

## *Retraction*

# **Retracted: Dynamic Correlation between Ozone and Volatile Organic Compounds in the Southeastern Coastal Region**

### **Scientific Programming**

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This article has been retracted by Hindawi following an investigation undertaken by the publisher [1]. This investigation has uncovered evidence of one or more of the following indicators of systematic manipulation of the publication process:

- (1) Discrepancies in scope
- (2) Discrepancies in the description of the research reported
- (3) Discrepancies between the availability of data and the research described
- (4) Inappropriate citations
- (5) Incoherent, meaningless and/or irrelevant content included in the article
- (6) Peer-review manipulation

The presence of these indicators undermines our confidence in the integrity of the article's content and we cannot, therefore, vouch for its reliability. Please note that this notice is intended solely to alert readers that the content of this article is unreliable. We have not investigated whether authors were aware of or involved in the systematic manipulation of the publication process.

Wiley and Hindawi regrets that the usual quality checks did not identify these issues before publication and have since put additional measures in place to safeguard research integrity.

We wish to credit our own Research Integrity and Research Publishing teams and anonymous and named external researchers and research integrity experts for contributing to this investigation.

The corresponding author, as the representative of all authors, has been given the opportunity to register their agreement or disagreement to this retraction. We have kept a record of any response received.

### **References**

- [1] H. Li and X. Nie, "Dynamic Correlation between Ozone and Volatile Organic Compounds in the Southeastern Coastal Region," *Scientific Programming*, vol. 2022, Article ID 8566454, 9 pages, 2022.

## Research Article

# Dynamic Correlation between Ozone and Volatile Organic Compounds in the Southeastern Coastal Region

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In order to investigate the sources and effects of atmospheric volatile organic compounds (VOCs) in the southeast coastal region and to formulate effective ozone control policies, 96 VOCs were measured in the southeast coastal region from September to October 2016 using an online gas chromatograph-mass spectrometer/flame ionization detector (Online-GC-MS/FID). The composition, daily trends, sources, and contribution to ozone production of 96 VOCs in the southeast coastal region were analyzed. The results of the study showed that the volume mixing ratio of alkanes was the highest, followed by aromatic hydrocarbons; the daily variation trend of alkanes and aromatic hydrocarbons was obvious, with a double-peaked feature; propane, isoprene, and aromatic hydrocarbons in the atmosphere of the southeast coastal region came from liquefied petroleum gas (LPG), natural sources, and industrial emissions, respectively. The analysis of the activity of VOCs shows that aromatic hydrocarbons and alkanes are the most important contributors to OFP in the southeast coastal region, with toluene, m-/paraxylene, and ethylene being the species that contribute the most to OFP. Therefore, the control of VOC emissions from anthropogenic sources is a priority for ozone pollution control in the southeast coastal region in the future.

## 1. Introduction

VOCs can be divided into natural source VOCs and anthropogenic VOCs. Reference [1] estimated global emissions of natural source VOCs at 1150 Tg, which is much greater than that of anthropogenic VOCs [2]. Studies have shown that natural sources of VOCs are involved in plant growth, reproduction, and defense and have important effects on other biological, atmospheric chemical, and physical processes [3]. BVOCs are present in low concentrations in the atmosphere compared to other gases in the atmosphere, but most of them are highly reactive and can react chemically with anthropogenic pollutants (especially nitrogen oxides) under certain temperature and light conditions, resulting in significant photochemical pollution [4].

At present, the representative models of BVOCs are BEIS, G95, BEIS2, GLOBEIS, MEGAN, etc. In this study, the

MEGAN2.1 model, which is widely used internationally, is a model for the emission of gaseous pollutants and aerosols from natural sources, based on a large amount of experimental data and the G95 algorithm, and further refining the mechanism and surface data [5].

The MEGAN model is not only a good replacement for the previous model but also has higher resolution and can meet the requirements of both regional and global scale simulations and has been commonly used in BVOCs emission studies at home and abroad. Many scholars have previously estimated BVOCs emissions in China using different modeling algorithms, and some studies have simulated some regions in China, such as Beijing, Hong Kong, Pearl River Delta, and Yangtze River Delta, but few studies have been conducted on BVOCs emissions with high spatial and temporal resolution for the northern inland regions of China. Therefore, in this study, the high-resolution leaf area index

(LAI) and vegetation functional type (PFT) data of the southeast coastal region were obtained from MODIS remote sensing images, and the meteorological data of the study area were modeled with the help of WRF model, and the final simulation was carried out by MEGAN2.1 model to obtain the high spatial and temporal resolution BVOCs emission inventory of the southeast coastal region [6]. The results of this study can provide a basis for future atmospheric research on photochemical pollution and ozone formation and will help to improve the atmospheric quality in northern China and further reduce the impact of atmospheric pollution on the ecological environment and human health.

The atmosphere on the Earth's surface determines the climate and environment on the planet, and it has a significant impact on biological and life processes on the Earth's surface; the composition and content of various chemical components in the atmosphere and their inter-conversion directly affects the environmental conditions on the Earth's surface, where the distribution of certain chemicals in the atmosphere (e.g., acid rain, ozone) on the Earth's surface has a direct impact on the biosphere and has become a major local environmental problem in some regions [7]. Nonmethane hydrocarbons (NMHCs) are trace gases produced by a variety of biological and geological processes on Earth, and although, they are present in small amounts in the atmosphere, they are decisive for certain atmospheric chemical processes. The amount of NMHC released is  $1.273 \text{ Tg C} \cdot \text{yr}^{-1}$  ( $1.273 \times 10^{12} \text{ g C}$  content per year), and in densely populated urban and industrialized areas, anthropogenic releases of NMHC occupy an undervalued position, but globally, the vast majority of NMHC is released from nature [8], with only a small fraction coming from the oceans and most of the rest from terrestrial ecosystems. The majority of the rest comes from vegetation in terrestrial ecosystems, especially woody plants, which contribute more than 90% ( $1,150 \text{ Tg C} \cdot \text{yr}^{-1}$ ) of the global NMHC emissions [9]. Plant VOCs are mainly volatilized into the atmosphere through the foliage of plants and have hundreds of components and structures, but two groups of compounds account for more than half of them: isoprene ( $\text{C}_5\text{H}_8$ ), which contains five carbon atoms, and monoterpenes, which contain ten carbon atoms, such as  $\alpha$ -pinene; the two types of volatile compounds released from plants total 500 and  $125 \text{ Tg C} \cdot \text{yr}^{-1}$  [10], respectively.

Many plants are capable of releasing VOCs under certain natural conditions and these compounds play a key role in the succession of ecosystems, for example, to mitigate heat stress [11], to protect against insect predation [12], and to meet the nitrogen requirements of the early stages of ecosystem succession by taking gaseous nitrogen from the air [13]. VOCs are chemically active and can undergo complex chemical reactions with atmospheric  $\text{HO}$  and  $\text{H}_2\text{O}$ , etc. The rate of VOC release from plants and their atmospheric content control the concentration of OH ions in the atmosphere, which in turn determines the atmospheric concentration of methane ( $\text{CH}_4$ ) and CO, which in turn influences the radiative balance in the atmosphere and hence the spatial and temporal distribution of global heat and precipitation, with a strong impact on the regional and

global environment and climate [14]. On the other hand, numerous studies have confirmed [15] that VOC has a significant impact on the photochemical synthesis of ozone in the near-earth troposphere and that the increase of ozone concentration in the troposphere can lead to serious ecological consequences such as forest decline and crop yield reduction [16]; atmospheric VOC also plays an important role in the global carbon cycle [17]. Therefore, the determination of atmospheric biogenic volatile compounds (BVOCs), especially the fluxes of VOC released by plants in various ecosystems, is important for the successful implementation of tropospheric ozone control.

Different plant taxa release different types and amounts of VOCs. For example, isoprene is one of the most abundant VOCs released by plants, and its release is dependent on sufficient light and high temperatures [18]. Among the angiosperms, *Quercus*, *Platanus*, *Populus*, *Rhamnus*, *Salix*, and *Eucalyptus* are typical isoprene releasers, while *Acer*, *Citrus*, and *Magnolia* are the main terpene releasers. Moreover, other genera mainly release terpenoids. Studying the phylogeny of plants and their interrelationship with VOC release developed a global VOC release model that provides a good explanation of the inter-relationship between the structure of temperate ecosystems and their atmospheric environment. However, this model is based on the species and capacity of different plant groups to release VOCs, requiring field and laboratory testing and analysis of a large number of plant species, which is not only a large amount of work but also results in large differences in the amount released due to different testing conditions and environments.

Studies in several regions have shown that VOC release is significantly correlated with the ecosystem type and closely related to the environmental conditions in which the ecosystem is located [19]. Further studies have also shown that plant VOC release in various ecosystems has an ecosystem succession-related pattern, with early to middle successional stages of ecosystems having a strong capacity to release isoprene, and plants with strong isoprene release mostly being the main components of this successional stage [20], while later successional plant species are mostly terpene releasers [21]. Succession is a process of ecosystem development that results in a constant turnover of vegetation types with different community structure and species composition (different successional stages). During the succession of an ecosystem, its productivity, biomass, nutrient cycling, and energy flow are widely predictable [6]. If VOC release is linked to ecosystem succession, then a systematic pattern of VOC release can be identified along the ecosystem succession sequence, and this pattern can be used to develop a succession-based VOC release model that can replace the cumbersome species-based VOC release model.

## 2. Research Methodology and Driving Data (Methods and Data)

**2.1. Study Area and Emission Model.** The southeastern coastal region is located at longitudes  $113^{\circ}27'$  to  $119^{\circ}50'$  E and latitudes  $36^{\circ}05'$  to  $42^{\circ}40'$  N, with a north-south length

of 735 km and an east-west width of 576 km, and a temperate monsoon climate. The study area was divided into  $245 \times 192$  grids at a distance of 3 km.

The MEGAN model, version 2.1, which is widely used internationally, was used to estimate BVOCs in agricultural, rural, and urban ecosystems. MEGAN2.1 was updated from MEGAN2.0 and MEGAN2.02, which not only expanded the emission categories but also added model control processes [7]. Previous models for estimating emissions of BVOCs have included one or more “other VOCs” in an attempt to include all emissions. However, “other VOCs” cannot be converted to known compound classes, or even from mass to substance, so this approach has significant limitations. To address this issue, the MEGAN2.1 model removes the category “other VOCs” and converts “other VOCs” into 73 specific categories of compounds.  $F_i$  is calculated as follows:

$$F_i = \gamma_i \sum \varepsilon_{i,j} \chi_j \rho, \quad (1)$$

where  $\varepsilon_{i,j}$  is the standard condition for vegetation type  $j$  (leaf area index LAI = 5, solar altitude angle of  $60^\circ$ , atmospheric light quantum flux transmittance of 0.6, air temperature of 303 K, air humidity of  $14 \text{ g} \cdot \text{kg}^{-1}$ , wind speed of  $3 \text{ m} \cdot \text{s}^{-1}$ , soil moisture of  $0.3 \text{ m}^3 \cdot \text{m}^{-3}$ , and sunrise photon flux of  $200 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  for the past 24 to 240 h).  $\chi_j$  is the proportion of this vegetation type in the corresponding grid;  $\rho$  is the fugacity factor, usually taken as a constant 1;  $\gamma_i$  is the emission activity factor, which is used to correct vegetation emissions according to changes in surrounding meteorological conditions (temperature, light, humidity, etc.), according to the following algorithm:

$$\gamma_i = C_{CE} \cdot \text{LA} \cdot \gamma_{P,i} \cdot \gamma_{T,i} \cdot \gamma_{A,i} \cdot \gamma_{SM,i} \cdot \gamma_{C,i}, \quad (2)$$

where CCE is the canopy environmental coefficient, taken as 0.57 in MEGAN; LAI is the leaf area index;  $\gamma_{P,i}$  represents the environmental regulation parameter related to light radiation;  $\gamma_{T,i}$  represents the regulation parameter related to temperature;  $\gamma_{A,i}$  represents the regulation parameter related to leaf age;  $\gamma_{SM,i}$  represents the regulation parameter related to soil moisture, which is only used for estimating isoprene and is defaulted to 1.0 for other emission categories;  $\gamma_{C,i}$  represents the emission parameter related to  $\text{CO}_2$ . The technical route of this paper is shown in Figure 1.

## 2.2. Data Preparation

**2.2.1. LAI Profile.** In this study, the 2017 MODIS leaf area index standard product MOD15A2H was used with a spatial resolution of 500 m and a temporal resolution of 8 d. Arcgis10.2 was used to stitch, reproject, crop, and resample the maps, and then ENVI5.3 was used to convert the output to obtain LAI data files in the study area.

**2.2.2. Types of Vegetation Function.** PFT The vegetation functional types in this study were classified using the MODIS land use standard product MCD12Q1 at a spatial resolution of 500 m. The images were stitched, reprojected, cropped, and resampled using Arcgis10.2, then were

converted and exported using ENVI5.3 to form a 3 km resolution grid, with the proportion of each vegetation type calculated separately within each grid. The proportion of each vegetation type was calculated for each grid. Table 1 shows the area distribution of various vegetation types in the southeast coastal area.

**2.2.3. Determination of EF Emission Factors.** The model applied in this study is MEGAN2.1, where the emission factors are measured under standard conditions, and the national emission factor averages [8] are used for the emission rates of specific categories of isoprene, monoterpene, and hemiterpene, while the default values in the model are used for the emission rates of specific categories of other VOCs. The emission factor unit in the MEGAN model is  $\mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ , whereas the emission factor unit in the literature is  $\mu\text{g}(c) \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  (in dry weight). So, this paper uses leaf biomass density ( $\text{g} \cdot \text{m}^{-2}$ , in dry weight) for conversion.

**2.2.4. Meteorologically Driven Data.** This study uses the latest release of WRF4.0 model data in 2018 as the meteorological driver data. MCIP was used to convert the WRF data into the standard input data of MEGAN2.1, where the projection of the MEGAN model is by default the same as the meteorological data, the Lambert equirectangular projection. The variables include temperature data (canopy temperature at 2 m above ground level and surface temperature for differential soil temperature), air humidity data (air humidity data at 2 m above ground level), wind speed data (canopy wind speed), soil data (soil moisture, soil temperature), solar radiation (downward shortwave radiation), etc.

## 3. Results and Discussion

**3.1. Characteristics of Atmospheric VOC Concentration Levels and Composition in the Southeast Coastal Region.** The composition of the VOCs varied considerably, with alkanes accounting for the largest proportion (56%), followed by OVOCs (13%) and aromatic hydrocarbons (12%). The top 10 compounds in terms of concentration were propane, n-butane, acetone, isobutane, toluene, isopentane, ethane, methylene chloride, acetylene, and n-pentane (Figure 2).

Table 2 shows the comparison of VOC concentrations in the southeastern coastal region and some major cities in China and abroad, and it can be seen that propane and toluene have the highest concentrations in each city. The concentrations of these species in the southeast coastal region are closer to those in Guangzhou and Hong Kong, and the high concentrations of propane, isobutane, and n-butane compared to other cities are related to the high number of buses and taxis using LPG (liquefied petroleum gas) fuels in the Hong Kong-Zhuhai-Macao region. Compared to Hong Kong and other cities in the PRD region, isopentane and methylene chloride concentrations in atmospheric VOCs are also high in the southeast coastal region, suggesting that oil volatilization and the chemical industry contribute to



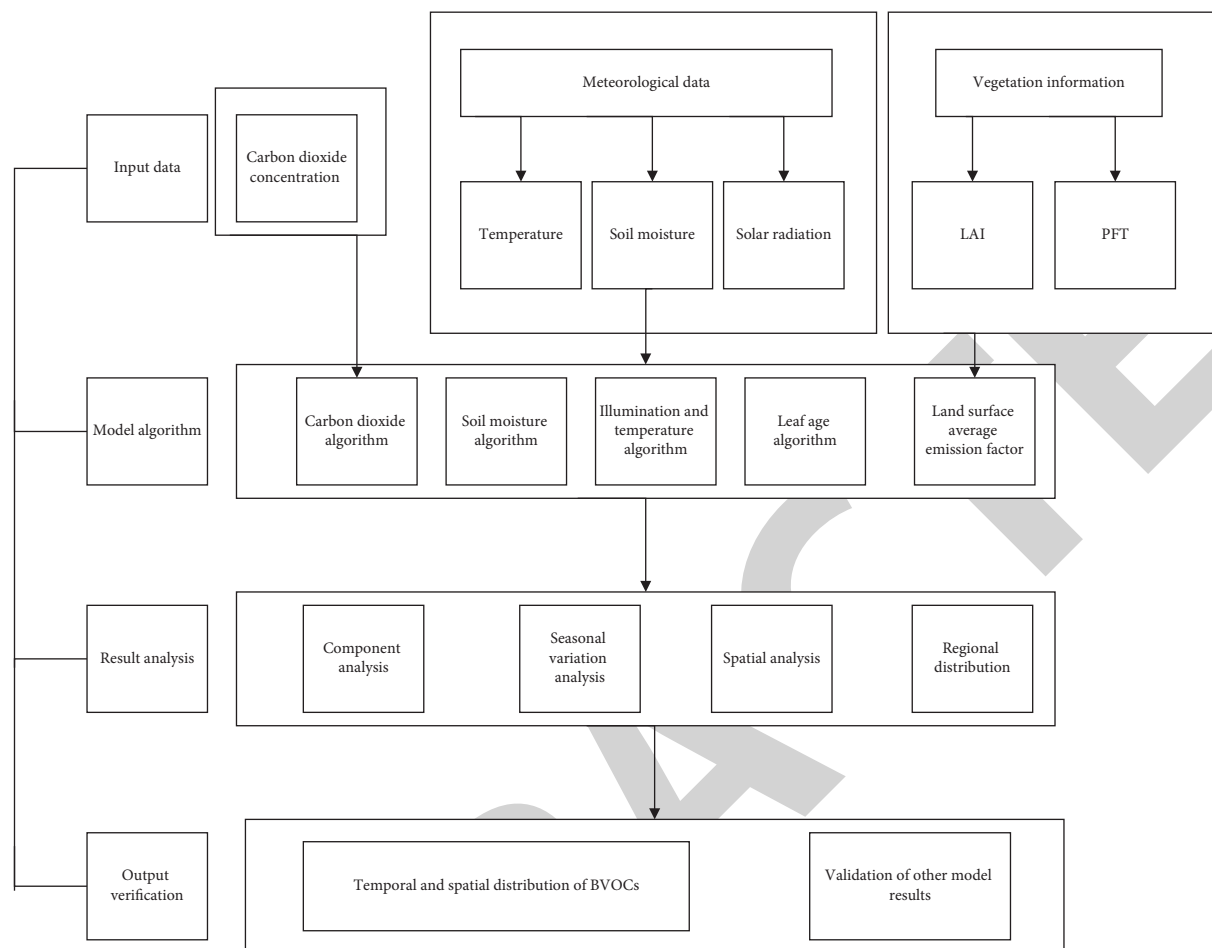


FIGURE 1: Technology roadmap for this study.

atmospheric VOCs in the southeast coastal region. The gasoline used in the PRD is mainly composed of lighter C4–C7 hydrocarbons, of which toluene and isopentane are the most abundant species, and atmospheric isopentane in the southeast coastal region may also come from the evaporation of gasoline fuels during the production process of the petrochemical industry. In addition, the source of methylene chloride may be the storage tank emissions from the chlorination plant. It can be seen that changes in atmospheric VOC concentrations in the southeast coastal region are influenced by various sources such as LPG exhaust, oil and solvent volatilization, and industrial production .

**3.2. VOCs' Daily Variation Characteristics.** The daily variation of alkanes, most olefins, and aromatic hydrocarbons in atmospheric VOCs in the southeastern coastal region shows a typical bimodal feature, with high concentrations in the morning and evening and lower concentrations at noon, see Figure 3. The strong convection in the midday, the boundary layer is elevated, which is conducive to the dilution and mixing of VOCs, and the strong sunlight in the midday consumes a large amount of VOCs in photochemical reactions, resulting in lower concentrations in the midday [9].

Acetonitrile (CH<sub>3</sub>CN), a tracer of biomass burning [10], did not vary significantly from day to day, but its concentration tended to increase in the evening, as shown in Figure 3. The concentration of acetonitrile increased significantly in individual evening sampling periods, with high values reaching  $2.67 \times 10^{-9}$ , much higher than the average concentration level, indicating that episodic biomass burning occurred in the evening.

Isoprene is an important indicator of emissions of biogenic (plant-derived) VOCs and its emission rate is dependent on light and temperature [11]. Isoprene is an important indicator of VOCs emissions from biogenic sources (plant sources). The regression results of MACR and MVK with 1,3-butadiene were 0.003 and 0.09, respectively, excluding the factor of motor vehicle exhaust emissions [12], indicating that isoprene and its oxidation products in atmospheric VOCs in the southeast coastal region are mainly from natural sources. The results of the regressions were 0.003 and 0.09, respectively, excluding motor vehicle emissions.

The daily variation of OVOCs (aldehydes and ketones) is characterized by single peaks, with high values lasting for a long time, with higher concentrations between 8:00 and 18:00 and lower concentrations at night, and with little variation in concentration, see Figure 3. For example, acetone is

TABLE 1: Vegetation types and areas in the southeastern coastal zone.

ID	Vegetation type	km <sup>2</sup>
1	Evergreen coniferous forest	4
3	Deciduous coniferous forest	3
4	Deciduous broad-leaved forest	9563
5	Thicket	1542
6	Grassland	81998
7	Cultivated land	101681

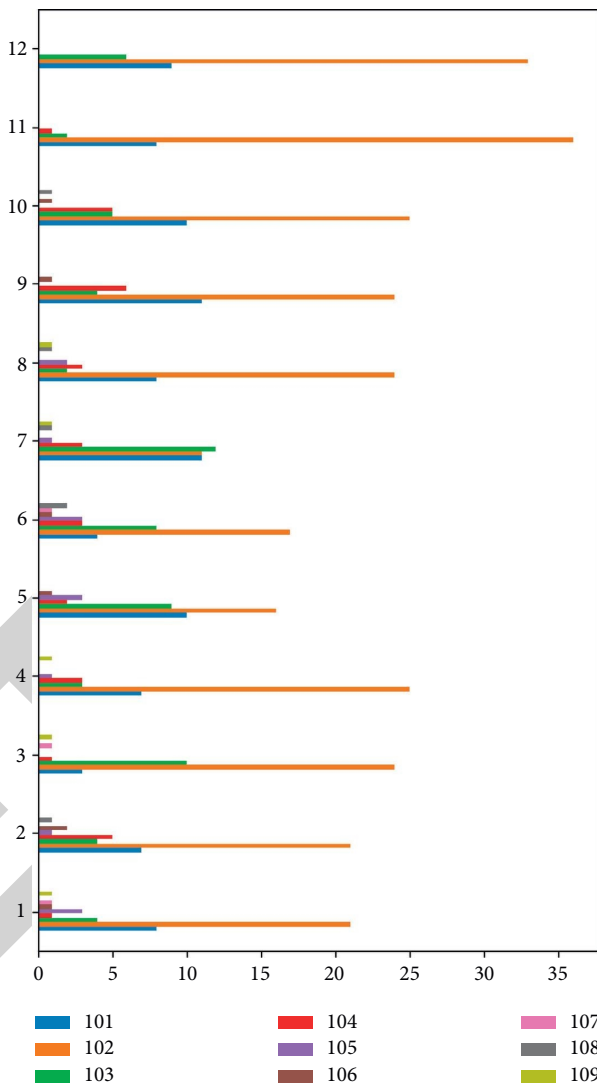


FIGURE 2: Top 10 VOC species in Zhuhai.

the species with the highest volumetric mixing ratio of atmospheric OVOCs in the southeast coastal region, and its source is both primary emissions from petroleum refining and petrochemical compounding processes [13] and secondary production from atmospheric oxidation of

precursors such as propane [14]. Due to the subtropical location of the southeastern coastal region, the strong midday light, long light hours, high temperatures, and strong photochemical reactions, and the long duration of high values of OVOCs, it is suggested that OVOCs in the

TABLE 2: Comparison of VOCs species concentrations between the southeast coastal region and selected cities in China and abroad.

Species	Our study	Guangzhou	Hong Kong	Shanghai	Nanjing	Beijing
Ethane	1.58	3.36	2.34	-	6.97	3.37
Propane	6.05	6.32	3.35	4.81	3.28	3.22
Isobutane	1.88	3.01	2.6	1.43	1.51	1.6
N-butane	3.25	3.69	4.34	2.04	1.69	1.7
Isopentane	1.62	1.05	0.66	2.29	1.12	1.99
N-hexane	0.4	0.62	0.23	0.68	0.67	0.23
2-Methylpentane	0.4	0.61	0.23	0.68	0.34	0.14
Ethylene	1.08	2.78	1.86	-	5.67	4.25
Propylene	0.27	0.69	0.54	0.84	2.45	0.53
Isoprene	0.16	0.07	-	0.12	0.54	0.47
Benzene	0.39	0.95	0.73	1.81	3.14	0.75
Toluene	1.85	4.83	2.56	4.7	2.2	1.02
M/p-Xylene	0.75	0.94	0.60	1.5	0.95	0.29
Dichloromethane	1.42	—	0.90	0.95	—	—
Acetaldehyde	0.70	—	1.92	—	—	—
Acetylene	1.13	2.5	—	—	3.13	—
Acetone	2.59	—	4.15	—	—	—

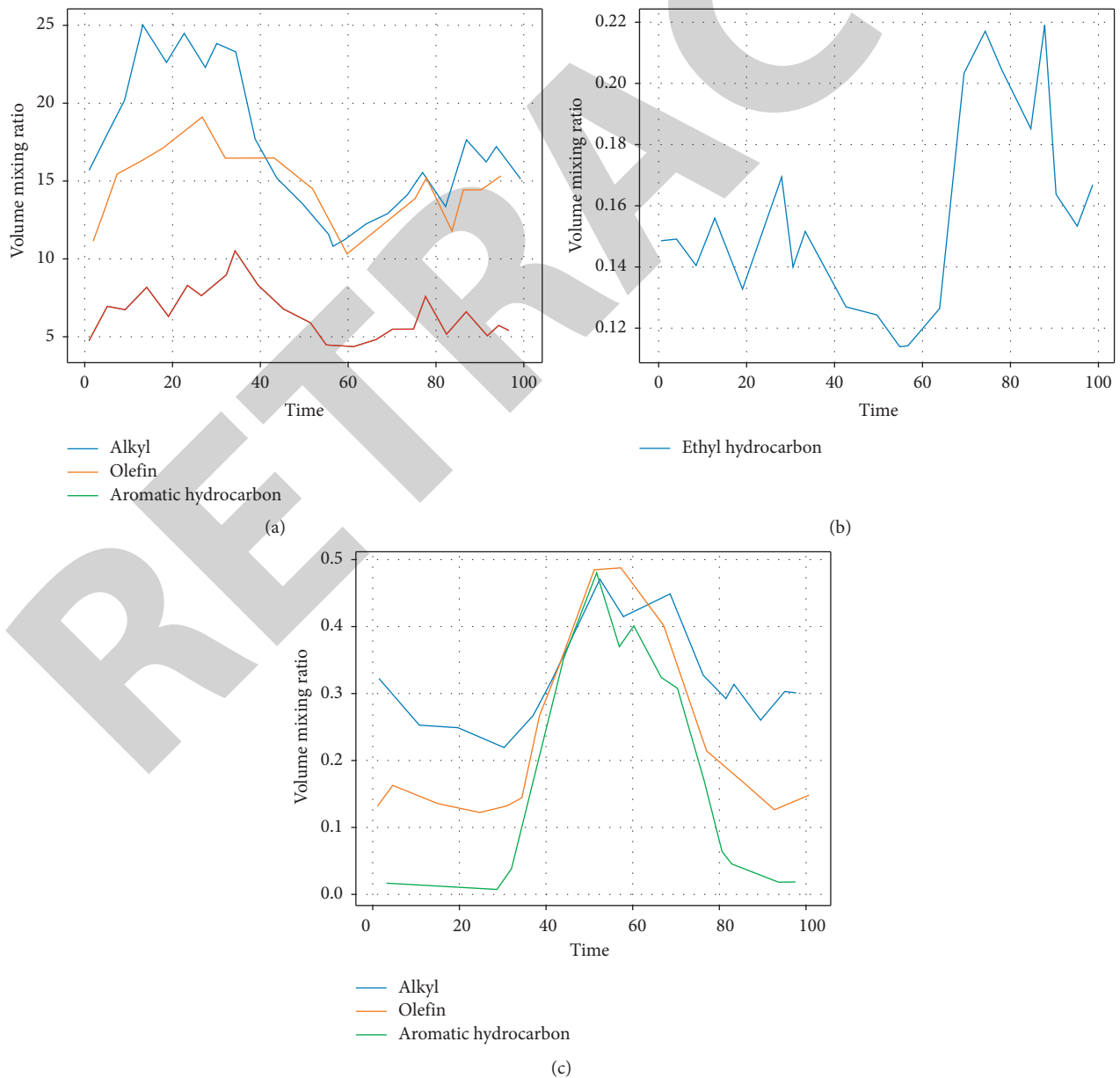


FIGURE 3: Diurnal variation of VOC species in Zhuhai.

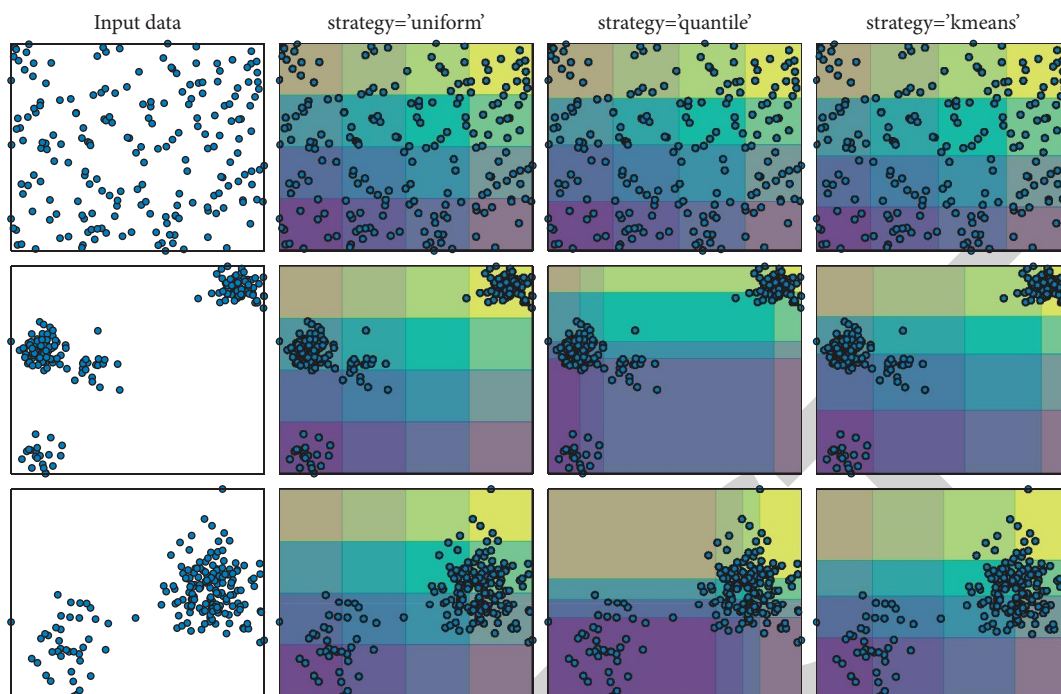


FIGURE 4: Regression analysis between selected species.

southeastern coastal region are mainly derived from secondary production by photochemical reactions, in addition to the effects of primary emissions.

### 3.3. Source Analysis

**3.3.1. Species-Specific Regression Analysis.** Studies have shown that the main sources of VOCs can be determined from the regression analysis of tracer compounds and compounds with different lifetimes [15]. Propane is the most concentrated VOC in the atmosphere in the southeast coastal region, with a mean volume mixing ratio of  $(6.0 \pm 4.4) \times 10^{-5}$ . The regression results between propane and n-butane and isobutane are shown in Figure 4, with  $R^2$  0.57 and 0.78, respectively, and those between ethylene and acetylene (characteristic compounds of combustion and industrial emissions) are shown in Figure 4, with  $R^2$  0.40 and 0.19. Since propane, isobutane and n-butane are all important components of LPG, it is clear that propane in the atmosphere of the Southeast Coastal Region is mainly derived from LPG. volatilization of liquefied petroleum gas (LPG) [16].

Isoprene is mostly emitted from natural sources, with some contribution from motor vehicle exhaust, and 1,3-butadiene is often seen as a marker for motor vehicle emissions. 1,3-butadiene regression results with isoprene are shown in Figure 4,  $R^2 = 0.02$ , indicating that isoprene in the

atmosphere in the southeast coastal region is mainly emitted from natural sources.

**3.3.2. Reverse Trajectory Analysis.** The HYSPLIT4.9 inverse trajectory model was used to analyze the inverse trajectories of the air masses during the sampling period. According to the time resolution of the sampling, one track was calculated every 1 h. The inversion time was 72 h and the altitude was 500 m. The track curves during the sampling period were clustered and analyzed, and five types of inversion tracks were obtained. The inland air masses in the northeastern direction dominated the sampling period, accounting for 33% of the total. The proportion of alkanes, olefins, aromatic hydrocarbons, OVOCs, and other VOCs in each trajectory was calculated and the results are shown in Figure 5. The lowest concentration was olefins, which were around 5%. The total concentrations of VOCs measured were significantly higher when the air masses were from inland (Tracks I and II) than when the air masses were from the sea (Tracks III and V). Moreover, anthropogenic VOCs such as aromatic hydrocarbons are higher in absolute concentration and proportion than marine air masses when the air masses are from inland. This indicates that the contribution of inland air masses to VOCs in the southeast coastal region is higher than that of marine air masses and that the influence of inland areas,



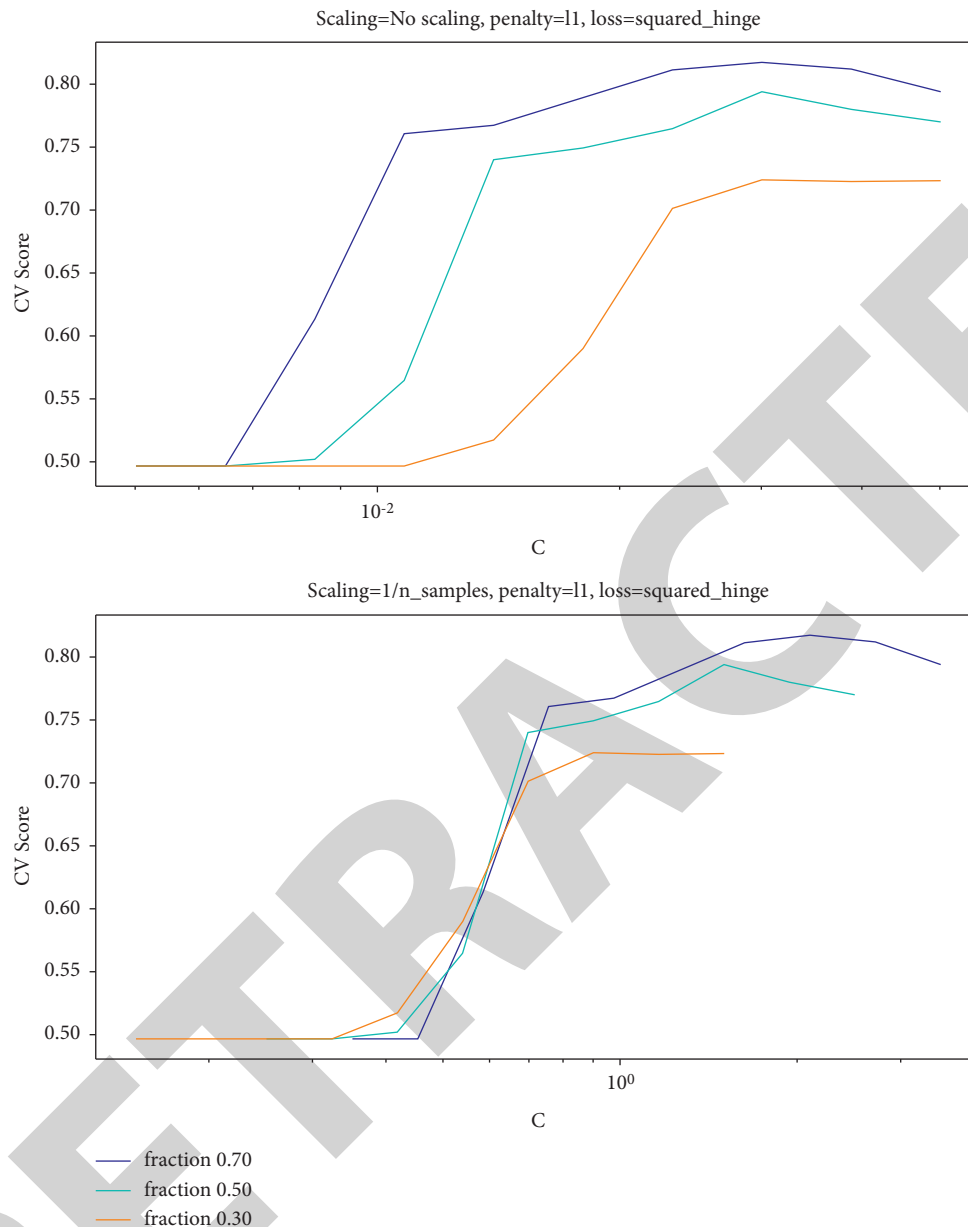


FIGURE 5: Proportion of each VOCs species at different trajectories.

especially the Pearl River Delta region (air mass I), on anthropogenic VOCs in the southeast coastal region is particularly pronounced.

#### 4. Conclusions

In this paper, 96 VOCs were measured in the atmosphere of the southeast coastal region, and their composition, daily trends, sources, and contribution to ozone production were analyzed. The results of the study show that the volume mixing ratio of alkanes is the highest, followed by aromatic hydrocarbons; the daily variation trend of alkanes and aromatic hydrocarbons is obvious, with a bimodal characteristic, and their influence on the ozone potential (OFP) is mainly from aromatic hydrocarbons.

#### Data Availability

The experimental data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest regarding this work.

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