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Air pollution in Germany: Spatio-temporal variations and their driving factors based on continuous data from 2008 to 2018☆

Xiansheng Liu [a,b], Hadiatullah Hadiatullah [c], Pengfei Tai [d], Yanling Xu [e], Xun Zhang [f,g,*], Jürgen Schnelle-Kreis [a], Brigitte Schloter-Hai [a], Ralf Zimmermann [a,b]

[a] Joint Mass Spectrometry Center, Cooperation Group Comprehensive Molecular Analytics, Helmholtz Zentrum München, German Research Center for Environmental Health, Ingolstädter Landstr. 1, 85764, Neuherberg, Germany
[b] Joint Mass Spectrometry Center, Chair of Analytical Chemistry, University of Rostock, 18059, Rostock, Germany
[c] School of Pharmaceutical Science and Technology, Tianjin University. 300072, Tianjin, China
[d] School of Geography and Tourism, Qufu Normal University, 276826, Rizhao, China
[e] College of Plant Health and Medicine, Qingdao Agricultural University, 266109, Qingdao, China
[f] Beijing Key Laboratory of Big Data Technology for Food Safety, School of Computer and Information Engineering, Beijing Technology and Business University, 100048, Beijing, China
[g] Key Laboratory of Resources Utilization and Environmental Remediation, Institute of Geographical Sciences and Natural Resources Research, Chinese Academy of Sciences, 100101, Beijing, China

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ABSTRACT

This study analyzed long-term observational data of particulate matter ($PM_{2.5}$, PM_{10}) variability, gaseous pollutants (CO, NO_2, NO_X, SO_2, and O_3), and meteorological factors in 412 fixed monitoring stations from January 2008 to December 2018 in Germany. Based on Hurst index analysis, the trend of atmospheric pollutants in Germany was stable during the research period. The relative correlations of gaseous pollutants and meteorological factors on $PM_{2.5}$ and PM_{10} concentrations were analyzed by Back Propagation Neural Network model, showing that CO and temperature had the greater correlations with $PM_{2.5}$ and PM_{10}. Following that, $PM_{2.5}$ and PM_{10} show a strong positive correlation ($R^2 = 0.96$, $p < 0.01$), suggesting that the reduction of $PM_{2.5}$ is essential for reducing PM pollution and enhancing air quality in Germany. Based on typical PM_{10}/CO ratios obtained under ideal weather conditions, it is conducive to roughly estimate the contribution of natural sources. In winter, the earth's crust contributed about 20.1% to PM_{10}. Taken together, exploring the prediction methods and analyzing the characteristic variation of pollutants will contribute an essential implication for air quality control in Germany.

1. Introduction

Air pollution has negative impacts on human health, ecological environment, climate, and socio-economic development. The current air pollution situation and driving factors have drawn more attention in recent years (Streets et al., 2007; He et al., 2001; Wang et al., 2001; Gulliver and Briggs, 2004). Epidemiological and toxicological studies showed that long-term exposure to outdoor air pollution in large European cohorts was associated with natural mortality (Strak et al., 2019), especially about fine particulate matter (Wilson and Suh, 1997; Pope et al., 2002; Zanobetti and Schwartz, 2009; Perez et al., 2009; Schwartz, 2000; Samet et al., 2000). At present, some European countries have adopted a monitoring and measures series to control the air pollution problem, which successfully achieved better progress in the field (Waluś et al., 2018).

In the previous studies, researchers used external field detection, laboratory analysis, numerical simulation calculations, and satellite remote sensing to study various physical and chemical characteristics of $PM_{2.5}$ and their temporal and spatial evolution characteristics (Friberg et al., 2018; Xue et al., 2017). Eldred et al. (1997) used observational data from the IMPROVE monitoring network, which revealed the $PM_{2.5}$ concentration was highest in summer, and sulfate performed as main contributor to air pollution. Dawson et al. (2007) investigated the effects of meteorological factors on PM concentration using a three-dimensional chemical transport model. Querol et al. (2004) studied the spatio-temporal distribution of PM in 7 European cities from 1998 to 2002. In those studies comparison, it was revealed that PM_{10} had the highest concentration in Spain and Germany, and the lowest in

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* Corresponding author. Beijing Key Laboratory of Big Data Technology for Food Safety, School of Computer and Information Engineering, Beijing Technology and Business University, 100048, Beijing, China.
E-mail address: zhangxun@btbu.edu.cn (X. Zhang)

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Sweden. The highest and lowest concentrations of $PM_{2.5}$ occurred in Austria and Sweden, respectively.

Throughout these studies, the spatio-temporal variation of $PM_{2.5}$ and PM_{10} concentrations in the atmosphere and its driving factors were previously performed by Song et al. (2017) and Chai et al. (2014). The process affecting air pollution is very complex and not only affected by the source of pollutants, but also meteorological conditions (He et al., 2017) and various chemical reactions (Xie et al., 2015). Therefore, it is essential to study PM combined with gaseous pollutants and meteorological factors. However, there is a strong non-linear relationship between PM concentration changes, meteorological conditions, and gaseous pollutants (Munir, 2016). Moreover, traditional multiple linear regression models for predicting PM mass concentration have significant limitations, such as, they are unable to capture PM mass concentration and parameters (Grivas and Chaloulakou, 2006; Chaloulakou et al., 2003). Due to certain conditions, the duration of continuous observations was short, implicating the short-term air pollution concentration change and chemical composition analysis (Kamińska, 2018). Therefore, it is imperative to explore long-term air pollution study, spatio-temporal variations, and their driving factors in Germany.

Based on the above reasons, the annual trend and characteristic variations in the pollutant concentration are necessary to further predict and control air pollution. This study analyzes a dataset of gaseous pollutants (carbon monoxide (CO), nitrogen dioxide (NO_2), nitrogen oxides (NO_X = NO + NO_2), sulfur dioxide (SO_2), ozone (O_3)) and particulate matter ($PM_{2.5}$ and PM_{10}) recorded at 412 monitoring sites in Germany, for 11-years (January 2008 to December 2018). The aims are as follows: 1) to detect the spatio-temporal characteristic variations of $PM_{2.5}$ and PM_{10} in Germany. 2) to quantify the influence of gaseous pollutants and meteorological factors on $PM_{2.5}$ and PM_{10} concentrations based on the artificial BP neural network. To the best of our knowledge, this is the first time large dataset used to systematically probe the variations in characteristics of the seven critical air pollutants and the associated health effects in Germany.

2. Methods

2.1. Monitoring data

The 24-h averages data for $PM_{2.5}$, PM_{10}, CO, SO_2, NO_2, and NO_X and 8 h averages data for O_3 were obtained from the Federal Environment Agency (https://www.umweltbundesamt.de/en/) and utilized to calculate monthly and annual averages at each monitoring location. The observations included daily $PM_{2.5}$, PM_{10}, CO, O_3, SO_2, NO_2, and NO_X concentrations at 412 monitoring sites in Germany from 2008 to 2018, characterizing the spatio-temporal variability of the pollution concentrations. A detailed description of the stations for the different pollutants was listed in Table S1.

2.2. Meteorological data

The routine meteorological data at 222 monitoring sites in Germany from January 2008 to December 2018 were obtained by the German Weather Service (Deutscher Wetterdienst) and used to analyze the relation to air pollution. The observations include a form of precipitation (only rain, only snow, rain and snow, FP), a daily precipitation height (PH), a daily average wind speed (WS), a daily sunshine duration (SD), a daily value snow depth (SnD), a daily average of coverage (C), a daily average of vapor pressure (VP), a daily mean air pressure (AP), a daily average relative humidity (RH), and a daily average temperature (T). To ensure the accuracy of data analysis, the meteorological data were obtained from the close location with fixed monitoring stations (pollutant monitor) and further analyzed to observe the effect of meteorological factors on particulate matter concentrations.

2.3. Time series method

In order to study the annual variation and variation characteristics of atmospheric pollutant concentration time series intuitively and quickly, this study uses rescaled range (R/S) analysis followed by fractal dimension (D) that can analyze the internal regularity of complex atmospheric phenomena.

2.3.1. Rescaled range (R/S) analysis

The formula for R/S analysis (Hurst, 1965) is as follows:

$$\bar{x}(j) = \frac{\sum_{i=1}^{j} x(i)}{j},\ j = 1, 2, 3 \ldots \tag{1}$$

$$x(i,j) = \sum_{k=1}^{i}\left(x(k) - \bar{x}(j), 1 \le i \le j \right. \tag{2}$$

$$R(j) = \max_{1 \le i \le j} x(i,j) - \min_{1 \le i \le j} x(i,j),\ j = 1, 2, 3 \ldots \tag{3}$$

$$S(j) = \left[\frac{1}{j} \sum_{i=1}^{j} (x(i) - \bar{x}(j))^2 \right]^{\frac{1}{2}}, j = 1, 2, 3 \ldots \tag{4}$$

where x_i, x(i, j), R(j) and S(j) are the mean, cumulative dispersion, range and standard deviation of the given time series. So the R/S analysis is the ratio between range and standard deviation.

If x_i is a random sequence that is independent of each other and has a limited variance, ie Brownian motion, then

$$\frac{R(j)}{S(j)} = \left(\frac{\pi j}{2} \right)^{H} \tag{5}$$

where H is the Hurst index of the time series. The magnitude of the H-index can reflect the future atmospheric pollutants of the time series.

(1) If H = 0.5, the time series of air pollution changes are random, and the current air pollution information will not affect the future.
(2) If 0.5 < H < 1, it indicates that the time series has long-term persistence, and the overall change in air pollution in the future will continue the overall trend of the past. The larger H is, the stronger the persistence; the closer H is to 1, the overall change in air pollution in the future continues the overall trend in air pollution in the past.
(3) If 0 < H < 0.5, it indicates that the time series has long-term anti-sustainability. The total change in air pollution in the future will be contrary to the overall trend of the past. The closer H is to 0, the stronger the anti-sustainability.

2.3.2. Fractal dimension (D)

The Hurst index (H) of the one-dimensional Brownian motion has the following relationship to its fractal dimension D:

$$D = 2 - H \tag{6}$$

The Hurst index is closely related to the fractal dimension D of the fractional Brownian motion, reflecting the persistence and anti-persistence of the fractional Brownian motion (Baillie, 1996).

2.4. Statistical analysis

A coefficient of variation (CV) or a coefficient of divergence (CD) was applied to the heterogeneous particle distributions to describe the relative intra-urban concentration heterogeneity (Zhaobin et al., 2013). The CD_{jk} method for identifying the differences in atmospheric pollutant profiles, described in detail by (Pakbin et al., 2010), was defined as follows:

$$CD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{X_{ij} - X_{ik}}{X_{ij} + X_{ik}}\right)^2} \quad (7)$$

where the x_{ij} and x_{ik} represent the observation (concentration of atmospheric pollutants in this case) for variable x in the ith of total p observations at the paired sampling sites j and k (Krudysz et al., 2009). If the value of CD_{jk} approaches zero, the atmospheric pollutant composition in j and k are similar, and if it approaches one, they are significantly different (Pakbin et al., 2010). Thus, the CD_{jk} can provide a relative measure of homogeneity in the concentration fields (Pinto et al., 2004).

The coefficient of variation (CV, i.e., standard deviation (STD) divided by the mean value (x)) was also used to describe the degree of the spatial variation of air pollutant concentration regions, expressed by:

$$CV = \frac{STD}{\overline{X}} \quad (8)$$

2.5. Back propagation (BP) neural network

Artificial neural networks (ANN) (Van Gerven and Bohte, 2017) can be used to forecast short and middle long-term concentration levels for some of the well-known pollutants (Viotti et al., 2002). In this study, back propagation (BP) neural network was chosen, which is used in artificial neural networks to calculate a gradient required for the calculation of the weights to be used in the network (LeCun et al., 2015).

2.6. Natural source contribution to PM_{10}

In a city, gaseous pollutants are mainly derived from urban anthropogenic emissions during a certain period. For example, near-surface gaseous pollutants are mainly derived from the combustion or conversion of fossil fuels and other organic matter, and other sources contribute to their insignificance (Pochanart et al., 2004). However, the particulate matter differs from the gaseous pollutants, including the combustion process (including the secondary conversion of gaseous pollutants) and the natural source contribution of the crustal material (wind and dust).

Depending on the difference between the two factors, it is possible to select the monitoring data of pollutants under ideal meteorological conditions (such as snowfall and low speed wind) whose natural sources contribute a slight impact to the inhalable particulate matter (PM_{10}). At this time, it is challenging to resuspend the crustal material. In the atmosphere, atmospheric particulate matter and gaseous pollutants have the same source of anthropogenic pollution, and there should be a significant positive correlation. At a certain time, the percentage contribution (referred to anthropogenic source) is relatively stable due to a slight change of fuel structure, hence, its ratio emission can be assumed to be a constant. Following the ratio, the contribution rate of natural sources to PM_{10} can be resolved according to the change of ratio.

Data analysis was performed using the SPSS 18.0 software. For the statistical analysis, the one-way analysis of variance (ANOVA) and the correlation analysis with Bivariate Correlations Analysis were completed. The spatial distributions of the average atmospheric pollutant concentrations were simulated using the Kriging interpolation model by Arcgis 10.3.

3. Results and discussion

3.1. Overview of air pollutants

This study analyzed the annual average mass concentrations of the pollutants during the past four years (2015–2018) (Fig. 1) to make a clear comparison. Significant spatial differences in air pollutants concentrations among Germany were observed, and the ranges of annual average values were shown in Table S2. Moreover, the cumulative population distribution of the annual values of $PM_{2.5}$, PM_{10}, $PM_{2.5}/PM_{10}$, CO, O_3, SO_2, NO_2, and NO_X during the past four years (2015–2018) was investigated to make a better understanding of the exposure German population to air pollution. From 2015 to 2018, half of the German population was exposed to annual average values higher than 12.6 μg/m^3 for $PM_{2.5}$, 18.1 μg/m^3 for PM_{10}, 0.32 mg/m^3 for CO, 48.3 μg/m^3 for O_3, 2.03 μg/m^3 for SO_2, 21.9 μg/m^3 for NO_2, and 35.3 μg/m^3 for NO_X, respectively, suggesting during that period only 7.79%, 67.4%, 85.6%, 100% of the population lived in areas that meet the annual standards of the World Health Organization (WHO) air quality guidelines (AQG) of 10, 20, 40, 100 μg/m^3 for $PM_{2.5}$, PM_{10}, NO_2, and O_3, respectively. In addition, when compared with the EU concentration standard for $PM_{2.5}$ and PM_{10} (25 and 40 μg/m^3), the entire German population has been exposed below their standard concentration from 2008 to 2018 (Figure S1).

3.2. Atmospheric pollutant characteristics

The fractal characteristics of the atmospheric pollutant monitoring data were studied by using the time series domain rescaling analysis method. Table S3 showed the Hurst-index (H) and fractal dimension (D) of $PM_{2.5}$ and PM_{10} in different multi-time scales and different areas. Meanwhile, this study also analyzed the H and D of CO, O_3, SO_2, NO_2, and NO_X (Table S4). The results showed that the H was larger than 0.5, indicating the time series of atmospheric pollutants as a trajectory of the fractional Brownian motion shows persistence, that is, a trend of increasing concentration of atmospheric pollution in the past means a future growth trend, and a reduction trend in the past means a future reduction trend, which can be maintained in some extents. It also implied that the air pollutant statistics show a certain degree of non-Gaussian (non-random) distribution. This phenomenon was further confirmed by the long-term change trend of $PM_{2.5}$ and PM_{10} (Figure S1 and S2), showing the air pollutants stability during the study period. Fractal studies are disordered systems with specific characteristics. As fractal constraints change, the fractal dimension will change accordingly (Baillie, 1996). Due to the linear relationship between H and D, the change in H reflects the change in D. Therefore, when the value of H changes greatly, it is the variation of the factors that restrict the system, which is called the variation point. To this end, the study divides the raw data into two parts with the year-end date (December 31) as the demarcation point?i.e, the starting point of the previous part and the starting point of the latter part) and performs R/S analysis on the two parts, respectively. The corresponding H index is recorded as H_i and H_{i+1} and then the absolute value $\Delta H = |H_{i+1} - H_i|$ of the difference between H_i and H_{i+1} is obtained, and the ΔH is obtained accordingly. The point with the largest value is regarded as the maximum point of variation, and the variations year can be diagnosed accordingly. Because the maximum point of this variation is compared with the other sample points analyzed, it is relative.

The results of the segmentation analysis are shown in Fig. 2. As shown in Fig. 2, for PM_{10} and $PM_{2.5}$, the largest of $|H_{i+1} - H_i|$ is found in 2009. Following that, the most variable atmospheric pollutant were found in the rural areas ($\Delta H = 0.52$ for $PM_{2.5}$; $\Delta H = 0.41$ for PM_{10}). The multiple factors may influence the air pollution changes, such as building completed area, thermal power generation, gross industrial output value, and wind speed (Yao et al., 2020). In the previous study, the average urban traffic $PM_{2.5}$ concentrations exceeded the WHO standards in the vast majority of European member states in 2009 (Kiesewetter and Amann, 2014). Moreover, regarding to urban $PM_{2.5}$ levels under the EU Clean Air Policy Package (Kiesewetter and Amann, 2014), the source contribution to ambient $PM_{2.5}$ in Germany is high, influencing the implementation of air pollution policy starting from 2009. The main source contribution to rural $PM_{2.5}$ comes from

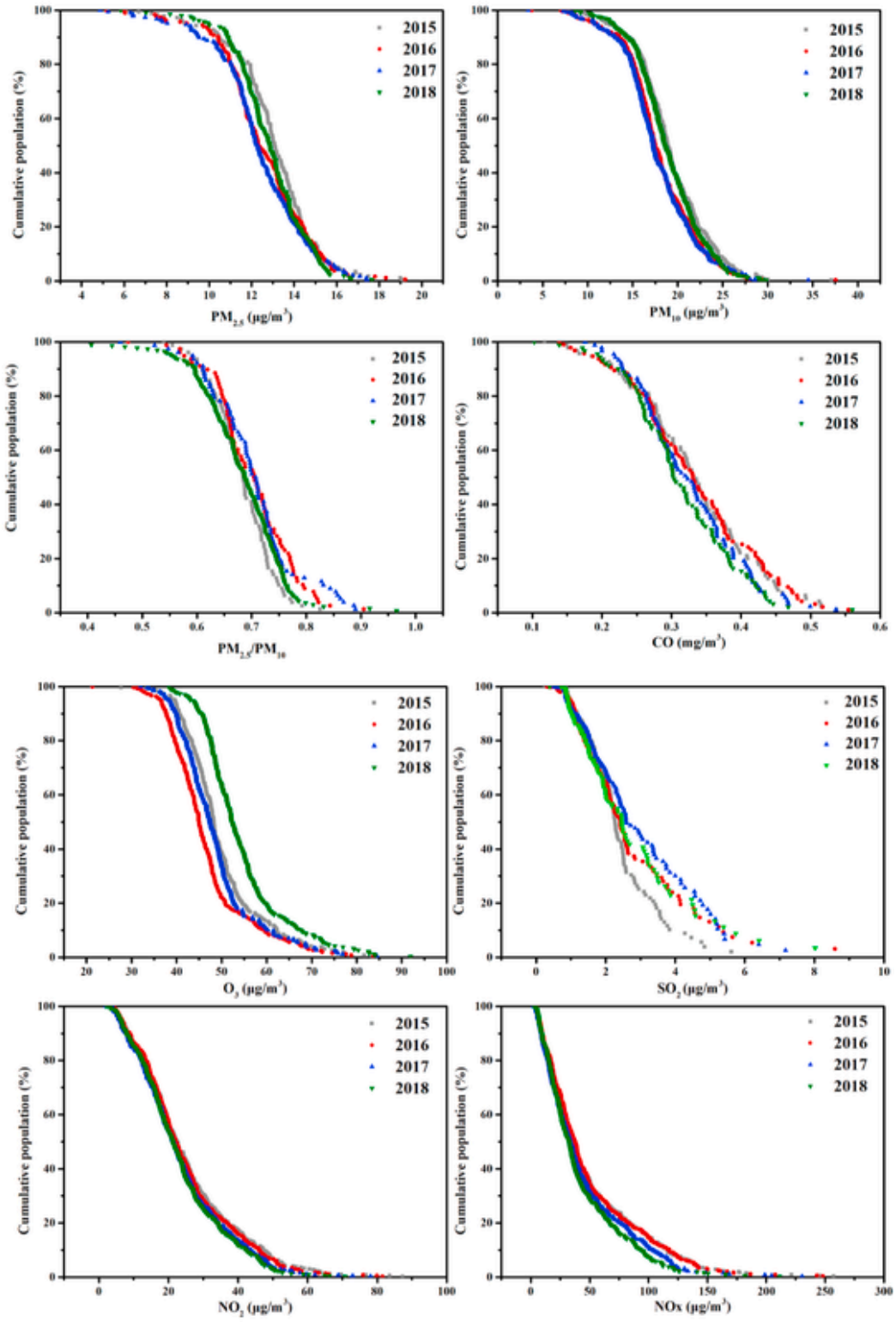

Fig. 1. Cumulative distribution of the annual average of air pollutants in Germany from 2015 to 2018.

sulfates, residential heating, nitrates, industry, re-suspended dust, and sea salt and dust-long range transport (Pokorná et al., 2018). Moreover, the industrial emission (SO_2 and NO_X) and traffic emission (NO_X) mainly interacted with Ammonia, which only obtained from rural agriculture, following, the house heating in the rural area also contributed to the $PM_{2.5}$ concentration. Therefore, both factors may influence the high contribution to $PM_{2.5}$ concentration from rural area. Simultaneously, in our study, the variability of air pollution was also large in 2016 and 2017. It is worth noting that $PM_{2.5}$ variation across many years in the urban industrial, which is not observed in PM_{10}, implied that $PM_{2.5}$ and PM_{10} might have different source contributions. These results were consistent with the previous study that these differences

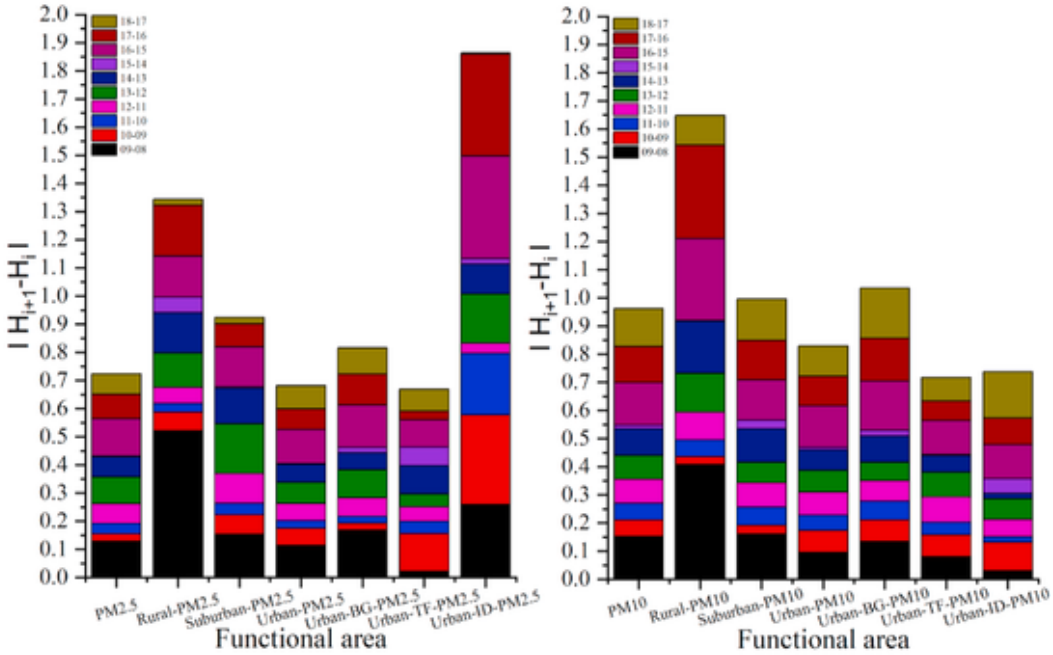

Fig. 2. Segmental analysis of atmospheric pollutants in different functional areas from 2008 to 2018 in Germany (BG, background; TF, traffic; ID, industry).

were primarily related to different source profiles (Huang et al., 2014).

3.3. Spatial variations

The spatial distribution of the annual average mass concentrations of seven air pollutants ($PM_{2.5}$, PM_{10}, CO, O_3, SO_2, NO_2, and NO_X) at each air quality monitoring station across Germany are shown in Figure S3. In order to observe the spatial distribution in different types of areas, the distribution of $PM_{2.5}$ and PM_{10} was analyzed in rural, suburban, and urban areas (Figure S4). In general, as the center of economic culture, air pollution is commonly more severe in Berlin and Brandenburg, comparable with our previous study in terms of the spatial distribution of PM_{10} (Liu et al., 2020).

In order to represent the overall spatial variations of air pollutant concentrations in Germany, the daily average mass concentrations of air pollutants at over 400 fixed monitoring stations over a period of eleven years was performed, the result showed that SO_2 has the largest spatial variations (42.7%), followed by $PM_{2.5}$ (CV = 12.1%), PM_{10} (CV = 10.0%), CO (CV = 8.7%), NO_2 (CV = 7.1%), NO_X (CV = 5.6%) and O_3 (CV = 2%). The largest spatial variation was located in Berlin for CO (CV = 20.1%), Niedersachsen for NO_2 (CV = 13%), Mecklenburg-Vorpommern for NO_X (CV = 24.3%), Bayern for O_3 (CV = 4.88%), Bremen for $PM_{2.5}$ (CV = 19%) and Thüringen for PM_{10} (CV = 16.5%). However, some areas in Germany cannot be monitored by fixed stations, which may influence the spatial distribution of air pollutant concentrations. Therefore, we selected the Kriging interpolation model to provide the continuous spatial distribution for each factor based on our daily metric data. The results are consistent as described by the cumulative distribution of the annual average of air pollutants in Fig. 1. More than that the spatial changes of pollutants and hot spots in various German regions can be identified (Fig. 3).

3.4. Correlations between air pollutants

3.4.1. Correlations of gaseous pollutants on $PM_{2.5}$ and PM_{10} concentrations

In this section, the BP neural network algorithm was used to select the five common types of pollutants (CO, O_3, SO_2, NO_2, and NO_X) to analyze and compare their correlations on $PM_{2.5}$ and PM_{10}. Fig. 4 showed that the gaseous pollutants with a greater correlation on $PM_{2.5}$ and PM_{10} were CO and SO_2. CO and SO_2 are mainly derived from the combustion of fuel, urban automobile exhaust and tail gas discharged from industrial plants, comparable with the basic situation of many German industrial and transportation vehicles. The second driving gaseous pollutants factors were NO_X and O_3, respectively. Although the nitrogen content is minimal in the car's fuel, the high-temperature environment in which the automobile's internal combustion engine operates causes a large production of nitrogen oxides (NO_X) released into the air (Cyrys et al., 2012; Mavroidis and Ilia, 2012). Ozone in the atmosphere is mainly formed by the photochemical reaction of nitrogen oxides and volatile organic compounds and is the main component of photochemical smog (Pusede et al., 2015). The main sources of nitrogen oxides are automotive exhaust and chemical production.

Then, we performed spearman analysis to further analyze the positive and negative relationship between $PM_{2.5}$, PM_{10} and gaseous pollutants (Table S5). The results showed that the $PM_{2.5}$ and PM_{10} were positively correlated with gaseous pollutants, including CO, NO_2, NO_X, and SO_2, and negatively correlated with O_3. The previous study showed the inverse relation between O_3 and PM based on seasonal time (Jia et al., 2017). Briefly, the negative correlation was found in the winter, and positive correlation was found in the summer. These phenomena may be influenced by the different photochemical reactions in different seasons (Khoder, 2009).

3.4.2. Effect of meteorological factors on $PM_{2.5}$ and PM_{10} concentrations

Previous studies have shown a close relationship between meteorological conditions and air pollution processes (Yoo et al., 2015). However, the effects of meteorological factors on particulate pollution were typically discussed in qualitative methods (Wang et al., 2010; Chen et al., 2008). Therefore, the quantitative analysis of $PM_{2.5}$ and PM_{10} mass concentrations and meteorological parameters was discussed in this section. The BP neural network was used to calculate the influence of various meteorological elements in Germany on $PM_{2.5}$ and PM_{10}. The results showed that, the effects of meteorological elements on $PM_{2.5}$ and PM_{10} are similar except daily value snow depth (SnD) (Fig. 5). The temperature is the most important driving factor, that reached 21.1% and 35.6% (weight correlation) to $PM_{2.5}$ and PM_{10}, respec-

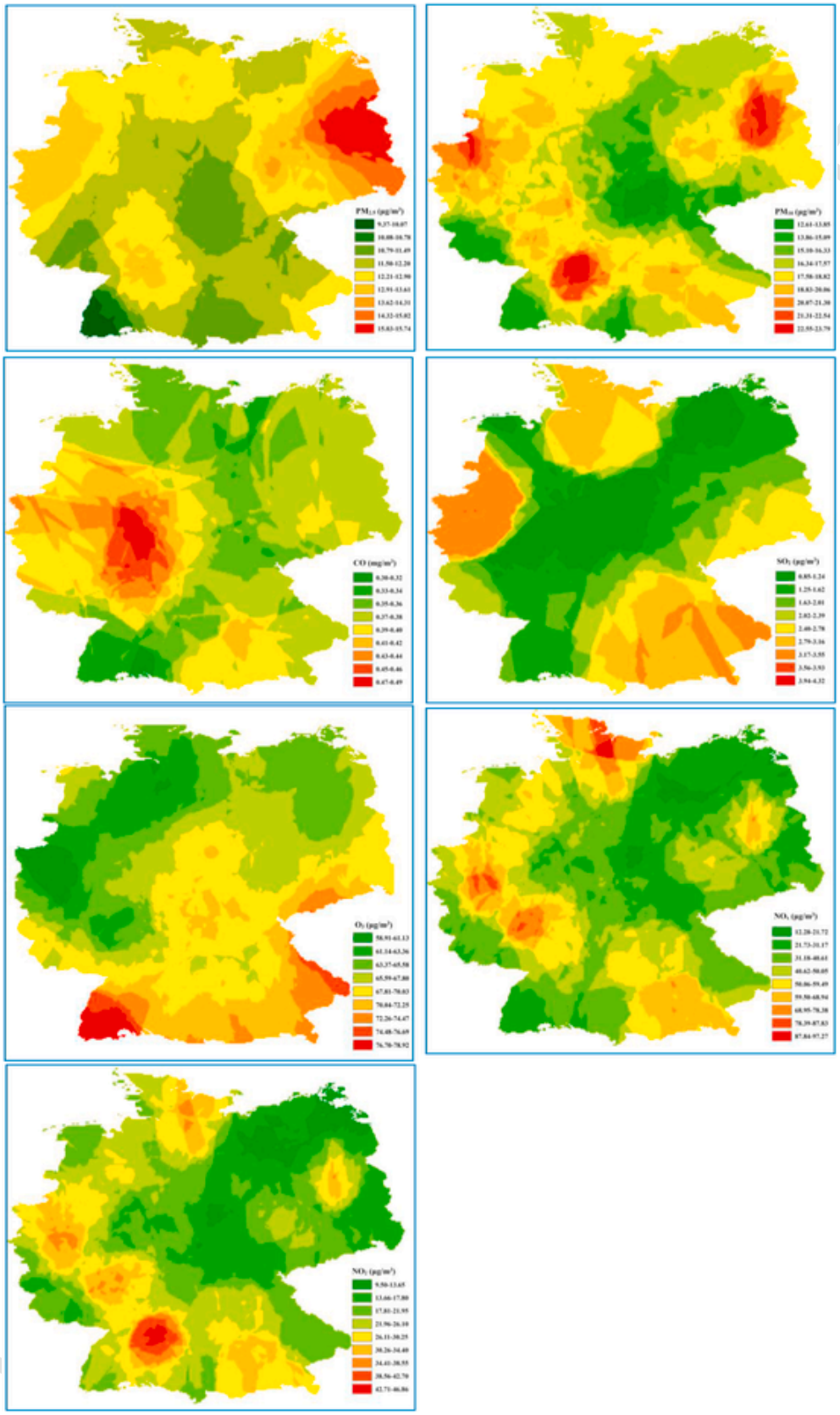

Fig. 3. Annual average mass concentrations of seven air pollutants ($PM_{2.5}$, PM_{10}, CO, SO_2, O_3, NO_X, and NO_2) maps obtained by Ordinary Kriging from 2008 to 2018.

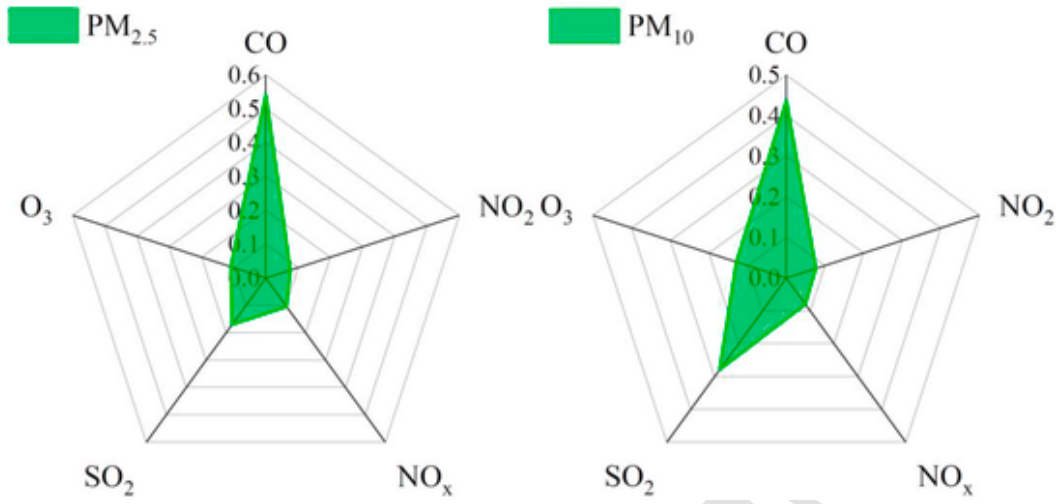

Fig. 4. The normalized coefficients of gaseous pollutants on $PM_{2.5}$ and PM_{10}.

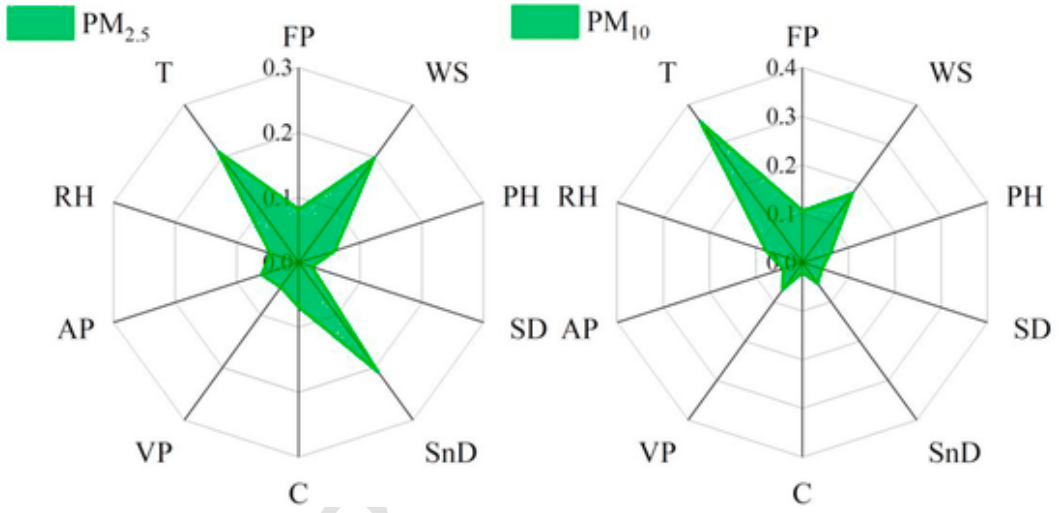

Fig. 5. Impact of meteorological factors on $PM_{2.5}$ and PM_{10} (FP, precipitation form (only rain, only snow, rain and snow); WS, a daily mean wind speed (m/s); PH, a daily precipitation height (mm)?SD, a daily sunshine duration (h); SnD, a daily value snow depth (cm); C, a daily average of coverage (1/8); VP, a daily average of vapor pressure (hPa); AP, a daily mean air pressure (hPa); RH, a daily average relative humidity (%); T, a daily average temperature (°C)).

tively. The second driving meteorological factors have slightly different effects on $PM_{2.5}$ and PM_{10}. For $PM_{2.5}$, the second driving factors are snowfall thickness (20.7%) and wind speed (19.9%). For PM_{10}, the second driving factor is wind speed (17.4%).

Then, we performed spearman analysis to show the positive and negative relationship between $PM_{2.5}$, PM_{10} and meteorological factors (Table S6). Generally, the $PM_{2.5}$ were negatively correlated with meteorological factors, including FP, WS, PH, C, VP, and T. Following that, the PM_{10} were also negatively correlated with meteorological factors, including FP, WS, PH, C, VP, AP, and T. However, RH was positively correlated both $PM_{2.5}$ and PM_{10} but less impact. This result was similar with previous study that RH has less impact to the PM concentration, but its fluctuation will raise the concentration of PM (Zhang et al., 2016). Moreover, it has already found that temperature (T) and wind speed (WS) were essential meteorological predictors. For example, low temperature could change the dynamics of air movement, trap air pollutants, and create a build-up of pollution near the ground (Zhang et al., 2018). Therefore, a change in temperature may effect on the PM concentration. Accordingly, the higher the wind speed, the cleaner air involved in pollutants per unit time. Moreover, under the control of the strong wind generated by the cold air transit, the particles can hardly accumulate rapidly, so that the concentration of the particulate matter can be maintained at a relatively low level for a long time. The effect of snowfall (SnD) on $PM_{2.5}$ is mainly the removal effect. During the process of snowfall, the aerosol particles can be captured by the Brownian diffusion or inertial wall-impacting processes, thereby removing $PM_{2.5}$ from the air. However, the effects of pressure on $PM_{2.5}$ and PM_{10} are relatively small, contradictory to the previous study (Cheng et al., 2015). This phenomenon may be influenced by the precipitation effect which played a major role in $PM_{2.5}$ pollution removal (Zalakeviciute et al., 2018). Meanwhile, to confirm that meteorological factors also affect particulate matter by affecting gaseous pollutants. Therefore, we also analyzed the gaseous pollutants-meteorological factors correlation (Table S6). The results showed that gaseous pollutants (CO, NO_2, NO_X, and SO_2) have negative relations with wind speed and temperature, and positively correlated with air pressure during year-round, indicating the meteorological factors could affect the variation of the gaseous pollutants as same as PM. In the previous study, the similar trend was found in New York City (Ito et al., 2007). In contrast, O_3 has the opposite correlation with the above meteorological factors compared to the other four gaseous pollutants. These trends may be affected by different photochemical reaction in different season (Khoder, 2009).

3.4.3. Correlations between PM size fractions

The correlation between $PM_{2.5}$ and PM_{10} showed a high positive correlation, which consistent with several studies performed in California (Motallebi et al., 2003), Netherland (Janssen et al., 2013), and China (Zhou et al., 2016). These analyses may provide new knowledge about source characterization of atmospheric particles, and help to evaluate the situation of $PM_{2.5}$ when the routine monitoring of PM_{10} is available (since the $PM_{2.5}$ data is less or scarce in Germany). However, due to different sources, fine particles ($PM_{2.5}$) and coarse particles ($PM_{10\text{-}2.5}$) should be considered as a separate class of pollutant (Payam, 2010). In our study, we found a high correlation between $PM_{2.5}$ *vs.* PM_{10} ($R = 0.96$, $p < 0.01$) than $PM_{10\text{-}2.5}$ *vs.* PM_{10} ($R = 0.44$, $p < 0.01$) (Fig. 6), indicating the $PM_{2.5}$ concentrations are the major contributors to the average PM_{10} concentrations at many sites in Germany. And the relation between $PM_{2.5}$ *vs.* $PM_{10\text{-}2.5}$ is weak but highly significant ($R = 0.26$, $p < 0.01$), suggesting that $PM_{2.5}$ and $PM_{10\text{-}2.5}$ are generally influenced by different sources. The similar report was found in the UK that the relation between $PM_{10\text{-}2.5}$ *vs.* $PM_{2.5}$ is lower than PM_{10} *vs.* $PM_{2.5}$ (Liu and Harrison, 2011). Taken together, the $PM_{2.5}$ and $PM_{10\text{-}2.5}$ may have distinct different behaviour due to their various sources and properties contribution, which further prove that coarse and fine particles have a different toxic effect in epidemiological studies (Wilson and Suh, 1997).

To further confirm the relation between $PM_{2.5}$, $PM_{10\text{-}2.5}$ and PM_{10}, the study has also analyzed the correlations in different types of areas (Figure S5), which showed the strong relations between $PM_{2.5}$ and PM_{10} in all the types of areas, especially in the urban area ($R = 0.97$, $p < 0.01$). In addition, to further reflect this relation in the urban areas, the study was continuously analyzed the relations in the different urban functional areas (Figure S6). Industrial areas have the lowest correlations for $PM_{2.5}$ *vs.* PM_{10} and $PM_{2.5}$ *vs.* $PM_{10\text{-}2.5}$, comparing with others three functional areas, and background area have the lowest correlations for $PM_{10\text{-}2.5}$ vs. PM_{10}, comparing with other three functional areas, suggesting that different source may be found in the different urban functional areas.

Therefore, the source of PM can be analyzed through the ratio of $PM_{2.5}$ - PM_{10}. It is well known that the fine particles primarily originate from combustion processes and gas-to-particle conversion processes in the atmosphere. In terms of mass concentration, the higher the $PM_{2.5}/PM_{10}$, the higher the contribution rate of the secondary particles; the lower the ratio, the higher the contribution rate of the dust source. By analyzing the ratio of $PM_{2.5}$ - PM_{10} in different types of urban areas, it is found that urban background has the highest ratio (0.67), while urban industrial area has the lowest ratio (0.55). The sparse vegetation urban industrial areas may be one reason for the small ratio of $PM_{2.5}$ to PM_{10} (He et al., 2017).

3.4.4. Natural source contribution to PM_{10} in winter

Naturally, after snowing, the ground was covered by snow, which made the particulate matter difficult to reach the atmosphere area, hence, the contribution of air pollutant to atmospheric particulate matter based on natural source is limited (i.e., dust). Thus, in snowfall days, atmospheric particulate matter mainly comes from fossil fuels and the combustion of other organic matter (i.e., urban anthropogenic sources), which has similar pollution source with gaseous pollutants. In this regard, the natural source contribution of PM_{10} in winter can be inferred.

In order to estimate the natural source contribution of PM_{10} in the winter, we selected the monitoring data of pollutants under ideal meteorological conditions (i.e., snowfall days (daily value snow depth ≥ 5 cm) and low speed wind). In that condition, it is difficult to obtain the crustal elements and dust. The statistical monitoring data of pollutants after snowing showed that the trend of particulate matter and gaseous pollutants were completely similar, meaning that when PM_{10} concentration was high, the similar trend was also found for CO (Fig. 7a). Considering the relatively stable nature of CO in gaseous pollutants, the concentration of PM_{10} and CO was further analyzed by regression analysis (Fig. 7b), showing the strong relation between them ($R = 0.86$, $p < 0.01$).

The average ratio of PM_{10} to CO concentration is $5.3 \bullet 10^{-2}$ in winter snowfall days, which can be considered as the reference value P. When the ratio of PM_{10} to the anthropogenic CO is greater than this value, it can be assumed that PM_{10} also has other pollution sources, mainly for surface contribution or external transportation, especially if there are many surface sand sources or sand dust. Based on atmospheric pollutant data collected from winter (Dec., Jan., and Feb.) during 2008–2018 in Germany, the ratios of PM_{10} to anthropogenic CO winter are $6.0 \bullet 10^{-2}$ (Dec.), $7.1 \bullet 10^{-2}$ (Jan.), and $7.0 \bullet 10^{-2}$ (Feb.) Based on the value P ($5.3 \bullet 10^{-2}$), it can be estimated that the contribution of German natural sources to atmospheric PM_{10} accounts for about 20.1% (5.58 μg/m^3) in winter, which is consistent with the previous study, that natural sources contribute with 6 μg/m^3 of mineral dust to the annual PM_{10} levels in Eastern Spain (Rodrıguez et al., 2004).

4. Conclusions

This paper comprehensively used the particulate matter ($PM_{2.5}$ and PM_{10}), gaseous pollutants (CO, NO_2, NO_X, SO_2, and O_3), and meteorological factors of the monitoring sites in Germany of the past 11 years to analyze the pollution characteristics of particulate pollutants in Germany. In this study, based on the Hurst index, the atmospheric pollutants, specially $PM_{2.5}$ and PM_{10}, revealed a stable trend from 2008 to 2018 in Germany ($H > 0.5$). By analyzing the correlations of different gaseous pollutants and meteorological conditions on the concentration of $PM_{2.5}$ and PM_{10} using Back Propagation Neural Network model, it

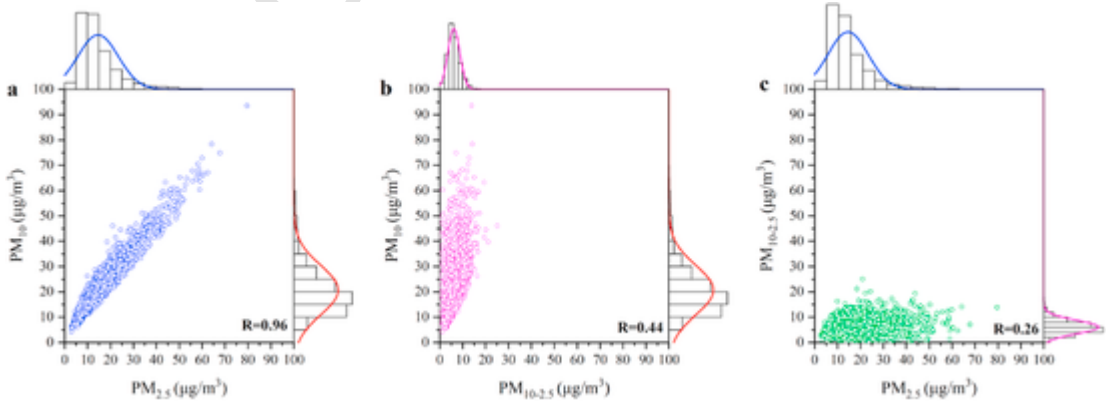

Fig. 6. The correlation between annual average concentrations of $PM_{2.5}$ *vs.* PM_{10} (a), $PM_{10\text{-}2.5}$ *vs.* PM_{10} (b), and $PM_{2.5}$ *vs.* $PM_{10\text{-}2.5}$ (c) base on 11 years of data collection all over Germany.

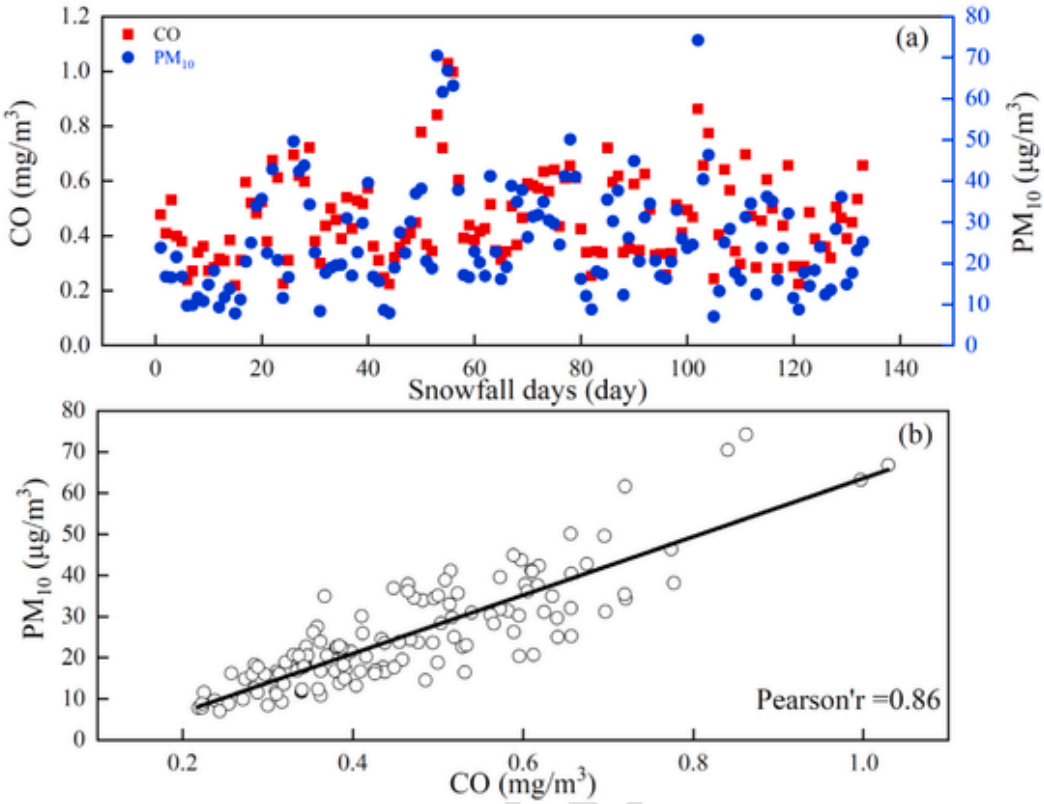

Fig. 7. Daily variations of PM_{10} and CO in snowfall days (a) and the correlation between PM_{10} and CO (b) in winter.

was found that CO and temperature had greater correlations with $PM_{2.5}$ and PM_{10} in Germany. Regarding on correlations between different PM size fractions, a high correlation between $PM_{2.5}$ *vs.* PM_{10} indicated that the $PM_{2.5}$ concentrations were the major contributors to the average PM_{10} concentrations at many sites in Germany. And the weak correlation between $PM_{2.5}$ *vs.* $PM_{10\text{-}2.5}$ suggested that $PM_{2.5}$ and $PM_{10\text{-}2.5}$ were generally influenced by different sources. Based on typical PM_{10}/CO ratios obtained under ideal weather conditions (i.e., snowfall days (daily value snow depth $\geq$ 5 cm) and low speed wind), it is conducive to roughly estimate the contribution of natural sources. In winter, the earth's crust contributed about 20.1% to PM_{10} (average 5.58 μg/m^3).

Author contributions

Xiansheng Liu: Data curation, Investigation, Methodology, Software, Supervision, Writing – original draft, Writing – review & editing. Hadiatullah Hadiatullah: Methodology, Writing – original draft. Pengfei Tai: Software. Yanling Xu:. Xun Zhang: Funding acquisition, Project administration. Jürgen Schnelle-Kreis: Data curation. Brigitte Schloter-Hai: Writing – review & editing. Ralf Zimmermann: Visualization

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.envpol.2021.116732.

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