

# Emission and Fate Assessment of Methyl Tertiary Butyl Ether in the Boston Area Airshed Using a Simple Multimedia Box Model: Comparison with Urban Air Measurements

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## ABSTRACT

Expected urban air concentrations of the gasoline additive methyl tertiary butyl ether (MTBE) were calculated using volatile emissions estimates and screening transport models, and these predictions were compared with Boston, MA, area urban air measurements. The total volatile flux of MTBE into the Boston primary metropolitan statistical area (PMSA) airshed was calculated based on estimated automobile nontailpipe emissions and the Universal Quasi-Chemical Functional-Group Activity Coefficient computed abundance of MTBE in gasoline vapor. The fate of MTBE in the Boston PMSA was assessed using both the European Union System for the Evaluation of Substances, which is a steady-state multimedia box model, and a simple airshed box model. Both models were parameterized based on the meteorological conditions observed during air sampling in the Boston area. Measured average urban air concentrations of 0.1 and 1  $\mu\text{g}/\text{m}^3$  MTBE during February and September of 2000, respectively, were comparable to corresponding model predictions of 0.3 and 1

$\mu\text{g}/\text{m}^3$  and could be essentially explained from estimated temperature-dependent volatile emissions rates, observed average wind speed (the airshed flushing rate), and reaction with ambient tropospheric hydroxyl radical ( $\cdot\text{OH}$ ), within model uncertainty. These findings support the proposition that one can estimate gasoline component source fluxes and use simple multimedia models to screen the potential impact of future proposed gasoline additives on urban airsheds.

## INTRODUCTION

Numerous investigators have found that liquid gasoline and gasoline vapor components constitute a substantial portion of tropospheric volatile organic pollutants in the United States.<sup>1</sup> We therefore anticipate that new gasoline additives that are both relatively volatile and abundant in fuel, such as methyl tertiary butyl ether (MTBE), accumulate in urban air to significant concentrations. As part of an effort to control toxic volatile compounds and urban air pollution precursors emitted from motor vehicles, the Clean Air Act Amendments of 1990 mandated 2% by weight oxygen ( $\text{O}_2$ ) addition to fuels in areas affected by the federal Reformulated Gasoline Program (RFG).<sup>2</sup> To fulfill this requirement, MTBE has been added to gasoline in amounts of 10–15% by volume in several metropolitan areas in the United States.<sup>3</sup> Gasolines in much of the New England region have been amended with at least 11% vol/vol MTBE year-round since 1995.<sup>2</sup>

We expect MTBE to constitute a significant portion of fuel vapor, because it is a highly volatile, major fuel component. Therefore, relatively high MTBE concentrations in the urban air of RFG-affected areas and possibly also measurable ambient MTBE concentrations in more remote areas are expected. Tropospheric MTBE concentrations typically in the range of 5–25  $\mu\text{g}/\text{m}^3$  have been

## IMPLICATIONS

Past experiences of serious environmental harm from tetraethyl lead and MTBE demonstrate that methods are needed to estimate, a priori, the likely environmental air and water concentrations of newly proposed gasoline additives. In this paper, it was shown that simple and established modeling concepts could successfully predict Boston-area average atmospheric MTBE concentrations resulting from volatilization of unburned fuel. This approach would allow policy-makers to accurately estimate urban air concentrations of new gasoline additives. Industry and regulators could therefore anticipate and avoid the resulting environmental costs, before new compounds are added to gasoline.

observed in "megalopolis" urban centers, including Mexico City, Mexico (4–29  $\mu\text{g}/\text{m}^3$  in March 1997<sup>4</sup>); downtown Cairo, Egypt (a single measurement of 2.7  $\mu\text{g}/\text{m}^3$  on a morning of June 1997); and Los Angeles and surrounding suburbs, California (17  $\pm$  10  $\mu\text{g}/\text{m}^3$  during the summers of 1995 and 1996<sup>5,6</sup>). Although it is significantly smaller than any of these metropolitan giants, Porto Alegre, Brazil (which is similar in size to Boston, having a population of  $\sim$ 3 million, including suburban districts) had measured ambient MTBE air concentrations of 24  $\pm$  16  $\mu\text{g}/\text{m}^3$ , based on year-round measurements from 1996 to 1997.<sup>7</sup>

MTBE air concentrations in more remote suburbs or mid-sized urban areas are generally lower but range more widely, typically from 0.5 to 10  $\mu\text{g}/\text{m}^3$ , based on measurements conducted in Cape Cod, MA ( $\sim$ 0.4  $\mu\text{g}/\text{m}^3$  in July–August 1995<sup>7</sup>); Providence, RI (median  $\sim$ 1.9  $\mu\text{g}/\text{m}^3$ , maximum 6.8  $\mu\text{g}/\text{m}^3$  year-round in 1997–1998<sup>8</sup>); Brookhaven, NY ( $\sim$ 0.8  $\mu\text{g}/\text{m}^3$  during July–August 1995<sup>7</sup>); Glassboro, NJ (annual median  $\sim$ 0.3  $\mu\text{g}/\text{m}^3$ , maximum 7.9  $\mu\text{g}/\text{m}^3$  from 1996 to 1998<sup>9</sup>); Turnersville and Rowan College, NJ ( $\sim$ 1.6  $\mu\text{g}/\text{m}^3$  from April to December 1997<sup>10</sup>); Chico and Fresno, CA (annual average  $\sim$ 9  $\mu\text{g}/\text{m}^3$ , maximum 45  $\mu\text{g}/\text{m}^3$  in 1995–1996<sup>6</sup>); and Roseville, CA (average  $\sim$ 5  $\mu\text{g}/\text{m}^3$ , maximum 12  $\mu\text{g}/\text{m}^3$  in 1995–1996<sup>6</sup>). In areas that are rural or somewhat removed from high oxygenate-use areas, measured ambient MTBE concentrations may still vary widely, as is evidenced from monitoring in several areas of Vermont (median  $\sim$ 0.1–0.6  $\mu\text{g}/\text{m}^3$ , maximum 2.7  $\mu\text{g}/\text{m}^3$  during the fall months of 1997<sup>8</sup>); and Shenandoah National Park, VA ( $\leq$ 0.03  $\mu\text{g}/\text{m}^3$  during July–August 1995<sup>7</sup>). It is also worth noting that Grosjean et al.<sup>7</sup> observed strong year-round correlations between measured MTBE concentrations and urban air concentrations of other gasoline combustion-related species such as carbon monoxide (CO) ( $r^2 \sim$  0.80) and acetylene ( $r^2 \sim$  0.83), suggesting that MTBE emission rates are strongly linked to total traffic volume.

MTBE is not only volatile but is also relatively soluble in water (Table 1), thereby posing a contamination threat to water supplies from leaking underground fuel tanks and gasoline spills.<sup>11–13</sup> Recent work has shown that a screening approach similar to that proposed here can be used to distinguish gasoline constituents that may cause this problem.<sup>14</sup> Additionally, equilibrium MTBE partitioning between air and water favors accumulation of MTBE in the aqueous phase, especially at decreased temperatures (see Table 1). Following Pankow et al.,<sup>15</sup> Baehr and coworkers<sup>9,16</sup> investigated the possibility that atmospheric MTBE could result in low-level contamination of shallow groundwater in urban areas. In southern New Jersey, Baehr et al.<sup>9,16</sup> concluded that although precipitation transported measurable amounts of dissolved MTBE into the subsurface, MTBE apparently degraded in

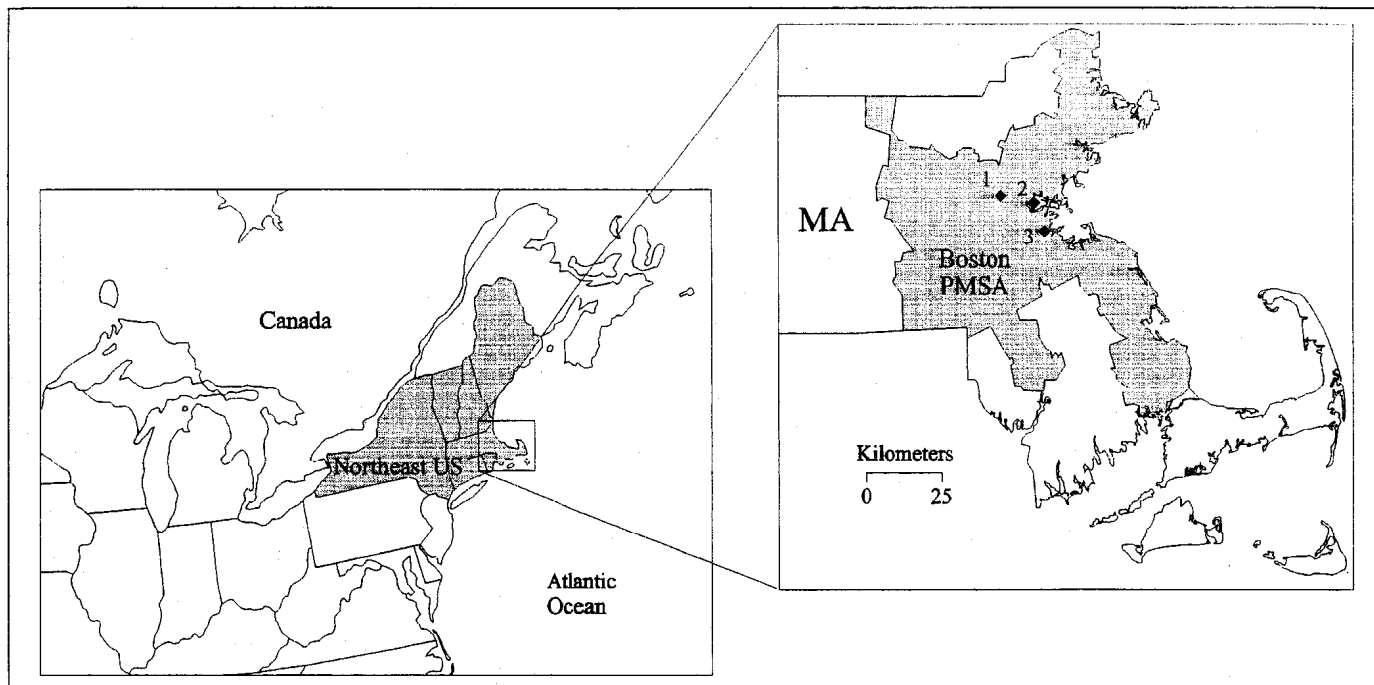
**Table 1.** Physical, chemical, and biological properties of MTBE.

Property	Value
Molecular formula	$\text{C}_8\text{H}_{12}\text{O}$
Molecular weight (g/mol)	88.15
Melting point ( $^{\circ}\text{C}$ )	$-109$
Boiling point ( $^{\circ}\text{C}$ )	55.2
Henry's law constant $K_H$ (–) at 20 $^{\circ}\text{C}^a$	$1.7 \times 10^{-2}$
Henry's law constant $K_H$ (–) at $-5$ $^{\circ}\text{C}^a$	$1.4 \times 10^{-3}$
Vapor pressure (atm) at 20 $^{\circ}\text{C}^b$	0.272
Vapor pressure (atm) at $-5$ $^{\circ}\text{C}^b$	0.0877
Solubility in water (mg/L) at 25 $^{\circ}\text{C}$	$4.8 \times 10^4$
$\log K_{OW}$ at 25 $^{\circ}\text{C}$	0.94–1.3 (1 taken)
$\log K_{OC}$ at 25 $^{\circ}\text{C}$	0.55–0.91 (0.9 taken)
$K_{bio-water}$ (d)	assumed nondegradable
$K_{bio-soil}$ (d)	assumed nondegradable
$K_{OH air}$ ( $\text{cm}^3/\text{molecule}/\text{sec}$ )	$2.83 \times 10^{-12}$
$K_{OH air}$ (d) <sup>c</sup>	0.5 $\pm$ 0.2 (summer), 0.2 $\pm$ 0.1 (winter)
Half-life in air (d) <sup>c</sup>	1 (summer), 3 (winter)

<sup>a</sup>From the relationship derived by Baehr et al. (ref 9); <sup>b</sup>Extrapolated from data at higher temperatures (ref 26), assuming constant  $\Delta H^{vap}$ ; <sup>c</sup>Derived assuming an  $\cdot\text{OH}$  concentration of  $2 \times 10^6 \pm 1 \times 10^6$  molecule/ $\text{cm}^3$  (summer) or  $1 \times 10^6 \pm 5 \times 10^5$  molecule/ $\text{cm}^3$  (winter).

the unsaturated zone too quickly to explain observed saturated zone concentrations at most monitoring sites. Achten et al.<sup>17</sup> measured MTBE concentrations in rainwater and snow over a 2-yr period (1998–2000) over the urbanized area of Frankfurt, Germany, and found significantly increased MTBE concentrations in winter precipitation (up to 85 ng/L in rainwater, which corresponds to a calculated equilibrium air concentration of  $\sim$ 0.5  $\mu\text{g}/\text{m}^3$ ) and nondetectable MTBE concentrations in precipitation during warmer months ( $<$ 10 ng/L). In subsequent monitoring of winter precipitation (November 2000–February 2001) at 11 rural and six urban sites in Germany, Achten et al.<sup>17</sup> consistently observed higher MTBE concentrations in snow than in rainwater at individual sampling locations. The results of these studies suggest that, at least in some areas, the unsaturated zone may act as a slow sink for MTBE transporting from either atmospheric or subsurface contamination sources, and precipitation appears to transport MTBE from the troposphere to the surface much more effectively at decreased temperatures ( $\leq$ 0–5  $^{\circ}\text{C}$ ).

To our best knowledge, no work to date has attempted to quantify the source emission rate of MTBE to an urban airshed or to use such calculations to explain measured MTBE concentrations in urban air. The objectives of this study were, therefore, to (1) estimate the total local flux of MTBE to the Boston primary metropolitan statistical area (PMSA) (Figure 1) based on estimated evaporative fuel emissions rates from automobiles and equilibrium gasoline vapor-phase composition calculations,



**Figure 1.** The Northeast United States and Boston PMSA regions used to parameterize the models; the Boston area Lexington (1), Cambridge (2), and Quincy (3) sampling sites.

(2) predict summer and winter MTBE concentrations in Boston air and surface water using a simple multimedia mass balance model, and (3) measure MTBE air concentrations in Boston during both the summer and winter to evaluate model prediction results. In particular, it was desirable to show that all modeling calculations could be performed without extensive a priori information about the behavior of MTBE in the environment or in gasoline. This would demonstrate, for scientists and regulators alike, the potential efficacy of a simple modeling approach for screening the probable urban air concentrations of a volatile gasoline additive such as MTBE.

## MODELING AND EXPERIMENTAL METHODS

### Estimation of Regional MTBE Emission Rates into the Urban Airshed

Automobiles were assumed to constitute the primary source of MTBE emissions into the Boston PMSA airshed. Other contributions, such as those from watercraft two-cycle engines, leaking underground fuel tanks or fuel-distribution pipelines, or fuel-refining facilities, were considered negligible. It should be noted, however, that in areas of the United States with significant petroleum-refining activity, this industry may introduce substantial quantities of MTBE directly into the environment.<sup>18</sup> To calculate MTBE emissions from automobiles in the Boston area, fuel vapor emission rates from automobiles first were assessed. Recently, Pierson et al.<sup>19</sup> extensively reviewed literature and data regarding various nontailpipe hydrocarbon emissions from automobiles, including

dynamometer and sealed housing evaporative determination (SHED) tests, roadway and tunnel chemical mass balance (CMB) source apportionment studies, and other reports. Based on these investigations, Pierson et al.<sup>19</sup> concluded that a typical 1990–1994 U.S. automobile emits ~77 g of nontailpipe hydrocarbons per day at ~20 °C from running (20%), diurnal (13%), hot soak (55%), refueling (7%), and crankcase (4%) losses. Because current (2000) fuel consumption rates in Massachusetts (580 gal/yr/vehicle) are slightly higher than the national average fuel consumption rates assumed by Pierson for 1993 (510 gal/yr/vehicle), we inflated this emission estimate by 12% to 86 g/day/vehicle at 20 °C. Pierson et al.<sup>19</sup> additionally estimated that the nontailpipe emissions rate may change by a factor of 2 for every  $12 \pm 5$  °C change in temperature. Therefore, at -5 °C (winter conditions in Boston), the nontailpipe emission for a single vehicle was assumed to be ~22 g/day/vehicle. It is not entirely clear what portion of nontailpipe emissions is constituted of complete, volatilized fuel rather than equilibrium fuel vapor (fuel vapor will generally be enriched in lower-molecular-weight components such as MTBE). As a modeling simplification, nontailpipe emissions were assumed to consist completely of fuel vapor.

Liquid-phase nonideality coefficients were computed for components of a model composition of base gasoline amended with 11% MTBE by volume using the Universal Quasi-Chemical Functional-Group Activity Coefficient (UNIFAC).<sup>20–23</sup> The base gasoline composition was simulated from 17 major hydrocarbon components of a typical

gasoline, based on a survey of several U.S. gasolines measured at several different laboratories.<sup>24,25</sup> UNIFAC-derived activity coefficients were combined with literature Antoine constants<sup>26</sup> and the oxygenated gasoline composition to estimate the simulated fuel mixture total vapor pressure and vapor-phase mass fraction of MTBE at several temperatures, using the standard approach.<sup>27,28</sup> These calculations indicated that the mass fraction of MTBE in fuel vapor is 10.5–11% by mass at temperatures ranging from –5 to 20 °C.

The Boston PMSA contains ~3.3 million residents who own a total of ~2.8 million vehicles.<sup>29</sup> Scaling the estimated volatile fuel emission rates and the calculated mass fraction of MTBE in fuel vapor on the vehicle population, predicted MTBE emission rates into the Boston PMSA are

$$(86 \text{ g fuel/day/vehicle} \times 0.11 \text{ g MTBE/g fuel} \times 2.8 \times 10^6 \text{ vehicles}) = 2.7 \times 10^4 \text{ kg MTBE/day} \quad (1)$$

during a typical summer day (20 °C) and

$$(22 \text{ g fuel/day/vehicle} \times 0.11 \text{ g MTBE/g fuel} \times 2.8 \times 10^6 \text{ vehicles}) = 6.7 \times 10^3 \text{ kg MTBE/day} \quad (2)$$

in the winter (–5 °C). By comparison, emissions from point sources in Massachusetts reported by the Toxic Release Inventory (TRI) totaled 136 kg MTBE/day into air and 0.22 kg MTBE/day into surface water in 1999.<sup>30</sup> This supports the assumption that volatile emissions from automobiles are by far the most significant source of MTBE in the Boston area airshed. Using similar calculations, Northeast United States automobile emission rates were found to be  $\sim 3 \times 10^5$  kg MTBE/day during the summer and  $8 \times 10^4$  kg MTBE/day during the winter, assuming an estimated vehicle population of 25 million and current (2000) national average fuel use rates of 747 gal/yr.<sup>29</sup>

### Environmental Parameterization

During air sampling experiments, weather data observed at four regional U.S. National Weather Service (NWS) stations located around the Boston PMSA (Boston Logan airport; Worcester, MA; Providence, RI; and Hartford, CT) were collected (Table 2). Temperature data were relevant to thermodynamic and source emission rate calculations. The model ceiling, or scale of lower atmospheric mixing, was estimated from observed lower cloud height data. Tropospheric air mass advective velocities were extrapolated from regional NWS 10-m anemometer (wind speed) data. An empirical model of the vertical wind profile suggested that effective lower troposphere air mass advection rates were approximately a factor of 2 greater than

**Table 2.** Environmental characteristics of the Northeast United States and the Boston PMSA.

Characteristic	Northeast United States	Boston PMSA
Population	$3.3 \times 10^7$	$3.3 \times 10^6$
Area (km <sup>2</sup> )	$2.84 \times 10^6$	$5.17 \times 10^3$
Air		
Height (m) <sup>a</sup>	900 ± 200 (winter) 1000 ± 300 (summer)	900 ± 200 (winter) 1000 ± 300 (summer)
Temperature (°C) <sup>a</sup>	–5 ± 4 (winter) 20 ± 4 (summer)	–5 ± 4 (winter) 20 ± 4 (summer)
Wind speed at 10 m (m/sec) <sup>a</sup>	4.0 ± 1.2	5.5 ± 1.4 (winter) 3.5 ± 0.9 (summer)
Wind direction	W (winter), SW (summer)	W (winter), SW (summer)
Precipitation (mm/yr)	1100 <sup>b</sup>	200 (winter) <sup>c</sup> , 470 (summer) <sup>c</sup>
Water		
Fraction of surface area	0.03	0.05
Average depth (m)	5	5
Soil		
Volume fraction water	0.2	0.2
Volume fraction air	0.2	0.2
Fraction organic carbon	0.02	0.02
Sediment		
Volume fraction solids	0.2	0.2
Fraction organic carbon	0.05	0.05

<sup>a</sup>Reported variability of some values reflects upper bound estimates of uncertainty based on observed diurnal averages; <sup>b</sup>True annual average for the Northeast region; <sup>c</sup>Annualized values extrapolated from precipitation observed during experiments.

the wind speeds observed at a height of 10 m,<sup>31</sup> based on the conditions observed during monitoring experiments. Precipitation data were recorded to assess whether rain or snow might have washed out MTBE in the urban atmosphere to a significant extent. Tropospheric hydroxyl radical ( $\cdot\text{OH}$ ) concentrations were estimated based on literature summertime tropospheric measurements at several locations in the United States and Europe. Reported averages were relatively consistent, typically ranging from  $2 \times 10^6$  to  $5 \times 10^6$  molecule/cm<sup>3</sup> during the daytime, and significantly lower at night.<sup>32–36</sup> Diurnally averaged tropospheric  $\cdot\text{OH}$  concentrations for all calculations were therefore assumed to be  $\sim 2 \times 10^6$  molec/cm<sup>3</sup> during summer months and  $1 \times 10^6$  molecule/cm<sup>3</sup> during winter months.

### EUSES Multimedia Model

The European Union System for the Evaluation of Substances (EUSES) version 1.0 multimedia environmental fate model was employed to predict diurnally averaged MTBE concentrations in air, soil, surface water, and sediment in the Boston PMSA.<sup>37</sup> EUSES was designed as a

decision-support system to evaluate the risks of commercial and industrial substances to humans and the environment. It has been successfully applied to the environmental exposure screening of 68 compounds in Japan.<sup>38</sup> EUSES is composed of six modules, including a nested multimedia mass balance model, SimpleBox version 2.0, which is equipped to simultaneously calculate steady-state contaminant concentrations in air, water, and soil on global, regional, and local scales. In this study, the regional scale was calibrated for the Northeast United States (defined as the states of Maine, Vermont, New Hampshire, Massachusetts, Rhode Island, Connecticut, and New York), and these air and surface water concentrations were used as advective inputs to the local-scale environment, the Boston PMSA. These scales were chosen because oxygenated fuel is used throughout urban centers in the Northeast, unlike many other areas of the United States.<sup>3</sup>

Additionally, large population centers in the region (e.g., New York City) were suspected to be the most relevant source of MTBE to incoming air masses at the local scale. Separate model calculations were made for both typical summer and typical winter settings, based on environmental parameters observed during air sampling experiments. EUSES model calculations were tailored to MTBE using environmental media partition coefficients and estimated pseudo-first-order environmental media degradation rate constants (see Table 1). The EUSES risk characterization module was used to evaluate the potential risks to both humans and the environment, based on estimated environmental MTBE concentrations in air, water, soil, and sediment. The risk assessment method for the environment is based on the ratio of predicted environmental concentrations and predicted noneffect concentrations (PNECs), which is indicated as the RCR (risk characterization ratio). The method of risk assessment for human exposures is based on the comparison of no observed adverse effect level and total daily exposure level for humans, and this ratio is indicated as the margin of safety (MOS).

### Airshed Box Model Calculations and Uncertainty Analysis

In addition to EUSES calculations, a nested simple box model of the regional (Northeast United States) and local (Boston PMSA) airsheds was constructed, incorporating the processes that were believed to be most important in determining MTBE transport in the environment. Based on the relative time scales of estimated MTBE degradation rates (see Table 1) and environmental processes (see Table 2), the most critical factors affecting steady-state MTBE concentrations in the urban airshed were believed to be incoming air concentration, advection (wind) and

reaction with tropospheric ·OH. Degradation rates of MTBE in surface water and soil were considered negligible relative to MTBE atmospheric advective transport and reaction with ·OH. Under these assumptions, only atmospheric processes were necessary to evaluate the steady-state concentration of MTBE in the troposphere. The governing equation describing the steady-state MTBE flux (mol/m<sup>3</sup>/day) in each of the two boxes (regional scale and local scale) reflect total MTBE emissions to the urban airshed (term 1), the MTBE concentration in incoming air (term 2), the MTBE concentration leaving the well-mixed airshed (term 3), and reaction with ·OH (term 4):

$$\left(\frac{dC_{\text{air}}}{dt}\right)_{\text{steady state}} = 0 = \left(\frac{\text{Emission rate}}{V_{\text{air}}}\right) + \left(\frac{C_{\text{air,in}}}{V_{\text{air}}}\frac{dV_{\text{air}}}{dt}\right) - \left(\frac{C_{\text{air}}}{V_{\text{air}}}\frac{dV_{\text{air}}}{dt}\right) - k_{\text{OH}}\{\text{OH}\}C_{\text{air}} \quad (3)$$

where  $C_{\text{air}}$  is the spatially averaged MTBE concentration of the air mass in the box (mol/m<sup>3</sup>),  $V_{\text{air}}$  is the volume of air mass (m<sup>3</sup>),  $k_{\text{OH}}$  is the ·OH rate constant (m<sup>3</sup>/molecule/day), {OH} is the atmospheric ·OH concentration (molecules/m<sup>3</sup>), and  $dV_{\text{air}}/dt$  reflects the rate at which the air mass volume is flushed with incoming wind (m<sup>3</sup>/day). Eq 3 was solved to find  $C_{\text{air}}$  as a function of the other (known) variables by setting  $dC_{\text{air}}/dt = 0$  (the steady-state condition).

$$C_{\text{air}}^{\text{steady state}} = \frac{\frac{\text{Emission rate}}{V_{\text{air}}} + \frac{C_{\text{air,in}}}{V_{\text{air}}}\frac{dV_{\text{air}}}{dt}}{\frac{1}{V_{\text{air}}}\frac{dV_{\text{air}}}{dt} + k_{\text{OH}}\{\text{OH}\}} \quad (4)$$

The incoming air mass boundary condition,  $C_{\text{air,in}}$ , for the regional scale was set to zero, and the calculated  $C_{\text{air}}$  for the regional scale was used as the air mass boundary condition for the local scale. Using this analytical formulation, the overall uncertainty of the  $C_{\text{air}}$  prediction was computed from the estimated uncertainties of model parameters (see Table 2) using first term-truncated Taylor series error propagation analysis.<sup>39</sup>

### Experimental Procedures

MTBE air concentration measurements were conducted at the surface in three locations of the Boston area during February and September of 2000. The sampling sites included a suburb to the northwest of Boston (Lexington; site 1), the Massachusetts Institute of Technology (MIT) Parsons Laboratory just northwest of Boston (Cambridge; site 2), and near heavily trafficked commuter routes just south of Boston (Quincy; site 3) (see Figure 1). Samples were taken in the winter experiment from February 2 to 4

(weekdays), and from February 4 to 6 (a weekend). Summer sampling was performed from September 8 to 10 (weekdays) and from September 10 to 12 (a weekend). Ambient air was monitored using a passive diffusion sampling method,<sup>40</sup> which employed stainless-steel tubes packed with adsorbent and designed for thermal desorption with the ATD-400 system (Perkin-Elmer Ltd.). The methodology adopted here was based on techniques developed elsewhere.<sup>41</sup> Packed Tenax TA (0.2 g), a 2,6-diphenylene oxide polymer, was used as adsorbent. This method has been extensively applied in previous work, and the overall uncertainty was estimated to be less than 50% in measurements of volatile organic compounds (VOCs).<sup>42</sup> Another study showed that variability in mean measured concentrations of ambient VOCs among different laboratories was less than 50% at both urban and rural sampling sites.<sup>43</sup> After 48-hr exposure in the environment, sampling tubes were sealed for transport using Teflon caps and then thermally desorbed at 200 °C and analyzed using an ATD-gas chromatography-mass spectrometry (GC-MS) system. A gas chromatograph (Hewlett Packard 5890 series II) with an HP-5 capillary column (0.25 i.d., 30 m length, 0.25 µm film thickness) was operated using a temperature program ramping from 35 to 150 °C. MTBE was quantified using the 73 m/e SIM ion fragment.

The MTBE concentration in air was calculated using the detected amount of MTBE in a tube sample and the uptake rate of MTBE. The uptake rate,  $R_u$  (cm<sup>3</sup>/sec), was calculated as

$$R_u = \frac{D_{\text{air}}A}{L} \quad (5)$$

where  $D_{\text{air}}$  is the diffusion coefficient of MTBE in air (0.084 cm<sup>2</sup>/sec at 25 °C, 0.07 cm<sup>2</sup>/sec at -5 °C),<sup>44</sup>  $A$  is the tube cross-sectional surface area (0.191 cm<sup>2</sup>), and  $L$  is the length from the sampler inlet to the adsorbent surface (1.5 cm). Using these parameters,  $R_u$  was determined to be 0.64 cm<sup>3</sup>/min at 25 °C and 0.53 cm<sup>3</sup>/min at -5 °C. The averaged air concentration of MTBE,  $C_{\text{MTBE,avg}}$  (µg/cm<sup>3</sup>), during the exposure period was then calculated as

$$C_{\text{MTBE,avg}} = \frac{M}{R_u t} \quad (6)$$

where  $M$  is the total mass of MTBE collected (µg), as quantified by GC-MS, and  $t$  is the duration of exposure (48 hr).

## RESULTS AND DISCUSSION

**Measured Concentrations of MTBE in Urban Air**  
Measured atmospheric MTBE concentrations in the Boston area were ~1–2 µg/m<sup>3</sup> during the summer

experiments (September) and 0.1–0.2 µg/m<sup>3</sup> during the winter experiments (February) (Table 3). These tropospheric MTBE levels are approximately an order of magnitude lower than those typically found in some megacities (discussed in the Introduction). Observed differences in average wind speed (flushing time), wind direction, and temperature (see Table 2) are most likely to explain the measured disparity between summer and winter MTBE air concentrations. Before model calculation results are considered, the effect of each of these factors on expected MTBE air concentrations is discussed.

**Air Transport.** Wind came primarily from the west-northwest at an average of ~5.5 m/sec during the winter experiment, and from the west-southwest at an average of 3.5 m/sec during the summer experiment. This implies that the urban air mass flushing rate was considerably higher in the winter experiment, decreasing average MTBE concentrations in urban air during this time. Recorded wind direction data suggest that the air mass over Boston might have come from nearby urban centers during the summer experiment (e.g., New York City), whereas wind direction data suggest rural air mass boundary conditions during the winter experiment (upstate New York). In other words, incoming air may have been significantly more contaminated with MTBE from upwind urban areas during the summer experiment than during the winter experiment.

**Precipitation.** Precipitation occurred during both the summer (rain) and winter (snow) experiments, creating the possibility for so-called washout, or scavenging and subsequent deposition of tropospheric MTBE via air-water partitioning. Because the volatility of MTBE decreases rapidly with decreasing temperature (see Table 1) and, additionally, because snow may act as a more effective sorbent than an equivalent mass of rain,<sup>45</sup> MTBE deposition rates should be enhanced during winter months. Indeed, Achten et al.<sup>17</sup> repeatedly observed higher MTBE

**Table 3.** Ambient air concentrations (µg/m<sup>3</sup>) of MTBE in winter and summer experiments (duplicate samples).

Location	Winter <sup>a</sup>	Summer <sup>b</sup>
Lexington, weekday	0.12, 0.17	0.29, 0.35
Lexington, weekend	< 0.04, < 0.04	1.0, 1.1
Cambridge, weekday	0.17, 0.09	1.1, 1.2
Cambridge, weekend	0.093, 0.08	1.7, 1.7
Quincy, weekday	0.12, 0.18	0.92, 0.93
Quincy, weekend	0.11, 0.17	2.1, 2.2

<sup>a</sup>Weekday = Feb 2–4, 2000, weekend = Feb 4–6, 2000; <sup>b</sup>Weekday = Sept 10–13, 2000, weekend = Sept 8–11, 2000.

concentrations in winter precipitation than in summer precipitation over Germany. To assess the maximum plausible effect of washout, we considered the possibility that the accumulated snowfall of the winter experiment ( $\sim 0.55 \text{ kg/m}^2$  over the monitoring period) was fully saturated with adsorbed MTBE. Assuming an estimated snow surface area of  $150 \text{ m}^2/\text{kg}^{46}$  and a calculated ice-air distribution coefficient,  $K_{\text{ice-air}}$ , of 0.057 m,<sup>47-49</sup> this would imply that  $\sim 0.5\%$  of the total atmospheric MTBE was transferred to the sorbed (deposited) phase. Therefore, it seems unreasonable that sorption to falling snow could have substantially affected MTBE levels in urban air during the winter experiment.

**Emission Rate Dependence on Temperature.** Ambient temperatures in the area were consistently  $\sim -5^\circ\text{C}$  during the winter experiment and  $20^\circ\text{C}$  during the summer experiment. Pierson et al.<sup>19</sup> suggest that nontailpipe emissions from automobiles may change by approximately a factor of 4 over a  $25^\circ\text{C}$  temperature change; however, it is unclear that this generalization extrapolates to temperatures as low as  $-5^\circ\text{C}$ . In long-term monitoring experiments in the temperate regions of Porto Alegre, Brazil, and Glassboro, NJ, investigators found little correlation between measured MTBE concentrations in urban air and seasonality.<sup>7,50</sup> Because other seasonally dependent factors may also have been important in these cases, it can only be concluded that the relationship between seasonal temperature variation and nontailpipe emission rates is uncertain.

### Traffic Variability

A final factor that may have contributed to the difference between measured summer and winter MTBE concentrations in Boston-area air is overall traffic volume, which is believed to be slightly lower in midwinter (after the Christmas holiday) than during late summer.<sup>51</sup> MTBE levels were also consistently increased in urban areas (Quincy and Cambridge) relative to outlying suburbs (Lexington) and were highest during summer weekends. These differences probably have to do with the increased traffic density in the inner city and increased traffic during high tourist season (summer weekends).

### EUSES Prediction of MTBE Concentrations in the Environment

EUSES predicted MTBE concentrations of 1 and  $0.2 \mu\text{g}/\text{m}^3$  in the Boston PMSA (Table 4) based on model parameterization using the summer and winter experimental conditions, respectively (see Table 2). These calculated MTBE concentrations were comparable to the observed September and February MTBE concentrations of  $\sim 1$  and  $0.1$

**Table 4.** Predicted environmental concentrations of MTBE in the Northeast United States and the Boston PMSA for two seasons.

Predicted Environmental Concentrations	Winter	Summer
Northeast United States		
In air, EUSES ( $\mu\text{g}/\text{m}^3$ )	0.2	0.6
In air, airshed box model ( $\mu\text{g}/\text{m}^3$ )	$0.2 \pm 0.2$	$0.6 \pm 0.5$
In surface water, EUSES ( $\mu\text{g}/\text{L}$ )	8E-03	0.03
In soil, EUSES ( $\mu\text{g}/\text{kgdwt}$ )	2E-03	9E-03
In sediment, EUSES ( $\mu\text{g}/\text{kgdwt}$ )	0.02	0.06
Boston PMSA		
In air, EUSES ( $\mu\text{g}/\text{m}^3$ )	0.2	1
In air, airshed box model ( $\mu\text{g}/\text{m}^3$ )	$0.3 \pm 0.3$	$1 \pm 1$
In surface water, EUSES ( $\mu\text{g}/\text{L}$ )	0.01	0.05
In soil, EUSES ( $\mu\text{g}/\text{kgdwt}$ )	3E-03	0.02
In sediment, EUSES ( $\mu\text{g}/\text{kgdwt}$ )	0.02	0.09

Note: Predicted environmental concentrations in air and water include masses sorbed to suspended materials.

$\mu\text{g}/\text{m}^3$ , suggesting that the model successfully captured the general magnitude of MTBE emissions and local tropospheric mixing in the Boston PMSA environment. The parameters that primarily drove the predicted 5-fold difference between summer and winter air concentrations were the temperature-controlled MTBE emission rate and wind speed. Calculated regional-scale MTBE air concentrations were of lower, but comparable, magnitude to predicted air concentrations in the Boston PMSA (see Table 4). At the regional scale, the emission contributions of large urban areas such as New York City are averaged with the diluting contribution of sparsely populated areas such as rural Connecticut. However, it seems likely that New York City might create a substantial upwind MTBE plume under certain wind conditions, which could significantly affect local Boston urban air concentrations. It is important to stress that such transient boundary condition deviations from averaged behavior were considered secondary effects and were, therefore, neglected for the purposes of the simple screening model being evaluated here. EUSES predicted steady-state surface water MTBE concentrations on the order of  $\sim 0.01 \mu\text{g}/\text{L}$  during both the summer and winter (see Table 4), which is well below U.S. Environmental Protection Agency (EPA)-recommended drinking water levels of  $20 \mu\text{g}/\text{L}$ .<sup>52</sup> Finally, it was useful to consider the expected overall mass distribution of a chemical among air, water, soil, and sediment. EUSES calculations predicted that, on average, the overwhelming majority of MTBE in the environment would be found in air (99.9%). This calculated result derives principally from the relatively high volatility of MTBE, and it indicates that advective and

reactive processes in the atmosphere, rather than in soil or water, will primarily control the final fate of MTBE in the environment.

### **Box Model-Predicted MTBE Concentrations in Urban Air and Uncertainty Analysis**

In box model computations, it was assumed that MTBE transport in the urban environment was dominated by atmospheric processes, based on the estimated rates of air mass flushing and atmospheric degradation (considered most important) relative to the rates of degradation in soil and water (considered negligible in comparison). The box model approach conferred the advantages of (1) a simple estimate of the relative importances of various atmospheric sinks and (2) a transparent analysis of parameter-driven prediction uncertainty. Box model calculations corroborated EUSES results, predicting MTBE concentrations of  $1 \mu\text{g}/\text{m}^3$  (summer) and  $0.3 \mu\text{g}/\text{m}^3$  (winter) in Boston PMSA urban air and  $0.6 \mu\text{g}/\text{m}^3$  (summer) and  $0.2 \mu\text{g}/\text{m}^3$  (winter) in the Northeast region (see Table 4). This demonstrated that in EUSES calculations, the key processes affecting MTBE transport were MTBE emission rate into the atmosphere, air mass turnover (advective) rate, airshed (box) volume, and MTBE reaction rate with tropospheric  $\cdot\text{OH}$  (eq 3). Additionally, a comparison of box model transport sink terms suggested that at the regional level (Northeast United States), advective flushing was responsible for  $\sim 80\%$  of MTBE removal from the system and reaction with  $\cdot\text{OH}$  was responsible for  $\sim 20\%$  of MTBE removal, depending on conditions. At the local level (Boston PMSA), advective flushing and reaction with  $\cdot\text{OH}$  on average explained  $\sim 95$  and  $\sim 5\%$  of MTBE removal from the system, respectively. The simple analytical formulation of the box model enabled straightforward application of first-order error propagation analysis, allowing transformation of estimated parameter uncertainties (see Table 2) into an estimated uncertainty of the predicted airshed concentration. This error propagation calculation suggested that box model-predicted MTBE air concentrations were precise to within approximately a factor of 2, indicating that model calculations reasonably capture observed MTBE air concentrations. Therefore, EUSES and box model calculations suggested that the expected urban air concentrations of a volatile gasoline additive such as MTBE can be estimated using a simple screening transport model. Finally, EUSES and box model calculations indicated that metropolitan-scale emissions are most important in determining the local tropospheric concentrations of MTBE.

### **Risk Characterization of MTBE**

A risk characterization was performed for both environmental and human exposures using the applicable EUSES

module, based on the predicted environmental concentrations of MTBE in air, water, soil, and sediment. Although data concerning the effects of MTBE on either the environment or humans are limited, RCR and MOS values could be estimated. The RCR (the ratio of the predicted environmental concentration to the PNEC) was  $10^{-4}$ – $10^{-5}$  for surface water, soil, and sediment compartments, indicating that MTBE is not anticipated to endanger ecosystems at predicted environmental levels. The MOS (the ratio of no observed adverse effect level to the total estimated daily exposure level for humans) was  $10^5$ – $10^6$ , suggesting that MTBE is unlikely to cause adverse health effects at predicted environmental levels.

### **CONCLUSIONS**

Measured MTBE air concentrations in the Boston area were  $\sim 1$  and  $0.1 \mu\text{g}/\text{m}^3$  during summer and winter measurement experiments, respectively—approximately an order of magnitude less than that found in extended metropolitan areas such as Mexico City and Los Angeles. Screening calculations using a multimedia box model, EUSES, suggested that Boston PMSA airshed MTBE concentrations could be accurately predicted based on estimated emission rates and the parameterization of simple environmental transport and transformation processes. Additional calculations using an airshed box model indicated that locally measured MTBE air concentrations essentially could be explained from the local emission rate, average wind speed (airshed flushing rate), and reaction with ambient tropospheric  $\cdot\text{OH}$ . These results validated the accuracy of MTBE volatile emission calculations, which were based on estimates of nontailpipe (volatile gasoline) emissions from automobiles and thermodynamic calculations of the occurrence of MTBE in gasoline vapor. The significant disparity in MTBE air concentrations between the summer and winter experiments might be explainable by the difference in estimated gasoline emission rates from vehicles at warm ( $20^\circ\text{C}$ ) versus cold ( $-5^\circ\text{C}$ ) temperatures. However, because monitoring data from other studies do not appear to support this rationale, it is suggested only tentatively. Previous workers such as Achten et al.<sup>17</sup> have demonstrated that winter precipitation is likely to contain significantly more concentrated MTBE than is summer precipitation. However, mass transfer calculations show that precipitation is very unlikely to effectively scavenge MTBE from the troposphere. Screening model calculations were parameterized using the environmental conditions observed solely during two 4-day measurement periods in September and February of 2000. However, these conditions were sufficiently representative of summer and winter conditions in Boston that the calculated results were considered generalizable.



The most important implication of this study is that careful emissions and fate analysis could be used as a screening tool to evaluate the expected urban air concentrations of relatively volatile components in future fuel formations. It is worth noting that application of the model to additives that are significantly less volatile or more hydrophilic (water-soluble) than MTBE may require the incorporation of other environmental transport processes that were considered negligible in this study (e.g., adsorption to terrestrial surfaces). However, previous work has already evaluated the efficacy of box model screening calculations that include these processes.<sup>38</sup> The relatively simple formulation of the model presented here strongly suggests that (1) the volatile emissions-related source flux of any gasoline additive to an urban airshed may be accurately estimated and (2) the urban atmospheric concentrations of volatile gasoline components such as MTBE may be accurately assessed for screening purposes. Consequently, these findings suggest that scientists, regulators, and industries may quantitatively anticipate pollution to the urban atmosphere resulting from the volatile emission of novel gasoline additives, before these compounds are added to gasoline.

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