Ambient Concentrations of Ethanol and Methyl tert-Butyl Ether in Porto Alegre, Brazil, March 1996–April 1997

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · FEBRUARY 1998

Impact Factor: 5.33 · DOI: 10.1021/es970788u

Environ. Sci. Technol. **1998**, *32,* 736−742

Ambient Concentrations of Ethanol and Methyl *tert*-Butyl Ether in Porto Alegre, Brazil, March 1996−April 1997

E. GROSJEAN,† D. GROSJEAN,*,† R. GUNAWARDENA,‡ AND R. A. RASMUSSEN‡

DGA, Inc., 4526 Telephone Road, Suite 205, Ventura, California 93003-5633, and Department of Environmental Science and Engineering, Oregon Graduate Institute of Science and Technology, P.O. Box 91000, Portland, Oregon 97291-1000

While air quality and other perceived benefits of oxygenated fuel programs are currently the topic of much debate, there are very few reports of ambient concentrations of oxygenated fuels (e.g., ethanol) and fuel additives (e.g., ethanol, methyl *tert*-butyl ether, hereafter called MTBE) in urban air. Ambient concentrations of MTBE and ethanol have been measured by GC−FID and GC−MS analysis of samples collected in electropolished canisters at a downtown location in Porto Alegre, Brazil, where 17% of the vehicles run on ethanol, 74% run on a mixture of 85% gasoline and 15% MTBE, and 9% use diesel fuel. During the ca. 1-year period of March 20, 1996−April 16, 1997, ambient levels of MTBE ranged from 0.2 to 17.1 ppbv (average = 6.6 ± 4.3 ppbv); those of ethanol ranged from 0.4 to 68.2 ppbv (average = 12.1 ± 13.3 ppbv). Ambient levels of ethanol and MTBE are compared to those of carbon monoxide (for which vehicle exhaust accounts for ca. 99% of total emissions in the city of Porto Alegre) and of acetylene. Linear regression of the ambient concentration data (44 samples) yielded near-zero intercepts and slopes of 11.40 ± 0.45 for acetylene (ppbv) vs CO (ppmv), 1.73 ± 0.20 for MTBE (ppbv) vs CO (ppmv), 0.153 ± 0.016 for MTBE (ppbv) vs acetylene (ppbv), and 4.64 ± 0.78 for ethanol (ppbv) vs CO (ppmv). These slopes together with an estimated vehicle exhaust emission rate for CO in mid-1996 are used to estimate vehicle emission rates of 2338 ± 393 t/year for ethanol and 1668 ± 193 t/year for MTBE.

Introduction

We report ambient concentrations of ethanol (CH_3CH_2OH) and methyl *tert*-butyl ether [2-methoxy-2-methyl propane, $CH_3OC(CH_3)_3$, hereafter called MTBE] in Porto Alegre, Brazil, during the ca. 1-year period of March 20, 1996−April 16, 1997. Porto Alegre (latitude 30°02′ S, longitude 51°14′ W, elevation 10 m, city population = 1.3 million, metropolitan area population = 3.2 million) is the capital of Rio Grande do Sul, the southernmost state in Brazil. The combination of vehicle fuels used in Porto Alegre is unique in the world. There are ca. 600 000 vehicles of which ca. 74% are light-duty vehicles that use a mixture of 85% gasoline and 15% MTBE, ca. 17% are light-duty vehicles that use ethanol, and ca. 9% (buses and trucks) that use diesel fuel (*1*). Cars that run on ethanol were introduced ca. 20 years ago when Brazil, to reduce oil imports and with unfavorable sugar prices on the world market, initiated a large-scale program to produce ethanol from sugar cane and mandated the use of ethanol as a vehicle fuel (*2, 3*). The ethanol fuel is hydrated ethanol (ca. 5% water) and contains small amounts of gasoline (≤5%). The diesel fuel has a low sulfur content (0.5%) and contains no ethanol and no MTBE. To our knowledge, there are no light-duty vehicles that run on gasoline alone in Brazil: a mixture of 78% gasoline and 22% anhydrous ethanol (E22G78) is currently used in all states but one, i.e., the state of Rio Grande do Sul (including Porto Alegre) where a mixture of 85% gasoline and 15% MTBE is used instead of E22G78. In addition, cars that run on the gasoline−MTBE mixture in Porto Alegre are not different from those sold in the rest of Brazil, i.e., their engines are tuned (fuel/air ratio, etc) to run on E22G78.

While Porto Alegre features a unique combination of vehicle fuels including MTBE and ethanol, considerable attention is also currently being given to MTBE and ethanol as oxygenated fuels worldwide, with focus on their impact on urban air quality. Ethanol, which has long been used in Brazil (*2, 3*) as a fuel and as a fuel additive (currently E22G78), is also used as a fuel additive in a number of states in the United States, where the 1990 Amendments to the Clean Air Act mandate the addition of oxygenates to vehicle fuels (*4*−*7*). MTBE is used as a fuel additive in several states in the United States (where MTBE is a major component of reformulated gasolines), in Mexico (*8*), and in several countries in Europe, e.g., Italy (*9*). Air quality and other benefits of oxygenated fuel programs continue to be the topic of much debate (*4*−*8, 10*−*15*). Perhaps surprisingly considering the widespread use of ethanol and MTBE as oxygenated fuel and fuel additives worldwide, there are very few peer-reviewed or other reports of ambient levels of ethanol, MTBE, or both in urban air (see Results and Discussion). Thus, the database presented in this paper is of value not only with respect to fuel policy and air quality issues in Porto Alegre and in Brazil but also in the more general context of the impact of oxygenated fuels on urban air quality. The results presented here have been obtained as part of a larger study that combines field measurements, smog chamber experiments, and computer kinetic modeling studies of the impact of vehicle emissions on air quality in Porto Alegre (*16*).

Experimental Methods

The sampling station was located a few blocks from the center of town and on a 30 m wide divider strip in the middle of a major highway that brings a large portion of the vehicle traffic—cars, trucks, and buses—to and from the center of Porto Alegre. The monitoring station was also located near a major terminal for interstate and intrastate buses (Rodoviaria).

Samples were collected in 850-mL SUMMA electropolished stainless steel canisters using a FC 1121 pump connected to a purge and tee assembly. The sampling duration was 1 min. The samples were collected during the period of maximum vehicle traffic (typically 8:30 a.m.) as indicated by continuous measurements of ambient CO. Samples were collected ca. once a week from March to July 1996; ca. once every two weeks from August 1996 to February 1997; once a week again from March 20 to April 3, 1997; and

* Corresponding author phone: 805-644-0125; fax: 805-644-0142.
† DGA, Inc.
‡ Oregon Graduate Institute of Science and Technology.

S0013-936X(97)00788-8 CCC: $15.00
Published on Web 02/03/1998

TABLE 1. Ambient Concentrations of MTBE and Ethanol in Downtown Porto Alegre, Brazil, March 20, 1996−April 16, 1997

date (1996−1997)	MTBE (ppbv)	ethanol (ppbv)	date (1996−1997)	MTBE (ppbv)	ethanol (ppbv)
3-20	3.1	9.0	9-12	9.3	28.7
3-27	0.2	15.9	9-25	2.9	3.7
4-4	15.7	46.1	10-9	5.6	8.5
4-10	3.3	5.0	10-23	3.8	7.3
4-17	0.6	3.6	11-9	6.6	8.7
4-24	9.4	12.7	11-20	4.2	7.1
5-2	6.0	16.6	12-4	12.2	19.9
5-8	4.9	0.5	12-18	2.6	3.8
5-15	3.6	7.3	1-17	8.2	3.9
5-22	7.2	18.7	1-21	6.1	2.5
5-29	8.2	13.0	1-29	11.1	6.9
6-5	13.3	26.8	2-14	1.2	0.7
6-12	9.9	20.5	2-19	12.4	2.2
6-19	4.6	10.1	3-20	7.6	3.0
6-26	4.9	12.1	3-27	2.1	0.4
7-3	2.1	2.1	4-3	9.1	4.5
7-10	1.8	1.7	4-8	9.9	no data
7-17	5.8	7.7	4-9	5.7	15.2
7-24	15.6	10.3	4-10	3.0	11.7
7-31	4.5	2.5	4-14	9.7	31.2
8-14	1.9	2.2	4-15	17.1	68.2
8-28	2.8	6.5	4-16	9.2	31.8

on three consecutive days April 8−10 and April 14−16, 1997. The canisters were pressurized to ca. 30 psig and returned to the laboratory for analysis by gas chromatography with flame ionization detection (GC−FID) and by gas chromatography−mass spectrometry (GC−MS). The methods are described in detail elsewhere (*16*, *17*) and follow U.S. EPA guidelines. MTBE was measured by GC-FID, and ethanol was measured by GC−MS. GC−FID analyses are carried out using a HP5890A gas chromatograph and a HP5980 flame ionization detector. Aliquots of air from the canister samples are loaded on a cryotrap (glass beads in 6 in. × 1/8 in. stainless steel tubing) at liquid oxygen temperature, desorbed from the cryotrap at ca. 90 °C, and injected onto the head of the GC column where the sample is cryofocused at −60 °C. The volume of sample loaded on the cryotrap depends on the total concentration, which is predetermined by analysis of the sample using EPA method TO-12 (the optimal mass loading for analysis is ca. 1.5 μg). GC−FID analysis involves the use of a DB-1 capillary column, 60 m long × 0.25 mm diameter × 1.0 mm thickness. The temperature is programmed according to the following sequence: −60 °C for 5 min and −60 °C to +200 °C at ca. 4 °C/min. GC−MS analyses are carried out using a HP5890A gas chromatograph and a HP5970 mass selective detector. The sample loading procedure, the capillary column, and the operating conditions are essentially the same as those described above for GC-FID analysis. Data acquisition involves the use of a HP 9000/300 computer with HP 59970 MS ChemStation software, and the mass spectral libraries used for compound identification include the NIST Database and the NIST/EPA/MSDC Mass Spectral Database version 2.0. Quantitative analysis involves the use of a primary reference standard (NIST benzene SRM, 254 ppbv) and of a secondary working standard (neohexane, 220 ppbv, daily average of 3 injections are within ±2%). Standards of MTBE and ethanol were used to verify retention time (GC−FID and GC−MS) and compound structure (GC-MS). Comprehensive validation studies of the canister sampling/GC−FID and GC−MS methods, including studies showing that MTBE and ethanol are stable in SUMMA electropolished stainless steel canisters, have been reported previously (*16*−*24*). Under the conditions employed for analysis, both MTBE and ethanol are baseline resolved from closely eluting compounds, i.e., MTBE elutes after 2,3-dimethylbutane and before 2-methylpentane and ethanol elutes after 3-methyl-1-butene and before 2-methylbutane. For a sample size of ca. 1.5 μg (determined by screening using the TO-12 method), analytical detection limits correspond to ambient air detection limits of 0.1 ppbv (0.36 μg m^{-3}) for MTBE and 0.4 ppbv (0.75 μg m^{-3}) for ethanol.

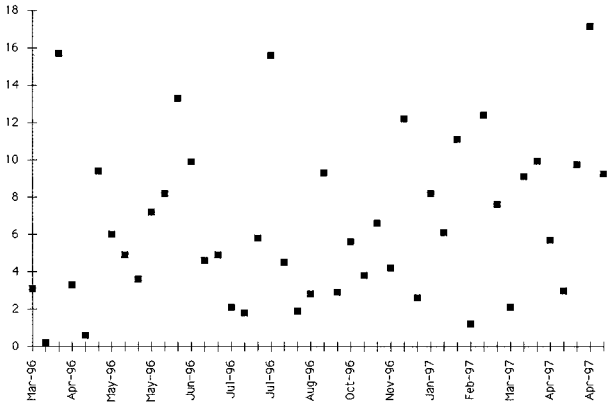

FIGURE 1. Time series plot of ambient concentrations of MTBE (ppbv) from 44 samples collected at a downtown Porto Alegre, RS, Brazil, location from March 20, 1996 to April 16, 1997.

Results and Discussion

Ambient Concentrations of Ethanol and MTBE. Listed in Table 1 are the ambient concentrations of ethanol and MTBE measured from March 20, 1996 to April 16, 1997, at a downtown location (Rodoviaria) in Porto Alegre, RS, Brazil. Ambient concentrations of ethanol ranged from 0.4 to 68.2 ppbv; those of MTBE ranged from 0.2 to 17.1 ppbv ("concentrations" reported in units of ppbv, as is the case in this section, are mixing ratios). During the ca. 1-year period studied (and with the caveat that the sampling frequency changed several times during that period, see Experimental Methods), ambient concentrations of ethanol averaged 12.1 ± 13.3 ppbv, those of MTBE averaged 6.6 ± 4.3 ppbv, and the average ethanol/MTBE concentration ratio was 1.83. On a ppbC basis, i.e., in units typically used for computer kinetic modeling, ethanol and MTBE averaged 24.2 and 33.0 ppbC, respectively, and the average ethanol/MTBE concentration ratio was 0.73. On a mass concentration basis relevant to human exposure, ethanol averaged 22.7 μg m^{-3}, MTBE averaged 23.8 μg m^{-3}, and the average ethanol/MTBE concentration ratio was 0.95. Thus, ambient concentrations of ethanol and MTBE are roughly of the same magnitude (average ethanol/MTBE concentration ratios of 1.83, 0.73, and 0.95 in units of ppbv, ppbC, and μg m^{-3}, respectively). This observation is not inconsistent with fleet data given in the Introduction, i.e., 17% of the vehicles run on ethanol (which contains ≤5% gasoline) and 74% of the vehicles run on a mixture of 85% gasoline and 15% MTBE (compare 0.17 × 0.95 = 0.162 for ethanol to 0.74 × 0.15 = 0.111 for MTBE). A more detailed discussion of ambient concentrations of ethanol and MTBE vs vehicle emissions is presented in the next section.

Examination of scatterplots of the data in Table 1 versus sampling date (shown in Figure 1 for MTBE) did not indicate seasonal variations in the ambient concentrations of ethanol and MTBE. Such seasonal variations, if they exist, may have been difficult to observe from the present data for two reasons. First, the sampling frequency was not constant during the 1-year period studied. Second, the amplitude of the seasonal variations may be less than the day-to-day differences in ambient concentrations of ethanol and MTBE (e.g., compare data for April 6−8 and for April 14−16, 1997). Such day-to-day differences reflect day-to-day changes in

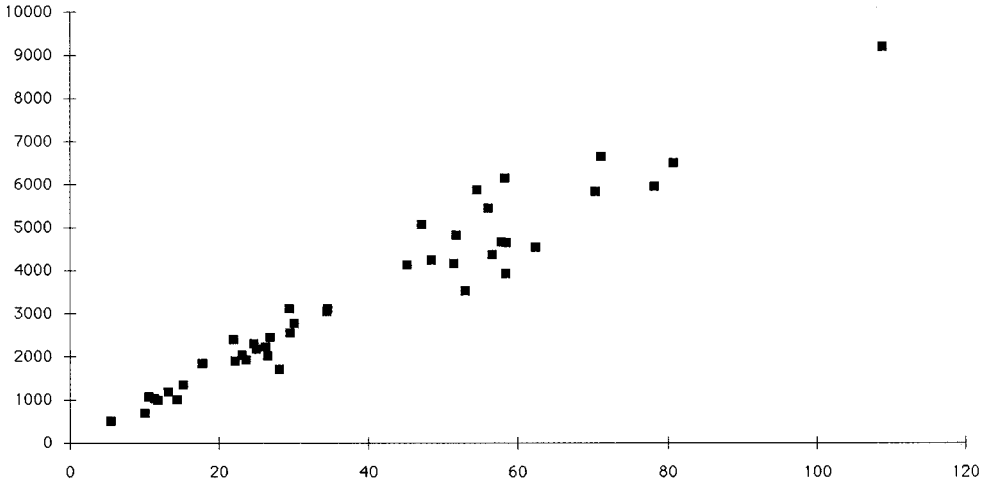

FIGURE 2. Scatterplot of ambient CO (ppbv) vs ambient acetylene (ppbv). Linear regression parameters are given in Table 2.

TABLE 2. Summary of Linear Regression Parameters for Correlations between Ambient Levels of Ethanol and MTBE and Those of CO and Acetylene

y[a]	*x*[a]	slope[b]	intercept[b]	*R*
acetylene	CO	11.40 ± 0.45	0.69 ± 1.74	0.969
CO	acetylene	0.0824 ± 0.0033	0.149 ± 0.146	0.969
MTBE	CO	1.73 ± 0.20	0.79 ± 0.78	0.799
ethanol	CO	4.64 ± 0.78	3.12 ± 2.96	0.683
MTBE	acetylene	0.153 ± 0.016	0.64 ± 0.71	0.831
ethanol	acetylene	0.401 ± 0.063	3.25 ± 2.84	0.702

[a] Data for 44 samples collected at a downtown Porto Alegre location (Rodoviaria) from March 20, 1996 to April 16, 1997. Concentration units are ppmv for CO and ppbv for ethanol, MTBE, and acetylene. [b] Unit-weighted linear least-squares regressions, slope, and intercept ± 1 STD. Intercept units are ppmv for CO and ppbv for ethanol, MTBE, and acetylene.

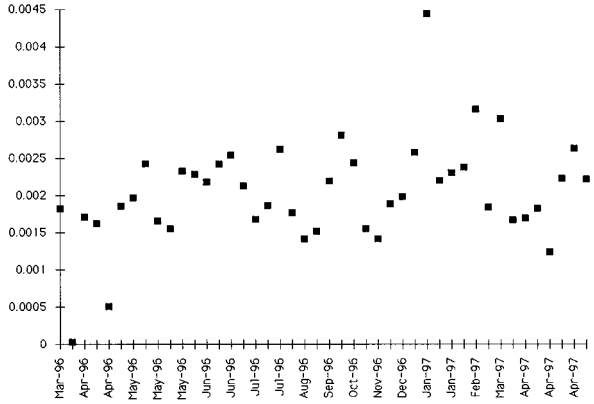

FIGURE 3. Time series plot of the MTBE/CO concentration ratio (ppbv/ppbv), Porto Alegre, March 20, 1996−April 16, 1997.

meteorology and in vehicle traffic density in the vicinity of the sampling location.

Ambient Concentrations of Ethanol and MTBE vs Vehicle Emissions. Air quality in downtown Porto Alegre is strongly influenced by vehicle emissions: a recent emission inventory for carbon monoxide indicates that vehicle exhaust contributes 98.9% of the total city-wide CO emissions (*1*). The ambient CO concentrations we measured (along with ethanol and MTBE) at the downtown location ranged from 987 to 9186 ppbv and averaged 3339 ± 1970 ppbv (March 20, 1996 to April 16, 1997, $n = 44$). In contrast, CO concentrations we measured in two samples collected at a "background" location some 30 km southeast of Porto Alegre (and upwind of the city on the days of sample collection) were 78 (November 27, 1996) and 100 ppbv (November 28, 1996). The concentrations of ethanol and of MTBE measured in these two samples were below detection (≤0.4 ppbv for ethanol and ≤0.1 ppbv for MTBE). Thus, ambient levels of CO, ethanol, and MTBE in downtown Porto Alegre are much higher than those measured at the background location. As noted above, ambient levels of CO reflect vehicle emissions. The contributions of vehicle emissions to ambient levels of ethanol and MTBE are examined below.

Vehicle emissions include exhaust and evaporative emissions. Compounds that are not present in the fuel but are present in the exhaust, for example, CO and acetylene, can be used as indicators of vehicle exhaust emissions. As is shown in Figure 2, ambient concentrations of CO and those of acetylene in downtown Porto Alegre correlate well (*16*), with near-zero intercepts (Table 2) whose numerical values are comparable to the concentrations of CO and acetylene measured at background locations relevant to the geographical location of Porto Alegre (southern hemisphere, marine and/or coastal Atlantic Ocean locations, see ref *25*). Thus, it appears legitimate to use both CO and acetylene as indicators of vehicle exhaust emissions. A time series plot of the MTBE/CO ambient concentration ratios (Figure 3; a similar plot, not shown, was constructed for the MTBE/acetylene ratio) indicates that the MTBE/CO ratio was fairly constant during the 1-year period studied, and this even though MTBE is emitted by only one type of vehicles (those fueled with the gasoline−MTBE mixture) whereas CO is emitted by vehicles that use all three fuels (ethanol, gasoline−MTBE, and diesel). Linear regression of the data (MTBE vs CO, MTBE vs acetylene, ethanol vs CO, and ethanol vs acetylene) yielded the slopes, intercepts, and correlation coefficients that are listed in Table 2. The corresponding scatterplots are shown in Figures 4−7. While MTBE correlates reasonably well with CO (Figure 4) and with acetylene (Figure 5), there is more scatter in these correlations than is the case for the correlation of acetylene vs CO (Table 2). This observation is consistent with the fact that the percentages of vehicles that use gasoline + MTBE, ethanol, or diesel (of which only those using gasoline + MTBE emit MTBE) in the vicinity of the sampling location are likely to vary from one sample to the next. The correlations of ethanol vs CO (Figure 6) and ethanol vs acetylene (Figure 7) show substantially more scatter than those for MTBE (Table 2). This observation suggests (sample-to-sample variations in percentages of gasoline−MTBE, ethanol, and diesel vehicles notwithstanding) that exhaust emissions of unburned ethanol may be accompanied by substantial evaporative emissions, for which neither CO nor acetylene can be used as indicators. Evaporative emissions of ethanol from light-duty vehicles that run

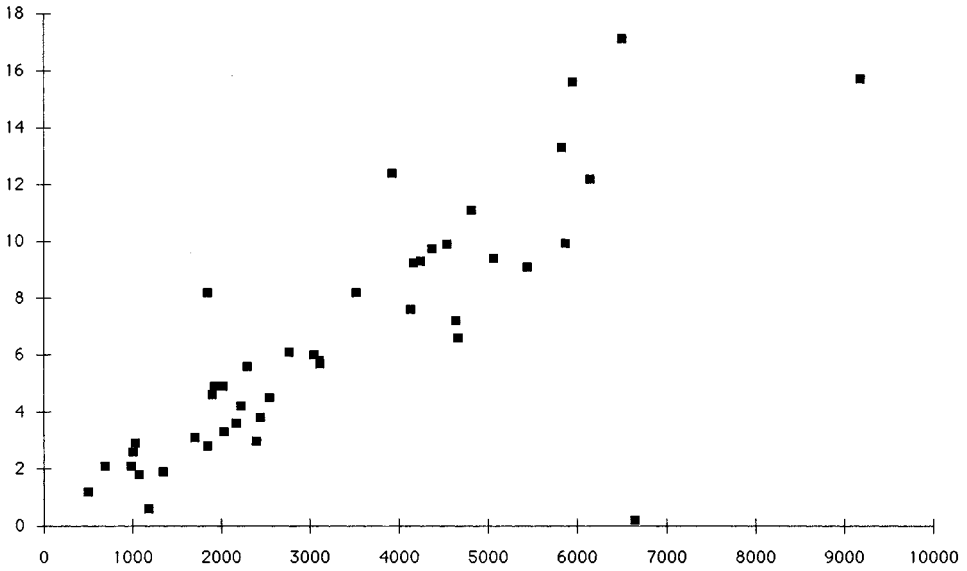

FIGURE 4. Scatterplot of ambient MTBE (ppbv) vs ambient CO (ppbv). Linear regression parameters for this scatterplot and those shown in Figures 5−7 are given in Table 2.

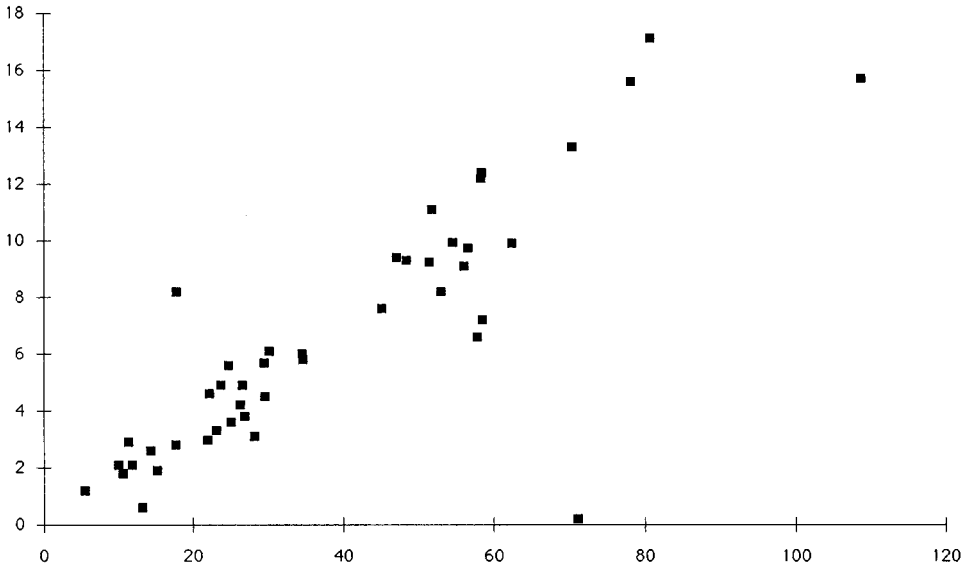

FIGURE 5. Scatterplot of ambient MTBE (ppbv) vs ambient acetylene (ppbv).

on ethanol have received attention in Sao Paulo, Brazil (*26*), where ca. 28% of the vehicles run on ethanol and where high ambient concentrations of ethanol have been measured within the metropolitan area (*27*), see discussion below.

Comparison with Literature Data for Other Locations. Little information is available regarding concentrations of ethanol and MTBE at urban locations other than Porto Alegre, and much of this information is not available in peer-reviewed form. For ethanol, reported concentrations include 0.7 ppbv in downtown Los Angeles in 1993, i.e., prior to the introduction of reformulated gasolines (R. A. Rasmussen, unpublished data) and 3−5 ppbv at four southern California locations in 1996 (*28*), i.e., after the introduction of California Phase II reformulated gasolines, which in southern California include MTBE (not ethanol) as the oxygenated additive. These low values compare to the high ambient ethanol concentrations reported in Sao Paulo, Brazil, where measurements were made in 1990 at two locations (*27*). With a detection limit of 80 ppbv (note that this limit of detection is higher than the highest ambient concentration of ethanol we measured in Porto Alegre, i.e., 68.2 ppbv), ethanol was observed in 21% of the samples collected at one location (Mooca, reported concentrations = 180, 200, 300, and 310 ppbv) and in 83% of the samples collected at the other location (Cerqueiro Cesar), where the highest and second highest concentrations were 2260 and 1900 ppbv. In addition, five samples collected in a Sao Paulo tunnel yielded ethanol concentrations of 1080−1440 ppbv (*27*). For MTBE, ambient levels include low values (<1 ppbv) at several locations in the United States (R. A. Rasmussen, unpublished data): Cape Cod, 39−201 pptv (four samples, July−August 1995); Shenandoah National Park, ≤7 pptv (14 samples, July−August 1995), Brookhaven, 33−416 pptv (16 samples, July−August 1995), and Wisconsin, ≤177 pptv (62 samples, August 1994−December 1996, with all but five samples yielding no detectable MTBE with a detection limit of 12 pptv). In California, where urban levels of MTBE were probably low prior to the introduction of MTBE-containing reformulated gasolines (e.g., 0.8 ppbv in a sample collected in 1993 in downtown Los Angeles, R. A. Rasmussen, unpublished data), higher concentrations have been measured in recent years, reflecting the use of MTBE as an oxygenated fuel additive. The results of two recent (1995−1996) monitoring surveys (*28, 29*) indicate that ambient levels of MTBE (Table 3) averaged 0.6−7.2 ppbv at four southern

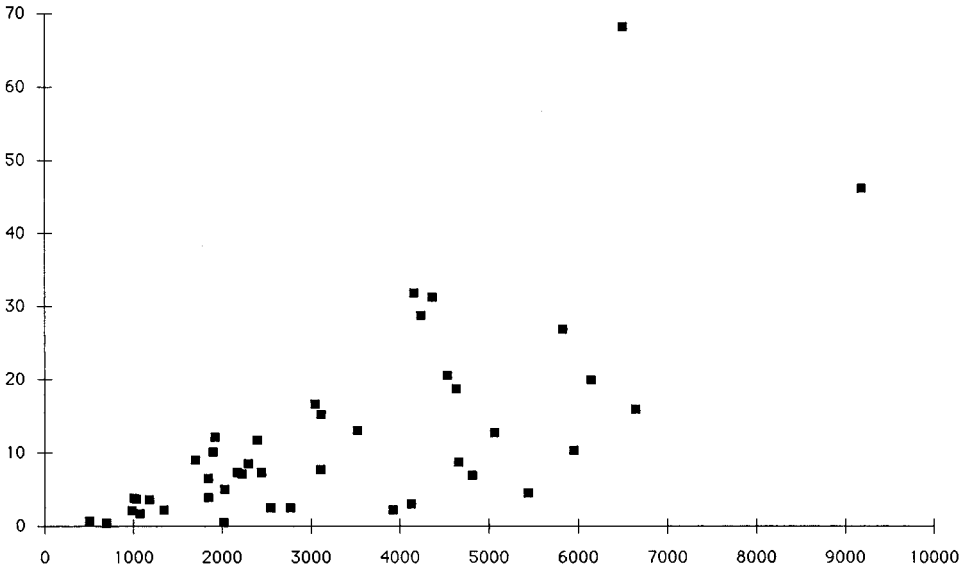

FIGURE 6. Scatterplot of ambient ethanol (ppbv) vs ambient CO (ppbv).

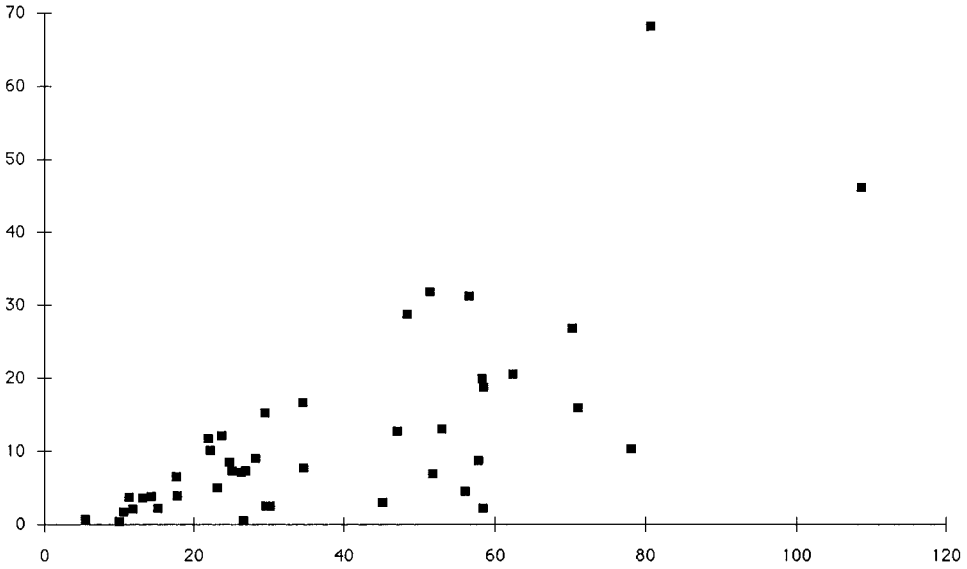

FIGURE 7. Scatterplot of ambient ethanol (ppbv) vs ambient acetylene (ppbv).

California locations (sampling duration = 3 h) and 1.3−4.8 ppbv at seven California locations (sampling duration = 24 h). More information on ambient levels of MTBE in California should soon become available, e.g., from a continuation of the monitoring study described in ref *29* (M. Poore, personal communication, 1997) and from measurements made as part of the 1997 Southern California Ozone Study (*30*).

Photochemical Considerations. Once emitted into urban air, ethanol and MTBE are expected to be oxidized in reactions initiated by their reaction with the hydroxyl radical. The oxidation of ethanol (*31* and references cited therein) leads to acetaldehyde and subsequently to peroxyacetyl nitrate (PAN) and to formaldehyde, depending on the NO_2/NO ratio and on temperature. The oxidation of MTBE leads to *tert*-butyl formate, formaldehyde, and methyl acetate (*32*−*34*). The average concentrations measured in this study, when multiplied by the oxygenate-OH reaction rate constant or by Carter's (*35*) maximum incremental reactivity (MIR) coefficient, indicate that ethanol is more important than MTBE, and this by a factor of ca. 1.5, with respect to removal of OH and production of ozone in Porto Alegre. This observation is of interest considering that only 17% of the vehicles in Porto Alegre run on ethanol (*1*). However, as discussed in detail elsewhere (*16*), neither ethanol nor MTBE are major contributors to photochemical reactions in Porto Alegre, where the overall reactivity (removal of OH and formation of ozone) is dominated by several alkenes, alkylbenzenes, CO, acetaldehyde, and formaldehyde (*16*). Reactivity ranking calculations show a negligible role for MTBE in Porto Alegre, and ethanol typically ranks 10−15 among reactive VOC (*16, 36*). Emissions of acetaldehyde rather than emissions of unburned ethanol probably constitute the major contribution of ethanol-fueled vehicles to photochemical precursors of ozone in Porto Alegre air (*16, 25, 36*).

Estimated Vehicle Emissions of Ethanol and MTBE in Porto Alegre. Since vehicles account for 98.9% of the total CO emissions in the city of Porto Alegre (*1*) and since ethanol and MTBE are also emitted by vehicles as discussed in the preceding sections, it is possible to estimate emission rates for ethanol and MTBE in Porto Alegre using the emission rate for CO and the average MTBE/CO and ethanol/CO ambient concentration ratios. This approach involves a number of assumptions including the representativeness of the sampling location with respect to city-wide traffic pattern, vehicle fleet composition (percentage of ethanol, gasoline−

TABLE 3. Ambient Concentrations of MTBE at California Locations

location	year	sampling duration (h)	MTBE (ppbv) range	MTBE (ppbv) average	ref
Los Angeles	1993	4[a]	0.8		*d*
Azusa	1995[b]	3		4.6 ± 0.3	28
	1996[b]	3		5.8 ± 0.5	28
Burbank	1995[b]	3		6.6 ± 0.5	28
	1996[b]	3		7.2 ± 0.6	28
Los Angeles	1995[b]	3		5.3 ± 0.4	28
	1996[b]	3		6.4 ± 0.5	28
Santa Monica	1995[b]	3		0.9 ± 0.1	28
	1996[b]	3		0.6 ± 0.2	28
Burbank	1996[c]	24	1.3−8.8	4.8	29
Los Angeles	1996[c]	24	1.1−6.9	2.6	29
Long Beach	1996[c]	24	0.9−6.0	2.6	29
Chico	1996[c]	24	1.0−7.7	2.3	29
El Cajon	1996[c]	24	0.4−5.0	2.5	29
Fresno	1996[c]	24	0.6−12.4	2.6	29
Roseville	1996[c]	24	0.7−3.4	1.3	29

[a] Sample collected at night. [b] Samples collected during the summer (June−September) from 6 to 9 a.m. in Azusa, Burbank, and Los Angeles and from 1 to 4 p.m. in Santa Monica. [c] Samples collected from February to October. [d] R. A. Rasmussen, unpublished data.

MTBE, and diesel vehicles), vehicle fleet age, and other factors that influence vehicle emissions.

The only reported vehicle emission rate for CO is that issued by the State of Rio Grande do Sul environmental protection agency for the year 1991 and is 237 781 t/year (*1*). We use this value as the starting point to estimate CO emissions in 1996. To do this, we examine information on vehicle fleet from 1992 to September 1995 (*1*), we use the 1992−1995 average fleet growth per year to estimate the number of vehicles in 1991, we use the incremental increase in the number of vehicles for the 9-month period January−September 1995 as an estimate of the incremental increase for the following 9-month period October 1995−June 1996, and for simplicity we neglect—in the absence of verifiable data—reductions in CO emissions that may accompany the phasing-out of older vehicles and the introduction of newer models (these should presumably emit less CO as a result of recent emission control technology). We also neglect, again in the absence of verifiable data, possible changes from 1991 to mid-1996 in the total number of kilometers driven and in changes in daily, weekly, and seasonal traffic patterns in the Porto Alegre metropolitan area. With these assumptions, the estimated vehicle emission rate for CO in 1996 is the product of the 1991 emission rate and the 1996/1991 ratio in the number of vehicles, i.e., $1.29 \times 237\,781 = 306\,737$ t/year. We multiply this value by the ethanol/CO and MTBE/CO ambient concentration ratios measured in this study, i.e., by the slopes given in Table 2 of the linear regressions for the data shown in Figure 4 for MTBE and Figure 5 for ethanol, and multiply these figures by the appropriate molecular weight ratios. The emission rates thus calculated are 2338 ± 393 t/year for ethanol and 1668 ± 193 t/year for MTBE, where the stated uncertainties are those associated with the slopes of the regressions given in Table 2 (one standard deviation) and, given the number of assumptions made, are lower limits for actual uncertainties on emission rates. These estimates may serve as a guide to construct, in future work, more precise inventories for vehicles emissions of ethanol and MTBE in Porto Alegre.

Acknowledgments

Financial support from Petróleo Brasileiro S. A. (Petrobras) is gratefully acknowledged. We thank Mr. Pacheco Netto, Mr. Ubirajara Soares (FEPAM, Porto Alegre), Mr. Marcos Linck, Mr. Marcelo Lock (Petrobras-REFAP, Canoas), Ms. Ana Maria Cruzat, and Ms. Tatiana Dieter for assistance in field operations and Mr. Don Stearns, Mr. Bob Watkins, Mr. Jim Mohan, and Mr. Bob Dalluge for assistance in sample analysis. We also thank Mr. Hubmaier Andrade, Ms. Ana Maria Machado, Mr. Vincente Schmall (Petrobras, Rio de Janeiro), Mr. Nilce Costa, Mr. Leonardo Souza, and Ms. Andrea Moreira (Petrobras-CENPES, Rio de Janeiro) for technical input and Mr. Michael W. Poore (State of California Air Resources Board, Sacramento, CA) and Dr. Barbara Zielinska (Desert Research Institute, Reno, NV) for discussions of their results. Ms. Brenda A. Brennan prepared the draft and final version of the manuscript. Presented in part as Paper No. 2092, Symposium on Oxygenated Fuels and Urban Air Quality in the Americas, Fifth Chemical Congress of North America, Cancun, Mexico, November 11−15, 1997.

Literature Cited

(1) Fundação Estadual de Proteção Ambiental (FEPAM). *Proposta preliminar de localização dos estações de amostragem da qualidade do ar*; Report. Porto Alegre RS, Brazil, March 1995.
(2) Grosjean, D.; Miguel, A. H.; Tavares, T. M. *Atmos. Environ.* **1990**, *24B*, 101.
(3) Murgel, E. M. *Ambiente* **1987**, *1*, 62 (published by CETESB, Sao Paulo, SP, Brazil).
(4) National Research Council. *Toxicological and performance aspects of oxygenated motor vehicle fuels;* National Academy Press: Washington, DC, 1996.
(5) Ainsworth, S. J. *Chem. Eng. News* **1991**, *June 10*, 13.
(6) Anderson, E. V. *Chem. Eng. News* **1991**, *Sept. 20*, 9.
(7) Reichhardt, T. *Environ Sci. Technol.* **1995**, *29*, 36A.
(8) Bravo, H. A.; Camacho, C. R.; Guadalupe, R. R.; Sosa, E. R.; Torres, J. R. *Atmos. Environ.* **1991**, *25B*, 285.
(9) Possanzini, M.; diPalo, V.; Petricca, M.; Fratarcangeli, R.; Brocco, D. *Atmos. Environ.* **1996**, *22*, 3757.
(10) Calvert, J. G.; Heywood, J. B.; Sawyer, R. F.; Seinfeld, J. H. *Science* **1993**, *261*, 23.
(11) Beaton, S. P.; Bishop, G. A.; Zhang, Y.; Ashbaugh, L. L.; Lawson, D. R.; Stedman, D. H. *Science* **1995**, *268*, 991.
(12) Mannino, D. M.; Etzel, R. A. *J. Air Waste Manage. Assoc.* **1996**, *46*, 20.
(13) Anderson, L. G.; Lanning, J. A.; Barrell, R.; Miyagishima, J.; Jones, R. H.; Wolfe, P. *Atmos. Environ.* **1996**, *30*, 2113.
(14) Squillage, P. J.; Zogorski, J. S.; Wilber, W. G.; Price, C. V. *Environ. Sci. Technol.* **1996**, *30*, 1721.
(15) Zhang, Y.; Stedman, D. H.; Bishop, G. A.; Beaton, S. P.; Guenther, P. L. *Environ. Sci. Technol.* **1996**, *30*, 1445.
(16) Grosjean, E.; Rasmussen, R. A.; Grosjean, D. *Atmos. Environ.* In press.
(17) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A. *Environ. Sci. Technol.* **1997**, *31*, 2356.
(18) Singh, H. B. *Report EPA-450/4-80-008*; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1980.
(19) Oliver, K. D.; Pleil, J. D.; McClenny, W. A. *Atmos. Environ.* **1986**, *20*, 1403.
(20) McClenny, W. A.; Pleil, J. D.; Evans, G. F.; Oliver, K. D.; Holdren, M. W.; Winberry, W. T. *J. Air Waste Manage Assoc.* **1991**, *41*, 1308.
(21) Pate, B.; Jayanty, R. K. M.; Peterson, M.; Evans, G. F. J. *Air Waste Manage. Assoc.* **1992**, *42*, 460.
(22) Apel, E. C.; Calvert, J. G.; Fehsenfeld, F. C. *J. Geophys. Res.* **1994**, *99*, 16651.
(23) Brymer, D. A.; Ogle, L. D.; Jones, C. J.; Lewis, D. L. *Environ. Sci. Technol.* **1996**, *30*, 188.
(24) Zielinska, B.; Sagebiel, J. C.; Harshfield, G.; Gertler, A. W.; Pierson, W. R. *Atmos. Environ.* **1996**, *30*, 2269.
(25) Grosjean, E.; Grosjean, D. *Porto Alegre Air Quality Study. Volume 1: Field Measurements*; Final report prepared for Petróleo Brasileiro S.A. by DGA, Inc., Ventura, CA, 1998.
(26) Companhia de Technologia de Saneamento Ambiental (CETESB). *Relatório de qualidade do ar no Estado de São Paulo-1994*; São Paulo, SP, Brazil, 1995.
(27) Companhia de Technologia de Saneamento Ambiental (CETESB). *Medições de álcoois e aldeídos na atmosphera de São Paulo*; São Paulo, SP, Brazil, Nov 1990.
(28) Zielinska, B.; Shire, J.; Harshfield, G.; Pasek, R. *Paper 97-RP139.06*; 90th Annual Meeting of the Air Waste Management Association Toronto, Canada, June 8−13, 1997.

(29) Poore, M.; Chang, B.; Niyati, F.; Madden, S. *Paper ENVR 215*, 213rd National Meeting of the American Chemical Society, San Francisco, CA, April 13−17, 1997.
(30) Fujita, E. M.; Bowen, J. L.; Green, M. C.; Moosmüller, H. *1997 Southern California Ozone Study (SCOS97) Quality Assurance Plan*; Report prepared for California Air Resources Board, Desert Research Institute, Reno, NV, April 4, 1997.
(31) Grosjean, D. *J. Brazil. Chem. Soc.* In press.
(32) Japar, S. M.; Wallington, T. J.; Richert, J. F. O.; Ball, J. C. *Int. J. Chem. Kinet.* **1990**, *22*, 1257.
(33) Tuazon, E. C.; Carter, W. P. L.; Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1991**, *23*, 1003.
(34) Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; McIver, C. D.; Bufalini, J. J. *Int. J. Chem. Kinet.* **1991**, *23*, 907.
(35) Carter, W. P. L. *J. Air Waste Manage. Assoc.* **1994**, *44*, 881.
(36) Grosjean, E.; Grosjean, D. *J. Brazil. Chem. Soc.* In press.

Received for review September 4, 1997. Revised manuscript received December 10, 1997. Accepted December 13, 1997.

ES970788U