoracic' deposition (2.1 to 5.8 μm) within the human respiratory system. The mass of Ni from the moderate pollution of sample A and heavy pollution of sample C was concentrated in the respirable range (1.1 to 2.1 μm), and from the heavy pollution of sample B, concentrated within the inhalable fraction (e.g., 3.3-5.8 μm). The mass concentrations of Co, Ni, and Cu showed no significant variation with increased particle size on the non-haze days.

## 4. Discussion

### 4.1 Correlation between concentrations of WSTE and particle-induced DNA damage

The levels of the typical WSHM above the detection limits were obtained by HR-ICP-MS. The connection between the concentrations of the typical WSHM and the corresponding DNA damage at the particle dosage of 100 μg/ml were analyzed (Table 2). According to the correlation analysis, the correlation coefficient was higher than the critical value of 0.449 at the 0.01 significance level with a sample number N=30, indicating that the types of WSTE and DNA damage were related. The correlation coefficients of four heavy metals were significantly higher than other elements, namely Cr, Zn, Cd, and Pb (Table 2).

The relationship between the DNA damage and the levels of total WSTE was markedly positive, with a correlation coefficient of 0.558, indicating that the total WSTE had a significant role in particle-induced oxidative potential. The individual heavy metals Pb, Cr, Cd and Zn also showed a markedly positive correlation with DNA damage, and their correlation coefficients were higher than the critical value of 0.449. The correlation coefficient between DNA damage and Pb was the highest, with a coefficient of 0.595. The correlation coefficients of water-soluble Cu, Ni, and Co were 0.316, 0.303, and 0.114, respectively, and all of them were lower than the critical value of 0.449.

## 4.2 Comparison between the DNA damage induced by the water-soluble fractions of size-segregated haze particles before and after the CAP

To improve the air quality of Beijing, the government implemented a series of control measures in 2017, called the "Comprehensive Action Plan" (abbreviated to "CAP"). The data for the particle-induced DNA damage before the CAP originated from Sun et al. (2014), who investigated the airborne particles collected in 2010. Particulate matter collected over the described size ranges indicated a different pattern of oxidative capacity before and after the implementation of the CAP (Sun et al, 2014). Fig.4 shows the variations of the particle-induced DNA damage over the particle size range in haze days before and after the CAP. Since the PM ranged from 0.056 μm to 0.32 μm in 2010 were much smaller than those in 2018 (i.e., 0.43 to 0.65 μm), the size limit of 0.056 μm to 0.32 μm could not be used for comparison. The size range of 0.43-10 μm in 2018 was closer to that reported in 2010 (i.e., 0.32-10 μm), and thus the DNA damage caused by these two particle fractions were utilized for comparison. It was noted that although the sizes were marginally different, the overall trends were self-evident.

Overall, the level of DNA damage in 2018 was reduced in comparison to the levels in 2010. The DNA damage was highest in the 0.43-1.1 μm size range after the CAP policy was initiated, whereas the DNA damage was highest in the 1.0-3.2 μm size range before the CAP, implying that after the CAP, the greater oxidative potential moved to the finer particle size, especially those smaller than 2.0 μm (Fig.4). Previous studies have shown that the heavy metals were generally enriched in smaller particles which is a globally observed phenomenon (Lyu et al., 2017; Tan et al., 2016; Sun et al., 2014; Song and Gao, 2011). In addition, it was reported that the secondary particles have smaller particle sizes and carry more trace elements (Gao et al., 2015; Dong et al., 2020).

The highest value of the average DNA damage in 2018 decreased when compared with that in 2010 (Fig.5). It was noted that the DNA damage induced by the large particle size range (i.e., > 5.0 μm) slightly increased in 2018 in comparison with that in

2010, which needs to be investigated further in the future, although this small variation might be related to more aged secondary particles after the CAP (Shao et al., 2021). Fig.5 displayed the significant reduction in DNA damage by fine particles (i.e., 1 μm to 3 μm aerodynamic diameter), however the particle-induced DNA damage after the CAP exhibited an insignificant decreasing trend with the increase of the particle size. This possibly suggested a less obvious trend, whereby the greater oxidative potential has translocated into the finer PM fraction, especially in particles smaller than 2.0 μm.

### 4.3 Comparison between the WSHM compositions of size-segregated haze particles before and after the CAP

Heavy metals are believed to influence the radical generating capacity and then effect the variation of the oxidative damage (Tian et al., 2021; Shao et al., 2017). To study the causes of oxidative damage before and after the CAP, the mass concentration of WSHM from different sized particles during haze days was compared and analyzed. Fig.6 demonstrated that the mass concentrations of WSHM Pb, Cr, Cd, and Zn in size-segregated particles, which were positively correlated with DNA damage before and after the CAP, were enriched in the small particle size range for both before and after the CAP. Despite this, the highest values before the CAP were observed in the less than 1.4 μm size range, and the highest values after the CAP were identified in the less than 1.6 μm size range. This indicated that after the CAP, the mass concentration of WSHM was still enriched in the fine size range, although the particle size range has widened to less than 2.0 μm, which may be related to the more complicated secondary formations of particles (Shao et al., 2021).

The Pb and Cr masses were concentrated in the small size range of 0.43-2.1μm after the CAP in this study, and this was like the studies on the mass-size distribution of heavy elements in heavy pollution episodes in Beijing in winter before the CAP, which found that the Pb and Cr were mainly concentrated in the 1-2 μm size range (Li et al., 2012; Tan et al., 2016). The highest mass concentrations of Cd and Zn appeared in the 0.56-1.0μm size range in the Beijing atmosphere after the Olympic games (Li et

al., 2012). These facts illustrated that Pb, Cr, Cd, and Zn were enriched in the fine size range.

For the individual elements, the mass concentration of water-soluble Pb and Cr in size-segregated particles was significantly increased, whereas that of Cd and Zn was decreased over the particle size range after the CAP (Fig.6). In the 1-3 μm size range, the mass concentrations of Cd and Zn in 2018 were lower than that in 2010, corresponding to the variation of the average DNA damage as shown in Fig.5.

The source apportionment of Zn and Cd in airborne PM found that coal-burning emissions was the major contributor (Li et al., 2017; Liu et al., 2021). The major control measures of the Clean Air Action Plan and CAP include coal-fired emissions, industrial emissions, vehicle emissions, dust emissions, and other measures. These measures greatly controlled coal combustion (Li et al., 2020; Xu and Zhang, 2020). The mass concentration of Zn, where Cd slightly decreased after the CAP, suggested that the reduction of coal-burning emissions played an important role in alleviating Beijing's air pollution.

Source apportionment in the Beijing atmosphere showed that traffic-related emission was the dominant source of Cr (Huang et al., 2018b). According to the data of the Beijing Municipal Bureau of Statistics, car ownership in Beijing increased from 4.81 million in 2010 to 6.08 million in 2018 (http://jtgl.beijing.gov.cn), which has resulted in the mass concentration of Cr increasing after the CAP. Therefore, vehicle emission controls should be increased.

Since 2003, Pb has been prohibited in gasoline, whereas the mass concentration of Pb increased after the CAP. Therefore, this suggests that Pb may come from other sources, such as regional transport (Lv et al., 2021; Wang et al., 2017; Zhang et al., 2019) and yellow traffic paint (O'Shea et al., 2021), although this inference needs to be further validated by more detailed studies.

## 5. Conclusions

(1) The DNA damage induced by water-soluble components at the particle dosage

of 100μg/ml in the smaller size ranges of 0.43-1.1μm was higher than that in the large size ranges of 4.7-10μm, and the DNA damage in the haze days was higher than that in the non-haze days.

(2) After the CAP, the DNA damage induced by the water-soluble components at the particle dosage of 100μg/ml was slightly higher in the size range less than 1μm, implying that the oxidative potential of finer particles increased after the CAP. Although the DNA damage was slightly higher in the size range less than 0.6μm after the CAP, the DNA damage significantly decreased in the size ranges 1-3 μm after the CAP.

(3) Before and after the CAP, the positive correlation between the DNA damage and the water-soluble Pb, Zn, Cd, and Cr showed that these water-soluble heavy metals were most likely responsible for the oxidative potentials.

(4) The mass concentration of Zn, Cd slightly decreasing after the CAP, suggested that the reduction of coal-burning emissions played an important role in alleviating Beijing's air pollution. However, the mass concentration of Pb and Cr increasing after the CAP implied that Pb and Cr were affected by other factors, such as regional transport and traffic-related sources, although this inference needs to be further validated by more detailed studies.

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**Figures and Tables**



Tables:

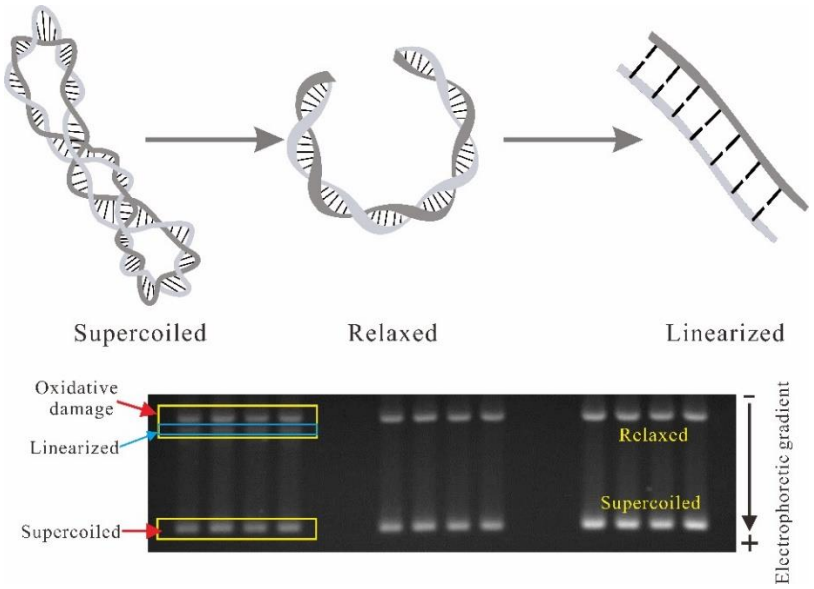


Fig.1 Schematic illustration showing the principle of the plasmid scission assay.

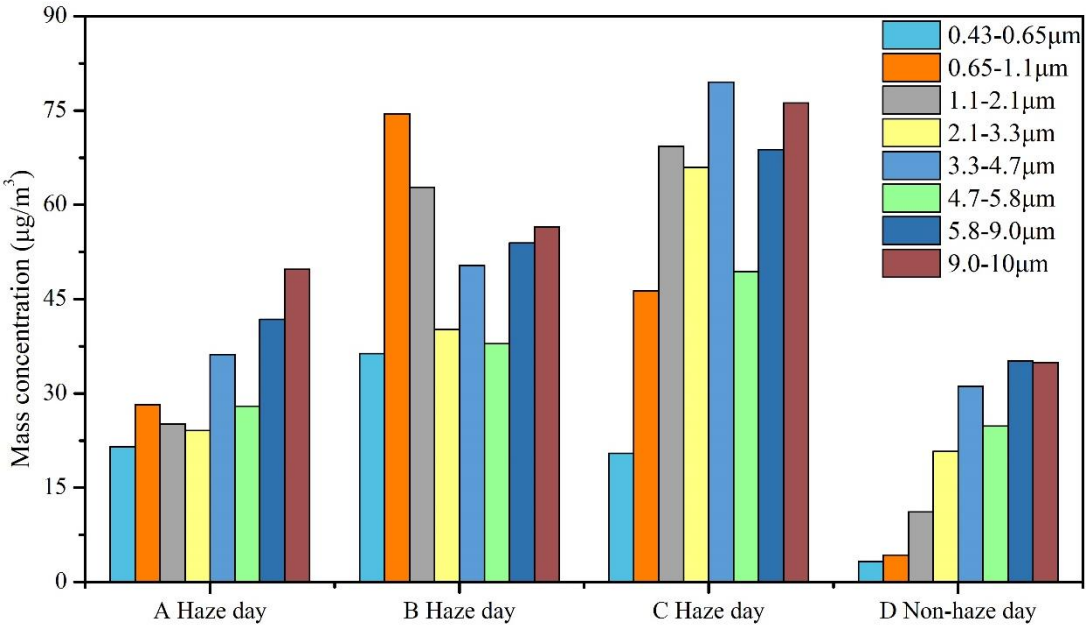


Fig.2 Mass concentrations of size-segregated particulate matter in the size range from 0.43 μm to 10 μm

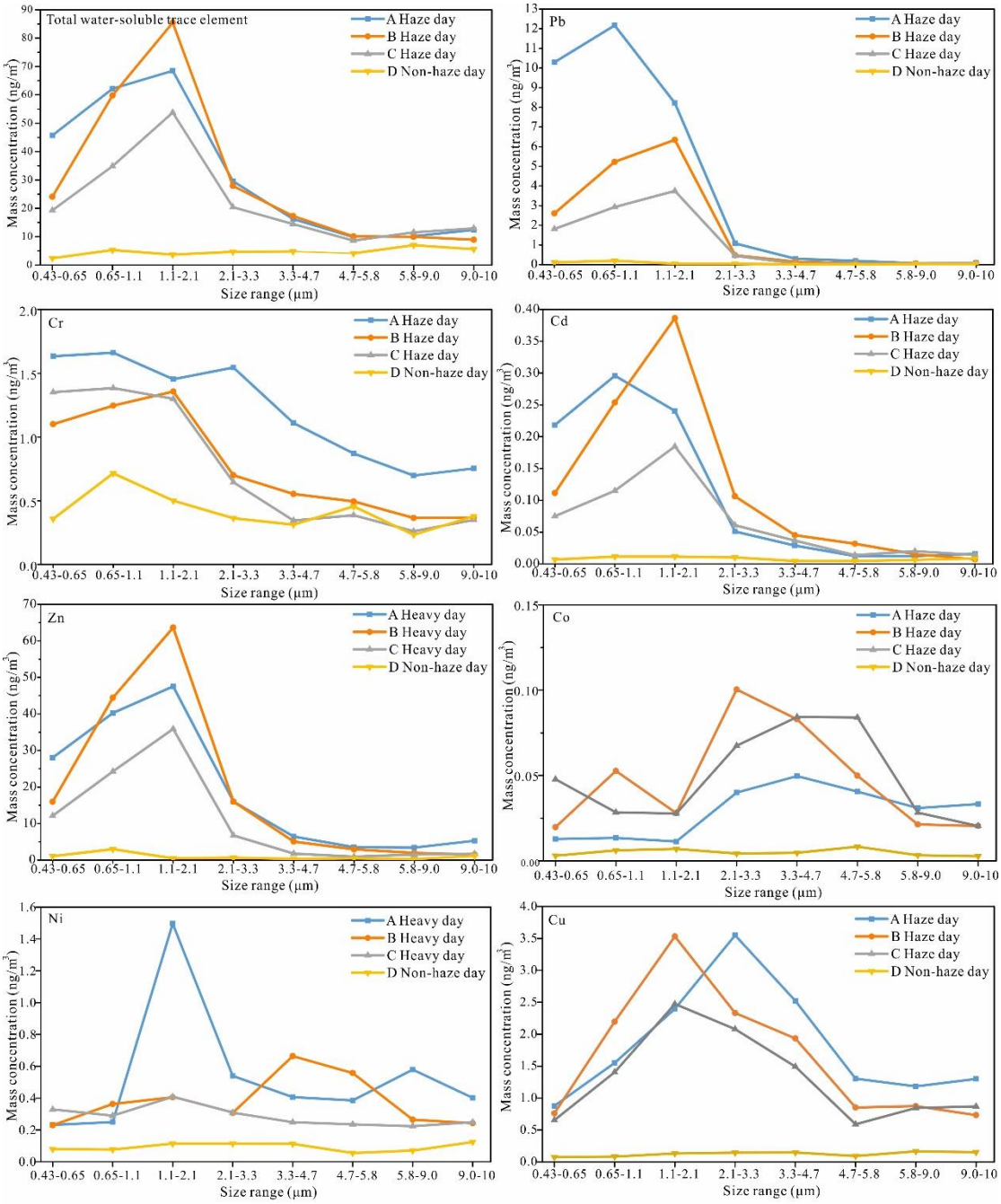


Fig.3 Mass-size distribution of total WSTE and individual water-soluble Pb, Cr, Cd, Zn, Co, Ni, and Cu over the particle size range with different particle sizes in haze and non-haze days

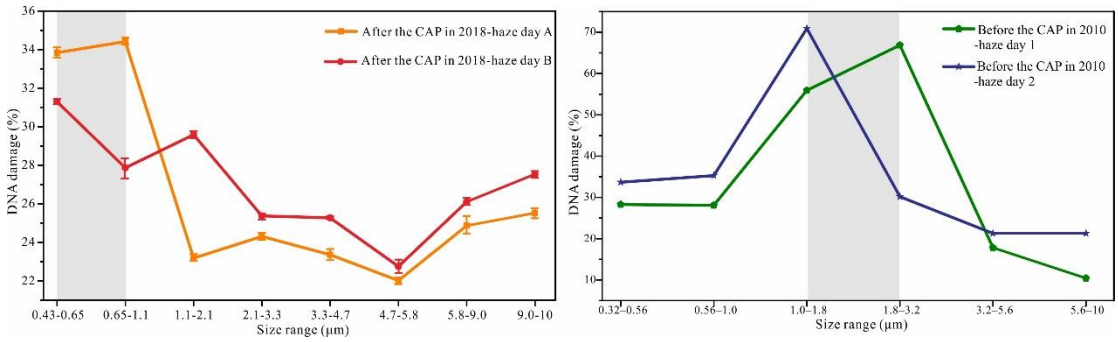


Fig.4 The particle-induced DNA damage at the particle dosage of 100 μg/ml over the particle size range in haze days before and after the CAP. The data in 2010 is from Sun et al. (2014). The grey shadow areas represent the maximum of DNA damage in different particle size ranges in haze days.

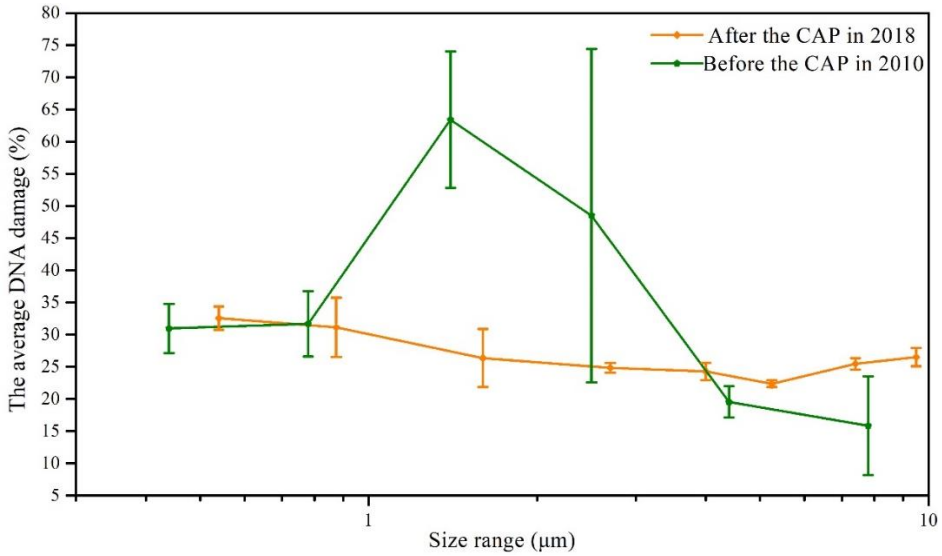


Fig.5 The average DNA damage induced by size-segregated particles at the particle dosage of 100 μg/ml in haze days before and after the CAP. The data in 2010 is from Sun et al. (2014).

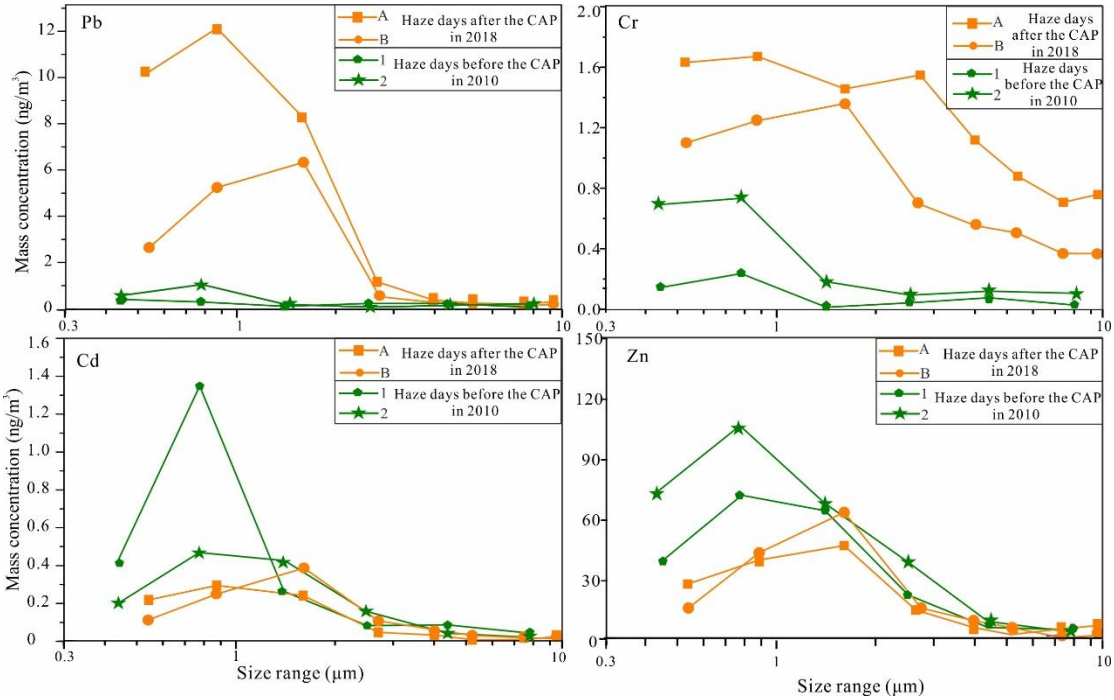


Fig.6 A comparison of the mass concentration of WSHM before and after the CAP. The data in 2010 is from Sun et al. (2014).

Table 1 Plasmid DNA damage rate (%) induced by size-segregated airborne particles at the particle dosage of 100 μg/ml for samples

| Size range (μm) | A Haze day | B Haze day | C Haze day | D Non-haze day | Blank |
|---|---|---|---|---|---|
| 0.43-0.65 | 33.84 | 31.29 | 31.58 | — | < 10 |
| 0.65-1.1 | 34.42 | 27.87 | 30.17 | — | |
| 1.1-2.1 | 23.18 | 29.58 | 25.10 | 16.94 | |
| 2.1-3.3 | 24.31 | 25.37 | 22.85 | 17.45 | |
| 3.3-4.7 | 23.36 | 25.27 | 26.13 | 19.34 | |
| 4.7-5.8 | 22.02 | 22.75 | 25.21 | 18.32 | |
| 5.8-9.0 | 24.87 | 26.10 | 23.60 | 13.68 | |
| 9.0-10 | 25.53 | 27.54 | 26.27 | 18.56 | |

Table 2 The Pearson correlation between the concentrations of WSHM (μg/g) and DNA damage rate at 100 μg/mL for the size-segregated particles

| The type of elements | total | Pb | Cr | Cd | Zn | Cu | Co | Ni |
|---|---|---|---|---|---|---|---|---|
| Correlation coefficient | 0.558[a] | 0.595[a] | 0.593[a] | 0.590[a] | 0.533[a] | 0.316 | 0.303 | 0.114 |

[a] Significantly correlated at the 0.01 level (both sides).

Supplementary material

Fig.S1 The hourly variation of $PM_{2.5}$ mass concentration during the pollution period

Table S1 Meteorological condition during the sampling periods

Table S2 Contents of 7 typical WSHM in size-segregated particles during the sampling periods

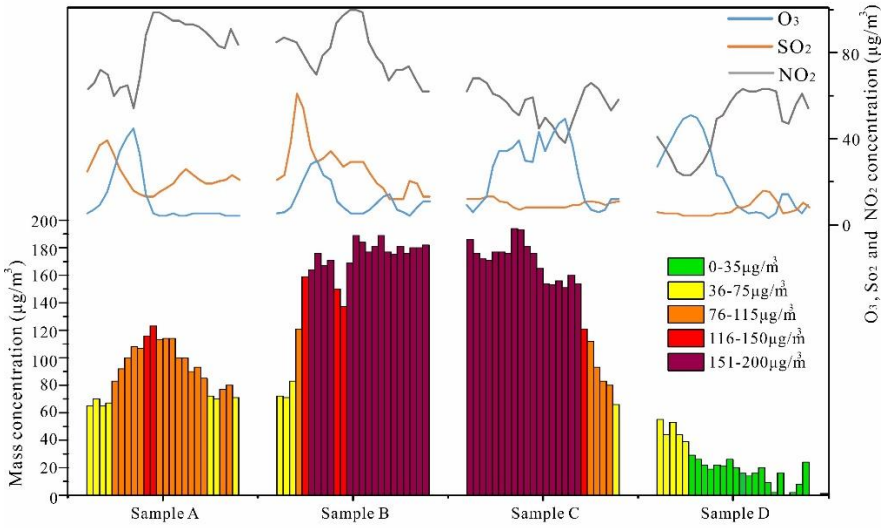


Fig.S1 The hourly variation of $PM_{2.5}$, $NO_2$, $SO_2$, $O_3$ mass concentration during the pollution period

Table S1 Meteorological condition during the sampling periods

| Time period | No. | Temperature(℃) | | | Relative humidity(%) | | | Pressure(hPa) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Mini. | Max. | Ave. | Mini. | Max. | Ave. | Mini. | Max. | Ave. |
| 2018.11.30-2018.12.01 | A | 3.7 | 9.1 | 7.9 | 43.5 | 51.2 | 46.8 | 1018.7 | 1019.4 | 1018.9 |
| 2018.12.01-2018.12.02 | B | 5.2 | 5.8 | 5.4 | 47.7 | 95.9 | 52.6 | 1009.7 | 1020.2 | 1018.6 |
| 2018.12.02-2018.12.03 | C | 5.3 | 7 | 5.9 | 13.9 | 100 | 44.9 | 1010.9 | 1016.2 | 1014.3 |
| 2018.12.03-2018.12.04 | D | 3.2 | 5.7 | 4.5 | 13.4 | 14.9 | 14 | 1017.1 | 1023.4 | 1019.9 |

According to the analysis of monitoring data and meteorological data, C was seriously influenced by wind-blown mineral dust.

Table S2 Contents of 7 typical WSHM in size-segregated particles during the sampling periods (Unit: ppt)

| Size range (μm) / Trace elements | 0.43-0.56 | 0.56-1.1 | 1.1-2.1 | 2.1-3.3 | 3.3-4.7 | 4.7-5.8 | 5.8-9 | 9-10 | 0.43-0.56 | 0.56-1.1 |
|---|---|---|---|---|---|---|---|---|---|---|

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cr | 15541 | 22352 | 16673 | 18828 | 17115 | 11879 | 8616 | 7266 | 13252 | 11244 |
| Co | 316 | 416 | 466 | 605 | 618 | 155 | 166 | 123 | 246 | 193 |
| Ni | 2202 | 3346 | 17165 | 6577 | 6259 | 5257 | 7148 | 3873 | 2762 | 3277 |
| Cu | 8333 | 20840 | 27506 | 43265 | 38910 | 17783 | 14616 | 12532 | 9165 | 19815 |
| Zn | 266517 | 541056 | 545199 | 194726 | 99197 | 47873 | 42060 | 51197 | 191974 | 401097 |
| Cd | 2077 | 3977 | 2758 | 623 | 445 | 170 | 151 | 156 | 1344 | 2290 |
| Pb | 97877 | 163697 | 94267 | 13089 | 4638 | 2596 | 791 | 887 | 31335 | 47172 |

| Size range (μm) / Trace element | 1.1-2.1 | 2.1-3.3 | 3.3-4.7 | 4.7-5.8 | 5.8-9 | 9-10 | 0.43-0.56 | 0.56-1.1 | 1.1-2.1 | 2.1-3.3 | 3.3-4.7 | 4.7-5.8 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cr | 15517 | 9136 | 6310 | 7055 | 5242 | 4931 | 13782 | 14746 | 12972 | 6895 | 3664 | 3763 |
| Co | 571 | 1083 | 1145 | 399 | 756 | 265 | 208 | 300 | 838 | 900 | 716 | 270 |
| Ni | 4634 | 3999 | 7567 | 7945 | 3796 | 3238 | 3350 | 3081 | 4065 | 3288 | 2631 | 2287 |
| Cu | 40374 | 30453 | 22044 | 12140 | 12541 | 9798 | 6675 | 14953 | 24681 | 22217 | 15840 | 5743 |
| Zn | 727730 | 208432 | 57446 | 42204 | 28069 | 20698 | 123609 | 258221 | 357903 | 72140 | 18664 | 9277 |
| Cd | 4418 | 1387 | 516 | 453 | 220 | 100 | 766 | 1225 | 1843 | 651 | 390 | 135 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pb | 72557 | 6165 | 1698 | 833 | 730 | 733 | 18480 | 31153 | 37387 | 4756 | 638 | 503 |

| Size range (μm) / Trace element | 5.8-9 | 9-10 | 0.43-0.56 | 0.56-1.1 | 1.1-2.1 | 2.1-3.3 | 3.3-4.7 | 4.7-5.8 | 5.8-9 | 9-10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Cr | 2635 | 3067 | 12843 | 14892 | 6819 | 3619 | 3616 | 5293 | 2270 | 3718 |
| Co | 286 | 419 | 97 | 67 | 113 | 47 | 50 | 81 | 60 | 30 |
| Ni | 2247 | 2174 | 2822 | 1584 | 1547 | 1133 | 1295 | 631 | 677 | 1213 |
| Cu | 8511 | 7619 | 2635 | 1731 | 1806 | 1458 | 1718 | 1066 | 1624 | 1491 |
| Zn | 15082 | 15172 | 38589 | 62049 | 6377 | 6124 | 3554 | 5293 | 2159 | 11260 |
| Cd | 202 | 126 | 247 | 242 | 160 | 102 | 55 | 55 | 63 | 83 |
| Pb | 237 | 470 | 3973 | 4072 | 620 | 456 | 80 | 100 | 267 | 282 |