Biomass burning and anthropogenic sources of CO over New England in the summer 2004

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[1] During the summer of 2004 large wildfires were burning in Alaska and Canada, and part of the emissions were transported toward the northeast United States, where they were measured during the NEAQS-ITCT 2k4 (New England Air Quality Study–Intercontinental Transport and Chemical Transformation) study on board the NOAA WP-3 aircraft and the NOAA research vessel *Ronald H. Brown*. Using acetonitrile and chloroform as tracers the biomass burning and the anthropogenic fraction of the carbon monoxide (CO) enhancement are determined. As much as 30% of the measured enhancement is attributed to the forest fires in Alaska and Canada transported into the region, and 70% is attributed to the urban emissions of mainly New York and Boston. On some days the forest fire emissions were mixed down to the surface and dominated the CO enhancement. The results compare well with the FLEXPART transport model, indicating that the total emissions during the measurement campaign for biomass burning might be about 22 Tg. The total U.S. anthropogenic CO sources used in FLEXPART are 25 Tg. FLEXPART model, using the U.S. EPA NEI-99 data, overpredicts the CO mixing ratio around Boston and New York in 2004 by about 50%.

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1. Introduction

[2] Forest fires are known to be a major source of CO, VOCs and aerosols on a global scale [*Andreae and Merlet*, 2001; *Crutzen and Andreae*, 1990]. Although most forest fires are found in tropical regions, fires in boreal forests can have an influence on the air quality in the midlatitude Northern Hemisphere. In the summer of 1995 large forest fires in northern Canada caused 52–74% of the variance in ground level carbon monoxide (CO) measurements and were responsible for 10 to 30 ppbv ozone enhancements throughout the southeastern United States over a two week period [*McKeen et al.*, 2002; *Wotawa and Trainer*, 2000]. In 1998 forest fires in Canada caused 58% of the CO enhance-

ment in Mace Head, Ireland [*Forster et al.*, 2001]. During July 2002, wildfires burning in Quebec, Canada, increased CO mixing ratios to 525–1025 ppbv at various ground sites in New England for a couple of days [*DeBell et al.*, 2004].

[3] In July and August of 2004, a large-scale atmospheric chemistry and transport study was conducted over North America and Europe within the framework of the ICARTT collaboration (International Consortium for Atmospheric Research on Transport and Transformation). As part of the NOAA contribution to ICARTT, the NEAQS-ITCT 2k4 (New England Air Quality Study–Intercontinental Transport and Chemical Transformation) study was conducted, which involved airborne measurements using the NOAA WP-3 research aircraft based out of Portsmouth, New Hampshire and ship-based measurements using the NOAA research vessel *Ronald H. Brown* in the Gulf of Maine. During the NEAQS-ITCT 2k4 study period extensive forest fires were burning in Alaska and western Canada. Smoke and enhanced CO from the forest fires were observed over the continental United States [*de Gouw et al.*, 2006; *Pfister et al.*, 2005] and even as far away as Europe as seen by the DLR Falcon aircraft (H. Schlager et al., personal communication, 2005).

[4] Acetonitrile (CH_3CN, methyl cyanide) is known to be a useful tracer for forest fire emissions and biomass burning in general [*Hamm and Warneck*, 1990]. Recently it was shown that acetonitrile was enhanced in a forest fire plume, but not in the Los Angeles Basin or in a power plant plume

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[*de Gouw et al.*, 2003c]. The long atmospheric lifetime of about 7 months [*Singh et al.*, 2003] makes acetonitrile a good indicator for forest fire emissions even after long-range transport [*de Gouw et al.*, 2004].

[5] Chloroform ($CHCl_3$, trichloromethane) has significant anthropogenic industrial sources (pulp and paper manufacturing, water treatment, and other industrial facilities) [*Aucott et al.*, 1999; *Laturnus et al.*, 2002; *McCulloch*, 2003], and is also emitted to the atmosphere from natural sources (offshore seawater and soil processes). Atmospheric background mixing ratios of chloroform are about 7 pptv in the Southern Hemisphere and about factor of two higher in the Northern Hemisphere [*Cox et al.*, 2003; *O'Doherty et al.*, 2001]. Close to the anthropogenic sources over the continent, chloroform enhancements will be predominantly caused by the anthropogenic sources. The long lifetime in the atmosphere (6 months), about as long as CO, makes chloroform a good tracer for anthropogenic emissions in the atmosphere over New England.

[6] The NOAA WP-3 sampled plumes from the Alaskan and western Canadian fires on multiple flights after transport times ranging from a few days to two weeks [*de Gouw et al.*, 2006]. In the marine boundary layer the *Ronald H. Brown* saw enhancements of CO and acetonitrile on multiple days. Both platforms together sampled urban plumes on more than 100 occasions along the U.S. East Coast, mainly from New York and Boston, but also from various other cities in the northeastern United States. In this paper, we use the measurement data of acetonitrile, a biomass burning tracer, and of chloroform used as an anthropogenic tracer, to estimate the contribution of biomass burning and anthropogenic sources to the CO enhancement in the troposphere over New England. The results from the measurements are compared to the atmospheric transport model FLEXPART [*Stohl et al.*, 1998]. Using VOCs tracers to estimate the contribution of different sources to the CO mixing ratio has be successfully used in previous studies [*Barnes et al.*, 2003; *Reiner et al.*, 2001].

2. Measurements

2.1. Aircraft and Ship Measurements

[7] Research goals of the NEAQS-ITCT 2k4 study included a detailed characterization of (1) the primary emissions of gas-phase and aerosol species on the North American continent, including emissions from eastern U.S. cities (Boston and New York), forest vegetation, and point sources such as power plants, (2) the chemical transformation leading to the formation of secondary pollutants (ozone and aerosol), and (3) the transport processes involved, including local and long-range transport to Europe. The NOAA research vessel *Ronald H. Brown* operated in the Gulf of Maine between Boston, Massachusetts, and Nova Scotia from 5 July until 12 August 2004. The NOAA WP-3 aircraft conducted 18 research flights between 5 July and 15 August 2004, from Portsmouth, New Hampshire. The *Ronald H. Brown* and the WP-3 both carried an extensive set of instruments to characterize the gas-phase and aerosol properties of the atmosphere. A full description of the payloads is beyond the scope of this paper.

2.2. Carbon Monoxide Measurements

[8] CO was determined on the WP-3 aircraft using a vacuum ultraviolet fluorescence measurement [*Holloway et al.*, 2000]. The precision of the measurements is estimated to be 2.5%. Variability in the determination of zero levels results in an absolute uncertainty of about 1 ppbv in the values reported. The field standard was compared to NIST Standard Reference Material (SRM) 2612a (10 ppmv nominal CO in air). The concentration of the calibration standard is known to within 2%. The overall accuracy of the 1s measurements is thus estimated to be 5%.

[9] On the *Ronald H. Brown*, CO was measured via a modified AeroLaser GmbH (Garmisch-Partenkirchen, Germany) AL5002 Ultra-Fast CO analyzer, a commercially available vacuum-UV resonance fluorescence instrument [*Gerbig et al.*, 1999]. For the campaign, data were collected at 1 Hz and averaged to a 1-min resolution; the total uncertainty is estimated at 3%, with a limit of detection of 1.5 ppbv.

2.3. Acetonitrile Measurements

[10] Acetonitrile and many other volatile organic compounds (VOCs) were measured on the WP-3 aircraft with a PTR-MS instrument (Proton-Transfer-Reaction Mass Spectrometer) from Ionicon Analytik [*de Gouw et al.*, 2003a]. Acetonitrile was measured for 1 s every 17 s. During a ship-based intercomparison PTR-MS measurements of acetonitrile have been compared with an online GC-MS instrument [*de Gouw et al.*, 2003b], and possible interferences have been studied by combining PTR-MS with a gas chromatographic preseparation method [*de Gouw et al.*, 2003a, 2003c; *Warneke et al.*, 2003]. For a detailed description of the PTR-MS instrument, the reader is referred to these references. The PTR-MS was calibrated for acetonitrile and other VOCs between the flights using a standard mixture containing 500 ppbv that was diluted to sub-ppbv levels. The calibration accuracy is estimated to be better than 15%.

[11] Acetonitrile measurements on the ship were done using a newly developed PIT-MS (Proton Transfer Ion Trap-Mass Spectrometry) and an online GC-MS (gas chromatography-mass spectrometer) instrument. The PIT-MS instrument is similar to a PTR-MS but uses an ion trap mass spectrometer (IT) instead of a quadrupole as a detector. The use of an IT can improve the measurement frequency and the selectivity of PTR-MS [*Prazeller et al.*, 2003; *Warneke et al.*, 2004]. The instrument was described in detail by [*Warneke et al.*, 2005a] and no details will be given here. The time resolution of the PIT-MS acetonitrile measurements was 2 min and the detection limit 73 pptv. Calibration measurements were done every 2 days using a standard mixture. Acetonitrile measurements compared well with the online GC-MS, which is described below, during the whole cruise [*Warneke et al.*, 2005b].

2.4. Chloroform Measurements

[12] During every flight, up to 80 whole air samples (WAS) were collected in electropolished stainless steel gas canisters. The canisters were transported to the NCAR laboratory in Boulder, where they were analyzed within a few days for hydrocarbons, chloroform and other halocarbons using several gas chromatography techniques. The

sampling and the subsequent analysis of the canisters is described by [*Schauffler et al.*, 1999, 2003] and references therein. The overall accuracy for the chloroform measurements is about 10%.

[13] On the *Ronald H. Brown*, chloroform was measured using an online GC-MS. A detailed description of this instrument and its analysis procedure is given elsewhere [*Goldan et al.*, 2004]. The GC-MS instrument analyzed 350 mL air samples with a 5-min acquisition time every 30 min. More than 100 VOCs including acetonitrile, chloroform and many oxygenated compounds, hydrocarbons, halocarbons and alkyl nitrates can be identified and quantified with this instrument. The detection limit of the GC-MS instrument is <0.5 pptv and the measurement precision is about 2%. A chloroform calibration was performed only once before the campaign and therefore the overall accuracy for this compound is rather high with about 30%. The overall accuracy for acetonitrile is mainly dependent on the quality of the calibration standard used and is believed to be within 10%. In the following analysis we have used the PIT-MS measurements, whenever a higher time resolution was desired and the GC-MS measurements, whenever the higher sensitivity and accuracy was beneficial.

2.5. FLEXPART Transport Model

[14] FLEXPART is a Lagrangian particle dispersion model used to describe the long-range transport of pollutants in the atmosphere [*Stohl et al.*, 1998, 2005]. For the results shown here, FLEXPART was run backward in time: small boxes were created along the flight and ship track and in every box 40000 particles were released and tracked for 20 days backward in time. The model output, with a global resolution of $1° × 1°$ and over North America of $0.25° × 0.33°$, 60 vertical levels and 1 day, consists of a response function to emission input (i.e., an emission sensitivity), which is proportional to the residence time of the particles in a given volume. If folded with the gridded emission fluxes from an emission inventory and integrated over the volume of the atmosphere or parts of it, a mixing ratio at the aircraft or ship location is obtained. The transport was described in FLEXPART using meteorological data from both the ECMWF (European Center for Medium-Range Weather Forecasts), and GFS (Global Forecast System) model of the National Center for Environmental Prediction (NCEP).

[15] The emission inventory used here for the Alaskan and Canadian fires in the summer of 2004 was produced using data taken from the Webpage of the Center for International Disaster Information (CIDI) (http://www.cidi.org/wildfire) and satellite observations by the MODIS instruments aboard the Aqua and Terra satellites. The daily areas burned per geographic province from the CIDI were smoothed with a 3-day running mean. The actual fire locations were determined using the number of fire hot spots detected by satellites. The hot spots were counted daily on a $1 × 1°$ grid and for every 3-day period the maximum daily number of hot spots was taken in order to account for possible missing detections during cloudy periods. The areas burned in the fire provinces were then attributed to the grid cells by weighting with the number of hot spots. Finally, a constant emission factor of $4.5 × 10^5$ kg CO per km^2 burned was used to obtain daily CO

emission fields [*Forster et al.*, 2001; *Wotawa and Trainer*, 2000]. The emissions of forest fires were evenly distributed over the lowest 1, 3 and 10 km of the atmosphere, respectively, to mimic the rapid vertical transport in fire-induced convective clouds that can be associated with large-scale forest fires [*Lavoue et al.*, 2000]. In the analysis presented here only the 10 km injection height results were used, because they generally delivered the best comparison with the measurements. A detailed comparison of FLEXPART with measurements for all observed fire plumes on the WP-3 is given by *de Gouw et al.* [2006].

[16] The anthropogenic CO inventory for North America used in FLEXPART is based on the U.S. EPA NEI-99 inventory (National Emissions Inventory, base year 1999, version 3) [*U.S. Environmental Protection Agency (U.S. EPA)*, 2004a]. This inventory was derived at 4-km horizontal resolution from spatial surrogates [*U.S. EPA*, 2004b] for each U.S. county and Canadian province, and average ozone season day (June through August). It includes county level estimates of on-road, off-road, area, and point sources. The 4-km resolution emissions, available through a graphics information system interface [*Frost and McKeen*, 2004], were then aggregated into the FLEXPART model output grid. Outside North America the $1° × 1°$ CO emissions from the EDGAR 1995 (version 3.2) inventory are used [*Olivier and Berdowski*, 2001].

3. Results and Discussion

3.1. CO Source Distribution Estimate Using VOCs

[17] In Figure 1, the altitude profiles of CO, acetonitrile (biomass burning tracer) and chloroform (anthropogenic tracer) measured on the WP-3 are shown. Most fire plumes were found between 2–5 km altitude, which can be seen in the strong acetonitrile enhancements at this altitude (Figure 1a). In contrast, the altitude profile of chloroform has the maximum at the surface (Figure 1b). The WP-3 sampled the anthropogenic emissions mainly from Boston and New York close to the source region, whereas the biomass burning emissions were transported over a long distance at higher altitudes to the measurement location. The New York and Boston plumes were usually transported from these cities along the New England coast at low altitudes and then over the ocean, where they were regularly found at an altitude of 0.5–1 km above the ocean surface as can be seen in Figure 1b. The CO altitude profile in Figure 1c is separated into two categories: (1) all the data and (2) data without influence of biomass burning (acetonitrile < 150 pptv) [*Schneider et al.*, 1997]. With this separation it becomes clear that for these data most observed strong CO enhancements in the free troposphere are caused by biomass burning emissions, but even at altitudes below 2 km biomass burning caused some of the large CO enhancements. The CO altitude profile without biomass burning influence resembles the chloroform profile well with the highest mixing ratios in the boundary layer and decreasing in the free troposphere.

[18] Figure 2 shows scatterplots of CO versus acetonitrile and chloroform for all data from all flights. In Figure 2a (CO versus acetonitrile) all the data are shown with the open black circles. The colored points are a subset of data where canister samples, and therefore chloroform measurements,
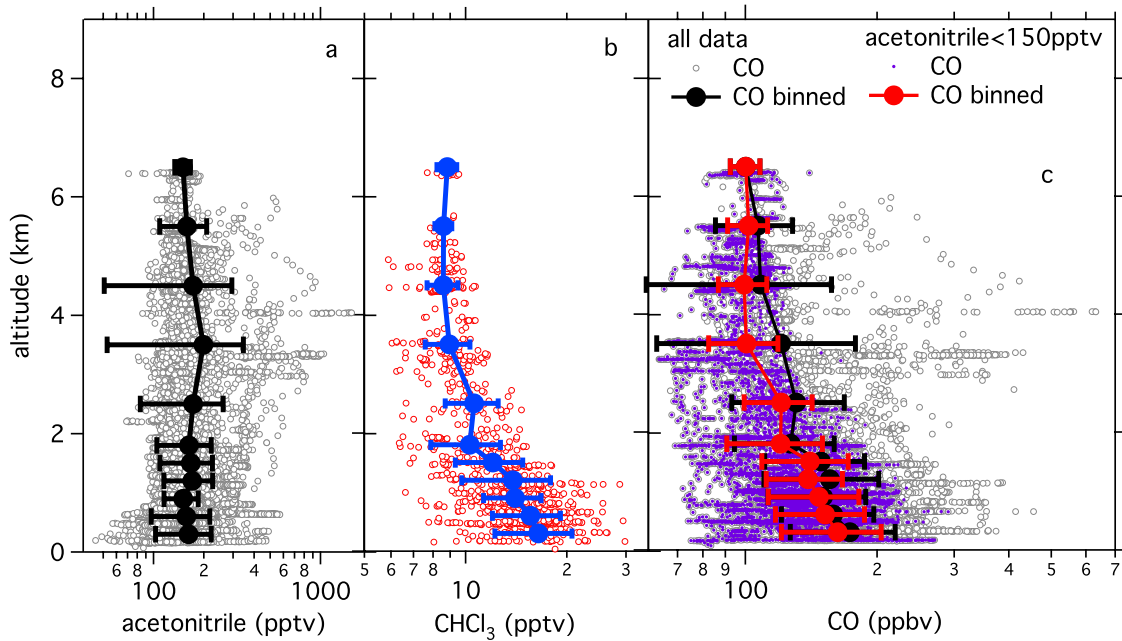
Figure 1. (a) Altitude profile of acetonitrile. (b) Altitude profile of chloroform. (c) Altitude profile of CO with and without biomass burning influence. The error bars are the standard deviation within each altitude bin. Measurements were made on the NOAA WP-3 aircraft.

were available. The latter points are averaged over the canister collection time and color coded with the chloroform mixing ratio. In Figure 2a two different populations can be clearly seen: (1) the emissions from the urban centers Boston and New York with high CO mixing ratios and small acetonitrile enhancements and (2) the fire plumes showing a good correlation between CO and acetonitrile. In the urban emission population chloroform was high, where-

as in the biomass burning population chloroform was not enhanced as can be seen from the color code. Local burning in urban centers, such as residential fires or waste burning, might cause the small acetonitrile enhancements in the urban emission population. The black curve in Figure 2a is a linear fit through the measurements of the most intense fire plumes with acetonitrile mixing ratios above 400 pptv. The linear fit procedure used in the manuscript is a two-
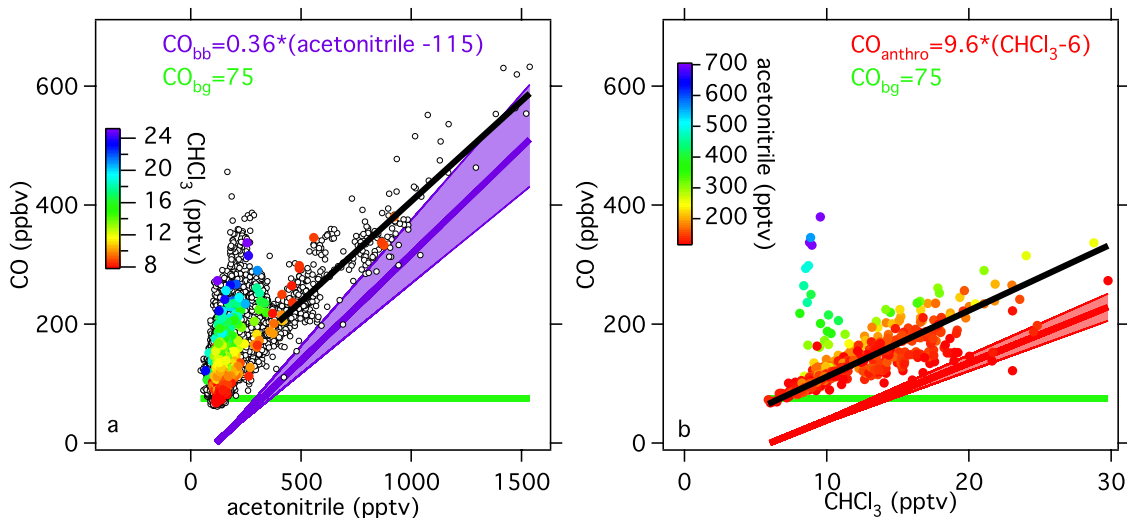

Figure 2. (a) Scatterplot of CO versus acetonitrile on the NOAA WP-3. The black solid line shows a linear fit for all data with acetonitrile larger than 400 pptv. The purple line shows the CO_{bb} estimated from the CO-acetonitrile enhancement ratio. The purple area indicates the error estimated from the enhancement ratios of the individual fire plumes. The atmospheric background of CO is estimated as 75 ppbv (green line). The open black circles are all the measured data and on top are the same data color coded whenever chloroform measurements were available. (b) Scatterplot of chloroform versus CO on the NOAA WP-3. The color code indicates the acetonitrile mixing ratio. The black solid line shows a linear fit and the solid red line indicates CO_{anthro}.

sided, or orthogonal distance regression (ODR) analysis, which minimizes the orthogonal distance between the data points and the fitted line [*Bakwin et al.*, 1997]. The slope of the linear fit shows that 0.36 ± 0.06 ppbv of CO per pptv of acetonitrile were observed over New England that were emitted from the forest fires. Using this enhancement ratio ($ER_{CO\text{-acetonitrile}}$) the amount of CO resulting from biomass burning (CO_{bb}) can be estimated.

$$CO_{bb} = ER_{CO\text{-acetonitrile}} \times \Delta\text{acetonitrile}$$
$$= 0.36 \times (\text{acetonitrile} - 115 \text{ pptv}) \qquad (1)$$

[19] CO and acetonitrile atmospheric background mixing ratios of 75 ppbv (CO_{bg}) and 115 pptv, respectively, were estimated from the lowest values in the free troposphere during times when very clean air was measured and from the altitude profiles in Figure 1. The CO_{bg} is shown in Figure 2 by the green solid lines. The CO_{bb} is shown in Figure 2a by the solid purple line. The purple shaded area around CO_{bb} reflects the estimated error, which is taken as the minimum ($ER_{CO\text{-acetonitrile(min)}} = 0.30$ ppbv/pptv) and maximum ($ER_{CO\text{-accetonitrile(max)}} = 0.42$ ppbv/pptv) enhancement ratios from the individual fire plumes with acetonitrile mixing ratios larger than 400 pptv that were taken from [*de Gouw et al.*, 2006]. This estimated error is larger than the error in the linear fit (± 0.003 ppbv/pptv) in Figure 2a.

[20] Because $ER_{CO\text{-acetonitrile}}$ is determined over New England, the estimation of CO_{bb} in the same region should be valid for all fire plumes, even though the actual emission ratio at the fire location is not known. The enhancement ratios in the individual fire plumes showed no trend with the plume age and therefore the difference in lifetime of CO and acetonitrile should not influence this analysis. [*de Gouw et al.*, 2006] have shown that most of the individual fire plumes were lofted to high altitudes and then transported to the measurement region with comparable transport mechanisms. During this transport, the chemistry in the plumes was rather slow because of low OH concentrations [*de Gouw et al.*, 2006]. Because acetonitrile is a very good tracer for biomass burning and there are only small differences in the observed enhancement ratios of all the fire plumes, the above described method for calculating CO_{bb} should be applicable also outside the most intense fire plumes all over New England and that assumption will be tested in this work.

[21] With the same method, but chloroform as a tracer, the anthropogenic contribution to CO (CO_{anthro}), can be calculated. Chloroform is a good tracer for this method for the following reasons: (1) Chloroform is highly correlated with CO in the urban plumes, and (2) the atmospheric lifetime of chloroform is close to that of CO, so that the observed enhancement ratios are relatively independent of air mass age. Chloroform has an OH rate coefficient of 1.0×10^{-13} cm^3 molecules^{-1} s^{-1}, which is close to CO with 2.4×10^{-13} cm^3 molecules^{-1} s^{-1} (1 atm and 298K) [*Atkinson et al.*, 2005]. (3) Chloroform has a very small biomass burning and a large industrial source [*Keene et al.*, 1999]. Chloroform is thought to have a globally significant oceanic source [*Keene et al.*, 1999] and therefore the CO_{anthro} estimation might yield an overestimate close to the ocean surface. During this experiment, however, no enhanced chloroform mixing ratios were observed in the marine boundary during vertical profiles with the WP-3 over the ocean. Also the large difference between the Northern and Southern Hemispheric background chloroform mixing ratios indicates the dominance of terrestrial/anthropogenic sources in the Northern Hemisphere [*O'Doherty et al.*, 2001]. It can be therefore assumed that the oceanic source has only a small influence on the calculation of CO_{anthro}.

[22] We did consider other species as tracers for the anthropogenic emissions, such as aromatic VOCs and other halocarbons. However, the aromatics also have a biomass burning source and most other halocarbons have very different lifetimes than CO and are therefore not usable for this analysis. Dichloromethane (CH_2Cl_2) and tetra-chloroethylene (C_2Cl_4) have no biomass burning source and lifetimes close to that of CO, but were not as highly correlated with CO as chloroform and therefore not used in this analysis.

[23] The scatterplot of CO with chloroform from all flights (Figure 2b) is color coded with the acetonitrile mixing ratio. In the biomass burning plumes, recognizable by the elevated acetonitrile, no chloroform enhancements are measured, whereas in the urban plumes a good correlation with CO is observed. The linear fit through the data without biomass burning influence (acetonitrile < 150pptv) (black line in Figure 2b) yields a slope of 9.6 ± 1.0 ppbv pptv^{-1} (CO chloroform^{-1}). Using this enhancement ratio and an atmospheric chloroform background of 6 pptv, the anthropogenic CO contribution, CO_{anthro}, is calculated as:

$$CO_{anthro} = ER_{CO\text{-chloroform}} \times \Delta CHCl_3 = 9.6 \times (CHCl_3 - 6 \text{ pptv})$$
$$(2)$$

[24] The atmospheric background for chloroform was estimated by looking at measured values in clean air and from the altitude profile in Figure 2b, which is somewhat lower than might be expected from literature values [*Cox et al.*, 2003; *O'Doherty et al.*, 2001]. CO_{anthro} is shown in Figure 2b with the red solid line and the red shaded region is from the minimum and maximum enhancement ratios of individual urban plumes that were encountered during the campaign.

[25] For completion, the scatterplot of acetonitrile versus chloroform is shown in Figure 3. The two compounds are, as expected, not correlated: acetonitrile is only high in the fire plumes, chloroform is only high in the urban plumes. No enhancements can be seen from the respective other tracer in either plume. This means that for the most part the urban and forest fire plumes were well separated in the atmosphere.

[26] As a validation for this method of estimating the source contributions of CO the sum of CO_{bg}, CO_{bb} and CO_{anthro} is compared to the measured CO mixing ratio in Figure 4. The calculation agrees well with the measurement with a linear correlation coefficient r of 0.92. This shows that the CO measurements on the WP-3 can indeed be explained by a superposition of a background, a biomass burning and an anthropogenic term that were calculated using VOC enhancement ratios.
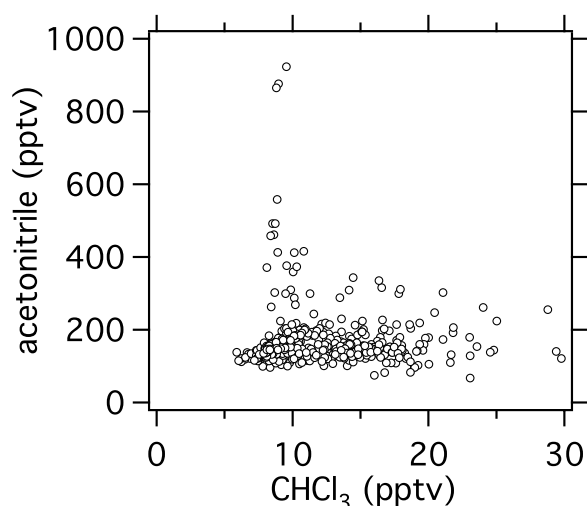
Figure 3. Scatterplot of acetonitrile versus chloroform for the NOAA WP-3.

[27] The scatterplots of CO versus acetonitrile and chloroform measured with the GC-MS on the *Ronald H. Brown* are shown in Figure 5. Only small enhancements of acetonitrile were observed in the marine boundary layer (Figure 5a). The clear distinction of biomass burning and urban plumes as seen in the aircraft measurements is not present in the marine boundary layer. The scale in Figure 5a is set the same as in Figure 2 (CO versus acetonitrile on the WP-3 shown with the grey dots in the background) to compare the small acetonitrile enhancements measured in the marine boundary layer to the intense fire plumes observed on the WP-3. The color code indicates the chloroform mixing ratio and it can be seen that in many cases acetonitrile and chloroform were enhanced at the same time. This would result from the biomass burning plumes being mixed to the surface over land at night and then transported out over the ocean together with urban plumes because of the stability of the marine boundary layer. Furthermore small urban sources of acetonitrile might exist such as biofuel use or possibly small emissions from industry or vehicle exhaust [*Holzinger et al.*, 2001]. Therefore an enhancement ratio of CO specifically with acetonitrile is not expected. CO and chloroform are also well correlated in the marine boundary layer. The slope of the linear fit (10.2 $\pm$ 1.2 ppbv pptv^{-1} (CO chloroform^{-1})) in Figure 5b is similar to the one of the aircraft measurements. The possible ocean source of chloroform would result in a lower slope and therefore an overestimation of CO_{anthro} calculated using equation (2). On the other hand, the biomass burning influence that cannot be separated from the urban plumes, as was discussed earlier, would cause a higher slope.

[28] For the *Ronald H. Brown* the sum of CO_{bg}, CO_{bb} and CO_{anthro} does not compare to the measured CO mixing ratio as well as the WP-3 measurements, but still agrees fairly well with a slope of the linear fit of 1.5 and a linear correlation coefficient r of 0.77.

3.2. Case Study With Strong Biomass Burning Influence at the Surface

[29] For the flight on 11 July 2004 over the Boston urban area, the estimation of the biomass burning, anthropogenic

and background contribution to CO is shown in Figure 6. This flight was a night flight at low altitudes over the city. In Figure 6a the WP-3 flight track is shown on top of the map of the area, including the Massachusetts urban area outlines. The flight track is color-coded with acetonitrile showing enhancements above the 115 pptv background most of the time. This indicates that biomass burning emissions mixed down to low altitudes and influenced the air quality in and around the city of Boston. Using FLEXPART the average age of these biomass burning emissions was estimated to be 10 $\pm$ 3 days [*de Gouw et al.*, 2006]. The measured forest fire plume was therefore emitted around 1 July 2004. Using equation (1), CO_{bb} was calculated for this flight and is shown in Figure 6b. Chloroform measurements were not available for this flight and CO_{anthro} was calculated by subtracting CO_{bg} and CO_{bb} from the measured CO, which seems to be a very good approximation as can be seen from the good correlation in Figure 4. CO_{anthro}, CO_{bb} and CO_{bg} are shown in Figure 6b as a stacked sum. Even over the urban center at low altitude, biomass burning is clearly a larger contributor to the CO enhancement than anthropogenic sources for this flight. The anthropogenic contribution was higher only during short periods of this flight, which were found mainly to the west of Boston, where the urban outflow was measured and the acetonitrile enhancement was small. Altitude profiles of CO, acetonitrile and CO_{bb}, CO_{anthro} and CO_{bg} for this flight are shown in Figure 7. Even at the lowest flight levels, which were below 500 m, the biomass burning dominates over the anthropogenic contribution. At higher altitudes, between 1 and 4 km, several layers with biomass burning emissions were detected, which were the largest contributor to CO. Above 4 km, CO mixing ratios were close to the estimated background mixing ratio of 75 ppbv.

[30] The average CO_{bb}, CO_{anthro} and CO_{bg} for this flight, given in Table 1, were 70 $\pm$ 12 ppbv, 38 $\pm$ 12 ppbv and 75 ppbv, respectively. This means 41 $\pm$ 6% of the CO, measured over Boston during this flight, was atmospheric
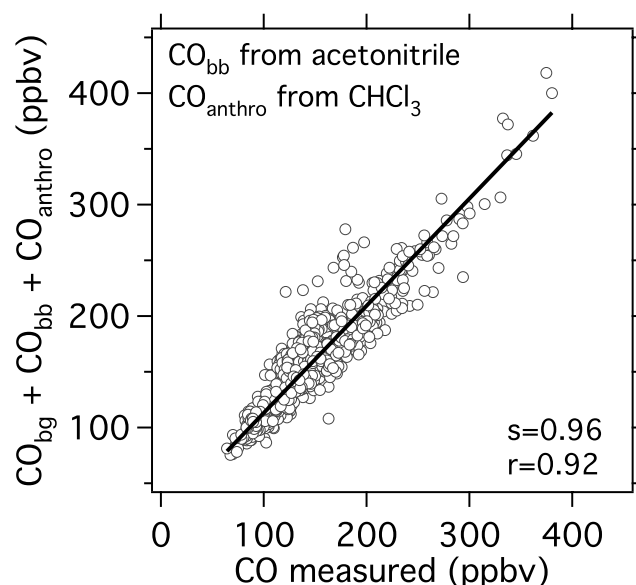

Figure 4. Scatterplot of CO_{bg} + CO_{bb} + CO_{anthro} versus measured CO.
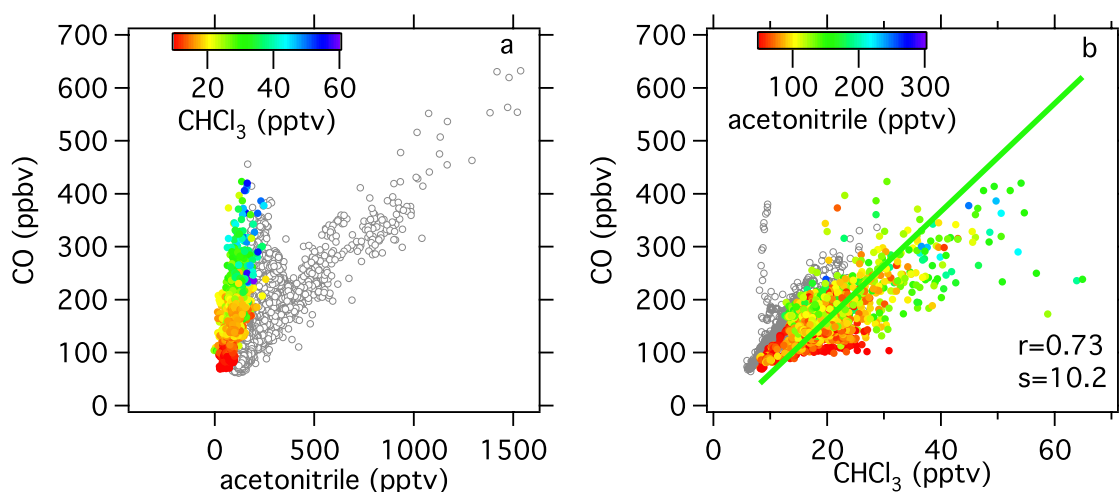
Figure 5. Scatterplot of acetonitrile and chloroform versus CO on the NOAA *Ronald H. Brown*. The color code indicates the chloroform or acetonitrile mixing ratio, respectively. The grey dots in the background are the NOAA WP-3 data from Figure 2.

background, $38 \pm 6\%$ from biomass burning emissions, and only $21 \pm 6\%$ from anthropogenic sources.

[31] During the same period, the *Ronald H. Brown* was downwind from Boston for several days. On 11 July 2004, the ship traveled into the Boston Harbor, where very high CO enhancements from local sources, such as small crafts and industrial facilities, were observed that are not reflected

in the chloroform measurements. This is partly because the CO enhancements were of such short duration that they were not captured with the GC-MS instrument that takes 5-min samples every 30 min, and partly because these local CO sources might not emit chloroform. The observed chloroform CO correlation during the WP-3 flights likely results from prior mixing of the various anthropogenic
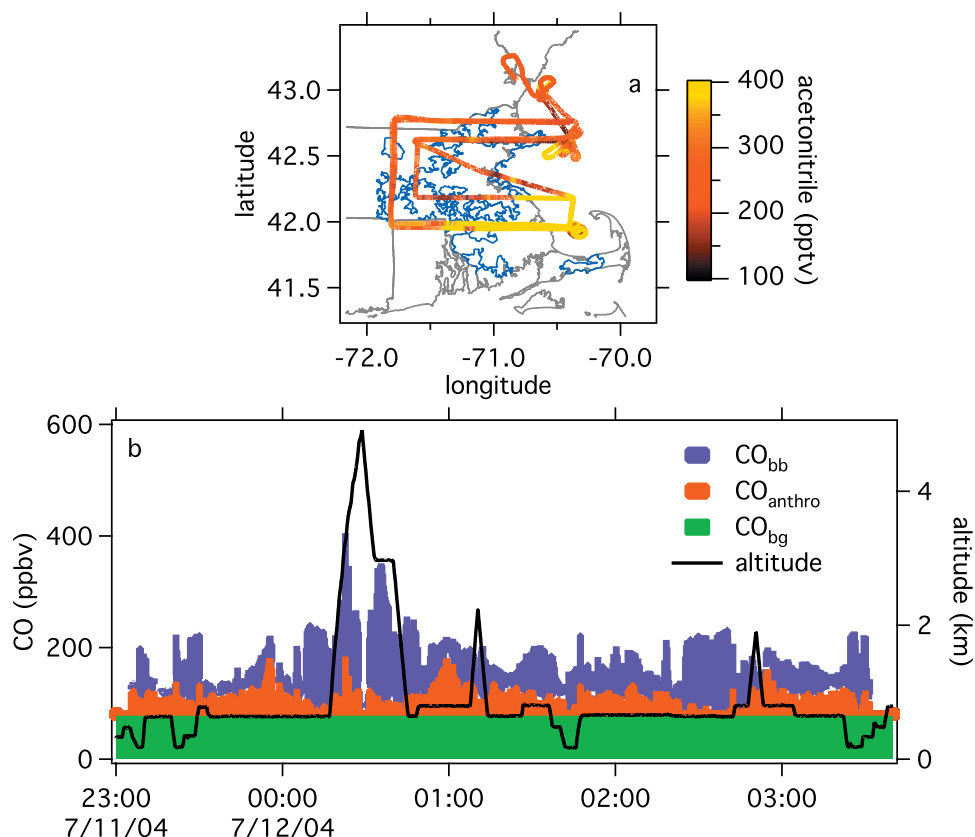

Figure 6. NOAA WP-3 flight on 11 July 2004. (a) Flight track on a map of the study area including the outlines of urban areas including Boston, Massachusetts. The color code shows the acetonitrile mixing ratio. (b) Time series of CO_{bb}, CO_{anthro}, and CO_{bg} as a stacked sum.
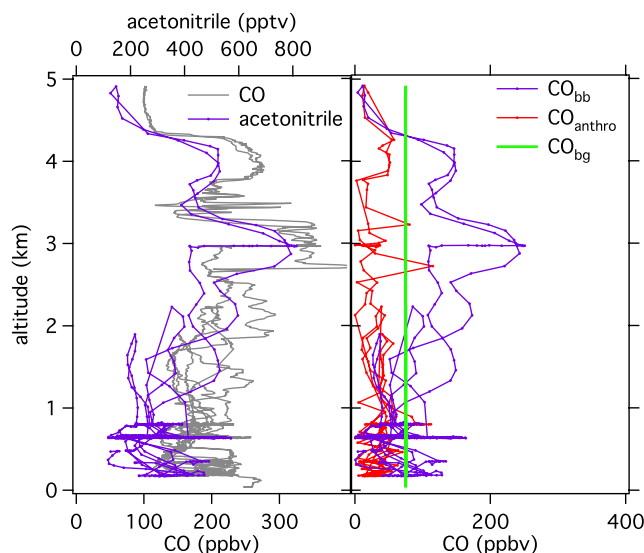
acetonitrile (pptv)

Figure 7. Altitude profile of measured CO and acetonitrile and calculated CO_{bb}, CO_{anthro}, and CO_{bg} from the flight on 11 July 2004 over Boston, Massachusetts.

sources in the urban areas. On the *Ronald H. Brown* a good correlation of CO with chloroform was always found downwind of the city centers. The ship track from 11 to 15 July 2004, color-coded with acetonitrile measured by PIT-MS, is shown in Figure 8a. Even in the marine boundary layer enhanced acetonitrile values were found during this episode. Most likely the biomass burning plume was mixed down to the surface over land late afternoon and from there transported out over the ocean together with the Boston plume. This results in a good correlation of acetonitrile and CO downwind of Boston. Over the ocean the surface layer was very stable and therefore the forest fire plumes could not be mixed down to the surface directly. Additional dilution likely occurred during the transport in the marine boundary layer, explaining the lower mixing ratios of acetonitrile and therefore CO_{bb} measured on the *Ronald H. Brown*. The lowest measured values were around 75 pptv, which we used here as the acetonitrile background. Ocean uptake is likely an effective sink for acetonitrile in the Gulf of Maine and would explain the lower measured background (S. Kato et al., Uptake and emissions of volatile organic compounds in the marine boundary layer during the 2004 New England Air Quality Study, manuscript in preparation, 2006). Using this value, CO_{bb}, CO_{anthro} and CO_{bg} are calculated using equations (1) and (2) with an acetonitrile background mixing ratio of 75 pptv for those four days and shown in Figure 8b as a stacked sum together with the measured CO mixing ratio. In the marine boundary layer downwind of Boston the anthropogenic fraction clearly dominates, but even here a clear influence of biomass burning was detected during this time period.

[32] The average CO_{bb}, CO_{anthro} and CO_{bg} calculated for the time period, shown in Figure 8b, are given in Table 1. Here $44 \pm 2\%$ were from the atmospheric background, $11 \pm 2\%$ of the CO was from biomass burning and $45 \pm 2\%$ from anthropogenic sources.

[33] To better demonstrate that biomass burning had a significant influence on CO even in the marine boundary

layer, the CO_{bb} calculated from acetonitrile and from FLEXPART is shown in Figure 8c for the first half of the cruise. Compared to the atmospheric background and the anthropogenic contribution, CO_{bb} is small, but CO enhancements of about 60 ppbv are frequently observed during this time period.

3.3. CO Source Contribution

[34] The average altitude profile of the CO source contribution along the flight and ship track for the whole campaign is shown in Figure 9 and averages of the entire data sets are given in Table 1. Figure 9a shows the CO_{bg}, CO_{bb} and CO_{anthro} mixing ratios, Figure 9b the fraction of the total CO signal and Figure 9c the fraction of CO_{bb} and CO_{anthro} to the CO enhancement. The aircraft measurements were averaged over different altitude bins, shown with the full circles, and the standard deviation within each altitude bin is given with the error bars. The results from the *Ronald H. Brown* measurements (open triangles) in the marine boundary layer of the Gulf of Maine are also shown in Figure 9 and Table 1 and are comparable to the lowest flight level of the airborne measurements. The atmospheric background is the overall largest contributor to the CO mixing ratio. Anthropogenic sources are the largest contributor to CO at low altitudes. Biomass burning is more important than anthropogenic sources at altitudes between 3 and 5 km, but even in the boundary layer a significant influence of the forest fire emissions can occasionally be detected. This shows that the air quality at the U.S. East Coast could be significantly influenced by forest fire emissions from Alaska and Canada. Especially for certain periods, as shown in Figures 6–8, the influence can be substantial. New England is an area with very high anthropogenic emissions from the densely populated areas around Boston and New York and also with strong biogenic emissions from the large forested areas mainly in New Hampshire and Maine.

Table 1. CO Source Contribution Along the Flight (NOAA WP-3) and Ship Track (NOAA *Ronald H. Brown* (RHB))[a]

	Background	Biomass Burning	Anthropogenic
Total CO Mixing Ratio, ppbv			
Total WP-3	75	18 ± 3	50 ± 3
Flight 11 Jul 2004	75	70 ± 12	38 ± 12
Total RHB	75	12 ± 3	82 ± 3
11–14 Jul 2004	75	19 ± 4	78 ± 4
Total CO, %			
Total WP-3	52	13 ± 1	35 ± 1
Flight 11 Jul 2004	41	38 ± 6	21 ± 6
Total RHB	44	7 ± 1	49 ± 1
11–14 Jul 2004	44	11 ± 2	45 ± 2
CO Enhancement, %			
Total WP-3	N/A	26 ± 7	74 ± 7
Flight 11 Jul 2004	N/A	65 ± 18	35 ± 18
Total RHB	N/A	13 ± 3	87 ± 3
11–14 Jul 2004	N/A	20 ± 4	80 ± 4
FLEXPART, ppbv			
Total WP-3	N/A	19	74
Flight 11 Jul 2004	N/A	37	38
Total RHB	N/A	17	147
11–14 Jul 2004	N/A	25	105

[a]The available error estimates are calculated using the minimum and maximum enhancement ratios from individual fire or urban plumes.
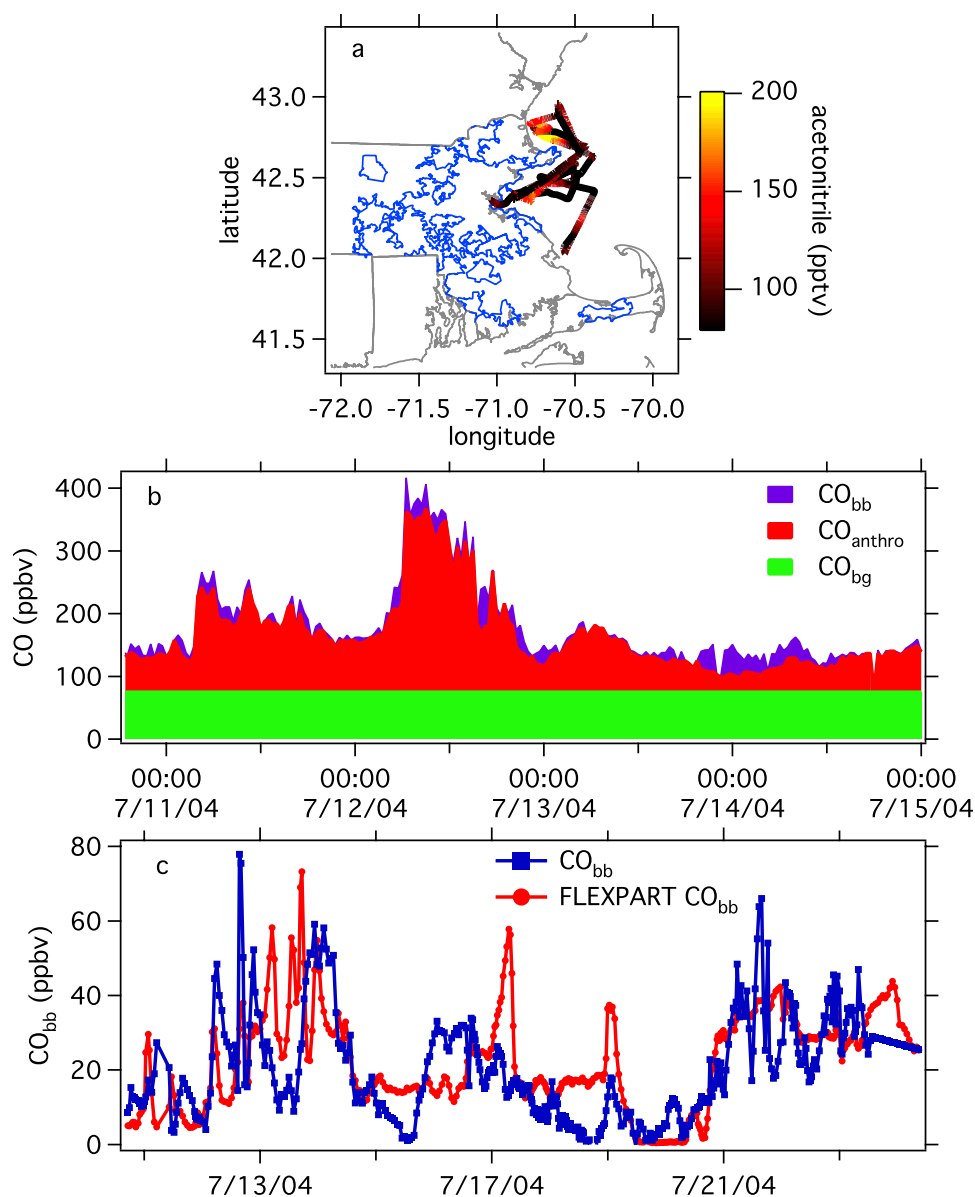
Figure 8. (a) Ship track of the NOAA *Ronald H. Brown* from 11 to 15 July 2004 in the Gulf of Maine close to Boston, Massachusetts. The color code shows the acetonitrile mixing ratio. (b) Time series of CO_{bb}, CO_{anthro}, and CO_{bg} as a stacked sum together with the measured CO. (c) Time series from 11 to 24 July 2004 of CO_{bb} and FLEXPART CO_{bb}.

Biomass burning emissions can increase the burden of air pollutants in this area even further during the summer months.

[35] Here it should be mentioned that the CO source contribution is only valid along the flight and ship track, respectively. The values of both CO_{bb} and CO_{anthro} presented in Figure 9 and Table 1 may be an overestimation of the regional averages, because the flights and the ship track were designed to investigate mainly the biomass burning and/or urban plumes.

3.4. Comparison With FLEXPART

[36] The transport model FLEXPART gave in general an excellent description of the forest fire plumes observed from the WP-3 [*de Gouw et al.*, 2006]. The average altitude

profiles of CO_{bb} and CO_{anthro} calculated with FLEXPART along the flight and ship track are shown in Figure 10a together with the measured altitude profile, including the *Ronald H. Brown* measurements, taken from Figure 9a. The measured and modeled altitude profiles for CO_{bb} agree very well over the whole altitude range, whereas CO_{anthro} from FLEXPART is higher below 2 km than the measurements, but agrees well in the free troposphere. FLEXPART also shows that anthropogenic sources dominate in the boundary layer and biomass burning in the free troposphere between 3 and 5 km.

[37] Scatterplots of CO_{bb} and CO_{anthro} versus FLEXPART are shown in Figures 10b–10e for the ship and the aircraft measurements. The quality of the fits is between r = 0.55 and r = 0.67, which is rather low for reasons that will be
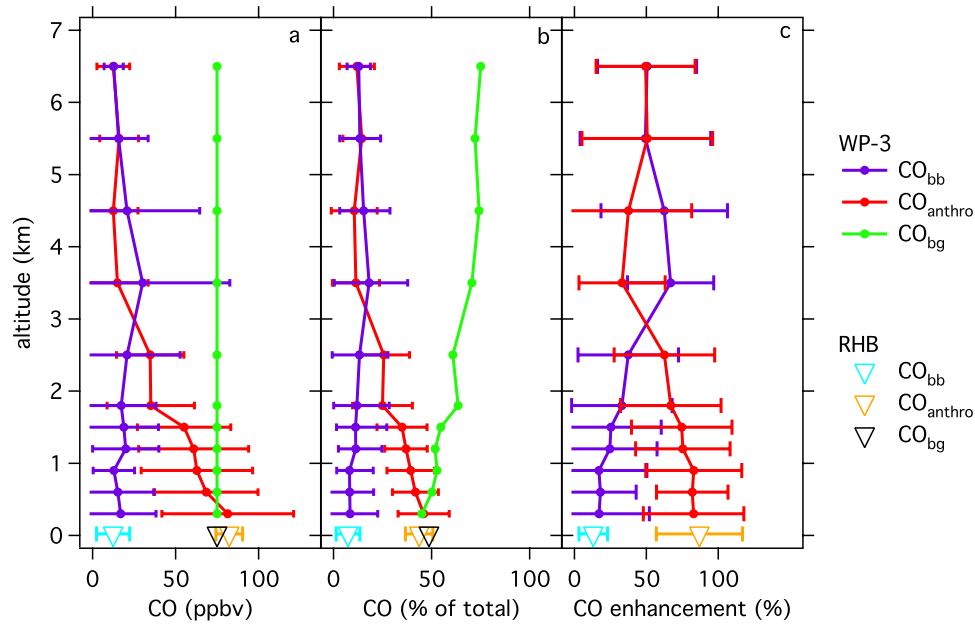
Figure 9. Average altitude profile of CO_{bb}, CO_{anthro}, and CO_{bg}: (a) Mixing ratio. (b) Contributions to total CO. (c) Contribution to CO enhancement. The error bars are the standard deviation within each altitude bin. The NOAA *Ronald H. Brown* measurements are indicated with the open triangles in each altitude profile.

described below. The slopes in Figures 10b and 10d show that CO_{bb} measurements and FLEXPART agree within 20%, but FLEXPART might underestimate CO_{bb} by 10–20%, which could have two reasons: (1) The transport of particles in the model was restricted to 20 days, whereas some of the observed fire plumes might have contributions from fires older than 20 days, and (2) the emissions in the model could be underestimated. The total fire emissions in Alaska and Canada used in FLEXPART (shown in

Figure 11) in the time period of the measurement campaign (2 June to 14 August 2004) are 22 Tg CO. The good quantitative agreement indicates that the emission estimate in FLEXPART is quite accurate.

[38] Using MOPITT data (Measurement of Pollution in the Troposphere) and a chemistry transport model [*Pfister et al.*, 2005] estimate the total CO emissions of the Alaskan and Canadian wildfires to be 30 ± 5 Tg for June to August 2004. The CO emissions from this calculation are also
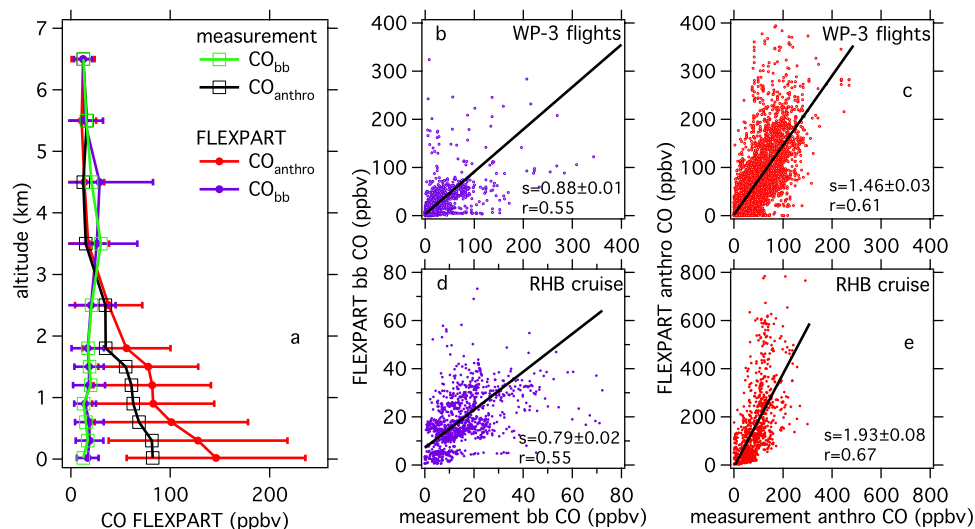

Figure 10. Comparison of the measured CO source contribution with FLEXPART. (a) Measured altitude profiles, including NOAA *Ronald H. Brown* measurements, of CO_{bb} and CO_{anthro} taken from Figure 9a. The error bars on the FLEXPART results are the standard deviation within each altitude bin. (b–e) Scatterplots of CO_{bb} and CO_{anthro} calculated using VOC enhancement ratios versus FLEXPART model results for the aircraft and the ship measurements.
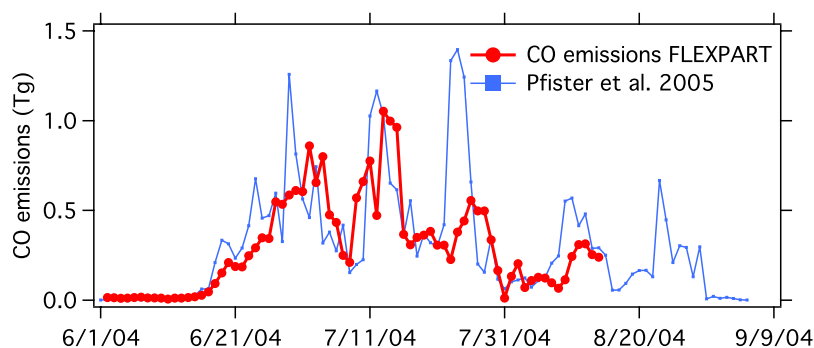
Figure 11. Biomass burning CO emission estimates for 2 June to 14 August 2004 used in FLEXPART and by *Pfister et al.* [2005].

shown in Figure 11. From 2 June until 14 August the emissions are 26 Tg in the Pfister et al. study, which is in good agreement with the FLEXPART estimate.

[39] In comparison to the biomass burning emissions, during the same time period the anthropogenic CO emissions used in FLEXPART in the United States were about 25 Tg. In the free troposphere FLEXPART agrees well with the measurements, but overestimates the anthropogenic CO emission by about 50% in the boundary layer (Figures 10a and 10c) and as much as a factor of 2 in the marine boundary layer (Figure 10e). The over prediction of the anthropogenic CO can be caused by three reasons: (1) The CO emissions in the inventory could be too high as was also found by [*Parrish*, 2006]. The anthropogenic CO inventory for North America used in FLEXPART is based on the U.S. EPA NEI-99 inventory (National Emissions Inventory, base year 1999, version 3) [*U.S. EPA*, 2004a]. A reduction in CO emissions form 1999 to 2004 would therefore also result in

an over prediction. (2) The vertical mixing from the surface layer to higher altitudes can be underestimated. (3) Especially for the measurements on the *Ronald H. Brown*, the emissions along the coast in FLEXPART could be mixed into the marine boundary layer when in reality they are transported on top of the marine boundary layer.

[40] To rationalize part of the scatter in Figures 10b–10e the time series of CO_{bb} is shown together with FLEXPART for the flight on 9 July 2004, in Figure 12a. It can be seen that FLEXPART predicts the time and location of the forest fire plume very well, although the predicted mixing ratio in the separate layers of the plume is sometimes overpredicted and sometimes underpredicted. This causes a large scatter in the correlation of CO_{bb} versus the model, shown in Figure 12b. The slope is s = 0.82 and r = 0.67. The large scatter has four reasons: (1) A constant emission factor of 4.5×10^5 kg CO per km^2 burned that was used to obtain daily CO emission fields. Different fires might have varying
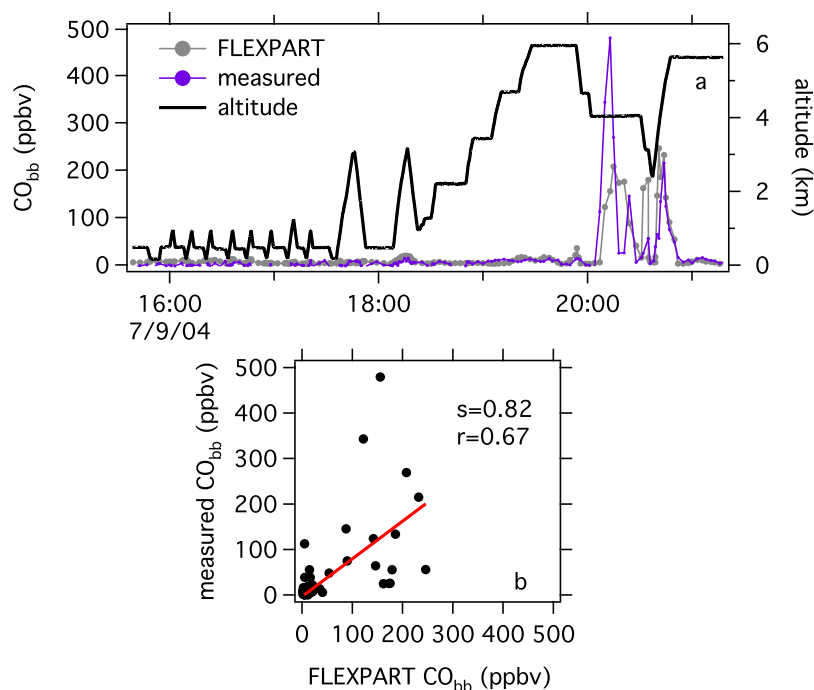

Figure 12. (a) Time series of CO_{bb} calculated using acetonitrile and FLEXPART for the NOAA WP-3 flight on 9 July 2004. (b) Scatterplot of CO_{bb}.

emission factors. (2) The temporal variations of the fires are not known well enough. Both the hot spots and the daily fire reports were averaged with a 3-day running mean, because satellite images miss the hot spots in the presence of clouds and the daily fire reports are not always accurate. Also the hot spots and daily fire reports were averaged on a $1 \times 1°$ grid. (3) Errors in the used wind field. (4) The emissions of forest fires in FLEXPART were evenly distributed over the lowest 10 km of the atmosphere to mimic the rapid vertical transport in fire-induced convective clouds that can be associated with large-scale forest fires [*Lavoue et al.*, 2000]. In reality, however, the distribution of emissions will be far from even across the altitude range, with the largest fractions at the surface and at the altitude to which the convective clouds rise. The altitude dependence of the emissions is strongly influenced by the size, temperature, and type of fire. Large forest fires tend to burn hot and produce fire induced convection that can rapidly transport fire emissions even into the lower stratosphere [*Fromm and Servranckx*, 2003; *Jost et al.*, 2004]. Peat fires are usually smoldering fires, which do not produce strong convection, and therefore the emissions can get trapped in the boundary layer [*Bertschi et al.*, 2003; *Sinha et al.*, 2003]. In the earlier part of the campaign forest fires in Alaska might have dominated the emissions and later in the campaign peat fires in Canada could have had a strong influence. The observed scatter is nonsystematic and therefore the slope of the correlation plots of Figure 10 might not be significantly affected.

4. Conclusions

[41] The emissions of large forest fires, burning in Alaska and western Canada in June to August 2004, were transported to the continental United States. During the NEAQS-ITCT2004 study the smoke plumes were intercepted several times with the NOAA WP-3 aircraft and with the NOAA *Ronald H. Brown* research ship in the New England area. Using the enhancement ratios of CO with acetonitrile, which proved to be an excellent tracer for biomass burning emissions, the contribution of biomass burning to the CO mixing ratio was determined. With the same method the anthropogenic fraction of CO was determined using chloroform as a tracer. The atmospheric background mixing ratio was set at 75 ppbv. During a flight on 11 July 2004 over Boston, Massachusetts, the CO enhancement from biomass burning (about 60% of the total enhancement) was larger than the anthropogenic contribution. CO transported from forest fires, burning in Alaska and Canada, caused higher CO mixing ratios, even at low altitudes, than the urban emissions close by. Along the flight track of the WP-3 in July and August 2004, about 30% of the CO enhancement was caused by forest fire emissions in Alaska and Canada and about 70% by anthropogenic sources. The overall altitude profile showed that anthropogenic sources were responsible for most of the CO enhancement at low altitudes, while biomass burning caused larger enhancements in the free troposphere between 3 and 5 km. This demonstrated that the air quality in this region, already burdened with anthropogenic emissions from urban areas such as New York and Boston, was influenced by biomass burning.

[42] Chloroform measurements indicate that in New England the main source is anthropogenic and that the ocean and biomass burning are only very minor sources.

[43] A comparison with the FLEXPART transport model showed that the total CO biomass burning emissions in Alaska and Canada were about 22 Tg for 2 June to 14 August 2004. The total anthropogenic CO sources used in FLEXPART are 25 Tg. The FLEXPART model, using the U.S. EPA NEI-99 emissions, overpredicts the CO mixing ratio around Boston and New York in 2004 by about 50%.

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