

Contents lists available at ScienceDirect

# Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

## Molecular characterization of organic aerosols in Taiyuan, China: Seasonal variation and source identification



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GRAPHICAL ABSTRACT

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## HIGHLIGHTS

- Molecular composition and variation of OAs were studied in a typical mining city.
- OA molecules in summer were more oxidative, while in winter were shown more condensed.
- Biogenic OSs and PANHs were predominant in summer and winter OAs respectively.
- Air mass transportation contributed a certain amount of PM<sub>2.5</sub> in Taiyuan.

## ARTICLE INFO

Article history: Received 21 April 2021 Received in revised form 26 July 2021 Accepted 29 July 2021 Available online 2 August 2021

Editor: Jianmin Chen

Keywords: Organic aerosol (OA) Orbitrap MS Molecular characterization Seasonal variation Source identification





## ABSTRACT

Fine particulate matter (PM<sub>2.5</sub>) samples collected in 2018 in Taiyuan, a typical industrial and mining city in North China Plain (NCP), were characterized based on ultrahigh-performance liquid chromatography (UHPLC) coupled with orbitrap mass spectrometry. Potential molecular identifications based on precise molecular weight were conducted to obtain the compositional and source information of organic aerosols (OAs) in this city. Evident variation trends were observed during the sampling period in the composition, degree of oxidation and saturation of the obtained molecules. The proportion of CHOS- and CHO+ were increased from winter to summer and then decreased, conversely the proportion of CHN+ was decreased from winter to summer and then increased. By reclassifying the molecules, OA molecules were observed to be more saturated and oxidized in summer. It was caused by the high abundance of organosulfates (OSs) in summer, and aromatic amines/N-heterocycle aromatic hydrocarbons (PANHs) in winter. Molecular identification indicated that the OSs were basically originated from biogenic source isoprene or monoterpene, while the aromatic amines and PANHs were related to anthropogenic emissions of fossil fuel combustion, like other cities in the NCP area. The prevailing northwesterlies in winter may bring coal-burning pollutants from other cities, while the high abundance of organosulfates in summer may be related to the PM<sub>2.5</sub> transportation from Shijiazhuang. This study firstly demonstrates the molecular composition characteristics, potential sources, and geographical origins of PM<sub>2.5</sub> in Taiyuan, which gives a comprehensive understanding of PM<sub>2.5</sub> in a typical industrial and mining city.

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#### 1. Introduction

Atmospheric aerosol is a suspension mixture of fine solid particles or liquid droplets in the air, and is also known as particulate matter (PM) (Rabha and Saikia, 2020). As a substantial portion of atmospheric aerosol, organic aerosols (OAs) constitute up to 90% of the submicron particulate mass (Johnston and Kerecman, 2019; Kroll et al., 2011), and have shown broad effects on atmospheric processes, climate, ecology, and public health (Hallquist et al., 2009; Pinto et al., 2010; Pöschl, 2005). In accordance with its sources, OAs could be attributed to primary organic aerosols (POAs) originated from the direct emission of biogenic or anthropogenic sources and secondary organic aerosols (SOAs) formed by the reaction of several gaseous precursors (e.g., NO<sub>x</sub>, SO<sub>2</sub>) in the atmosphere (Mather et al., 2003; Seinfeld and Pankow, 2003). The composition of OAs is labile owing to the diversity of origins, the intricacy of multiple chemical reactions as well as the change of meteorological and geographic conditions (Goldstein and Galbally, 2007; Jimenez et al., 2009; Liu et al., 2009). Previous studies reported that OAs contained a variety of organic species, such as hydrocarbons, alcohols, aldehydes, carboxylic acids, organosulfates, organonitrates and organic amines (Gentner et al., 2012; Sheesley et al., 2003; Unger et al., 2008). Only 10- 30% of these components have been specifically identified so far due to their high complexity and variety (Hoffmann et al., 2011). Hence, the elucidation of the chemical composition and variation of OAs at the molecular level is an important yet challenging task.

A variety of methods have been utilized to the chemical determination of OAs including gas chromatography (GC)/liquid chromatography (LC) mass spectrometry (GC-MS/LC-MS), two-dimensional GC equipped with time-of-flight mass spectrometry ( $GC \times GC$ -ToF MS), high-resolution mass spectrometry coupled with electrospray ionization (ESI-HRMS) and unit mass resolution aerosol mass spectrometry (UMR-AMS) (Alam and Harrison, 2016; Chauhan, 2014; Jiang et al., 2016; Tao et al., 2014; Wu et al., 2018; Zhang et al., 2011). Among these methods, ESI-HRMS especially ultrahigh-resolution mass spectrometry (UHRMS) like Fourier transform ion cyclotron resonance mass spectrometry (FT ICR-MS) and orbitrap mass spectrometry have been widely adopted in recent years, to obtain accurate molecular composition information of OAs based on their high mass resolution and accuracy (Lin et al., 2012; Nizkorodov et al., 2011; Noziere et al., 2015; Wang and Schrader, 2015). Based on the UHRMS, several studies have been carried out recently to explore the specific molecular composition in megacities like Beijing, Shanghai, Guangzhou, Hong Kong and Mainz to indicate the temporal and spatial changes of OAs (Kuang et al., 2018; Wang et al., 2019b; Wang et al., 2018; Wang et al., 2016). Most of these studies in China are focused on the hotspots including the North China Plain (NCP), Yangtze River Delta (YRD) and Pearl River Delta (PRD) area (Zhang and Cao, 2015). However, quite a few studies reported that the rapid increase of fine particulate matter (PM<sub>2.5</sub>) concentrations not only contribute to the local air pollution, but also have a territorial influence through transportation (Xie et al., 2019; Zheng et al., 2015). Molecular characterization of OAs in the surrounding areas of these hotspots is also of fundamental importance.

Taiyuan, the capital and largest city of Shanxi province, is located in the west of the NCP area and surrounded by mountains from the east (Taihang Mountains), west (Lvliang Mountains) and north (Xizhou Mountains). As a main manufacturing and mining base of China, Taiyuan has enormous coal usage for electricity generation and other industrial activities like coking, steeling and chemical production (He et al., 2015). With the combined effects of unfavorable dispersion conditions, typical continental monsoonal climate and a high level of industrialization and urbanization, Taiyuan has suffered from serve air pollutions and was one of the most polluted cities in the world (Mu et al., 2019; Wei et al., 2018). Moreover, it is situated along the air pollution transmission pathway of the Beijing-Tianjin-Hebei (BTH) region, and the mining and industrial activities could increase the pollution levels in this area due to the transportation of airborne contaminants (Li et al., 2020; Mu et al., 2019). Therefore, evaluating the molecular composition and seasonal variation of OAs in Taiyuan is of great significance to further alleviate the air pollution in BTH. Most of the previous studies in Taiyuan were focused on the analysis of the carbonaceous components in  $PM_{2.5}$  and did not consider the specific characterization of the molecular composition of OAs in different seasons, to give a further investigation of their typical characteristics (He et al., 2015; Meng et al., 2007; Mu et al., 2019). This hindered the comprehensive understanding of the regional pollution level and source apportionment of OAs in Taiyuan.

In this study, a comprehensive investigation on the seasonal variation of OAs' molecular composition was conducted through the annual collection and measurement of PM<sub>2.5</sub> samples from January 2018 to December 2018 in Taiyuan. The targets of this research covered (1) Determine the specific molecular composition of OAs based on UHRMS to present its characteristics and seasonal variation trend; (2) Investigate the individual OA components under different meteorological conditions and anthropogenic influences, to reveal its potential sources in different seasons. The dominance pattern of SOAs was further discussed to reveal its local traits based on the identification of organic acids and organosulfates (OSs); (3) Analyze the air mass trajectories in different seasons based on HYSPLIT4 mode and clustering analysis to study its geographical transportation.

#### 2. Materials and methods

#### 2.1. Sample collection and pretreatment

24-h integrated PM<sub>2.5</sub> samples were collected onto 90 mm diameter quartz microfiber filters (QMA, Whatman International Ltd., UK) with a medium volume air sampler (ADS-2062E, AMAE (Shenzhen) Co., Ltd., China) from January to December 2018 in Taiyuan. The sampling site was located at Shanxi University (37°47′42.70″ N, 112°34′52.51″ E), where no obvious pollution sources (e.g., industrial facilities) might cause positive effects around in Taiyuan, China (Song et al., 2020; Zhang et al., 2018). Table S1 contained the detailed sampling date, atmospheric and meteoric conditions during the sampling periods. All quartz filters were baked at 550 °C for 5 h in the muffle furnace before sampling. Filters were then wrapped with aluminum foil and stored at a -80 °C freezer for further analysis.

The extraction procedure was performed in reference to earlier studies with modification (Wang et al., 2018). Briefly, a 4 cm<sup>2</sup> fraction of the filter was extracted with 2 mL acetonitrile-water (8/2, v/v) in an ultrasonic bath for 30 min. Samples were extracted 3 times with the same procedure. Then the extracts were pooled together and filtered through a 0.22  $\mu$ m Teflon syringe filter to remove insoluble impurities. The filtered sample was then blown with nitrogen to near dryness. Finally, the residual was redissolved in 1 mL acetonitrile-water (1/9, v/v) solvent for subsequent determination.

#### 2.2. UHRMS analysis

Sample analysis was conducted with an ultrahigh-resolution mass spectrometer (Q Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer; Thermo Scientific, USA) coupled to an UHPLC system (Dionex Ulti-Mate 3000, Thermo Scientific, USA). Analytes were separated using a Waters Acquity BEH C18 column ( $1.7 \mu$ m,  $2.1 \times 100 m$ m) with mobile phases consisting of (A) 2% acetonitrile and 0.04% formic acid in ultrapure water and (B) 2% ultrapure water in acetonitrile. Elution procedure used in the gradient mode with a flow rate of 300 µL/min and the following gradients: 2% B for 1.5 min, increased linearly to 20% B in 1 min and hold for 5 min, increased linearly to 98% B in 1 min and hold for 2.5 min, back to 2% B in the next 5 min and hold for 1 min. The injection volume of each sample was 20 µL and blank filter samples were also analyzed for background subtraction.

The spray voltage of the ESI source equipped for Q-Exactive MS was -3.3 kV in the negative ion mode (ESI–) and 4.0 kV in the positive ion mode (ESI+). The sheath and auxiliary gases were 45 psi and 10 psi respectively. 320 °C capillary temperature and 55 S-lens RF level was adopted. The scanning range was set to m/z 80– 800 with a resolution of 140,000 at m/z 200. The MS system was pre-calibrated using sodium acetate solution to ensure the mass accuracy of the measurements was less than 3 ppm.

#### 2.3. Data processing

The obtained LC-MS spectrums were processed with Xcalibur software (V4.3.7, Thermo Scientific, USA) to subtract the blank sample for the elimination of background peaks from contaminants and other interferences. Then the data were proceeded by MZmine (V2.53) software, which enables several LC-MS data processing functions (Lin et al., 2012; Pluskal et al., 2010; Tao et al., 2014; Wang et al., 2017a). The processing workflow and parameters referred to previous studies and were described in the supporting information (Wang et al., 2017a; Wang et al., 2021c). It should be noted that the compositional elemental of these formulas was constrained as  $C_{1-40}H_{0-100}O_{0-40}N_{0-5}S_{0-2}$  and *m/z* tolerance was 3 ppm for both ESI modes.

#### 2.4. Statistical analysis

A certainly obtained compound was expressed as formula  $C_cH_hO_oN_nS_s$ , where c, h, o, n, and s correspond to the numbers of carbon, hydrogen, oxygen, nitrogen, and sulfur atoms in the molecular formula, respectively. To get a deeper insight into these molecules, several indicators were calculated to character their features including double bond equivalent (DBE), aromaticity equivalent ( $X_c$ ), Carbon oxidation state ( $OS_c$ ) and Kendrick mass defect (KMD).

DBE represents the total amount of double bonds and cyclic rings in a molecule, and was widely used to indicate the level of unsaturation for a certain compound obtained from UHRMS (Kuang et al., 2018; Wang et al., 2019a; Wang et al., 2017a). DBE was calculated based on Eq. (1):

$$DBE = c - \frac{h}{2} + \frac{n}{2} + 1 \tag{1}$$

To achieve a better identification of the aromatic/condensed aromatic molecules in OA, X<sub>c</sub> was also calculated with Eq. (2):

$$X_c = \frac{3[DBE - (m \times o + n \times s)] - 2}{DBE - (m \times o + n \times s)}$$
(2)

where *m* and *n* represent the fraction of oxygen/sulfur involved in the  $\pi$ -bond structure of the molecule. X<sub>c</sub> was defined as 0 when *DBE* – (*m* × *o* + *n* × *s*)≤0 and the detailed value selection of *m* and *n* were described by Yassine et al. (2014). Herein, we adopt m = n = 0.5 for compounds obtained in ESI–, while m = n = 1 for compounds obtained in ESI+ in reference to (Wang et al.)'s method.

OS<sub>c</sub> was defined as the charge a carbon atom would take if it were to lose all electrons in bonds with more electronegative atoms, but gain all electrons in bonds with less electronegative atoms, and was usually

used as an index to indicate the degree of oxidation of  $PM_{2.5}$  species (Kroll et al., 2011). For a certain compound with the ratio of O/C and H/C, the calculation of OS<sub>c</sub> was based on Eq. (3):

$$OS_c \approx 20/C - H/C$$
 (3)

The KMD was commonly used to identify molecules with related molecular formulas by sorting the compounds according to their differences in the homologous series like  $CH_2$ . In this study, we use KMD to represent homologous series that differ by one ethyl and the calculation was bases on Eqs. (4) and (5):

$$KM = IUPAC \ mass \times \left(\frac{14.00000}{14.01565}\right)$$
 (4)

$$KMD = Nominal \ mass - KM \tag{5}$$

where *IUPAC mass* is the exact mass of a compound calculated from the m/z value measured by the mass spectrometer and "Nominal Mass" is the rounded integer mass of a compound (Hughey et al., 2001).

Besides these indicators described above, other follow-up data analysis was applied using SPSS 11.0 (SPSS Inc., Chicago, USA). Pearson correlation analysis with a two-tailed test was employed to explore the correlation between the portion of detected organic species and atmosphere quality parameters. All differences were regarded as statistically significant at P<0.05.

## 2.5. Backward air mass trajectory analysis

Analysis of the air movement trajectory in different seasons was conducted using the HYSPLIT4 (Hybrid Single Particle Lagrangian Integrated Trajectory, version 4) backward trajectory model, to identify the movement path of the air mass carrying PM<sub>2.5</sub> and indicates the potential geographical origins. The sampling point in Taiyuan City (112.58E, 37.79N) was used as the starting point, selecting a height of 100 m, a 24-h backward trajectory simulation was performed in different seasons during 2018.

#### 3. Result and discussion

#### 3.1. Overall variation

After UHRMS characterization, data processing and statistical analysis, a total of 174–489 and 776–2013 molecules were obtained from ESI – and ESI+, which were assigned into 28 and 32 species respectively (see fig. S1). The comparison of the molecular composition portion between Taiyuan and other cities were listed in Table 1. A similar chemical species proportion was observed in January to the results obtained from Beijing in January 2014, which was a heavily polluted period with a high level of PM<sub>2.5</sub> (Wang et al., 2018). Specifically, the proportion of all species obtained from ESI+ and CHO, CHOS species obtained from ESI– were quite similar between Taiyuan and Beijing. However, the proportion of CHON components was lower in Taiyuan (24.2% vs. 48%), while the part of CHONS was higher (21.3% vs. 5%). The high proportion of CHONS in Taiyuan was mainly contributed by the molecule

Table 1

Molecular composition portion comparation of each subgroup in PM<sub>2.5</sub> between Taiyuan with other cities.

City	Date	CHO-/CHO+	CHON-/CHON+	CHONS-/CHONS+	CHOS-/CHOS+	CHN-/CHN+	Reference
Taiyuan	January 2018	42.2/20.5	24.2/43.4	21.3/8.9	12.3/0	0/27.3	This study
Beijing-H	January 2014	35/21	48/36	5/4	12/0	0/39	(Wang et al., 2018)
Beijing-L	January 2014	24/22	53/40	7/3	16/0	0/35	(Wang et al., 2018)
Shanghai	January 2014	40/4	44/24.7	4/0/3	12/0	0/71	(Wang et al., 2019b)
Guangzhou	January 2014	42/8	39/29	5/1	14/0	0/62	(Wang et al., 2019b)
Changchun	January 2014	30/13	55/46.5	5/0.5	10/0	0/40	(Wang et al., 2019b)
Mainz	January 2015	23/13	40/74	22//2	15/0	0/11	(Wang et al., 2018)

 $C_{10}H_{17}NO_7S$ , which has been reported to be  $\alpha$ -pinene-derived pinanediol mononitrate, indicating the important role of biogenic monoterpene precursor in Taiyuan (Gómez-González et al., 2012; Wang et al., 2018). The identification of CHON— compounds (Table 2) showed that most of them were nitro aromatic phenol compounds stemmed from vehicle emission or biomass burning, which revealed a relatively low level of traffic and biomass burning activities in Taiyuan, 2018 compared to Beijing, 2014 (Tong et al., 2016; Zhang, 2012).

To describe the specific composition of OAs in different months, detected molecules were classified into different subgroups and their monthly variation in abundance was shown in Fig. 1. It could be seen that the dominant abundance of CHO and CHOS compounds in ESI—, while CHO, CHON and CHN compounds in ESI+. Interestingly, the proportion of CHOS in ESI— showed a conspicuous fluctuating trend of rise and then fall with the time varied from January to December in 2018. A similar trend was also observed for CHO in ESI+, with the proportion of CHN compounds showed an inversely drop and then rise trend. These trends meant a particularly obvious difference in the chemical composition compared between winter and summer. That is, more CHN, CHON and CHONS compounds but fewer CHOS compounds were identified in winter, while more CHOS and CHO compounds were observed in summer. The variation of molecular composition may indicate the change of

#### Table 2

Potential identities and sources apportion for the most intense species from each month at different ionization modes.

Formula	Neutral mass	DBE	Month	RI	Potential identity	Source	Reference
C10H13NO3	195.0823	5	1-	1.00	5-Methyl-2-(1-methylethyl) 4-nitrophenol	Traffic, coal combustion or biomass burning	(Zhang, 2012)
C10H7NO3	189.0353	8	1-	0.85	4-Nitro-1-naphthol	biomass burning	(Zhang, 2012)
C9H11NO4	197.0615	5	1-	0.84	(2S)-2-Amino-3-(3,4-dihydroxyphenyl) propanoic acid	biomass burning	(Tong et al., 2016)
C9H16O4	188.0976	2	2-, 3-, 6-, 8-, 11-, 12-	1.00, 0.89, 0.91, 0.55, 1.00, 0.71	Azelaic acid	Oxidation product of unsaturated fatty acid. food cooking	(Gysel et al., 2018; Ho et al., 2010)
C9H8O4	180.0350	6	2-	0.82			
C8H16O4S	208.0697	1	2-, 11-, 12-	0.63, 1.00, 0.66			
C16H32O3	272.2279	1	3—	1.00	3-Hydroxyhexadecanoic acid	Bioaerosol emissions	(Watson and Chow, 2018)
C16H30O3	270.2122	2	3—	0.98	2-Oxo-tetredecanoic acid	Cooking emissions and oils	(Qi et al., 2019)
C3H6O3	90.0244	1	4-	1.00		Bonfire burn period	(Priestley et al., 2018)
C10H1707NS	295.0653	3	4-, 5-, 6-, 9-, 10-	0.96, 1.00, 1.00, 1.00, 1.00	Pinanediol mononitrate	$\alpha$ -Pinene, $\beta$ -pinene, $\alpha$ -terpinene, terpinolene	(Gómez-González et al., 2012)
C8H6O4	166.0193	6	4-	0.80	Phthalic acid	Vehicle exhaust	(Williams et al., 2007)
C4H8O6S	183.9969	1	5-	0.95	Isoprene-derived secondary organosulfate	Bioaerosol emissions	(Hughes et al., 2021)
C6H10O7S	226.0074	2	5-	0.92	Isoprene-derived secondary organosulfate	Bioaerosol emissions	(Tao et al., 2014)
C22H27NO5	385.1816	10	6—, 7—, 9—, 10—	0.86, 1.00, 0.45, 0.86	C C C C C C C C C C C C C C C C C C C		
C5H8O7S	211.9918	2	7—	0.84	Isoprene-derived secondary organosulfate	Bioaerosol emissions	(Bryant et al., 2020)
C17H26O4	294.1758	5	8-	1.00	Secondary ozonide from β-pinene ozonolysis	Bioaerosol emissions	(Slade et al., 2019)
C18H36O3	300.2592	1	8-	0.89	3-Hydroxyoctadecanoic acid	Bioaerosol emissions	(Watson and Chow, 2018)
C9H9NO7S	275.0027	6	9—	1.00			,
C9H15NO8S	297.0446	3	10-	0.88	Nitrated monoterpene-derived organosulfate	SOA	(Lin et al., 2013)
C9H14O4	186.0819	3	11-	0.68	$\alpha$ -Pinene, pinic acid	Oxidation products of BVOCs	(Daellenbach et al., 2019)
C8H9NO4	183.0459	5	12-	1.00	Nitrophenol species	Brushwood	(Fleming et al., 2018)
C9H7N	129.0651	7	1+,5+	1.00, 0.91	Quinoline	Tobacco smoke	(Wang et al., 2017a)
C10H9N	143.0808	7	1+, 4+, 5+, 12+	0.87, 0.39, 1.00, 0.16	1-Naphthalenamine; 2-Naphthylamine	Aluminum smelter; tobacco smoke	(Ge et al., 2011)
C11H11N	157.0964	7	1+	0.86	1-Naphthalenemethylamine	Cookfire	(Fleming et al., 2018)
C7H3N	101.0338	7	2+, 4+, 9+, 10+, 12+	1.00, 1.00, 1.00, 1.00, 1.00			2010)
C6H15N	101.1277	0	2+	0.94	Triethylamine; Hexylamine; Dipropylamine	Cattle; swine; solvent; sewage; ambient air: Tobacco smoke	(Ge et al., 2011)
C10H14N2	162.1230	5	2+, 11+, 12+	0.20, 0.25, 0.60, 0.25	Diisopropylamine; n-Propylisopropylamine	Tobacco smoke	(Wang et al., 2017a)
C5H11NO2	117.0863	1	3+	1.00	n riepjisepropjianine		
C5H8N2O	112.0709	3	3+	0.63			
C5H10N2	98.0917	2	3+,11+	0.35, 0.56	Dimethylaminopropionitrile		
C6H11NO	113.0913	2	4+	0.67	ε-Caprolactam	Industry	(Cheng et al., 2006)
C16H22O4	278.1591	6	5+, 6+, 7+, 8+	0.75, 0.93, 1.00, 1.00	Aliphatic acid		(Lin et al., 2012)
C16H35NO2	273.2741	0	6+,7+,8+	1.00, 0.72, 0.77	Sphinganine		(Loo et al., 2020)
C7H11N3	137.1026	4	6+, 10+, 11+	0.85, 0.23, 1.00		Straw residue burning	(Wang et al., 2017b)
C8H4O3	148.0233	7	7+,8+	0.64, 0.65	Phthalic	Anhydride naphthalene	(Riva et al., 2015)
C17H11N	229.0964	13	9+	0.34	Benzo[ <i>a</i> ]acridine/benzo[ <i>c</i> ]acridine	Coal combustion	(Jalees et al., 2020)
CI9HIIN	253.0964	15	9+	0.30	Polycyclic aromatic N-heterocycle hydrocarbons	Coal combustion	(Lintelmann et al., 2010)



Fig. 1. Annual variation in abundance percentages of detected CHO, CHON, CHONS CHOS, CHN compounds as well as the average H/C, O/C and DBE obtained from ESI- (left) and ESI+ (right) in PM2.5 collected from Taiyuan during 2018.

macroscopic properties of OAs like oxidative and aromaticity. Fig. 1 showed the average O/C, H/C ratio and DBE of the obtained molecules in each month. Both O/C and H/C ratios showed a relatively high level in summer compared to winter. As an indicator of the unsaturation level, DBE showed a converse tendency that raised steeply during winter and reached a peak in January. In line with the previous studies in Shanghai (Wang et al., 2017a), these results may prove that the molecules were gradually becoming saturated and oxidized from winter to summer, and then becoming unsaturated from summer to winter.

To specifically illustrate the change based on molecule level, we identified the molecules with the most intense abundance obtained in each month and listed their formula, neutral mass, DBE, relative intensity (RI), potential identification and source/precursor in Table 2. Assignments of compounds and their source/precursors were according to the accurate mass formula in association with previous chamber and field studies. From the result of molecular identification, the most abundant CHOS compounds obtained in ESI- were organosulfates, which were mostly formatted from the photochemical reaction of anthropogenic or biogenic sources precursors, and were reported to be promoted in summertime (Meade et al., 2016). It could be noted that a slight decrease of CHOS molecules was observed in April (Fig. 1), with a proportion of only 26.8% compared to March (37.8%) and May (39.7%). It was due to one of the sample days was April 12, which was a moderately rainy day and may result in the wet deposition of quite a few organosulfates (Altieri et al., 2009). The regularity in abundance proportion was also observed for CHN and CHO compounds in ESI+. The CHN compounds have mainly consisted of polycyclic aromatic Nheterocycle hydrocarbons (PANHs or azaarenes), which were

particularly considered to be markers for the combustion of coal (Alves et al., 2017; Bandowe et al., 2016). It is reasonable that CHN compounds increased remarkably during the central heating period of Taiyuan from October to April. The CHO compounds identified in ESI+ were mainly originated from the photooxidation of anthropogenic volatile organic compounds (AVOCs), which showed high abundance in summer with intensive illumination and oxidation effects (Wang et al., 2017a).

An anomalous low proportion of CHON, with a relatively high proportion of CHN molecules, was observed in September. By investigating the implementation of local policies, we found a special joint law enforcement action was carried out for pollution control of diesel vehicles and bulk material transport vehicles on 30 August. This may effectively decrease the emission of nitrated PAHs (CHON) in September, as the exhaust emissions of diesel vehicles were proved to an important source of nitrogen PAHs (Alves et al., 2017; Liu et al., 2017a). To specifically analyze the composition of high abundance CHN compounds in September, we have plotted the DBE-carbon number diagram of the most abundant CHN<sub>1</sub> class in CHN species in Fig. S3. Series of aromatic compounds with a difference of DBE = 3 (difference of one benzene ring) indicated these compounds may be aromatic amines (aminobenzene, amino naphthalene, aminophenanthrene, etc.) or PANHs. The identification of the most abundant molecules of C17H11N and C19H11N indicates they were most likely to be benzo acridine and 10-azabenzo pyrene (Jalees et al., 2020; Lintelmann et al., 2010). This may indicate that the series of aromatic compounds were more likely to be PANHs, which may be related to the coal combustion of local steelworks and thermal power plants. The result was further confirmed by the monthly

report on ambient air quality in Shanxi Province in September 2018 that Taiyuan had the highest level of  $NO_2$  and  $PM_{10}$  during that month leading to the worst comprehensive index of urban ambient air quality among 11 cities in Shanxi Province (Shanxi Province Environmental Monitoring Center, 2018).

As the seasonal variation showed obvious regularity, these changes might have been associated with the local atmosphere quality and meteorological conditions. The concentration of trace gases  $(O_3, NO_2, SO_2)$ and CO), mass loadings (PM<sub>2.5</sub>, PM<sub>10</sub>) and temperature during the sampling period was collected from Shanxi Province Environmental Monitoring Center (2021). Detailed data were shown in Table S1, while the Pearson correlation coefficients of detected molecular proportions with the atmosphere quality parameters were shown in Fig. 2. Positive correlations were observed between the proportion of CHOS - with O<sub>3</sub> (r = 0.51, P < 0.05) and temperature (r = 0.68, P < 0.01), while a negative correlation was found between CHOS- and SO<sub>2</sub> (r =-0.41, P < 0.01). It seemed that the relationship between the proportion of CHOS – and the concentration of  $SO_2$  was unreasonable, as  $SO_2$ is an important anthropogenic source marker of OSs (Cai et al., 2020) We hypothesized that the OSs in this area mainly came from biogenic source and was less associated with the gaseous SO<sub>2</sub>. The CHOS- molecules may be formed through the photooxidation of natural source precursors (e.g., isoprene) on acidic sulfate particles (Wang et al., 2017a). Former research also indicated that isoprene oxidation contributes significantly to the formation of OSs in the summer of the mid-Atlantic United States (Meade et al., 2016). Similarly, The CHO+ compounds may be also formatted by the photooxidation due to their high correlations with the strong oxidative O<sub>3</sub> and high temperature. Different from CHOS- and CHO+, the CHN+ molecules showed a negative correlation with  $O_3~(r=-0.45,\,P<0.05)$  and the temperature (r=-0.32), which revealed differentiation of their sources and formation pathways. As the identified CHN+ compounds were mainly aromatic amines and PANHs (Table 2), anthropogenic NH<sub>3</sub> emissions mixed with anthropogenic/biogenic SOAs were reported to be their primary source (O'Brien et al., 2013). The anthropogenic emission would be highly enhanced in winter due to the central heating using coal and bio-fuel burning. The different formation pathways and origins explained the difference in correlation results. The specific source attributions about CHO, CHOS and CHN compounds would be discussed in the sections below. These overall molecular variation results may imply the characteristics of OAs in Taiyuan: with the high level of O<sub>3</sub> in summer, quite a few OSs and CHO compounds were formatted, which increased the average O/C and H/C. While in winter anthropogenic sources were predominant with the massive burning of fossil fuels, caused a high level of unsaturated aromatic pollutants like PAHs, and PANHs. Jiang et al. (2016) have investigated the molecular composition of OAs in Beijing during hazy days in the winter of 2014, and also found high abundance of PAHs derived OSs and high condensed CHON and CHO molecules.

#### 3.2. Specific molecular species variation and potential sources

#### 3.2.1. CHO compounds

The CHO compounds obtained in different ionization modes were usually different as CHO- were usually considered as deprotonate compounds like alcohols or acids and carbonyls, while CHO+ molecules were usually esters, peroxides, or carbonyls (Lin et al., 2012). To clarify its specific composition, molecules were subdivided into four seasons for further discussion. The VK diagrams of CHO compounds obtained from positive and negative modes were shown in Fig. 3. Many studies have subdivided the CHO compounds into different regions to define their attribution (Cottrell et al., 2013; Kroll et al., 2011; Tu et al., 2016; Wang et al., 2021a). Here we combined their findings and define 5 groups as A: Aliphatic compounds (H/C  $\ge$  1.5, O/C  $\le$  0.5); B: Low oxidated aromatic compounds (H/C  $\leq$  1.0, O/C  $\leq$  0.5); C: High oxidized functional compounds like alcohols, esters, and peroxides (OSc  $\geq$  0, O/  $C \ge 0.6$ ); D; High reduced functional compounds like organic acids and carbonyls (OSc  $< 0, 0/C \ge 0.6$ ); E: Moderate oxygenation compounds  $(OSc \ge 0, O/C \ge 0 \text{ and } H/C \le 1.2)$  (Kourtchev et al., 2016; Tu et al., 2016). In ESI-, It could be seen a wide distribution of CHO molecules



**Fig. 2.** Pearson correlation coefficients of detected molecular proportions with the atmosphere quality parameters monitored the same day with the samples from Taiyuan during 2018–2019. Numbers with \* and \*\* represent significance at P < 0.05 and P < 0.01 respectively.

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**Fig. 3.** Van Krevelen (VK) diagrams of the CHO molecules obtained from ESI- (left) and ESI+ (right). The color represents molecules with different aromaticity equivalent (Xc). The pie chart is the proportion of different components. The red, blue, orange and green pots represent pyrene core structural compounds (Xc  $\ge 2.833$ ), anthracene core structural compounds ( $2.800 \le Xc < 2.833$ ), naphthalene core structural compounds ( $2.500 \le Xc < 2.714$ ) and aliphatic compounds (Xc  $\ge 2.800$ ). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Fig. 4. Carbon oxidation state (OSc) plots for CHO- and CHO+ compounds. The black dash ovals area marked as LV-OOA, SV-OOA, BBOA and HOA correspond to low-volatility, semi-volatile oxidized organic aerosol, biomass burning organic aerosol and hydrocarbon-like organic aerosol.

in the group A, C and D in spring, summer and autumn, which belong to aliphatic compounds, high oxidized functional compounds and high reduced functional compounds. Relatively, most of the CHO molecules in winter belong to low oxidated aromatic compounds in region B. Molecule distributions in ESI+ also indicate the same result that a larger proportion of CHO molecules attributed to region B in winter. This result may indicate a high level of aromaticity of the OAs in the winter Taiyuan. To further confirm this, we have introduced the parameter of aromaticity equivalent (Xc), which was used to determine the presence of pyrene core structural compounds ( $Xc \ge 2.833$ ), anthracene core structural compounds ( $2.800 \le Xc < 2.833$ ), naphthalene core structural compounds ( $2.714 \le Xc < 2.800$ ), aromatic (benzene core structural) compounds (2.500  $\leq$  Xc < 2.714) and aliphatic compounds (Xc <2.500) in OAs (Yassine et al., 2014). As the pie charts in Fig. 3 showed, the average percentage of total fractions of naphthalene, anthracene and pyrene core structural compounds in winter was 67.5%, which was much higher than that in spring (8.5%), autumn (8%) and summer (5.5%). These results certificated the former conclusion in 3.1 and indicate a large proportion of low-oxygen-containing condensed aromatic components in the winter OAs of Taiyuan.

The difference in compositional characteristics of CHO compounds from different seasons was probably related to the variety of emission sources and/or reactions. As the most abundant species in the obtained molecules, the CHO compounds take an average portion of 32% of the total molecules. This indicated that CHO compounds could represent the properties of the OAs to a certain extent and the source evaluation of them was of great importance. It is reported to use carbon oxidation state (OSc) plots to determine the potential source of the organic aerosol components (Kroll et al., 2011). Molecules with OSc between 0.25 and 1.0, carbon number between 4 and 13 and OSc between -0.5 and 0.25, carbon number between 5 and 18 were usually defined as lowvolatility and semi-volatile oxidized organic aerosol (LVOA and SVOA), which were produced by multistep oxidation reactions. In contrast, molecules contained 7-23 carbon atoms with an OSc ranged from -1.25 to -0.25 and were considered as primary biomass burning organic aerosol (BBOA), which was directly emitted into the atmosphere. Other molecules with more than 18 carbon atoms and -1 to -2 OS<sub>C</sub> values were implied to be hydrocarbon-like organic aerosol (HOA) (Kourtchev et al., 2015; Kourtchev et al., 2016). Fig. 4 showed the OSc plots for CHO- and CHO+ compounds and it was clear that most of the molecules obtained in winter were BBOA with high condensation structures. This result indicated that anthropogenic biomass burning source made the most important contribution to the OAs of Taiyuan during winter, which was consistent with the results from other megacities in China like Beijing, Shanghai, Guangzhou and Changchun (Wang et al., 2019b; Wang et al., 2017a; Zhang et al., 2013).

## 3.2.2. CHOS & CHONS compounds

The identification of the CHOS and CHONS compounds indicates most of them (91–100%) were OSs with  $O/S \ge 4$ , which is an important tracer for multiphase chemical processes leading to SOA formation (Meade et al., 2016; Tao et al., 2014; Wang et al., 2016). Here we focused on the main component of OSs in CHOS compounds to determine its composition and source. Former studies have shown that sulfatederived aerosol acidity could enhance the generation of OSs and other SOAs from biogenic precursors, and thus highlights the importance of organic acids as an indicator of SOAs' characteristics (Chan et al., 2011; Nozière et al., 2010). Fig. 5 illustrated the absolute intensity of identified organic acids originated from the anthropogenic/biogenic source and the ratios of these two sources. As important markers, the ratios of adipic acid to azelaic acid (C6/C9) and phthalic acid to azelaic acid (Ph/C9) have been widely used to reflect the relative contributions of anthropogenic versus biogenic SOA (Hansen et al., 2014; Yu et al., 2021). Here we adopt the ratios of C6/C9 and Ph/C9 to evaluate the source contribution of anthropogenic/biogenic (A/B) acids to SOA. The source of organic acidic SOA varies significantly in Taiyuan during 2018–2019. Samples in winter showed the highest C6/C9 (0.31  $\pm$ 0.06) and Ph/C9 ratios ( $3.59 \pm 0.67$ ), indicating a strong anthropogenic contribution in that season. Besides in winter, the C6/C9 and Ph/C9 ratios following the order of autumn (0.23  $\pm$  0.02, 2.44  $\pm$  0.17), summer  $(0.22 \pm 0.01, 1.74 \pm 0.23)$  and spring  $(0.20 \pm 0.01, 1.41 \pm 0.35)$ . Relatively lower ratios in summer and spring may indicate a comparable contribution from anthropogenic and biogenic precursors (Hansen et al., 2014). Similar results were also found in Beijing during 2017 (Yu et al., 2021). It was noteworthy that a remarkably high level of phthalic acid was observed in February and October, whose precursor was mainly considered as PAHs. This result may due to the Spring festival in February and central heating in October, which would cause a high level of PAHs through fireworks, cooking and coal burning (Zhang et al., 2019). A high level of phthalic acid was also observed in



Fig. 5. Intensity of identified organic acids derived from the anthropogenic/biogenic source and the ratio of C6/C9 and Ph/C9. Benzoic acid, phthalic acid, adipic acid and pimelic acid were usually considered as anthropogenic source SOA; Terpenylic acid, DTAA (diaterpenylic acid acetate), pinic acid, MBTCA (3-methyl-1,2,3-butanetricarboxylic acid), suberic acid and azelaic acid were biogenic source SOA.

the winter of Seoul, and other cities in the NCP area including Beijing, Tianjin and Shijiazhuang, which was also related to massive biomass burning in the cold season (Lee et al., 2012; Shen et al., 2018).

Similar to organic acids, the OSs could also be attributed to anthropogenic and biogenic sources. According to the report of earlier researches, 19 identified OSs were used to determine the source of the CHOS compounds. The number, molecular formula, suggested identification/precursor were listed in Table S2, while the absolute abundance of each compound and ratio between anthropogenic/biogenetic was shown in Fig. 6. It should be noted that the identified OSs and ratios are based on the studies before, quite a few unknown OSs may also have a certain amount of contribution from these sources. Here we take 19 of these OSs to determine their potential sources. It can be seen that the most abundant anthropogenic source OSs were  $C_6H_{10}O_7S$  (A2), which was reported as the product from cyclohexene photooxidation in the presence of SO<sub>2</sub> under high-NO<sub>x</sub> conditions (Liu et al., 2017b). Whereas the most abundant biogenic source OSs were C<sub>10</sub>H<sub>17</sub>NO<sub>7</sub>S (B14), which have been reported to be generated due to the oxidation of  $\alpha$ -pinene in the smog chamber (Surratt et al., 2008) and was frequently detected in Lahore (Kundu et al., 2013), mid-Atlantic United States (Meade et al., 2016) and Shanghai (Wang et al., 2021b). It is apparent that a high abundance of biogenic OSs was appeared in summer (May to July), which may be related to the high temperature, ozone concentration and light intensity, as these parameters showed a high level of correlations with the CHOS compounds in Fig. 3. The trend of the ratio was consistent with the result of organic acids (see Fig. 5), which showed a relatively lower in summer and higher in winter. However, the values of the ratio are all less than 1, showing an absolute biogenic dominant tendency (Hansen et al., 2014). This is consistent with the hypothesis we proposed in 3.1 that the formatted OSs in Taiyuan were mainly biogenic sources. Similar observations were also found in other studies. (Wang et al., 2021b) have recently quantified the concentration of 35 OSs in Shanghai and found that isopreneand monoterpene-derived biogenic OSs take an average accounting for more than 31% of the quantified OS concentrations, and suggesting the important contribution of biogenic emissions to the production of OSs and SOA in Shanghai. Also, they have indicated that the abundance of the biogenic OSs, particularly those arising from isoprene, exhibited a significantly high level in summer. Although these identified compounds were only part of the total OSs molecules, their determination and comparison were still meaningful as they were represented in the composition and source of the total CHOS compounds due to their high abundance.



**Fig. 6.** The intensity of identified 19 organosulfates from anthropogenic (A) and biogenic (B) sources, and the ratio of the total intensity between A and B. Specific information about these organosulfates are listed in Table S2.

#### 3.2.3. CHON & CHN compounds

As the most abundant species in ESI+, the CHON and CHN took an average portion of 43% and 26% of the total detected molecules. This is reasonable as many of these molecules may contain amino groups, which are readily to be protonated in ESI+. Fig. 7 shows the KMD diagrams for the CHN+ compounds. Molecules that differ only in ethyl group numbers were illustrated on the same horizontal line, which also have the same degree of unsaturation (Hughey et al., 2001). It was clear that series of aromatic compounds like benzene core structural nicotine ( $C_{10}H_{14}N_2$ , KMD = 0.5917), naphthalene core structural 1-naphthalenamine ( $C_{10}H_9N$ , KMD = 0.8011), anthracene core structural aminoanthracene ( $C_{14}H_{11}N$ , KMD = 0.1203) and pyrene core structural aminopyrene ( $C_{16}H_{11}N$ , KMD = 0.1471). The molecule identification of CHN compounds also indicates a bulk of PANH compounds like quinoline (C<sub>9</sub>H<sub>7</sub>N), benzo[a]/[c]acridine (C<sub>7</sub>H<sub>11</sub>N), which were believed from coal combustion as we described before (Table 2 and Fig. S5) (Jalees et al., 2020; Lintelmann et al., 2010). Fig. 7 showed a clear relation that the higher values of KMD correspond to the high condensed aromatic compounds, which was in accord with earlier observations (Wang et al., 2017a). Compared to other seasons, winter showed a significant number of high condensed aromatic compounds with 12-23 DBE and 15–29 carbon atoms (those above the dashed line in Fig. 7). These compounds are assigned to PANHs with four or more aromatic rings, which were reported to have been strong mutagenesis and potentially carcinogenic (Wang et al., 2018). It was also reported that similar high condensed PANH compounds were observed in the ambient OAs in Beijing in January 2014 (Jiang et al., 2016; Wang et al., 2018). These findings suggested that a certain number of PANHs with several detrimental effects were formed in the winter, which was probably originated from the massive fossil fuel combustion (especially coal) for centralized heating in Taiyuan (Alves et al., 2017; Bandowe et al., 2016).

The identification of CHON compounds suggests that most of these molecules contain amino functional groups in ESI+ and nitro groups in ESI- (Figs. S4-5, Table 2). This was due to the ionization tendency that amines are prone to be protonated in ESI+ mode, while nitro group compounds were preferential to be deprotonated in ESImode. To confirm these results, we adopt O/N and average DBE to estimate the functional group and degree of unsaturation and the results were shown in Fig. 8. Most of CHON- compounds (>85%) showed an O/N ratio larger than 3, which may associate with nitro (-NO<sub>2</sub>) or nitrooxy (-ONO<sub>2</sub>) groups in these formulas. Quite a few CHON- compounds have an O/N ratio of more than 4, indicating that these compounds contain additionally oxidized groups (e.g., hydroxy group) besides the nitrooxy group. Different from CHON-, most of the CHON+ compounds (>74%) have an O/N ratio of less than 3, which were assigned to have reduced nitrogen-containing functional groups like amines (Wang et al., 2018). For different months, compounds with O/N ratio  $\leq$  1 dominate (~65%) for CHON+ samples in December, January and February. This is an indication that reduced nitrogen compounds take a significant proportion among CHON+ compounds in winter, which was proved to originate from the pyrolytic and oxidative reaction (e.g., smoldering burning) of PANHs (Lin et al., 2012; Wang et al., 2018). The average DBE also verified the results that the CHON molecules in both negative and positive mode are showed a high value in the winter, indicating a high degree of unsaturation.

#### 3.3. Geographical origins

As it was reported that air mass transportation from Shanxi, especially Taiyuan has a potential contribution to the air pollution to other BTH cities like Shijiazhuang and Beijing (Xie et al., 2019; Zhu et al., 2011). Evaluating the geographical origins of air masses in Taiyuan is of great importance to mitigate the regional aerosol pollution in China. Fig. 9 showed the 24-h backward trajectory clustering analysis of air masses from different seasons in Taiyuan. In spring, the air masses showed a multidirectional origin, the most abundant masses were



Fig. 7. CH<sub>2</sub>-Kendrick diagrams of CHN+. The color represents molecules with different aromaticity equivalent (Xc).

from the southwest (1, 27.25%) and east (5, 25.39%), which originated from Shaanxi and Hebei province respectively. In summer, the proportion of air masses from Hebei province has increased from 25.39% to 43.12%. It was reported an intense SOA formation in the summer and autumn of Shijiazhuang (capital of Hebei), with adequate gaseous oxidants ( $O_3$ ) and proper atmospheric conditions (Xie et al., 2019). The high level of SOA may also contribute to a certain amount of the OSs in Taiyuan, as the OSs were observed to attain a peak value in summer.

The air mass transportation in autumn and winter was similar. Longdistance transportation (13 in autumn, 16 and 17 in winter) from Inner Mongolia was caused by the prevailing westerlies during autumn and winter, and was considered as clean air masses due to their rapidly



Fig. 8. Distribution of CHON compounds based on their O/N ratio and the average DBE of these molecules obtained from ESI- (left) and ESI+ (right).



Fig. 9. The 24-h backward trajectory clustering analysis for different seasons in Taiyuan (The numbers in bracket are the serial numbers of the trajectories and the proportions of air masses are expressed as a percentage).

moving from areas of forests and grasslands (Lv et al., 2015). From a similar direction but differ in length, other clusters in the northwest were originated from Yulin city in Shannxi province (12 in autumn and 15 in winter). These clusters make a certain proportion of the total clusters in autumn (34.95%) and winter (36.92%). Yulin is a typical industrial and coal-burning city, and was proved to have a dominant contribution to PM<sub>2.5</sub> from coal combustion (Lei et al., 2020; Lei et al., 2018). Besides that, other clusters from the southeast also contribute a certain proportion in autumn (14 for 39.65%) and winter (18 for 22.37%), which comes from Changzhi and Shijiazhuang respectively. Anthropogenic emissions were reported to be significant in these areas (Zhao et al., 2012) and strong regional transport from Hebei and other locations in Shanxi were documented in previous studies (Pu et al., 2015). This may be related to the high portion of coal-burning aromatic amines/PANHs and PAH-sourced organic acids identified in autumn and winter. Air pollutants might be brought via trajectories from Shannxi, Hebei, and other cities in Shanxi, where were considered as severe haze polluted areas during autumn and winter.

#### 4. Conclusions

Based on the 24-h integrated  $PM_{2.5}$  samples collection in Taiyuan in each month of 2018, specific molecular composition of  $PM_{2.5}$  was determined to study its seasonal variation and potential source, which helped to further probe into its chemical characteristics. More than 1500 organic compounds were identified in  $PM_{2.5}$  samples every month based on the unambiguous elemental composition obtained from UHRMS, which provided meaningful information of these species and enriched the database of the molecular composition of  $PM_{2.5}$  in a typical industrial and mining city.

A high level of CHOS and CHO compounds were observed in summer, while abundant unsaturated CHN molecules in winter, implying an intense photooxidation in summer and influence of anthropogenic activities in winter. Pearson correlation analysis and specific molecular identification indicated that CHO compounds were mostly organic acids and anhydrides, while CHOS were organosulfates formatted through the photooxidation pathway with an intensive illumination and oxidation effect in summer. CHN compounds were mainly aromatic amines and PANHs relating to anthropogenic emissions. Besides the PANHs with several detrimental effects, a certain amount of pyrene core structural compounds and PAH-produced acids were discovered in autumn and winter, indicating serve pollution caused by massive fossil fuel combustion (especially coal) in Taiyuan like other megacities Beijing, Tianjin, and Shijiazhuang. Analysis of the organic acids and OSs also confirmed the high level of anthropogenic source SOAs formatted in winter. OSs showed an evident peak value in summer and were basically dominant by biogenic sources like Shanghai. Backward trajectory clustering analysis implied a potential contribution of high-level OSs from eastern Shijiazhuang in summer, as well as fossil fuel combustion-related pollutants from northwest Yulin in autumn and winter.

In summary, coal-burning-related contaminants still had a significant influence on the severe air pollution in Taiyuan, especially in autumn and winter. The high atmospheric oxidative capacity results in the massive formation of SOAs in summer. Air mass transportation from nearby high polluted cities also aggravates the contamination. Thus, more efforts should be applied to reduce the local coal-burning and oxidant emissions. Cross-boundary control strategies are also needed to alleviate the air pollutions in Taiyuan.

#### **CRediT authorship contribution statement**

Wei Wang: Writing original draft, Data curation, Formal analysis, Methodology. Yanhao Zhang: Data curation, Writing- review & editing, Methodology. Bin Jiang: Methodology, Resources. Yanyan Chen: Resources. Yuanyuan Song: Resources. Yingtao Tang: Resources. Chuan Dong: Resources. Zongwei Cai: Supervision, Manuscript editing and revising, Resources, 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.

#### Acknowledgments

We thank the National Natural Science Foundation of China (91843301 and 91543202) for financial support.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2021.149419.

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