

Urban air measurements using PTR-MS in Tokyo area and comparison with GC-FID measurements

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Abstract

Ambient air at a suburban area in Tokyo was measured by proton transfer reaction mass spectrometry (PTR-MS) and GC-FID simultaneously. Good correlations were obtained for hydrocarbon concentrations between GC-FID and PTR-MS, but concentrations differed by factor of 0.52–2.15, depending on the hydrocarbon. This shows that the calculated PTR-MS data needs to be corrected by standard gas measurements. Isoprene measured by PTR-MS is influenced by other species and the results of isoprene is not reliable at low concentration. Oxygenated volatile organic carbons showed higher concentrations during summer than in fall. This reflects the enhanced photochemical reactivity in summer. On the other hand, aromatic hydrocarbons, emitted mainly from car exhaust, did not show a difference between summer and fall. The ratios of aromatic hydrocarbons can be used as an indicator of photochemical reaction. Enhanced photochemical reactions were expected from these ratios during summer.

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1. Introduction

Tokyo is one of the biggest city in the world (population is ca. 12 million in Tokyo metropolitan). By the successful control of automobile exhaust, air quality in Tokyo area has become considerably better than other mega-cities in the world. But high oxidants produced by photochemical reaction appear during hot summer days and the improvement of air quality is still an important issue. High oxidant concentration tends to appear in semi-urban areas rather than in the city center. This is roughly explained as follows: NO_x emitted in urban area is transported to semi-urban areas and produces ozone (O₃) by the reaction with higher reactive hydrocarbons emitted from plants there. To understand the photochemical reaction mechanism and obtain knowledge to control the air quality, continuous measurements of volatile organic carbons (VOCs) are required. Observations

of more reactive species like oxygenated volatile organic carbons (OVOCs), which are usually produced during the oxidation processes, are limited. Proton transfer reaction mass spectrometry (PTR-MS) can measure VOCs continuously, and it also can measure reactive species. Measurements by PTR-MS have great advantage to understand the reactions in urban area.

PTR-MS has been developed by Lindinger et al. [1,2], and is now applied to various atmospheric measurements in urban air [3–5], in remote sites [6,7], in ocean [8,9], and in aircraft [10–14]. Although PTR-MS is a very powerful tool to measure VOCs, we need to be careful of quantification. Since the monitored species are determined only by mass number, there could be interference species (and fragment peaks) at the same mass [15]. Also humidity dependence exists for some species [15,16]. In this paper, PTR-MS measurements were compared with GC-FID data, in sub-urban air in Tokyo area. Measurements were made in summer and in fall. In formal expression, the observed signals by PTR-MS should be expressed as protonated benzene

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($m/z = 79$), etc. They are simply expressed benzene (M79), etc. in this paper for simplicity.

2. Method

2.1. Measurement location

Measurement of ambient air was carried out on the campus in Tokyo Metropolitan University (TMU, 35°37'N, 139°23'E), which is located about 30 km west of the city center of Tokyo. The location is illustrated in Fig. 1 with the city center and Tokyo metropolitan area. Kanto area (ca. 40 million population), which spreads over Kanto plain, is also roughly illustrated. TMU is located in residential area and there is much vegetation near the university campus. But TMU is considered as an intermediate of suburban–urban area because there is considerable traffic and pollutant transportation from city center.

2.2. PTR-MS

The PTR-MS was provided by IONICON, Austria. There are already detail explanations about PTR-MS in scientific literatures [1,2,15,16]. During the measurements, the PTR-MS instrument was operated at standard condition (2 mbar and 590 V at drift tube). This corresponds to an E/N (electric field/molecule number density) in drift tube of about 140 Td (townsend) ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$). Ambient air was introduced from the window in the laboratory, which was on third floor in the engineering building. Air was taken through 1/4 PFA tube with pump at about 4 l/min, and branched to PTR-MS inlet by 1/8 PFA tube. Zero air was regularly injected to check zero level. 30 min

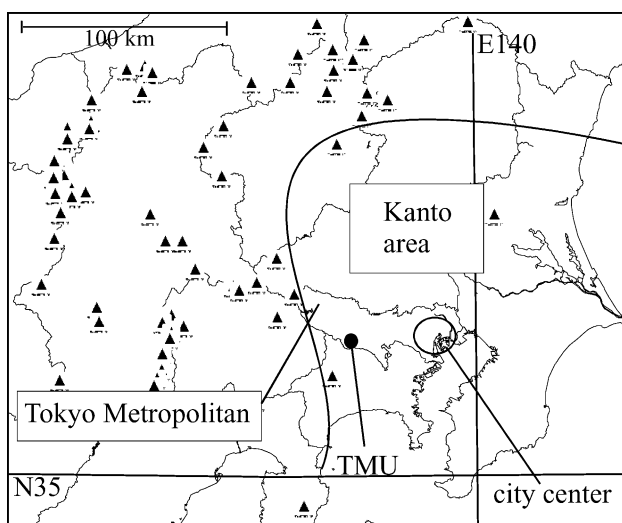


Fig. 1. The map of the measurement location. Tokyo Metropolitan University (TMU) is indicated by a solid circle. Tokyo metropolitan and Kanto area are also shown. City center of Tokyo is indicated by a circle. Triangles indicate mountains.

of zero measurement was followed by 30 min of ambient air using an electromagnetic valve and a timer. Zero air was generated by a charcoal trap at first, but this can not remove methanol and may affect the ion reactions in the drift tube since there is no water in the zero air. Later, a heated Pt catalysis (Thermo Environmental Instruments, Model 96) was used for zero air generation to keep water level constant. Ambient air measurements were carried out in summer (from August 1 to August 16, 2002) and in fall (from October 21 to November 27, 2002).

One advantage of PTR-MS measurements is that the absolute concentration of VOCs can be deduced theoretically. The targeted VOC concentration can be calculated by the following equation:

$$[\text{VOC}] = \frac{i[\text{VOCH}^+]}{k i[\text{H}_3\text{O}^+]t} \quad (1)$$

Here $[\text{VOC}]$ is the number density of the VOC, $i[\text{VOCH}^+]$ and $i[\text{H}_3\text{O}^+]$ is the measured ion count by the detector at mass number of corresponding protonated species, k is rate constant for the proton transfer reaction of VOC and H_3O^+ , t is reaction time (average residence time in drift tube). Since the right side in Eq. (1) are known parameters or measured values, the number density of VOC can be calculated. But some factors need to be taken account in practical calculation.

2.2.1. Transmission factor

The ion counts ($i[\text{VOCH}^+]$, $i[\text{H}_3\text{O}^+]$) need to be corrected by the loss at the quadrupole mass filter and by the loss from drift chamber to detection chamber. This is called the transmission factor, which is different for each mass number.

2.2.2. Isotope

Most VOCs have its isotope peaks, because carbon contains about 1.1% of ^{13}C . If the carbon number in the VOC increases, the existence of the isotope peak becomes more important. For example, terpenes have 10 carbon atoms in a molecule, and they have about a 10% isotope peak (M137:M138 is about 9:1).

2.2.3. Fragmentation

Some species undergo fragmentation, especially terpenes [17]. For higher E/N condition, the fragmentation tends to occur easier. In order to get true concentration of targeted VOC, all the fragment peaks should be counted in addition to the main mass peak. For example, at our measurements setting, α -pinene has peaks at M137/M138 (main peak/its isotope) and M81/M82 (fragment peak/its isotope). Their intensities are about 40 and 60%, respectively. If only M137 is taken into account, the results will be only about 40% of the true value.

2.2.4. Water cluster

The reagent ion H_3O^+ makes clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ($n = 1, 2, \dots$) in the drift tube, especially at lower E/N condition.

At our instrument setting ($E/N = 140$ Td), only M37 ($n = 1$) and M55 ($n = 2$) can be observed. Some VOCs can react with H_3O^+ (H_2O) $_n$ and the reaction rate constant is almost the same as H_3O^+ . In this case, the sum of H_3O^+ and H_3O^+ (H_2O) $_n$ should be the reagent ion. If the VOC does not react with H_3O^+ (H_2O) $_n$, only H_3O^+ should be the reagent ion. But the real situation is more complicated. Some of the clusters dissociate before the detection chamber, and the detected ion does not give the true distribution of clusters in the drift tube [15,16]. In practical measurements, it is better to check if the targeted VOC has a sensitivity dependence on the water concentration (humidity dependence).

Other important considerations during practical measurements is the voltage setting of the detector (secondary electron multiplier; SEM). The present PTR-MS instrument gives high load to the SEM and the decay of SEM is fast. The charge voltage to SEM needs to be maintained to keep constant sensitivity. If the SEM voltage setting is not proper (lower voltage), the signal has mass dependence (heavier mass yields less signal) and the calculated concentration become lower.

2.3. GC-FID

To compare with the results of the PTR-MS measurement, ambient air was also measured by GC-FID from November 14 to November 21, 2002. Ambient air was sampled at the same inlet of the PTR-MS using a T connector, and concentrated by a three-stage pre-concentrator (Entech7000). 500 ml of air was concentrated at a rate of 150 ml/min and the sampling time was about 4 min. The concentrated air was injected into the GC-FID (HP6890). GC-FID measurements were taken every 4 h automatically using scheduling programs. The column was HP-1 (length 60 m, inner diameter 0.32 mm, film thickness 1.0 μm). Temperature control was as follows: -50°C at first 6 min, then rise to 10°C at $15^\circ\text{C}/\text{min}$, and rise 190°C at $5^\circ\text{C}/\text{min}$. Identifications and concentrations were determined by comparison with diluted standard gas (Matheson, Enviro-MAT, mixture of 56 hydrocarbons at 1 ppm). With this method, hydrocarbons from C2 to C10 can be analyzed in one run [18].

O_3 concentration in ambient air was also measured at the same period (Thermo Environmental Instruments: Model 49C). The data were logged every minute by personal computer. In this paper, only the hourly average values of O_3 were used.

3. Results and discussion

3.1. Comparison with GC-FID and PTR-MS

GC-FID and PTR-MS measurement results of ambient air at TMU campus obtained in November 2002 were compared. The common species measured by both instruments are isoprene (M69), benzene (M79), toluene

Table 1
List of species compared with GC-FID and PTR-MS measurements

Category	Species	Mass number (m/z) of protonated ion	Rate constant with H_3O^+ ($10^{-9} \text{ cm}^3/\text{s}$) ^a
Isoprene	Isoprene	69	2
Benzene	Benzene	79	1.9
Toluene	Toluene	93	2.2
C8-benzene	<i>o</i> -Xylene	107	2.2
	<i>m</i> -Xylene		
	<i>p</i> -Xylene		
	Ethylbenzene		
C9-benzene	1,3,5-Trimethylbenzene	121	2
	1,2,4-Trimethylbenzene		
	<i>n</i> -Propylbenzene		
	<i>iso</i> -Propylbenzene		
Terpenes	α -Pinene	137	2
	β -Pinene		
	Limonene		
	Camphene		

^a These values are quoted from calculated values in Lindinger et al. [1].

(M93), C8-benzene (M107: *o*-, *m*-, *p*-xylene, ethylbenzene), C9-benzene (M121: 1,3,5-, 1,2,4-trimethylbenzenes, *n*-, *iso*-propylbenzenes), terpenes (M137: α -pinene, β -pinene, limonene, camphene). The ion reaction rate constants with H_3O^+ for calculation are summarized in Table 1. The observed results for benzene from November 14 to November 17 are shown in Fig. 2. The results of PTR-MS is not subtracted by the regularly injected zero air in this figure to show the zero level. It can be seen that there is good agreement between the results of PTR-MS and GC-FID. Correlation plots of benzene and other VOCs measured by PTR-MS and GC-FID are shown in Fig. 3. Values of PTR-MS are the average of 4 min corresponding to the air sampling time for GC-FID measurements. The PTR-MS results in Fig. 3 were calculated using Eq. (1), considering isotope, transmission, and fragment corrections. The correlation of the benzene plot is satisfactory. The intercept of

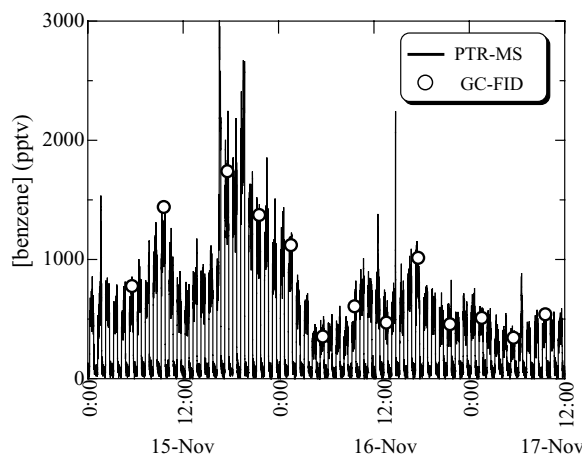


Fig. 2. Comparison of benzene concentration measured by PTR-MS and GC-FID at Tokyo Metropolitan University campus in November 2002.

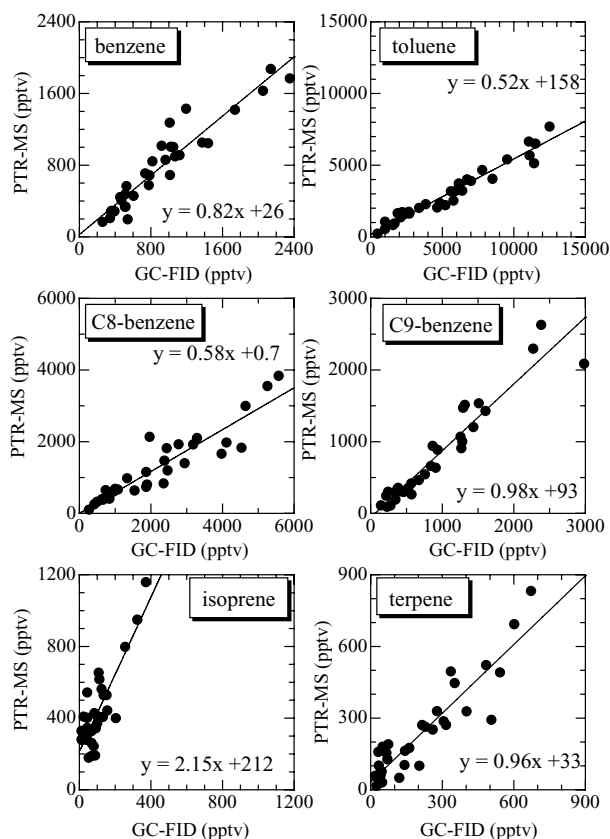


Fig. 3. Correlation plots of PTR-MS data against GC-FID data.

the least square fitting line is near zero (through the origin). This indicates that the targeted mass has no interference by other species or fragments. But the slope (absolute concentration) indicates a bias between the two techniques (0.82). For other VOCs, the linearity of the correlation plots are also good. But the slopes of the PTR-MS and GC-FID correlations are in different for each species. There is no systematic trend for these slopes. If standard gas of known concentration is available, it is better to use standard gas to calibrate PTR-MS instrument rather than to estimate the concentrations using Eq. (1). It should be noted that the fitting line of isoprene has a significant intercept. This indicate that there is an interference at M69 [15]. Checking the intercept of the correlation plots is a good method to check for interference. Even if there are absolute concentration differences for some VOCs and interference for isoprene, the measurements by PTR-MS are well correlated with GC-FID. When the calibration is properly applied and some corrections are carefully considered, PTR-MS can provide trustful data of actual atmospheric measurements at high frequency.

3.2. Ambient air measurement at Tokyo Metropolitan University campus

3.2.1. Measurements in summer

The PTR-MS measurement results during summer in 2002 at TMU campus are shown in Fig. 4. Aromatic VOC con-

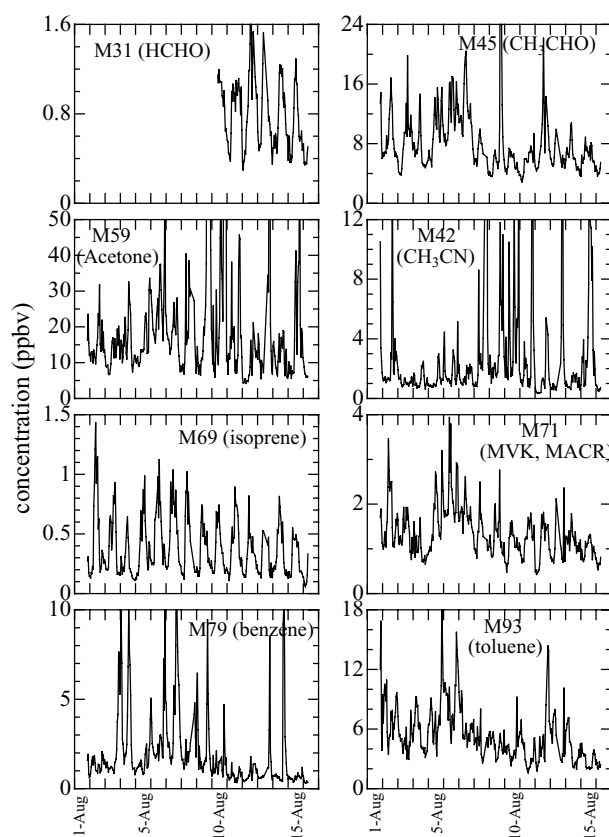


Fig. 4. Ambient air measurement results at Tokyo Metropolitan University campus in August 2002.

centrations were corrected by the GC-FID data. Isoprene is also corrected by GC-FID data, but we did not subtract the background interference. Some OVOC results are also shown here. They were not compared with other measurements method, and were not calibrated by standard gas at that time. Later, standard gasses of some VOCs (acetaldehyde, acetone, acetonitrile) generated by diffusion tubes and permeation tubes became available and the data obtained before was corrected by them. Formaldehyde and methyl vinyl ketone/methacrolein were not calibrated by standard gas and their concentrations were determined by Eq. (1). Therefore, the absolute concentrations of these species have large uncertainty. But we believe that the results of these OVOCs are still informative since the concentration changes would be proper.

Formaldehyde (HCHO) plays an important role in atmospheric chemistry. But HCHO measurements in ambient air by PTR-MS have not been reported previously. Since the difference of proton affinity between H_2O and HCHO is only slight, the backward reaction ($\text{HCHOH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$) progresses [19]. The observed HCHO (M31) concentration will be an equilibrium condition, and this will have a humidity dependence. The M31 data in Fig. 4 show clear diurnal variation, high during daytime and low during night. In Fig. 5, the average diurnal variations are shown for the same species in Fig. 4. The diurnal variation of M31 is more clear

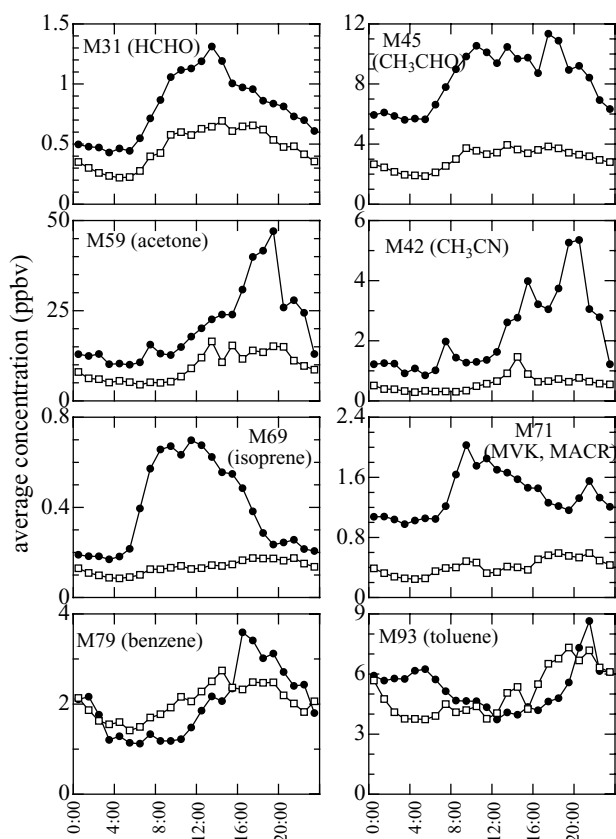


Fig. 5. Average diurnal variations in summer (solid circle) and fall (open square).

in Fig. 5. This is consistent with the expected production of HCHO (oxidation by hydrocarbons and direct emission from car exhaust). They are enhanced during daytime. The average diurnal variations observed in fall are also shown in Fig. 5. The amplitude of the diurnal variation and average concentrations are smaller in fall.

Acetaldehyde (CH_3CHO) makes a signal at M45 in PTR-MS measurements. CH_3CHO measurements by GC-PTR-MS [15,20] ensure that the M45 does not have an interference, other than CO_2 , in urban air. The influence of CO_2 can be cancelled by subtracting zero air which contain CO_2 as the same concentration of ambient air. The M45 signal in Fig. 4 is higher in daytime and lower in night. The diurnal variation is clear in Fig. 5. As well as M31, the average concentration and diurnal variation of CH_3CHO is smaller in fall. Since CH_3CHO is also produced during oxidation of VOC and car exhaust, this concentration change is reasonable.

Acetone (CH_3COCH_3) has various sources and they are not well defined yet. There are reports that M59 in PTR-MS measurements are the sum of acetone and 1-propanal [15,20]. But acetone is always dominant in ambient air and so the M59 can be attributed primarily to acetone. The M59 signal in Fig. 4 is different from other species related to photochemical production. The very high peaks are likely caused by very local emission of acetone. Fig. 5 shows that

acetone tends to become high at evening to night rather than daytime. This trend is similar to aromatic VOCs, suggesting similar anthropogenic sources. The average concentration in fall is smaller than in summer.

Acetonitrile (CH_3CN) has a relatively long lifetime in the atmosphere (about 1.5 years). Since it is emitted from burning process [21], CH_3CN is used as an indicator of forest fire [22]. But the sources and sinks of CH_3CN are not well known yet. In Fig. 4, there are many spikes probably related to local sources. Holzinger et al. [3] reported that the contribution of car exhaust was minor and CH_3CN can be used as an indicator of biomass burning, even in areas where there is considerable traffic density. But our measurements of urban air show significantly higher average CH_3CN concentration than remote places, suggesting strong sources in urban areas. The average diurnal variations show higher concentration at evening to night, similar to acetone and aromatics. The average concentration is also higher in summer than in fall.

Isoprene (2-methyl-1,3-butadiene) is emitted from plants in enormous amount [23], and the emission is related to the sunlight intensity and temperature. Isoprene gives a signal at M69 by PTR-MS measurements, but there is interference at this mass number [15] as demonstrated in Section 3.1. When isoprene concentrations are high enough, such as in a forest, the interference described in Section 3.1 becomes negligible. The M69 results in Fig. 4 show higher concentration during daytime. There is clear diurnal variation in average concentration in Fig. 5. Since there are many trees in and around TMU campus, this diurnal variation should be caused by isoprene emission from plants during daytime. The diurnal variation faded in fall since the activity of plants become smaller in this season.

Methyl vinyl ketone and methacrolein (MVK and MACR) are oxidation products from isoprene. Both MVK and MACR show signal at M71 and only the sum of them can be monitored by PTR-MS. There are some reports about the observation of MVK and MACR [14]. Since standard gases for MVK and MACR are not available in these measurements, the concentration shown here is not calibrated and was calculated using Eq. (1). In Fig. 4, the concentrations are higher than isoprene. The concentration ratio between isoprene and MVK + MACR will change as time after isoprene emitted. Higher concentration of MVK + MACR than isoprene is often observed at various places. But the much higher calculated concentration observed here could be an overestimate. MVK and MACR also show higher concentration during daytime in summer. Slightly higher concentration during night would correspond to the longer lifetime of MVK, compared to isoprene. The diurnal variation vanished in fall. From these results, M71 signal change may reflect the concentration of MVK and MACR properly.

Benzene is harmful to human and is mainly emitted from car exhaust in urban areas. Its concentration measured by the PTR-MS instrument (M79) is in good agreement with the GC-FID result as explained in Section 3.1. There are some sporadic peaks in Fig. 4, which are probably related to

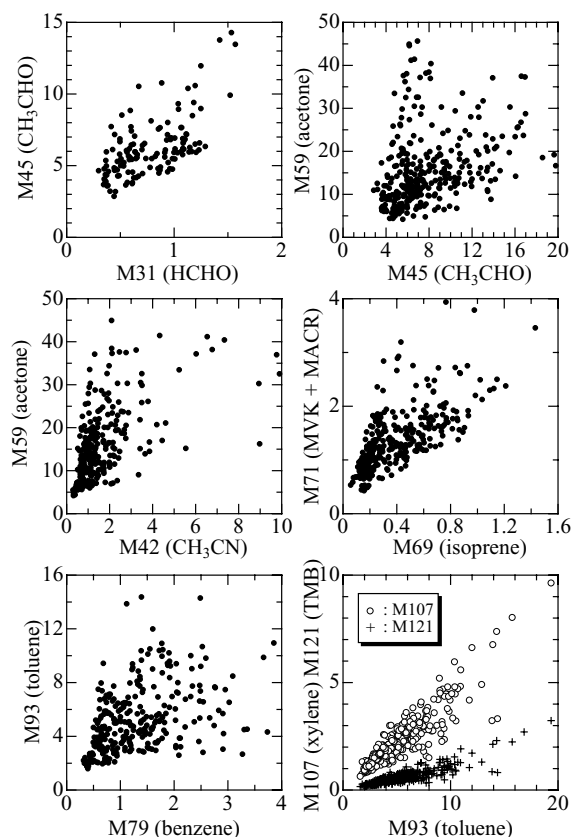


Fig. 6. Correlation plot of the measurement results in summer.

very local emission from the engineering department. The average diurnal variation of Benzene in Fig. 5 is not clear, but concentrations tend to become higher in the afternoon. The average concentration is similar in summer and in fall.

Toluene (M93), C8-benzenes (M107, xylenes and ethylbenzenes), C9-benzenes (M121, trimethylbenzenes and propylbenzenes) show quite similar concentration changes. They are mainly emitted from car exhaust. Therefore, only the result of toluene is shown in Fig. 4. The observed concentrations are toluene > C8-benzenes > C9-benzenes. This order reflects the volatility and the emission strength. They tend to become higher during night because of nocturnal surface inversion layer.

In Fig. 6, correlation plots of some species at TMU in summer are shown. M45 (CH₃CHO) and M31 (HCHO) show good correlation. They are both aldehydes and they have some common sources. From this good correlation, M31 would reflect HCHO variations correctly, except for the absolute concentration. M59 (acetone) and M45 (CH₃CHO), show slight correlation. It seems like that there are two different slopes, indicating the source of acetone has various sources. M59 (acetone) and M42 (CH₃CN) show some correlation, except for very high concentration of CH₃CN. M69 (isoprene) and M71 (MVK and MACR) show good correlation. Since isoprene is oxidized by OH and O₃ immediately in the atmosphere, MVK and MACR will have similar con-

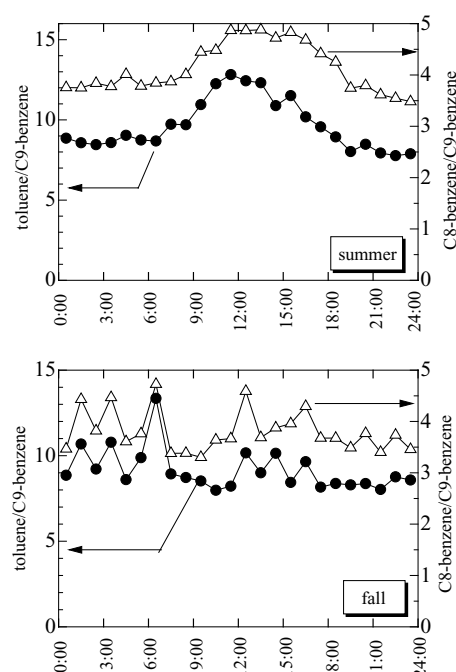


Fig. 7. Average diurnal variation of aromatic hydrocarbon ratios in summer and fall. Solid circles indicate toluene/C9-benzene, and open triangles indicate C8-benzene/C9-benzene.

centration changes like isoprene. Therefore good correlation between them is reasonable. M93 (toluene) and M79 (benzene) show some scatter, especially at high benzene concentrations. They usually show good correlation in urban area. This scatter is caused by local emission of benzene near the sampling site. M93, M107 (C8-benzenes), and M121 (C9-benzenes) show good correlation indicating their common sources, mainly from car exhaust.

3.2.2. Aromatic hydrocarbon ratios

Although toluene, C8-benzene, and C9-benzene have similar origin, each is removed at different rates. The ratio of aromatics can be used as an indicator of the air mass age [5]. The reaction rate constants with OH radical (the unit is 10⁻¹² cm³/molecule/s) are listed in parentheses for aromatics [24]. Toluene (5.96), ethylbenzene (7.1), *p*-xylene (14.3), *m*-xylene (23.6), *o*-xylene1 (13.7), 1,3,5-trimethylbenzene (57.5), 1,2,4-trimethylbenzene (32.5). Heavier species have a faster reaction rate with OH radical. In Fig. 7, average diurnal change of toluene/C9-benzene and C8-benzene/C9-benzene are plotted for summer and fall data. In these ratios, less reactive species are divided by the more reactive species. Although each ratio obtained in fall shows a constant value through the day, the ratios obtained in summer shows a clear diurnal cycle having a peak in the daytime. It should be noted that the ratios are similar between fall data and night time data obtained in summer.

There is an apparent difference between summer and fall ratios. When photochemical reaction with OH radical is enhanced during daytime, these ratio will increase.

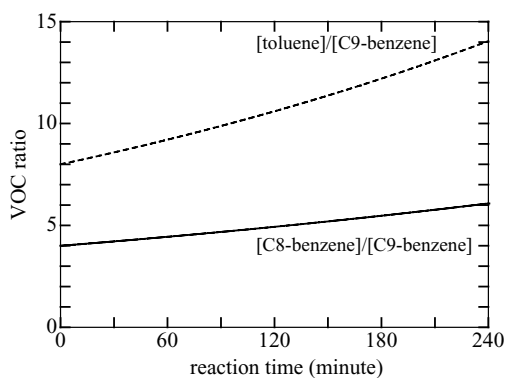


Fig. 8. Calculated toluene/C9-benzene and C8-benzene/C9-benzene decrease by OH radical reaction. OH radical concentration is assumed 1×10^6 radicals/cm³, and reaction rate constants are 5.96×10^{-12} , 16×10^{-12} , and 45×10^{-12} cm³/molecule/s for toluene, C8-benzene, and C9-benzene, respectively.

The increase of these ratios indicates the enhanced removal by OH. A simple calculation is performed if this ratios change can be explained by OH reaction or not. When toluene, C8-benzene, and C9-benzene are removed only by reaction with OH, the ratios will change with time as shown in Fig. 8. Here initial concentrations are assumed 6000 pptv, 3000 pptv, and 750 pptv for toluene, C8-benzene, and C9-benzene. OH concentration is constant at 1×10^6 radicals/cm³. Reaction rate constants are assumed as 5.96×10^{-12} , 16×10^{-12} , and 45×10^{-12} cm³/molecule/s for toluene, C8-benzene, and C9-benzene. At a reaction time of 120 min, toluene/C9-benzene increases from 8 to about 11, and C8-benzene/C9-benzene increases from 4 to about 5. In Fig. 7, the average concentration of toluene/C9-benzene increase from 9 (night) to 12 (daytime), and C8-benzene/C9-benzene increase from 3.5 (night) to 5 (daytime). Therefore, the daytime ratio increases in Fig. 7 in summer are explained by the reaction with OH. In actual urban air, fresh VOCs are always supplied from car exhaust and polluted air moves in/out. Therefore the assumed OH concentration (1×10^6 radicals/cm³) and the reaction time (120 min) do not indicate the actual urban air situation. When the build up time from morning to noon is 4 h, the average OH concentration will be 0.5×10^6 radicals/cm³. When the supply of car exhaust is considered, this OH concentration should be much higher value.

O₃ is photochemically produced from NO_x and hydrocarbons in the troposphere. The hourly O₃ data was plotted against C8-benzene/C9-benzene ratio for summer and fall in Fig. 9. When photochemical reactions are enhanced, O₃ concentration and C8-benzene/C9-benzene ratio both increase as indicated by the arrow in Fig. 9. The summer data shows this trend as indicated by the arrow, but the fall data did not show such correlation. These difference clearly show the difference of photochemical production ability in summer and in fall. Photochemical reactions are very important in urban air to the production of oxidants and other species. The ratios of aromatic VOC can work as an indicator of

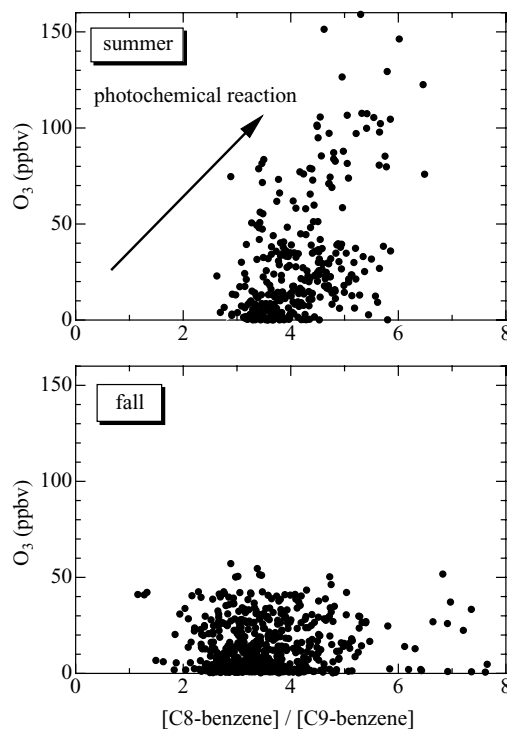


Fig. 9. Relation between ozone and C8-benzene/C9-benzene ratio in summer and fall. When photochemical reaction progresses, both ozone and C8-benzene/C9-benzene will increase.

photochemical reactions in urban air and they can help in the analysis of complex air behavior.

4. Conclusion

GC-FID and PTR-MS measurements of VOCs were made during summer and fall in Tokyo area. A comparison of the GC-FID and PTR-MS measurements showed differences in the absolute concentration. The PTR-MS data was corrected using the GC-FID data. This continuous data obtained by PTR-MS is an advantage for urban air monitoring since the analysis by GC method requires a lot of work. In addition, OVOC, which are more difficult to measure, can be measured by PTR-MS. The ratios of aromatic VOCs show an enhanced photochemical reactivity in summer. Because urban air shows high variability of many species, these kind of analysis need high frequency data like PTR-MS. The high frequency data obtained by PTR-MS will be great advantage to discuss about reactive species like OH radicals in the urban air.

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