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# Atmospheric alcohols and aldehydes concentrations measured in Osaka, Japan and in Sao Paulo, Brazil

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## Abstract

The use of alcohol fuel has received much attention since 1980s. In Brazil, ethanol-fueled vehicles have been currently used on a large scale. This paper reports the atmospheric methanol, ethanol and isopropanol concentrations which were measured from May to December 1997, in Osaka, Japan, where alcohol fuel was not used, and from 3 to 9 February 1998, in Sao Paulo, Brazil, where ethanol fuel was used. The alcohols were determined by the alkyl nitrite formation reaction using gas chromatography (GC-ECD) analysis. The concentration of atmospheric alcohols, especially ethanol, measured in Sao Paulo were significantly higher than those in Osaka. In Osaka, the average concentrations of atmospheric methanol, ethanol, and isopropanol were  $5.8 \pm 3.8$ ,  $8.2 \pm 4.6$ , and  $7.2 \pm 5.9$  ppbv, respectively. The average ambient levels of methanol, ethanol, and isopropanol measured in Sao Paulo were  $34.1 \pm 9.2$ ,  $176.3 \pm 38.1$ , and  $44.2 \pm 13.7$  ppbv, respectively. The ambient levels of aldehydes, which were expected to be high due to the use of alcohol fuel, were also measured at these sampling sites. The atmospheric formaldehyde average concentration measured in Osaka was  $1.9 \pm 0.9$  ppbv, and the average acetaldehyde concentration was  $1.5 \pm 0.8$  ppbv. The atmospheric formaldehyde and acetaldehyde average concentrations measured in Sao Paulo were  $5.0 \pm 2.8$  and  $5.4 \pm 2.8$  ppbv, respectively. The  $C_2H_5OH/CH_3OH$  and  $CH_3CHO/HCHO$  were compared between the two measurement sites and elsewhere in the world, which have already been reported in the literature. Due to the use of ethanol-fueled vehicles, these ratios, especially  $C_2H_5OH/CH_3OH$ , are much higher in Brazil than these measured elsewhere in the world. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Methanol; Ethanol; Formaldehyde; Acetaldehyde; Brazil; Osaka; Alternative fuel

## 1. Introduction

There has been an increased interest in use of ethanol and other alcohol fuels as alternative energy sources. The use of alternative fuels has received much attention as a method to minimize the country's reliance on foreign energy sources. Most countries have established

programs for the development of alternative energy sources with the purpose of reducing their dependence on petroleum (Wang et al., 1990). From the viewpoint of air quality, a major advantage of alcohol fuels is the practical elimination of tetraethyl lead, which is an anti-knock additive in the fuel. In addition, the use of alcohol fuel can lead to the reduction of CO, NO<sub>x</sub> (nitrogen oxides) and hydrocarbon emissions (Bishop and Stedman, 1990; Chang et al., 1991).

Mexico, Argentina, the United States, some countries in South Africa and European Community became

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enthusiastic supporters of the “Gasohol” program after having heard about the positive aspects of the “Brazilian Proalcool Program”. Brazil is the country that has attempted the large-scale use of alcohol as an automobile fuel. The use of an ethanol–gasoline blended fuel was introduced about 20 years ago. The fraction of ethanol-fueled cars has increased to 19% of the total vehicles in 1985. Nowadays, there are more than 3,000,000 light duty cars, which is estimated to be more than 35% of the total vehicles, exclusively driven using hydrated ethanol. A mixture of 78% gasoline and 22% anhydrous ethanol is currently used as the vehicle fuel throughout Brazil. However, there are very few reports regarding the ambient levels of ethanol. Recently, Grosjean et al. (1998) reported the ambient levels of ethanol measured in Porto Alegre, Brazil, where 17% of vehicles run on ethanol. The atmospheric ethanol had been measured by GC-MS analysis for samples collected in electropolished canisters. The ambient ethanol concentrations ranged from 0.4 to 68.2 ppbv (parts per billion per volume). It is expected that in Sao Paulo, Brazil, where 28% of the vehicles run on ethanol, the atmospheric ethanol concentrations are significantly high compared to that measured in a place where alcohol fuel has not been used (Bailey and Meagher, 1986).

Moreover, documented evidence shows that the use of oxygenated fuels can be a potential emission source of aldehydes, which is more toxic and reactive in the atmosphere than alcohols (Gaffney et al., 1997). The reaction of acetaldehyde with the OH free radical in the atmosphere leads to the formation of the peroxyacetyl radical, which can react with nitrogen dioxide to form peroxyacetyl nitrate (Cofer et al., 1985). Formaldehyde (HCHO) and acetaldehyde (CH<sub>3</sub>CHO) are the most abundant carbonyl compounds in the atmosphere (Anderson et al., 1996). The use of ethanol-fueled vehicles popularly leads to a high level of atmospheric acetaldehyde since the combustion of ethanol in spark-ignition engines results in the increased emissions of primary acetaldehyde (Grosjean et al., 1990).

We report the results of the atmospheric alcohol and aldehyde concentrations measured in Osaka, Japan, where alcohol-fueled vehicles have not been introduced, and in Sao Paulo, Brazil, where ethanol-fueled light duty vehicles are in high use.

## 2. Experimental sections

### 2.1. Description of sampling sites

Samples of the atmospheric alcohols and aldehydes were taken in Osaka, Japan, and in Sao Paulo, Brazil.

In Osaka, samples were collected near Route 310, one of the main routes that runs through Sakai city, southeast Osaka Prefecture, connected to other cities,

with heavy traffic, on 1–2 May, 16–17 June, 18–19 July, 13–14 August, 15–16 October, 20–21 November, and 17–18 December. Sampling days were chosen by the same weekday. Samples in Sao Paulo were collected at the border of the Sao Paulo University campus, which was closed to heavy traffic, Arnaldo, one of the largest routs of the city, in Consolacao, Western Sao Paulo.

### 2.2. Alcohol measurements

Ambient air was sucked up by atmospheric pressure into 200 ml Pyrex glass bottles, which were previously evacuated. Forty milliliters of pure nitrogen dioxide (1 atm) was injected into the bottle to get a 200 ppmv concentration. A 200  $\mu$ l of 1% HCFC-123 (CHCl<sub>2</sub>CF<sub>3</sub>) in nitrogen, which was used as an internal standard, was also injected into the bottle. Alcohols were allowed to react with nitrogen dioxide for 30 min. The alkyl nitrite formed after the 30-min reaction was analyzed by GC-ECD. Prior to sampling, the glass bottles have to be treated as following: the bottles were cleaned and treated with chromic acid mixture for at least 1 h, rinsed several times with pure water, dried up, evacuated by a vacuum pump, and then wrapped with aluminum foil to avoid irradiation of UV-visible light which produces photochemical reactions of nitrogen dioxide as well as alkyl nitrite during and after the reaction. The pure water for cleaning had been prepared using distilled water with KMnO<sub>4</sub> added, and then purified using a Mill-Q Labo (resistivity > 18.2 M $\Omega$  cm). The air samples were collected in triplicate every time. The relative standard deviation results for the three samples collected were always less than 10% (Nguyen et al., 1999).

A GC analysis was done using a Shimadzu GC-4CM gas chromatography which was fitted with a Teflon column (3 mm inner diameter, and 4 m long). Tricresyl phosphate on Chromosorb W-AW (60–80 meshes) was packed in the column. The temperature of the injection port, detector, and column was set at 25°C.

The detection limits determined by a signal-to-noise ratio of 3:1 were 0.9, 0.7 and 1.8 ppbv for methanol, ethanol, and isopropanol, respectively, under the condition mentioned above with a 500  $\mu$ l injection. The analytical method has already been described in detail in the literature (Nguyen et al., 1999).

### 2.3. Aldehyde measurements

Aldehydes were sampled for 1 h at a flow rate of 1.0 l min<sup>-1</sup> using the Sep-pak 2,4-dinitrophenylhydrazine (DNPH)–silica cartridges (Waters/Millipore Corp.), which has less ozone influence on the aldehydes determination than the C<sub>18</sub> cartridges. The cartridges consist of DNPH-coated silica packed in a Waters

Sep-Pak Plus cartridge equipped with end caps and plugs as described in detail elsewhere (Arnts and Tejada, 1989; Kuwata and Uebori, 1979; Zhou and Mopper, 1990). The cartridges trap the aldehydes gases by reacting them with DNPH in the cartridges to form the corresponding stable 2,4-dinitrophenylhydrazones derivatives. High-performance liquid chromatography (HPLC) grade acetonitrile was used to elute the derivatives from the cartridges. The solution samples were analyzed by using HPLC from a Waters Co. HPLC system and a  $C_{18}$ ,  $39 \times 300$  mm column with UV detection at 360 nm using a Waters Co. 486 UV detector (mobile phase: acetonitrile–water: 60/40% by volume; flow rate:  $1 \text{ ml min}^{-1}$ ; injection volume:  $20 \mu\text{l}$ ). The calibrations were made each time before analyzing the atmospheric aldehyde samples and the correlation coefficients ( $R^2$ ) values were always greater than 0.99.

### 3. Results and discussion

#### 3.1. Ambient concentration of alcohol measured in Osaka, Japan

The diurnal variations in the ambient methanol, ethanol, and isopropanol concentrations measured once a month from May 1997 to December 1997 in Sakai, Osaka, are shown in Fig. 1. For all the measurements, three samples were collected in three different glass bottles at the same time and the results were average of these values. The error bars in Fig. 1 show one standard deviation of the measured alcohol results. The measured concentrations of atmospheric methanol ranged from 0.3 to 17.3 ppbv with an average of  $5.8 \pm 3.8$  ppbv, those of ethanol ranged from 1.4 to 21.9 ppbv with an average of  $8.2 \pm 4.6$  ppbv, and those of isopropanol ranged from 1.6 to 28.9 ppbv with an average of  $7.2 \pm 5.9$  ppbv. Except on 17 December (cloudy), all the sampling days were sunny. Although seasonal variations in the ambient concentrations of alcohol were not clear, the month-to-month differences in atmospheric methanol and isopropanol concentrations were slightly higher than those of ethanol. This indicates that some of the emission sources of methanol and isopropanol do vary according to seasonal changes, for example, the emission from plants sources is higher in the summer than in the other seasons (Kirstine et al., 1998; MacDonald and Fall, 1993). Moreover, the atmospheric methanol and isopropanol levels showed peaks at noon, and these also reflect the influence of emissions from biological sources. Generally, the alcohol concentrations show peaks during the night. This can be explained by the effect of boundary layer thermal inversions or reactions with pollutants such as OH,  $\text{NO}_2$ . A higher wind speed during the day than at night was also one of the reasons for the high concentration of alcohols at night.

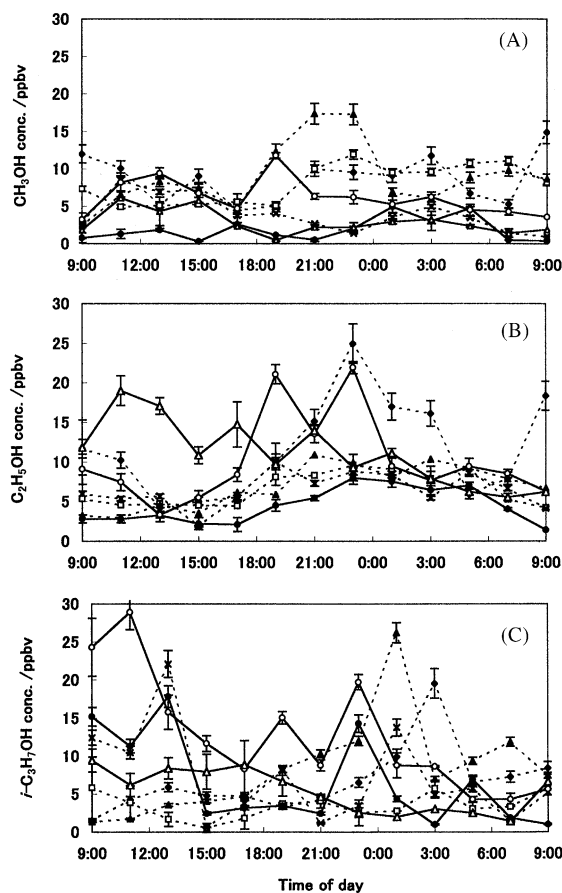


Fig. 1. Diurnal variations of atmospheric  $\text{CH}_3\text{OH}$  (A),  $\text{C}_2\text{H}_5\text{OH}$  (B), and  $i\text{-C}_3\text{H}_7\text{OH}$  (C) concentrations measured in Osaka, Japan (1997) Values shown are the averages for three samples collected at the same time and error bars show one standard deviations (SDV). (—◆—) 1–2 May, (—□—) 16–17 June (—▲—) 18–19 July, (—×—) 13–14 August (—●—) 15–16 October, (—○—) 20–21 November (—△—) 17–18 December.

#### 3.2. Ambient concentration of alcohol measured in Sao Paulo, Brazil

The atmospheric alcohol concentrations measured in Sao Paulo, Brazil, are listed in Table 1. Table 1 also presents the temperature and relative humidity measured at Sao Paulo site along with each alcohol measurement. Two glass bottles were used for sampling at each measurement. The results, which are the average values of the two, are shown in Table 1 with one standard deviation. The ambient levels of methanol, ethanol, and isopropanol ranged from 20.8 to 51.1 ppbv with an average of  $34.1 \pm 9.2$  ppbv, from 109.9 to 242.7 ppbv with an average of  $176.3 \pm 38.1$  ppbv, and from 27.6 to 65.7 ppbv with an average of

Table 1  
Alcohols concentrations (ppbv) measured in Sao Paulo, Brazil (1998). Values are shown with one standard deviation

Day	Time	Temperature (°C)	RH (%)	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> OH/CH <sub>3</sub> OH	<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH
Feb-03	10:15	26.0	77	34.7 ± 1.5	177.4 ± 28.6	5.1	58.1 ± 5.3
	11:50	26.8	54	20.8 ± 4.4	170.1 ± 45.3	8.2	29.8 ± 9.3
	14:45	29.4	54	37.2 ± 4.6	242.7 ± 18.2	6.5	52.3 ± 7.1
Feb-04	16:55	30.0	54	29.5 ± 1.3	203.7 ± 4.9	6.9	49.6 ± 5.7
	09:25	26.0	67	27.1 ± 2.6	222.9 ± 13.0	8.2	32.4 ± 7.8
	11:05	30.3	59	24.9 ± 8.3	202.4 ± 20.1	8.1	31.0 ± 5.4
Feb-05	10:55	29.6	54	29.7 ± 0.5	160.4 ± 34.7	5.4	27.6 ± 2.0
	12:26	30.0	52	37.6 ± 6.5	153.0 ± 31.9	4.1	32.1 ± 5.1
	13:56	31.4	43	46.6 ± 6.2	147.0 ± 4.4	3.2	65.7 ± 10.7
Feb-09	15:46	30.9	54	51.1 ± 8.8	128.3 ± 4.2	2.5	62.2 ± 10.5
	15:15	31.0	71	37.6 ± 0.6	109.9 ± 1.6	2.9	55.1 ± 2.7
	Average			34.1 ± 9.4	176.3 ± 38.1	5.2	44.2 ± 13.7
Osaka (average)	Summer	22–30	32–87	7.0 ± 1.6	6.6 ± 2.1	0.9	6.4 ± 2.6

44.2 ± 13.7 ppbv, respectively. The measurement results showed that atmospheric alcohol concentrations had little variation for samples taken on the same day. It can be suggested that the photochemical degradation of alcohol is low. For measurements taken on three days from 3 to 5 February 1998, the day-to-day variations of atmospheric alcohol levels were high. Among the measured alcohols, the ethanol concentrations were especially high. The use of ethanol fuel for light duty vehicles made the atmospheric concentrations of ethanol for all measurements higher than those of methanol and isopropanol. It was very clear that the ambient levels of alcohol measured in Sao Paulo were higher than those measured in Osaka. Especially, the atmospheric ethanol concentrations were more than 20 times higher than those measured in Osaka in the summer. It should be noted that measurements in Sao Paulo were done at about the same temperature, humidity, and wind speed (Table 1) as conditions in Osaka in summer.

### 3.3. Comparison with other atmospheric alcohol measurements by other studies

Atmospheric ethanol concentrations in Sao Paulo, 1990, reported by Mooca were 180, 200, 300, and 310 ppbv (Table 2), which were close to the results from this work. Pereira et al. (1999) reported the atmospheric ethanol concentration of 36.2 ppbv in Sao Paulo, which is much lower than our results. The atmospheric ethanol concentrations measured at other sites around the world are lower than those in Brazil, and have a range from less than 1 to several ppbv, which are not very different from those measured in Osaka in this study.

### 3.4. Ethanol-to-methanol ratios

Several studies reported that the emission of methanol from plants is one of major sources (MacDonald and Fall, 1993; Fall, 1999). In this paper, we used the ethanol-to-methanol ratio to measure the anthropogenic to natural sources. Diurnal variations of ethanol-to-methanol ratios in summer and winter in Osaka are shown in Fig. 2. The summer results were the average of measurements from June to August. The winter results were the average of measurements from October to December. On the sampling day in the summer, the temperature and relative humidity were 22–30°C and 32–87%, respectively. Those in the winter were 6–18°C and 26–90%, respectively. The wind speed recorded on the sampling days did not change much during the summer and winter, and had the tendency of a higher wind speed in daytime of 1.3–2.8 m s<sup>-1</sup> than the nighttime of 0.1–1 m s<sup>-1</sup>. The ethanol-to-methanol ratios were lower in the daytime than those in the nighttime for both the summer and winter results. The ethanol-to-methanol ratios were higher for the winter measurement than for the summer ones. These variations are related to the activity of plants. Plants emit more methanol in daytime than in the nighttime and in the summer than in the winter.

The ethanol-to-methanol ratios for the measurements in Sao Paulo and the average ratio for the Osaka summer data are also listed in Table 1. The ratios for Sao Paulo were significantly higher than the ratios of Osaka. Table 2 lists the methanol, and ethanol concentrations, and the ethanol-to-methanol ratios measured around the world, which were obtained from the average value by this study and results reported by Goldan et al. (1995a, b), Grosjean et al. (1998), Kirstine et al. (1998), Leibrock and Slemr (1997), and Pereira

Table 2  
Methanol, ethanol average concentrations and ethanol-to-methanol ratios results by other study and by this work

Site	Year	MeOH conc. (ppbv)	EtOH conc. (ppbv)	EtOH/MeOH	Note	Ref.
The US						
Los Angeles	1993		0.7			Grosjean et al. (1998)
California	1996		3–5			Grosjean et al. (1998)
Boulder	1991			0.7 <sup>a,b</sup>	Summer	Goldan et al. (1995b)
Nationwide	1985			1.0 <sup>a,b</sup>	Winter	Goldan et al. (1995b)
Alabama	1990	12.1	1.7	0.1 <sup>a</sup>	Summer	Goldan et al. (1995a)
Australia (Victoria)	1997			0.5–0.9 <sup>a,b</sup>	Summer (from grass and clovers)	Kirstine et al. (1998)
Germany (Wank)	1995	2.25	0.25	0.11 <sup>a</sup>	Summer	Leibrock and Slemr (1997)
Japan (Osaka)	1997	7.0	6.6	0.9	Summer	
		3.6	8.5	2.4	Winter	This work
Brazil						
Sao Paulo	1998	34.1	176.3	5.2	Summer	This work
	1990		180, 200, 300,310			Grosjean et al. (1998)
	1990		1080–1440		Tunnel	Grosjean et al. (1998)
	Not mentioned	19.6	36.2	1.9 <sup>a</sup>		Pereira et al. (1999)
Porto Alegre	1996–1997		0.4–68.2			Grosjean et al. (1998)
Salvador	Not mentioned	9.8	65.4	6.7 <sup>a</sup>		Pereira et al. (1999)
Rio de Janeiro	Not mentioned	14.0	66.4	4.7 <sup>a</sup>		Pereira et al. (1999)

<sup>a</sup> The values EtOH/MeOH for the literatures cited was calculated in this work.

<sup>b</sup> This value was deduced from the emission strength of EtOH and MeOH reported in the literature.

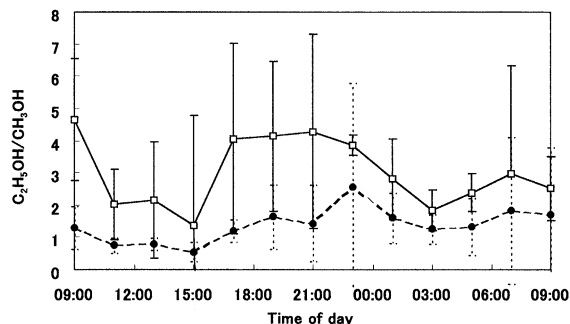


Fig. 2. (A)  $C_2H_5OH$ -to- $CH_3OH$  ratio related to time of day and season, Osaka (1997) (—●—). Summer: average of measurement results from June to August (—□—). Winter: average of measurement results from October to December. Error bars indicate 1 SDV of average ratios.

et al. (1999). In general, the ratios for summer are lower than those of winter based on all the reports. The ethanol-to-methanol ratios in Japan, Germany, and the United States were from 0.1 to 1.0. In this study, the ethanol-to-methanol ratio measured in Sao Paulo, Brazil, was 5.2, about 4–5 times higher than those measured in other places around the world. It should be noted that ethanol-to-methanol ratio of 5.2 in Brazil was measured in the daytime of summer, the season of the high methanol emissions from plants. The ethanol-to-methanol ratio from the study of Pereira et al. (1999), for the three largest cities in Brazil were also rather high, up to 6.7 for Salvador. This reflects the important role of the emission source of alcohol from alcohol-fueled vehicles in Brazil compared to the emission from biological sources.

### 3.5. Ambient concentrations of aldehydes

The increase in the ambient aldehydes is paid more attention than their parent alcohols because aldehydes are more reactive than alcohols. Therefore, it is important to examine the differences in ambient aldehyde concentration due to ethanol-fueled use.

It was reported that  $C_{18}$  cartridges have interferences at a high concentration of ozone (Arnts and Tejada, 1989; Kleindienst et al., 1998). Therefore, in this study, the DNPH-silica gel cartridges but not the  $C_{18}$  cartridges were used for the aldehyde measurements. Moreover, the ozone concentrations at the sampling sites were usually less than 60 ppbv. The available ozone measured results in two weeks from late July to early August in Osaka were usually less than 120 ppbv. In the winter, the ozone concentrations were much lower. According to report of the CETESB, Sao Paulo-1998, the annual averages of 1-h maximal ozone concentrations were always less than 60 ppbv

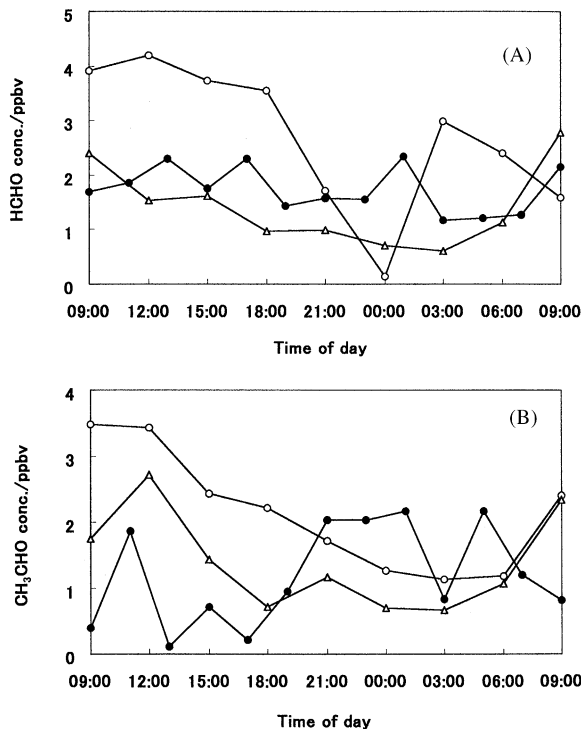


Fig. 3. Diurnal variations of atmospheric HCHO (A) and  $CH_3CHO$  (B) concentrations measured in Osaka, Japan (1997). (—●—) 15–16 October (—○—) 20–21 November (—△—) 17–18 December.

(from 1982 to 1997 data). Therefore, in total, the ozone interference with the formaldehyde measurements is negligible.

The ambient concentrations of aldehydes measured in Osaka, Japan, on 15–16 October, 20–21 November, and 17–18 December are shown in Fig. 3. The atmospheric formaldehyde concentrations were 0.1–4.3 ppbv with an average of  $1.9 \pm 0.9$  ppbv, and the acetaldehyde concentrations were 0.6–3.5 ppbv with an average of  $1.5 \pm 0.8$  ppbv. Propanal concentrations measured in Osaka ranged from 0.1 to 0.5 ppbv (not shown).

The diurnal variations of aldehydes measured in Osaka have the same tendency as been shown and discussed in other studies (Anderson et al., 1996; Possanzini et al., 1996). The aldehyde concentrations began to rise early in the morning (05:00–06:00) due to atmospheric reactions of alkenes and alkanes and showed maxima corresponding to the 09:00–13:00 period when the vehicle emission increased and then decreased from before sunset when the solar radiation started decreasing due to the reaction of aldehydes with hydroxyl radicals. Formaldehyde showed a slower decreased tendency than acetaldehyde due to the lower reaction rate with hydroxyl radical of the former than the latter. The aldehyde concentrations decreased in the

Table 3  
Aldehydes concentration (ppbv) measured in Sao Paulo, Brazil (1998). Values are shown with one standard deviation

Date	Time	HCHO	CH <sub>3</sub> CHO	CH <sub>3</sub> CHO/HCHO	C <sub>2</sub> H <sub>5</sub> CHO
Feb-03	09:50	4.8 ± 0.3	5.9 ± 0.4	1.2	0.7 ± 0.03
	11:25	9.7 ± 0.1	10.2 ± 1.0	1.1	1.4 ± 0.1
	14:20	5.0 ± 0.3	5.5 ± 0.4	1.1	0.8 ± 0.03
	16:30	8.3 ± 0.1	7.0 ± 0.5	0.8	0.8 ± 0.3
Feb-04	09:00	6.1 ± 0.2	7.0 ± 0.3	1.2	0.8 ± 0.2
	10:40	3.1 ± 0.8	3.5 ± 1.1	1.1	0.4 ± 0.2
Feb-05	10:30	5.7 ± 2.2	6.0 ± 1.9	1.1	0.5 ± 0.1
	12:01	4.3 ± 2.7	4.8 ± 2.7	1.1	0.7 ± 0.4
	13:31	4.6 ± 1.3	4.8 ± 2.6	1.0	0.3 ± 0.1
	15:21	2.1 ± 1.1	3.9 ± 2.3	1.8	0.5 ± 0.1
Feb-09	14:50	1.4 ± 0.1	1.0 ± 0.2	0.7	0.1 ± 0.1

nighttime at 20:00–23:00 by the reaction of aldehydes with nitrate radicals.

The average concentrations of formaldehyde and acetaldehyde measured in the summer in Sakai, Osaka, near heavy traffic were 7.5 and 3.8 ppbv, respectively (unpublished data) as shown in Table 4.

Table 3 lists the concentrations of aldehydes measured in Sao Paulo, Brazil. For every measurement, 2–4 sep-pak cartridges were used for simultaneously collecting the samples and the measured results shown in Table 3 are average of these with one standard deviation. The formaldehyde and acetaldehyde concentrations were 1.4–9.7 ppbv with an average of  $5.0 \pm 2.8$  ppbv and 1.0–10.2 ppbv with an average of  $5.4 \pm 2.8$  ppbv, respectively. The atmospheric propanal concentrations measured in Sao Paulo ranged from 0.1 to 1.4 ppbv.

Table 4 lists the aldehyde concentrations by this study and concentrations reported in the literature for different sites around the world (Ferrari et al., 1999; Gaffney et al., 1997; Grosjean et al., 1990, 1988, 1982; Komazaki et al., 1999; Possanzini et al., 1996; Tanner et al., 1988). The aldehyde concentrations in Brazil were not very high when compared to those measured at other places around the world. The range of aldehyde concentrations is rather wide, from about 1 ppbv to more than 10 ppbv. The ratio of acetaldehyde-to-formaldehyde has been paid much attention in other studies (Gaffney et al., 1997; Grosjean et al., 1990). The acetaldehyde-to-formaldehyde ratios can be used as a measure of the anthropogenic to natural sources in the atmosphere (Gaffney et al., 1997; Grosjean et al., 1990). It is expected that the emission of acetaldehyde by the incomplete combustion of ethanol lead to an increase in the acetaldehyde-to-formaldehyde ratios due to the use of ethanol-fueled vehicles (Gaffney et al., 1997; Grosjean et al., 1990, 1988, 1982; Tanner et al., 1988). It was reported that ethanol-fueled vehicles emit much more acetaldehyde than formaldehyde (Grosjean et al., 1990).

The acetaldehyde-to-formaldehyde ratios based on the measurements in Brazil are listed in Table 3. The average ratios obtained from this study and results reported by literature are shown in Table 4. In general, the ratio ranges from 0.3 to 0.8 (lower than 1) for all measurements of aldehydes around the world, except those in Brazil. For almost all the literature values, the acetaldehyde-to-formaldehyde ratios measured in Brazil were greater than 1. This is a further indication of an anthropogenic source.

### 3.6. Anthropogenic-to-biogenic ratio

In this study, the ethanol-to-methanol ratio was used to express anthropogenic-to-biogenic. In the literatures, acetaldehyde-to-formaldehyde ratio has been considered as the anthropogenic-to-biogenic ratio.

Comparing the ratios of acetaldehyde-to-formaldehyde and ethanol-to-methanol, it was found that the ethanol-to-methanol ratios are similar to the acetaldehyde-to-formaldehyde ratios from most measurements around the world (Tables 2 and 4). However, the ethanol-to-methanol ratios are much higher than the acetaldehyde-to-formaldehyde ratios in Brazil. The highest reported ratio of acetaldehyde-to-formaldehyde was 3.4 for Brazil (Grosjean et al., 1990) while the ethanol-to-methanol maximum ratio was 8.2 in this study (Table 1), and 6.7 by Pereira et al. (1999). In summer, the ethanol-to-methanol ratio measured in Sao Paulo was more than five times higher than those measured in Osaka while the acetaldehyde-to-formaldehyde ratio in Sao Paulo was 1.5 times as high as that in Osaka.

Aldehydes are so reactive and their reactions in the atmosphere are very complicated. Thus, the acetaldehyde-to-formaldehyde ratio can change depending upon the detailed chemistry. Aldehydes react with hydroxyl radical, and photolyzed rapidly. Reaction rate of OH

Table 4  
Average concentrations of formaldehyde, acetaldehyde and acetaldehyde-to-formaldehyde ratios results by other studies and by this work

Site	Year	HCHO conc. (ppbv)	CH <sub>3</sub> CHO conc. (ppbv)	CH <sub>3</sub> CHO /HCHO	Note	Ref.
The US						
Los Angeles	1980	11–39	3–24	0.5		Grosjean et al. (1982)
Claremont	1985	6.1	5.0	0.8	Day	Grosjean et al. (1988)
		3.8	2.8	0.7	Night	
Denver's	1991	2.71	1.43	0.5	Summer	Anderson et al. (1996)
		3.92	1.64	0.4	Winter	
		0.94	0.77	0.8	Summer	
Germany (Wank)	1995	17.0	9.3	0.6	Summer	Leibrock and Slemr (1997)
Italy (Rome)	1994	11.2	4.6	0.4	Winter	Possanzini et al. (1996)
		5.6	1.5	0.3	Autumn	
France (Creteil campus)	1993–1995	13.9	6.6	0.5	Summer	Ferrari et al. (1999)
New Mexico		3.2–16.8	1.4–7.3	0.4	Winter	Gaffney et al. (1997)
		1.9	1.5	0.8	Winter	
Japan Osaka	1997	7.5	3.8	0.5	Summer	This work
Kawasaki	1997	7.7	4.1	0.5	Winter	Komazaki et al. (1999)
Brazil						
Sao Paulo	1998	5.0	5.4	1.1	Summer	This work
		3.5–19.3	1.8–18.0	0.8–3.4		
Salvador	1988	2.3–26	9.2–35	2.2–2.3		Grosjean et al. (1990)
Rio de Janeiro	1985	15.0	17.3	1.2		Tanner et al. (1988)

with acetaldehyde is larger than that of OH with formaldehyde. This makes the loss rate due to OH reaction of acetaldehyde higher than that of formaldehyde. However, aldehydes photolyze fairly rapidly, especially in the summertime, and photolysis of formaldehyde is much more intense than that of acetaldehyde, the photodissociation coefficient of formaldehyde is higher than that of acetaldehyde. This factor leads to higher loss rate due to photolysis of formaldehyde than acetaldehyde. In total, the loss of aldehydes in atmosphere in summer can be considered as the loss of formaldehyde due to photolysis and loss of acetaldehyde due to the reaction with OH radical. It is not simple to make comparison in the loss rates between formaldehyde and acetaldehyde since they depend on specific condition. Depending on the condition, one may be quickly delighted that the acetaldehyde-to-formaldehyde ratio is high, which is the original result of the use of ethanol fuel.

Since aldehydes are not stable, it is not a good way to use acetaldehyde-to-formaldehyde ratio to express the anthropogenic-to-biogenic ratio. Alcohols are much more stable than aldehydes. As presented in the earlier section, ethanol-to-methanol ratio is higher in the winter than in the summer, higher in urban areas than in rural areas corresponding to the higher emission of methanol from plants in the summer than winter and rural than urban areas. The ethanol-to-methanol ratio might be able to express the anthropogenic-to-biogenic ratio and the effect of ethanol-blended-fuel use better than the acetaldehyde-to-formaldehyde ratio does.

In conclusion, in Sao Paulo, Brazil, the use of ethanol-fueled vehicle leads to the high concentrations of ethanol, and high ratio of ethanol-to-methanol. The ethanol-to-methanol ratio is used to show anthropogenic-to-biogenic ratio.

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