Atmos. Chem. Phys. Discuss., 13, 3135–3178, 2013
www.atmos-chem-phys-discuss.net/13/3135/2013/
doi:10.5194/acpd-13-3135-2013

Atmospheric Chemistry and Physics Discussions

Trends in emissions and concentrations of air pollutants in the lower troposphere in the Baltimore/Washington airshed from 1997 to 2011

H. He[1,2], J. W. Stehr[1], J. C. Hains[3], D. J. Krask[3], B. G. Doddridge[4], K. Y. Vinnikov[1], T. P. Canty[1], K. M. Hosley[1], R. J. Salawitch[1,2,5], H. M. Worden[6], and R. R. Dickerson[1,2,5]

[1]Department of Atmospheric and Oceanic Sciences, University of Maryland, College Park, MD 20742, USA
[2]Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20740, USA
[3]Maryland Department of the Environment, Baltimore, MD 21230, USA
[4]Chemistry and Dynamics Branch, NASA Langley Research Center, Hampton, VA 23681, USA
[5]Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA
[6]National Center for Atmospheric Research, Boulder, CO 80305, USA

Received: 5 January 2013 – Accepted: 20 January 2013 – Published: 4 February 2013

Correspondence to: H. He (hhe@atmos.umd.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Trends in the composition of the lower atmosphere (0–1500 m altitude) and surface air quality over the Baltimore/Washington area and surrounding states were investigated for the period from 1997 to 2011. We examined emissions, ground-level observations and long-term aircraft measurements to characterize trends in air pollution. The USEPA Continuous Emissions Monitoring System (CEMS) program reported substantial decreases in point sources resulting from national and regional control measures; these decreases are definitely reflected in the ground-level observations. The decreasing trend of CO column contents is ~8.0 Dobson Unit (DU) decade^{-1}, corresponding to ~350 ppbv decade^{-1} in the lower troposphere. Satellite observations of long-term, near-surface CO show ~40 % decrease over western Maryland between 2000 and 2011, the same magnitude as indicated by aircraft measurements over upwind regions of Baltimore/Washington aished. After compensating for inter-annual temperature variations, historical aircraft measurements suggest the daily net production of tropospheric ozone over Baltimore/Washington area decreases from ~20 ppbv in the late 1990s to ~7 ppbv in the early 2010s during the ozone season. A decrease in the long-term ozone column content is observed as ~2.0 DU decade^{-1} in the lowest 1500 m, corresponding to ~13 ppbv decade^{-1} decrease. Back trajectory cluster analysis demonstrates that emissions of air pollutants from Ohio and Pennsylvania through Maryland influence column contents of downwind ozone in the lower atmosphere. The trends of air pollutants reveal the success of regulations implemented over the last decade and the importance of region wide emission controls over the eastern United States.

1 Introduction

Ozone controls much of the chemistry in the lower atmosphere, such as hydroxyl radical (OH) production and the lifetimes of atmospheric species including methane (CH_4),

ACPD
13, 3135–3178, 2013

carbon monoxide (CO), and volatile organic compounds (VOCs) (Levy, 1971; Logan et al., 1981; Seinfeld and Pandis, 2006). Tropospheric ozone is a good absorber of thermal radiation, acting as the third most important anthropogenic contributor to radiative forcing of climate (Fishman et al., 1979b; IPCC, 2007; Ramanathan and Dickinson, 1979). High concentrations of ground-level ozone also threaten human health (Anderson, 2009; Jerrett et al., 2009; WHO, 2003) and cause damage to ecosystems (Adams et al., 1989; Ashmore, 2005; Chameides et al., 1999). Thus, ozone is one of the six criteria air pollutants in the National Ambient Air Quality Standards (NAAQS), and regulated by the US Environmental Protection Agency (EPA).

As a secondary air pollutant, tropospheric ozone is mainly produced through photochemical reactions involving CO and VOCs catalyzed by nitrogen oxides (NO_x) (Crutzen, 1974; EPA, 2006; Fishman et al., 1979a), while troposphere-stratosphere air exchange contributes a small portion (Holton et al., 1995; Levy et al., 1985; Wild et al., 2003). In the US, ozone pollution drew public attention after the "Los Angeles Smog" in the 1950s (Haagen-Smit, 1952; Haagen-Smit and Fox, 1956), and emissions of ozone precursors, mainly NO_x and VOCs from anthropogenic sources, have decreased significantly under regulation, resulting in lower ground-level ozone (EPA, 2012c). Long-term records of tropospheric in the US have been investigated through ground-level observations (Jaffe and Ray, 2007; Lefohn et al., 2008, 2010; Oltmans et al., 1998; Oltmans et al., 2006) and ozone sondes (Yorks et al., 2009), however long-term trends are not clearly observed. Analysis of these long-term ozone measurements can also shed light on the change of "baseline" ozone to estimate the flux of air pollutants entering and exiting North America, which is essential for regulations of ambient air quality (Chan and Vet, 2010; Cooper et al., 2010; Lin et al., 2012; Oltmans et al., 2008).

In the Mid-Atlantic States, ozone is a major air pollutant in the summer (EPA, 2012a) and the Baltimore/Washington area has failed to meet mandated attainment deadlines (EPA, 2012b). For a better understanding of air quality, the Regional Atmospheric Measurement Modeling and Prediction Program (RAMMPP, http://www.atmos.umd.edu/~RAMMPP) was formed to conduct a state-of-the-art scientific research through in

ACPD
13, 3135–3178, 2013

situ measurements (Hains et al., 2008; Marufu et al., 2004; Taubman et al., 2004a,b, 2006), air quality forecasting, mesoscale dynamics modeling (Shou and Zhang, 2010; Zhang et al., 2009, 2011), and chemical transport modeling (Castellanos et al., 2009, 2011; Loughner et al., 2011; Yegorova et al., 2011). As a key component of RAMMPP, aircraft measurements of air pollutants have been conducted during the ozone season (May to September) over the last 15 yr. Presently the RAMMPP aircraft has the ability to measure CO, O_3, sulfur dioxide (SO_2), nitrogen dioxide (NO_2), aerosol absorption, aerosol scattering, particle counts, aerosol size distribution, and meteorological variables (temperature, pressure, and relative humidity).

RAMMPP aircraft flights started with tropospheric O_3 and CO measurements in 1997, providing a 15-yr record of summertime tropospheric ozone for investigating ozone trends in the Baltimore/Washington airshed. Previous studies typically focused on the trends of ground-level ozone over rural areas (Jaffe and Ray, 2007; Lefohn et al., 2008, 2010; Cooper et al., 2012). It is also important to study ozone in the free troposphere (FT). Ozone and its precursors aloft have longer lifetimes and can be transported farther than at the surface, influencing air quality in downwind regions (Jaffe, 2011; Neuman et al., 2012). The Baltimore/Washington nonattainment area is downwind of the Ohio River Valley, where a large number of power plants are located, and upwind of other nonattainment areas such as Philadelphia, New Jersey and New York City. Distinguishing local ozone production from regional transport is critical for effective policy and control measures.

In this article, we present a study on tropospheric ozone and its precursors (CO and NO_x) in the Mid-Atlantic region and upwind state based on emissions data and in situ measurements, to investigate trends in summertime air pollution over the last 15 yr. Section 2 presents the data sets and methods. In Sect. 3, we discuss the trends of emissions in the Baltimore/Washington airshed, and the trends of tropospheric ozone and carbon monoxide observed by the RAMMPP aircraft and EPA Air Quality System (AQS) network. One case study on regional transport is conducted using a back trajectory clustering technique to reveal the relationship between upstream anthropogenic

ACPD
13, 3135–3178, 2013

emissions and downstream air quality. Finally, we discuss the importance of emission regulations for improving ozone pollution in the nonattainment Baltimore/Washington airshed, and implications for future control measures.

2 Data and method

For a comprehensive study of ozone pollution in the Baltimore/Washington airshed, two emissions datasets were used: the EPA National Emissions Inventory (NEI) and the CEMS data for states of Maryland (MD), Virginia (VA), West Virginia (WV), Pennsylvania (PA) and Ohio (OH) (the Mid-Atlantic and one upwind state, hereafter named the "research domain"). The NEI emissions inventory, a comprehensive and detailed estimate of emissions on both criteria and hazardous air pollutants from all sources on the county scale, is prepared every three years, based on emissions measurements and model results (e.g. http://www.epa.gov/ttnchie1/net/2008inventory.html). In the NEI inventory, emissions are grouped into five categories: point, nonpoint, onroad, nonroad, and event (details are listed in Table S1 of the Supplement). In this study, detailed NEI data (2002, 2005, and 2008) and summaries of annual national data (available at http://www.epa.gov/ttn/chief/trends/index.html) were utilized to study the trends of ozone precursor emissions from point and mobile sources. Since NEI only contains annual emission estimates, to investigate daily changes of emissions, we examined the CEMS data from continuous monitoring of point sources, i.e. major power plants and industries, for the EPA Clean Air Market (prepackaged data available at http://ampd.epa.gov/ampd/). The CEMS data include NO_x, SO_2 and carbon dioxide (CO_2), and have temporal resolution as high as hourly from individual point source. Daily CEMS data for NO_x emissions from sources within the research domain from 1997 to 2011 were used in this study.

Ground-level measurements of NO_x, CO and O_3, in the Baltimore/Washington area, were acquired from the EPA AQS website (http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm), to study trends of ground-level air pollution. EPA

ACPD
13, 3135–3178, 2013

NO_x measurements are achieved through conversion of NO_2 to NO by a hot molybdenum catalyst, followed by the chemiluminescent reaction of NO with O_3. Interferences come from other oxidized reactive nitrogen species such as peroxyacyl nitrates (PAN) and alkyl nitrates (Dunlea et al., 2007; Fehsenfeld et al., 1987), which are also converted to NO. Correcting these measurements for potential interferences is beyond the scope of this study, but these interfering NO_y species all originate from NO_x, so we can use the EPA NO_x record as an estimate of actual ambient NO_x concentration trend.

CO is emitted mainly by automobiles and incomplete combustion such as biomass burning, so CO emissions are not monitored as are NO_x and SO_2 emissions from point sources in the CEMS program. The USEPA estimates national CO emissions using emission models such as Motor Vehicle Emissions Simulator (MOVES). Tropospheric CO can been measured from satellites, such as Measurements of Pollution In The Troposphere (MOPITT) on Terra (Deeter et al., 2003), Atmospheric Infrared Sounder (AIRS) on Aura (Warner et al., 2007), Tropospheric Emission Spectrometer (TES) on Aura (Luo et al., 2007), Infrared Atmospheric Sounding Interferometer (IASI) on METOP-A (George et al., 2009), and Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) on Envisat (Buchwitz et al., 2004). Launched in 1999, MOPITT has proven useful for tracking the long-term trend of tropospheric CO on regional scales (Worden et al., 2012). A ~ 15 % decrease is reported in the column content over the eastern US between 2000 and 2011. We used the MOPITT level 3 monthly products version 5 using near and thermal infrared radiances (MOP03JM.005, http://eosweb.larc.nasa.gov/PRODOCS/mopitt/table_mopitt.html). Because the RAMMPP aircraft measurements focus on CO in the lower troposphere, the MOPITT "near-surface CO retrievals" (surface to 900 hPa) are applied (see details in Deeter et al., 2012). Although MOPITT multispectral retrievals have variable sensitivity to near-surface CO over different land surface types, we note that the Mid-Atlantic region considered in this study showed significant improvement in sensitivity for retrievals with near and infrared radiances compared with thermal infrared only (Worden et al., 2010). For the MOPITT multispectral observations used

ACPD
13, 3135–3178, 2013

in this analysis, sensitivity to CO typically peaks in the surface layer from 1000 hPa to 900 hPa and falls off exponentially with a scale height around 1 km, making them suitable for comparison with our aircraft measurements.

RAMMPP aircraft observations of tropospheric O_3 and CO date back to 1997, providing a 15-yr record of summertime ozone pollution. The sampling platform for the early 2000s was discussed extensively in previous studies (Hains et al., 2008; Taubman et al., 2004b); details on the current sampling platform are listed in Table S2 of the Supplement. Here, a brief summary on O_3 and CO measurements is provided. Ozone is measured using a commercially available analyzer (Model 49/49C, Thermo Environmental Instruments, TEI, Franklin Massachusetts), based on the absorption of ultraviolet radiation. The analyzer is routinely serviced and calibrated with an in-house primary ozone calibrator (TEI Model 49PS) fed on zero-grade air. The instrument is compared to the National Institute of Standard and Technology (NIST) standard, and the precision can reach 1 parts per billion by volume (ppbv) for 10-s average data (Taubman et al., 2006). Observations of ambient CO are conducted using a modified commercially available nondispersive infrared gas filter correlation analyzer (TEI Model 48) with enhanced precision of about 30 ppbv for one minute moving average of 10-s data (Dickerson and Delany, 1988). The detector is regularly calibrated with a NIST traceable CO gas standard (Scott Marrin Inc., Riverside, CA). Processed airborne measurements are available at the RAMMPP website (http://www.atmos.umd.edu/~RAMMPP/, data access is available upon request).

RAMMPP flight plans are based on air quality forecasts, issued by Maryland Department of the Environment (MDE), usually for days with predicted poor air quality. Most of the research flights were performed on hot summer days with weak surface winds and/or stagnation. In the last 15 yr, around 1000 research profiles (defined as a spiral over a fixed location to measure the vertical distribution of air pollutants, hereafter named research spirals) were carried out over more than 100 airports from Georgia to Vermont. Here we examine research spirals conducted in the Baltimore/Washington airshed. Figure 1 shows the locations of the selected airports and a typical flight route

ACPD
13, 3135–3178, 2013

(see statistics of research spirals in Fig. S1 of the Supplement). On average, ~40 research spirals were conducted each year (except 2006), providing robust statistics for long-term trends.

To reveal the effects of regional transport and photochemical production of tropospheric ozone in the Baltimore/Washington airshed, two flights are conducted during a typical day: one flight over the upwind area in the morning and one over the downwind area in the afternoon. On a typical westerly transport (Fig. 1), the morning flight samples air over Luray, Winchester, and Cumberland in western MD; the afternoon flight covers Harford County, and Easton in eastern MD. Another important transport process of atmospheric pollutants in the Mid-Atlantic region is the low level jet (LLJ) during the summer (Corsmeier et al., 1997; Higgins et al., 1997), which transports ozone and its precursors from the south. When a LLJ had been forecasted, we conducted research spirals over southern VA, such as Williamsburg, VA (37.24° N, 76.72° W), during the morning flight, called southerly transport flights.

Generally, the air mass measured in the morning is considered as the background air entering the Baltimore/Washington area with residual ozone and its precursors from the previous day, while in the afternoon the observed ozone levels are regarded as the sum of residual ozone and ozone produced during the daytime. The difference between ozone measured in the morning and in the afternoon is considered an estimate of the net daily production of ozone in the Baltimore/Washington area.

To interpret the trends of ozone pollution throughout the region, the column contents of tropospheric O_3 and CO are used. During the 15 yr operation, research flight plans changed somewhat, e.g. the maximum height of research spirals increased from 1500 m a.g.l. (above ground-level) before the year 2000 to ~3000 m a.g.l. afterwards. In this study, tropospheric column contents of air pollutants were obtained from altitude profiles integrating from the surface to 1500 m a.g.l., for consistency.

Numerous studies have shown that back trajectory analyses are capable of representing the general wind flow under specific synoptic conditions (Stohl, 1998; Stohl et al., 1995; Stunder, 1996). To study the transport of air pollutants, Hains et al. (2008)

ACPD
13, 3135–3178, 2013

applied a hierarchical clustering technique to the RAMMPP aircraft measurements in the Mid-Atlantic region for the period 1997 to 2003; they identified a strong correlation between integrated NO_x emissions from point sources and ozone concentrations. We follow a similar approach by conducting a case study of long-term aircraft profiles over the Harford County airport (located ~ 50 km to the northwest and generally downwind of Baltimore).

3 Trends of emissions and RAMMPP aircraft measurements

3.1 Trends of NEI and CEMS emissions

NO_x and CO are important anthropogenic precursors of tropospheric ozone. Onroad and nonroad internal combustion sources release the majority of anthropogenic CO and around half of the anthropogenic NO_x, with the other half emitted from point sources such as electricity generating units, construction equipment, and other industrial sources. In this study, CO and NO_x emissions estimates from onroad and nonroad sources were obtained from the NEI emission data; daily NO_x emissions from point sources were acquired from CEMS emission data.

The EPA NEI program provides two emission estimates: (1) a comprehensive and detailed estimate of air pollution emissions from different sectors at county level every three years; (2) annual estimates of national emissions, which can be used to define national trends. The national emissions trends on mobile sources between 1997 and 2011 (CO and NO_x) were scaled with total emissions from the research domain in 2002, 2005, and 2008 to project the trends of emissions near the Baltimore/Washington airshed over the last 15 yr. We found that the research domain release ~ 4 % and ~ 5 % of the national NO_x and CO emissions, respectively (Fig. S2 in the Supplement). Between 1997 and 2011, large decreases of NO_x and CO emissions, ~ 50 % and ~ 60 %, respectively (using 1997 emissions as a baseline), were observed in the whole US. Here, we assume that onroad and nonroad emissions have the same trends in the

ACPD
13, 3135–3178, 2013

research domain as for the entire US, consequently the large reduction of precursors should affect the tropospheric ozone in the Baltimore/Washington airshed.

Long-term trends of monthly CEMS NO_x emissions (Fig. 2a) show that NO_x emissions from point sources decreased by ~80 % in the last 15 yr for each state, except a ~50 % decrease in PA (using 1997 emissions as a baseline). Several characteristics are observed: (1) between 1997 and 2002, a slow decrease of NO_x emissions for all states; (2) a large reduction after 2003, due to the EPA NO_x State Implementation Plan (SIP) call; (3) OH, PA, and WV NO_x emissions were only controlled in ozone season between 2003 and 2009 resulting in a square wave pattern for this period; (4) 2003–2008, further slow decreases for all states, followed by substantial reductions in MD, OH, and WV, but slight increases in PA and VA after 2009. During the same period, CO_2 emissions from point sources, i.e. amount of fossil fuel burned, stayed at similar levels (Fig. S3 in the Supplement).

Figure 2b presents locations of the major point sources, indicating the large NO_x sources in the Ohio River Valley and western PA. These air pollutants released in the upwind regions of the Baltimore/Washington airshed exert a significant influence on downwind air quality under the prevailing westerly winds during the ozone season. We also computed the ratio of NO_x and CO_2 emissions for each source. Figure 2c shows that the point sources with high NO_x/CO_2 ratio during the ozone season exist mainly in the Ohio River valley, and these "hot spots" (details listed in the Table S3) are suitable targets for the future NO_x emission reductions.

3.2 Trends of ground-level observations

To study ozone photochemistry, we analyzed the EPA CO, NO_x, and O_3 observations in the afternoon (12 p.m. to 6 p.m.) during the ozone season. Ozone monitors are located throughout this area, while the CO and NO_x observations are mainly conducted along the Interstate 95 corridor between Baltimore and Washington DC (Fig. S4 in the Supplement). Figure 3 shows the long-term trends of annual mean ground-level concentrations during the summer. The long-term ozone measurements show large

ACPD
13, 3135–3178, 2013

inter-annual variations, because ozone production is not only determined by emissions but also weather, especially temperature. A discernible decrease (~ 6.0 ppbv decade^{-1}, Fig. 4) is observed, suggesting a general decreasing trend of ambient ozone in the Baltimore/Washington area.

For the long-term CO trend, ground-level observations show a non-monotonic but steady decreasing trend from ~ 600 ppbv to ~ 350 ppbv or ~ 180 ppbv decade^{-1} decrease (linear regression coefficient $r = -0.90$). If the regional background CO concentration is assumed as ~ 150 ppbv, then the reduction is from ~ 450 ppbv to ~ 200 ppbv, corresponding to a ~ 55 % decrease since 1997. During the same period, the NEI annual CO emissions decreased from $\sim 13.5 \times 10^6$ t to $\sim 5.5 \times 10^6$ t (Fig. S2 in the Supplement), suggesting a ~ 59 % decrease since 1997. Therefore, after correcting for the background CO, the trends of ground-level CO observations and the NEI CO emissions are similar.

Long-term ambient NO_x measurements demonstrated a sharp decrease (from ~ 20 ppbv to ~ 8 ppbv) after 2003, while a gradual decreasing trend in annual NEI emissions (CEMS data plus automobile emissions) was observed. This sharp decrease coincides with the large reduction of NO_x emissions from point source during the EPA SIP call (Fig. 2a). Here we estimated the daily mean NO_x emissions during the ozone season through incorporating daily CEMS emissions (point sources) and scaled mobile emission estimates from NEI annual data (scaled by factor of 4 %). Figure 5 indicates that total emissions from both point sources and mobile sources decreased significantly, ~ 60 % and ~ 50 %, respectively. Point source emissions had a sharp decrease around 2003 due to the EPA SIP call, while estimated mobile emissions decreased gradually. The contribution of NO_x from point sources to the total emissions decrease from ~ 70 % in the late 1990s to ~ 50 % in the early 2010s, which confirms the efficacy of EPA NO_x SIP call.

We compared the CEMS, scaled NEI, and total NO_x emissions with the EPA AQS observations using the linear regression analysis (Fig. 6), revealing good correlation between these three emission estimates and ground-level NO_x observations. The slope

ACPD
13, 3135–3178, 2013

of emissions versus observations is 0.0042 ppbv/ton for CEMS and 0.0024 ppbv/ton for NEI mobile emissions alone. Therefore, if we assume emissions from point sources and mobile sources have an equivalent effect on surface concentrations of NO_x, point sources contribute ~60 % of the ambient ground-level NO_x concentrations. The daily CEMS measurements provide a unique opportunity to investigate the effects of emissions on surface NO_x observations. Considering that ground-level NO_x concentrations are controlled by other parameters such as advection, temperature, turbulence, and concentration of VOCs, the CEMS data correlate surprisingly well with observed ground-level NO_x concentrations.

Total daily CEMS NO_x emissions in the research domain decreased from ~3500 t yr^{-1} to ~1000 t yr^{-1} in the last 15 yr (Fig. 5), corresponding to a ~6.5 ppbv (~4.5 ppbv decade^{-1}) decrease of the ground-level NO_x concentrations. In the eastern US, ozone production is largely NO_x-sensitive, so the decrease in ambient NO_x concentration is expected to mitigate ozone pollution. We used the ozone production efficiency (OPE), defined as the net number of O_3 molecules produced per molecule of NO_x emitted (or processed to other NO_y species) (Hirsch et al., 1996; Liu et al., 1987). Literature values range from 5 mol mol^{-1} in the urban areas (Kleinman, 2000; Nunnermacker et al., 2000) to ~50 mol mol^{-1} in the clean marine atmosphere (Wang et al., 1998). Here we applied the value of 2–8 mol mol^{-1} for the Baltimore/Washington airshed (Kleinman et al., 2002), leading to 9–36 ppbv decade^{-1} as projected decrease of ambient ozone. The reported decrease of ozone observed by ground-level monitoring network is less (~6.0 ppbv decade^{-1}, Fig. 4), which could be caused by the complicated chemical mechanism of tropospheric ozone (Lin et al., 1988; Shon et al., 2008; Sillman, 1995; Walcek and Yuan, 1995).

ACPD
13, 3135–3178, 2013

3.3 Trends of aircraft measurements

3.3.1 Vertical distribution of tropospheric O_3 and CO

Long-term aircraft measurements show that tropospheric ozone has large day-to-day variations; for instance, all tropospheric ozone altitude profiles obtained in summer 2001 are shown in Fig. 7. In the lower atmosphere, ozone is reasonably well mixed with a local maximum near 1000 m, around the top of planetary boundary layer (PBL). In the morning upwind flights (Fig. 7b), ozone concentrations near the surface are relatively low compared with the values in the FT (higher than 1000 m), suggesting that ozone is lost due to dry deposition and reactions with NO_x during the night. With the low photochemical production and weak mixing in the morning, ozone concentrations stay low until close to noon. Relatively high concentrations of ozone observed in the FT are in the residual layer, reflecting ozone production on previous days. With the rise of the PBL during daytime, air in the residual layer is entrained and mixed, transporting the residual-layer pollutants downward. In the afternoon, tropospheric ozone is produced through photochemical reactions and the mean ozone altitude profile shows a quasi-uniform concentration (Fig. 7c). The afternoon mean ozone profile also has a local maximum at ~1000 m, with ozone ~18 ppbv higher than the ground-level value. Pollutants aloft observed in both morning and afternoon do not immediately influence the local air quality, however transport of these pollutants exerts significant effects on air pollution in the downwind areas.

We conducted similar analysis on all the CO altitude profiles obtained in 2001 (Fig. 8). A relatively uniform concentration of ~250 ppbv CO was observed in the FT; maximum CO concentrations were observed near the surface. These measurements reflect atmospheric CO sources on the Earth's surface and on average an exponential decrease within the PBL. With a lifetime of about one month, CO can be transported upward and well mixed in the FT, so CO is a good chemical tracer to investigate advection in the lower atmosphere (Castellanos et al., 2011; Loughner et al., 2011). The mean CO profiles from upwind and downwind research spirals exhibit similar vertical

ACPD
13, 3135–3178, 2013

distributions (Fig. S5 in the Supplement), indicating that CO pollution in the Baltimore/Washington airshed is a regional problem. CO is concentrated within the PBL, as is NO_x, so the production of ozone is enhanced in the lower atmosphere.

3.3.2 Estimate of photochemical production of tropospheric ozone

Ozone production is closely related to temperature (Bloomer et al., 2009; Camalier et al., 2007; EPA, 2006; Jacob and Winner, 2009), so we must take the inter-annual variations of ambient temperature into account to study the long-term trend of tropospheric ozone. Here, we use the climate penalty factor (CPF), defined as $\frac{d[O_3]}{dT}$. One previous study reported CPF as $\sim 3.2\,\text{ppbv}\,^{\circ}\text{C}^{-1}$ prior to 2002 and $\sim 2.2\,\text{ppbv}\,^{\circ}\text{C}^{-1}$ after 2002 in the eastern US (Bloomer et al., 2009). Here, we first obtained a "standard" temperature altitude profile by averaging all the temperature profiles, and then normalized ozone concentration profiles by applying the CPF ($3.2\,\text{ppbv}\,^{\circ}\text{C}^{-1}$ before 2002 and $2.2\,\text{ppbv}\,^{\circ}\text{C}^{-1}$ after 2002) to the temperature deviations from the "standard" temperature profile and calculated column contents.

Figure 9 shows the long-term trend of lower tropospheric ozone column contents after adjustment for variations in temperature using the CPF. The upwind ozone column contents are taken as the background air entering the Baltimore/Washington area, with ozone mainly in the residual layer; the downwind contents represent the total of background plus ozone generated by local photochemical reactions. The afternoon flights are usually finished around 4 p.m. when the ozone maximum is reached, so the difference between morning and afternoon flights accounts for the daily production of tropospheric ozone in the Baltimore/Washington area. Negative values are observed for 1999 and 2008, when a relative small number of research flights were conducted. The mean net production in the last 15 yr is estimated as 2.3 ± 2.0 DU ($1\,\text{DU} = 2.69 \times 10^{16}\,\text{molecules}\,\text{cm}^{-2}$) per day where 2.0 DU represents the $\pm 1\,\sigma$ variability. When assuming the ozone is well-mixed in the lower atmosphere, this value equals a $\sim 15 \pm 13$ ppbv ozone increase in the lowest 1500 m.

ACPD
13, 3135–3178, 2013

It is notable that the net daily production of ozone decreased from $\sim 3.0\,\mathrm{DU\,day^{-1}}$ in late 1990s to $\sim 1.0\,\mathrm{DU\,day^{-1}}$ in early 2010s, corresponding to $\sim 20\,\mathrm{ppbv\,day^{-1}}$ to $\sim 7\,\mathrm{ppbv\,day^{-1}}$, respectively. This shows that the daily ozone production within the Baltimore/Washington area has decreased significantly, $\sim 60\,\%$ and $\sim 10\,\mathrm{ppbv\,decade^{-1}}$. This magnitude of decrease is higher than the decreasing trends revealed by the ground-level measurements (see Fig. 4), suggesting that ozone transported into the Baltimore/Washington airshed plays an important role in determining the downwind ozone pollution. Since most of the RAMMPP research flights have been conducted in the air quality action days, our estimates can be treated as the upper limit of net daily production of ozone in the Baltimore/Washington airshed.

3.3.3 Long-term trends of tropospheric O_3 and CO

Here we focus on the O_3 and CO measurements in the afternoon flights, when the maximum ground-level ozone is usually observed. The annual mean O_3 and CO column contents are plotted showing the long-term trends (Fig. 10). We used the Savitzky-Golay Smoothing (Bromba and Ziegler, 1981; Gorry, 1990; Savitzky and Golay, 1964), which preserves the feature of the data while reducing the influences of noise and missing data. Figure 10a shows a $\sim 2.0\,\mathrm{DU\,decade^{-1}}$ decrease of ozone column contents. Assuming ozone in the lower atmosphere is well mixed, the decrease of column contents is equivalent to $\sim 13\,\mathrm{ppbv\,decade^{-1}}$ in the lower atmosphere. This value is much higher than a $4 \sim 6\,\mathrm{ppbv\,decade^{-1}}$ decrease of ground-level ozone reported in the eastern US (Bloomer et al., 2010; Cooper et al., 2012). The reason could be that RAMMPP research flights were usually conducted on air quality action days, suggesting that these days, i.e. bad air quality events, have been improved more than normal conditions during the ozone season.

To test the effects of variations of ambient temperature, we also calculated the long-term ozone column contents without applying the CPF (Fig. 10b). The difference between the ozone column contents with and without CPF adjustment is discernible,

ACPD
13, 3135–3178, 2013

especially for years 2009 to 2011. Figure 10b shows a monotonic increase of ozone column contents from 2009 to 2011, suggesting increasing trend. However, the statistics of daily mean temperature shows that the year 2009 has a cool summer, compared with hot summer in 2010 and 2011 (Fig. S6 in the Supplement). After compensating the effects of ambient temperature with the CPF, the ozone column contents in 2010 and 2011 have been decreased.

The long-term CO column contents show a $\sim 8.0\,\mathrm{DU\,decade^{-1}}$ decrease (Fig. 10c). Based on the vertical distribution of CO (Fig. 8), CO concentrations decay exponentially above the surface within the PBL to near constant value aloft. So the $8.0\,\mathrm{DU\,decade^{-1}}$ decrease in CO column contents can be interpreted as a $\sim 350\,\mathrm{ppbv\,decade^{-1}}$ decrease on the ground-level, less than the nationwide decrease (data available at http://www.epa.gov/airtrends/). One possible explanation is that the national trend is calculated based on the 2nd maximum of annual 8-h average, i.e. measurements in CO episodes, which usually arise on cold winter days with a temperature inversion. RAMMPP research flights are normally carried out during the ozone season, when CO pollution is not as severe and strong convection transporting CO upward. Figure 10 also shows that O_3 and CO column contents are well correlated, in particular after the EPA SIP call; for instance, in 2009, both high CO and high O_3 columns were observed. These large inter-annual variations in CO column contents cannot be explained by the NEI emissions trends (Fig. S2) and have not been observed by ground-level observations (Schwab et al., 2009). CO is usually emitted alongside with NO_x from automobile emissions or other incomplete combustion such as biomass burning. Therefore, a high concentration of CO might be an indicator of high NO_x, which would also boost the production of ozone. Airborne NO_2 measurements were not available in RAMMPP aircraft before 2011, so this hypothesis of intercepting automobile exhausts or wildfire plumes cannot be verified and future studies are needed to elaborate these issues. However, when we used the 7 yr Savitzky-Golay method to smooth the data, the $\sim 8.0\,\mathrm{DU\,decade^{-1}}$ decrease, $\sim 15\,\%$ relatively, can be treated as the long-term trend of column CO in the lower atmosphere with uncertainties from airborne sampling.

ACPD
13, 3135–3178, 2013

To investigate the long-term CO trends from the space, we used the monthly MOPITT near-surface CO retrievals from 2000 to 2011 (Deeter et al., 2003, 2012). Since MOPITT equator crossing time is around 10:30 a.m. (local time), we used the morning RAMMPP CO column contents observed in western MD. Only data in summer (JJA) were selected to reduce the effect of CO seasonal variations, and we calculated the observed annual mean (Fig. 11). Linear regression analyses of long-term RAMMPP aircraft measurements, MOPITT observations, and NEI emissions were conducted, with high correlation for MOPITT observations ($r = -0.86$) and NEI emissions ($r = -0.99$). However, the correlation is low for RAMMPP aircraft measurements in the morning, which could be caused by the sampling uncertainty mentioned above. The overall reduction (based on the value of 2000) is estimated as $\sim 40\,\%$ ($\sim 3.5\,\%\,yr^{-1}$) for both RAMMPP measurements and MOPITT observation, and $\sim 60.0\,\%$ ($\sim 4.5\,\%\,yr^{-1}$) for the NEI emissions. The decreasing trend of MOPITT CO observed over western MD, $\sim 3.5\,\%\,yr^{-1}$, is higher than the value ($\sim 1.5\,\%\,yr^{-1}$) reported in eastern US (Worden et al., 2012). In Worden et al. (2012) MOPITT total column CO data in all seasons were analyzed, while we only focused on summertime observations of near-surface CO. We would expect to see a larger trend in near-surface values compared to total column CO because the near-surface CO is substantially influenced by surface-based pollution sources (Fig. 8).

4 Clustering analysis on the regional transport of CEMS emissions

The CEMS program monitors point sources equipped with tall smokestacks such as power plants and industrial boilers. A study conducted by the US Government Accountability Office (US G.A.O) tracked 284 tall smokestacks at 172 coal-fired power plants in 34 states, of which 205 are 62.5 to 213 m tall, 63 are 213 to 305 m tall, and 12 are higher than 305 m (G.A.O., 2011). About one-third of these tall stacks are located in PA, WV and OH along the Ohio River Valley. Such high smokestacks can disperse air pollutants over great distances. Since the Baltimore/Washington region is

ACPD
13, 3135–3178, 2013

often downwind of the Ohio River Valley, emissions from point sources are expected to exert substantial effects on the downwind air pollution. We aggregated the CEMS emission data by state, because point sources are regulated by each state.

We studied regional transport with a hierarchical clustering technique using measurements from 63 RAMMPP research spirals over Harford County airport from 1998 to 2011. We utilized the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (version 4, http://www.arl.noaa.gov/ready/hysplit4.html) to calculate 48-h back trajectories. The time of each aircraft spiral was used to initialize the model with release heights of 500, 1000, and 1500 m a.g.l., respectively. Details on the model and meteorological fields are listed in Table S4 of the Supplement. The accuracy of these trajectories is adequate to track the general circulation patterns that transport the air pollutants (Stohl, 1998; Stohl et al., 1995).

Location and altitude information of each HYSPLIT back trajectory was archived and the back trajectories ending at 1000 m over Harford County airport were selected to investigate the transport processes. The clusters are identified by their circulation patterns (Fig. 12). Three major clusters, OH/PA, PA, and WV/VA arise; two minor clusters, recirculation and stagnation (containing less than 10 members each), are embedded underneath these spaghetti-like clusters (Table 1). Emissions of NO_x from OH and PA are $\sim$4 and $\sim$6 times higher than emissions from MD, and the OH/PA cluster corresponds to the prevailing westerly winds during the ozone season. A simplified approach was developed to evaluate the influence of upwind emissions: if the back trajectory passes over OH and PA, total emissions are estimated as:

$$\text{Emission}_{\text{total}} = \text{Emission}_{\text{MD},i} + 0.5\text{Emission}_{\text{PA},i-1} + 0.25\text{Emission}_{\text{OH},i-1} \quad (1)$$

Where the subscript i represents the flight date, and $i-1$ represents upwind emissions from the day before (Table 1). The coefficients of 0.5 and 0.25 are used under a simple assumption based on the distance between the upwind sources and air pollutants over eastern MD, i.e. PA is next to MD so half of the CEMS emissions are assumed to be

ACPD
13, 3135–3178, 2013

transported into MD while OH is farther away, so the coefficient is assumed to be 0.25. Our analysis is insensitive to the exact value of these coefficients as will be discussed below.

Figure 13 shows CEMS emissions versus the measured surface to 1500 m a.g.l. column ozone contents. Linear regression analyses were conducted for each cluster (r values are listed in Table 1), and only the OH/PA cluster shows a strong correlation between upwind emissions and downwind air pollution. We also correlated ozone column contents with emission estimates assuming double (high estimate) and half (low estimate) of the coefficients in Table 1; see also Fig. S7 in the Supplement. Ozone over the Harford County airport shows a strong positive correlation with emissions from the OH/PA cluster with little sensitivity to the exact value of these coefficients. However, the correlation between ozone column contents and MD emissions is low (Fig. S8 in the Supplement), suggesting that emissions from MD alone are a poor prediction of ozone pollution within this state. In summary, emissions of NO_x in OH and PA substantially influence the ground-level air quality in the Baltimore/Washington area during the ozone season. Interstate/regional transport should be taken into account in plans to improve future air quality in the Baltimore/Washington area.

5 Discussion and conclusions

We investigated the long-term trends of air pollution in the lower troposphere in the Baltimore/Washington airshed through a comprehensive study using emissions, aircraft and satellite measurements, and a clustering technique.

The EPA CEMS program continuously monitors the emissions from major point sources including power plants and industrial boilers, and the data for the research domain were used to investigate the interstate transport of air pollutants. The long-term trends of CEMS emissions demonstrate a significant decrease of NO_x emissions over the last 15 yr. The EPA NO_x SIP call (2003–2004) has been effective in reducing the NO_x emissions from point sources, which helped improving local and regional air

ACPD
13, 3135–3178, 2013

quality, especially ground-level ozone. The EPA AQS NO_x observations decline by an amount similar to that of the CEMS emissions, with both time series exhibiting a sharp decrease after the EPA NO_x SIP call.

The aircraft measurements of O_3 and its precursor CO were integrated to obtain column contents, and categorized into upwind and downwind groups. The difference of tropospheric ozone column contents in these two groups was used to estimate the daily net photochemical production of ambient ozone: $\sim 3.0\,\mathrm{DU\,day^{-1}}$ in the late 1990s and $\sim 1.0\,\mathrm{DU\,day^{-1}}$ in the early 2010s for column contents, equivalent to $\sim 20\,\mathrm{ppbv\,day^{-1}}$ and $\sim 7\,\mathrm{ppbv\,day^{-1}}$ when averaged over the lowest 1500 m of the atmosphere. The decreasing trends of CO and O_3 were found to be $\sim 8.0\,\mathrm{DU\,decade^{-1}}$ and $\sim 2.0\,\mathrm{DU\,decade^{-1}}$, respectively, equivalent to $\sim 350\,\mathrm{ppbv\,decade^{-1}}$ and $\sim 13\,\mathrm{ppbv\,decade^{-1}}$ decreases. Because RAMMPP research flights are mostly conducted on the air quality action days, the substantial ozone decrease suggests that ozone pollution on the bad air quality days has been improved significantly. MOPITT spaced-based observations and RAMMPP morning aircraft flights both show $\sim 40\,\%$ ($\sim 3.5\,\%\,\mathrm{yr^{-1}}$) decrease over western MD, while the NEI emissions suggest $\sim 60\,\%$ ($\sim 4.5\,\%\,\mathrm{yr^{-1}}$) reduction between 2000 and 2011.

To investigate the effects of long-range transport of air pollutants, in particular from power plants with high smokestacks, back trajectories were calculated using the NOAA HYSPLIT model. These trajectories fell into several clusters, and total NO_x emissions were estimated for the geographic origins corresponding to each cluster. We performed a linear regression analysis for each cluster, and found that transport from OH and PA through MD has greatest effect on column contents of air pollutants in the Baltimore/Washington airshed. Ozone over eastern MD correlates strongly ($r = 0.86$) with air following this multiscale trajectory. The next highest correlation is with a recirculation pattern involving MD, VA, and PA ($r = 0.56$).

According to the NEI inventory, $\sim 90\,\%$ of CO and $\sim 50\,\%$ NO_x, important precursors for ozone pollution, are emitted by mobile sources (onroad and nonroad vehicles). In this study, annual mobile emissions from USEPA NEI inventory were used to track the

ACPD
13, 3135–3178, 2013

long-term trend, but seasonal and diurnal variations of mobile emissions are not directly available. Future research should focus on numerical modeling to study the seasonal and diurnal variability of mobile emissions, and these results will be useful to study the effects of regional/local measures on air quality.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/13/3135/2013/acpd-13-3135-2013-supplement.pdf.

Acknowledgement. We thank MDE for supporting the RAMMPP program. We thank Juying Warner for helpful comments. The National Center for Atmospheric Research (NCAR) is sponsored by the National Science Foundation. The NCAR MOPITT project is supported by the National Aeronautics and Space Administration (NASA) Earth Observing System (EOS) program.

References

Adams, R. M., Glyer, J. D., Johnson, S. L., and McCarl, B. A.: A reassessmen of the economic-effects of ozone on United-States agriculture, JAPCA J. Air Waste Ma., 39, 960–968, 1989.

Anderson, H. R.: Air pollution and mortality: a history, Atmos. Environ., 43, 142–152, 2009.

Ashmore, M. R.: Assessing the future global impacts of ozone on vegetation, Plant Cell Environ., 28, 949–964, 2005.

Bloomer, B. J., Stehr, J. W., Piety, C. A., Salawitch, R. J., and Dickerson, R. R.: Observed relationships of ozone air pollution with temperature and emissions, Geophys. Res. Lett., 36, L09803, doi:10.1029/2009GL037308, 2009.

Bloomer, B. J., Vinnikov, K. Y., and Dickerson, R. R.: Changes in seasonal and diurnal cycles of ozone and temperature in the eastern US, Atmos. Environ., 44, 2543–2551, 2010.

Bromba, M. U. A. and Ziegler, H.: Application hints for Savitzky–Golay digital smoothing filters, Anal. Chem., 53, 1583–1586, 1981.

ACPD
13, 3135–3178, 2013

Buchwitz, M., de Beek, R., Bramstedt, K., Noël, S., Bovensmann, H., and Burrows, J. P.: Global carbon monoxide as retrieved from SCIAMACHY by WFM-DOAS, Atmos. Chem. Phys., 4, 1945–1960, doi:10.5194/acp-4-1945-2004, 2004.
Camalier, L., Cox, W., and Dolwick, P.: The effects of meteorology on ozone in urban areas and their use in assessing ozone trends, Atmos. Environ., 41, 7127–7137, 2007.
Castellanos, P., Stehr, J. W., Dickerson, R. R., and Ehrman, S. H.: The sensitivity of modeled ozone to the temporal distribution of point, area, and mobile source emissions in the eastern United States, Atmos. Environ., 43, 4603–4611, 2009.
Castellanos, P., Marufu, L. T., Doddridge, B. G., Taubman, B. F., Schwab, J. J., Hains, J. C., Ehrman, S. H., and Dickerson, R. R.: Ozone, oxides of nitrogen, and carbon monoxide during pollution events over the eastern United States: an evaluation of emissions and vertical mixing, J. Geophys. Res.-Atmos., 116, D16307, doi:10.1029/2010JD014540, 2011.
Chameides, W. L., Li, X. S., Tang, X. Y., Zhou, X. J., Luo, C., Kiang, C. S., St John, J., Saylor, R. D., Liu, S. C., Lam, K. S., Wang, T., and Giorgi, F.: Is ozone pollution affecting crop yields in China?, Geophys. Res. Lett., 26, 867–870, 1999.
Chan, E. and Vet, R. J.: Baseline levels and trends of ground level ozone in Canada and the United States, Atmos. Chem. Phys., 10, 8629–8647, doi:10.5194/acp-10-8629-2010, 2010.
Cooper, O. R., Parrish, D. D., Stohl, A., Trainer, M., Nedelec, P., Thouret, V., Cammas, J. P., Oltmans, S. J., Johnson, B. J., Tarasick, D., Leblanc, T., McDermid, I. S., Jaffe, D., Gao, R., Stith, J., Ryerson, T., Aikin, K., Campos, T., Weinheimer, A., and Avery, M. A.: Increasing springtime ozone mixing ratios in the free troposphere over western North America, Nature, 463, 344–348, 2010.
Cooper, O. R., Gao, R. S., Tarasick, D., Leblanc, T., and Sweeney, C.: Long-term ozone trends at rural ozone monitoring sites across the United States, 1990–2010, J. Geophys. Res.-Atmos., 117, D22307, doi:10.1029/2012jd018261, 2012.
Corsmeier, U., Kalthoff, N., Kolle, O., Kotzian, M., and Fiedler, F.: Ozone concentration jump in the stable nocturnal boundary layer during a LLJ-event, Atmos. Environ., 31, 1977–1989, 1997.
Crutzen, P. J.: Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air, Tellus, 26, 47–57, 1974.
Deeter, M. N., Emmons, L. K., Francis, G. L., Edwards, D. P., Gille, J. C., Warner, J. X., Khattatov, B., Ziskin, D., Lamarque, J. F., Ho, S. P., Yudin, V., Attie, J. L., Packman, D., Chen, J., Mao, D., and Drummond, J. R.: Operational carbon monoxide retrieval algo-

ACPD
13, 3135–3178, 2013

rithm and selected results for the MOPITT instrument, J. Geophys. Res.-Atmos., 108, 4399, doi:10.1029/2002jd003186, 2003.
Deeter, M. N., Worden, H. M., Edwards, D. P., Gille, J. C., and Andrews, A. E.: Evaluation of MOPITT retrievals of lower-tropospheric carbon monoxide over the United States, J. Geophys. Res.-Atmos., 117, D13306, doi:10.1029/2012jd017553, 2012.
Dickerson, R. R., and Delany, A. C.: Modification of a commercial gas filter correlation CO detector for enhanced sensitivity, J. Atmos. Ocean. Tech., 5, 424–431, 1988.
Dunlea, E. J., Herndon, S. C., Nelson, D. D., Volkamer, R. M., San Martini, F., Sheehy, P. M., Zahniser, M. S., Shorter, J. H., Wormhoudt, J. C., Lamb, B. K., Allwine, E. J., Gaffney, J. S., Marley, N. A., Grutter, M., Marquez, C., Blanco, S., Cardenas, B., Retama, A., Ramos Villegas, C. R., Kolb, C. E., Molina, L. T., and Molina, M. J.: Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, Atmos. Chem. Phys., 7, 2691–2704, doi:10.5194/acp-7-2691-2007, 2007.
EPA: Air Quality Criteria for Ozone and Related Photochemical Oxidants, Report Nos. EPA/600/R-05/004sf, US Environmental Protection Angency, Office of Research and Development, Research Triangle Park, NC, February 2006, 2006.
EPA: Mid-Atlantic Air Quality, avialable at: http://www.epa.gov/reg3artd/airquality/airquality.htm (last access: December 2012), 2012a.
EPA: Federal Register Notices Related to 8-hour Ozone Designations and Classifications, available at: http://www.epa.gov/oar/oaqps/greenbk/gfrnrpt4.html (last access: December 2012), 2012b.
EPA: Air Quality Trends, avialable at: http://www.epa.gov/airtrends/aqtrends.html (last access: December 2012), 2012c.
Fehsenfeld, F. C., Dickerson, R. R., Hubler, G., Luke, W. T., Nunnermacker, L. J., Williams, E. J., Roberts, J. M., Calvert, J. G., Curran, C. M., Delany, A. C., Eubank, C. S., Fahey, D. W., Fried, A., Gandrud, B. W., Langford, A. O., Murphy, P. C., Norton, R. B., Pickering, K. E., and Ridley, B. A.: A Ground-based intercomparision of NO, NO_x, and NO_y measurement techniques, J. Geophys. Res.-Atmos., 92, 14710–14722, 1987.
Fishman, J., Solomon, S., and Crutzen, P. J.: Observational and theoretical evidence in support of a significant in situ photo-chemical source of tropospheric ozone, Tellus, 31 432–446, 1979a.
Fishman, J., Ramanathan, V., Crutzen, P. J., and Liu, S. C.: Tropospheric ozone and climate, Nature, 282, 818–820, 1979b.

ACPD
13, 3135–3178, 2013

GAO: Information on Tall Smokestacks and their Contribution to Interstate Transport of Air Pollution, United States Government Accountability Office (GAO), Washginton DC, 2011.
George, M., Clerbaux, C., Hurtmans, D., Turquety, S., Coheur, P.-F., Pommier, M., Hadji-Lazaro, J., Edwards, D. P., Worden, H., Luo, M., Rinsland, C., and McMillan, W.: Carbon monoxide distributions from the IASI/METOP mission: evaluation with other space-borne remote sensors, Atmos. Chem. Phys., 9, 8317–8330, doi:10.5194/acp-9-8317-2009, 2009.
Gorry, P. A.: General least-squares smoothing and differentiation by the convolution (Savitzky–Golay) method, Anal. Chem., 62, 570–573, 1990.
Haagen-Smit, A. J.: Chemistry and physiology of Los-Angeles smog, Ind. Eng. Chem., 44, 1342–1346, 1952.
Haagen-Smit, A. J. and Fox, M. M.: Ozone formation in photochemical oxidation of organic substances, Ind. Eng. Chem., 48, 1484–1487, 1956.
Hains, J. C., Taubman, B. F., Thompson, A. M., Stehr, J. W., Marufu, L. T., Doddridge, B. G., and Dickerson, R. R.: Origins of chemical pollution derived from Mid-Atlantic aircraft profiles using a clustering technique, Atmos. Environ., 42, 1727–1741, 2008.
Higgins, R. W., Yao, Y., Yarosh, E. S., Janowiak, J. E., and Mo, K. C.: Influence of the Great Plains low-level jet on summertime precipitation and moisture transport over the central United States, J. Climate, 10, 481–507, 1997.
Hirsch, A. I., Munger, J. W., Jacob, D. J., Horowitz, L. W., and Goldstein, A. H.: Seasonal variation of the ozone production efficiency per unit NO_x at Harvard Forest, Massachusetts, J. Geophys. Res.-Atmos., 101, 12659–12666, 1996.
Holton, J. R., Haynes, P. H., McIntyre, M. E., Douglass, A. R., Rood, R. B., and Pfister, L.: Stratosphere-troposphere exchange, Rev. Geophys., 33, 403–439, 1995.
IPCC: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report (AR4) of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp., 2007.
Jacob, D. J. and Winner, D. A.: Effect of climate change on air quality, Atmos. Environ., 43, 51–63, 2009.
Jaffe, D.: Relationship between Surface and Free Tropospheric Ozone in the Western US, Environ. Sci. Technol., 45, 432–438, 2011.
Jaffe, D. and Ray, J.: Increase in surface ozone at rural sites in the western US, Atmos. Environ., 41, 5452–5463, 2007.

ACPD
13, 3135–3178, 2013

Jerrett, M., Burnett, R. T., Pope, C. A., Ito, K., Thurston, G., Krewski, D., Shi, Y. L., Calle, E., and Thun, M.: Long-term ozone exposure and mortality, New Engl. J. Med., 360, 1085–1095, 2009.

Kleinman, L. I.: Ozone process insights from field experiments – Part II: Observation-based analysis for ozone production, Atmos. Environ., 34, 2023–2033, 2000.

Kleinman, L. I., Daum, P. H., Lee, Y. N., Nunnermacker, L. J., Springston, S. R., Weinstein-Lloyd, J., and Rudolph, J.: Ozone production efficiency in an urban area, J. Geophys. Res.-Atmos., 107, 4733, doi:10.1029/2002jd002529, 2002.

Lefohn, A. S., Shadwick, D., and Oltmans, S. J.: Characterizing long-term changes in surface ozone levels in the United States (1980–2005), Atmos. Environ., 42, 8252–8262, 2008.

Lefohn, A. S., Shadwick, D., and Oltmans, S. J.: Characterizing changes in surface ozone levels in metropolitan and rural areas in the United States for 1980–2008 and 1994–2008, Atmos. Environ., 44, 5199–5210, 2010.

Levy, H.: Normal atmosphere: large radical and formaldehyde concentrations predicted, Science, 173, 141–143, 1971.

Levy, H., Mahlman, J. D., Moxim, W. J., and Liu, S. C.: Tropospheric ozone: the role of transport, J. Geophys. Res.-Atmos., 90, 3753–3772, 1985.

Lin, M. Y., Fiore, A. M., Horowitz, L. W., Cooper, O. R., Naik, V., Holloway, J., Johnson, B. J., Middlebrook, A. M., Oltmans, S. J., Pollack, I. B., Ryerson, T. B., Warner, J. X., Wiedinmyer, C., Wilson, J., and Wyman, B.: Transport of Asian ozone pollution into surface air over the western United States in spring, J. Geophys. Res.-Atmos., 117, D00v07, doi:10.1029/2011jd016961, 2012.

Lin, X., Trainer, M., and Liu, S. C.: On the nonlinearity of the tropospheric ozone production, J. Geophys. Res.-Atmos., 93, 15879–15888, 1988.

Liu, S. C., Trainer, M., Fehsenfeld, F. C., Parrish, D. D., Williams, E. J., Fahey, D. W., Hubler, G., and Murphy, P. C.: Ozone production in the rural troposphere and the implications for regional and global ozone distributions, J. Geophys. Res.-Atmos., 92, 4191–4207, 1987.

Logan, J. A., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Tropospheric chemistry: a global perspective, J. Geophys. Res.-Oc. Atm., 86, 7210–7254, 1981.

Loughner, C. P., Allen, D. J., Pickering, K. E., Zhang, D. L., Shou, Y. X., and Dickerson, R. R.: Impact of fair-weather cumulus clouds and the Chesapeake Bay breeze on pollutant transport and transformation, Atmos. Environ., 45, 4060–4072, 2011.

ACPD
13, 3135–3178, 2013

Luo, M., Rinsland, C. P., Rodgers, C. D., Logan, J. A., Worden, H., Kulawik, S., Eldering, A., Goldman, A., Shephard, M. W., Gunson, M., and Lampel, M.: Comparison of carbon monoxide measurements by TES and MOPITT: influence of a priori data and instrument characteristics on nadir atmospheric species retrievals, J. Geophys. Res.-Atmos., 112, D09303, doi:10.1029/2006jd007663, 2007.

Marufu, L. T., Taubman, B. F., Bloomer, B., Piety, C. A., Doddridge, B. G., Stehr, J. W., and Dickerson, R. R.: The 2003 North American electrical blackout: an accidental experiment in atmospheric chemistry, Geophys. Res. Lett., 31, L13106, doi:10.1029/2004gl019771, 2004.

Neuman, J. A., Trainer, M., Aikin, K. C., Angevine, W. M., Brioude, J., Brown, S. S., de Gouw, J. A., Dube, W. P., Flynn, J. H., Graus, M., Holloway, J. S., Lefer, B. L., Nedelec, P., Nowak, J. B., Parrish, D. D., Pollack, I. B., Roberts, J. M., Ryerson, T. B., Smit, H., Thouret, V., and Wagner, N. L.: Observations of ozone transport from the free troposphere to the Los Angeles basin, J. Geophys. Res.-Atmos., 117, D00v09, doi:10.1029/2011jd016919, 2012.

Nunnermacker, L. J., Kleinman, L. I., Imre, D., Daum, P. H., Lee, Y. N., Lee, J. H., Springston, S. R., Newman, L., and Gillani, N.: NO_y lifetimes and O_3 production efficiencies in urban and power plant plumes: analysis of field data, J. Geophys. Res.-Atmos., 105, 9165–9176, 2000.

Oltmans, S. J., Lefohn, A. S., Scheel, H. E., Harris, J. M., Levy, H., Galbally, I. E., Brunke, E. G., Meyer, C. P., Lathrop, J. A., Johnson, B. J., Shadwick, D. S., Cuevas, E., Schmidlin, F. J., Tarasick, D. W., Claude, H., Kerr, J. B., Uchino, O., and Mohnen, V.: Trends of ozone in the troposphere, Geophys. Res. Lett., 25, 139–142, 1998.

Oltmans, S. J., Lefohn, A. S., Harris, J. M., Galbally, I., Scheel, H. E., Bodeker, G., Brunke, E., Claude, H., Tarasick, D., Johnson, B. J., Simmonds, P., Shadwick, D., Anlauf, K., Hayden, K., Schmidlin, F., Fujimoto, T., Akagi, K., Meyer, C., Nichol, S., Davies, J., Redondas, A., and Cuevas, E.: Long-term changes in tropospheric ozone, Atmos. Environ., 40, 3156–3173, 2006.

Oltmans, S. J., Lefohn, A. S., Harris, J. M., and Shadwick, D. S.: Background ozone levels of air entering the west coast of the US and assessment of longer-term changes, Atmos. Environ., 42, 6020–6038, 2008.

Ramanathan, V. and Dickinson, R. E.: Role of stratospheric ozone in the zonal and seasonal radiative energy balance of the Earth troposphere system, J. Atmos. Sci., 36, 1084–1104, 1979.

ACPD
13, 3135–3178, 2013

Savitzky, A. and Golay, M. J. E.: Smoothing and differentiation of data by simplified least squares procedures, Anal. Chem., 36, 1627–1639, 1964.
Schwab, J. J., Spicer, J. B., and Demerjian, K. L.: Ozone, trace gas, and particulate matter measurements at a rural site In Southwestern New York State: 1995–2005, J. Air Waste Manage. Assoc., 59, 293–309, 2009.
Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd edn., John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 2006
Shon, Z.-H., Madronich, S., Song, S.-K., Flocke, F. M., Knapp, D. J., Anderson, R. S., Shetter, R. E., Cantrell, C. A., Hall, S. R., and Tie, X.: Characteristics of the NO-NO_2-O_3 system in different chemical regimes during the MIRAGE-Mex field campaign, Atmos. Chem. Phys., 8, 7153–7164, doi:10.5194/acp-8-7153-2008, 2008.
Shou, Y. X. and Zhang, D. L.: Impact of environmental flows on the daytime urban boundary layer structures over the Baltimore metropolitan region, Atmos. Sci. Lett., 11, 1–6, 2010.
Sillman, S.: The use of NO_y, H_2O_2, and HNO_3 as indicators for ozone-NO_x-hydrocarbon sensitivity in urban locations, J. Geophys. Res.-Atmos., 100, 14175–14188, 1995.
Stohl, A.: Computation, accuracy and applications of trajectories – a review and bibliography, Atmos. Environ., 32, 947–966, 1998.
Stohl, A., Wotawa, G., Seibert, P., and Krompkolb, H.: Interpolation errors in wind fields as a function of spatial and temporal resolution and their impact on different types of kinematic trajectories, J. Appl. Meteorol., 34, 2149–2165, 1995.
Stunder, B. J. B.: An assessment of the quality of forecast trajectories, J. Appl. Meteorol., 35, 1319–1331, 1996.
Taubman, B. F., Marufu, L. T., Piety, C. A., Doddridge, B. G., Stehr, J. W., and Dickerson, R. R.: Airborne characterization of the chemical, optical, and meteorological properties, and origins of a combined ozone-haze episode over the eastern United States, J. Atmos. Sci., 61, 1781–1793, 2004a.
Taubman, B. F., Marufu, L. T., Vant-Hull, B. L., Piety, C. A., Doddridge, B. G., Dickerson, R. R., and Li, Z. Q.: Smoke over haze: aircraft observations of chemical and optical properties and the effects on heating rates and stability, J. Geophys. Res.-Atmos., 109, D02206, doi:10.1029/2003jd003898, 2004b.
Taubman, B. F., Hains, J. C., Thompson, A. M., Marufu, L. T., Doddridge, B. G., Stehr, J. W., Piety, C. A., and Dickerson, R. R.: Aircraft vertical profiles of trace gas and aerosol pollution

ACPD
13, 3135–3178, 2013

over the mid-Atlantic United States: statistics and meteorological cluster analysis, J. Geophys. Res.-Atmos., 111, D10s07, doi:10.1029/2005jd006196, 2006.
Walcek, C. J. and Yuan, H. H.: Calculated influence of temperature related factors on ozone formation rates in the lower troposphere, J. Appl. Meteorol., 34, 1056–1069, 1995.
Wang, Y. H., Logan, J. A., and Jacob, D. J.: Global simulation of tropospheric O_3-NO_x-hydrocarbon chemistry 2. Model evaluation and global ozone budget, J. Geophys. Res.-Atmos., 103, 10727–10755, 1998.
Warner, J., Comer, M. M., Barnet, C. D., McMillan, W. W., Wolf, W., and Maddy, E.: A comparison of satellite tropospheric carbon monoxide measurements from AIRS and MOPITT during INTEX-A, J. Geophys. Res.-Atmos., 112, D12s17, doi:10.1029/2006jd007925, 2007.
WHO: Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide, Wolrd Health Organisation, Bonn, 2003.
Wild, O., Sundet, J. K., Prather, M. J., Isaksen, I. S. A., Akimoto, H., Browell, E. V., and Oltmans, S. J.: Chemical transport model ozone simulations for spring 2001 over the western Pacific: comparisons with TRACE-P lidar, ozonesondes, and Total Ozone Mapping Spectrometer columns, J. Geophys. Res.-Atmos., 108, 8826, doi:10.1029/2002jd003283, 2003.
Worden, H. M., Deeter, M. N., Edwards, D. P., Gille, J. C., Drummond, J. R., and Nedelec, P.: Observations of near-surface carbon monoxide from space using MOPITT multispectral retrievals, J. Geophys. Res.-Atmos., 115, D18314, doi:10.1029/2010jd014242, 2010.
Worden, H. M., Deeter, M. N., Frankenberg, C., George, M., Nichitiu, F., Worden, J., Aben, I., Bowman, K. W., Clerbaux, C., Coheur, P. F., de Laat, A. T. J., Detweiler, R., Drummond, J. R., Edwards, D. P., Gille, J. C., Hurtmans, D., Luo, M., Martínez-Alonso, S., Massie, S., Pfister, G., and Warner, J. X.: Decadal record of satellite carbon monoxide observations, Atmos. Chem. Phys., 13, 837–850, doi:10.5194/acp-13-837-2013, 2013.
Yegorova, E. A., Allen, D. J., Loughner, C. P., Pickering, K. E., and Dickerson, R. R.: Characterization of an eastern US severe air pollution episode using WRF/Chem, J. Geophys. Res.-Atmos., 116, D17306, doi:10.1029/2010jd015054, 2011.
Yorks, J. E., Thompson, A. M., Joseph, E., and Miller, S. K.: The variability of free tropospheric ozone over Beltsville, Maryland (39° N, 77° W) in the summers 2004–2007, Atmos. Environ., 43, 1827–1838, 2009.
Zhang, D. L., Shou, Y. X., and Dickerson, R. R.: Upstream urbanization exacerbates urban heat island effects, Geophys. Res. Lett., 36, L24401, doi:10.1029/2009gl041082, 2009.

ACPD
13, 3135–3178, 2013

Zhang, D. L., Shou, Y. X., Dickerson, R. R., and Chen, F.: Impact of upstream urbanization on the urban heat island effects along the Washington-Baltimore corridor, J. Appl. Meteorol. Clim., 50, 2012–2029, 2011.

ACPD
13, 3135–3178, 2013

Table 1. Characteristics and emission estimates of each cluster.

Cluster	Upwind states	Emissions estimate	r^b	n^c
1	OH and PA	$MD_i + 0.5PA_{i-1} + 0.25OH_{i-1}$	0.86	18
2	PA	$MD_i + 0.5PA_{i-1}$	0.16	22
3	WV or VA	$MD_i + 0.5VA_{i-1}$ or $MD_i + 0.5WV_{i-1}$	−0.08	12
4	Recirculation	$MD_i + 0.5VA_{i-1} + 0.5\ PA_{i-1}$	0.53	4
5	Stagnation[a]	MD_i	0.04	7

[a] The background flight was incorporated into the stagnation cluster because it shares the same estimate of upwind emissions.
[b] Linear regression coefficient r is calculate for each group in Fig. 13a.
[c] Number of research spirals.

ACPD
13, 3135–3178, 2013

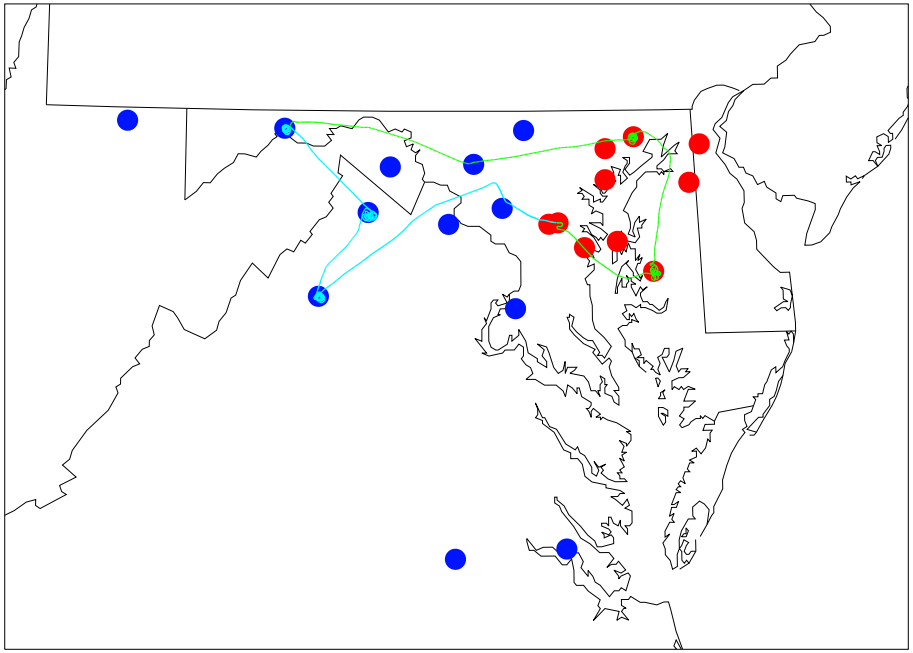

Fig. 1. Locations of the selected RAMMPP research spirals in the Baltimore/Washington airshed. Blue/Red dots show the locations of morning/afternoon spirals; Cyan/Green lines show the route of morning/afternoon flights during a typical westerly transport flight pattern after 2000. Five airports extensively covered by this flight pattern are (from the lower left, clockwise): Luray, VA (38.67° N, 78.50° W, 65 spirals), Winchester, VA (39.14° N, 78.14° W, 57 spirals), Cumberland, MD (39.62° N, 78.76° W, 71 spirals), Harford County, MD (39.57° N, 76.20° W, 64 spirals), and Easton, MD (38.80° N, 76.07° W, 72 spirals).

ACPD
13, 3135–3178, 2013

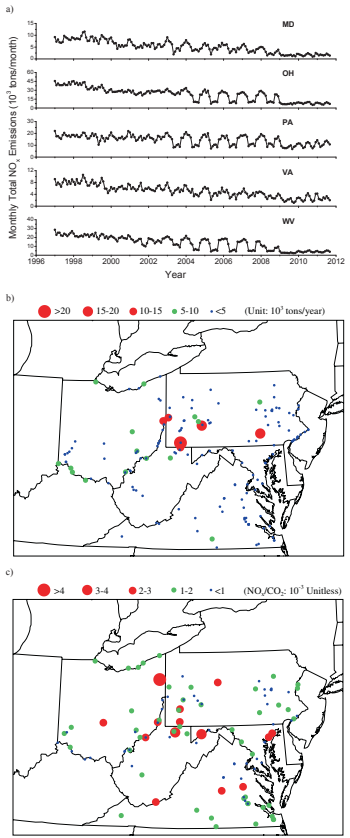

Fig. 2. CEMS NO_x emissions in the research domain. **(a)** Long-term trends of monthly NO_x emissions (unit: 10^3 t); **(b)** locations of major NO_x point sources; **(c)** map of NO_x/CO_2 ratios (unit: mol mol^{-1}). (**b** and **c**) are based on the annual emissions data in 2010.

ACPD
13, 3135–3178, 2013

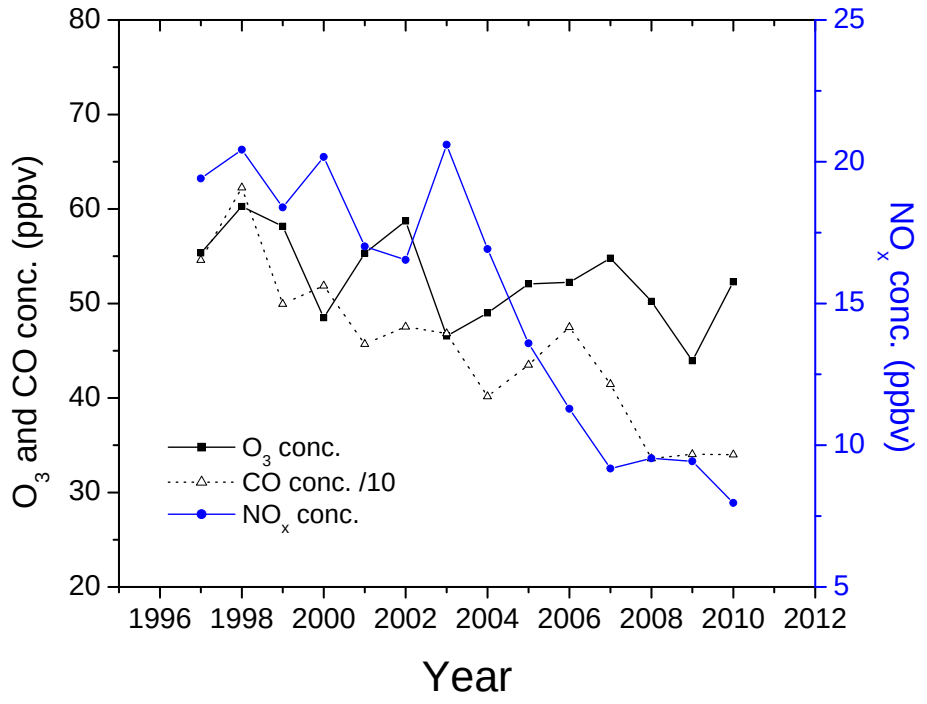

Fig. 3. Long-term trends of ground-level O_3, CO, and NO_x observed in the Baltimore/Washington area. CO concentrations are scaled by 10 for clarity. To investigate the ozone chemistry, measurements in the afternoon (12 p.m. to 6 p.m.) during the ozone seasons are used, and annual mean values are calculated.

ACPD
13, 3135–3178, 2013

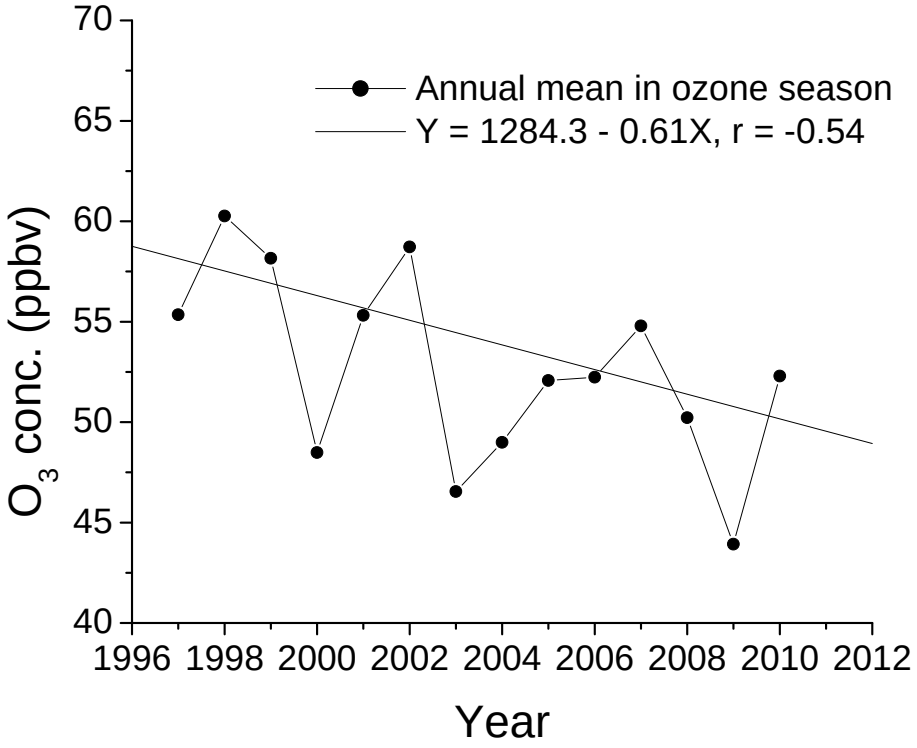

Fig. 4. Linear regression analysis of long-term EPA AQS ozone observations in MD/DC/NOVA Ozone data is same as in Fig. 3, and linear regression of ozone with respect to year, i.e. *Y*: ozone concentrations, *X*: year.

ACPD
13, 3135–3178, 2013

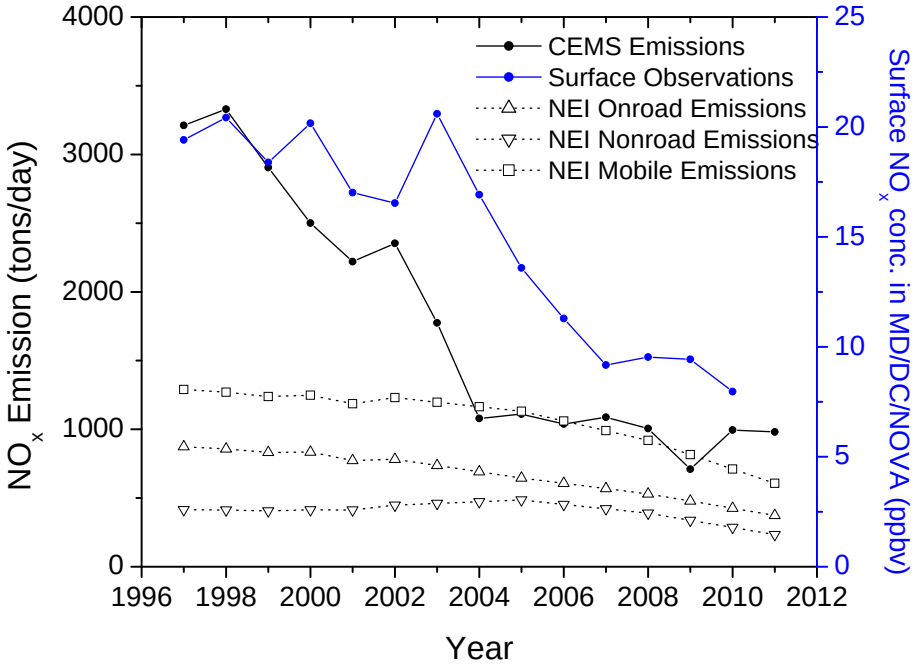

Fig. 5. Long-term trends of estimated daily NO_x emissions (CEMS and scaled NEI in the research domain) and EPA AQS ground-level observations in the Baltimore/Washington area. NEI mobile emissions are the sum of onroad and nonroad mobile emissions.

ACPD
13, 3135–3178, 2013

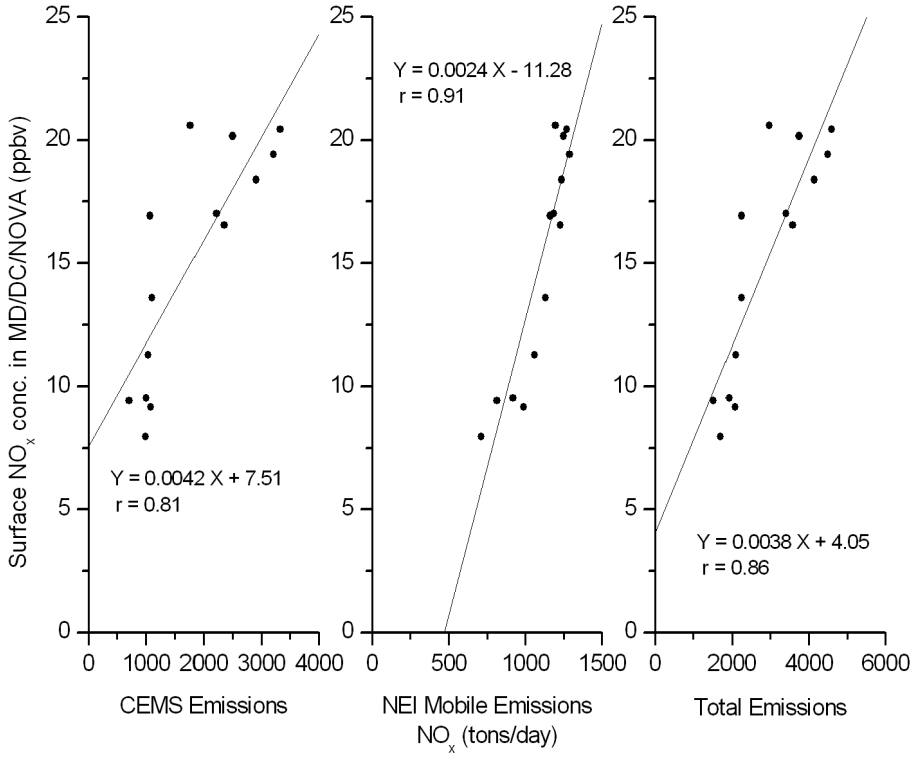

Fig. 6. Linear regression analysis of the long-term CEMS, NEI, and (CEMS + NEI) NO_x emissions with the EPA AQS observations, left: CEMS emissions only; middle: NEI mobile emissions (interpreted from annual estimate) only; right: total emissions (CEMS emissions + NEI mobile emissions).

ACPD
13, 3135–3178, 2013

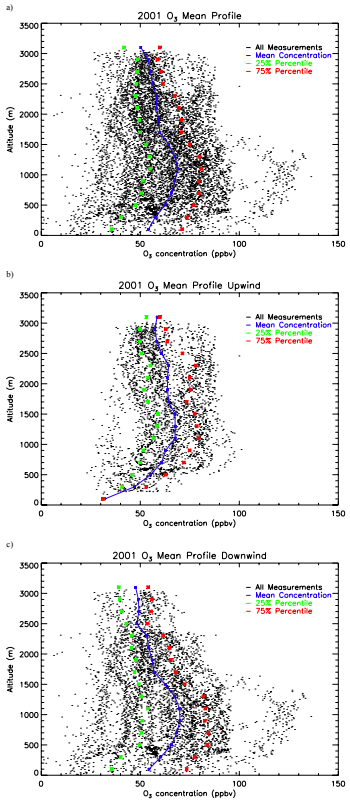

Fig. 7. Vertical distributions of tropospheric ozone over the Baltimore/Washington region in 2001 (**a**: all spirals; **b**: only the upwind spirals; **c**: only the downwind spirals). Measurements are grouped every 200 m according to the altitude; 25 % percentile, mean and 75 % percentile are calculated for each layer.

ACPD
13, 3135–3178, 2013

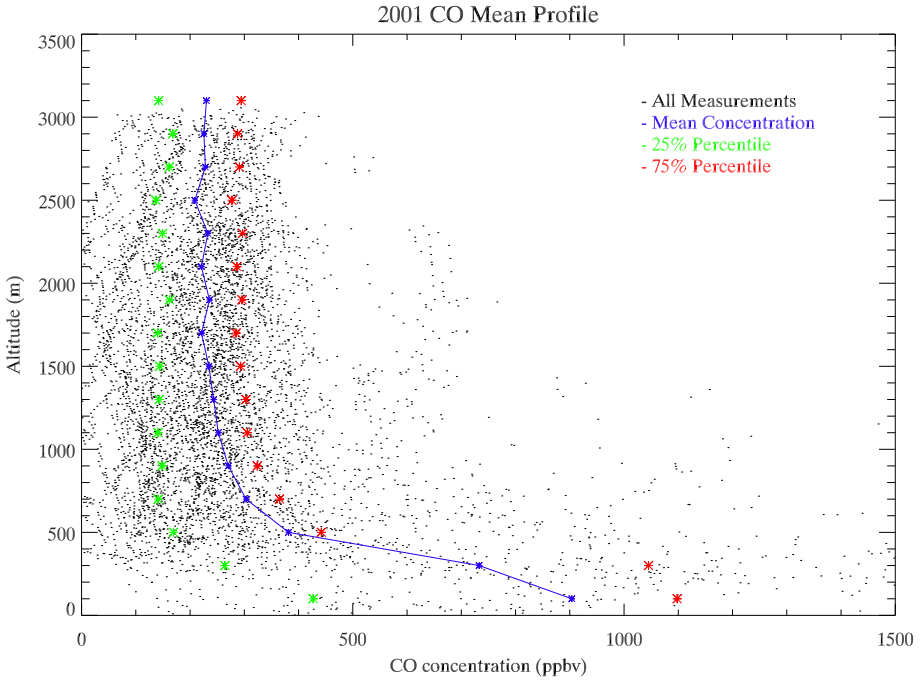

Fig. 8. Vertical distributions of tropospheric CO over the Baltimore/Washington region in 2001 (all spirals). The 25 % percentile, mean and 75 % percentile are calculated as in Fig. 7.

ACPD
13, 3135–3178, 2013

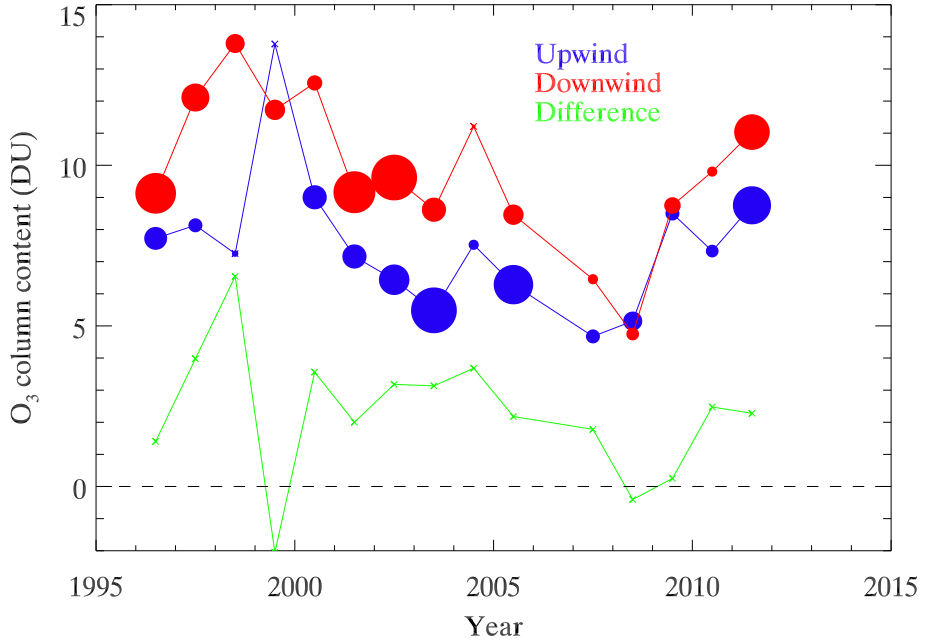

Fig. 9. Lumped long-term annual mean tropospheric ozone column contents. The size of bubble is proportional to the number of research spirals. Blue/Red bubbles show the mean ozone column contents in the upwind/downwind regions. Green line shows the difference. * Tropospheric ozone concentrations in the lower 1500 m are integrated to calculate the ozone column contents.

ACPD
13, 3135–3178, 2013

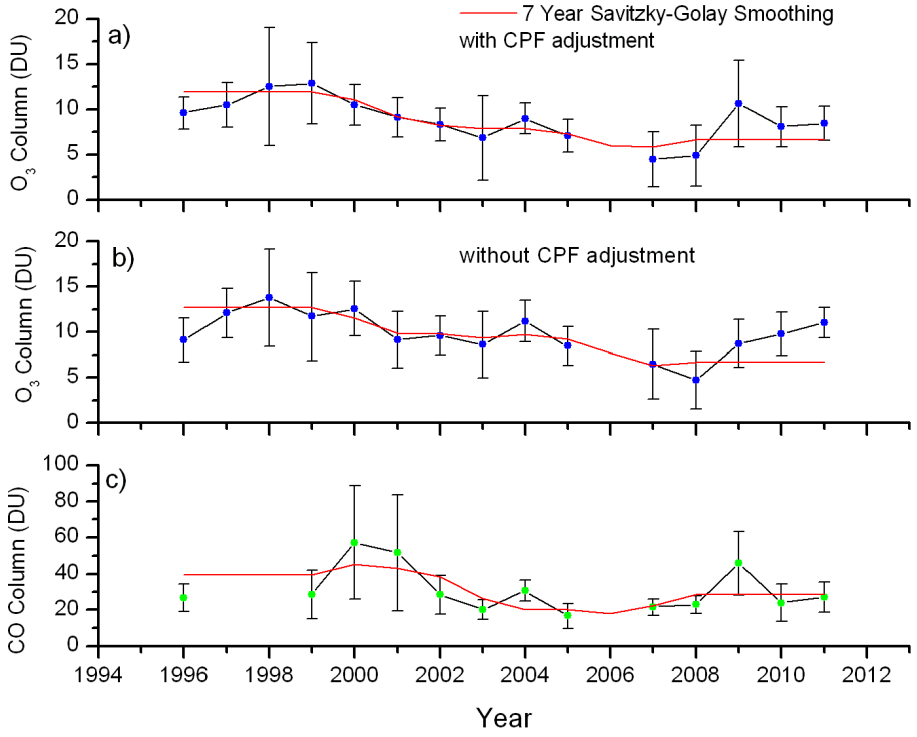

Fig. 10. Long-term trends of annual mean afternoon O_3 and CO column contents over the downwind region of the Baltimore/Washington area (**a** O_3 column contents with CPF adjustment; **(b)** O_3 column contents without CPF adjustment; **(c)** CO column contents). Error bars present the one standard deviation. Red line is the 7 yr Savitzky–Golay smoothing.

ACPD
13, 3135–3178, 2013

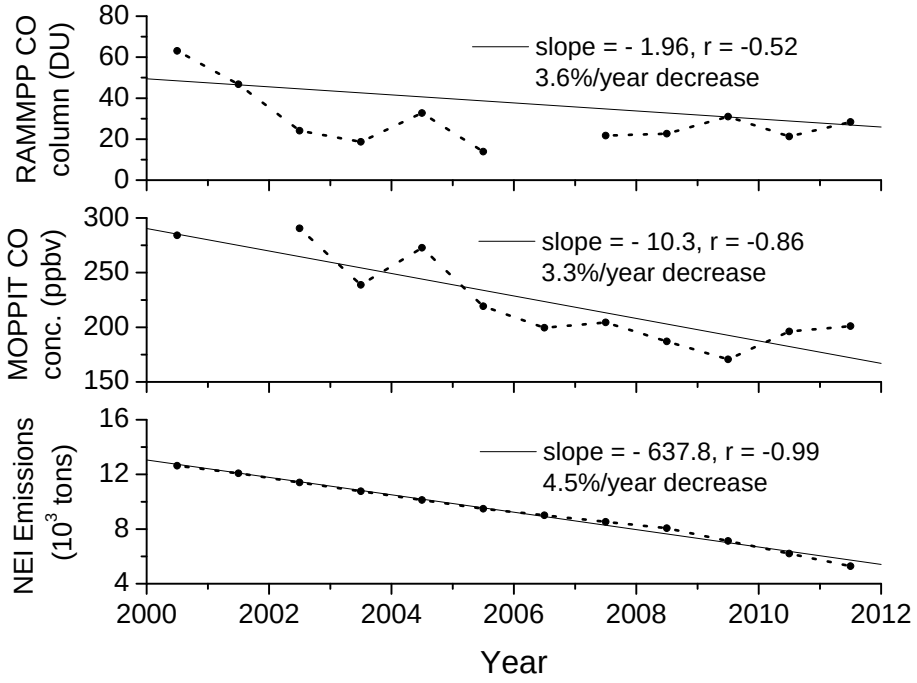

Fig. 11. The long-term trends of RAMMPP measurements, MOPPIT observations, and NEI emissions. **(a)** Annual mean RAMMPP morning CO column contents over western MD; **(b)** annual mean MOPITT near-surface CO concentrations; **(c)** annual NEI emissions. Lines show the results of linear regression analysis.

ACPD
13, 3135–3178, 2013

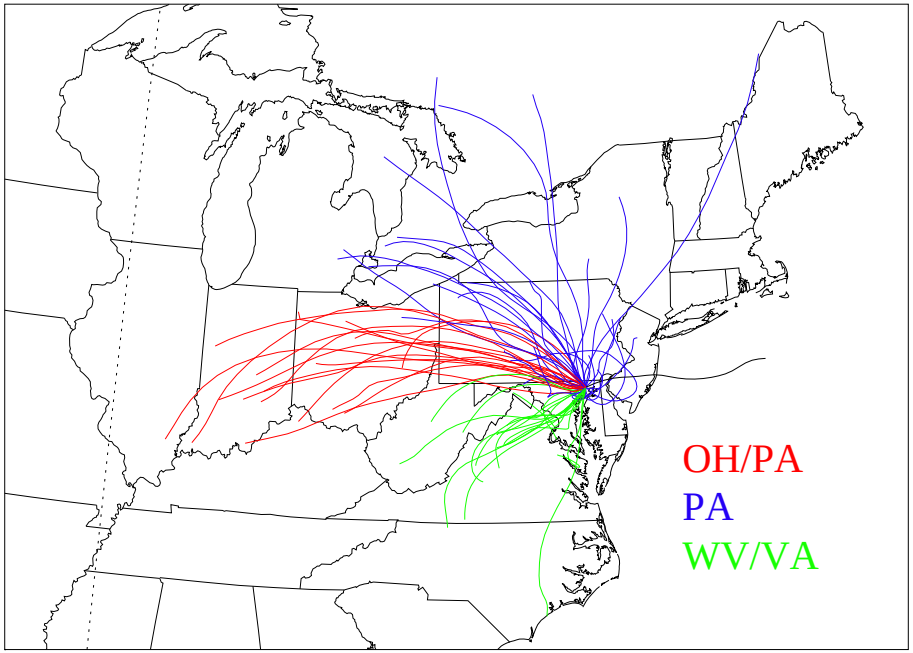

Fig. 12. Results of clustering RAMMPP research flights over Harford County airport (black line shows the background flight on 9 September 2003). Red: OH/PA cluster; Blue: PA cluster; Green: WV/VW cluster.

ACPD
13, 3135–3178, 2013

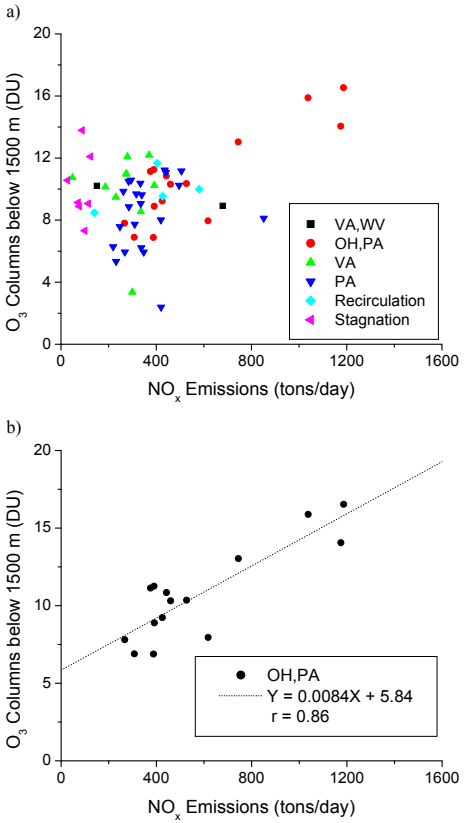

Fig. 13. RAMMPP ozone column contents versus CEMS NO_x emissions (**a**: all clusters; **b**: OH/PA cluster only). Linear regression was conduced O_3 columns contents versus estimated NO_x emissions in OH/PA cluster.

ACPD
13, 3135–3178, 2013