Measurement of Airborne Carbonyls with Pentafluorophenyl Hydrazine (PFPH)-Coated Tenax Tube using an Integrated Automatic Sampler in a Rapid Developing City in Pearl River Delta (PRD) Region, China

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Abstract: Airborne carbonyls can be formed from primary and secondary sources which are widespread in the environments. Their abundances are always related to the degree of capitalization of a city or area. More sensitive measurement of active airborne carbonyls (*e.g.*, formaldehyde and acetaldehyde) is thus critical to interpret their roles in the atmosphere. In this study, an observation was conducted in a rapid development city of Huizhou, where located in Pearl River Delta (PRD) Region in southern China. Monocarbonyls and dicarbonyls were collected onto pentafluorophenyl hydrazine (PFPH)-coated Tenax glass tubes by a modified automatic carbonyl sampler (ACS), which is originally adopted for sampling with default 2,4-dinitrophenylhydrazine (DNPH) cartridges. The tubes were analyzed by thermal desorption (TD)-gas chromatography/mass spectrometry (GC/MS) method. The results show that the collection efficiencies for both target carbonyls were consistent between a regular sampler and the ACS at a flow rate of 100 ml/min, demonstrating that the reliability and feasibility on the application of ACS for the carbonyls collection with the PFPH-coated tubes. The mean molar ratio of formaldehyde to acetaldehyde (1.17) in Huizhou suggests that the primary emission source was dominant in the city. According to the diurnal variations of the carbonyls, primary pollutants [*e.g.*, nitrogen dioxide ($NO_{2,}$) and sulfur dioxide (SO_2)] and secondary pollutant [*e.g.*, ozone (O_3)], active carbonyls could be produced from both primary and secondary sources in daytime. Vehicle emission is expected to be more dominant in rush hours (*i.e.*, early morning and evening). The peaks of formaldehyde around noontime were mainly attributed to increases of atmospheric photo-oxidation of other organics. The work indicates the advantages of using the PFPH-coated tubes for determination of diurnal variation on the atmospheric carbonyls with an aid of less labor-intensive automatic sampler.

Keywords: Carbonyls, Autosampler, Developing city, PFPH, Derivatization.

INTRODUCTION

Carbonyls, including aldehydes and ketones, are ubiquitous in both indoor and outdoor environments. These airborne compounds can be formed in combustion processes of natural and anthropogenic sources [1-4]. Secondary atmospheric reactions through oxidations of volatile organic compounds (VOCs) are also major contributors [5-7]. Low molecular weight (LMW) carbonyls are active in the photochemistry of the troposphere. Formaldehyde and acetaldehyde are the most abundant carbonyls in the ambient air [8-10] which act as sources of free radicals such as hydroxyl (•OH), hydroperoxyl (•HO2), acetyl (•CH_3CO), subsequently initiating atmospheric reactions for formation of ozone (O_3), nitric acid, peroxyacytyl nitrate (PANs), and other smog components [11-13]. The relative contributions of secondary versus primary sources are varied in locations and times (*i.e.*, seasons). Zhang *et al*. (2014) reported an obvious enhancement of carbonyls to carbon monoxide (CO) ratios during haze days, with the uplift factor of 1.5-4.2 in winter compared to 1.2-1.9 in the summer, because of more active photochemical reactions in hot weather and high solar radiation [14]. The dominant in-situ formation pathways for formaldehyde and acetaldehyde have been illustrated as reactions between alkoxy radicals (RO•) and oxygen (O_2) [15]. Additionally, due to more intense photochemical reactions resulted from biogenic VOCs, the contribution of secondary sources in rural area (~53%) was higher than that in urban area (~33%) for carbonyls [16]. Friedfeld *et al.* (2002) reported a positive correlation of formaldehyde with O_3 and CO with statistical regression models [17]. The ratio of secondary to primary sources of formaldehyde was

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found to be 1.7 in Houston, U.S. in summer of 2000. Possanzini *et al.* (2002) also found that 80 – 90 % of formaldehyde and acetaldehyde were photochemically produced in the summer but the percentage dropped to ~35 % in the winter of 1994 – 1997 in downtown Roma, when direct emission from traffic was dominant [18].

Different collections and measurement methods for airborne carbonyls have been developed since 1980's [19-21]. Among those approaches, the Compendium Methods of TO-11A established by the United States Environmental Protection Agency (U.S.EPA) is the most conventional method for active air sampling onto 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbent cartridges (USEPA, 1999). However, the DNPH-coated cartridge method usually requires coupling with high pressure liquid chromatography (HPLC)-Ultraviolet (UV) detection. Due to the limitation of solvent elution, it requires a long sampling time (*i.e.*, 12-24 h) and thus short temporal variation (*e.g.*, 1-2 h) could not be obtained. In addition, the artifacts of DNPH are widely reported such as interferences from atmospheric O_3 and NO_2 and polymerization of its hydrazones [22-25]. Therefore, the DNPH method is not the best measurement for all airborne carbonyls.

Alternative derivatizing agents such as *O*-(2,3,4,5,6-pentafluorobenzyl)- hydroxylamine (PFBHA) and pentafluorophenyl hydrazine (PFPH) have been examined and demonstrated for better performances in carbonyls monitoring [26, 27]. In this study, home-prepared PFPH-coated Tenax sorbent tubes were applied for the carbonyl collection, and the sampled tubes were then analyzed with thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) method [27]. An automatic carbonyl sampler (ACS), a default instrument originally designed for connection of DNPH-coated cartridges, was adopted for the PFPH tubes. Speedy derivatization reaction rates between PFPH and carbonyls and high sensitivity allow smaller sampling volume or shorter sampling time than the conventional DNPH method. The autosampler are also less labor intensive in continuous collection of a maximum of eight samples, which pre-installed inside the sampler.

Air samples were collected in Huizhou, Guangdong Province, China (114.4E, 22.7N), where is a key development city in Pearl Delta River (PRD) Region. The city has a population of 483 million in 2018 (http://news.ijntv.cn/qyzx/2019-03-25/03252FO-2019.html). Industry and logistic are the two major business sectors in Huizhou, additionally with large numbers of construction works for highways and residential and commercial buildings. The objectives of this study are: 1) to demonstrate the feasibility on the use of the regular automatic sampler for carbonyl collection with the PFPH-coated tube; and 2) to determine the temporal variations of the target carbonyls and compare their relationships with other primary [*i.e.*, NO_2 and sulfur dioxide (SO_2)] and secondary (*i.e.*, O_3) pollutants.

2. EXPERIMENTAL SECTION

2.1. Sampling Site

Air samples were collected on the roof top of a four-stories height building (>10 m above the ground level), which is situated in the center of Huizhou city (Figure **1**). Many railway and road construction works

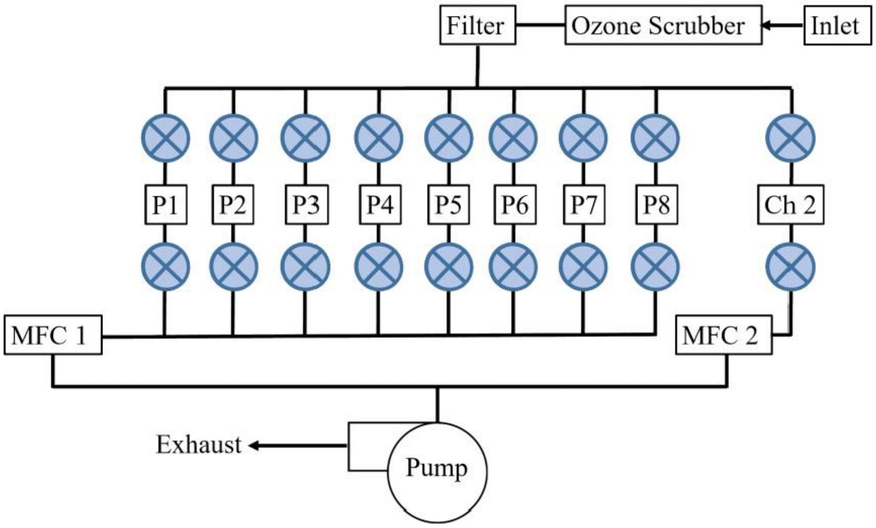

Figure 1: Symmetric diagram of an automatic carbonyl sampler.

were being conducted around the site (<5 km), but no large-scale industrial activity or other obvious pollution sources were found nearby. However, there were large numbers of diesel-fueled heavy-duty vehicles (*i.e.*, trucks for transportation of goods or construction materials) and light gasoline-fueled light-vehicles around the area.

2.2. Sampling with ACS

Sampling was conducted between January 14 and January 22, 2019. An ACS (Model 8000, ATEC, Malibu, CA, USA) were moderately adapted to fit the connection of PFPH-coated tubes. Figure **2** shows a schematic diagram of the modified ACS, which consists of eight sampling channels and one blank position. The flow rate of ACS was set at a minimum flow rate of 100 ml min^{-1} and calibrated by a flow calibrator (Defender 510, Mesa Lab, Butler, NJ, USA). Leak check was performed prior to a new set of sampling tubes were loaded onto the ACS. Atmospheric O_3 and particulate matters (PMs) were removed from the inlet gas stream by an O_3 scrubber and a filter installed upstream. The time sequence was programmed digitally on the panel. All sampling tubes were sealed and transported in a cooler box (~0 °C) to prevent any potential loss of derivatives and background interferences. The sample tubes were stored in a desiccator at room temperature (22±2 °C) for a maximum of 72 h before chemical analysis.

Figure 2: Map shows the location of sampling site (red dot) in Huizhou, Guangdong.

Collection efficiencies of the PFPH-coated tubes at the operation flow rate were examined by passing the test atmospheres and ambient airs through two identical tubes connected in series. The collection efficiency was calculated as 100 % (1 - A_b/A_f), where A_f and A_b are the amounts of a carbonyl collected on the front and the back tubes, respectively. The test atmospheres containing carbonyls at 5-10 ppbv levels were prepared in a Tedlar bag through liquid injection and subsequent vaporization [27]. The sampling times were set to vary from 1 and 3 h, corresponding to the total sampled volumes of 6 and 18 L.

2.3. Chemical Analysis

The sample loaded PFPH tube was exchanged with the injector liner in an GC/MS (Agilent 7890 GC/5975 MS, Santa Clara, CA, USA) system. The TD step took place in the GC injector port. Detailed analytical procedures and instrumental setting were shown in previous publication (Ho and Yu, 2004). In brief, the GC injector temperature was first lowered to 50 °C while the sampling tube was inserted in the injector port. Once the sample loaded, the injector temperature was ramped to 250 °C and kept at this temperature until the end of analysis. The injector was maintained in the splitless mode throughout the GC program. The initial GC oven temperature was 30 °C while the desorption step, and then stepwise increased to the final temperature of 250 °C. The unreacted PFPH and its derivatives were subsequently separated on the HP-5MS capillary column (5% diphenyl/95% diethyl polysiloxane, 30 m x 0.25 mm i.d. x 0.25-ím film thickness) and detected by the MSD at selective ion monitoring (SIM) mode. The quantification ions for the target compounds were shown in Table **1**.

The calibration procedures were shown in Ho and Yu (2004). The calibration curves were established by plotting the ratio of selective monitored ion peak areas between a given carbonyl and 4-fluorobenzladehyde (served as internal standard) versus the number mole of the carbonyl compound on the calibration sample tubes. The R^2 values for all target carbonyls were >0.990. All the carbonyls have LODs at sub-nmol levels, ranging from tens to hundreds pico-mol per sampling tube (Table **1**). The LODs in nmol per sample tube are translated into mixing ratios in the sub ppbv range for a sample volume of 6 and 18 L, which corresponds to sampling for 1 and 3 h at a flow rate of 100 mL/min.

3. RESULTS AND DISCUSSIONS

3.1. Collection Efficiencies with ACS

Table **2** lists the collection efficiencies of the PFPH sampling tubes determined using the test atmosphere in laboratory with usual pump and ambient air on field with ACS. For the test atmosphere tests, the collection efficiencies of >81% were achieved for all target carbonyls except acetaldehyde (71.5±6.2%), which was consistent with a relatively lower value of ~75 % shown in Ho and Yu (2004). Collection efficiencies for *n*-heptanal, *n*-octanal, *n*-nonanal, and benzaldehyde were all >85%. Di-carbonyls, including glyoxal and methylglyoxal, had the collection efficiencies of 81.6±5.1% and 85.5±2.3%, respectively.

Higher collection efficiency (>84%) of the target carbonyls were seen in the field samples collected by ACS because their mixing ratios were generally lower than those in the test atmospheres. Formaldehyde and acetaldehyde, the two most abundant carbonyls, had the collection efficiencies of 87.9±3.5% and 74.2±7.6%, respectively. Humidity, temperature, and other meteorological factors may also interfere the derivatization and results in better collection efficiencies. For this reason, the collection efficiencies determined in field measurements were used for the calculation of sample concentrations. In addition, the consistent collection efficiencies between the test atmospheres and field measurements prove the reliability and feasibility in use of the ACS for carbonyl sampling with PFPH-coated tubes.

3.2. Ambient Carbonyls Levels

The 3-h integrated ambient carbonyl concentrations after collection efficiencies correction were shown in Table **3**. Higher mixing ratios were observed during daytime sections (*i.e.*, 06:00-09:00 and 15:00-18:00) while primary emission sources (*i.e.*, vehicle emission in rush hours) and photochemical reactions were strong. In addition, all of the carbonyls showed lower concentrations in weekends than weekdays, due to less emissions from traffic and near-by factories. The average molar composition of the target carbonyls was shown in Figure **3**. Formaldehyde was the most abundant carbonyl in the ambient airs in Huizhou, ranging from 1.99 to 15.6 ppbv. It contributed to 34.3 % of the total quantified carbonyls on the molar bias. Acetaldehyde was the second most abundant carbonyl (29.3%), ranging from 1.66 to 13.3 ppbv. The sum of formaldehyde and acetaldehyde accounted for ~63% of the total quantified carbonyls. The mean molar ratio of

Table 2: Collection Efficiencies for the Target Carbonyls Determined in the Test Atmosphere with Regular Sampler and the Ambient air with ACS

Carbonyl	Test Atmosphere				Field Measurement	
	Conc.	Amount	Collection Efficiency [a]		Collection Efficiencies [b]	
	(ppbv)	(nmol/tube)	Average	SD	Average	SD
monocarbonyls						
formaldehyde	10	0.82	80.4 %	3.1 %	87.9 %	3.5%
acetaldehyde	10	0.82	71.5 %	6.2 %	74.2 %	7.6%
propanal	5	0.41	82.3 %	3.4 %	84.5 %	4.4%
acrolein	5	0.41	85.2 %	2.3 %	87.3 %	3.6%
n-butanal	5	0.41	86.2 %	1.7 %	90.4 %	2.6%
2-butanone	5	0.41	83.2 %	3.0 %	91.5%	3.4%
heptanal	5	0.41	85.6 %	2.1 %	91.2%	3.4%
octanal	5	0.41	90.3 %	2.3 %	90.3%	3.2%
nonanal	5	0.41	93.4 %	2.4 %	94.2%	2.9%
benzaldehyde	5	0.41	92.7 %	2.6 %	94.5 %	2.8%
tolualdehyde	5	0.41	91.5 %	3.2%	91.6%	3.5%
dicarbonyls						
glyoxal	5	0.41	81.6 %	5.1 %	84.6 %	5.6%
methylglyoxal	5	0.41	85.5 %	2.3 %	88.4 %	4.1%

[a] Test atmosphere samples were collected from a standard-containing Tedlar bag for 20 minutes;
[b] Field samples were collected for 1 h.

Table 3: Mixing Ratios of Carbonyls (ppbv) Quantified in Huizhou during the Sampling Period

	Weekdays		Weekend	
	Range	**SD**	**Range**	**SD**
monocarbonyls				
formaldehyde	2.60-15.6	2.34	1.99-6.12	1.63
acetaldehyde	2.71-13.3	1.89	1.66-6.02	1.35
propanal	0.12-3.53	0.62	0.09-1.36	0.36
acrolein	0.23-2.36	0.26	0.16-1.54	0.12
n-butanal	0.11-1.08	0.33	bd-0.88	0.22
2-butanone	bd*-0.43	0.52	bd-0.32	0.18
heptanal	bd-0.36	0.32	bd-0.30	0.16
octanal	bd-0.31	0.36	bd-0.25	0.17
nonanal	bd-0.39	0.12	bd-0.29	0.05
benzaldehyde	bd-0.89	0.23	bd-0.35	0.12
tolualdehyde	bd-0.69	0.36	bd-0.42	0.12
dicarbonyls				
glyoxal	bd-2.81	0.49	bd-1.55	0.23
methylglyoxal	0.20-3.72	0.36	0.09-1.36	0.29
Total quantified carbonyls	6.58-35.8	3.65	2.35-19.3	2.63

* bd represents below limit of detection.

formaldehyde to acetaldehyde was 1.17 in this study. Corrêa *et al.* (2003) reported acetaldehyde was more abundant than formaldehyde in samples collected at roadside locations in Brazil, due to the use of ethanol-containing diesel [28]. Diesel-fueled vehicle combustion was an expected source of carbonyls due to large amount of trucks for transportation of construction materials and goods around the sampling area. Our results prove that the content of ethanol was insignificant in the diesel fuels utilized in southern China. Our findings were more consistent with the findings reported in street canyons in Guiyang and at urban center in Guangzhou, both of which are located in southern China, with the ratio of formaldehyde to acetaldehyde of ~2 and ~1.2, respectively [29, 30].

Other carbonyls existed at much lower levels. The mixing ratios of *n*-propanal did not exceed 4.0 ppbv during the entire sampling period, whereas *n*-butanal ranged from 0.09 to 1.08 ppbv. The average molar compositions of propanal and *n*-butanal were 7.8 % and 2.4 %, respectively. Two aromatic carbonyls, benzaldehyde and tolualdehyde (sum of o-, p- and m-isomers), were detected in a range of 0.05 to 0.89 ppbv and 0.06 to 0.79 ppbv. The mean contribution of benzaldehyde was 2.0 % whereas tolualdehyde was 1.5 %. High molecular weight (HMW, n>6) carbonyls such as heptanal, octanal, and nonanal presented in all the ambient samples. The sum of their molar contribution was approximately 2.4%. These carbonyls have emission sources other than vehicular combustion. In addition, an unsaturated carbonyl of acrolein had the maximum mixing ratio of 2.36 ppbv. The mixing ratios of 2-butanone (MEK) ranged from 0.06 and 0.43 ppbv. Its contribution was 0.9% to the total quantified carbonyls. Two dicarbonyls, glyoxal and methylglyoxal, were scarcely reported in gaseous measurement. Their mixing ratios ranged from 0.07 to 2.80 and 0.09 to 3.70 ppbv, respectively. Quantification of acetone was excluded in this study due to large variation in its background level in PFPH tubes [27].

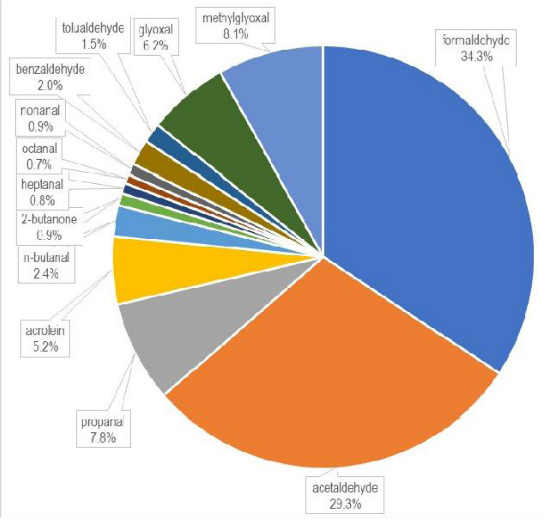

Figure 3: Average carbonyl molar composition in the ambient airs in Huizhou.

3.3. Correlation of Carbonyls with Gaseous Pollutants

Ambient concentrations of major gaseous pollutants, including SO_2, NO_2, and O_3, were measured on field. Physical parameters including temperature, relative humidity (RH), and atmospheric pressure were determined at the sampling location as well.

Formaldehyde and acetaldehyde could be formed from both primary and secondary sources [1, 5, 16]. Their correlations with other gaseous pollutants were investigated to gain insight into the relative contribution of primary and secondary sources. Plot of 3-h ambient concentrations of formaldehyde, acetaldehyde, and the major gaseous pollutants are shown in Figure **4**. The 3-h average concentrations of the major gaseous pollutants were obtained by taking averages from the hourly readings. It is obvious that both mixing ratios of formaldehyde and acetaldehyde increased from noon to evening, but then decreased from nighttime to mid-night. Their concentrations increased again in the early morning. Similar trends were seen for NO_2. Both reached to a maximum in the early evening, corresponding to the local traffic rush hour (*i.e.*, off-duty). Similarly, corresponding to the morning rush hours (06:00 - 09:00), the NO_2 concentrations were found to increase in this period. The variation of SO_2 concentration was not obvious. Low sulfur-containing diesels were commonly used, consequently vehicular emissions are minor sources for SO_2 [31, 32]. This can be attributed to the lack of link of SO_2 level with traffic flow. O_3, produced from secondary photochemical reactions, showed an opposite trend to that of NO_2. The mixing ratio of O_3 increased after the sunrise and reached its maximum around noon time. It decreased in the afternoon and dropped to a low level at night. No photochemical reaction is available without sunlight and its formation was therefore suppressed during nighttime. If NO_2 is assumed to be a marker for vehicular emission, it is reasonable to believe that primary sources are the dominant sources for formaldehyde and acetaldehyde in the developing city of Huizhou.

The lifetimes of formaldehyde and acetaldehyde in the atmosphere were ~1.5h and ~1 day, respectively [33, 34]. Due to their rapid photochemical degradation, temporal variation in shorter time intervals could demonstrate better correlations between the two carbonyls and other known primary and secondary pollutants. One-hour integrated carbonyls concentrations were further obtained for two consecutive sampling days (Figure **5**). Similar to the findings observed for the 3-h interval measurement, O_3 showed the maximum mixing ratio at noon time just

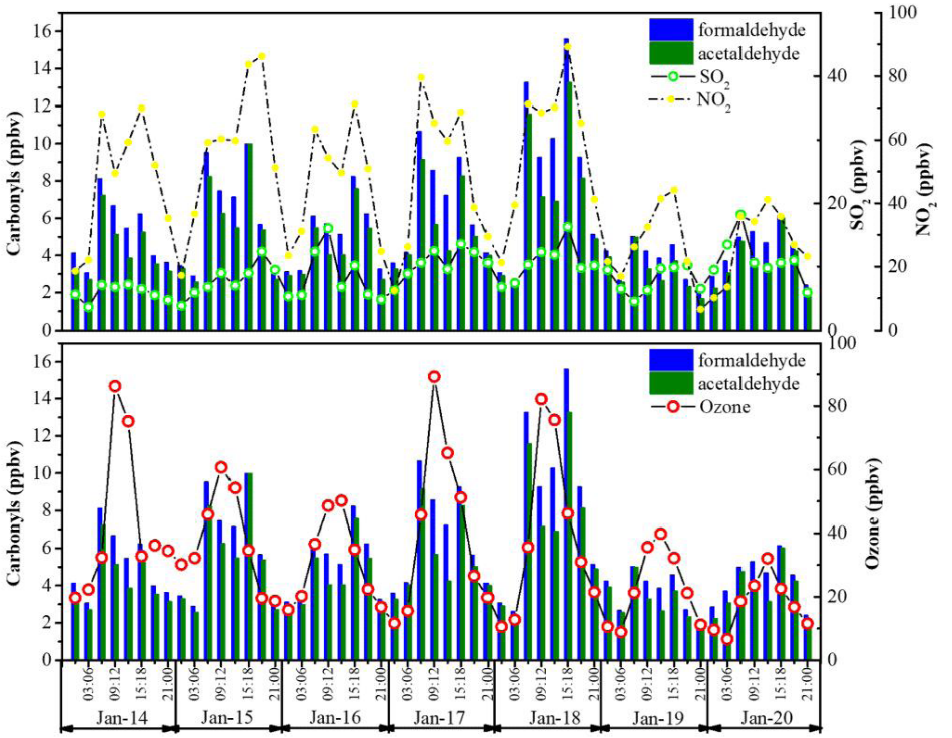

Figure 4: Trends of concentrations of formaldehyde, acetaldehyde, and other primary and secondary gaseous pollutants in 3-h interval.

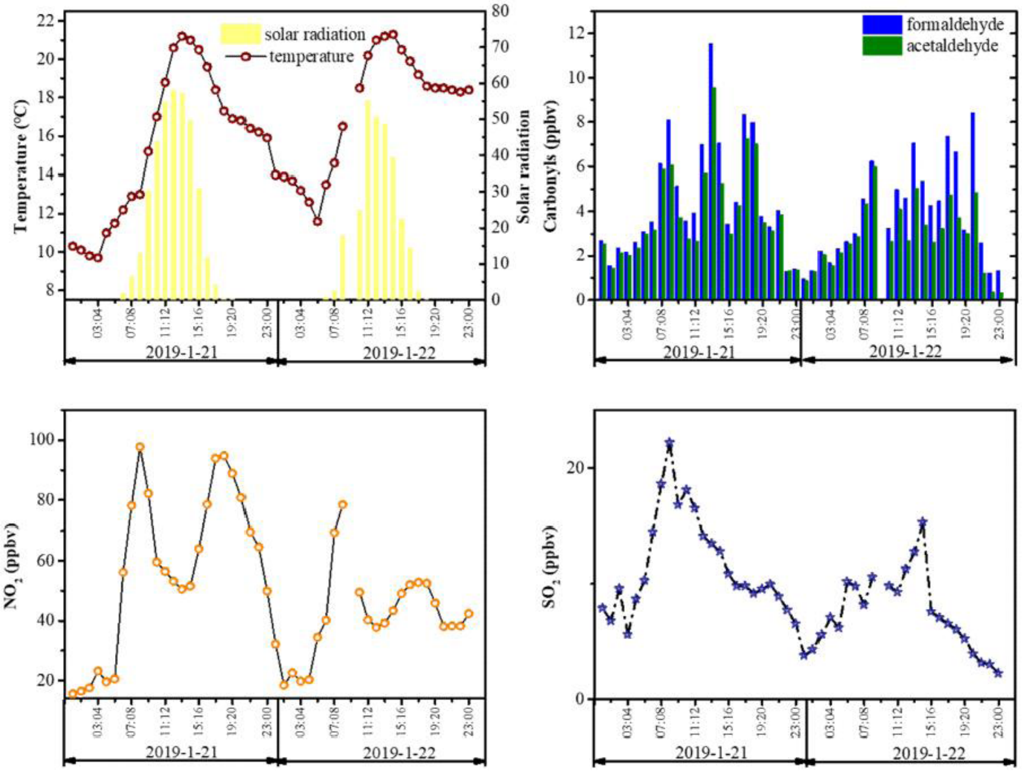

Figure 5: Trends of concentrations of physical parameters, formaldehyde, acetaldehyde, primary and secondary gaseous pollutants in 1-h interval.

after the NO_2 reached a peak level in the morning. The ambient O_3 returned to lower levels from afternoon to night, whereas mixing ratio of NO_2 increased to another peak in the evening. The abundances of formaldehyde and acetaldehyde increased with sunlight and reached at a high level at noon time. Even though the concentrations of formaldehyde and acetaldehyde declined in the early afternoon, they increased to another peak in the early evening, together with the primary pollutant of NO_2. Our findings demonstrated that the active carbonyls were produced from both primary and secondary sources in daytime, and primary sources were more dominant in the early morning and the late afternoon (*i.e.*, rush hours). The formations of formaldehyde and acetaldehyde started in the morning when more NO_2 was emitted into the environment. Even though the NO_2 concentration then decreased, the carbonyls and O_3 were continuously formed at noon time, attributed to their photochemical formation thru atmospheric oxidation of other organics. Such secondary formation processes are thus the dominant pathways for the early-afternoon peak of formaldehyde and acetaldehyde. In the evening, primary sources were believed to be dominant again, indicated by the simultaneous increases in NO_2 and the carbonyls.

CONCLUSION

The use of ACS for carbonyl sampling with PFPH-coated tubes is less labor intensive and adopt to shorter time interval offline measurement. The investigation of diurnal variation of most abundant carbonyls in the atmosphere is therefore made possible. The results of this study clearly demonstrate the advantage of new approach over the traditional DNPH method. Compared with the concentration variations of NO_2, SO_2, and O_3, active carbonyls such as formaldehyde and acetaldehyde were found to be produced from both primary and secondary sources. Secondary formations were dominant around the noontime whereas the primary sources such as vehicular emission were dominant during the early morning and evening rush hours.

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