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Volatile Organic Compound Emission Inventory for Pesticide Spraying in an Agricultural City of Northeast China: Real-Time Monitoring and Method Optimization

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Abstract: Atmospheric volatile organic compounds (VOCs), such as olefins and aromatics, released from synthetic chemical pesticide sprays can increase regional air pollution, public health risks, and food security risks. However, significant uncertainties remain regarding the measurement methods and chemical profiles of VOC emissions. Using an agricultural city, Changchun City in Northeast China, as a case study, we quantified real-time concentration and composition data based on online monitoring instruments for the year 2023. This study optimized data collection methods for emission factors and activity levels and developed a high-precision emission inventory of VOCs in pesticides at the city scale. The emission factors for VOCs from the seven categories of pesticides were estimated as follows: 78 g/kg (nicosulfuron and atrazine, oil-dispersible [OD] and suspension emulsion [SE], respectively), 4 g/kg (chlorpyrifos and indoxair conditioningarb, suspension concentrate [SC]), 5 g/kg (fluopicolide and propamocarb hydrochloride, SC), 217 g/kg (MCPA-dimethylammonium, aqueous solution [AS]), 34 g/kg (glyphosate, AS), 575 g/kg (beta-cypermethrin and malathion, emulsifiable concentrate [EC]), and 122 g/kg (copper abietate, emulsion in water [EW]), depending on the pesticide formulation components and formulation types. The orchard insecticide exhibited the highest emission factors among all pesticides owing to its emulsifiable concentrate formulation and 80% content of inactive ingredients (both factors contribute to the high content of organic solvents in the pesticide). The major components of VOC emissions from pesticide spraying were halocarbons (27–44%), oxygenated VOCs (OVOCs) (25–38%), and aromatic hydrocarbons (15–28%). The total VOC emissions from pesticide spraying in the Changchun region accounted for 10.6 t, with Yushu City contributing 28% of the VOC emissions and Gongzhuling City and Dehui City contributing 18.7% and 16.0%, respectively. Herbicides were the main contributors to VOC emissions because of their high emission factors and extensive use in fields (used for spraying maize and rice, the main crops in Changchun City). May and June exhibited the highest VOC emissions from pesticide application, with May accounting for 57.0% of annual pesticide emissions, predominantly from herbicides (95.1%), followed by insecticides (4.9%). June accounted for 30.1% of the annual pesticide emissions, with herbicides being the largest contributor of VOC emissions. An emission inventory of VOC with a monthly scale and spatial grid resolutions of 0.083° and 0.5° in 2023 was developed. These emission factors and inventories of pesticide applications provide valuable information for air quality modeling. This study also provides an important scientific basis for enhancing regional air quality and mitigating the environmental impact of pesticide use in major grain-producing areas.

Keywords: emissions factors; volatile organic compounds; pesticide spraying; emission inventory; real-time measurements

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1. Introduction

Volatile organic compounds (VOCs) are important precursors of ozone (O_3) and secondary organic aerosols, which are found extensively in the atmosphere. They play a significant role in many photochemical reactions, which have significant impacts on atmospheric oxidation capacity and air quality [1,2]. Long-term exposure to high concentrations of VOCs can elevate the risk of acute or chronic diseases and significantly inhibit the growth of crops, such as soybeans and rice [3–5]. Therefore, it is necessary to continue conducting VOC monitoring activities and understand the sources and types of VOCs in polluted areas. This information can provide an important scientific basis for reducing regional O_3 concentrations.

As VOC emissions from the transportation and petrochemical industries continue to decrease in China, there is a growing need to monitor and quantify other anthropogenic sources that contribute to increasing VOC emissions [6,7]. China is an important agricultural producer country, and agricultural sources have a significant potential to emit air pollutants [8]. However, current research on agricultural sources is relatively limited compared with that on industrial and transportation sources. This is primarily attributed to the perceived insufficiency of the established representative monitoring stations in rural regions. However, the seasonal variability and duration of O_3 and VOC concentrations are more pronounced in rural areas than in urban areas. These variations are influenced by the implementation of various agricultural management practices [9,10]. In addition, research on agricultural source emission inventories has mainly focused on straw burning, ammonia emissions, and farmland wind erosion [7,11], and there is often a scarcity of direct measurement data regarding pesticide source parameters in China [12,13]. This limitation hinders our capacity to comprehend, forecast, and manage the influence of VOC emissions from agricultural sources on air quality and human health owing to insufficient estimations of emissions from these sources.

Authoritative calculation methods for VOC emissions from pesticide applications include the methods of the "Emission Factor Documentation For AP-42 Section 9.2.2" (AP-42) [14], "EEA air pollutant emission inventory guidebook 2023" (EEA method) [15], and "Technical Guidelines for Compilation of Volatile Organic Compound Emission Inventory from Sources in China" (referred to as Guidelines), etc. [16]. However, there are several concerns regarding the emission factors (EFs) for pesticide applications. The AP-42 and EEA methods consider the values of emission factors to be dependent on the active ingredients in pesticides and the vapor pressure of the active ingredients, and the range of values is 2.7 to 580 kg/mg. The EEA method provides specific emission factor values for pesticide spraying, and activity level data consider the effects of the active ingredient content and density on the basic quantity of the pesticide [17,18]. The Guidelines provide emission factors for seven types of pesticides, with emission values ranging from 276 to 576 g/kg. The primary pathway for pesticide emissions into the air is through pesticide applications in the field [15]. The lack of direct emission factor data for pesticide application can lead to inaccurate assessments of regional VOC emission characteristics [19,20]. Furthermore, when estimating VOC emissions from pesticide spraying using the emission factors from the three aforementioned methods, challenges arise due to the unavailability of data on the VOC content of non-active and inactive ingredients in pesticide types [14,15]. In China, pesticides of the same type may exhibit variations in their formulation or inactive ingredient content across different companies (http://www.chinapesticide.org.cn/zwb/dataCenter (accessed on 2 February 2021)). Moreover, agricultural pesticide application systems have evolved, introducing new types of pesticides that are being widely used. These factors significantly contribute to the complexity of conducting regional VOC emission studies for pesticide spraying sources, often resulting in rough estimations or neglect of the impact of pesticide spraying sources on VOC and other important atmospheric pollutants. To address these challenges, it is crucial to augment pesticide emission data with localized data from various countries and conduct in-depth investigations into the VOC emission characteristics of pesticide spraying sources and their effects on regional air quality.

The primary industry in Changchun, which includes agriculture, forestry, animal husbandry, and fishery (excluding support services), contributes to approximately 6 to 8% of the region's gross domestic product, as indicated on the government website <https://data.stats.gov.cn/easyquery.htm?cn=B01> (accessed on 12 January 2015). The cultivated area covers approximately 1.64 million hectares. Situated at the heart of the Northeast China Plain, the region boasts a suitable soil texture, making it an ideal location for studying agricultural emissions from sources typical of grain-producing areas [19]. Pesticide application is essential for field crop management, with a significant volume of pesticides (ranging from 300 to 7500 milliliters per hectare based on a survey questionnaire). Based on this, it is estimated that the annual total VOC emissions from pesticide spraying of >20,000 tons are sprayed during crop cultivation to mitigate yield losses due to pests and diseases. The organic solvents present in the pesticide spraying process have the potential to volatilize and disperse into the air, affecting the atmospheric composition of farmlands and their surrounding areas.

The aim of this study was to conduct measurements of VOC emission concentrations and components after pesticide spraying in agricultural fields, calculate emission factors, and characterize the spatial and temporal distributions of high-resolution VOC emissions resulting from pesticide spraying in Changchun, Jilin. The proposed agricultural inventory aims to improve the accuracy of air quality models by providing input data on agricultural VOC emissions and their spatial and temporal distributions. Additionally, considering the anticipated increase in agricultural contributions to total emissions in the absence of specific control measures, an agricultural inventory will be instrumental in formulating national and local policies for controlling VOC emissions from pesticide spraying.

2. Methodology and Data

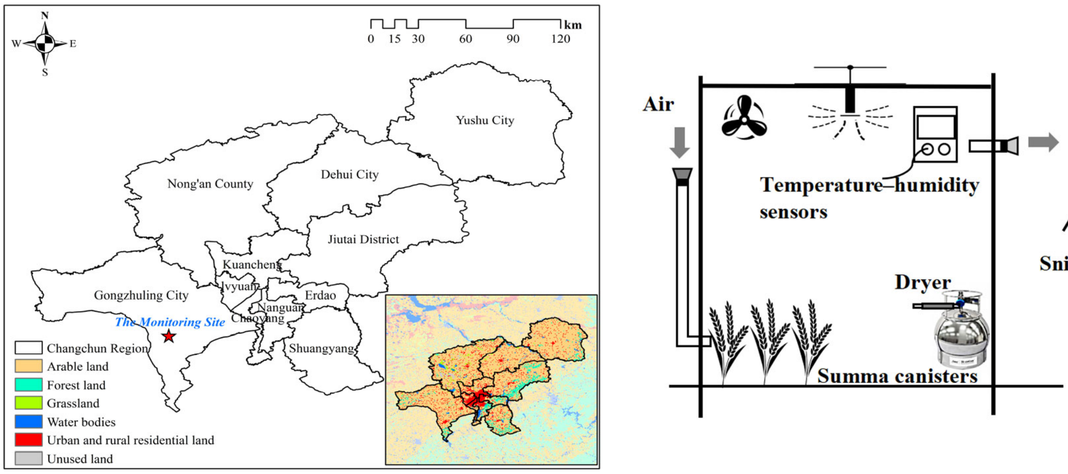
2.1. Study Region and Field Observations

The study area was situated in Changchun, Jilin Province, covering Changchun District, Nong'an County, and three county-level cities: Gongzhuling, Yushu, and Dehui. The longitude and latitude ranges of the study area were 124°18′–127°15′ E and 43°5′–45°15′ N, which was used to develop a regional high-precision VOC emission inventory for pesticide spraying.

VOC measurements were conducted from 3 to 8 September 2023. Before conducting the experiment, we collected survey questionnaires regarding pesticide application in Changchun City. The questionnaires covered several aspects, including the primary types of pesticides used and the frequency, timing, and dosage per unit area of pesticide application (Table 1). It was observed that pesticide application in Changchun mainly occurred between March and October, with multiple types of pesticides being sprayed 1–3 times during this period. The experiments commenced on 3 September due to the suitable temperatures in September, which reduced the impact of temperature fluctuations within the experimental chamber. Based on the experiment, VOC emission factors from pesticide application in Changchun were obtained to calculate the VOC emissions in Changchun for the year 2023. Additionally, we conducted more in-depth experimental research on the effects of different temperatures, atmospheric pressures, and vegetation growth conditions on VOC emission factors. These calibration parameters broadened the applicability of the VOC emission factors. The monitoring site was an agricultural field located 462 m east of Dongxing village in Changchun City, Jilin (124°47′ E, 43°37′ N). The sampling site was surrounded by vegetation, and there was no significant industrial activity within a 5 km radius of the site. Therefore, the sampling sites were not affected by the nearby atmospheric pollution sources. The geographical location is shown in Figure 1a.

Table 1. The details of pesticide application based on a survey questionnaire in Changchun City.

	Crop Type	Pesticide Type	Pesticide Name	Frequency of Pesticide Application	Time of Pesticide Application
1	Temperate fruit	Herbicides	Glyphosate	3	June and July
2	Temperate fruit	Insecticides	Beta-cypermethrin and malathion	3	June, July, and August
3	Temperate fruit	Fungicides	Copper abietate	3	April, June, and August
4	Maize	Herbicides	Nicosulfuron and atrazine	1	May
5	Maize/Rice	Insecticides	Indoxair conditioningarb and chlorpyrifos	3	May, June, and July June, July, and August
6	Maize/Rice	Fungicides	Fluopicolide and propamocarb hydrochloride	3	March, September, and October June, July, and August
7	Rice	Herbicides	MCPA-dimethylammonium	3	June and July



(**a**) (**b**)

Figure 1. Study region (**a**) and experimental equipment (**b**) (The red star indicates the locations of experimental monitoring stations).

2.2. Sample Collection and Chemical Analysis

In this study, a static chamber was constructed from a 304 stainless steel branch enclosure covered with a transparent fluorinated ethylene propylene (FEP) film [21,22], as shown in Figure 1b. The chamber was cuboid in shape with dimensions of 500 × 300 × 300 mm.

During pesticide, herbicide, and fungicide spraying periods on maize, wheat, peanuts, and orchards, VOC emissions were monitored online at the field site. Real-time meteorological parameters, including air temperature, humidity, light intensity, wind speed, and air pressure, were recorded using a meteorological monitor (Zoglab HWS3000, Hangzhou, China). The Sniffer4D is an atmospheric navigation monitoring system (Sniffer4D V2, Soarability, Shenzhen, China) that measures the concentration of VOC per second (unit: ppm). Summa canisters were used to identify the individual VOC species during pesticide spraying. The Summa canister pressure was evacuated to a vacuum (<10 Pa) in preparation for the experiment. During the sampling process, the method outlined in "Ambient air-determination of volatile organic compounds–collected by specially-prepared canisters and analyzed by gas chromatography/mass spectrometry" (HJ 759-2015) was followed, using a constant flow sampling technique. Additionally, the cleanliness and airtightness of the Summa canister were inspected. The collected air samples were concentrated using a pre-concentrator (Nutech 8900DS, Houston, TX, USA) and analyzed using a gas chromatography–mass spectrometry detector (GC-MS). Bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene were the internal standards used for analysis.

Before sample analysis, the GC-MS was tuned using mass spectrometer checks and calibration gases. Quantification was performed using the internal standard method, with a standard curve consisting of six concentration gradients. The coefficient of determination (R^2) for the standard curve needed to be >0.99. The midpoint concentration of the standard curve (2×10^{-9}) was analyzed every 24 h, and the deviation of the results from the initial concentration needed to be <30%. The retention time of the internal standard in the sample needed to not deviate by >20 s from the retention time in the most recently plotted standard curve. Each batch of samples included at least one transport blank, which involved transporting a clean sampling canister filled with high-purity nitrogen to the sampling site to ensure consistency in the treatment process (including exposure at the site, transportation, storage, and laboratory analysis). Random samples were selected for duplicate analysis during the sample analysis, and the variance between the two analyses was within 20%. One laboratory blank was analyzed for every ten samples to ensure that the concentrations of the target compounds were below the detection limit. Each pesticide testing site was sufficiently distant and free of interference to ensure accurate results.

The pesticides used in the planting management process included insecticides for maize and rice (chlorpyrifos and indoxair conditioning, respectively), herbicides for maize (nicosulfuron and atrazine) and rice (MCPA-dimethylammonium), fungicides for maize and rice (fluopicolide and propamocarb hydrochloride), herbicides for orchards (glyphosate), insecticides for orchards (beta-cypermethrin and malathion), and fungicides for orchards (copper abietate). Table 2 presents the detailed information of pesticides utilized in Changchun.

Table 2. Details of pesticides that were used in Changchun.

Number	Type of Pesticide	Name	Active Ingredients	Pesticide Formulation	Active Ingredient Content
1	Dryland herbicides (for maize)	Nicosulfuron	Nicosulfuron	Oil dispersible [1]	40 g/L
		Atrazine	Mesotrione, atrazine, acetochlor	Suspoemulsion [2]	50%
2	Paddy and dryland insecticides (for maize and rice)	Indoxair conditioningarb	Emamectin benzoate, indoxacarb	Suspension concentrate [3]	9%
		Chlorpyrifos	Chlorfenapyr	Suspension concentrate [3]	240 g/L
3	Paddy and dryland fungicides (for maize and rice)	Fluopicolide and propamocarb hydrochloride	Fluopicolide, propamocarb hydrochloride	Suspension concentrate [3]	587.5 g/L
4	Paddy herbicides (for rice)	MCPA-dimethylammonium	MCPA	Aqueous solution [4]	750 g/L
5	Orchard herbicides	Glyphosate	Glyphosate	Aqueous solution [4]	41%
6	Orchard insecticides	Beta-cypermethrin and malathion	Beta-cypermethrin, malathion	Emulsifiable concentrate [5]	20%
7	Orchard fungicides	Copper abietate	Copper abietate	Emulsion in water [6]	20%

[1] OD: oil dispersible; [2] SE: suspension emulsion; [3] SC: suspension concentrate; [4] AS: aqueous solution; [5] EC: emulsifiable concentrate; [6] EW: emulsion in water.

2.3. Formulae for Establishing VOC Emissions

The following formulae were used to estimate the VOC emissions of the pesticide spray categories:

$$E = A \times EF \times (1 - ER/100) \quad (1)$$

where E is the VOC emission from pesticide spraying, A is the pesticide application quality in this study (kg/ha), EF is the emission factor of the mass of VOCs volatilized per unit mass of pesticide applied (μg/mg or mg/g), and ER is the overall emission reduction efficiency, for example, reducing the amount of pesticide sprayed per unit area of cultivated land (%) [16].

2.4. Formulae for Estimating the Values of the Localized VOC Emission Factors

An atmospheric navigation monitoring system (Sniffer4D) was used to monitor the concentration of VOCs released from pesticides inside the static chamber. Based on the ideal gas state equation, $\mathrm{mg/m^3} = \frac{\mathrm{M}}{22.4} \times \frac{\mathrm{T_0}}{\mathrm{T_0+T}} \times \frac{\mathrm{P}}{\mathrm{P_0}} \times \mathrm{ppm}$ (in standard conditions, the temperature $\mathrm{T_0}$ is 273.15 K (0 °C), $\mathrm{P_0}$ is 101.325 kPa, and M is the molar mass of the gas), the VOC emission values (ppm) measured by Sniffer4D were converted into $\mathrm{mg/m^3}$. The component information is shown in Section 3.1. We simultaneously measured 65 types of VOCs using SUMMA canisters; the sum of these mass concentrations provided the total VOC concentration (ppm). We could calculate the mass concentration ($\mathrm{mg/m^3}$) of different VOCs based on their types (with known individual VOC species, molecular weight, and concentration). By comparing this value with the VOC concentration (ppm) measured by Sniffer4D, we obtained the mass concentration ($\mathrm{mg/m^3}$) of different VOC species per second. The sum of these concentrations gave the total VOC concentration ($\mathrm{mg/m^3}$) per second. t was defined as the interval from the beginning of pesticide application until the VOC concentration decreased to a level similar to that of the ambient concentration (when the VOC concentration stabilized). The emission factor was calculated using Equation (2) [23]:

$$EF_{voc} = \frac{\int_0^t F_{pesticides} \cdot V \cdot dt}{M} \cdot 100\% \tag{2}$$

where $F_{pesticides}$ indicates the VOC emission quality ($\mathrm{mg \cdot m^{-3} \cdot s^{-1}}$) during the observation period of pesticide spraying in the static chamber. V represents the volume of the static chamber ($\mathrm{m^3}$). t represents the time ($\mathrm{s^{-1}}$) (from the beginning of pesticide spraying until the complete dissipation of pesticide effects). M represents the pesticide application quality (g).

2.5. Activity Data

The acquisition of activity-level data involved two methods: (1) "the Guidelines" served as the pesticide application mass, sourced from the Changchun Statistical Yearbook [24]; (2) pesticide types and amounts sprayed per unit of farmland area were obtained through survey questionnaires. The amount sprayed per unit of farmland area was calculated by multiplying the respective planting areas of different crops to calculate the pesticide usage. In addition, data on pesticide types, components, and the amount used per unit of farmland area were also obtained from the "China Pesticide Information Network" available at http://www.chinapesticide.org.cn/zwb/dataCenter (accessed on 2 February 2021), which provided comprehensive pesticide-related information. The planting area data for different crops were obtained from the Global Crop Information Database published by the Spatial Production Allocation Model (SPAM) (https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/PRFF8V) (accessed on 15 July 2020) and the China Science Institute of Geography and Natural Resources, Chinese Academy of Sciences, and the Resource and Environment Data Cloud Platform (http://www.resdc.cn/Default.aspx) (accessed on 13 December 2023), which provided land use data.

2.6. Uncertainty Analysis of VOC Emissions

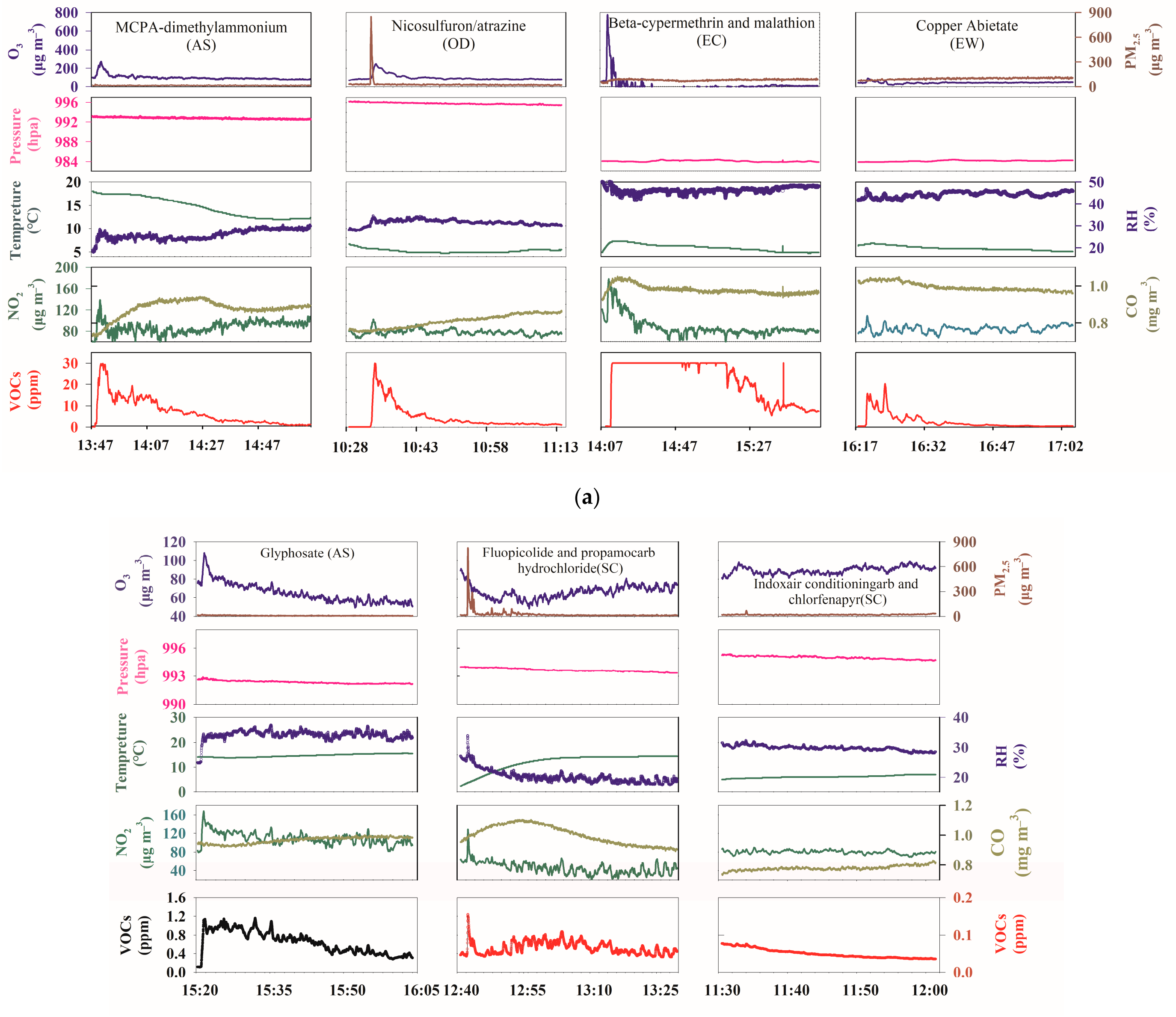
We used the Monte Carlo method to estimate the uncertainty of the emission inventory [25]. Uncertainties are influenced primarily by two key parameters: activity data and emission factors [26]. Our approach involved a four-step approach. First, we assumed that the activity data and emission factors could be represented by either a normal or a lognormal distribution. Subsequently, we extracted the single values of the analog activity and emission factors from the respective normal or lognormal distributions. The numerical values of the activity data and emission factors were used to calculate VOC emissions using the algorithms outlined in Table 1. We repeated the process of extracting values of activity and emission factors >20,000 times to calculate the VOC emissions iteratively. Finally, we estimated the standard deviations of these distributions, along with a 95% confidence interval.

3. Results and Discussion

3.1. VOC Concentrations and Temporal Variation

Figure 2a,b show the time series and concentrations of VOCs, $PM_{2.5}$ (particulate matter with a diameter <2.5 µm), O_3, NOx, CO, temperature, relative humidity, and pressure. Figure 2a shows the temporal sequence of the aforementioned parameters (from the start of pesticide spraying to the point where VOC concentration aligned with the environmental background level). The pesticides sprayed included paddy herbicides (MCPA-dimethylammonium), dryland herbicides (nicosulfuron and atrazine), orchard insecticides (beta-cypermethrin and malathion), and an orchard fungicide (copper abietate). Figure 2b illustrates the temporal sequences of parameters of an orchard herbicide (glyphosate), dryland and paddy fungicides (fluopicolide and propamocarb hydrochloride), and dryland and paddy insecticides (indoxair conditioningarb and chlorpyrifos). Throughout the measurement period, the ambient temperature ranged from 4.7 to 19.6 °C, and the relative humidity varied between 17.2 and 53.7%, with a prevailing north wind direction. This study revealed that shortly after pesticide spraying, the VOC concentrations in the static chamber rapidly increased to high values (though not necessarily the highest) and then gradually decreased to a low value, similar to the ambient background concentration after 30–120 min. For dryland herbicides, paddy herbicides, dryland and paddy insecticides, dryland and paddy fungicides, orchard herbicides, orchard insecticides, and orchard fungicides, the highest concentrations of emitted VOCs were 25.7 ppm, 29.8 ppm, 0.1 ppm, 0.2 ppm, 1.2 ppm, 30.1 ppm, and 22.2 ppm, with average VOC concentrations per second of 3.5 ppm, 7.1 ppm, 0.1 ppm, 0.1 ppm, 0.6 ppm, 22.1 ppm, and 2.5 ppm, respectively. Among the detected VOCs, orchard insecticides exhibited the highest levels of VOC emissions, whereas herbicides and orchard fungicides exhibited relatively high VOC emissions.

During the spraying of MCPA-dimethylammonium (a paddy herbicide), the O_3 concentration ranged from 73.0 to 271.4 $\mu g/m^3$, with an hourly average of 100.6 $\mu g/m^3$ and a median of 93.6 $\mu g/m^3$. The NO_2 concentration ranged from 47.5 to 138.2 $\mu g/m^3$, with an hourly average of 87.5 $\mu g/m^3$. In addition, the concentration of $PM_{2.5}$ varied between 9.0 and 31.0 $\mu g/m^3$, with an hourly average of 15.6 $\mu g/m^3$. This study revealed that the concentration peak values of O_3, NO_2, and VOCs occurred almost simultaneously, with the VOC concentration demonstrating a strong correlation with the O_3 concentration ($r^2 > 0.96$). This correlation may be attributed to the tendency of emulsifiable pesticides to promote VOC volatilization during pesticide application, consequently leading to a significant increase in the regional O_3 concentration. After the spraying of dryland herbicides (nicosulfuron and atrazine), orchard insecticides (beta-cypermethrin and malathion), orchard fungicides (copper abietate), and orchard herbicides (glyphosate), the O_3 concentration also rapidly increased in conjunction with the peak of VOCs. Similarly, the $PM_{2.5}$ concentration peaked after the use of dryland herbicides (nicosulfuron and atrazine, oil-dispersible [OD] and suspension emulsion [SE]), dryland and paddy insecticides (indoxair conditioningarb and chlorfenapyr, suspension emulsion [SC]), and dryland and paddy fungicides (fluopicolide and propamocarb hydrochloride, SC). Pesticides in suspension can significantly contribute to regional $PM_{2.5}$ concentrations, whereas pesticides of OD and SC often play a substantial role in VOC concentrations, undergoing rapid photochemical reactions under suitable environmental conditions, thereby increasing regional environmental O_3 levels. Furthermore, the formulation type of pesticides sprayed with higher solvent components (e.g., indoxair conditioningarb, with a solvent content of 91%; beta-cypermethrin and malathion with 80%; and copper abietate with 80%) tended to exhibit longer volatilization times and higher emission factor values. Notably, after spraying beta-cypermethrin and malathion, elevated VOC concentrations persisted for an extended period (>2 h), highlighting the need for particular attention to this category of pesticides.



(**a**)

(**b**)

Figure 2. (**a**). Time series of meteorological parameters and levels of air pollutants during pesticide spraying (e.g., paddy herbicides, dryland herbicides, orchard insecticides, and orchard fungicides). (**b**). Time series of meteorological parameters and levels of air pollutants during pesticide spraying (orchard herbicides, dryland and paddy fungicides, and dryland and paddy insecticides).

Figure 3 illustrates the proportions of alkanes, alkenes, aromatics, halogenated hydrocarbons, oxygenated VOCs (OVOCs), and sulfur-containing compounds. Halogenated hydrocarbons were the predominant type, constituting 27–44% of the total VOC (TVOC) concentration during pesticide spraying. OVOCs and aromatics accounted for approximately 25 to 38% and 15 to 28% of the TVOCs, respectively. Alkanes, alkenes, and sulfur-containing compounds made relatively minor contributions, representing <5, 6, and 2% of the TVOCs, respectively. Notably, during farmland herbicide spraying, halogenated hydrocarbons made a more significant contribution than other types of pesticide spraying, with 4-bromofluorobenzene, chloromethane, and methylene chloride being the primary halogenated species. The presence of OVOCs was primarily influenced by acetone, 2-butanone, and ethyl acetate. The contributions of OVOCs (38%) and aromatics (28%) from paddy herbicides were significantly higher than those of other types of pesticides.

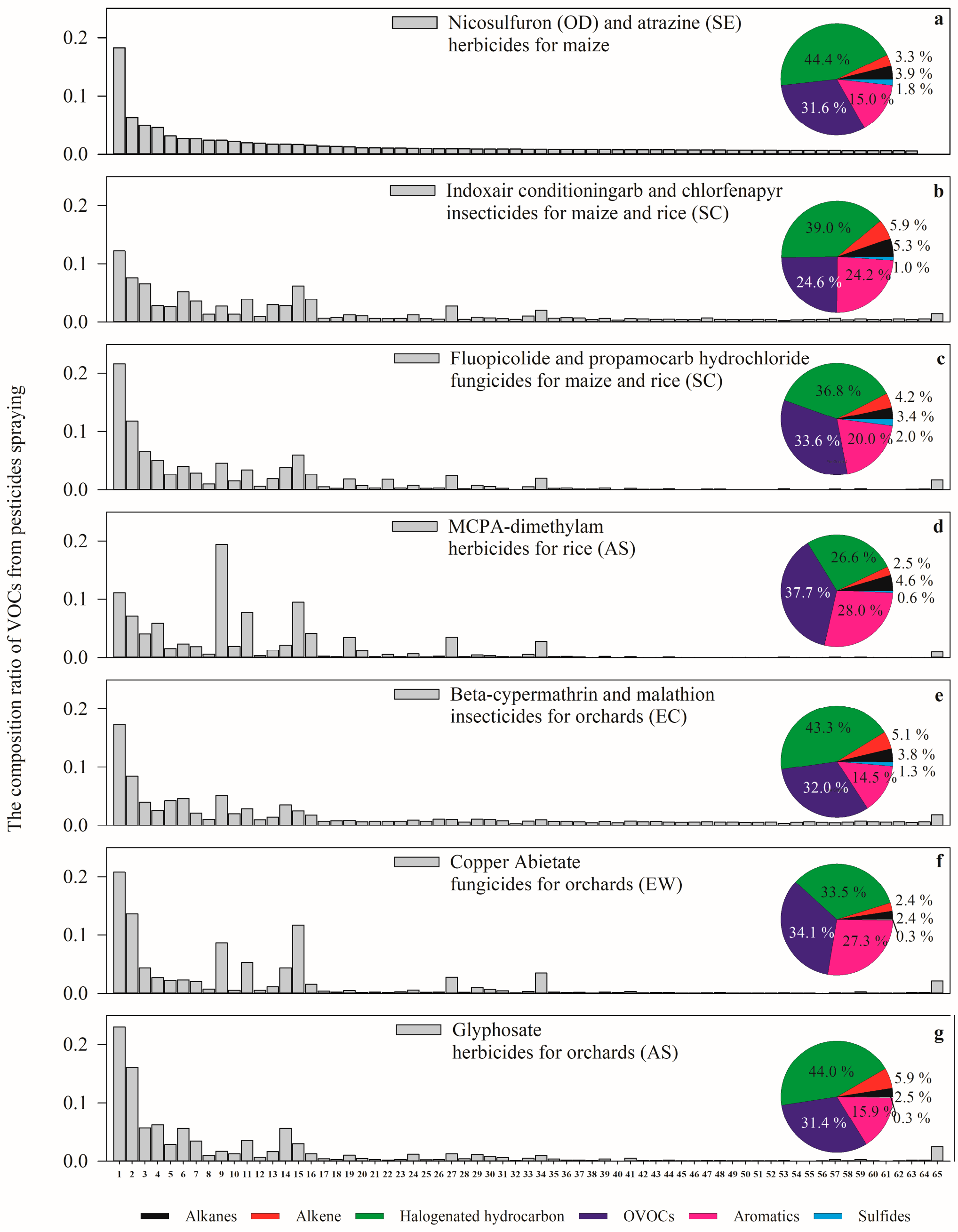


Figure 3. The relative contributions of the individual VOC species from pesticide spraying. Types of pesticides are as follows: (**a**) Nicosulfuron and atrazine (**b**) Indoxair conditioningarb and chlorpyrifos (**c**) Fluopicolide and propamocarb hydrochloride (**d**) MCPA-dimethylammonium (**e**) Beta-cypermethrin and malathion (**f**) Copper bietate (**g**) Glyphosate. (**1.** Acetone. **2.** 4-Bromofluorobenzene. **3.** Chloromethane. **4.** Methylene chloride. **5.** 2-Butanone. **6.** Propene. **7.** Benzene. **8.** Naphthalene. **9.** Ethyl acetate. **10.** 1,2-Dichloroethane. **11.** Toluene. **12.** 1,2,4-Trichlorobenzene. **13.** Acrolein. **14.** Dichlorodifluoromethane. **15.** m-Xylene. **16.** Hexane. **17.** 2-Hexanone. **18.** Hexachloro-1,3-butadiene. **19.** 2-Propanol. **20.** 1,2-Dichloropropane. **21.** 1,2-Dichlorobenzene. **22.** Carbon disulfide. **23.** 1,4-Dichlorobenzene. **24.** 1,2,4-trimethylbenzene. **25.** 1,3-dichlorobenzene. **26.** Chloroform. **27.** o-Xylene. **28.** 4-Methyl-2-pentanone. **29.** 1,1,2-trichloro-1,2,2-trifluoroethane. **30.** Carbon tetrachloride. **31.** Cyclohexane. **32.** Methyl tert-butyl ether. **33.** Styrene. **34.** Ethyl benzene. **35.** 1,3,5-Trimethylbenzene. **36.** Tetrahydrofuran. **37.** Methyl methacrylate. **38.** Benzyl chloride. **39.** 4-Ethyltoluene. **40.** Vinyl chloride. **41.** Heptane. **42.** Tetrachloroethylene. **43.** Bromomethane. **44.** 1,1,2-Trichloroethane. **45.** Dibromochloromethane. **46.** Ethylene dibromide. **47.** 1,1,2,2-tetrachloroethane.

48. Chlorobenzene. **49.** Trans 1,3-dichloropropene. **50.** Bromoform. **51.** Trichloroethylene. **52.** 1,1-Dichloroethane. **53.** 1,4-Dioxane. **54.** cis-1,3-Dichloropropene. **55.** 1,1-Dichlorethene. **56.** Vinyl acetate. **57.** 1,3-butadiene. **58.** Bromodichloromethane. **59.** 1,1,2,2-Tetrachloro-ethylene dichloride. **60.** trans-1,2-Dichloroethene. **61.** 1,1,1-trichloroethane. **62.** cis-1,2-dichloroethene. **63.** Dimethyl disulfide. **64.** Chlorethane. **65.** Trichlorofluoromethane.)

The most abundant VOC species resulting from pesticide spraying were acetone (11–23%), 4-bromofluorobenzene (6–14%), chloromethane (4–7%), methylene chloride (3–6%), 2-butanone (2–4%), and propylene (2–6%). This could be attributed to the use of the aforementioned organic solvents as pesticide adjuvants to dissolve the active ingredients of the pesticides.

3.2. The Calculation of Pesticide Source Emission Factors and Emissions Based on Localized Measurements in Changchun City

The volatilization of organic solvents used to dissolve active compounds in chemical pesticides during spraying resulted in VOC emissions. The EF_{VOCs} resulting from the pesticide spraying are listed in Table 3. Emission factors of TVOCs were calculated during the spraying of seven pesticides, and a brief analysis is presented here. The emission factors of TVOCs during pesticide spraying varied from 4 to 575 µg/mg, with significant variations observed among different types of pesticides, primarily influenced by the type of pesticide adjuvant and the concentration of active ingredients. Notably, when the pesticide adjuvant was in suspension (SC), the TVOC emission factor was significantly low (4 and 5 µg/mg); however, it significantly contributed to the increase in $PM_{2.5}$ concentration (as depicted in Figure 2). Conversely, other pesticide formulations, such as emulsifiable concentrates (ECs), aqueous solutions (ASs), and emulsions in water (EWs), could exhibit TVOC emission factors approximately 5 to 100 times higher than those of SC-based pesticides. The emission factor of beta-cypermethrin and malathion (EC) was the highest, making it one of the pesticide types requiring specific attention.

Table 3. The calculation of pesticide source emission factors based on localized measurements in Changchun City.

	Type of Pesticide	Names of Pesticides	Pesticide Formulations	VOC Emission Factor (µg/mg)
1	Dryland herbicide	Nicosulfuron and atrazine	OD, SE	78
2	Dryland and paddy insecticide	Chlorpyrifos and indoxair conditioningarb	SC	4
3	Dryland and paddy fungicide	Fluopicolide and propamocarb hydrochloride	SC	5
4	Paddy herbicide	MCPA-dimethylammonium	AS	217
5	Orchard herbicide	Glyphosate	AS	34
6	Orchard insecticide	Beta-cypermethrin and malathion	EC	575
7	Orchard fungicide	Copper abietate	EW	122

Table 4 presents the cumulative emissions of VOCs stemming from pesticide spraying activities across various districts of Changchun City, including maize (dryland), rice (paddy field), and orchards. The quantities of pesticide sprayed, as determined through field surveys, ranged from approximately 750 to 3000 g/ha. In this study, the emissions were calculated based on the minimal application rate per unit area. The total VOC emissions attributed to pesticide spraying in Changchun City for corn, rice, and orchards amounted to 10.4 t. Specifically, emissions from corn fields resulting from pesticide spraying were 6.6 t (accounting for 63% of the overall emissions), primarily influenced by the extensive regional cultivation of corn and the relatively low emission factors associated with this type of pesticide spraying. Paddy fields and orchards contributed 3.0 t (29%) and 0.8 t (8%) of VOC emissions, respectively. Nevertheless, the estimated pesticide spraying frequency for orchards was significantly underestimated in this study (presumed to be sprayed three times). Regarding pesticide types, herbicide spraying (in both paddy and dry fields) led to higher VOC emissions than insecticide and fungicide spraying. With respect to pesticide spraying in orchards, the infrequent use of herbicides, fungicides, and insecticides contributed more significantly to the overall VOC emissions.

Table 4. VOC emissions (kg) from pesticides sprayed at 750 g/ha.

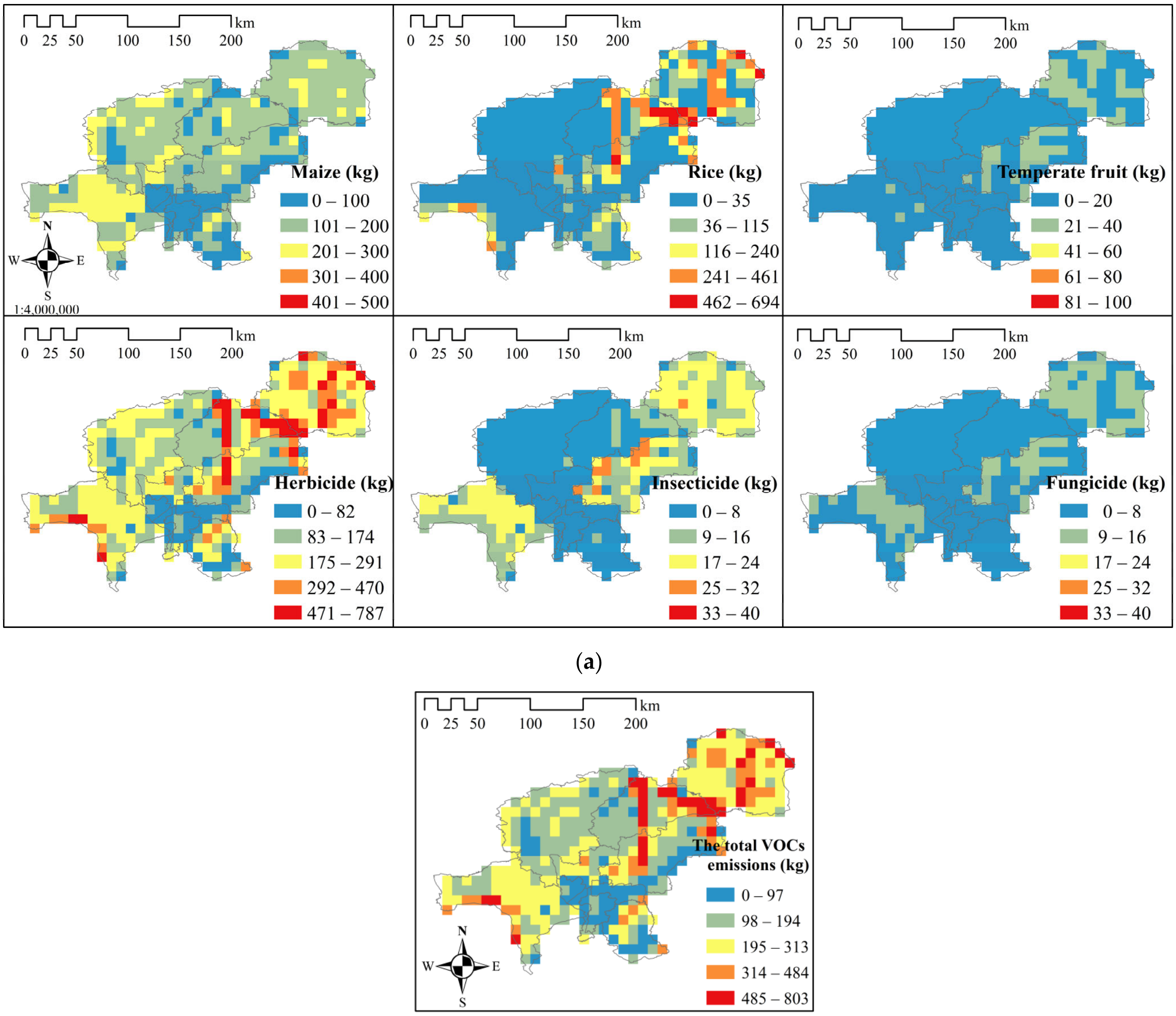
	CITY	MAIZE			RICE			TEMF		
		Herbicide	**Insecticide**	**Fungicide**	**Herbicide**	**Insecticide**	**Fungicide**	**Herbicide**	**Insecticide**	**Fungicide**
1	Changchun	1315	135	84	488	18	11	1	148	21
2	Dehui	6724	690	431	8101	299	187	1	277	39
3	Gongzhuling	12,594	1292	807	2342	86	54	7	2116	299
4	Jiutai	6751	692	433	4064	150	94	7	2043	289
5	Nonganxian	14,127	1449	906	92	3	2	0	61	9
6	Shuangyang	2827	290	181	1854	68	43	0	0	0
7	Yushu	12,278	1259	787	11,461	423	264	9	2629	372
	Total	56,616	5807	3629	28,402	1047	654	25	7275	1029

Note: (1) TEMF: temperate fruit. (2) If the amount of pesticide applied per hectare was 3000 g/ha, then the above emission quantities would be multiplied by four.

The VOC emissions resulting from pesticide spraying in various districts and counties of Changchun City and Yushu City contributed 28% of the total VOC emissions, followed by Gongzhuling City, Dehui City, and Nong'an County, which contributed 18.7, 15.9, and 15.8%, respectively, of the total VOC emissions. This distribution can be attributed to the larger maize cultivation area in Gongzhuling City and rice cultivation area in Dehui City, which are 1.6 and 2.0 times the size of the average maize and rice cultivation areas in Changchun City. Moreover, the maize and rice cultivation areas in Yushu City rank third and first, respectively, in the Changchun region. In 2023, the annual fertilizer application in Gongzhuling and Yushu was 2431 tons and 2414 tons, respectively, representing 1.50 and 1.51 times the average level in Changchun City. These areas were the focus of our study.

3.3. The Spatial Distribution of VOC Emissions from Pesticide Spraying in the Changchun Region

The spatial distribution of VOC emissions resulting from pesticide spraying in the Changchun region, as depicted in Figure 4a,b, at a resolution of 0.0833° × 0.0833° (matching the resolution of the crop-harvested area data from the SPAM), revealed significant spatial variations in emissions from corn, rice, and fruit tree cultivation. Furthermore, the spatial distribution characteristics of VOC emissions from insecticides, fungicides, and herbicides showed significant variation. The intensity of VOC emissions from pesticide spraying decreased in the following order: corn (76 kg/grid/a) > rice (35 kg/grid/a) > orchards (10 kg/grid/a). Regions with relatively high emission intensities included primary corn cultivation areas, such as Nong'an County and Gongzhuling City; primary rice cultivation areas, such as Yushu City; and primary orchard cultivation regions, such as Jiutai City. The maximum emission intensities per unit area were 329 kg/grid for corn cultivation, 724 kg/grid/a for rice cultivation, and 80 kg/grid/a for orchard cultivation. In terms of pesticide type, the average regional emissions for herbicides, insecticides, and fungicides were 98 kg/grid/a, 16 kg/grid/a, and 6 kg/grid/a, respectively. The herbicides exhibited the highest VOC emission intensity, with peak emissions concentrated in Yushu City and Dehui City, reaching a maximum intensity of 787 kg/grid/a. Counties exhibiting significant VOC emissions from insecticides included Jiutai and Yushu City, with a maximum intensity of 86 kg/grid/a. Similarly, counties with significant VOC emissions from fungicides included Dehui and Gongzhuling City, with a maximum intensity of 23 kg/grid/a.



(**a**)

(**b**)

Figure 4. (**a**). The spatial distribution of VOC emissions from pesticide spraying in the Changchun region (for three types of crops and three types of pesticides). (**b**). The spatial distribution of the total VOC emissions from pesticide spraying.

Yushu and Dehui cities were identified as the regions characterized by relatively high VOC emission intensities resulting from pesticide spraying. The highest emission intensity recorded was 847 kg/grid/a in Yushu City, Changchun region. On average, the VOC emission intensity in the Changchun region was 121 kg/grid/a. The increased VOC emission intensities observed in specific grid areas could be attributed to the high proportion of agricultural fields within these grids, particularly those allocated for corn cultivation (pesticides used in these cornfields have high emission factors).

3.4. Temporal Distribution of VOC Emissions from Pesticide Spraying in the Changchun Region

According to the questionnaire survey conducted before the experimental determination of pesticide application in farmland, the annual spraying frequency and timing of herbicide, insecticide, and fungicide applications were as follows (Table 1): Herbicides for maize were sprayed once in May, whereas those for rice and orchards were sprayed once in June. Insecticides for maize and rice were sprayed twice annually, with maize insecticide sprayed in May and July and rice sprayed in June and August. Orchard insecticides were sprayed three times annually in June, July, and August. Fungicides were sprayed once a year for maize and rice in March and June, respectively, and twice for orchards in April and August. The VOC emissions from pesticide application for a given month were calculated as follows. First, the types and frequencies of pesticide applications were identified during the month. Second, the total amount of pesticide applied was calculated by multiplying the crop area by the pesticide application rate per unit area. This value, which represented the activity level, was then multiplied by the emission factor to determine VOC emissions from a single pesticide application event. Finally, the VOC emissions for all pesticide application events that occurred within the month were summed to obtain the total VOC emissions. The monthly emissions and contribution rates of VOCs from pesticide application are illustrated in Figure 5.

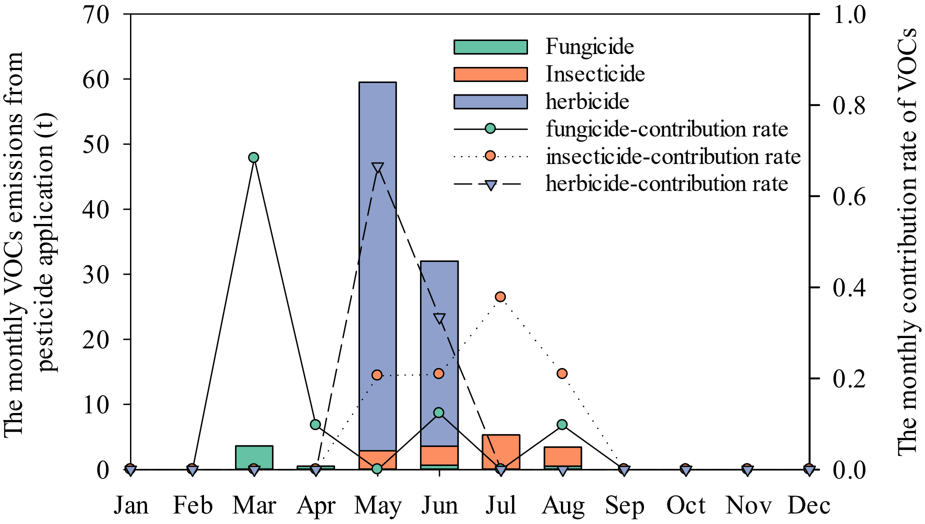


Figure 5. The monthly VOC emissions and contribution rates from pesticide spraying in the Changchun region.

Between September and February of the subsequent year, the emissions of VOCs resulting from pesticide application in the Changchun region remained at 0. Specifically, during May, high pesticide emissions were predominantly observed in the Jiutai and Shuangyang Districts, with orchards being the primary sprayed crops. Subsequently, in June, high pesticide emissions were observed in Yushu City, Dehui City, and Jiutai District, with rice as the primary sprayed crop. Pesticide emissions in May represented 57.0% of the total annual emissions, with herbicides being the major contributors to VOC emissions (contributing 95.1%), whereas insecticides contributed 4.9% to the total pesticide VOC emissions. In June, VOC emissions accounted for 30.1% of the total annual pesticide emissions, with herbicides being the largest contributor to VOC emissions. The pesticide VOC emissions in the Changchun area were most prevalent from May to August, with herbicides being the primary source of VOC emissions from March to June, peaking in May, which exhibited the highest emissions among herbicides. Insecticides were used from May to August, with the highest emissions occurring in July, contributing 37.7% of the insecticide VOC emissions. Fungicidal VOC emissions were predominantly observed in March (contributing 68.3%), with emissions also observed in April, June, and August.

3.5. Developing an Emissions Inventory of Pesticide Spraying Based on Statistical Data

Tables 5 and 6, along with Figure 6, illustrate the total emissions and spatial distribution of VOCs using emission factors and calculation methods provided by the guidelines. The activity level data corresponded to the amount of pesticide application extracted from statistical yearbooks [24]. The spatial resolution of the emissions at the county level is illustrated in Figure 6a. By reallocating the pesticide application quantities based on the crop planting area (Figure 6b), a finer resolution (0.05°) of the spatial characteristics of VOC emissions from pesticide spraying sources was achieved (Figure 6c). Consequently, two pesticide spraying emission inventories were compiled in this study: Inventory (1), based on localized emission factors and pesticide spraying quantities (derived by multiplying pesticide spraying quantities per unit area of farmland by crop planting data obtained from survey questionnaires, resulting in activity data with finer resolution), and Inventory (2), based on emission factors from the guidelines and pesticide usage quantities (sourced from statistical yearbooks at the county-level resolution).

Table 5. Details of two inventories in this study.

	Type	Activity Data	Emission Factor	Resolution
1	Inventory (1)	Pesticide spraying quantities (SPAM and survey questionnaires)	Based on real-time monitoring	1 km^2
2	Inventory (2)	Pesticide spraying quantities (Changchun statistical yearbooks)	Based on the ”Technical Guidelines for Compilation of Volatile Organic Compound Emission Inventory from Sources in China”	County-level

Table 6. VOC emissions from pesticide spraying, calculated based on the Statistical Yearbook.

Emission Factor	Regions	Pesticide Application Mass (t)	VOC Emissions (kg)
276~576 g/kg [16]	Changchun City	250	117
	Shuangyang District	745	350
	Jiutai District	1309	615
	Yushu City	2414	1135
	Nong’an County	2954	1389
	Dehui City	1141	536
	Gongzhuling City	2431	1143
	Total	11,244	5285

Technical Guidelines for Compilation of Volatile Organic Compound Emission Inventory from Sources in China (experimental implementation) [16].

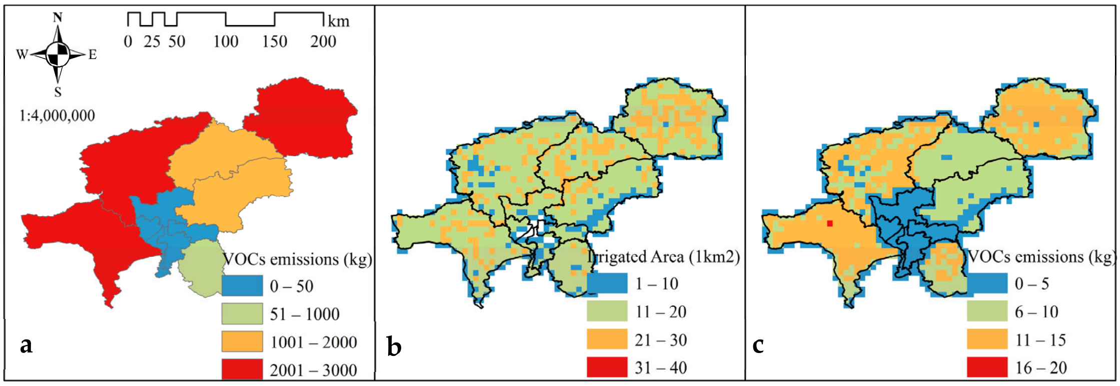


Figure 6. (**a**). The spatial distribution of VOC emissions from pesticide spraying at county-level. (**b**). The spatial distribution of irrigated area in Changchun. (**c**). The spatial distribution of VOC emissions from pesticide spraying at 1 km^2 resolution.

The emission factor values for Inventory (2) based on “the guidelines” (ranging from 276 to 576 g/kg) exceeded those of the localized emission factors (ranging from 4 to 575 g/kg). However, in terms of the calculated results, the regional VOC emissions from Inventory (2) were lower than those from Inventory (1). This discrepancy could be attributed to the pesticide application quantity based on statistical yearbook surveys (11,244 t) (from the "Changchun Bureau of Statistics") [24] being lower than the pesticide usage in agricultural fields obtained through questionnaire surveys and SPAM data (3444 t; indeed, this calculation was based on the minimum value of pesticide spraying per unit area) (data source: https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/PRFF8V) (accessed on 15 July 2020).

3.6. Uncertainty Analysis

To analyze the uncertainties in pollutant emissions, we propagated the uncertainties from pesticide application VOC emission estimates using a crystal ball model in a set of Monte Carlo simulations. It was assumed that the activity data and emission factors could be described by a normal distribution. For the bottom-up inventories of pesticide application, the VOC emissions in Inventory (1) were calculated based on three parameters: crop planting area, pesticide application rate per unit area, and emission factor. The VOC emissions in Inventory (2) were calculated based on two parameters: the pesticide usage amount and the emission factor. To calculate the uncertainties for both inventories, we set coefficients of variation for each parameter. Based on the studies of Cao et al. (2011) and Wei et al. (2011), emission estimates were uncertain owing to a lack of complete knowledge of pesticide application emission factors (with a coefficient of variation in the range of ±30 to ±300%) and variations at the activity level (with a coefficient of variation in the range of ±50 to ±500%) [27–29]. Therefore, for Inventory (1), we assumed that the located emission factor had a coefficient of variation of 80%, as the emission factors were based on actual field measurements of pesticide spraying, which had a lower margin of coefficient of variation. For Inventory (2), the variations in the emission factors were assumed to be 200%, as the data were derived from guidelines and characterized by a single value. The variation in the activity level for inventory (1) was 30% because of the detailed statistical data from the SPAM. The pesticide spraying amount per acre was obtained from questionnaire surveys conducted in actual field areas, with an assumed variation of 50%. The activity-level data for Inventory (2) were obtained from the statistical yearbooks of the National Statistics Bureau, with a coefficient of variation of 30%.

Based on Monte Carlo simulations, we calculated the uncertainties of VOC emissions from pesticide application in Inventories (1) and (2) to be (−155%, 283%) and (−284%, 292%), respectively, at 95% confidence intervals. The inclusion of more key parameters in the emission algorithm led to significant uncertainties in VOC emissions from pesticide spraying. Despite Inventory (1) using more parameters for calculation than Inventory (2), the uncertainties in the emissions calculated by Inventory (1) were found to be greater than those in Inventory (2). This disparity could be attributed to Inventory (2), which relied on non-local emission factors to estimate pollutant emissions and had a limited number of values and a high coefficient of variation. Therefore, to minimize the estimation error of VOC emissions from pesticide application sources, it was essential to obtain localized emission factors and the influencing factors of these emission factors (with low uncertainty) through field experiments and surveys.

We quantified the effect of reducing pesticide application frequency, lowering emission factors, and decreasing the amount of pesticide applied per hectare on VOC emissions, as illustrated in Figure 7. First, the reduction in pesticide application frequency significantly reduced VOC emissions. The effect varied among counties in Changchun. Overall, a reduction in pesticide application frequency from three times per year to two times per year could lead to a 30–40% decrease in VOC emissions. The effect of reducing pesticide application frequency on VOC emissions was relatively small in Nong'an County, whereas it was most significant in Dehui. This discrepancy was attributed to the predominant cultivation of maize in Nong'an County, (the area under maize cultivation accounted for approximately 87.8% of the total farmland area), where herbicides are applied once a year for maize cultivation, thereby diminishing the effect of reducing the frequency of other pesticides on VOC emissions. In contrast, maize cultivation covered 69.7% of the total farmland area in Dehui, resulting in a significant effect on VOC emissions by reducing the frequency of other pesticides.

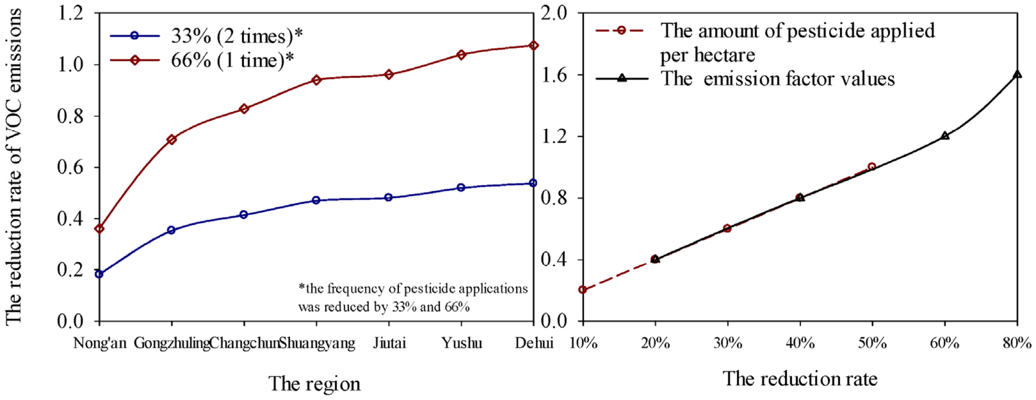


Figure 7. Sensitivity analysis of VOC emission reduction rates with emission factors, amount of pesticide applied per hectare, and pesticide application frequency.

The effect of reducing VOC emissions by decreasing emission factors was consistent across various counties in the Changchun region, demonstrating a linear relationship. The VOC emission reduction rate was approximately 40% for every 20% reduction in the emission factor. Similarly, reducing the amount of pesticides applied per hectare to lower VOC emissions showed a significant effect and followed a linear pattern. For every 10% reduction in the amount of pesticides applied per hectare, the emission reduction rate was approximately 20%. Among these sensitivity analyses, reducing the annual frequency of pesticide application had the most significant effect on VOC emissions reduction. However, lowering emission factors and reducing the amount of pesticides applied per hectare also played important roles in decreasing VOC emissions. These findings offer scientific support for proposing measures to reduce VOC emissions from pesticide applications.

4. Conclusions

This study involved the on-site monitoring of VOC emissions from seven pesticides in the Changchun area. This study revealed the following key findings: (1) The predominant pesticides used showed emission factor values varying from 4 to 575 g/kg, with the emission factors largely influenced by the pesticide formulations and the content of active ingredients. (2) The total VOC emissions attributed to pesticide spraying in Changchun City for maize, rice, and orchards were estimated to be 10.4 t. VOC emissions from pesticide spraying in drylands accounted for 63% of the total emissions, whereas paddy fields and orchards contributed 29% and 8%, respectively. (3) The regions with higher emission intensities were identified as Nong'an County, Gongzhuling, and Jiutai City. (4) Using the methods used in this study, it was determined that May and June are the peak periods for pesticide emissions. Specifically, May accounted for 57.0% of the annual pesticide emissions, with herbicides contributing the most (95.1%). June accounted for 30.1% of the annual pesticide emissions, with herbicides being the largest contributor of VOC emissions. (5) The key components responsible for VOC emissions from pesticide spraying were identified as halogenated hydrocarbons, OVOCs, and aromatics, with contribution rates ranging from 27 to 44, 25 to 38, and 15 to 28%, respectively.

There remain some issues that require further discussion. For instance, there are limited data on VOC emissions resulting from the use of pesticides with varying formulations and active ingredients in China. Therefore, we can assess the VOC emission characteristics of pesticides with different solvent formulations or with the same solvent formulation but varying organic solvent content. This will enable us to obtain adjustment factors for VOC emission rates associated with various pesticide formulations and solvent contents, thus extending the scope of VOC emission factors to pesticide application sources.

In this study, we measured the VOC emission characteristics of the seven most commonly used pesticides in Changchun in September 2023. According to survey data, the application of pesticides in Changchun was predominantly observed from March to October, with each pesticide being sprayed 1–3 times annually, and the types of pesticides used were fixed. Field experiments conducted in parallel indicated that the VOC emission characteristics of the same pesticide were relatively consistent. Therefore, the experiment was conducted from March to October to estimate the VOC emissions resulting from pesticide spraying in Changchun in 2023 (each month). This estimation was based on the annual or monthly pesticide application rates, emission factors, and spraying frequencies. Variations in temperature, atmospheric pressure, and vegetation growth conditions across different months influenced the VOC emission factors, potentially leading to estimation errors. The extent of these errors was assessed using Monte Carlo simulations; however, to reduce these errors, further investigations are required to evaluate the effects of temperature, humidity, soil conditions, and vegetation status on the measurement of VOC concentrations and compositions.

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Data Availability Statement: If you require access to the data presented in this study, please contact the corresponding author (fujing@iga.ac.cn) or the first author (lrm21@sdua.edu.cn).

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

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