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Traffic-Related Airborne VOC Profiles Variation on Road Sites and Residential Area within a Microscale in Urban Area in Southern Taiwan

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Abstract: The sampling sites, including roadsides and residential areas, were set up to collect ambient air and determine the volatile organic species it contained. For the roadside air, the average VOCs (volatile organic compounds) abundant at rush hour periods was two times that at non-rush hour periods. In the residential area, the VOC concentrationswere106 and 129 ppb during rush hour periods. The VOC concentration ratios of roadside and residential areas were in the range of 1.08–1.75 and the traffic emissions were related to the VOCs abundant in air. The highest VOC concentration was 168 ppb at midnight at residential sites and the VOC abundance could be two times that of roadside sites. This level of concentration could be attributed to the application of solvents and to human activity in a nearby motorcycle/vehicle maintenance plant, laundry rooms, etc. High abundant species were similar in both the roadside and residential air samples. These highly abundant species included toluene, acetone, acetonitrile, m,p-xylene and n-pentane, all of which can be emitted from traffic exhaust. Benzene, acrolein, formaldehyde, vinyl chloride and 1,3-butadiene were the main species with health impacts collected at both sites. In the micro-scale environment, the residential ambient air was affected by traffic flow from morning to night. In the midnight period, some local activities (a motorcycle/vehicle maintenance shop and laundry shops) affected the concentrations of certain VOCs (acetonitrile, toluene, hexane, 2-methylpentane, methyl cyclopentane and 3-methylpentane). The traffic and motor vehicles' effects were determined, which could be useful for air quality management and strategy development in an urban area.

Keywords: volatile organic compounds (VOCs); ozone formation potential (OFP); benzene; toluene; ethylbenzene; xylene; health impact

1. Introduction

In urban areas, air pollution can be an important environmental issue and have a serious health effect on people. In Europe, six main air pollution emission sources have been identified. These include road transport (41%), indoor space heating and air conditioning (15%), shipping (8.8%), energy production and distribution (6.2%), industrial processes (6.2%) (especially in metal industries) and agriculture (5.3%) [1]. Motorized road transport and fuel combustion are of concern because of their contribution to ill health and consequent social costs [2].

Air pollution has a significant economic impact, shortening lives, stimulating higher medical fees and lowering productivity because of the loss of working days across the economy [3]. Globally, roughly seven million premature deaths occur every year, and it is estimated that one eighth of all deaths occur as a result of the combined effects of air pollution [2].

Volatile organic compounds may be the highest priority air pollutants because of their health effects on humans, such as their chronic negative impact on humans' breathing and reproductive systems even at low levels of concentration. A major USEPA study reported that one third of the cancer risk in the United States can be attributed to ambient VOCs [4].

Most of these VOCs are emitted by mobile and area sources [5]. An investigation of the deterioration of air quality in Los Angeles suggested that Los Angeles residents had an increased risk for multiple negative health outcomes due to their exposure to urban air pollution, including traffic emissions [6–8]. In Los Angeles, benzene, n-pentane and n-hexane were correlated with carbon monoxide, which was emitted as a result of incomplete combustion and suggested that these VOCs were produced from motor vehicle emissions [9]. In urban environments, benzene, n-pentane and n-hexane were identified as being emitted from anthropogenic sources such as incomplete fuel combustion and vaporization, especially in motor vehicles [10].These vehicular emissions can undergo reactions to form secondary organic aerosols (SOA) and are regarded as one of the important precursors of SOA in the atmosphere in metropolitan areas [11].

Many airborne hazardous chemicals are released from industrial facilities and mobile sources into the atmosphere and it is thought that they could have a negative impact on human health. These negative effects include chronic effects such as damage to the human immune and nervous systems. Long-term exposure can produce irritation of the eyes, nose and throat, nausea, fatigue, loss of coordination, damage to the liver, kidneys and nervous system and cancer [12].

Airborne VOCs were monitored in the United States and results indicated that benzene, other aromatic hydrocarbons and chlorinated VOCs were present in the air in most urban areas [13]. In urban areas, VOCs are emitted from a complex mixture of emission sources including traffic, industry, solvents, waste burning and others. Generally, traffic is the main source of urban VOCs. Fossil fuel production and application procedures are also major VOC emission sources. Other sources in the United States of America and Europe include pesticides, coatings and inks, cleaning agents and personal care products [14]. According to an investigation by the Hong Kong Air Pollutant Emission Inventory, a total of 25,520 tons of VOCs were emitted in 2017. These emissions came from three principal sources: non-combustion emissions (57%), road transport (19%) and the navigation sector (17%) [15]. These data show that traffic emissions are an important VOC emission source in urban areas, especially in crowded cities and downtown areas. In downtown areas, the exhaust of motor vehicles is the most abundant source of airborne air pollutants. These exhaust-emitted pollutants are easily transformed and transported into the atmosphere, where they affect ambient air quality and impact human health, especially in metropolitan areas.

This study sought to determine the degree of pollution produced by traffic activities in Tainan, in Southern Taiwan. Volatile organic compounds, traffic flow, meteorological factors, ozone formation potential of VOCs and health impact of VOCs were determined in order to evaluate the air pollution characteristics of roadside and residential areas.

2. Experimental Methodology

2.1. Sampling Sites and Period of Data Collection

In total, six sampling sites were selected, including three sampling sites near the main highway and another three sampling sites at alleys in a community block in the southern district of downtown Tainan's metropolitan area (shown in Figure 1). The air samples were collected during four time periods (0700–0900 h, 1300–1500 h, 1700–1900 h and 2300–0100 h) on July 14, 17 and 22, 2014. The rush hour (RH) samples were obtained in the periods of 0700–0900 h, and 1700–1900 h, non-rush hour (NRH) samples were obtained during1300–1500 h, and the 2300–0100 h was regarded as the nighttime period. The shorter sampling days and limited analyzed samples may be a limitation for the application.

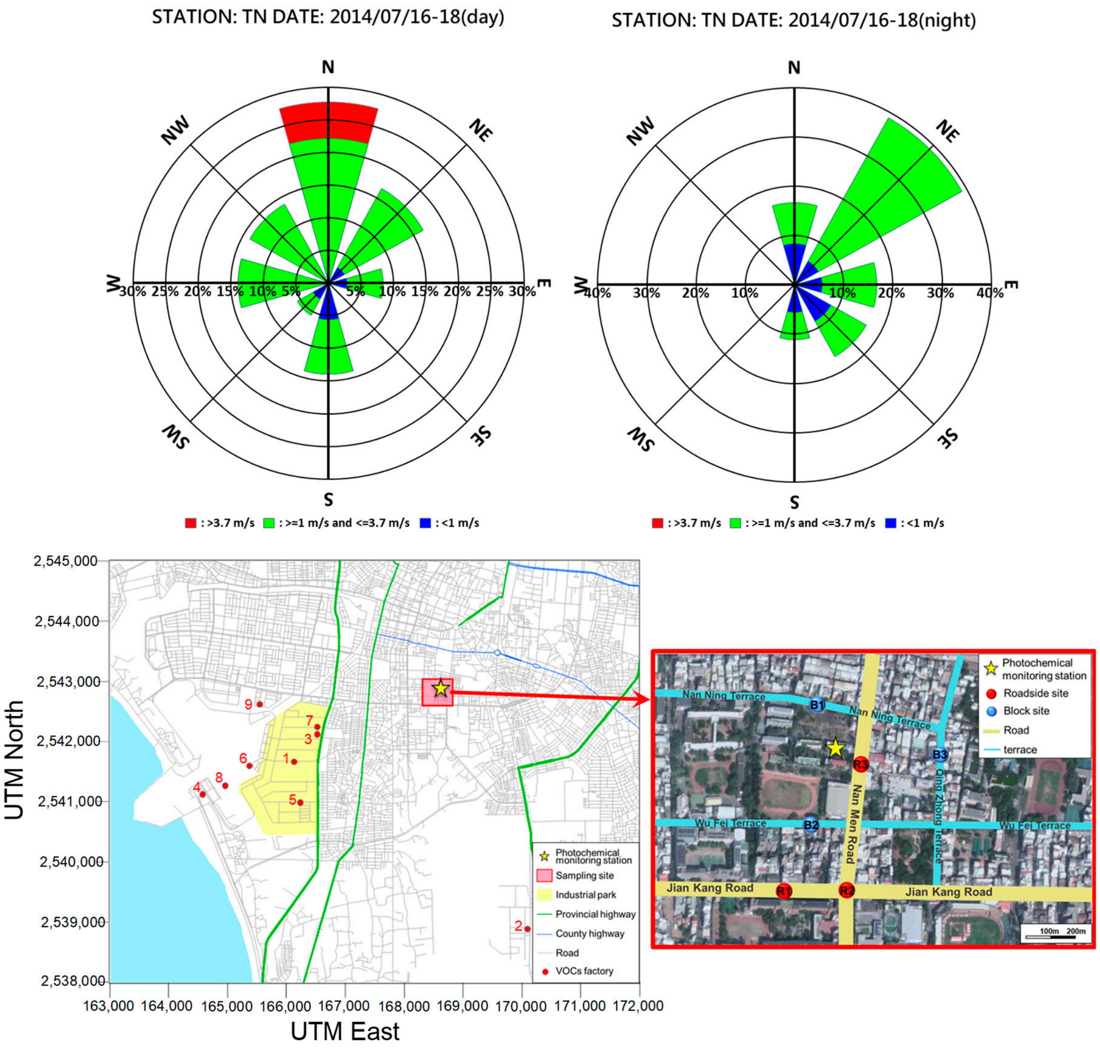

Figure 1. Sampling sites and air pollution emission sources. UTM: Universal Transverse Mercator.

The metropolitan area is spread over 2191.6 km^2 and had a population of around 1.88 million people in 2014. Downtown Tainan occupies an area of 175.6 km^2 and in 2014 had a population of 0.78 million people (population density was 4436 people per square kilometer). The population density of the southern district of downtown was 4604 people km^{-2}.

More than 1.90 million vehicles, including 0.64 million automobiles and 1.29 million motorcycles, are normally active annually in Tainan. According to the Taiwan Emission Data System (TEDs 9.0), the emission in Tainan of PM$_{2.5}$ was 5574 ton yr^{-1}, SOx was 3973 ton yr^{-1}, NOx was 23,333 ton yr^{-1}, NMHC (Non-methane hydrocarbons) was 42,025 ton yr^{-1} and CO was 40,353 ton yr^{-1}. Around29% PM$_{2.5}$, 74% NOx, 27% NMHC and 80% CO were emitted from mobile sources.

The meteorological parameters were determined at Tainan Station by the Central Weather Bureau [16]. High wind speed was determined in the daytime (2.61 ± 1.49 m s^{-1}) and the dominant wind came from the north. The average wind speed at night was determined (1.44 ± 0.96 m s^{-1}) and came from the northeast. The average wind speed at night was around30–50% lower than that during the day (shown as Figure 1). The temperature during the day (31.7 ± 2.4 °C) was around 2.4 °C higher than that at night (29.3 ± 1.0°C). The difference in humidity was significant during the daytime (70.5 ± 8.7%) and nighttime (77.4 ± 2.9%). The average solar radiation intensity was 1.58 ± 0.91 (0.12–2.95 MJ/m^2) MJ m^{-2}.

The traffic volume on the roads included in this study was 2–59 # hr^{-1} for buses and HDVs (heavy-duty vehicles), 497–2220 # hr^{-1} for passenger cars and LDVs (light-duty vehicles) and

842–4272 # hr^{-1} for motorcycles. The traffic volumes in the blocks included in this study were 0-15 # hr^{-1} for buses and HDVs, 68-208 # hr^{-1} for passenger cars and LDVs and 165-1082 # hr^{-1} for motorcycles. The PCU (passenger car unit) of roadside and residential sites were in the range of 752-3561 and 117-532, respectively. Highest traffic volumes were determined to occur at in the morning rush hour period for the roads and the nighttime rush hour period for the residential sites included in this study.

2.2. VOC Analysis

VOC samples were collected from the sampling sites by the canister system following the TO-15(Toxic Organics–15) method [17,18]. VOC species were pre-concentrated in a purge-and-trap system (Entech 7100 instrument) and afterwards analyzed in a gas chromatograph with mass spectrometer (GC/MS, GC: HP-6890 and MS: HP 5973N, Santa Clara, California, CA, USA). The GC was equipped with a fused silica capillary column (non-polar RTx-1, 105 m × 0.25 mm (ID) × 1.0 μm (film thickness)). Certified VOC standard gas (87 VOC species, Linde, New Jersey, NJ, USA) was diluted with ultra-high-purity nitrogen (99.995%) in dilution bottles and served as the VOC species calibration standard. Perfluorotributylamine was used as the standard to evaluate the performance and quality of the GC/MS. The relative standard deviation for all VOCs was <10%, and the accuracy ranged from 90 ± 5% (methanol) to 105 ± 6% (*p*-ethyltoluene).The method detection limit ranged from 0.10 (tetrachloroethylene and benzyl chloride) to 0.76 (methanol) ppb (shown in Table S1). A total of 87 VOCs were analyzed. These included halogenated (36 species), alkane (19 species), alkene (6 species), aromatic (17 species) and oxygenated/nitro (9 species) species.

2.3. Carbonyl Analysis

The derivation technique was applied to determine the aldehyde species. The gas sample was pumped into a cartridge that was pre-coated with dinitrophenylhydrazine (2,4-DNPH) (LpDNPH S10 Cartridge, Supelco Inc., Bellefonte, PA, USA) at a sampling flow rate of 1 L·min^{-1} for 2 h. The cartridges were then capped and stored until analysis. This cartridge had a capacity of 75 μg of formaldehyde, low background (<0.35 μg of aldehydes) and a sampling temperature in the range of 10–100 °C [19]. In order to determine the aldehyde species, the derivation technique was conducted. High-performance liquid chromatography (HPLC) was employed to separate and determine the DNPH derivatives of aldehydes. A Dionex system (Dionex TCC-100 Thermostatted HPLC column compartment and P680 HPLC pump, Waltham, MA, USA) with an ultraviolet detector (Thermo Finnigan UV 6000LP) and a computerized pump and an eluent delivery system were combined as the HPLC system. The separation column was a SupelcosilLC18 column (25 cm × 4.6 mm (ID), 5-μm particles). The gradient program was conducted in this study. The eluent was 60:40 acetonitrile: water, the flow rate was 1.2 mL·min^{-1}, the injection volume was 20 μL, and the detection wavelength was 360 nm. A total of 15 carbonyl compounds were analyzed in this work. The recovery was in the range of 84–110%, reproducibility (in terms of coefficient of variation) was 2.4–9.7% and linearity (in terms of the R-squared value of the regression line) was 0.992–0.998.

A series using two cartridges was conducted over a course of five runs to determine the breakthrough of carbonyls. Results showed that the carbonyl species concentrations were undetectable in the second cartridge for all five sets prior to the experiments. Thus, one cartridge was enough to absorb the carbonyls in the ambient air. The method detection limit was from 0.08 (propionaldehyde and benzaldehyde) to 0.21 (formaldehyde) ppb (shown in Table S1). Three duplicated analyses were done for each extracted carbonyl sample from the cartridge. The method detection limits of the analyzed VOC species are listed in Table S1.

This work investigated 87 VOC species and 15 carbonyl species in the area, which could be advantageous inexplainingindetail the characteristics of VOCs in the traffic-crowded downtownarea. The data could be important whendeveloping air quality control strategies in metropolitan areas, especially forcontrolling motor vehicles emissions.

2.4. Ozone Formation Potential (OFP) of VOC Species

Generally, MIR (maximum incremental reactivity) is popular in identifying the ozone formation potential of various VOC compounds. The equation is as follows [20]: MIR= $\max\{[\partial(O_3)_p/\partial E_i]\}$ for all VOCs/NO_x, (1) where $(O_3)_p$ is maximum ozone concentration, E_i is incremental of VOC concentration. The ambient VOC species, associated with the maximum incremental reactivity factors [21], were introduced to determine the ozone formation potential (OFP, in g-O_3 produced per g-VOCs) of the ambient air.

2.5. Risk Assessment

A health impact assessment was conducted to determine the potential VOC impact following the air monitoring comparison values (AMCVs) that are similar to the effects screening levels (ESLs), inhalation reference values (ReVs) and risk unit factors (URFs) which are used in air permitting and air monitoring.

The Texas Commission on Environmental Quality (TCEQ) presents the air monitoring comparison values (AMCVs) for different VOC species. AMCVs are screening levels used for evaluating measured levels of common air toxics and their potential impacts on human health [22].

After the screening procedures for our analyzed VOCs, the short-term exposure effects were insignificant due to their high abundance levels. Long-term exposure effects should be carefully considered for their impacts on human health. However, some species have final AMCVs, and some species are under review or interim; therefore, in total, 25 species were elected and their AMCVs were collected (shown in Table S2) to determine their health impact and the sum of the 25 species' health impacts.

3. Results and Discussion

3.1. VOCs Characteristics

3.1.1. Roadside Sites

At the roadside sampling sites, the average VOC concentrations were registered between 80 and 187 ppb. A comparison of the four sampling periods shows a high concentration during the rush hour periods (average concentration: 187 ppb in the morning and 152 ppb in the night) and a lowconcentration in the non-rush hour periods (average concentration: 93 ppb in the noon and 80 ppb in the midnight testing periods). At the roadside sampling sites, the following main VOCs were found: toluene (average concentration: 5.6–16.4 ppb), acetone (8.9–14.6 ppb), acetonitrile (10.7–17.2 ppb), m,p-xylene (2.8–10.8 ppb), n-pentane (2.3–8.7 ppb), 2-methylpentane (2.0–7.6 ppb),hexane (2.2–6.7 ppb), methyl cyclopentane (1.2–5.4 ppb), 2,2,4-trimethylpentane (1.0–5.0 ppb)and benzene (1.2–4.8 ppb). During rush hour periods, their average concentrations were higher than 4.0 ppb (shown in Table 1).

Methylene chloride, chloromethane (R-40 or HCC 40), chlorodifluoromethane (HCFC-22, or R-22), dichlorodifluoromethane (R-12) and trichlorofluoromethane (CFC-11, R-11) were the main chlorinated VOCs at the roadside sampling sites. Their concentrations were in the range of 0.82–1.76 ppb. Chlorinated VOCs such as these chlorinated methanes are widely used as chemical industry solvents, where they are used for metal degreasing, dry cleaning and as intermediates in the synthetic industry and for the manufacture of adhesives, pesticides, pharmaceuticals and refrigerants [23–26]. In the past several decades, chlorinated methanes have come to play an important part in industrial development and in the daily lives of individuals; however, they have high levels of toxicity and appear to contribute to cancer in humans [26].

Table 1. VOC species concentrations (ppbv) at roadside sites.

Sampling Periods **Compounds**	**07:00–09:00**	**13:00–15:00**	**17:00–19:00**	**23:00–01:00**
Toluene	16.41 ± 7.88	5.634 ± 1.72	14.73 ± 7.32	9.27 ± 10.83
Acetone	13.67 ± 7.27	14.63 ± 7.45	10.47 ± 5.88	8.91 ± 3.56
Acetonitrile	13.64 ± 8.88	11.04 ± 5.12	10.68 ± 9.50	17.20 ± 11.89
m,p-xylene	10.75 ± 5.23	3.23 ± 1.46	8.75 ± 3.85	2.78 ± 1.27
n-Pentane	8.73 ± 3.88	3.37 ± 1.25	7.72 ± 3.25	2.28 ± 0.97
2-Methylpentane	7.60 ± 3.26	2.72 ± 1.07	6.24 ± 2.67	2.02 ± 0.90
Hexane	6.68 ± 2.43	2.76 ± 0.66	6.18 ± 1.38	2.22 ± 0.37
Methylcyclopentane	5.45 ± 2.63	1.71 ± 0.77	4.17 ± 1.81	1.16 ± 0.58
2,2,4-trimethylpentane	5.03 ± 2.52	1.51 ± 0.73	4.14 ± 1.98	1.03 ± 0.48
Benzene	4.84 ± 2.31	1.65 ± 0.72	4.04 ± 1.77	1.22 ± 0.61
o-xylene	4.76 ± 2.31	1.39 ± 0.63	3.88 ± 1.71	1.16 ± 0.49
3-methylPentane	4.32 ± 1.74	1.78 ± 0.69	3.53 ± 1.27	1.22 ± 0.46
1,2,4-Trimethyl benzene	4.26 ± 2.15	1.19 ± 0.56	3.31 ± 1.52	0.92 ± 0.39
2-methylHexane	3.64 ± 1.73	1.17 ± 0.50	3.00 ± 1.36	0.93 ± 0.44
Heptane	3.51 ± 1.68	1.12 ± 0.48	2.86 ± 1.18	0.88 ± 0.38
trans-2-Pentene	3.40 ± 1.58	1.35 ± 0.58	2.74 ± 1.15	0.86 ± 0.35
Ethyl benzene	3.16 ± 1.54	0.90 ± 0.40	2.46 ± 1.08	0.72 ± 0.30
Propane	3.15 ± 2.31	2.27 ± 1.49	2.93 ± 2.70	2.42 ± 2.20
1,3-Butadiene	3.01 ± 0.78	0.89 ± 0.39	1.71 ± 0.69	0.84 ± 0.69
trans-2-Butene	2.95 ± 1.36	1.42 ± 0.54	2.72 ± 1.06	1.00 ± 0.35
20 species	128.97 (69) *	61.73 (66)	106.25 (70)	59.01 (74)
87 analyzed species	186.56 ± 73.39	92.97 ± 23. 93	152.24 ± 33.17	79.54 ± 24.13

* The values of parentheses indicate percentage of 20 species in 87 VOCs.

The carbonyl concentrations were in the range of 12–65 ppb at the roadside sites. Formaldehyde (2.8–10 ppb), acetaldehyde (3.7–9.4) and acetone (1.6–11 ppb) were the major species. Formaldehyde is used mainly to produce resins, which are used in particleboard products and as an intermediate in the synthesis of other chemicals. In ambient environments, acetaldehyde may be formed from the breakdown of ethanol. In a tunnel study, acetone was determined to be produced in motor vehicle exhaust [27]. In the downtown ambient air of Porto Allegre, Brazil, acetone was strongly related to vehicle exhaust emissions [28].

The group fractions of halogenated, alkanes, alkenes, aromatics and oxygenated species were in the range of 13.4–17.1%, 21.4–30.1%, 4.9–7.3%, 19.4–29.8% and 18.7–37.0%, respectively, over the different sampling periods (shown inFigure 2a). High alkane, aromatic and oxygenated species fractions were detected at the roadside sites. High alkanes (around30%) and aromatics (around30%) were abundant duringthe rush hour periods. Duringthe non-rush hour periods, the abundance of aromatics decreased and the fraction of oxygenated species became more abundant. The average concentration of oxygenated species was in the range of 29–37 ppb. The variation in their abundance was insignificant for different sampling periods.

The tunnel study indicated that the fractions in the VOCs were as follows: alkanes (44–62%), alkenes (10–14%), aromatics (5.1–6.6%), halocarbons (6.4–16%) and others (6.6–22%) [29]. Generally, ethane, ethylene, propane, propylene, isopentane, 2,3-dimethylbutane and toluene were the most dominant VOC species in vehicle exhaust emissions [29]. Aromatic VOCs have been shown to be significantly related to vehicular traffic and photochemical oxidation [30].

3.1.2. Residential Sites

In the residential sampling sites, the average VOCs concentrations were between 86–168 ppb. The sequence of average VOCs concentration was midnight (23:00–01:00:168 ppb), rush hour periods at night, (17:00–19:00: 129 ppb), rush hour periods in the morning, (07:00–09:00:106 ppb), non-rush hour periods at noon (13:00–15:00: 86 ppb).

Toluene (average concentration: 7.2–20.4 ppb), acetonitrile (12.3–20.1 ppb) and acetone (3.5–30.4 ppb) were highly concentrated at the residential sites. Most acetone and acetonitrile concentrations were higher at the residential sampling sites than that at the roadside sites (shown in Table 2). Toluene is an anthropogenic aromatic hydrocarbon produced mostly from the catalytic conversion reactions of petroleum and aromatic reactions of aliphatic hydrocarbons. It is used as a solvent for the coating, printing and leather industry and for the manufacture of paints and coatings, inks, adhesives, resins and pharmaceuticals. It is applied to the blending (benzene-toluene-xylene mixture) of gasoline for the improvement of octane ratings, too.

Table 2. VOC concentrations (ppbv) at residential sites.

Sampling Periods **Compounds**	**07:00–09:00**	**13:00–15:00**	**17:00–19:00**	**23:00–01:00**
Acetone	30.38 ± 12.94	13.62 ± 10.26	25.52 ± 25.78	3.50 ± 3.70
Acetonitrile	13.75 ± 8.36	12.35 ± 12.62	12.28 ± 4.81	20.14 ± 20.05
Toluene	7.18 ± 2.14	12.17 ± 20.00	10.93 ± 5.92	20.42 ± 26.69
n-Pentane	3.95 ± 1.99	3.18 ± 2.70	5.19 ± 2.62	3.51 ± 1.87
Hexane	3.54 ± 0.68	3.67 ± 4.06	3.88 ± 1.84	24.28 ± 32.48
m,p-xylene	3.19 ± 1.54	3.26 ± 3.93	6.35 ± 2.72	2.14 ± 1.53
2-Methylpentane	2.73 ± 1.26	1.73 ± 0.95	3.68 ± 1.77	12.00 ± 15.03
Propane	2.29 ± 0.92	1.58 ± 0.61	4.06 ± 2.56	4.80 ± 1.99
2-Butanone	2.04 ± 0.80	1.71 ± 2.36	2.01 ± 0.85	2.16 ± 1.57
Methylcyclopentane	1.95 ± 1.00	1.13 ± 0.65	2.40 ± 1.26	19.96 ± 27.33
Methylene chloride	1.70 ± 0.89	2.64 ± 3.15	2.68 ± 1.12	1.67 ± 0.81
3-methylPentane	1.69 ± 0.74	1.23 ± 0.63	2.14 ± 0.99	17.09 ± 24.03
trans-2-Butene	1.58 ± 1.19	1.16 ± 0.75	2.32 ± 1.18	0.68 ± 0.23
Benzene	1.51 ± 0.65	0.94 ± 0.54	2.30 ± 1.06	0.85 ± 0.41
o-xylene	1.45 ± 0.68	1.40 ± 1.60	2.68 ± 1.12	1.09 ± 0.78
2,2,4-trimethylpentane	1.38 ± 0.79	0.73 ± 0.47	2.21 ± 1.13	0.70 ± 0.28
Vinyl acetate	1.35 ± 1.03	0.93 ± 0.76	1.73 ± 0.81	0.49 ± 0.48
trans-2-Pentene	1.30 ± 0.87	0.97 ± 0.67	1.84 ± 0.92	1.32 ± 43
1,2,4-Trimethyl benzene	1.11 ± 0.64	0.62 ± 0.46	1.85 ± 0.93	0.68 ± 0.23
Chloromethane	1.07 ± 0.14	0.92 ± 0.20	1.16 ± 0.34	1.16 ± 0.25
20 species	85.15 (80) *	65.98 (76)	96.53 (75)	140.40 (83)
87 analyzed species	106.43 ± 43.84	86.44 ± 51.99	129.48 ± 59.15	168.29 ± 154.05

* The values inparentheses indicate percentage of 20 species in 87 VOCs.

In the residential sites, methylene chloride, chloromethane, chlorodifluoromethane, dichlorodifluoromethane and trichlorofluoromethane were also dominant halogenated species and their concentrations were in the range of 0.51–2.6 ppb.

The toluene, benzene and acetonitrile (methyl cyanide) concentrations could be due to traffic pollution from automobiles [31] as well as from biomass burning and fossil fuel burning [32,33]. According to a USEPA report, the sources of airborne acetonitrile include manufacturing and industrial facilities, automobile exhaust and volatilization from aquatic environments [34]. Acrylonitrile does not occur in nature and it also cannot be produced by chemical reactions in the atmosphere [35].

Oil refinery facilities, the architectural decoration industry, the storage and transport industries and the basic organic chemical industry are important sources of 1-butene in ambient air and their photochemical reactions contribute to the formation of ozone in the atmosphere [36].

In this study, the group fraction of chlorinated, alkanes, alkenes, aromatics and oxygenated species were in the range of 8.5–15.6%, 20.3–53.3%, 4.2–6.0%, 16.7–25.1% and 17.3–46.2%, respectively, for different sampling periods (shown in Figure 2b).

High alkane, aromatic and oxygenated species fractions were identified at the residential sites. High oxygenated species fractions were abundant in most sampling periods, except for the midnight period. The carbonyl concentrations were in the range of 13–17 ppb at the residential sites, where formaldehyde

(3.2–5.6 ppb), acetaldehyde (3.4–4.8) and acetone (1.6–3.0 ppb) were the major species. The variation incarbonyl species concentrations was higher at the roadside test sites than at the residential test sites. The average concentration ratios of VOC species at the roadside and residential sites were 2.85, 1.53, 1.49 and 0.82 for the sampling periods 07:00–09:00 h, 13:00–15:00 h, 17:00–19:00 h and 23:00–01:00 h, respectively. Results indicated that the VOC concentrations were higher at the roadside sites than at the residential sites during most sampling periods, except during the midnight period.

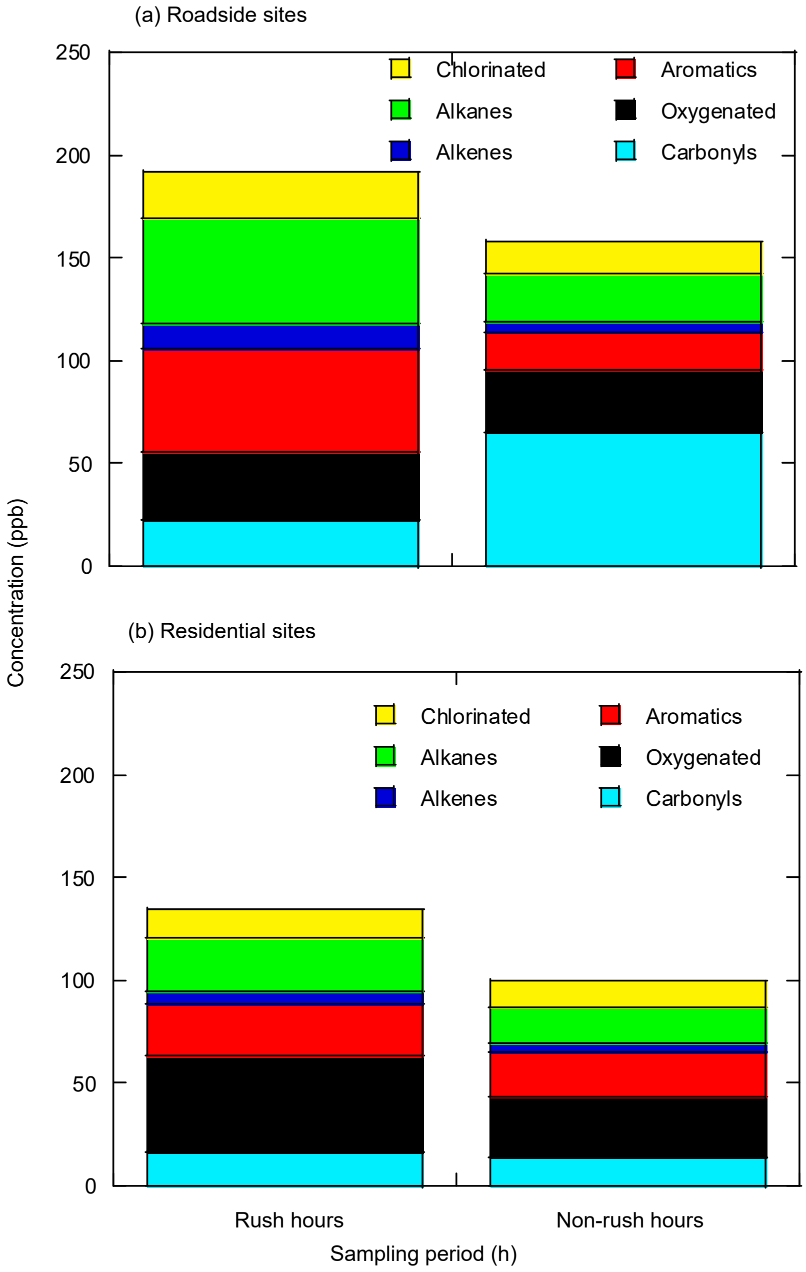

Figure 2. VOC groups distribution at roadside and residential sites for different sampling periods. (**a**) Roadsite sites, (**b**) Residential sites.

3.2. Ozone Formation Potential

Ozoneprecursors are related to the NOx and VOCs, whose effects on ozone formation are different according to the location and often very uncertain depending on the emission and meteorology [37]. In this study, VOCs' effects on ozone formation are evaluated road sites and residential areas in an urban area.

Maximum incremental reactivity factors [21] were calculated to determine the ozone formation potential (OFP) of VOCs for ambient air at both the roadside and block test sites. The OFP values in the ambient air of a total of 87 VOCs were 682–2233 $O_3 \cdot m^{-3}$ on average for the different sampling period. The OFP was significantly higher during the rush hour periods (2233 and 1782 $O_3 \cdot m^{-3}$ for the morning and night, respectively) and a low OFP was determined during the non-rush hour periods.

The OFP fraction profile was similar for different sampling times, with 3.6–5.1% for halogenated, 11–13% alkanes, 17–21% for alkenes, 52–60% for aromatics and 5.2–9.7% for oxygenated/nitro species (shown in Figure 3).

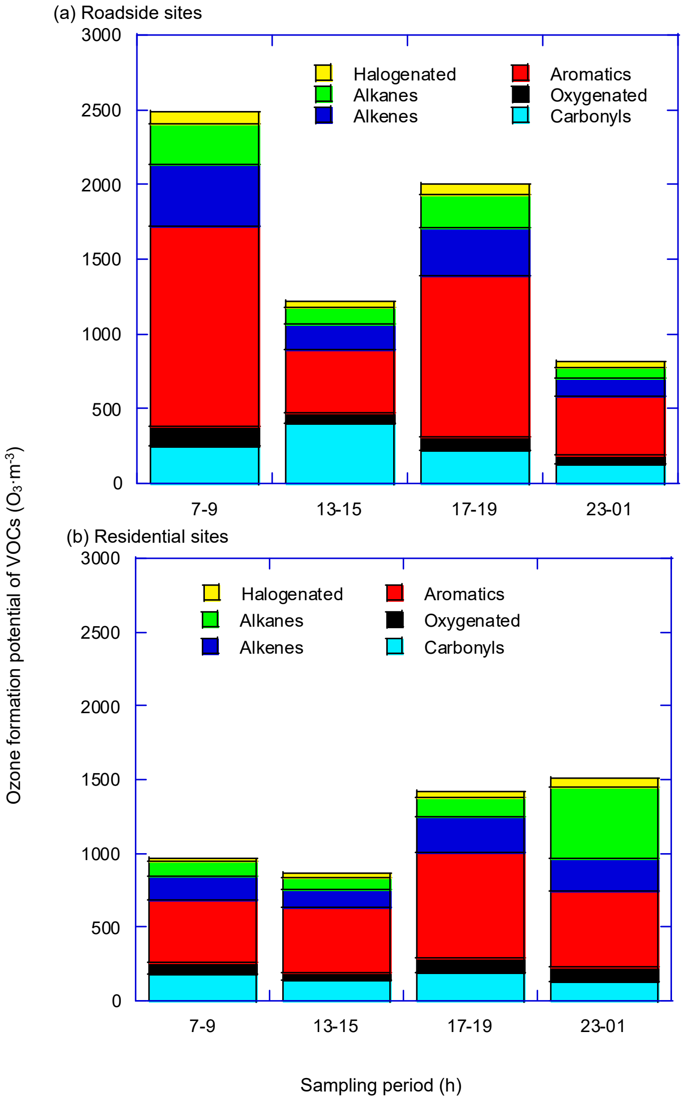

Figure 3. Ozone formation potential of VOC groups at roadside and residential sites for different sampling periods. (**a**) Roadsite sites, (**b**) Residential sites.

For aromatic species, the high-OFP species were xylene (94–363 $O_3 \cdot m^{-3}$ for m,p-xylene and 38–158 $O_3 \cdot m^{-3}$ for o-xylene), toluene (85–247 $O_3 \cdot m^{-3}$), 1,2,4-trimethylbenzene (40–185 $O_3 \cdot m^{-3}$) and ethyl toluene (19–102 $O_3 \cdot m^{-3}$, with around70% attributed to m-ethyl toluene) and 1,3,5-trimethylbenzene (15–74 $O_3 \cdot m^{-3}$).

The OFP of most alkanes was less than 40 $O_3 \cdot m^{-3}$. Methyl cyclopentane, 2-Methylpentane, n-pentane and 2,2,4-trimethylpentane were the major OFP alkane species. Trans-2-pentene (26–103 $O_3 \cdot m^{-3}$), trans-2-butene (35–102 $O_3 \cdot m^{-3}$), 1,3-Butadiene (23–84 $O_3 \cdot m^{-3}$) and cis-2-butene (21–65$O_3 \cdot m^{-3}$) were high-OFP alkene species.

Formaldehyde and acetaldehyde were in the range of 33–116 and 44–111 $O_3{\cdot}m^{-3}$, respectively, for the different sampling periods. The sequence of OFP of VOCs was rush hour at night (1013 $O_3{\cdot}m^{-3}$) ≈ midnight (1006 $O_3{\cdot}m^{-3}$) > rush hour in the morning (622 $O_3{\cdot}m^{-3}$) > non -rush hour at noon (591 $O_3{\cdot}m^{-3}$). The OFP of VOCs was lower at the block sites in comparison with the road sites, except in the midnight air sample. Based on the literature, high humidity and high temperature could lead to photochemical reactions under high-intensity solar radiation and the air pollutants can be accumulated under low air movement conditions [38–41]. Some weather conditions were similar to this study and related to photochemical reactions and affected the VOC concentration variation inSouthern Taiwan.

3.3. Ratio Analysis

At roadside, most VOCs at rush hour periods were 2–3 times higher than those at non-rush hour periods, expect acetone and acetonitrile (Figure 4). Based on the species correlation coefficient, a high relation was presented between different VOC species, besides acetone and acetonitrile. Results suggested that most VOCs can be emitted from vehicle exhaust. Acetone and acetonitrile could come from other sources (commercial sources such as repair stores, laundry etc., could be one of the reasons). Detailed investigations are necessary to identify the emission sources in the future.

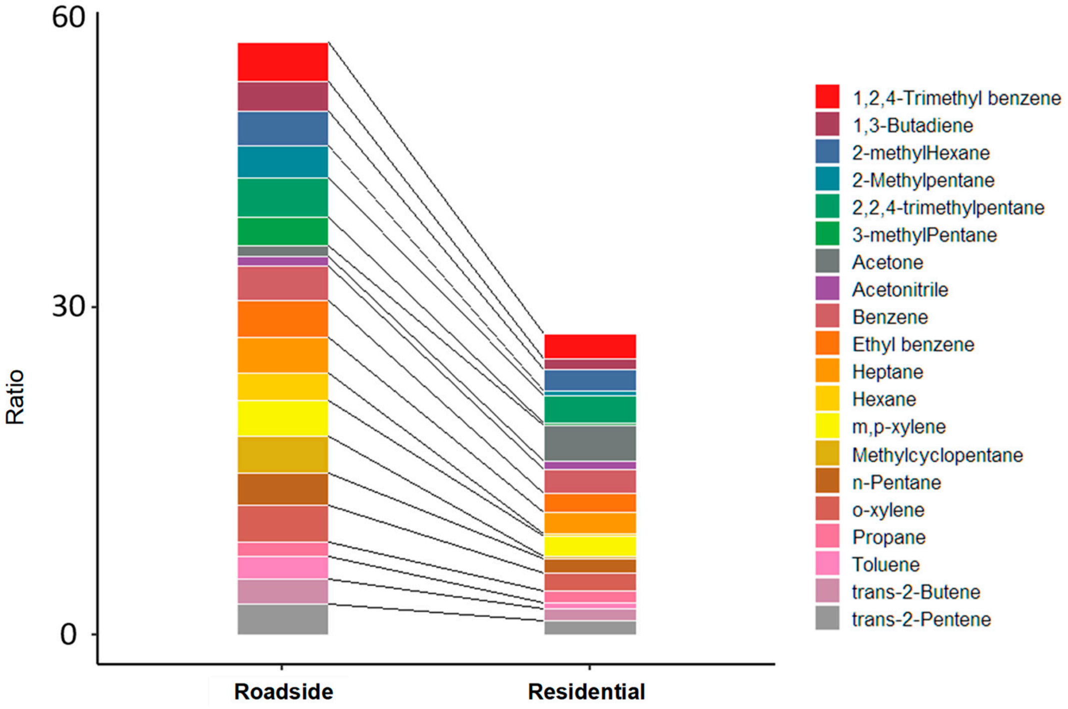

Figure 4. VOC species concentration ratios of rush hour periods and non-rush hour periods at roadside and residential sites.

At residential sites, the RH/NRH (Rush hours/non-rush hours) ratios of toluene, 2-methylpentane, hexane, methyl cyclopentane and 3-methylpentane were lower than one. Results indicated that highabundances as a result of human activities were detected duringnon-rush hour periods, especially in the midnight periods. In residential communities, there were minor industrial activities and commercial activities (laundry, motor vehicle repair shops, paint and restaurants) in the area that could be sources of VOCs.

At roadside sites, the nighttime and daytime ratios of VOCs were in the range of 0.65–1.13 (0.85 ± 0.12). In the residential site, high variations were determined 0.66–7.25 (2.21 ± 1.79) (Figure 5) and some 2-methylpentane, hexane, methyl cyclopentane and 3-methylpentane were found in the range of 3.52–7.25, which could reflect the lifestyle patterns (high human activities in the nighttime) of residents in residential areas. Urban planning is complex in the residential areas in Taiwan and human activities could lead tohigh exposure frequency and cause high risk in residential areas, especial at nighttime.

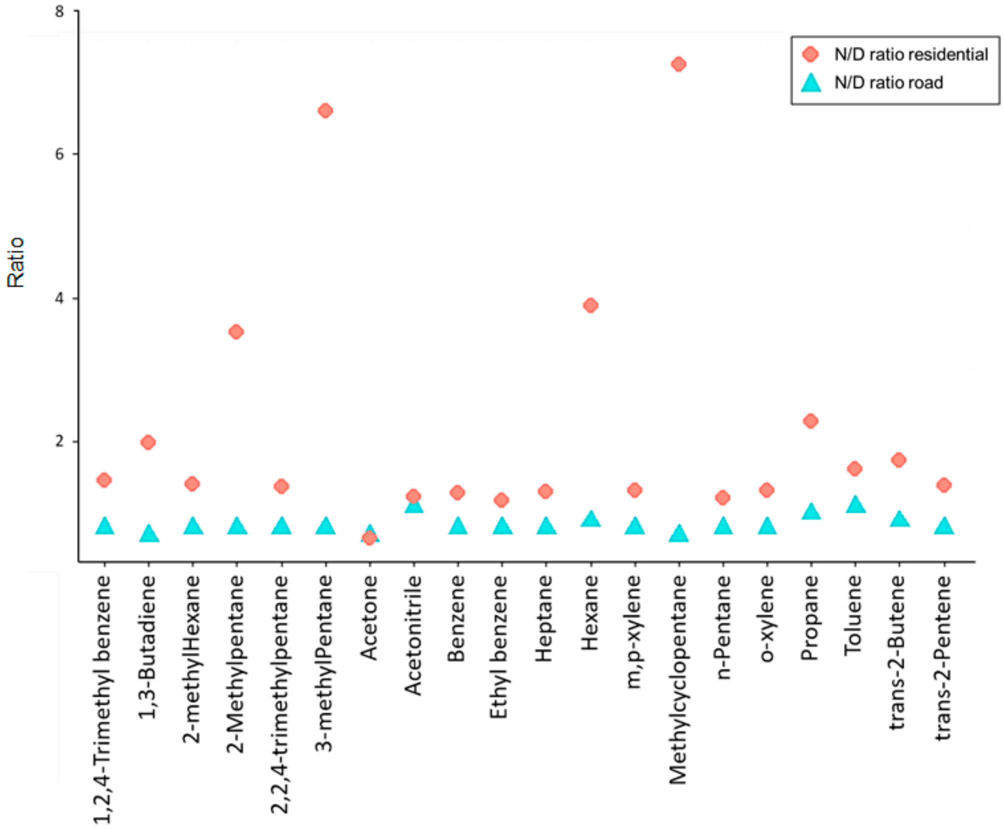

Figure 5. VOC species concentration ratios of nighttime and daytime at roadside and residential sites.

VOC concentrations were related to traffic volumes (PCU) at roadside sites. At residential sites, the relationship between VOC concentration and traffic volume was insignificant.

Fossil fuels such as crude oil, diesel and gasoline, benzene, toluene, ethylbenzene and (o-, m-and p-)xylenes are often detectable in ambient air when they undergo combustion. In addition, BTEX (benzene, toluene, ethylbenzene and xylene) are often used in industry as raw materials and additives to other substances. These chemicals can be used in the manufacture of synthetic materials and consumer products, and many chemical products which are used in daily life are related to VOC emissions.

Usually, toluene and benzene (T/B) are abundant in the ambient VOCs produced by traffic emissions, especially in urban areas [30,42]. Benzene is one of the constituents of motor vehicle fuel and toluene is produced in abundance as a result of the evaporation of solvents in paints [43]. A T/B ratio between 1.5 and 4.3 in ambient air indicates that that ambient air has been significantly influenced by traffic. T/B ratios larger than 4.5 indicate the presence of non-traffic sources such as solvent vaporization and application and industrial sources. [44]. In this study, average concentration levels were as follows: benzene, 1.5 μg m^{-3}; toluene, 4.7 μg m^{-3}; ethylbenzene, 2.0 μgm^{-3}; (m + p)-xylene, 5.0 μg m^{-3}; o-xylene, 2.3 μg m^{-3}. The toluene and benzene ratio was around 3, which suggests that they were the result of air pollution from traffic emissions [44]. Another study indicated that toluene and benzene ratios in the range of 0.65–13.9 were detected in vehicular traffic. The same study indicated that vehicular traffic might be the main contributing source in urban sites of xylene/benzene ratios ranging from 0.7 to 2.8. This study also confirmed that VOCs are transported to rural sites from nearby urban areas [30].

The average ratios of toluene and benzene detected in this study were 3.6 ± 0.62 and 4.9 ± 2.9 for rush-hour and non-rush-hour roadside traffic (shown in Table 3). The T/B ratios were in similarrangesto those of different cities (T/B ratios:1.3–9.5) around the world, as was the case for tunnel study (2.60) and motorcycle exhaust (4.87). The average ratios of toluene and benzene were 4.8 ± 0.92 and 12.4 ± 13.7 for rush-hour and non-rush-hour residential site measurements. Results indicated that these VOC emissions were not solely related to vehicle emissions; solvent applications could be an important source of VOCs in residential areas. In addition, the T/B ratios were slightly higher at block sites than roadside sites, which indicated that there are not only traffic emission effects on residential sites, but some area sources' emissions could be another important pollution source for the industries, businesses and residents within the complex metropolitan area.

Table 3. Benzene, ethylbenzene, toluene and xylene (BTEX) concentration ratios. RH: Rush hours. NRH: Non-Rush hours.

City/Country		T/B	B/T	X/B	X/E	References
Tainan (Taiwan)	RH-Roadside	3.6 ± 0.62	0.3 ± 0.04	3.1 ± 0.29	5.1 ± 0.4	This study
	NRH-Roadside	4.9 ± 2.91	0.3 ± 0.08	3.0 ± 0.35	5.3 ± 0.45	
	RH-Residential	4.8 ± 0.92	0.2 ± 0.03	3.6 ± 0.74	5.1 ± 0.46	
	NRH-Residential	12.4 ± 13.7	0.2 ± 0.12	4.0 ± 2.54	4.8 ± 0.79	
Taipei (Taiwan)		5.8	0.4	1.5	2.9	[45]
Kaohsiung (Taiwan)	Rush hour	9.5	0.1	1.1	0.6	
	Non-rush hour	8.7	0.1	0.9	0.7	
Taichung (Taiwan)		4.5–45.9	-	2.1–6.2	3.52–5.64	[46]
China, Japan, South Korea, Italy		1.3–6.4	0.2–0.8	0.5–2.9	1.1–10	[47,48]

In ambient air, m,p-Xylene is highly reactive and has a shorter lifetime than benzene and ethylbenzene. Therefore, the VOCs contained in air particles that travel a long distance from their sources could present low X/E and X/B ratios. Fresh air masses near emission sources contain high X/E and X/B ratios. The changing lifetime of X/E and X/B ratios has been applied as an indicator of the photochemical age of ambient air [49].

Obviously, mobile sources could be the main sources of VOCs at the traffic sites, where the fresh air mass was measured at B/T <0.4 and X/B >1.1 [47]. In this study, the average B/T ratios were 0.3 at the roadside test sites and 0.2 at the block test sites. In addition, the average X/B ratios were in the range of 4.8–5.3 for the ambient air of both sites. Results indicated that fresh mobile emission exhaust was the major source of VOCs.

3.4. Health Impacts

3.4.1. Roadside Sites

After exposure, the average health impact index was 5.05 and the sequence was rush hour in the morning (8.07),rush hour at night (6.14), non-rush hour at noon (3.88),non-rush hour at midnight (2.12) (shown as Figure 6a). The health impact at the roadside sampling sites could come from benzene (30–47%), acrolein (14–20%), vinyl chloride (16–21%), formaldehyde (14–26%), and 1,3-butadiene (2.5–4.3%). High fraction human health impacts were benzene, vinyl chloride, formaldehyde, acrolein, and 1,3-butadiene. If the HI ratio is higher than one indicated the long-term effects of this specie in ambient should be carefully concerned. Following the criteria, the benzene, acrolein, vinyl chloride, and formaldehyde were over the criteria at rush hour in the morning and benzene and formaldehyde at non-rush hour at noon, and benzene and vinyl chloride rush hour at night

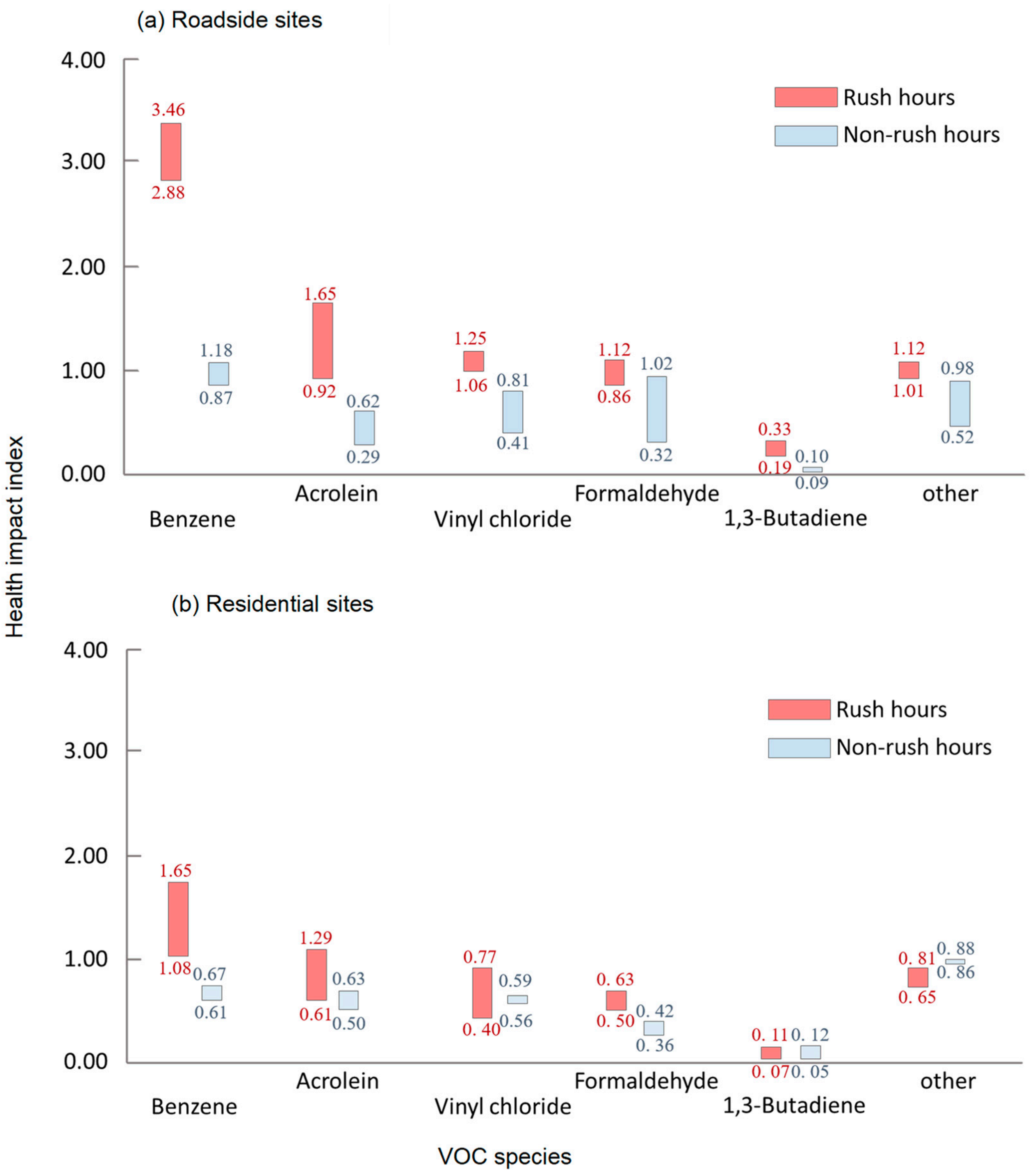

Figure 6. Health impacts of VOC species at roadside and residential sites for different sampling periods. (**a**) Roadsite sites, (**b**) Residential sites.

3.4.2. Residential Sites

The average health impact was 3.04 and the sequence was rush hour at night (4.48),rush hour in the morning (2.88), non-rush hour at midnight (2.45), non-rush hour at noon (2.35) (shown inFigure 6b). At the residential sites, the health impact mainly came from benzene (25–37%), acrolein (21–29%), vinyl chloride (14–24%), formaldehyde (11–22%) and 1,3-butadiene (2.0–4.9%). The concentrations of benzene during both rush hour periods and acrolein duringrush hour periods at night could be higher than AMCVs. Their abundance could have a long-term health effect on humans.

Butadiene is primarily used in the manufacture of synthetic elastomers (rubbers, latexes) and for producing raw materials for nylon. The primary sources of butadiene emissions on a national level are on-road and off-road mobile exhaust emissions due to the incomplete combustion of engines [50]. Industry is the main source of 1,3 butadiene, styrene-butadiene copolymer production, as well as polybutadiene and chloroprene/neoprene production [51].

At the roadside, VOC concentration could be related to traffic volumes. However, this relationship was insignificant in the residential sites (shown in Table 4). Results suggest thatVOCs could not only be emitted from motor vehicles; the commercial sources located in the residential sites could be another important source for the small industries, businesses and residential communities in complex urban areas. In this study, the AMCVs (health index) were related to the emission of traffic volumes, especially in motorcycles (shown in Table 4). Motor vehicle emissions could be the source with the mostimportant impact on human heath in urban areas.

Table 4. Correlation of traffic volumes, volatile organic compounds and ambient monitoring comparison value.

<table>
<tr><th colspan="7">(a) Roadside</th></tr>
<tr><th>Items</th><th>PCU</th><th>TVOC</th><th>AMCVs</th><th>BC</th><th>PC</th><th>MT</th></tr>
<tr><td>PCU</td><td>1</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>TVOC</td><td>0.71</td><td>1</td><td></td><td></td><td></td><td></td></tr>
<tr><td>AMCVs</td><td>0.82</td><td>0.99 *</td><td>1</td><td></td><td></td><td></td></tr>
<tr><td>BC</td><td>0.94</td><td>0.52</td><td>0.65</td><td>1</td><td></td><td></td></tr>
<tr><td>PC</td><td>0.98 *</td><td>0.57</td><td>0.7</td><td>0.97 *</td><td>1</td><td></td></tr>
<tr><td>MT</td><td>0.94</td><td>0.9</td><td>0.96 *</td><td>0.79</td><td>0.86</td><td>1</td></tr>
<tr><th colspan="7">(b) Residential</th></tr>
<tr><td>PCU</td><td>1</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>TVOC</td><td>−0.48</td><td>1</td><td></td><td></td><td></td><td></td></tr>
<tr><td>AMCVs</td><td>0.82</td><td>0.1</td><td>1</td><td></td><td></td><td></td></tr>
<tr><td>BC</td><td>−0.08</td><td>−0.69</td><td>−0.47</td><td>1</td><td></td><td></td></tr>
<tr><td>PC</td><td>0.94</td><td>−0.49</td><td>0.78</td><td>0.15</td><td>1</td><td></td></tr>
<tr><td>MT</td><td>0.97 *</td><td>−0.39</td><td>0.82</td><td>−0.27</td><td>0.84</td><td>1</td></tr>
</table>

Note: PCU: passenger car unit, TVOC: total volatile organic compound, AMCVs: ambient monitoring comparison values, BC: bus and heavy-duty vehicle, PC: passenger car, MT: motorcycle. * $p < 0.05$.

4. Conclusions

Traffic flow had a significant influence on the abundance of VOCs in roadside ambient air. VOC concentrations at rush-hour could be two times the concentration at non-rush hour times at the roadside test sites. At the residential sites, the VOC concentrations were still high at rush hour. High VOC concentrations at the residential measurement sites in the midnight period might be the result of human activities. Motorcycle/vehicle maintenance plants, laundry shops and places where solvents were being applied were located in the residential area where measurements were taken.

Toluene, acetone, acetonitrile, m,p-xylene, n-pentane and 2-methylpentane were the most abundant species at both sampling sites. Xylene, toluene, 1,2,4-trimethylbenzene, ethyl toluene, trans-2-pentene and trans-2-butene were the major species of OFP at both sites. The average health impact was 5.05 at the roadside sites and 3.04 at the residential sites. The health impact at the roadside sites was 1.7 times the risk at the residential sites. Benzene, acrolein, vinyl chloride, formaldehyde and 1,3-butadiene were the major sources of health impact. The study determined the traffic and motor vehicles' effects on the air quality near the roadside and residential community. The results could be useful for air quality management and urban planning and development, especially in emerging countries.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/11/9/1015/s1, Table S1: Method detection limit of analyzed VOC species (ppbv), Table S2: Ambient monitoring comparison values (AMCVs) for long-term exposure.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

References

1. World Health Organization. *Health Risks of Air Pollution in Europe—HRAPIE Project*; WHO: Copenhagen, Denmark, 2013.
2. World Health Organization. *Economic Cost of the Health Impact of Air Pollution in Europe: Clean Air, Health and Wealth*; WHO Regional Office for Europe: Copenhagen, Denmark, 2015.
3. European Environment Agency. *Air Quality in Europe—2018 Report*; EEA: Copenhagen, Denmark, 2018.
4. US EPA. *Cancer Risk from Outdoor Exposure to Air Toxics*; EPA-450/1-90-004a; EPA: Research Triangle Park, NC, USA, 1990.
5. Payne-Sturges, D.C.; A Burke, T.; Breysse, P.; Diener-West, M.; Buckley, T.J. Personal exposure meets risk assessment: A comparison of measured and modeled exposures and risks in an urban community. *Environ. Health Perspect.* **2004**, *112*, 589–598. [CrossRef] [PubMed]
6. Jerrett, M.; Burnett, R.T.; Ma, R.; Pope, C.A.; Krewski, D.; Newbold, K.B.; Thurston, G.; Shi, Y.; Finkelstein, N.; Calle, E.E.; et al. Spatial Analysis of Air Pollution and Mortality in Los Angeles. *Epidemiology* **2005**, *16*, 727–736. [CrossRef] [PubMed]
7. Ghosh, J.K.C.; Heck, J.E.; Cockburn, M.; Su, J.; Jerrett, M.; Ritz, B. Prenatal exposure to traffic-related air pollution and risk of early childhood cancers. *Am. J. Epidemiol.* **2013**, *178*, 1233–1239. [CrossRef]
8. Wilhelm, M.; Ghosh, J.K.; Su, J.; Cockburn, M.; Jerrett, M.; Ritz, B. Traffic-Related Air Toxics and Term Low Birth Weight in Los Angeles County, California. *Environ. Heal. Perspect.* **2011**, *120*, 132–138. [CrossRef] [PubMed]
9. Baker, A.K.; Beyersdorf, A.; Doezema, L.A.; Katzenstein, A.; Meinardi, S.; Simpson, I.J.; Blake, D.R.; Rowland, F.S. Measurements of nonmethane hydrocarbons in 28 United States cities. *Atmos. Environ.* **2008**, *42*, 170–182. [CrossRef]
10. Garcia-Gonzales, D.A.; Shamasunder, B.; Jerrett, M. Distance decay gradients in hazardous air pollution concentrations around oil and natural gas facilities in the city of Los Angeles: A pilot study. *Environ. Res.* **2019**, *173*, 232–236. [CrossRef]
11. Shah, R.U.; Coggon, M.M.; Gkatzelis, G.I.; McDonald, B.C.; Tasoglou, A.; Huber, H.; Gilman, J.B.; Warneke, C.; Robinson, A.; Presto, A.A. Urban Oxidation Flow Reactor Measurements Reveal Significant Secondary Organic Aerosol Contributions from Volatile Emissions of Emerging Importance. *Environ. Sci. Technol.* **2019**, *54*, 714–725. [CrossRef]
12. USEPA. Available online: https://www.epa.gov/indoor-air-quality-iaq/volatile-organic-compounds-impact-indoor-air-quality#Health_Effects (accessed on 20 March 2020).
13. Mohamed, M.F.; Kang, D.; Aneja, V.P. Volatile organic compounds in some urban locations in United States. *Chemosphere* **2002**, *47*, 863–882. [CrossRef]
14. McDonald, B.C.; De Gouw, J.; Gilman, J.B.; Jathar, S.H.; Akherati, A.; Cappa, C.D.; Jimenez, J.L.; Lee-Taylor, J.; Hayes, P.L.; McKeen, S.A.; et al. Volatile chemical products emerging as largest petrochemical source of urban organic emissions. *Science* **2018**, *359*, 760–764. [CrossRef]
15. The Government of the Hong Kong. Environmental Protection Department. Hong Kong Air Pollutant Emission Inventory—Volatile Organic Compounds. Available online: https://www.epd.gov.hk/epd/english/environmentinhk/air/data/emission_inve.html (accessed on 20 March 2020).
16. Taiwan Central Weather Bureau (TCWB). Climate statistics. Available online: http://www.cwb.gov.tw/V7/climate/monthlyMean/Taiwan_tx.htm (accessed on 3 September 2020).
17. US EPA. Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially—Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry(GC/MS). In *Selected Analytical Methods for Environmental Remediation and Recovery (SAM)*; EPA: Cincinnati, OH, USA, 1999.
18. US EPA. Reduction of Detection Limits to Meet Vapor Instrusion Monitoring Needs. In *Compendium Method TO-15-Supplement*; EPA: Research Triangle Park, NC, USA, 2009.

19. US EPA. *Compendium Method TO-11A. Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)*; EPA: Cincinnati, OH, USA, 1999.
20. Russell, A.; Milford, J.; Bergin, M.S.; McBride, S.; McNair, L.; Yang, Y.; Stockwell, W.; Croes, B. Urban Ozone Control and Atmospheric Reactivity of Organic Gases. *Science* **1995**, *269*, 491–495. [CrossRef]
21. Carter, W.P.L. *Updated Maximum Incremental Reactivity Scale and Hydrocarbon in Reactivities for Regulatory Applications*; University of California: Riverside, CA, USA, 2009.
22. Texas Commission on Environmental Quality (TCEQ). Air Toxics. Available online: http://www.tceq.state.tx.us/toxicology/AirToxics.html/#list (accessed on 15 May 2020).
23. Doherty, R.E. A History of the Production and Use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichloroethane in the United States: Part 1—Historical Background; Carbon Tetrachloride and Tetrachloroethylene. *Environ. Forensics* **2000**, *1*, 69–81. [CrossRef]
24. Doherty, R.E. A History of the Production and Use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichloroethane in the United States: Part 2—Trichloroethylene and 1,1,1-Trichloroethane. *Environ. Forensics* **2000**, *1*, 83–93. [CrossRef]
25. Scheutz, C.; Durant, N.D.; Hansen, M.H.; Bjerg, P.L. Natural and enhanced anaerobic degradation of 1,1,1-trichloroethane and its degradation products in the subsurface—A critical review. *Water Res.* **2011**, *45*, 2701–2723. [CrossRef] [PubMed]
26. Martin-Martinez, M.; Gómez-Sainero, L.; Alvarez, M.A.; Bedia, J.; Rodriguez, J.; Bedia, J. Comparison of different precious metals in activated carbon-supported catalysts for the gas-phase hydrodechlorination of chloromethanes. *Appl. Catal. B Environ.* **2013**, *132*, 256–265. [CrossRef]
27. Kirchstetter, T.W.; Singer, B.C.; Harley, R.A.; Kendall, G.R.; Hesson, J.M. Impact of California Reformulated Gasoline on Motor Vehicle Emissions. 2. Volatile Organic Compound Speciation and Reactivity. *Environ. Sci. Technol.* **1999**, *33*, 329–336. [CrossRef]
28. Grosjean, E.; Rasmussen, R.A.; Grosjean, D. Ambient levels of gas phase pollutants in Porto Alegre, Brazil. *Atmos. Environ.* **1998**, *32*, 3371–3379. [CrossRef]
29. Zhang, Q.; Wu, L.; Fang, X.; Liu, M.; Zhang, J.; Shao, M.; Lu, S.; Mao, H. Emission factors of volatile organic compounds (VOCs) based on the detailed vehicle classification in a tunnel study. *Sci. Total. Environ.* **2018**, *624*, 878–886. [CrossRef]
30. Kumar, A.; Singh, D.; Kumar, K.; Singh, B.B.; Jain, V.K. Distribution of VOCs in urban and rural atmospheres of subtropical India: Temporal variation, source attribution, ratios, OFP and risk assessment. *Sci. Total. Environ.* **2018**, *613*, 492–501. [CrossRef]
31. Holzinger, R.; Jordan, A.; Hansel, A.; Lindinger, W. Automobile Emissions of Acetonitrile: Assessment of its Contribution to the Global Source. *J. Atmos. Chem.* **2001**, *38*, 187–193. [CrossRef]
32. Hamm, S.; Warneck, P. The interhemispheric distribution and the budget of acetonitrile in the troposphere. *J. Geophys. Res. Space Phys.* **1990**, *95*, 20593. [CrossRef]
33. Holzinger, R.; Jordan, A.; Lindinger, W.; Scharffe, D.H.; Schade, G.; Crutzen, P.J.; Warneke, C.; Hansel, A. Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide. *Geophys. Res. Lett.* **1999**, *26*, 1161–1164. [CrossRef]
34. US EPA. *Health and Environmental Effects Profile for Acetonitrile*; Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development: Cincinnati, OH, USA, 1985.
35. Environment Canada (EC). *Priority Substances List Assessment Report: Acrylonitrile. Canadian Environmental Protection Act, 1999*; Environment Canada: Ottawa, ON, Canada, 2000.
36. Liang, X.; Chen, X.; Zhang, J.; Shi, T.; Sun, X.; Fan, L.; Wang, L.; Ye, D. Reactivity-based industrial volatile organic compounds emission inventory and its implications for ozone control strategies in China. *Atmos. Environ.* **2017**, *162*, 115–126. [CrossRef]
37. Sillman, S. The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments. *Atmos. Environ.* **1999**, *33*, 1821–1845. [CrossRef]
38. Elminir, H.K. Dependence of urban air pollutants on meteorology. *Sci. Total. Environ.* **2005**, *350*, 225–237. [CrossRef]
39. De Sario, M.; Katsouyanni, K.; Michelozzi, P. Climate change, extreme weather events, air pollution and respiratory health in Europe. *Eur. Respir. J.* **2013**, *42*, 826–843. [CrossRef]

40. Sheng, J.; Zhao, D.; Ding, D.; Li, X.; Huang, M.; Gao, Y.; Quan, J.; Zhang, Q. Characterizing the level, photochemical reactivity, emission, and source contribution of the volatile organic compounds based on PTR-TOF-MS during winter haze period in Beijing, China. *Atmos. Res.* **2018**, *212*, 54–63. [CrossRef]
41. Li, Y.; Yin, S.; Yu, S.; Yuan, M.; Dong, Z.; Zhang, D.; Yang, L.; Zhang, R. Characteristics, source apportionment and health risks of ambient VOCs during high ozone period at an urban site in central plain, China. *Chemosphere* **2020**, *250*, 126283. [CrossRef]
42. Elbir, T.; Cetin, B.; Cetin, E.; Bayram, A.; Odabasi, M. Characterization of volatile organic compounds (VOCs) and their sources in the air of Izmir, Turkey. *Environ. Monit. Assess.* **2007**, *133*, 149. [CrossRef]
43. Yuan, B.; Shao, M.; Lu, S.; Wang, B. Source profiles of volatile organic compounds associated with solvent use in Beijing, China. *Atmos. Environ.* **2010**, *44*, 1919–1926. [CrossRef]
44. Alfoldy, B.; Mahfouz, M.; Yigiterhan, O.; Safi, M.; Elnaiem, A.; Giamberini, S. BTEX, nitrogen oxides, ammonia and ozone concentrations at traffic influenced and background urban sites in an arid environment. *Atmos. Pollut. Res.* **2019**, *10*, 445–454. [CrossRef]
45. Liu, P.-W.G.; Yao, Y.-C.; Tsai, J.-H.; Hsu, Y.-C.; Chang, L.-P.; Chang, K.-H. Source impacts by volatile organic compounds in an industrial city of southern Taiwan. *Sci. Total. Environ.* **2008**, *398*, 154–163. [CrossRef] [PubMed]
46. Yang, H.-H.; Dhital, N.B.; Wang, Y.-F.; Huang, S.-C.; Zhang, H.-Y. Effects of short-duration vehicular traffic control on volatile organic compounds in roadside atmosphere. *Atmos. Pollut. Res.* **2020**, *11*, 419–428. [CrossRef]
47. Wang, X.; Sheng, G.-Y.; Fu, J.-M.; Chan, C.-Y.; Lee, S.; Chan, L.Y.; Wang, Z.-S. Urban roadside aromatic hydrocarbons in three cities of the Pearl River Delta, People's Republic of China. *Atmos. Environ.* **2002**, *36*, 5141–5148. [CrossRef]
48. Na, K.; Kim, Y.P. Seasonal characteristics of ambient volatile organic compounds in Seoul, Korea. *Atmos. Environ.* **2001**, *35*, 2603–2614. [CrossRef]
49. Zalel, A.; Yuval; Broday, D. Revealing source signatures in ambient BTEX concentrations. *Environ. Pollut.* **2008**, *156*, 553–562. [CrossRef] [PubMed]
50. US EPA. *Environmental Protection Agency, Locating and Estimating Air Emissions from Sources of 1,3-Butadiene*; EPA: Morrisville, NC, USA, 1996; 454/R-96-008.
51. Mullins, J.A. Industrial emissions of 1,3-butadiene. *Environ. Health Perspect.* **1990**, *86*, 9–10. [CrossRef]