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# Unveiling the importance of VOCs from pesticides applicated in main crops for elevating ozone concentrations in China

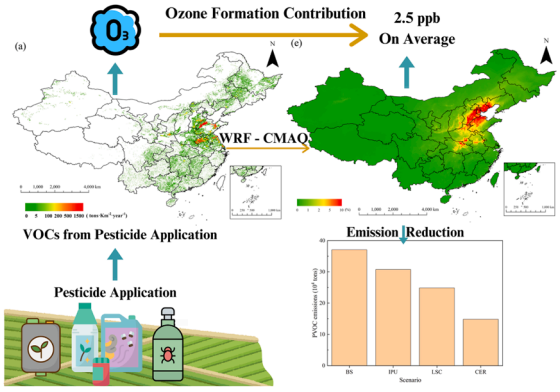
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## HIGHLIGHTS

- PVOC emissions across China in June 2019 accounted for ca. 30% of its annual emissions.
- PVOCs in the parts of North China Plain contributed 10% of the ozone formation.
- The reduction of PVOC emissions helps to control ozone pollution in China.

## GRAPHICAL ABSTRACT




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## ABSTRACT

Volatile organic compounds (VOCs) are considered as important precursors of ozone in the air, while the contribution of VOCs from pesticide application (PVOCs) to ozone production is unknown. Utilizing data from the Ministry of Agriculture and Rural Affairs of the People's Republic of China and ChinaCropPhen1km, this paper developed PVOC emission inventories with a resolution of 1 km for the main crops (rice, maize, and wheat) from 2012 to 2019 in China. The results revealed that pesticide application is an important VOC emission source in China. Specially, the PVOC emissions from the major grain-producing regions in June accounted for approximately 30% of the annual total PVOC emissions in the local regions. The simulation with the Weather Research and Forecasting Community Multiscale Air Quality model (WRF-CMAQ) indicated that the PVOC emissions increased the mean maximum daily 8-hour average (MDA8) ozone concentration across China by 2.5 ppb in June 2019. During the same period, PVOCs in the parts of North China Plain contributed 10% of the ozone formation. Under the comprehensive emission reduction scenario, it is anticipated that by 2025, the joint

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implementation of measures including reducing pesticide application, improving pesticide utilization efficiency and promoting solvent substitution will decrease PVOC emissions by 60% compared with 2019, thereby mitigating ozone pollution.

## 1. Introduction

Due to the continuous growth of the global population and the increasing demand for food, modern agriculture faces significant challenges [1]. Crop pests and diseases threaten both food quantity and quality, compelling the widespread application of pesticides in agricultural practices [2]. These pesticides serve as efficient and cost-effective tools for enhancing crop yields and safeguarding the global food supply. However, their extensive application has raised concerns due to adverse effects on the environment and human health [3,4]. Although researchers have a comprehensive understanding of the environmental fate of pesticide active ingredients [5], there remains a notable gap in our knowledge regarding the contributions of volatile organic compounds from the application of pesticides (PVOCs) to atmospheric ozone production.

Recent research has indicated that PVOCs contribute approximately 2% of the total anthropogenic VOCs in China [6]. Although the proportion of PVOCs in the total anthropogenic VOCs seems small, their impact on ozone formation cannot be overlooked. It was reported that ozone formation potentials resulting from pesticide application range from 0.1–3.2 kg ozone/kg product [6,7]. Furthermore, Kumar et al. demonstrated that PVOCs contributed 15 ppb of the ozone concentration, which corresponded to approximately 20% of the local background level during the summer of 2007 in a California citrus orchard [8]. These findings underscore the importance of PVOC emissions in ozone production.

Anthropogenic VOC emission sources in the Emissions Database for Global Atmospheric Research (EDGAR) include industry, transportation, agriculture (from the soil, waste burning and manure management), etc., whereas pesticide application is not included [9]. Although the Multi-resolution Emission Inventory for China (MEIC) [10] and China High Resolution Emission Database 3.0 A (CHRED 3.0 A) [11] encompass almost all VOC emission sources in China, pesticide application is still missing in MEIC and CHRED 3.0 A. Wang et al. evaluated PVOC emissions in China, but they did not provide a high-resolution emission inventory and the compositions of PVOCs [12]. The absence of a PVOC emission inventory makes it difficult to evaluate the contribution of PVOCs to ozone formation with air quality models.

This study was to develop PVOC emission inventories with a resolution of 1 km for the main crops in China at a multiyear scale from 2012 to 2019. Based on the PVOC emission inventories, the role of PVOCs in ozone formation in China was assessed utilizing the Weather Research and Forecasting Community Multiscale Air Quality (WRF-CMAQ) model. We compared the contributions of PVOCs and other anthropogenic VOCs to ozone formation and proposed further measures for reducing ozone production. Our findings in this paper aim to provide the public with a comprehensive understanding of the spatiotemporal distribution of PVOCs at a national level and to offer decision-makers valuable insights on ozone control strategies.

## 2. Method

### 2.1. Construction of PVOC emission inventory

#### 2.1.1. Estimation of PVOC emissions

Annual PVOC emissions were determined using Eqs. (1) and (2):

$$E_{y,i,k} = \sum_{j} \left( P_{y,i,j,k} \times EF_{j,k} \right) \quad (1)$$

$$E_y = \sum_{i,k} E_{y,i,k} \quad (2)$$

where the subscripts *y*, *i*, *j* and *k* represent the year, province, main crop type (rice, maize and wheat) and pesticide species, respectively. $E_{i,k,y}$ (ton·year$^{-1}$) represents the VOCs from pesticide *k* applied in province *i* in year *y*; $P_{y,i,j,k}$ (ton·year$^{-1}$) is the amount of pesticide *k* applied in crop *j* in province *i* during year *y*; $EF_{j,k}$ represents the emission factor (g·kg$^{-1}$) for VOCs emitted from pesticide *k* applied in crop *j*; $E_y$ (ton·year$^{-1}$) represents the total PVOC emissions in year *y* in China.

#### 2.1.2. Determination of pesticide application in crops

The mass of pesticides applicated in crops was determined using Eq. (3):

$$P_{y,i,j,k} = P_{y,i,k} \times \frac{S_{y,i,j}}{S_{y,i}} \quad (3)$$

where $P_{y,i,k}$ (ton·year$^{-1}$) is the mass of pesticide *k* applied in province *i* during year *y*. The annual provincial activity level data of pesticide application ($P_{y,i,k}$) in the main crops were sourced from the Ministry of Agriculture and Rural Affairs of the People's Republic of China (MARA), and it can be found in Fig. S1. Pesticide *k* applied in the main crops in China included insecticides (pyrethroids, emamectin benzoate, organophosphorus, neonicotinoids and carbamate), fungicides and herbicides (Fig. S2). $S_{y,i,j}$ (m$^2$) represents the area of cultivated land for crops *j* in province *i* during year *y*; $S_{y,i}$ (m$^2$) denotes the area of total cultivated land for the main crops in province *i* during year *y*; Data for $S_{y,i,j}$ and $S_{y,i}$ were sourced from China Rural Statistical Yearbooks [13] and High-resolution Crop Phenological Dataset for Three Staple crops in China (ChinaCropPhen1km) [14].

#### 2.1.3. Determination of emission factors

The compositions of solvents in the applied pesticides were obtained from a previous study [6]. According to the guidelines outlined in the Compilation of Air Pollutant Emissions Factors (AP-42) [15], it is assumed that all solvents in pesticides would volatilize into the air within 30 days after application, regardless of the application methods, temperature and other factors. Given this assumption, all solvents in the pesticides applied in the main crops were considered to fully volatilize as PVOCs into the air in this study.

#### 2.1.4. Determination of temporal PVOC emission characteristics

Temporal PVOC emission characteristics were determined using Eqs. (4) and (5):

$$P_{m,i,j} = \sum_{k} \left( \frac{S_{y,i,j}}{T_{y,i,j,k} \times S_{y,i}} \times P_{y,i,k} \right) \quad (4)$$

$$E_m = \sum_{i,k} \left( P_{m,i,j} \times EF_{j,k} \right) \quad (5)$$

where subscript *m* represents the month. $P_{m,i,j}$ (ton·month$^{-1}$) is the mass of pesticide applied in crop *j* in province *i* during month *m* during the farming seasons. The month of pesticide application is determined using data from the phenological calendar [16,17]. $T_{y,i,j,k}$ represents the number of months that pesticide *k* applied in crop *j* in province *i* across the farming seasons during year *y*; $EF_{j,k}$ represents the emission factor (g·kg$^{-1}$) for VOCs emitted from pesticide *k* applied to crop *j*; $E_m$ (ton·month$^{-1}$) represents PVOC emitted across China in month *m*.

#### 2.1.5. Spatial emission allocation

According to the Technical Guideline on City-level Air Pollutant Emission Inventory Development, the area of cultivated land is recommended as a surrogate parameter to spatially allocate PVOC emissions into grids [18]. ChinaCropPhen1km offers the spatial distributions of the main crops at a 1 km resolution in China. Therefore, we mapped PVOC emissions onto ChinaCropPhen1km using the Geographic Information System to obtain a PVOC emission inventory with a spatial resolution of 1 km.

### 2.2. WRF-CMAQ model configuration

We employed the WRF-CMAQ model to assess the contribution of PVOCs to ozone formation. The simulation of ozone generation was conducted using WRF version 3.9.2 and CMAQ version 5.2.1 on a domain covering China with 9 km horizontal resolution and 37 vertical layers. Final Operational Global Analysis (FNL) data ($1^\circ \times 1^\circ$) from the National Centers for Environmental Prediction (NCEP) were used to create the initial and lateral boundary conditions of meteorology. The physical and chemical parameterization schemes are summarized in Table S1. The CMAQ model encompasses 218 gas-phase reactions, 28 photolysis reactions, 77 gas-phase species and 21 emission species for ozone formation, as detailed in Yarwood et al. [19]. The Chinese anthropogenic emission inventory for 2019 from MEIC, the natural/-biogenic VOC emissions from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) [20], the PVOC emission inventory for 2019 (9 km) from this paper and the data on meteorological fields and environmental conditions were taken as the model input files for WRF-CMAQ to calculate the ozone concentrations.

### 2.3. Uncertainties of PVOC emission inventory

The Monte Carlo simulation was applied to estimate uncertainties of the PVOC emission inventory. The probability distribution of pesticide application was assumed to follow a normal distribution with a coefficient of variation of 10% (Table S2) [21].

We entered the uncertainty parameters and the gridded activity level data into the Monte Carlo model, enabling the generation of random values for activity data in each spatial cell. These values were subsequently multiplied by their respective emission factors to compute PVOC emissions. To assess the range of uncertainties in our estimates, we conducted a comprehensive set of 10,000 simulations utilizing a 95% confidence interval, as suggested by Zhou et al. [21].

### 2.4. Model verification

We adopted a model verification method akin to the one used in a previous ozone simulation case [22]. This verification focused on the simulation results of ozone concentration nationwide for June 2019, especially in the North China Plain (NCP). Surface ozone data in China were obtained from the China National Environmental Monitoring Center (CNEMC) network (http://www.cnemc.cn/). The CNEMC network has over 1500 air monitoring sites across more than 450 cities, reporting hourly surface ozone concentrations.

Previous research has indicated that ozone concentrations are typically distributed in a log-normal pattern [23]. Consequently, we applied a logarithmic transformation on both the observed and simulated ozone concentrations for quality control. This transformation is represented by Eqs. (6) and (7). As indicated by Eqs. (8) to (11), the Pauta criterion method was utilized to perform quality control at the level of 5% significance [24]. Specifically, data exceeding two standard deviations from the sample mean are considered outliers.

$$x_{o(i)} = \lg O_{3i}(obs) \tag{6}$$

$$x_{s(j)} = \lg O_{3j}(sim) \tag{7}$$

$$\bar{x}_o = \frac{1}{n}\sum_{i=1}^{n} x_{o(i)} \tag{8}$$

$$\bar{x}_s = \frac{1}{n}\sum_{j=1}^{n} x_{s(j)} \tag{9}$$

$$|D_o| = |x_{o(i)} - \bar{x}_o| > 2s \tag{10}$$

$$|D_s| = |x_{s(i)} - \bar{x}_j| > 2s \tag{11}$$

Where *obs* and *sim* represent the observed and simulated ozone concentration values, respectively. The terms $x_{o(i)}$ and $x_{s(j)}$ correspond to the logarithmic transformations of the observed and simulated ozone concentration values, respectively. $\bar{x}_o$ and $\bar{x}_s$ are the average values of $x_{o(i)}$ and $x_{s(j)}$, respectively. $D_o$ and $D_s$ are the absolute deviations of observed and simulated values, respectively. $s$ is the standard deviation.

### 2.5. PVOC emission projections for 2025

#### 2.5.1. Basic scenario (BS)

The Chinese government initiated the ″Program of Zero Growth in Pesticides Use in 2015″ and successfully achieved the ″Zero Growth″ goal by 2020 [25]. Building upon this achievement, MARA proposed more ambitious plans to further reduce pesticide application by 5% before 2025 [26]. In this scenario, the PVOC emissions in 2025 will be reduced to 95% of the emissions in 2019.

#### 2.5.2. Scenario of improving pesticide utilization (IPU)

According to the declaration announced by the Chinese government, the current pesticide utilization efficiency in China stands at 35%, which will increase to 43% by 2025 in this scenario [27]. This increase in pesticide utilization efficiency is expected to reduce pesticide application, thereby correspondingly decreasing PVOC emissions.

#### 2.5.3. Scenario of solvent substitution in pesticides (SSP)

Under the SSP scenario, the Chinese government has taken the initiative to replace current aromatic solvents with low-volatility or other environmentally friendly solvents following the standard ″Limit of Harmful Solvents of Emulsifiable Concentrate Pesticide″ [28]. The limits on solvents specified in this standard are outlined in Table S3. Based on these limits, an assessment was conducted to determine the anticipated reduction in PVOC emissions in 2025.

#### 2.5.4. Comprehensive emission reduction scenario (CER)

Under the CER scenario, we considered all the individual control measures mentioned above and estimated the maximum emission reduction potential of PVOCs in 2025.

## 3. Results and discussion

### 3.1. Spatiotemporal characteristics of VOC emissions from pesticide application

The distribution of pesticides applied in the main crops at the provincial level in China is presented in Fig. S2. Taking 2019 as an example, the application share of insecticides (pyrethroids, emamectin benzoate, organophosphorus, neonicotinoids and carbamate) was the largest, constituting 39.6% of the total pesticides applied in the main crops. Specifically, the applications of pyrethroids, emamectin benzoate, organophosphorus, neonicotinoids and carbamate made up 7.5%, 13.5%, 10.9%, 5.1% and 2.6% of the total pesticides, respectively. The consumption of fungicides and herbicides accounted for 21.7% and 38.7% of the total pesticides, respectively. The province with the highest amount of pesticide application was Shandong (7.5%), followed by Guangdong (6.6%), Henan (6.3%), Heilongjiang (6.2%), Jiangsu

(6.2%), Guangxi (5.8%), Yunnan (5.8%), Hubei (5.7%), Hunan (5.6%) and Anhui (5.2%). The amount of pesticide application in each remaining region was less than 5% of the total.

As illustrated in Fig. 1, the application of pesticides (insecticides, fungicides and herbicides) decreased by 17.0% from 2012 to 2019, resulting in a 16% reduction in PVOC emissions (Fig. S3). The reduction in pesticide application and PVOC emissions is largely due to the adoption of various practices, such as the "Unified Pest Prevention and Control", the "Precise Application of Pesticides" and the "Program of Zero Growth in Pesticides Use". Additional pesticide-related policies are detailed in Table S4. The PVOC emissions decreased by 9.5% in 19 provinces and increased by 10.6% in 11 provinces from 2012 to 2015 (Fig. S4). From 2015 to 2019, 28 provinces saw a decrease in PVOC emissions, with 4 provinces (Guizhou 45%, Beijing 38%, Shanxi 33% and Tianjin 32%) reducing the PVOC emissions by more than 30% (Fig. S5).

Wang et al. estimated that the PVOC emissions in 2018 were approximately $7.1 \times 10^5$ tons, using a constant emission factor of 0.47 tons VOCs/ton pesticide [12]. It should be noted that the emission factors for PVOCs vary depending on pesticide species. As reported by Chen et al. [6], only 40% of pesticides contain organic solvents that can volatilize into the air as PVOCs. Considering pesticide species and their solvent compositions, this study provided a more accurate estimate of PVOC emissions ($3.9 \times 10^5$ tons) in 2018. Compared with other anthropogenic VOC emissions [12], PVOC emissions were higher than those from dry cleaning, catering industry, electronics manufacturing, plastic processing industry, basic organic chemicals, petrol stations, power, synthetic leather manufacturing, iron and steel and shoemaking.

A detailed understanding of PVOC compositions is crucial for an in-depth analysis of their impact on the atmospheric environment. Based on the PVOC compositions from pesticide solvents (Table S5) reported by Chen et al. [6], this paper estimated the PVOC emissions from the main crops in China for 2019. As shown in Figs. S6-S10, aromatic hydrocarbons were the most important contributor to PVOCs, accounting for 38.5% of the total PVOCs. Specifically, the emissions of p-xylene, 1,2,4,5-tetramethylbenzene, o-xylene, ethylbenzene, pentamethyl-benzene, m-xylene, and 1,2,4-trimethylbenzene accounted for 14.2%, 10.1%, 7.5%, 4.8%, 0.9%, 0.8% and 0.2% of the total PVOC emissions, respectively. Methanol emissions accounted for 30.2% of the total PVOC emissions. The remaining emissions were mainly from alkanes, alkenes, chlorinated hydrocarbons, esters, etc., accounting for 31.3% of the total PVOC emissions.

The Monte Carlo simulation indicated that the uncertainty of the PVOC emission inventory fell within an acceptable range (Table S6), affirming the reliability of the emission inventory developed in this study. A statistical analysis showed that there were significant differences ($p < 0.01$) in PVOC emissions among provinces in 2019 (Table S7). As shown in Fig. 2a, the highest PVOC emissions occurred in Shandong (10.2%), followed by Henan (7.4%), Yunnan (7.3%), Guangdong (6.6%) and Hunan (6.2%). These provinces are the major grain-producing regions in China, producing 27.3% of the national grain in 2019 [13]. Given that our gridded inventory was derived by mapping PVOC emissions onto ChinaCropPhen1km, the spatial distribution of PVOC emissions should be similar to that of the main crops in China. Additionally, the application of pesticides in these regions accounted for 31.4% of the total pesticides applicated in the main crops in China, resulting in 37.7% of the total PVOC emissions. In contrast, the PVOC emissions in Beijing, Tianjin, Shanghai and Tibet accounted for less than 1% of the total PVOC emissions since these regions applied a few pesticides in their limited cultivated land. Furthermore, the different types and dosages of pesticides applied in the main crops also influence the distribution of PVOC emissions. In 2019, the PVOC emissions from rice, maize and wheat fields accounted for 41.4%, 41.4% and 17.2% of the total PVOC emissions, respectively. In northern China, especially Inner Mongolia, Ningxia, Jilin and Liaoning, the PVOC emissions from maize fields accounted for more than 80% of their total. In southern provinces, such as Guangdong, Fujian, Hainan, Zhejiang, etc., the PVOC emissions from rice fields accounted for over 95% of their total. The PVOC emissions from wheat fields in Tianjin, Shanxi and Hebei accounted for 30% of their total.

A distinct monthly variation existed in PVOC emissions. As illustrated in Fig. 2b, the PVOC emissions in the summer of 2019 (June, July and August) accounted for 70% of the annual total while the remaining

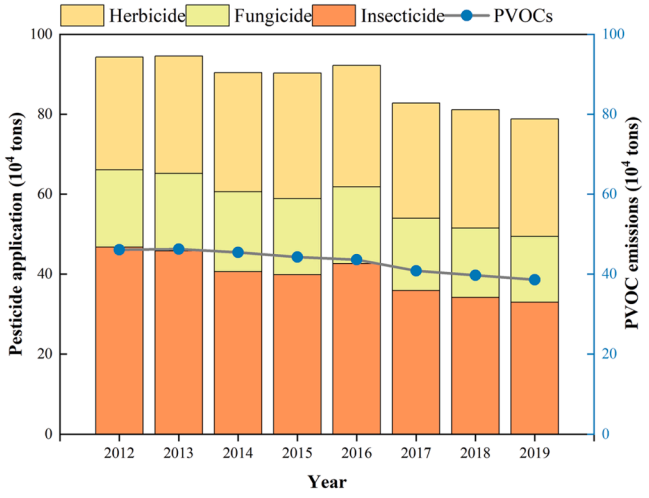



**Fig. 1.** Pesticide application and VOC emissions from pesticide application (hereafter referred to as PVOC emissions) from 2012 to 2019.

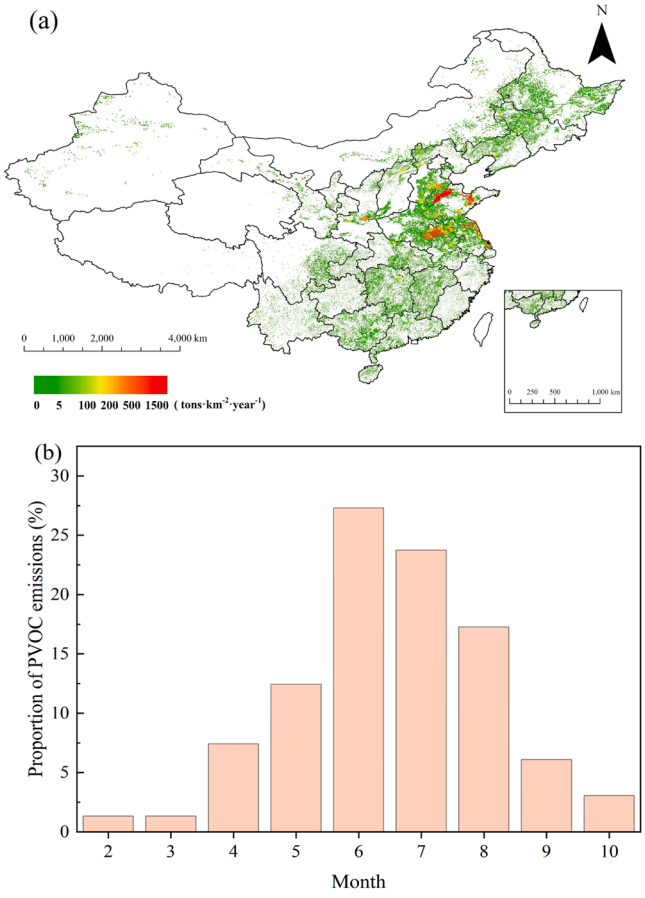



**Fig. 2.** Spatiotemporal distribution of PVOC emissions in 2019: (a) PVOC emissions with a resolution of 1 km; (b) Monthly distribution of nationwide PVOC emissions.

30% of the annual total occurred in the other seasons. Pesticide application in the agricultural production in China peaks in June each year, resulting in the highest PVOC emissions, which account for approximately 30% of the annual total. This peak in pesticide application coincides with the annual peak in pest and disease incidence in the agricultural production in China [16].

### 3.2. Impact of PVOC emissions on ozone formation in China

The contribution of PVOCs to ozone formation in June 2019 was explored with the WRF-CMAQ model. At the national scale, the observed and simulated mean maximum daily 8-hour average (MDA8) ozone concentrations in June 2019 were 46.46 and 39.75 ppb, respectively (Fig. 3a and b). Fig. 3c shows that the correlation coefficient (r) between the observed and simulated mean MDA8 ozone concentrations was 0.81, illustrating the reliability of the simulation results. As can be seen from Fig. 3a and b, the mean observed and simulated MDA8 ozone concentrations in NCP were higher than those in other regions. Consequently, we conducted a special model verification in this region. The results showed that the model accurately reproduced the spatial distribution of ozone ($r = 0.90$) and exhibited a small positive mean bias of 0.3 ppb for the mean MDA8 ozone concentrations measured in NCP in June 2019 (Fig. 3d).

In June 2019, the PVOC emissions increased the mean MDA8 ozone concentration across China by 2.5 ppb. NCP is one of the major grain-producing regions in China, and the estimated result indicated that PVOCs increased the mean MDA8 ozone concentrations in Hebei, Shandong, Tianjin, Beijing, Henan, Anhui and Jiangsu by 15, 10, 9, 8, 6, 4 and 3 ppb, respectively. Obviously, the contribution of PVOCs to ozone formation in major grain-producing regions mainly depends on the ratio of PVOC emissions to cultivated area, i.e., the intensity of PVOC emissions (ton/km$^2$). In these regions, the PVOC emissions constituted 6% of the total anthropogenic VOC emissions, with an average PVOC emission intensity of 0.41 ton/km$^2$. Specifically, PVOCs contributed 10% of the mean MDA8 ozone concentrations in Tangshan and Qinhuangdao, Hebei, as shown in Fig. 3e. In Qinhuangdao, the intensity of PVOC emissions (0.43 ton/km$^2$) was approximately 1.6 times higher than the average intensity in Hebei (Table S8). Moreover, the estimated emission intensity of PVOCs in Tangshan (4.1 ton/km$^2$) was nearly 15 times higher than the average intensity in Hebei.

Although the intensity of PVOC emissions in the major grain-producing regions of southern China was still comparably high, the contribution of their PVOC emissions to ozone formation was negligible. This can be attributed to the fact that substantial VOCs emitted from other anthropogenic sources dominated the ozone formation process [29,30]. For instance, the total anthropogenic VOC emissions in Yangtze River Delta (YRD) in June 2019 were $4.6 \times 10^5$ tons [10]. The research conducted in YRD revealed that the primary contributors to ozone enhancement were the transportation sector (63.1%) and the industrial sector (23.4%) [29]. The PVOC emissions estimated in this study constituted merely 1.40% of the total anthropogenic VOC emissions in this region, exerting little impact on ozone enhancement. Similarly, the total anthropogenic VOC emissions in Pearl River Delta (PRD) in June 2019 were $1.9 \times 10^5$ tons [10], and the estimated PVOC emissions accounted for only 1.02% of the total anthropogenic VOC emissions in PRD, with a limited contribution to ozone enhancement. Related research also indicated that the ozone formation in southern China was driven by VOCs from the transportation and the industrial sources [30].

In Beijing-Tianjin-Hebei (BTH), $1.5 \times 10^5$ tons of VOCs from industry and transportation contributed of 28 ppb to the mean MDA8 ozone concentration in the summer of 2007 [31]. The contribution of anthropogenic VOCs ($2.2 \times 10^5$ tons) to the mean MDA8 ozone concentration in this region reached 17.4 ppb in the summer of 2017 [32]. Compared with the VOCs from other anthropogenic sources in BTH, the mean MDA8 ozone concentration seems more sensitive to PVOCs with a high content of aromatic hydrocarbons (38.5%). According to a previous report [33], the maximum incremental reactivity (MIR) values of aromatic hydrocarbons are larger than those of other VOCs. This implies that PVOCs contribute more to ozone formation than other VOCs under the same emissions. Therefore, reducing PVOC emissions may be an effective way to control ozone concentration in the air.

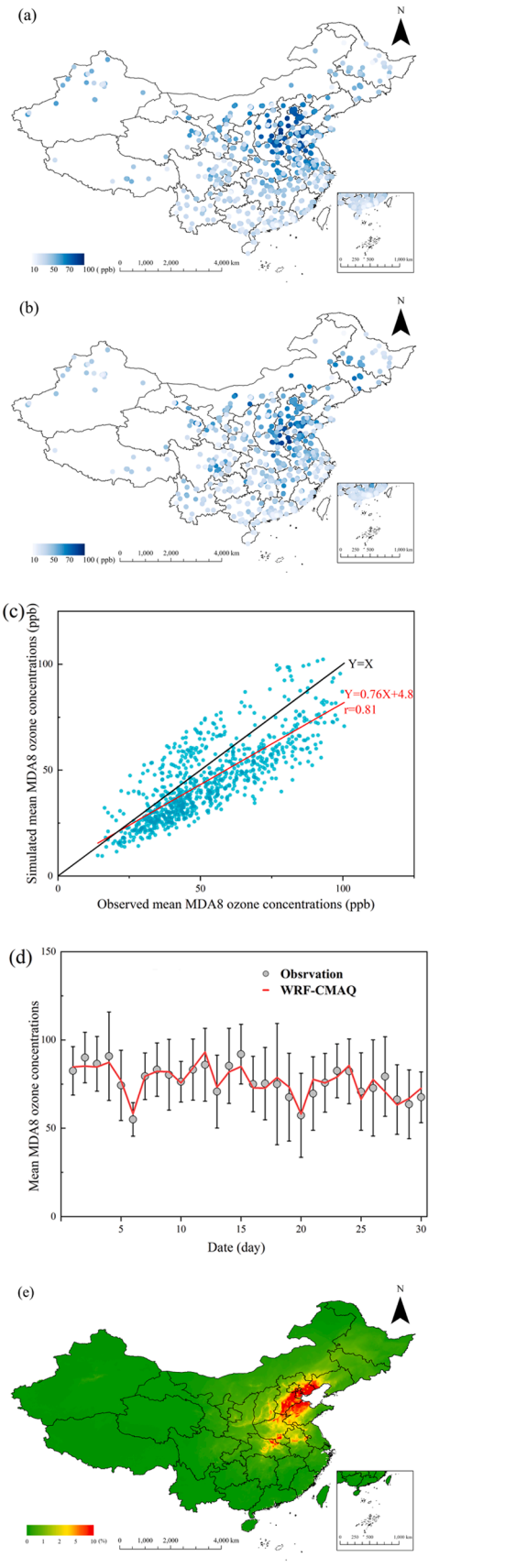
### 3.3. Implication of PVOC emission mitigation strategies

China has been actively addressing PVOC emissions to mitigate ozone formation. Generally, the substitution of high-volatility solvents with low-volatility ones, the restriction on the use of solvents in pesticide production and the improvement in pesticide utilization efficiency are considered as the effective paths of PVOC emission reduction [6,28]. Since 2009, the National Development and Reform Commission has no longer issued new approval certificates for pesticide products with harmful organic solvents [34], which accelerated the process of pesticide solvent substitution. Bio-derived solvents [35,36], mineral oils [37] and synthetic solvents [38] have been considered as suitable alternative solvents. Among these options, synthetic solvents show substantial potential in replacing harmful organic solvents due to their good solubility and low volatility [39]. The Chinese pesticide administration has introduced the ″List of Prohibited Pesticide Additives (Draft for Soliciting Opinions)″ to prohibit the use of hazardous and high-volatility solvents [40]. However, a detailed plan to achieve the goal of solvent substitution has not been outlined by MARA. In 2014, the standard ″Limit of Harmful Solvents of Emulsifiable Concentrate Pesticide″ [28] stipulated that the harmful solvent content in pesticides should be less than 22%. According to the results of previous research [6], many pesticides still do not meet the requirements of this standard. Nonetheless, solvent content limits for pesticide products in the standard may be met in the future by promoting the solvent substitution process mentioned above. During pesticide application, the low pesticide utilization efficiency will increase pesticide dosage, thereby enhancing PVOC emissions. In 2015, the pesticide utilization efficiency in China was 35% [27], which is still below those (55%−60%) in developed countries [41]. To reduce environmental pollution from pesticides, the Chinese government has set a target to increase pesticide utilization efficiency to 43% by 2025 [42]. In response, MARA issued the order ″Measures for the Administration of Pesticide Labels and Instructions″ [43], requiring pesticide producers to provide clarifications on how to apply pesticides. MARA also guided farmers to scientifically select pesticides and apply them safely and efficiently [44], thereby decreasing PVOC emissions.

Based on the identified paths of PVOC emission reduction, four scenarios are proposed in this study to assess the potential of PVOC emission reduction. Compared with the BS scenario, pesticide utilization efficiency will increase by 7% in the IPU scenario, resulting in a 17% reduction in PVOC emissions (Fig. 4). By solvent substitution, the PVOC emissions are expected to decrease by 33% in the SSP scenario. Although PVOC emissions are projected to be reduced under each scenario, they are expected to remain problematically high in 2025. Compared with the effect of PVOC emission reduction driven by a single policy, the comprehensive emission reduction scenario (CER) achieves a 60% reduction in PVOC emissions, which may provide an effective approach for the Chinese government to mitigate ozone formation in the future.

### 3.4. Uncertainty analysis

Many studies [45–47] have identified that major uncertainties in atmospheric modeling primarily stem from emission inventories, meteorological data and chemical reaction mechanisms rather than the models themselves. This study utilized three emission inventories: MEIC, MEGAN and PVOCs. MEIC was selected for its wide acknowledgment and application in air quality assessments at various scales, offering a credible basis for our simulation [29,30]. The MEIC team has reported that the level of uncertainty in air pollutant emissions is acceptable [48]. Furthermore, the reliability of the MEGAN inventory




*(caption on next column)*

**Fig. 3.** (a) and (b) show the spatial distribution of observed and simulated mean MDA8 ozone concentrations at 1653 Chinese urban sites in June 2019, respectively; (c) The correlation coefficient between observed and simulated mean MDA8 ozone concentrations; (d) Comparation of observed and simulated mean MDA8 ozone concentrations in North China Plain (NCP) in June 2019, and black bars represent the standard deviation of mean MDA8 ozone concentrations; (e) The contribution of PVOC emissions to ozone formation in June 2019.

was evidenced by the congruence between the tropospheric HCHO concentration from CMAQ model simulations using MEGAN and observed data [49]. Emission inventory uncertainties are commonly quantified by employing the Monte Carlo method [46]. As can be seen from Section 3.1, the uncertainties of the PVOC emission inventories fell within acceptable levels.

The WRF model is a mesoscale meteorological model extensively used for providing necessary meteorological fields in air quality models [45]. The key meteorological variables output by WRF, such as temperature, wind, boundary layer depth, clouds and radiation, can significantly influence ozone formation and its concentration in the air [50]. Aligning with common practices in this domain [10,22,51], we entered the data from the NCEP FNL Operational Model Global Tropospheric Analyses into the WRF model to simulate meteorological fields. Our team has previously applied the WRF model with the same data to evaluate the impact of air pollutant emissions from the iron and steel industry [51] and aviation sector [52] on the national air quality. This indicated that the meteorological variables output by WRF are reliable.

It is critical to select an appropriate chemical reaction mechanism because it determines the pathways in which the precursors are converted to ozone in the photochemical model. We have chosen the carbon bond mechanism for version 6 (CB6) because it describes tropospheric oxidant chemistry in a concise manner suitable for use in complex 3-dimensional atmospheric models [19,53–56]. Previous studies have widely applied CB6 to simulate ozone concentrations at home [57,58] and abroad [59], proving the reliability of CB6.

In summary, although emission inventories, meteorological data, and chemical mechanisms inherently possess uncertainties, our analysis substantiates that these uncertainties are within a tolerable range. Many studies have applied the WRF-CMAQ model to assess the contributions of air pollutants to air quality for various purposes [60–62], and demonstrated the reliable simulation results and acceptable uncertainties of the modeling system. This affirmation underscores the reliability of our modeling in evaluating the contribution of PVOCs to ozone generation.

## 4. Conclusion

In this study, the first PVOC emission inventory at a 1 km spatial resolution in China was constructed using pesticide application data and corresponding emission factors. PVOC emissions were mainly distributed in the major grain-producing regions, and the emissions in June accounted for approximately 30% of the annual total emissions. Notably, the PVOC emissions were found to contribute 2.5 ppb of the mean MDA8 ozone concentration across China in June 2019. The emission reduction strategy in the CER scenario will help reduce 60% of PVOC emissions in 2025.

## CRediT authorship contribution statement

**Bo Xin:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Xu Zhongjun:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – original draft, Writing – review & editing. **Ma Xiaotian:** Data curation, Investigation, Methodology, Visualization. **You Qian:** Data curation, Investigation,

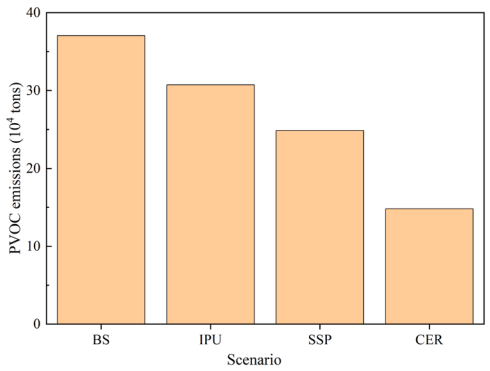



**Fig. 4.** PVOC emissions under different scenarios at the end of 2025 in China.

Methodology, Visualization. **Jiang Mengyun:** Data curation, Investigation, Methodology, Visualization. **He Youjiang:** Conceptualization, Data curation, Investigation, Methodology, Writing – review & editing. **Chen Shaobo:** Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing.

## Declaration of Competing Interest

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

## Data availability

The authors do not have permission to share data.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.133385.

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