Determination of Urban VOC Emissions Ratios and Comparison with Inventories

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ABSTRACT

During the NEAQS-ITCT2k4 campaign in New England, anthropogenic VOCs and CO were measured downwind from New York City and Boston. The emission ratios of VOCs relative to CO and acetylene were calculated using a method in which the ratio of a VOC with acetylene is plotted versus the photochemical age. The intercept at the photochemical age of zero gives the emission ratio. The emission ratios thus determined were compared to other measurement sets, including data from the same location in 2002, canister samples collected inside New York City and Boston, aircraft measurements from Los Angeles in 2002 and the average urban composition of 39 U.S. cities. All the measurements show fairly good agreement. The measured emission ratios also agree well with vehicle exhaust data indicating that a major source of VOCs in urban areas are automobiles. A comparison with an anthropogenic emission inventory shows a rather poor agreement, especially for the C_2-C_4 alkanes and most oxygenated species. The inventory overestimated toluene for example by almost a factor of three, which caused an air quality forecast model (WRF-CHEM) using this inventory to over-predict the toluene mixing ratio by about a factor of three as well.

INTRODUCTION

Volatile organic compounds (VOCs) are emitted into the atmosphere in large quantities from a variety of different natural and anthropogenic sources. VOCs are key ingredients in the formation of ozone and aerosols in polluted air, and play a significant role in determining regional air quality, in the chemistry of the global troposphere, and possibly in the global carbon cycle. On a global scale the biogenic VOC emissions, mainly isoprene, α- and β-pinene and methanol [1, 2], dominate over the anthropogenic sources. In and around urban areas, anthropogenic emissions of VOCs, which are in large part caused by production, storage and use of fossil fuels, usually are more important.

In this paper, we will focus on the determination of primary anthropogenic VOC emission ratios from mainly Boston and New York City during NEAQS-ITCT 2k4 (New England Air Quality Study – Intercontinental Transport and Chemical Transformation), which was a large-scale atmospheric chemistry and transport study conducted in July and August of 2004 in New England. Emission ratios of a large number of VOCs versus acetylene and CO were determined using the ship-based measurements in the Gulf of Maine downwind of the urban areas. The resulting emission ratio data are compared to data from a previous campaign in 2002 in the same area, to canister samples collected in Boston and New York City and to data from Los Angeles in 2002. The measured emission ratios are also compared to an anthropogenic emissions database based on EPA NEI-99 (Environmental Protection Agency National Emissions Inventory-99). This database includes four categories of emissions: on-road, off-road, area and point sources. We compare our results to the sum of those four categories, because the VOC measurements were made downwind of the urban areas and should include all the source categories. The database is used in various regional air quality forecast models such as the WRF-CHEM (Weather Research and Forecasting-Chemical Model). The results from WRF-CHEM are compared to the measurements from the NEAQS-ITCT 2k4 study to demonstrate how inaccuracies in the emission inventory translate into the model results.

BODY

Ship-based and Airborne Instrumentation

VOC measurements on the NOAA research ship Ronald H. Brown (RHB) were performed using an on-line GC-MS. A detailed description of this instrument and its analysis procedure is given elsewhere [3]. The GC-MS instrument analyzed 350 mL air samples with a 5-min acquisition time every 30 min. More than 100 VOCs including many oxygenated compounds, hydrocarbons, halocarbons and alkyl nitrates were identified and quantified with this instrument. CO was measured via a modified AeroLaser GmbH [Garmisch-Partenkirchen, Germany] AL5002 Ultra-Fast CO analyzer, a commercially-available vacuum-UV resonance fluorescence instrument [4].

Fast-response measurements of oxygenated VOCs, aromatics, acetonitrile, isoprene and monoterpenes were made on the NOAA WP-3D research aircraft with a PTR-MS instrument from Ionicon Analytik [5]. During every flight, up to 80 whole air samples (WAS) were collected in electro-polished stainless steel gas canisters. The canisters were transported to the NCAR laboratory in Boulder, where they were analyzed within a few days for hydrocarbons, halocarbons and C_1- to C_5- alkyl nitrates using several gas chromatography techniques. CO was determined on the WP-3 aircraft every second using a vacuum ultraviolet fluorescence measurement [6].

The Anthropogenic Emissions Database

The anthropogenic VOC emissions database (4 km horizontal resolution) is based upon the U.S. EPA 1999 National Emissions Inventory (NEI-99, version 3) released November 2003 (updated to March 2004 revisions), and the 4 km horizontal resolution spatial surrogates released by EPA in September of 2003. Emissions of several individual VOCs (e.g. ethane, propane, ethylene, propylene, acetylene, styrene, benzene, toluene, acetone, and acetaldehyde) are extracted from the database, and are used for comparisons in this study.

NOAA WRF-CHEM Model

The multi-scale air pollution prediction system used here is based on the Weather Research and Forecasting (WRF) model, which is coupled with the RADM2 chemical mechanism [7]. Biogenic and anthropogenic emissions, dry deposition, convective and turbulent chemical transport, photolysis, and advective chemical transport are all treated simultaneously with the meteorology "online". WRF-CHEM results presented here are from the “reference case” simulations documented in [8].

Determination of Emission Ratios

VOC emission ratios are determined from data collected on board the RHB in the Gulf of Maine downwind of Boston and New York City. The emission ratios are determined using a method that was introduced elsewhere [9]. In this method, summarized in the following, the ratio of a VOC with acetylene is plotted versus the photochemical age as shown in Figure 1 for ethyl benzene. The photochemical age was estimated using the measured ratio between toluene to benzene in the sampled air [10]:

Equation (1) $$\Delta t = \frac{1}{[OH](k_{toluene} - k_{benzene})} \times \left[\ln\left(\frac{[toluene]}{[benzene]}\Big|_{t=0} \right) - \ln\left(\frac{[toluene]}{[benzene]} \right) \right],$$

where $k_{toluene}$ and $k_{benzene}$ are the rate coefficients for the reaction with OH ($k_{toluene}=5.63\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_{benzene}=1.22\times10^{-12}$ cm^3 molecule^{-1} s^{-1}) [11], and [OH] is the average concentration of the hydroxy radical. The emission ratio of benzene and toluene ($\frac{[toluene]}{[benzene]}\Big|_{t=0}$) was set to 4.25 and determined by looking at fresh plumes from Boston and New York City during several flights of the NOAA WP-3D aircraft. Plumes were assumed to be fresh, when the NO_x/NO_y ratio was higher than 80%.

Figure 1: The ethyl benzene/acetylene ratio plotted versus the photochemical age of the air mass. The measurements include all data on the RHB from July 5 until August 12, 2004 filtered for biomass burning and power plants (N=1608). The red line is a linear fit where the emission ratio is determined at photochemical age zero.

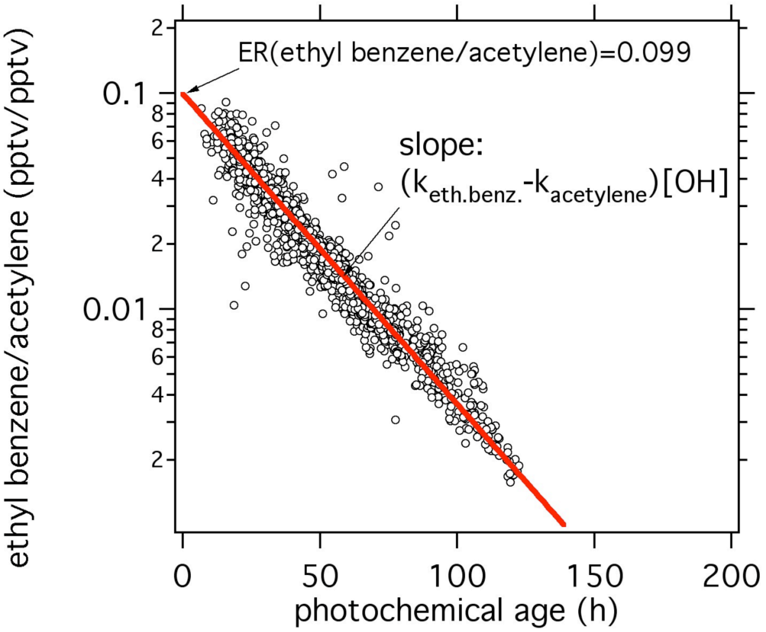


Figure 1 shows that the *[ethyl benzene*]/[*acetylene*] ratio decreases by an order of magnitude over the course of two days, because the OH rate coefficient of ethyl benzene (k=7×10^{-12} cm^3 molecule^{-1} s^{-1}) is larger than that of acetylene (k=0.83×10^{-12} cm^3 molecule^{-1} s^{-1}) [11]. The data in Figure 1 can be described by:

Equation (2) $$\frac{[VOC]}{[C_2H_2]} = ER_{VOC} \times \exp[-(k_{VOC} - k_{C_2H_2})[OH]\Delta t] \ ,$$

with [VOC] and [C_2H_2] the volume mixing ratios of a primary anthropogenic VOC (ethyl benzene in Figure 1) and acetylene, ER_{VOC} the emission ratio of the VOC with acetylene, k_{VOC} and $k_{C_2H_2}$ the rate coefficients of those compounds with OH [11] and Δt the photochemical age. In Figure 1, [OH] was set to 2.1×10^6 molecule cm^{-3}, which was calculated for this data set in the same way as described elsewhere [12]. The emission ratio ER_{VOC} is determined from the intercept on the y-axis of the linear fit (red line in Figure 1) and the rate coefficient k_{VOC} for the reaction with OH can be determined from the slope.

The emission ratios for all measured anthropogenic hydrocarbons versus acetylene are presented in Table 1 together with the emission ratios versus CO, which is used in many studies as the anthropogenic emissions marker instead of acetylene.

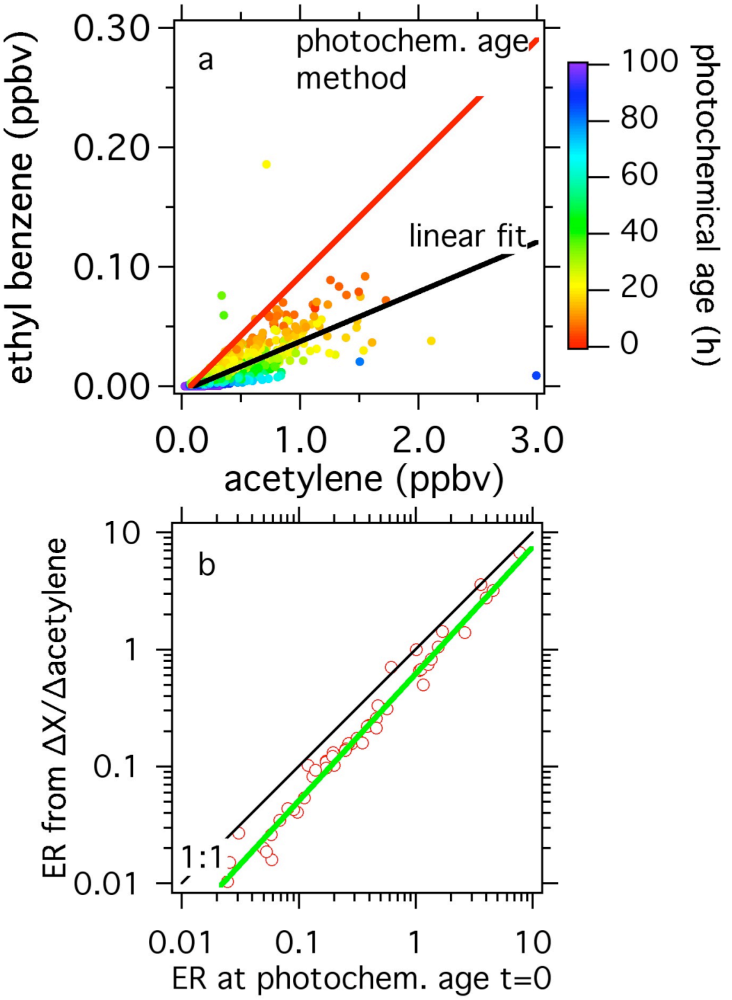
Table 1. Emission ratios of anthropogenic VOCs from Boston/New York City, Los Angeles and an anthropogenic emissions inventory based on EPA data. The estimated error on the measured emission ratios is 30%. Data in the first three columns were determined with the photochemical age method (see text) and therefore are the most accurate.

Compound	Boston/New York City 2004	Boston/New York City 2002	Boston/New York City CO 2004	Los Angeles 2002	Boston/New York City Baker et al	39 US Cities Seila et al	Vehicle Exhaust Harley et al.	Database
	pptv [pptv C_2H_2]$^{-1}$	pptv [pptv C_2H_2]$^{-1}$	pptv [ppbv CO]$^{-1}$	pptv [ppbv CO]$^{-1}$	pptv [ppbv CO]$^{-1}$	pptv [pptv C_2H_2]$^{-1}$	pptv [pptv C_2H_2]$^{-1}$	pptv [ppbv CO]$^{-1}$
ALKANES								
ethane	3.097	2.738	11.616	7.84	10.37	1.806	0.967	1.571
propane	2.187	2.505	7.733	12.39	5.50	1.214	0.023	0.357
n-butane	0.482	0.660	1.688	5.4	2.39	1.562	0.758	
iso-butane	0.287	0.373	1.012	2.58	1.80	0.574	0.086	
n-pentane	0.463	0.555	1.548	3.01	1.69	0.682	0.250	
iso-pentane	1.192	1.509	3.991	6.38	3.65	1.404	0.583	
cyclohexane	0.092	0.068	0.285			0.057	0	
methyl cyclopentane	0.180	0.135	0.566			0.165	0.060	
n-hexane	0.335	0.175	1.072		1.13	0.284	0.116	
2-methyl pentane	0.341	0.272	1.106			0.385	0.244	
3-methyl pentane	0.394	0.186	1.276			0.276	0.151	
2,2-dimethyl butane	0.033	0.050	0.120				0.070	
2,3-dimethyl butane	0.082	0.074	0.265			0.098	0.116	
methyl cyclohexane	0.065	0.118	0.202			0.075	0.041	
n-heptane	0.126	0.157	0.398		0.59	0.104	0.030	
2-methyl hexane	0.124	0.133	0.385			0.162		
3-methyl hexane	0.148	0.156	0.460			0.131		
2,3-dimethyl pentane	0.080	0.115	0.252					
2,4-dimethyl pentane	0.053	0.071	0.171			0.049		
2,2,3-trimethyl butane	0.009	0.012	0.031					
n-octane	0.062	0.085	0.197		0.08	0.050	0.018	
3-methyl heptane	0.042	0.082	0.131			0.043		
2-methyl heptane	0.054	0.102	0.171			0.048		
2,2,4-trimethyl pentane	0.148	0.576	0.476			0.132		

2,3,4-trimethyl pentane	0.055	0.170	0.171			0.048		
2,3,3-trimethyl pentane	0.061	0.209	0.194					
n-decane	4e-05		1e-4					
ALKENES								
ethylene	1.343	1.372	4.564	4.92	5.33	1.659	2.107	7.534
propylene	0.408	0.393	1.363	0.76	1.37	0.398	0.595	0.949
trans-2-pentene	0.032	0.057	0.097			0.090		
cis-2-pentene	0.016	0.029	0.050			0.112		
2-methyl-1-butene	0.076	0.102	0.250					
3-methyl-1-butene	0.018	0.037	0.058					
1-butene	0.041	0.058	0.139		0.21	0.229	0.071	
1-pentene	0.035	0.049	0.112					
cis-2-butene	0.017	0.030	0.059		0.10		0.107	
trans-2-butene	0.015	0.027	0.053		0.10	0.097	0.054	
acetylene	1.000	1.000	3.6	4.99	3.94		1.000	1.271
AROMATICS								
styrene	0.007	0.012	0.026					0.023
ethyl benzene	0.099	0.108	0.314		0.22	0.114	0.123	
(m+p)-xylene	0.387	0.346	1.159		0.64	0.351	0.330	
o-xylene	0.149	0.134	0.459	0.45	0.25	0.140	0.123	
1,2,4-trimethyl benzene	0.116	0.129	0.350			0.183	0.158	
1,2,3-trimethyl benzene	0.022	0.031	0.069			0.059	0.042	
1,3,5-trimethyl benzene	0.030	0.038	0.091			0.052	0.108	
1-ethyl-2-methyl benzene	0.033	0.036	0.100			0.050		
1-ethyl-(3+4)-methyl-benzene	0.116	0.124	0.349			0.140		
iso-propyl benzene	0.008	0.010	0.025					
n-propyl benzene	0.026	0.029	0.081					
benzene	0.171	0.210	0.617	0.95	1.09	0.326	0.474	0.599
toluene	0.846	0.792	2.622	3.51	3.79	0.749	0.967	6.439

A different method to determine emission ratios is to calculate the slope of the linear fit of the scatter plot of two compounds. Figure 2a shows the case of ethyl benzene versus acetylene. The color code indicates the photochemical age and it can be seen that the [*ethyl benzene*]/[*acetylene*] ratio is higher at younger ages. The linear fit through the data is shown by the solid black line. The emission ratio from the photochemical age method is shown by the red line in Figure 2a and lies close to all the points that have not been photochemically aged. The slope from the linear fit was determined for all the primary hydrocarbons listed in Table 1. The results are plotted in Figure 2b versus the photochemical age method from above. It can be seen that the values determined from the scatter plots are, for all compounds except two, lower than the method used here. Mixing with older air will cause the slopes from the correlation plots to change dependent on the lifetime and the mixing ratio of the investigated compounds in aged air masses.

Figure 2. (a) Scatter plot of ethyl benzene versus acetylene (same data as Figure 1a). The black line is the linear fit and the red line the emission ratio determined with the photochemical age method. (b) The emission ratios determined from scatter plots versus the ones determined with the photochemical age method for the 51 VOC species in Table 1, where each data point represents one compound. The emission ratios from the scatter plots are generally lower, because of chemistry and mixing with aged air masses.



Emission Ratios of Oxygenated VOCs

The calculation of the emission ratios of oxygenated VOCs (oxyVOCs) is further complicated by their photochemical production and possible biogenic sources [9, 13]. Therefore no linear fit can be used in a semi-logarithmic plot of the $[oxyVOC]/[acetylene]$ ratio versus photochemical age. The evolution of oxyVOCs can be described using the expression [9]:

$$\begin{aligned} &[oxyVOC] = ER_{oxyVOC} \times [C_2H_2] \times \exp[-(k_{oxyVOC} - k_{C_2H_2})[OH]\Delta t] + \\ \text{Equation (3)}\quad &ER_{precursor} \times [C_2H_2] \times \frac{k_{precursors}}{k_{oxyVOC} - k_{precursors}} \times \frac{\exp(-k_{precursors}[OH]\Delta t) - \exp(-k_{oxyVOC}[OH]\Delta t)}{\exp(k_{C_2H_2}[OH]\Delta t)} + \\ &([biogenics] + [background]) \end{aligned}$$

where the first term represents the removal of oxyVOCs by OH as described in Equation (1). The second term represents the production and subsequent removal of secondary anthropogenic oxyVOCs. The third term represents biogenic emissions, including photochemical production from biogenics, plus the local background mixing ratios. ER_{oxyVOC} and $ER_{precursor}$ are the emission ratios of the oxyVOC and the precursor and $k_{precursor}$ the rate coefficient with OH from the precursor to form oxyVOCs. The parameter k_{oxyVOC} is the rate coefficient of the oxyVOC with OH [11]. Photolysis reactions of the oxygenated species are not taken into account, because the photolysis loss rate is small compared to the OH loss rate [12]. ER_{oxyVOC}, $ER_{precursor}$, $k_{precursor}$, ([*biogenics*]+[*background*]) are determined from a linear least square fit that minimizes the difference between the measured oxyVOC mixing ratio and those calculated from Equation (3) [9]. The results of this analysis for the emission ratios of the measured oxyVOCs on the RHB are shown in Table 2.

Table 2. The emission ratios of oxygenated VOCs.

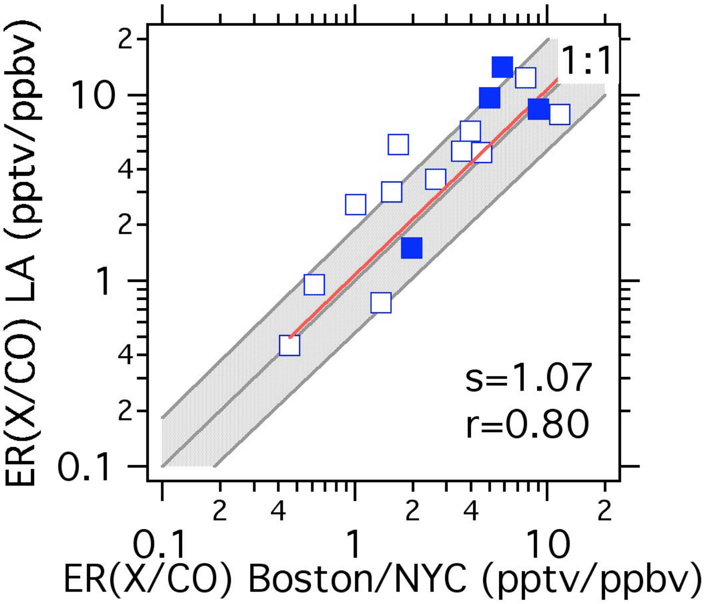
Compound	ER_{oxyVOC} (2004)	ER_{oxyVOC} (2002)	ER_{oxyVOC} (slope fresh urban plumes)	ER_{oxyVOC} (2004)	ER_{oxyVOC} (Los Angeles)	ER_{oxyVOC} (Vehicle Exhaust)	$ER_{database}$
	pptv [pptv C_2H_2]$^{-1}$	pptv [pptv C_2H_2]$^{-1}$	pptv [ppbv CO]$^{-1}$	pptv [ppbv CO]$^{-1}$	pptv [ppbv CO]$^{-1}$	pptv [pptv C_2H_2]$^{-1}$	pptv [ppbv CO]$^{-1}$
Acetaldehyde	0.2	0.8	5.0	0.7	9.7	0.1	0.5
Propanal	0.2	0.2	n/a	0.7	n/a	0.01	
Acetone	0.8	1.2	5.8	2.9	14.2	0.1	0.5
MEK	0.2	0.3	2.0	0.8	1.5	0.01	
Methanol	1.1	2.3	9.0	4.0	8.4		0.1
Ethanol	1.6	1.0	n/a	5.8	n/a		
Acetic acid	0.0	0.0	3.2	0.0	n/a		

Comparison with Other Recent Data Sets

In 2002 the emission ratios relative to acetylene were determined on a cruise of the RHB in roughly the same area downwind of Boston and New York City [9]. The comparison with the 2004 data is given in Table 1 and 2. Baker et al. [14] collected whole air canister samples at different ground sites in 28 US cities including Boston and New York City and a comparison with the current data is given in Table 1. A comparison with the average urban air composition from 39 US cities published by Seila et al. [15] is also included in Table 1. Also shown Table 1 and Table 2 is a comparison with VOC measurements from vehicle exhaust [16]. In the spring of 2002, the NOAA WP-3D aircraft conducted a research flight over the Los Angeles Basin [17, 18]. During this flight the emission ratios for all available VOCs were determined using the slopes of the correlation plots with CO. The comparison with the results from Boston and New York City is shown in Figure 3 as an example and the values are given in Table 1 and 2.

The emission ratios determined in this work generally agree well with recent measurements from urban areas even though these were done in different years or cities. For alkenes and aromatics they also agree well with vehicle exhaust measurements. For individual compounds there are clear differences between the cities, years and seasons and agreement within a factor of 2 is shown as an example by the grey shaded area in Figure 3. These differences can be caused for example by different fuel compositions, different industrial facilities, different evaporative sources, which are also dependent on ambient temperature, and many other possible differences between cities or years. Furthermore uncertainties in the measurements and the analysis can cause differences between the various data sets.

Figure 3. Comparison of the 2004 emission ratios with CO with data from a flight in the Los Angeles Basin in 2002, where each data point represents one compound (full squares are oxygenates). The solid red line is a linear fit through the data. The grey shaded area shows an agreement within a factor of two.



Comparison with the Anthropogenic Emissions Database

The anthropogenic VOC emissions database, based on the NEI-99 data, separates emissions into four categories: on-road, non-road, point, and area sources. The on-road emissions are mobile sources, which are mainly highway gasoline and Diesel cars and trucks. The non-road emissions are from mobile sources, which are off-highway vehicles such as 2-stroke lawn and garden equipment or construction, farming and mining equipment. The area sources are for example from evaporation during storage and transport of petroleum products like gasoline service stations or non-industrial solvent evaporation. Finally, the point sources are industrial operations or petroleum and solvent evaporation from, for example, surface coating operations. Small point sources are included in the area sources.

To compare the measured emission ratios with the VOC emissions database we have integrated the gridded VOC emissions for all available species and CO in squares that cover Boston, New York City and Los Angeles, respectively. The relative speciation of the four categories for the three cities, the total emissions and the emissions per square kilometer are given in Table 3. In Boston and New York City the area sources and in Los Angeles the on-road sources dominate. The point sources in all three cities are very small. In all three cities the emissions per square kilometer are about the same, but New York as the largest city has the largest total emissions.

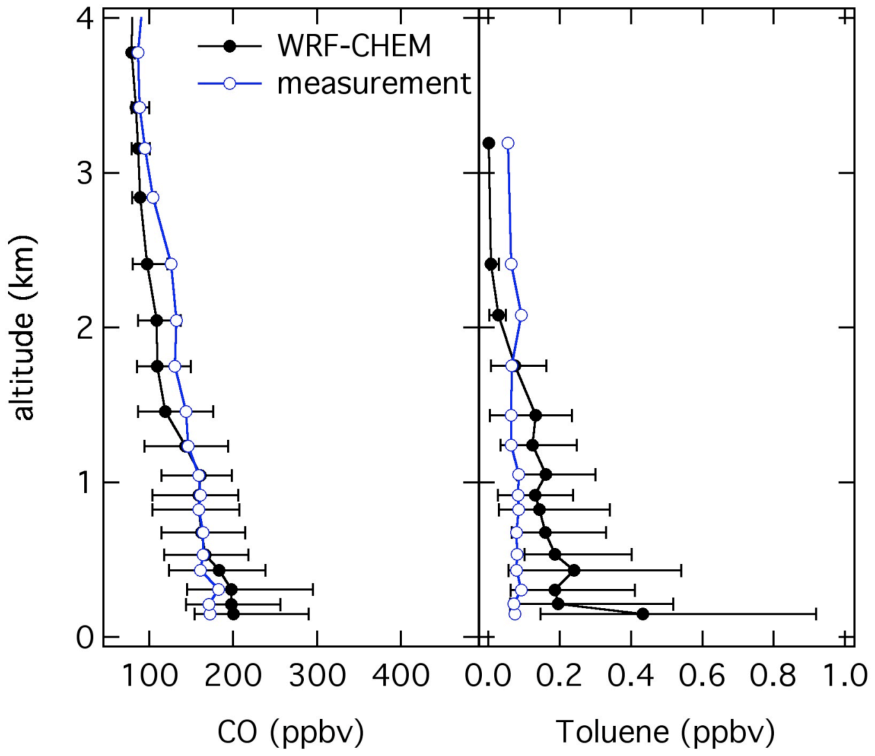
Table 3. Relative contributions of the different source categories to the VOC emissions, the total VOC emissions, and the VOC emissions per square kilometer of Boston, New York City and Los Angeles.

City	On-road VOC emission (%)	Non-road VOC emission (%)	Area VOC emission (%)	Point VOC emission (%)	Total VOC emission (tons/day)	VOC emissions in (kg/day/km^2)
Boston	28	24	45	3	211	139
New York City	32	17	47	4	1210	149
Los Angeles	40	25	32	3	908	148

After summing up the four categories, the total VOC/CO ratios for individual and lumped species were calculated. The ratios for all the available individual species are given in Table 1 and the comparison for Boston/New York and Los Angeles with the measurements is shown in Figure 4. The measurements and the database do not agree well, especially the alkanes and oxygenated VOCs are very different.

The main source for the alkanes are the area sources, which are the most difficult to determine accurately. In the emissions database the area sources are generally larger than the on-road emissions, but the good agreement of the measurements with the vehicle exhaust may indicate that the contribution of the area sources is overestimated in the database. Only recently it was shown that oxyVOCs are also emitted in large quantities from urban areas (eg [9, 13, 19-21]). The sources of oxyVOCs in urban areas is not well understood yet, but they are likely not primary automobile emissions [9]. The emissions database does not yet include those recent findings of large oxyVOC emissions, which cause the large discrepancies with the presented oxyVOC emission ratios.

Figure 4. Measured and modeled altitude profiles of toluene and CO.

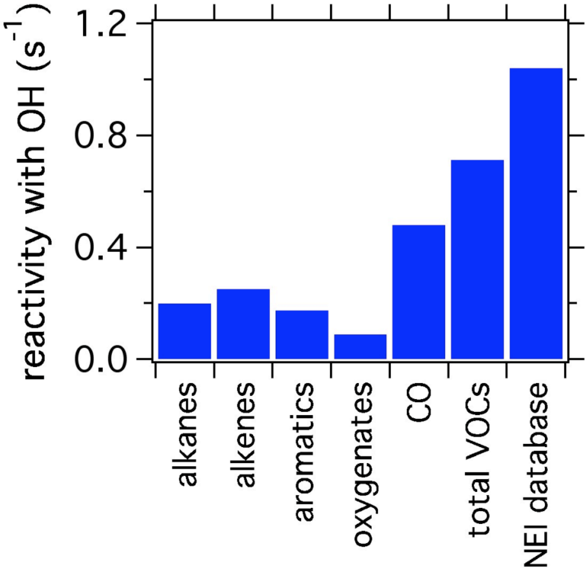


The prediction of toluene and CO from the WRF-CHEM model is compared in Figure 4 with the measurements of those two species. In Figure 4 an altitude profile of all the measurements from the NOAA WP-3D during the NEAQS-ITCT2004 campaign are compared with the WRF-CHEM results along the flight track. CO agrees fairly well, whereas toluene is over-predicted by almost a factor of 3, which is close to the difference in the emission ratios from the database and the measurements.

OH reactivity

The OH reactivity of a compound is calculated by multiplying its concentration with the OH rate coefficient. Shown in Figure 5 are the reactivities of CO (100 ppbv) and the different classes of compounds calculated from the measured emission ratios of the 2004 data. The total reactivity of all VOCs is about 50% larger than that of CO. Also shown in Figure 5 is the total reactivity of all the VOCs in the emissions database. The total reactivity of the database is about 30% larger than of the sum of the measured VOCs. The database includes more compounds in the lumped species than the measurements, but the ones that contribute most to the reactivity are measured. Using this database it might be difficult to predict individual compounds accurately as seen in Figure 4, but the small difference in total reactivity is promising in terms of ozone predictions.

Figure 5. VOC and CO reactivities with OH calculated from the measured emission ratios and a CO enhancement of 100 ppbv. Different classes of compounds and all the VOCs included in the EPA NEI-99 based database are shown.



CONCLUSIONS

Emission ratios versus CO of a large number of VOCs were determined for the urban areas Boston/New York City and Los Angeles and compared to other datasets. The measurements presented here compared well to other measurement data from urban areas and also to measurements of vehicle exhaust indicating that a large source of VOCs in urban areas is from vehicle exhaust. On the other hand the measured emission ratios did not compare well (R=0.29, slope of 0.57) with a frequently used anthropogenic emissions database, especially the alkanes and the oxygenated VOCs showed discrepancies of up to an order of magnitude. The urban emissions in the database are dominated by area sources and not by the on-road emissions. The toluene mixing ratios calculated with the WRF-CHEM model in the New England using this database are over-predicted by about a factor of three. This is about the same difference as between database and measurements. Using measured emission ratios for urban areas instead of inventories may therefore help to improve the quality of regional air quality forecast models. It is also important in future studies to find out the reasons for the discrepancies and apply the appropriate corrections to the speciation profiles of VOCs used in the inventories.

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KEYWORDS

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