Inter-comparison of ~~the~~ Elemental and Organic Carbon Mass Measurements from Three North American National Long-term Monitoring Networks at a co-located Site

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Keywords

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Abstract

Carbonaceous aerosol is a major contributor to the total aerosol load and being monitored by diverse measurement approaches. Here, ten years (2005-2015) of continuous carbonaceous aerosol measurements collected at the Centre of Atmospheric Research Experiments (CARE) in Egbert, Ontario, Canada on quartz-fiber filters by three independent networks (Interagency Monitoring of PROtected Visual Environments (IMPROVE), Canadian Air and Precipitation Monitoring Network (CAPMoN), and Canadian Aerosol Baseline Measurement (CABM)) were compared. Specifically, the study evaluated how differences in sample collection and analysis affected the ~~yield~~ concentrations of total carbon (TC), organic carbon (OC), and elemental carbon (EC). Results show that different carbonaceous fractions measured by various networks were consistent and comparable in general among the three networks over the ten years period, even with different sampling systems/frequencies, analytical protocols and artifact corrections. The CAPMoN TC, OC, and EC obtained from the DRI-TOR method were lower than those determined from the IMPROVE_A TOR method by 17%, 14% and 18%, respectively. When using transmittance for charring correction, the corresponding carbonaceous fractions obtained from the Sunset-TOT were lower by as much as 30%, 15%, and 75%, respectively. In comparison, the CABM TC, OC, and EC obtained from a thermal method (ECT9) were higher than the corresponding fractions from IMPROVE_A TOR by 20-30%, 0-15% and 60-80%, respectively. ~~When all measurements were normalized with respect to concentration measured in a common reference year, OC measurements agreed to within 29-48% and EC measurement to within 20% amongst the different networks. Fitted with a sigmoid function, elevated~~ Ambient OC and EC concentrations were found to elevate when ambient temperature exceeded 10 °C. These increased ambient concentrations of OC during summer were possibly attributed to the secondary organic aerosol (SOA) formation and forest fire emissions, while elevated EC concentrations were potentially influenced by~~attributed to~~ forest fire emissions and increased vehicle emissions. Results also show that the pyrolyzed organic carbon (POC) obtained from the EnCan-Total-900 (ECT9) protocol could provide additional information on SOA although more research is still needed. ~~The observations from this study suggest that carbonaceous aerosol measurements, especially EC, can be synchronized across networks if sample collection and analytical method in each network remain internally consistent. This study allows the generation of regional to continental-scale-harmonized concentration data sets for benchmarking of atmospheric chemical transport models that determine emission sources and sinks, and assess the effectiveness of government mitigation policies in improving air quality and reducing reliance on fossil fuel consumption.~~

Introduction

Carbonaceous aerosols, including ~~organic carbon (OC) and~~ elemental carbon (EC), ~~;~~ which is often referred to as black carbon (BC)~~),~~ and organic carbon (OC), make up a large fraction of the atmospheric fine particulate matter (PM) mass (Heintzenberg, 1989). Atmospheric OC and ~~EC~~ BC particles that are emitted directly into the atmosphere have both natural (e.g., biomass burning or forest fires) and anthropogenic (e.g., internal combustion engines) sources. A significant amount of the particulate OC is also formed in the atmosphere through oxidation and condensation of volatile organic compounds (e.g., isoprene and terpenes), which are emitted directly from vegetation. BC is a by-product of incomplete combustion of hydrocarbon fuels, generated mainly from fossil fuel combustion and biomass burning. Atmospheric particles have direct and indirect influences on climate, visibility, air quality, ecosystems, and adverse human health effects (Bond et al., 2013; Japar et al 1986; Lesins et al., 2002; Watson, 2002). Atmospheric BC absorbs solar radiation while OC primarily scatters (Schulz et al., 2006). However, BC and OC co-exist in atmospheric particles and the net radiative forcing of the aerosol particles depends on the particle size, composition, and the mixing state of the particles, while all of these variables also change as aerosol particles age (Fuller et al., 1999; Lesins et al., 2002). ~~Long-term atmospheric OC and EC measurements provide necessary benchmark data for understanding inter-annual trends and seasonal variations and for constraining BC sources (Collaud Coen et al. 2013). They are also needed for determining changes of emissions and their impacts on atmospheric processing and developing/verifying the effectiveness of future environmental and health-related policies (Chen et al. 2012).~~

~~Conducting long-term ambient BC mass measurements is challenging in part due to the lack of a universally accepted definition of BC.~~ Black carbon is a generic term in the literature and it is often interchanged with other terms such as EC, soot, refractory BC, light absorbing carbon, or equivalent BC (Petzold et al., 2013). Although BC is highly relevant to climate research, there is no universally agreed and clearly defined terminology concerning the metrics of carbonaceous aerosol. The use of different terminology is linked to the different methodologies used to measure different physical or chemical properties of BC. The scientific community generally accepts the definitions ~~from Bond et al. (2013)~~ that BC particles possess the following properties: (1) strongly absorbing in the visual spectrum with an inverse wavelength (λ) dependence (i.e., λ^{-1}) (Bond and Bergstrom 2006), (2) refractory in nature with a vaporization temperature near 4000 K (Schwarz et al., 2006), (3) insoluble in water and common organic solvents (Fung, 1990), (4) fractal-like aggregates of small carbon spherules ~~form~~ (Kittelson, 1998), (5) containing a large fraction of graphite-like sp^2-bonded carbon atoms (Bond et al., 2013; Petzold et al., 2013), ~~-~~and (~~5~~6) chemically inertness in the atmosphere~~, as graphitic carbon~~ (Bond et al. 2013). ~~BC is a generic term in the literature and is often interchanged with other terms such as EC, soot, refractory BC, light absorbing carbon, or equivalent BC (Petzold et al 2013). The use of different terminology is linked to the different methodologies used to measure different physical or chemical properties of BC.~~ In this article, the recommendation from Petzold et al. (2013) is adopted as the definition of BC whenever the context of climate effects impacted by strong light-absorption carbonaceous substance is mentioned. ~~In this study, the term BC is referred to a substance that absorbs a significant amount of visible light and was created during incomplete combustion, from either internal combustion engines or biomass burning.~~ EC is referred to as the carbon mass determined from the thermal evolution analysis (TEA) or thermal optical analysis (TOA) of carbonaceous materials at the highest temperature set point (e.g., >550 °C) under an oxygenated environment. It is also assumed that ambient EC and BC concentrations time series ~~resemble~~ correlate with each other.

TOA and TEA have been applied in many long-term monitoring networks with various protocols to quantify OC and EC concentrations from aerosol deposits on quartz-fiber filters (Birch and Cary, 1996; Cachier et al., 1989; Cavalli et al., 2010; Chow et al., 1993; Huang et al., 2006; Huntzicker et al., 1982) due to the simplicity in filter sample collection and the analytical procedures. TOA and TEA provide a direct measurement of the carbon mass in ~~as part of~~ the ~~gravimetric~~ collected PM mass. One of the limitations of TOA and TEA is the need for sufficient sampling time to accumulate enough mass for precise measurements (i.e., ensuring a high signal to noise ratio) which constrains the temporal resolution of such samples. In addition, EC and OC are defined differently in different protocols and could affect the absolute mass values measured. Generally, OC is quantified under a pure helium (He) atmosphere at a low heating temperature whereas EC is quantified under an oxygen (O_2)/He atmosphere at high temperatures. Estimates of total carbon (TC=OC+EC) derived from different TOA and TEA methods are generally consistent, whereby the differences in OC and EC estimates could vary from 20 to 90%, and often ~~agree within 10-20%, but~~ larger differences are found for EC, owing to its smaller contribution to TC (Cavalli et al., 2010; Chow et al., 1993; 2001; 2005; Countess 1990; Watson et al., 2005; Hand et al., 2012).

During thermal analysis, some of the OC chars to form pyrolyzed organic carbon (POC) when heated in the inert He atmosphere, darkening the filter (Chow et al., 2004; Watson et al. 2005). When O_2 is added, POC combusts ~~with~~ to EC, resulting in ~~and leads to~~ an overestimation of EC of the filter ~~in~~

~~the PM deposit~~. The formation of POC depends on the nature of the organic materials, the amount of the oxygenated compounds in the collected particles, the rate, duration, and temperature of the heating, and the supply of O_2 in the carrier gas (Cachier et al. 1989; Chan et al., 2010; Han et al. 2007; Yang and Yu, 2002). POC in TOA is estimated by monitoring reflectance and/or transmittance of a 633-650 nm laser beam, ~~with~~ which ~~the resulting EC method~~ is termed thermal optical reflectance (TOR) or thermal optical transmittance (TOT) method, respectively. When the reflected or transmitted laser signal returns to its initial intensity at the start of the analysis (i.e., at OC/EC split point), it is assumed that artifact POC has left the sample and the remaining carbon belongs to EC. The carbon mass before the split point is defined as OC whereas that after the split point is defined as EC. POC is defined as the mass determined between the time when O_2 is introduced and the OC/EC split point. Different from TOA, the TEA used in this study applies a different approach for POC determination (see below).

Quartz-fiber filters adsorb organic vapors (Chow et al., 2009; Turpin et al., 1994; Viana et al., 2006; Watson et al., 2010), resulting in non-PM contributions to OC and charring enhancement within the filter. These vapors are adsorbed passively when the filter is exposed to air and more so as air is drawn through the filter during PM sampling. Sampling at low filter face velocities for long period of time could lead to more adsorption (McDow and Huntzicker, 1990), while using high filter face velocities for longer sample durations may result in evaporation of semi-volatile compounds as negative artifact (Khalek, 2008; Sutter et al., 2010; Yang et al., 2011). The positive OC artifact from adsorption usually exceeds the negative evaporation artifact, especially at low temperatures, resulting in OC overestimation (Watson et al., 2009; WMO, 2016). This can be corrected by subtracting the OC concentration from field blanks or backup filters located downstream of a Teflon-membrane or quartz-fiber filter (Chow et al., 2010; Watson et al., 2005; 2010).

Previous studies further suggested that TOT could over-estimate the POC mass more than TOR, resulting in higher POC (and lower EC) because of the charring of the adsorbed organic vapors within the filter (Chow et al 2004; Countess 1990). Since only a portion (0.5-1.5 cm^2) of the filter is analyzed, inhomogeneous PM deposits add to measurement uncertainty when OC and EC are normalized to the entire filter deposit area. Deposits that are light or too dark can cause unstable laser signals that affect the OC/EC split (Watson et al., 2005).

The short lifetime of atmospheric aerosols (in days to weeks) and the different chemical and microphysical processing that occur in the atmosphere result in high spatial and temporal variations of aerosol properties. To facilitate the determination of the trends in emission changes and evaluation of the effectiveness of emission mitigation policies (Chen et al. 2012), long-term consistent atmospheric measurements are required, including aerosol carbon fractions. The emission sources of OC and EC at a regional and global scales are often constrained through the use of atmospheric transport models in conjunction of long-term OC and EC measurements (Collaud Coen et al., 2013; Huang et al., 2018). Usually an integration of datasets from different networks is necessary for sufficient spatial coverage. The objective of this study is to conduct an inter-comparison study for evaluating the comparability and consistency of ten years co-located carbonaceous aerosol measurements at Egbert made by three North American networks ~~This study evaluated the consistency and comparability of co-located carbonaceous aerosol measurements by three North American networks~~ (Interagency Monitoring of PROtected Visual Environments, Canadian Air and Precipitation Monitoring Network, and Canadian Aerosol Baseline Measurement~~IMPROVE, CAPMoN, CABM~~), ~~over 10 years.~~ all of which ~~These networks~~ use different sampling instruments, frequencies, ~~and~~ durations, analytical methods, and artifact corrections. This~~e~~ inter-comparison study is also expected to provide some suggestions/recommendations for ~~investigation identified potential issues and determined solutions for~~ improving the compatibility and consistency of long-term ~~the different~~ measurements. ~~When combining all measurements from all networks at various sites, it offers the possibility to create a regional- to continental-scale, harmonized carbon concentration dataset, which is important and necessary for constraining model input for understanding the OC and EC sources.~~

Sampling and Measurements

Sampling Site

The sampling station is the Center for Atmospheric Research Experiments (CARE) located near Egbert, Ontario (44°12′ N, 79°48′ W, 251 m a.s.l.), Canada. This station is owned and operated by Environment and Climate Change Canada (ECCC), and is located 70 km NNW of the city of Toronto. There are no major local anthropogenic sources within about 10 km of the site. Air that reaches this site from southern Ontario and the northeastern United States typically carries urban or anthropogenic combustion pollutants that were emitted within last two days (Rupakheti et al. 2005; Chan and Mozurkewich 2007; Chan et al., 2010). Air from the north generally contains biogenic emissions and is often accompanied with the presence of SOA during summer (Chan et al., 2010; Slowik et al., 2010). Table 1 compares the instrument and analytical specifications among the three networks.

The ~~IMPROVE~~ Interagency Monitoring of PROtected Visual Environment Network

The IMPROVE network, established in 1987, includes regional-scale ~~monitors~~ monitoring stations for detecting visibility trends, understanding long-~~range~~ term ~~transport~~trends, and evaluating atmospheric processes (Malm 1989; Malm et al., 1994; Yu et al., 2004). IMPROVE operates about 150 sites and provides long-term records of PM$_{10}$ and PM$_{2.5}$ (particles with aerodynamic diameter less than 10 and 2.5 microns, respectively) mass as well as PM$_{2.5}$ composition, including anions (i.e., chloride, nitrate, and sulfate), and carbon (OC and EC). IMPROVE 24-hour samples at Egbert were acquired once every third day from ~~2006~~ 2005 to 2015. The sampling period was from 08:00 to 08:00 local standard time (LST) except for August 16, 2006 through October 24, 2008 (from 00:00 to 00:00 LST). Module C of the IMPROVE sampler uses a modified air-industrial hygiene laboratory (AIHL) cyclone with a 2.5 µm cut point at a flow rate of 22.8 liters per minute (L/min). PM samples were collected onto a 25 mm diameter quartz-fiber filter (Tissue quartz, Pall Life Sciences, Ann Arbor, MI, USA), which were pre-fired at 900°C for four hours. Once sampled, filters were stored in freezer until they were ready to be analyzed in the DRI laboratory in Reno. All samples were analyzed by the IMPROVE_A thermal/optical reflectance protocol (Figure S1a; Supplementary information) (Chow et al., 2007) as shown in Table S1 (Supplementary information). The IMPROVE ~~measurements~~ data (denoted as IMPROVE_A TOR) were obtained from the website http://vista.cira.colostate.edu/IMPROVE (Malm et al., 1994; IMPROVE, 2017).

The ~~CAPMoN~~ Canadian Air and Precipitation Monitoring Network

CAPMoN was established in 1983 to understand the source impacts of acid rain-related pollutants from long-range transport to the Canadian soil and atmosphere ~~and soil~~. The network operates 30 regionally representatives sites (as of 2015) across Canada with most located in Ontario and Quebec. Measurements include PM, trace gases, mercury (both in air and precipitation), tropospheric ozone, and multiple inorganic ions in air and precipitation. In addition, a few number of sites include carbon (OC and EC) meausrements (https://www.canada.ca/en/environment-climate-change/services/air-pollution/monitoring-networks-data/canadian-air-precipitation.html).

Twenty-four-hour samples (08:00 to 08:00 LST) were acquired every third day from 2005 to 2015 using the Modified Rupprecht and Patashnick (R&P) Model 2300 PM$_{2.5}$ Speciation Sampler with ChemComb cartridges and PM$_{2.5}$ impactor plates with impactor foam to direct particles onto a 47 mm diameter tissue quartz-fiber filter (Thermo Scientific, Waltham, MA, USA) operated at 10 L/min ~~(Thermo Scientific, Waltham, MA, USA)~~. Samples were made on the same date when the IMPROVE samples were collected. A second parallel cartridge is configured with a 47 mm front Teflon-membrane filter and a quartz-fiber backup filter to estimate vapor adsorption artifact. All quartz-fiber filters were pre-fired at either 800°C or 900°C for over two hours and cooled at 105°C overnight and stored in freezer (-15 °C) before being used for sampling. All sampled filters were shipped cold and~~also~~ stored in freezer until they are ready ~~for~~ to be analyzed in the CAPMoN laboratory in Toronto~~analysis~~.

Carbon was determined using the Sunset laboratory-based carbon analyzer (Sunset Laboratory Inc., OR, USA; http://www.sunlab.com/) following the IMPROVE-TOT protocol from 2005 to 2007 (denoted as Sunset-TOT), then by DRI Model 2001 Thermal/Optical Carbon Analyzer following the IMPROVE-TOR protocol (denoted as DRI-TOR) from 2008 to 2015 (Chow et al., 1993). As shown in Table S1, the temperature settings for IMPROVE protocol (i.e., DRI-TOR) ~~protocol~~ for CAPMoN samples are lower than those of IMPROVE_A TOR protocol for IMPROVE samples by 20°C to 40°C (Figure S1b). Overall, Chow et al. (2007) found that ~~This~~ the small difference in the temperature-ramp between these protocols results in correlated but different OC, EC, and TC mass~~ (Chow et al., 2007)~~.

The ~~ECCC~~ Canadian Aerosol Baseline Measurement Network

The Climate Chemistry Measurements and Research (CCMR) Section in the Climate Research Division of ECCC has operated the Canadian Aerosol Baseline Measurement (CABM) network since 2005 to acquire data relevant to climate change (https://www.canada.ca/en/environment-climate-change/services/climate-change/science-research-data/greenhouse-gases-aerosols-monitoring/canadian-aerosol-baseline-measurement-program.html). The CABM network includes 6 sites (as of 2016) for aerosol chemical, physical, and optical measurements that cover ecosystems at coastal, interior urban/rural areas, boreal forests, and the Arctic. Measurements are intended to elucidate influences from various emission sources on regional background air, including biogenic emissions, biomass burning as well as anthropogenic contributions from industrial/urban areas.

The CABM filter pack system uses a $PM_{2.5}$ stainless steel cyclone (URG-2000-30EHS) operated at 16.7 L/min for sampling from 2006 to 2015 with an operator manually changing the 47 mm quartz-fiber filter on a weekly basis. All quartz-fiber filters were pre-fired at 900°C overnight prior being sampled. Once sampled, filters were shipped cold and then stored in freezer until they were ready to be analyzed in the CCMR laboratory in Toronto. A TEA method, EnCan-Total-900 (ECT9), developed by Huang et al. (2006) and refined later (Chan et al., 2010), was used to analyze the OC, POC, and EC on the quartz-fiber filters using a Sunset laboratory-based carbon analyzer. The ECT9 protocol was developed to permit stable carbon isotope (^{13}C) analysis of the OC and EC masses without causing isotope fractionation, as it was demonstrated by Huang et al. (2006). This method first heats the filter at 550°C and 870°C for 600 s each in the He atmosphere to determine OC and POC (including carbonate carbon; CC), respectively, and then combusts the sample at 900°C under 2% O_2 and 98% He atmosphere for 420 s to determine EC (Figure S1c and Table S1). The ECT9 POC definition (released as CO_2 at 870 °C) includes the charred OC, and some calcium carbonate ($CaCO_3$) that decomposes at 830°C, as well as any refractory OC that is not combusted at 550°C. Chan et al. (2010) found that POC determined by ECT9 was proportional to the oxygenated compounds (e.g., aged aerosol from atmospheric photochemical reaction) and possibly humic-like materials. Consistent with the IMPROVE_A TOR protocol (Chow et al., 2007), OC is defined as the sum of OC and POC, as CC is usually negligible in $PM_{2.5}$.

CABM sites are also equipped with Particle Soot Absorption Photometer (PSAP; Radiance Research, Seattle, WA, USA) that continuously monitor aerosol light absorption at 1 minute time resolution, as changes in the amount of light transmitted through a quartz-fiber filter. Assuming the mass absorption coefficient (MAC) for aerosol is constant at Egbert, the one minute PSAP absorption measurements ~~is~~ are linearly proportional to the BC or EC concentrations. In this study, five years of PSAP data (2010-2015) collected at Egbert was used to assess the impact of different sampling duration on the derived monthly averages EC values.

Differences in Sampling and Analysis among Networks

Depending on the sharpness (i.e., slope) of the inlet sampling effectiveness curve (Watson et al., 1983), different size-selective inlets may introduce measurement uncertainties. CAPMoN uses ~~an~~ impactors whereas CABM and IMPROVE use cyclones. Impactor may have larger pressure drops across the inlet that might enhance semi-volatile PM evaporation. Larger solid particles might bounce off when in contact with the impactor and be re-entrained in the $PM_{2.5}$ samples if the impactor is overloaded (Flagan and Seinfeld, 1998; Hinds, 1999). Atmospheric mass size distributions typically peak at about 10 µm with a minimum near 2.5 µm, therefore, the difference in mass collected with different impactors or cyclones among the three networks is not expected to be large (Watson and Chow, 2011). Analyzing OC and EC content by TEA or TOA also subject to a number of artifacts, including adsorption of volatile organic compound (VOC) gases by quartz-fiber filter, leading to positive artifact, and evaporation of particles, leading to negative artifact (Malm et al., 2011).

The small filter disc (25 mm diameter) and high flow rate (22.8 L/min) in the IMPROVE sampler result in a 5- to 7-fold higher filter face velocity (i.e., 107.7 cm/s) ~~versus 16-20 cm/s)~~ than that for the

CAPMoN and CABM samplers (16-20 cm/s). McDow and Huntzicker (1990) assert that higher filter face velocity may reduce sampling artifacts. However, very high face velocity (>100 cm/s) may enhance OC volatilization (Khalek 2008).

Both IMPROVE and CAPMoN ~~and IMPROVE~~ networks correct for vapor adsorption, while CABM network does not. For CAPMoN measurements, ~~subtracts~~ the organic artifact derived from ~~the~~ each 24-hour backup quartz-filter ~~parallel channel~~ was subtracted from the corresponding OC measurement.~~,~~ ~~whereas~~ For IMPROVE measurements (up until 2015), ~~used~~ monthly median OC value~~s~~ obtained from the backup quartz-filters from 13 sites (not including Egbert) was subtracted from all samples collected in the corresponding month. Monthly averaged OC values were then derived from the 24-hour artifact corrected measurements.

Multiple studies show that using the same TOA protocol on both DRI and Sunset carbon analyzers can produce comparable TC concentrations (Chow et al., 2005; Watson et al., 2005). However, large differences in EC are found between the reflectance and transmittance POC correction (Chow et al., 2004; 2005; Watson et al., 2005). Difference in OC and EC definitions among different TOA and TEA protocols introduces measurement uncertainties. Among the TOA methods, how POC is determined from the laser signals at different temperatures in the inert He atmosphere introduce uncertainties. Large uncertainties in laser transmittance were found for lightly- and heavily-loaded samples (Birch and Cary, 1996). For the CABM samples, the POC determined at 870 °C by ECT9 represents different OC properties and does not equal the charred OC obtained by Sunset-TOT, DRI-TOR, or IMPROVE_A TOR.

Both IMPROVE and CAPMoN data sets are once every third day 24-hour measurements collected on the same date while the CABM data is weekly integrated samples. A comparison between the integrated weekly samples and 24-hour samples have already been done by Yang et al. (2011) and therefore will not be repeated here. Based on two years of Egbert measurements (2005-2007), Yang et al. (2011) suggested that integrated weekly samples might experience reduced vapor adsorption but increased losses of semi-volatile organics leading to lower OC measurements. Weekly EC values were higher than those from 24-hour samples, which were attributed to the higher analytical uncertainties for the lower loadings on the 24-hr samples (Yang et al., 2011).

Five years (2010-2015) of real-time (1 min average) PSAP particle light absorption measurements (at 567 nm) was used here as a proxy common EC data set to assess the effect of different sample duration on monthly average EC concentrations. First, the 1 min PSAP data was averaged to 24-hour once in every three day samples and integrated weekly samples, respectively, and the comparison of the two data sets are compared in Figure 1a. The results demonstrate that both data sets capture the variations adequately. Monthly averages derived from the two sets of measurements show highly correlated results (r=0.78; Figure 1b) and a slope of 0.96 (Figure 1c). Assuming the variations in light absorption can represent the variations in EC, these results suggest that monthly averaged EC based on integrated weekly sampling is about 4% lower than the monthly averaged EC based on 24 hour sampling.

Results and Discussions

NIST urban dust standard comparison ~~(SRM 8785 & 1649a)~~

~~The consistency of the OCEC measurements obtained between the ECT9 and the IMPROVE_A method was assessed by measuring four replicates of the~~ The National Institute of Standards and Technology (NIST) Urban Dust Standard Reference Material (SRM) 8785 Air Particulate Matter on Filter Media is intended primarily for use to evaluate analytical methods used to characterize the carbon composition of atmospheric fine PM (Cavanagh and Watters, 2005; Klouda et al., 2005). These samples were produced by resuspension of the original SRM 1649a urban dust sample, followed by collection of the fine fraction ($PM_{2.5}$) on quartz-fiber filters (Klouda et al., 2005; May and Trahey, 2001). Past studies on SRM 1649a and SRM 8785 have shown consistent composition and both samples were supplied with certified values for OC and EC (Currie et al., 2002; Klouda et al., 2005). The consistency between the ECT9 and the IMPROVE_A TOR analytical methods was assessed by analyzing NIST SRM 8785 filters. ~~The~~ Four SRM 8785 filters with mass loading of 624-2262 μg were analyzed following the ECT9 method by the ECCC laboratory and the IMPROVE_A TOR protocol by the DRI laboratory during 2009-2010.

~~Figure 1 shows reasonable correlations with 21-25% higher TC and EC by the ECT9 method.~~ The values in the SRM 8785 certificate were reported in grams of OC or EC per grams of PM mass, which are average mass ratios based on analysis of a small numbers of randomly selected samples. Figure 2a-c shows that measurements by IMPROVE_A TOR protocol ~~by DRI~~ were within uncertainties of ~~compared well with~~ the certificate values. Ratios measured with ECT9 were greater, but not significantly different from the certificate values. When fitting the ECT9 measurements to the IMPROVE_A TOR measurements using a linear regression (Figure 3a-c), good correlations (r=0.9-0.99) were observed with 21-25% higher in values by the ECT9 method than the IMPROVE_A TOR.

The parameter EC/TC, calculated based on the reported certificate values, were compared with the average EC/TC values determined from the inter-comparison study (ICP) by the DRI group (using IMPROVE_A TOR) and the ECCC group (using ECT9) (Figure~~.~~ 2d). These results show that EC/TC reported by both ~~DRI and CCMR~~analytical methods were statistically the same as the certificate value.

Finally, the EC/TC value was further verified by analyzing ~~multiple~~ SRM 1649a samples with the ECT9 method. The combusted CO_2 from OC, EC, and TC were analyzed for the isotope ratios (i.e., $^{14}C/^{12}C$) expressed as a fraction of modern carbon (i.e., FM_i is the ratio of $^{14}C/^{12}C$ in the sample i, relative to a modern carbon standard) for individual mass fractions (i.e., FM_{TC}, FM_{OC}, and FM_{EC}). Using isotopic mass balance, the EC/TC ratio can be derived from Eq. [1]:

$$FM_{TC} = FM_{OC} \times \left(1 - \frac{EC}{TC}\right) + FM_{EC} \times \frac{EC}{TC} \qquad [1]$$

The $^{14}C/^{12}C$ ~~abundances~~ ratio were determined by off-line combustion method at the Keck Carbon Cycle accelerator mass spectrometry (KCCAMS) Facility at University of California Irvine. A FM_{TC} value of 0.512 was obtained, which is close to certificate values that range from 0.505 to 0.61 (Currie et al., 2002). Average measured values of FM_{OC} and FM_{EC} for the SRM 1649a via ECT9 were 0.634 (n=3) and 0.349 (n=3), respectively. This yields an EC/TC ratio of 0.425, which is comparable to the ECT9 value of 0.44, and close to the reported certificate value of 0.49 and the IMPROVE_A TOR value of 0.47 (Figure ~~2d~~3d), reconfirming a good separation of OC from EC using the ECT9 method. This analysis also confirms the consistency between the IMPROVE_A TOR and ECT9 methods.

Vapor Adsorption Corrections

Figure 4 shows the monthly averaged carbon concentration time series with and without the artifact correction for CAPMoN samples over the period from 2005 to 2015. Vapor adsorption contributes to a large amount of the measured OC (Figure 4a), but a negligibly amount to EC (Figure 4b) and POC after 2008 (Figure 4c). The median vapor adsorption artifact was 0.79 µg/m^3 from 2008 to 2015 for DRI-TOR, representing about 50.9% of the uncorrected OC, compared to 0.92 µg/m^3 (43.3% of uncorrected OC) using the Sunset-TOT before 2008 (Supplemental Figure S2). Linear ~~L~~least square regressions between corrected and uncorrected carbon in Figure 5 shows a slope of 0.52 for OC and 0.56 for TC with good correlations (r=0.93-0.94). Sunset-TOT measurements acquired prior 2008 are mostly scattered around the regression line, with higher concentrations. On average, about 48% of the uncorrected OC (0.84 μg/m^3) can be attributed to vapor adsorption. The low filter face velocity (15.5 cm/s) in CAPMoN samples could be one of the contributing factors.

Figure 5c indicates that artifact corrected EC concentrations are 7.8% (0.02 μg/m^3) lower than the uncorrected values~~after artifact correction~~. The~~se~~ artifact magnitude ~~levels are~~is close to the detection limit of 0.022 μg/m^3 (0.197 μg/cm^2) and within analytical uncertainties (Chow et al., 1993). Some Sunset-TOT EC measurements are scattered from the regression line, indicating a more accurate and consistent adsorption correction for DRI-TOR (Figure 5b). Although not expected to impact EC concentration, vapor adsorption directly affects POC correction and thus influences EC mass determination.

Figure 5d shows that 4.3% (0.01 μg/m^3) of POC was caused by vapor adsorption using the DRI-TOR protocol. For Sunset-TOT~~ (red open circles)~~, however, up to 21.1% (0.17 μg~~C~~/m^3) of the POC was detected on the backup filter. Note that POC is part of OC and is a charring correction in the DRI-TOR and Sunset-TOT protocols. Results show that ~~Filter ~~filter transmittance is influenced by both surface and within filter charring and EC from different sources have been observed to have different filter penetration depths (Chen et al., 2004; Chow et al., 2004~~), ~~). ~~an ~~Based on the available information from this study, an optical correction by reflectance appears to be more appropriate and give more consistent results when ~~POC/EC ratio ~~POC concentration is relatively large compared to EC ~~in measurements are high~~(Chen et al., 2004). Regardless, the absolute POC and EC concentrations were much lower than OC and the adsorption correction on TC is mostly attributed to the OC artifact.

Since the ~~CAPMoN ~~IMPROVE aerosol samples~~deposits~~ were acquired at a higher~~low~~ filter face velocity (107.7~~15.5~~ cm/s), it is expected that the magnitude of the vapor adsorption correction would be smaller for the IMPROVE samples~~ due to the use of higher filter face velocity~~. This is supported by the observations from Watson et al. (2009) at six anchor IMPROVE sites (i.e., Mount Rainier National Park, Yosemite National Park, Hance Camp at Grand Canyon National Park, Chiricahua National Monument, Shenandoah National Park, and Okefenokee National Wildlife Refuge), suggesting that vapor adsorption obtained from backup quartz filters represented about 23% of the uncorrected OC values.~~, whereas those obtained from field blanks were averaged to be about 18%. In comparison with the IMPROVE measurements at Egbert, the vapor adsorption obtained from field blank represent about 16% (or 0.18 μg/m^3) of the uncorrected OC measurements.~~ Filter fibers are saturated over a long sampling interval (Khalek, 2008; Watson et al., 2009), thus, artifacts for the CABM samples are expected to be lower relatively.

Comparison among IMPROVE, CAPMoN, and CABM ~~vs. IMPROVE~~ Measurements

Figure 6 shows the ~~Temporal~~ temporal variations of the monthly averaged IMPROVE_A TOR, CAPMoN Sunset-TOT, DRI-TOR, ~~CAPMoN~~ and CABM ECT9 measurements. ~~are comparable to the IMPROVE_A TOR protocol (Figure 6), showing a similar temporal pattern with elevated peaks found in mid-summer (July).~~ Also included in the figure are the monthly averaged temperature and the wind direction and speed (expressed in wind barbs). It is evident that better correlations of TC, EC and OC were found between the protocols that use same POC correction method (DRI-TOR and IMPROVE_A TOR) than between Sunset-TOT (which uses transmittance for POC correction) and IMPROVE_A TOR (Table 2). Especially correlation of EC between Sunset-TOT and IMPROVE_A TOR was poor. ~~High correlations are found for DRI-TOR OC and TC with IMPROVE_A measurements (r=0.90-0.91; Table 2) while lower correlations (r=0.78-0.79) are seen for Sunset-TOT data. Good correlations are observed between the DRI-TOR and IMPROVE_A TOR POC measurements (r=0.85) but much lower correlations are observed for Sunset-TOT and IMPROVE_A POC measurements (r=0.70). Correlations between DRI-TOR EC and IMPROVE_A TOR EC are high (r=0.81) but it is not the case between Sunset-TOT EC and IMPROVE_A TOR EC (r=0.33).~~

Comparisons of the monthly averaged carbonaceous measurements among different networks are summarized in Figure 7. When fitting the monthly averaged DRI-TOR and Sunset-TOT measurements to IMPROVE_A TOR measurements using a linear regression fit through the origin (i.e., Regression 1) typically yields less than unity slopes (0.64-0.97; Table 2), suggesting that the carbonaceous masses reported by CAPMoN were in general lower than those by IMPROVE. Fitting the measurements allowing an intercept (i.e., Regression 2) typically yields least square slopes close to unity (>0.92) with small intercepts.

The effect of using transmittance or reflectance for POC determination is apparent. The Sunset-TOT POC correction is larger because transmittance is affected by the charred OC within the filter. This is consistent with the larger regression slopes in POC (Regression 1: 1.8) between Sunset-TOT and IMPROVE_A TOR protocol than the slope in POC (1.0) between the DRI-TOR and IMPROVE_A TOR protocol.

~~CABM vs. IMPROVE Measurements~~

~~Figure 6 shows the temporal variations of the ECT9 CABM measurements with other networks. The temporal variations of the CABM measurements were consistent with the temporal trends of~~

~~measurements from the other two networks. While ECT9 OC concentrations are comparable (±~15%) with the IMPROVE_A TOR measurements, higher TC and EC concentrations are found in CABM samples.~~

The ECT9 versus IMPROVE_A TOR via Regression 1 slopes are equal to or greater than unity, ranging from 1.0 ~~2~~ to 1.8 (Table 2). Linear regression with intercept (i.e., Regression 2) yields lower slopes (0.6-1.7) with positive intercepts (0.06-0.18 $\mu g/m^3$), signifying higher TC and EC concentrations for ECT9 samples. Higher intercepts (0.12-0.18 $\mu g/m^3$) for TC, OC, and POC are consistent with ECT9 measurements uncorrected for vapor adsorption. However, the systematically higher TC, OC and EC by 21-25% via ECT9 relative to those via IMPROVE_A TOR in SRM 8785 could not be simply attributed to the uncorrected vapor adsorption.

In specific, ECT9 OC concentrations are 15% higher than the IMPROVE_A TOR measurements (Table 2) with good correlation (r=0.87; Table S2). ~~T~~the ECT9 method yielded 66-83% higher EC than IMPROVE_A TOR, with moderate correlation (r=0.74). Differences in combustion temperatures~~,~~ for OC/EC split determination~~, inhomogeneous deposition of mass loading on filter spots~~ could contribute to these discrepancies. Heating under an oxidative environment at a constant temperature of 900 °C in the ECT9 protocol could combust more highly refractory carbon than the IMPROVE_A TOR protocol, which only heats progressively from 580 °C to 840 °C. Another minor factor could include inhomogeneous deposition of mass loading on the filter spot. When plotted on different scales, Figure S3 shows that the two EC data sets track well, capturing both long-term trends and ~~short-term~~seasonal variations.

A slope approaching unity (1.00) was obtained when fitting the ECT9 POC to IMPROVE_A TOR POC through the origin (Figure 7d). Refitting the data allowing an intercept leads to a slope of 0.62 with a y-intercept (0.12; Table 2), comparable in magnitude to the vapor adsorption artifact. The correlation coefficient between ECT9 POC and IMPOVE_A TOR POC is low (r=0.46; Table S3). However, ~~there is a significant~~ correlation ~~found~~ between ~~the~~ IMPROVE_A TOR POC and IMPROVE_A TOR OC is much higher (r=0.91), and even to a lesser extent between IMPROVE_A TOR POC and IMPROVE_A TOR EC (r=0.71). In comparison, ECT9 POC has weak correlation with ECT9 OC (r=0.65) and ECT9 EC (r=0.37). These observations show that the POC definition in ECT9 is not dominated by charred OC correction and likely include the characterization of other oxygenated organic materials as observed in Chan et al. (2010). Additional research is needed to verify if ECT9 POC is proportional to SOA formation.

Seasonality in Carbon Concentration and Possible Origination

Figure 6 shows elevated carbon during summer, consistent with the observations from Yang et al. (2011) and Healy et al. (2017). A sigmoid function was applied here to characterize the relationship between ambient carbon concentration and ambient temperature. The Sigmoid function has a characteristic “S” shape and represents an integral of a Gaussian function. ~~Figure 9 shows elevated carbon during summer, consistent with the observations from Yang et al. (2011) and Healy et al. (2017).~~ Relationships between carbon concentrations and ambient temperatures are ~~shown~~ illustrated in Figure S5. Apparent increases in OC and TC concentrations are found when ambient temperatures exceed about 10 °C; a phenomenon not as apparent in EC. EC from the week-long CABM samples are more scattered.

The TC, OC, and EC from all measurements are averaged and shown in Figure ~~10~~ 8 with the following best-fitted sigmoid functions:

$$TC = 1.053 + \left\{\frac{3.558}{1+exp\left(\frac{23.081-T}{3.760}\right)}\right\}$$

[~~3~~2]

$$OC = 0.780 + \left\{\frac{1.838}{1+exp\left(\frac{20.089-T}{2.978}\right)}\right\}$$

[3~~4~~]

$$EC = 0.239 + \left\{\frac{1.446}{1+exp\left(\frac{34.776-T}{8.404}\right)}\right\}$$

[4~~5~~]

Equations [~~3~~2]-[~~5~~4] show that lower limits of the observed TC, OC, and EC concentrations are 1.05, 0.78, and 0.24 µgC/m^3, with the half way of the maximum growth curve occurring at about 23 °C, 20 °C, and 35 °C, respectively. The predicted maximum concentrations for TC, OC, and EC are 4.61, 2.62, and 1.69 µgC/m^3, respectively.

~~To determine the air mass origins, a Lagrangian particle dispersion transport model (FLEXible PARTicle dispersion model; FLEXPART) (Stohl et al., 2005) was applied to obtain daily five-day back-trajectories from Egbert from 2006 to 2015. Figure S6 summarizes the average FLEXPART footprints for summer (May-Oct) and winter (Nov-Apr) seasons, showing the probability of air masses originating from various regions. These results indicate regional contributions from boreal forest in the northern part of Ontario and Quebec, as well as anthropogenic emissions from the northern U.S. Five-day trajectories show larger concentrations from the N and NW, consistent with wind roses shown in Figure S4.~~

Preliminary analysis based on simple wind roses and Lagrangian particle dispersion transport model (FLEXible PARTicle dispersion model) (Stohl et al., 2005) was conducted (Supporting Materials). Results from the analysis appear to suggest that human activities ~~At low ambient temperatures, primary emissions~~ (e.g., local transportation, ~~residual~~ residential heating, and industrial activities), ~~account for most of the ambient OC and EC (Ding et al., 2014). Increased human activities (e.g., traveling by car and barbecuing) during warmer weather could lead to increased emissions. High ambient temperature also leads to increased~~ biogenic emissions (e.g., monoterpenes) from the boreal forest, ~~and increased~~ SOA formation, biomass burning, and transboundary transport could contribute to the variations of OC and EC at Egbert in a complicated way (Ding et al., 2014; Chan et al., 2010; Leaitch et al., 2011; Passonen et al., 2013; Tunved et al., 2006; ~~). The central and eastern boreal forest fire season typically occurs from May to August when ambient air is dry and hot, resulting in generally increased OC and EC emissions (~~Lavoué et al 2000; ~~). Transboundary transport of biomass burning emissions from the U.S. could also contribute to the higher concentrations in southern Ontario (~~Healy et al. 2017), which requires additional research to confirm. At Egbert, ~~Increasing~~ increasing ambient temperature from 10 °C to 20 °C leads to higher OC concentrations from 0.84 to 1.61 µgC/m^3 (91.7% increase) and EC concentration from 0.31 to 0.45 µgC/m^3 (45.2% increase). The temperature dependency of OC and EC suggests a potential climate feedback mechanism consistent with the observations from Leaitch at al. (2011) and Passonen et al. (2013).

Chan et al. (2010) showed that ECT9 POC possesses a positive relationship with oxygenated organics and aged aerosol particles. The seasonality in ECT9 POC is compared with the average OC and EC seasonality observed at Egbert (Figure ~~10d~~8d). Interestingly, the ECT9 POC concentration does not show a gradual exponential shape of function as for OC and EC ~~(Figures 10b and 10c)~~. Instead, it shows a small but obvious two-step function when plotted against ambient temperature. The ECT9 POC temperature dependent results (Figure ~~10~~8d) suggest constant sources of background emissions of possible oxygenated organic compounds that is independent from the measured OC, with additional secondary organic compound (SOA) formation at higher temperatures (e.g., >15 °C). Future study is needed to verify this.

~~Conclusions~~ Summary of the Inter-comparison Study

Ten years of OC and EC measurements at Egbert were obtained from three independent networks (IMPROVE, CAPMoN, CABM) and observable~~.~~ ~~Differences~~ differences in carbon concentrations were attributed to different sampling methods, analytical protocols, sampling time, and filter artifact corrections. Vapor adsorption did not affect EC values but contributed ~~about~~ 20-50%~~48% (or 0.84 μg/m^3)~~ of the measured OC, depending on the sampling filter face velocity. ~~for the CAPMoN network with the lowest filter face velocity of 15.5 cm/s. When sampling at a filter face velocity of 108 cm/s, the IMPROVE field blanks account for about 16% (or 0.18 μg/m^3) of the measured OC.~~ The higher TC and OC concentration of the CABM measurements by 20-30% and 15%, respectively, compared to the IMPROVE measurements could be partially due to the absence of vapor adsorption correction. These results are consistent with other inter-comparison study before data adjustments (Hand et al., 2012). The differences in analytical protocol also play a role in causing higher carbon values, supported by the higher TC, OC and EC values from the SRM8785 analysis obtained by the ECT9 method compared to those by IMPROVE_A TOR~~TC measurements differences were influenced by the uncorrected vapor adsorption artifact as a result of the OC artifact as in the CABM measurements.~~ method. Pyrolyzed OC (POC) from ECT9 is shown to be more than a ~~both DRI-TOR (i.e., IMPROVE) and IMPROVE_A TOR protocols~~ charring correction and more research is needed to develop its relationship with SOA.

Important observations from the inter-comparison study are: (1) CAPMoN DRI-TOR TC, OC, and EC are 5-17%, 7-16%, and 7-18% lower than the corresponding masses from IMPROVE_A TOR. (2) CAPMoN Sunset-TOT TC, OC, and EC are lower than the IMPROVE_A TOR values by up to 30%, 15%, and 75%. (3) CABM TC, OC and EC by ECT9 are higher than the IMPROVE_A TOR values by 20-30%, 0-15%, and 60-80%, respectively. ~~correlated with OC (r=0.91-0.92), indicative of the charring property of the measured OC. ECT9 POC was only weakly correlated with OC (r=0.65) and had weak correlations with POC from DRI-TOR and IMPROVE_A TOR (r=0.44 and 0.46), suggesting ECT9 POC includes compounds with different properties under high temperature gasification (870 °C).~~

Carbon concentrations observed from all three networks exhibited a non-linear positive dependency with ambient temperature, which~~and this relationship is~~ can be characterized by a sigmoid function. Although further research is needed, ~~Preliminary~~ preliminary observations suggested that increased anthropogenic activities, urban emissions, SOA formation, forest fire emissions, and long range transport could have an impact on the observed OC and EC at Egbert. ~~the increases in OC and TC concentrations when ambient temperatures rose beyond 10 °C during summer, is likely corresponding to the sum of SOA formation, influences of forest fires, and increased anthropogenic activities. The moderate increase in EC concentration with increasing ambient temperature is believed to be a result of increased primary emissions from anthropogenic activities.~~ The increase in OC concentration with temperature is consistent with the climate feedback mechanisms reported from various studies. The different characteristic temperature dependency of the ECT9 POC suggests the need for future investigation, which could provide additional insights of SOA formation from acquired carbonaceous measurements.

Suggestions Going Forward

Long-term measurements play important roles for detecting the trends in atmospheric compositions, constraining their emission changes, and allow for assessing the effectiveness of emission mitigation policies at regional scales (WMO, 2016; 2003), provided that the measurements are consistent and comparable across different networks. Recognizing the absence of a universally accepted carbonaceous standard, long-term inter-comparison studies become challenging and even more important. Echo the recommendations from the World Meteorological Organization (WMO) guidelines and recommendations for long-term aerosol measurements (WMO, 2016; 2003), this study illustrates the importance of measurement consistency (e.g., sampling method/procedures, analytical instrument/method/protocols and data processing, quality assurance and quality control protocols) within a network over a long period of time. As indicated in the guidelines, regular inter-comparison of filter samples should be encouraged. These activities include analyzing exchanged common filter samples and co-located filter samples. In addition, there is a need to develop proper reference materials for assessing comparability and consistency, and incorporating the use of such reference as part of the inter-comparison effort.

Nomenclature

AIHL	Air-industrial hygiene laboratory
AMS	Accelerator mass spectrometry
BC	Black carbon
CABM	Canadian Aerosol Baseline Measurement
CAPMoN	Canadian Air and Precipitation Monitoring Network
CARE	Center for Atmospheric Research Experiment
CCMR	Climate Chemistry Measurements and Research
DRI	Desert Research Institute
DRI-TOR	CAPMoN measurements using IMPROVE on DRI analyzer with TOR correction
EC	Elemental carbon
ECCC	Environment and Climate Change Canada
ECT9	EnCan-Total-900 protocol
FID	Flame ionization detector
FLEXPART	FLEXible PARTicle dispersion model
ICP	Inter-comparison study
IMPROVE	Interagency Monitoring PROtected Visual Environments
IMPROVE_A TOR	IMPROVE_A TOR protocol on DRI analyzer

KCCAMS	Keck Carbon Cycle accelerator mass spectrometry
MAC	Mass absorption coefficient
NIST	National Institute of Standard and Technology
OC	Organic carbon
PM	Particulate matter
POC	Pyrolyzed organic carbon
PSAP	Particle Soot Absorption Photometer
SOA	Secondary organic aerosol
SRM	Standard Reference Material
Sunset-TOT	IMPROVE TOT protocol on Sunset analyzer
TC	Total carbon
TEA	Thermal evolution analysis
TOA	Thermal optical analysis
TOR	Thermal optical reflectance
TOT	Thermal optical transmittance
UCI	University of California Irvine
WMO	World Meteorological Organization

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Supplementary Information:

The supplement related to this article, which includes ~~Additional~~ additional details on thermal/optical analysis, the experimental parameters used in different temperature protocols (IMPROVE, IMPROVE_A, ECT9), radiocarbon analysis, vapor adsorption uncertainty, seasonality of carbonaceous measurements, wind rose analysis, and FLEXPART back trajectory analysis at Egbert are ~~included~~ available online~~in the Supplementary Information~~.

Author Contributions:

TWC and LH wrote the paper, with KB, JW, JCC, CIC, GMS, KJ provide contributions to the article. All authors commented on the manuscript.

Competing interest:

The authors declare that they have no conflict of interest.

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Table 1 Specifications for the filter sampling systems and analytical instruments/methods used by the three networks.

	IMPROVE	CAPMoN		CABM
Data coverage period	2005-2015	2005-2007	2008-2015	2005-2015
Analytical instrument	DRI	Sunset	DRI	Sunset
Thermal/optical protocol	IMPROVE_A	IMPROVE	IMPROVE	ECT9
Pyrolyzed organic carbon detection	Reflect.	Transmit.	Reflect. & Transmit.	Retention time
Particle size selection method	Cyclone	Impactor plates	Impactor plates	Cyclone
Particle size cut off diameter (nm)	2.5	2.5	2.5	2.5
Sampling flow rate (L/min)	22.8	10.0	10.0	16.7
Filter media model	2500QAT-UP	2500QAT-UP	2500QAT-UP	2500QAT-UP
Quartz filter diameter (mm)	25	47	47	47
Filter deposition exposure area (cm^2)	3.53	10.75	10.75	13.85
Filter face velocity (cm/s)	107.65	15.50	15.50	20.09
Sampling frequency	Daily every 3 days	Daily every 3 days	Daily every 3 days	Integrated weekly
Daily sampled air volume (L/day)	31680	14400	14400	24048
Air volume per sample (m^3)	31.68	14.4	14.4	168.3
Positive artifact correction	Yes	Yes	Yes	No
Filter blank correction	Yes	No	No	Yes
Number of 24-h sample	1228	254	907	-
Number of weekly sample	-	-	-	476
Number of monthly averaged sample	124	28	93	117

Table 2 Regression results (slope, correlation coefficient, and total number of points) obtained when fitting various CABM (ECT9) and CAPMoN (Sunset-TOT & DRI-TOR) carbonaceous mass concentration time series against IMPROVE (IMPROVE_A TOR) measurements. IMPROVE_A TOR and ECT9 measurements cover the period from 2005 to 2015. Sunset-TOT and DRI-TOR measurements cover the periods for 2005-2008 and 2008-2015, respectively. Regression 1 indicates the best-fitted slope through the origin. Regression 2 is the best-fitted slope with intercept (in brackets).

	Regression 1	**Regression 2**	**R**	**N**
Sunset-TOT TC vs IMPROVE_A TOR TC	0.888±0.033	0.713±0.112 (0.301±0.186)	0.78	28
Sunset-TOT OC vs IMPROVE_A TOR OC	0.967±0.041	0.873±0.135 (0.125±0.170)	0.79	28
Sunset-TOT EC vs IMPROVE_A TOR EC	0.639±0.042	0.233±0.130 (0.171±0.053)	0.33	28
Sunset-TOT POC vs IMPROVE_A TOR POC	1.769±0.091	1.776±0.351 (-0.003±0.127)	0.70	28
DRI-TOR TC vs IMPROVE_A TOR TC	0.832±0.015	0.946±0.044 (-0.164±0.059)	0.91	93
DRI-TOR OC vs IMPROVE_A TOR OC	0.835±0.017	0.934±0.046 (-0.116±0.050)	0.90	93
DRI-TOR EC vs IMPROVE_A TOR EC	0.818±0.019	0.929±0.072 (-0.032±0.020)	0.81	93
DRI-TOR POC vs IMPROVE_A TOR POC	0.986±0.028	1.230±0.080 (-0.073±0.023)	0.85	93
ECT9 TC vs IMPROVE_A TOR TC	1.304±0.022	1.197±0.065 (0.164±0.093)	0.88	107
ECT9 OC vs IMPROVE_A TOR OC	1.149±0.021	1.004±0.056 (0.179±0.064)	0.87	107
ECT9 EC vs IMPROVE_A TOR EC	1.834±0.046	1.661±0.149 (0.056±0.046)	0.74	107
ECT9 POC vs IMPROVE_A TOR POC	0.998±0.031	0.615±0.082 (0.124±0.025)	0.59	107

Figure 1~~3~~ (a) Real-time Particle Soot Absorption Photometer (PSAP) measurements averaged to match the corresponding sampling frequencies used in different networks. (b) Monthly PSAP measurements derived from (a). (c) Comparison of the different sets of measurements from (b) with the 1:1 line shown in red.

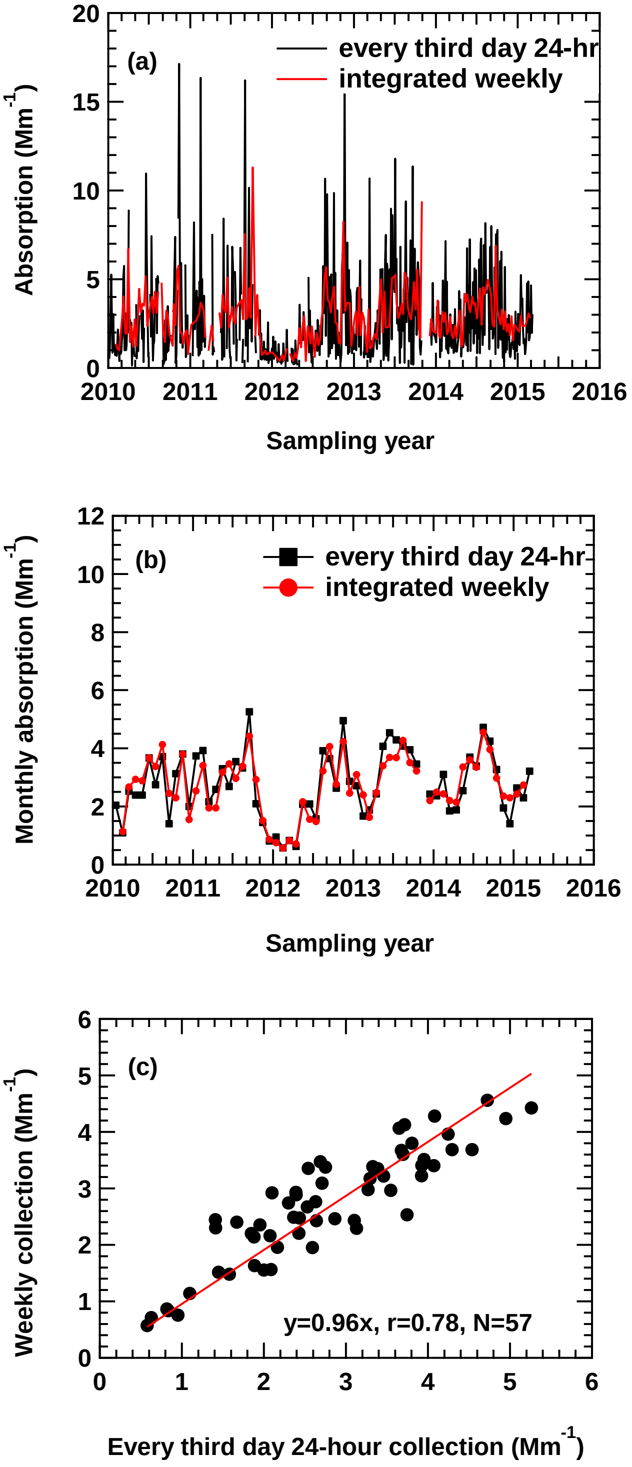


Figure ~~1~~ 2 Comparison of the TC, OC, and EC measurements of the NIST SRM samples reported by the ECCC and DRI groups during the inter-comparison study (ICP) conducted between 2009 and 2010. "Reported" represent the published value in the NIST SRM certificate (Cavanagh and Watters, 2005). Error bars represent uncertainties covering 95% confidence interval. In (d), the ECT9 value (in green) represents the calculated EC/TC ratio determined based on stable carbon isotope measurement obtained from the SRM 1649a sample (Currie et al., 2002).

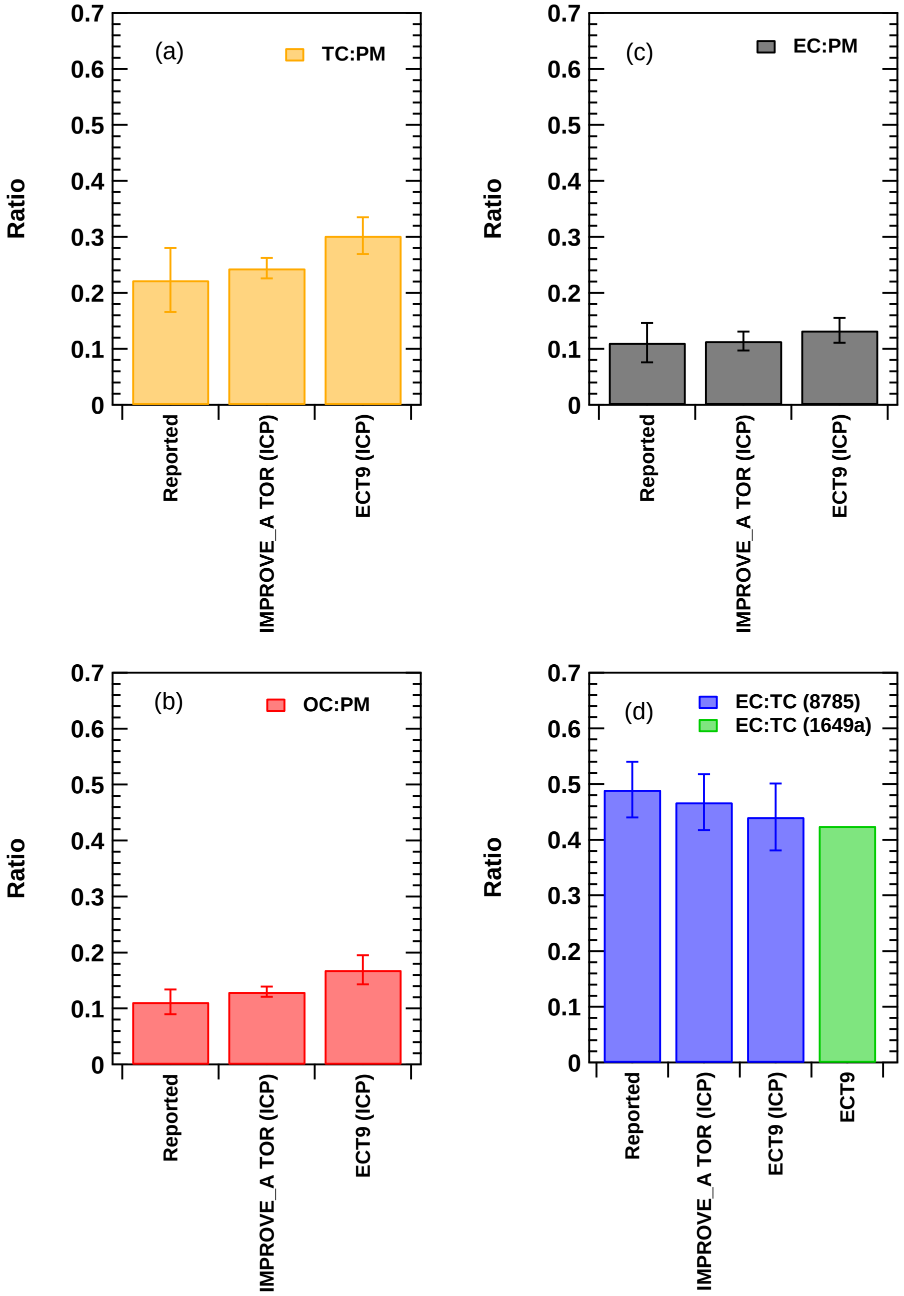


Figure 3~~1~~ Comparison of: (a) TC, (b) OC, and (c) EC concentrations obtained from the same NIST SRM 8785 filters reported by ECCC following the TEA (ECT9) method and by DRI following the IMPROVE_A TOR protocol during the inter-comparison study in 2009/2010.

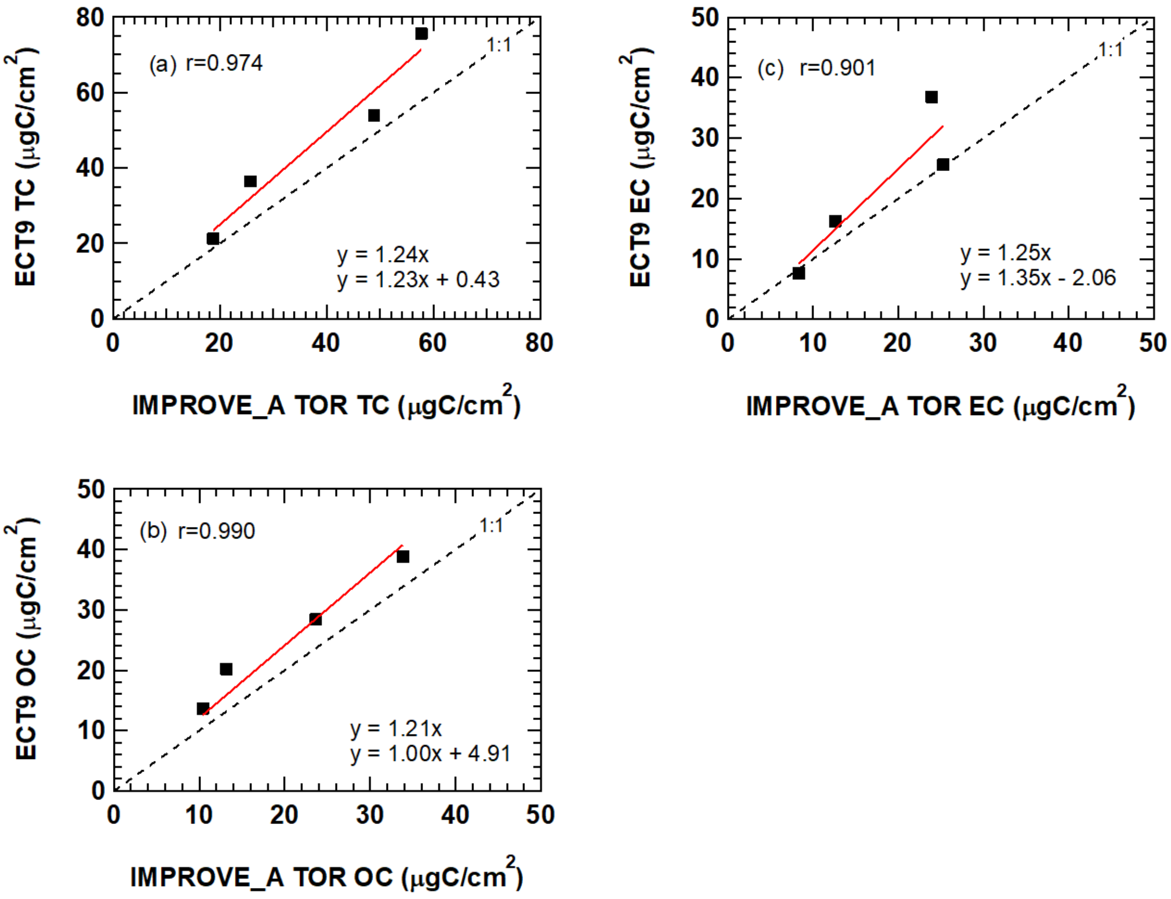


Figure 4 Monthly averaged CAPMoN (a) OC, (b) EC, and (c) POC mass concentration time series with and without vapor adsorption correction. Note that the y-axes in Figures 4b and 4c are on different scale.

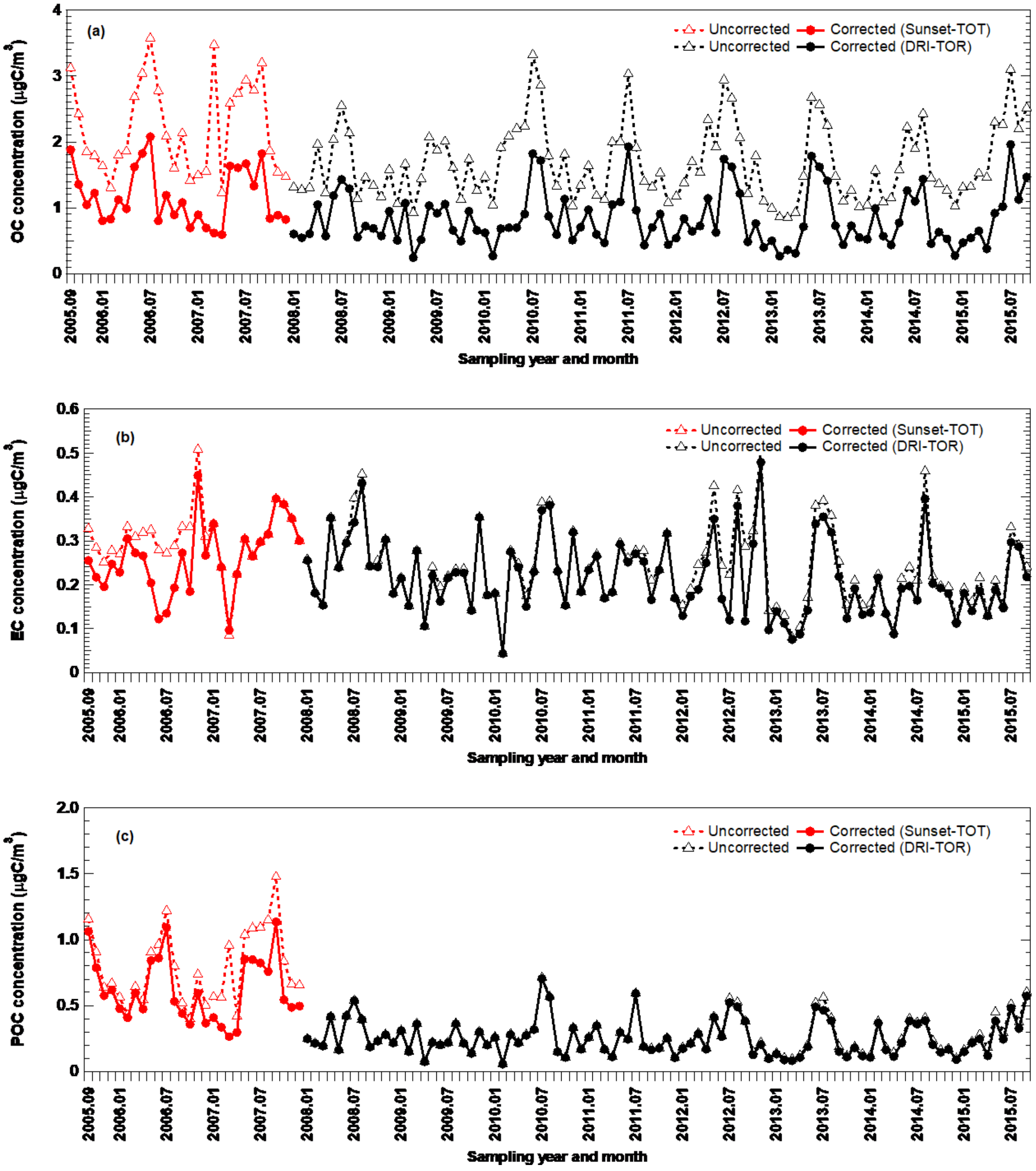


Figure 5 Relationship between the monthly averaged CAPMoN vapor adsorption corrected and uncorrected measurements for (a) TC, (b) OC, (c) EC, and (d) POC. Black solid markers represent the TOR measurements (2008-2015) analyzed by the DRI analyzer (i.e., DRI-TOR). Red open markers represent the TOT measurements before 2008 analyzed by the Sunset analyzer (i.e., Sunset-TOT). The red line represents the best-fitted linear regression of all the DRI-TOR measurements through the origin. All the corresponding statistics (i.e., best-fitted slope, correlation coefficient, total number of measurement points) are included in the legend.

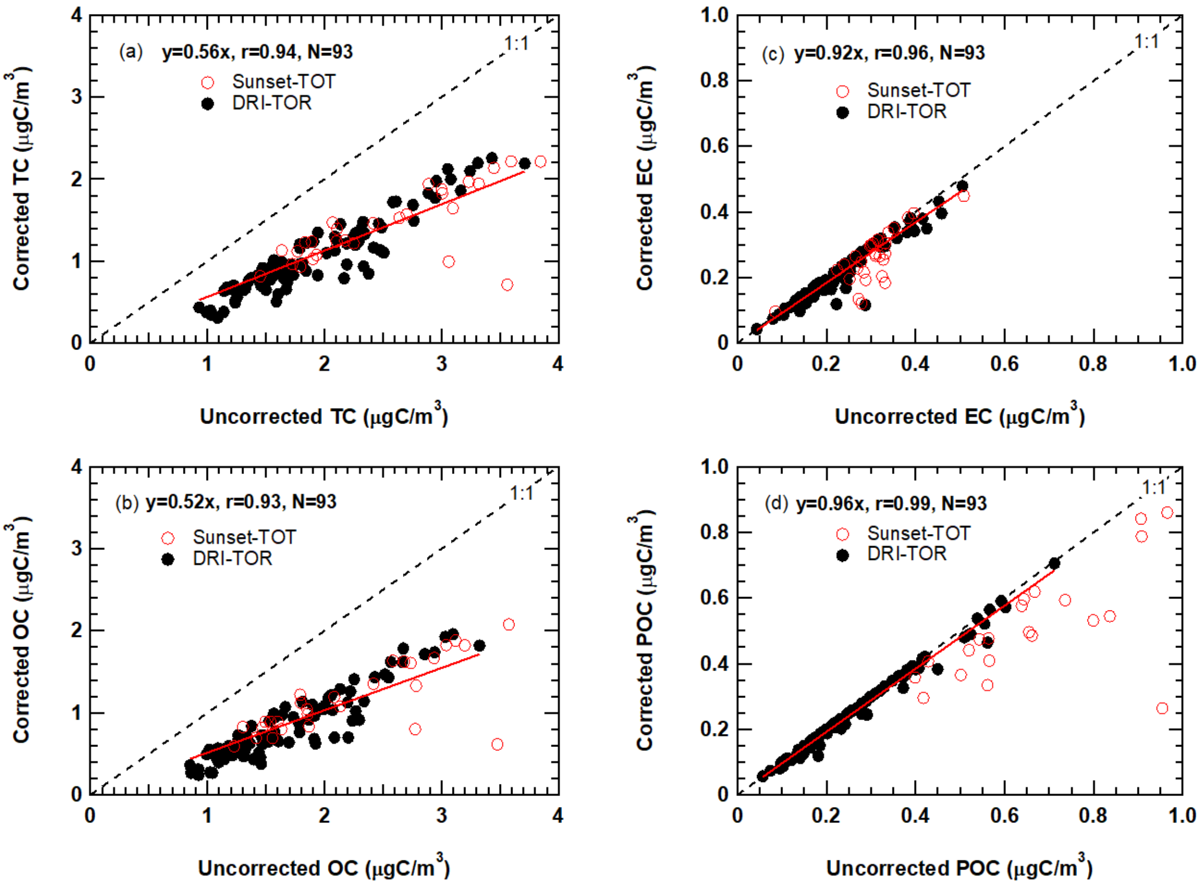
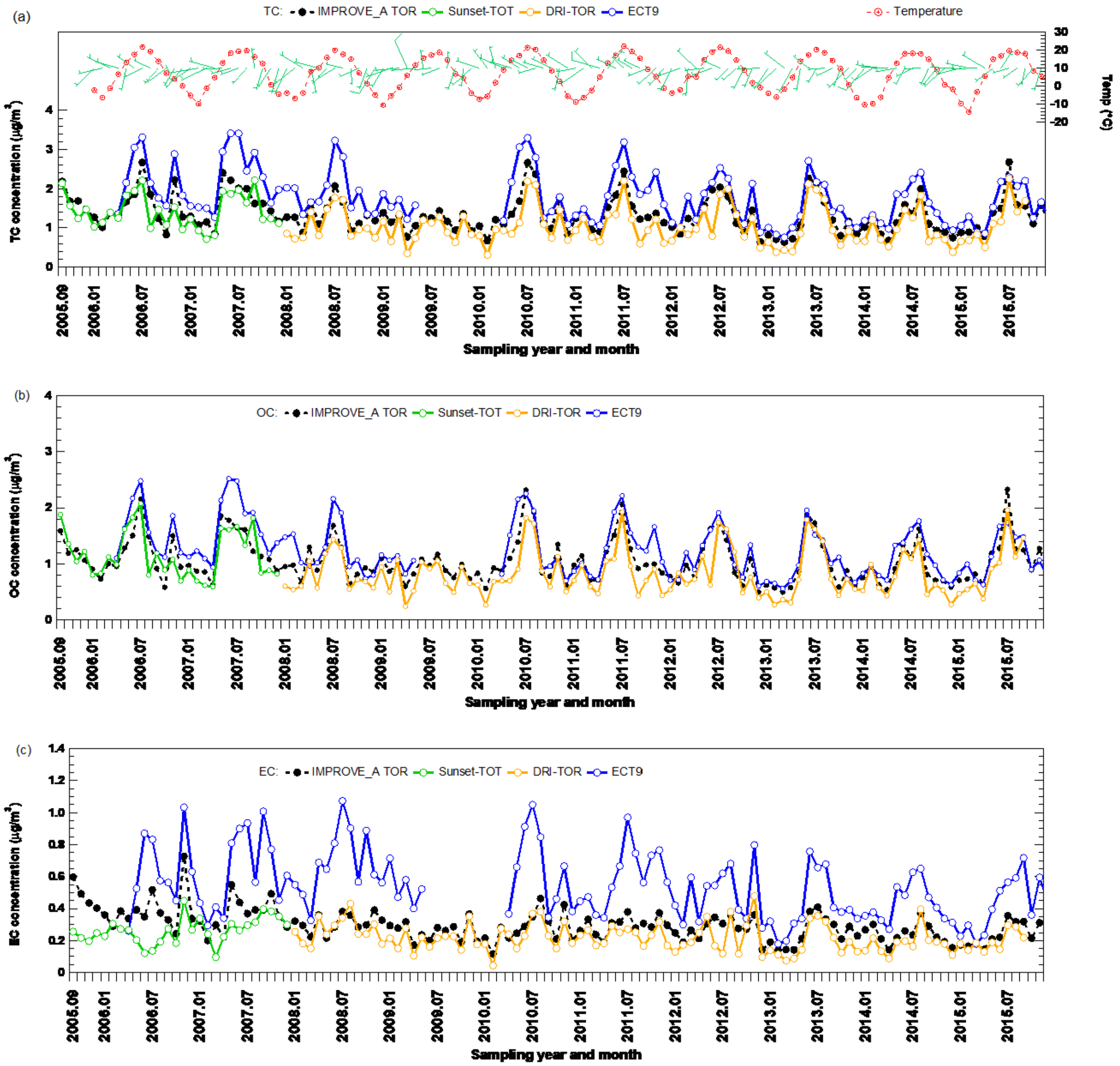


Figure 6 Monthly averaged (a) TC, (b) OC, (c) EC, and (d) POC concentration time series obtained from three different networks at Egbert. CAPMoN measurements before 2008 were obtained using Sunset-TOT method (in green) while measurements starting 2008 were obtained using DRI-TOR method (in orange).



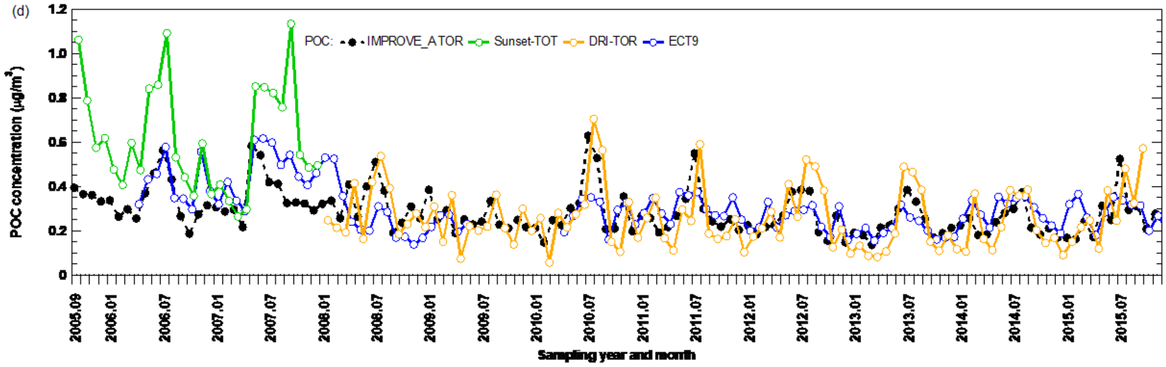


Figure 7 Comparison of the monthly averaged carbonaceous mass concentrations from the ~~CAPMoN~~ DRI-TOR (red circles and orange triangles) and ~~CABM~~ ECT9 (black squares) ~~networks~~ protocols against IMPROVE_ A TOR protocol. The different straight lines represent the linear regression best fitted line through the origin (i.e., Regression 1). The fitted parameters for all corresponding data sets with (Regression 2) and without (Regression 1) the y-intercept are summarized in Table 2.

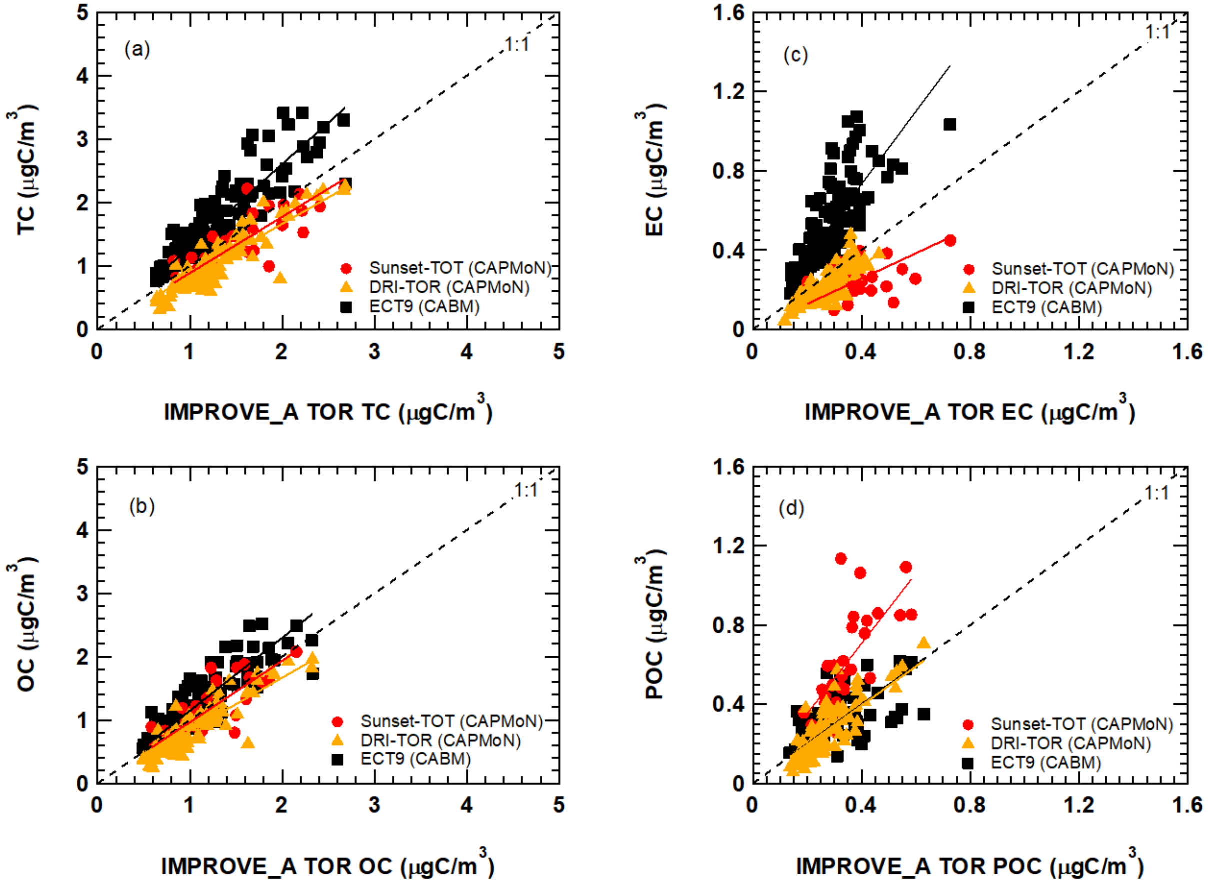
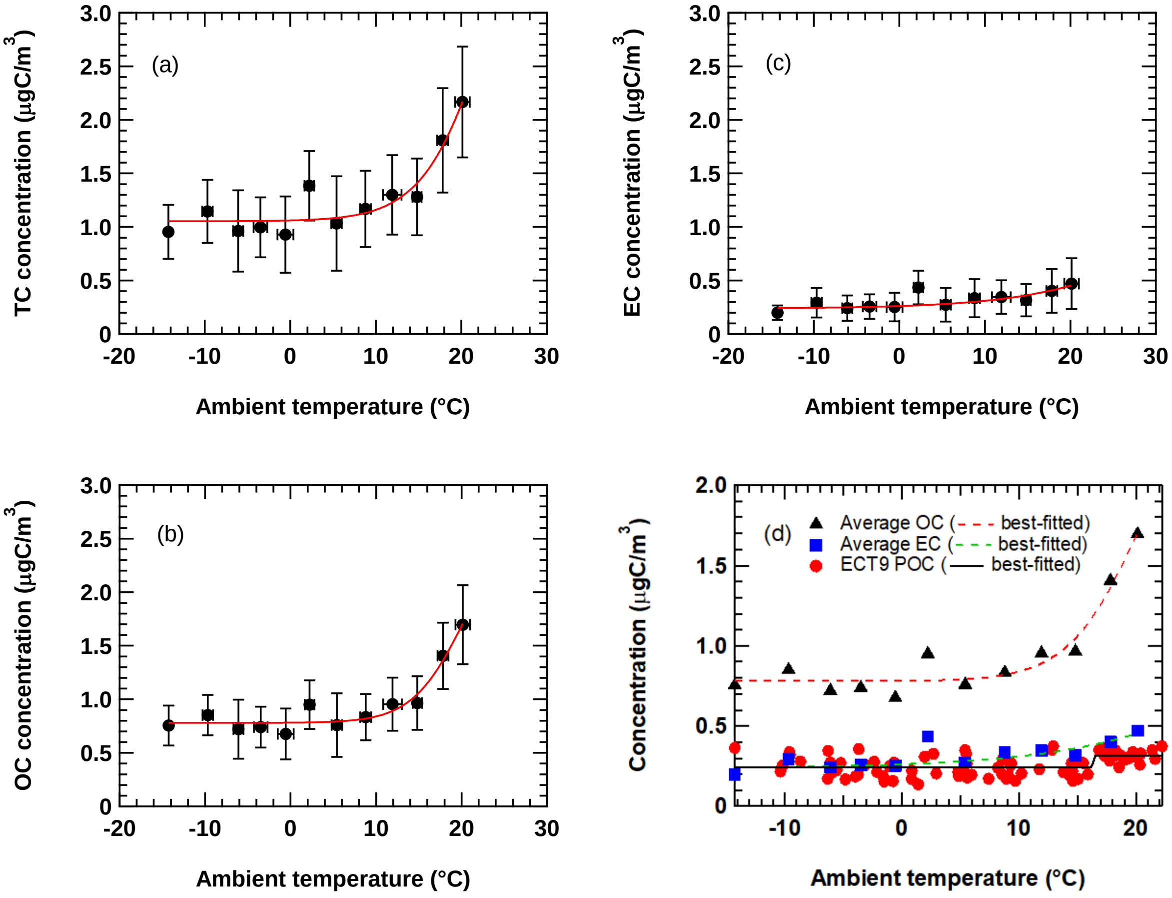


Figure ~~10~~ 8 Figure shows the relationship of averaged (a) TC, (b) OC, and (c) EC concentrations from all networks as a function of ambient temperature. Each data point represent the average value of all network measurements within a 3°C temperature range. Uncertainties are standard deviations of the measurements. Red curve represents the best-fitted Sigmoid function. Figure 10(d) shows the seasonality of ECT9 POC compared to the average OC and EC seasonality. Black solid curve represents the best-fitted Sigmoid function on all ECT9 POC measurements.



Supplementary Information for: Inter-comparison of the Elemental and Organic Carbon Mass Measurements from Three North American National Long-term Monitoring Networks at a co-located Site

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~~11~~ 13 pages, 2 table, and 6 figures

Supplementary Material:

Nomenclature

AIHL	Air-industrial hygiene laboratory
AMS	Accelerator mass spectrometry
BC	Black carbon
CABM	Canadian Aerosol Baseline Measurement
CAPMoN	Canadian Air and Precipitation Monitoring Network
CARE	Center for Atmospheric Research Experiment
CCMR	Climate Chemistry Measurements and Research
DRI	Desert Research Institute
DRI-TOR	CAPMoN measurements using IMPROVE on DRI analyzer with TOR correction
EC	Elemental carbon
ECCC	Environment and Climate Change Canada
ECT9	EnCan-Total-900 protocol
FID	Flame ionization detector
FLEXPART	FLEXible PARTicle dispersion model
ICP	Inter-comparison study
IMPROVE	Interagency Monitoring PROtected Visual Environments
IMPROVE_A TOR	IMPROVE_A TOR protocol on DRI analyzer
KCCAMS	Keck Carbon Cycle accelerator mass spectrometry
MAC	Mass absorption coefficient
NIST	National Institute of Standard and Technology
OC	Organic carbon
PM	Particulate matter
POC	Pyrolyzed organic carbon
PSAP	Particle Soot Absorption Photometer
SOA	Secondary organic aerosol
SRM	Standard Reference Material
Sunset-TOT	IMPROVE TOT protocol on Sunset analyzer
TC	Total carbon
TEA	Thermal evolution analysis
TOA	Thermal optical analysis
TOR	Thermal optical reflectance
TOT	Thermal optical transmittance
UCI	University of California Irvine
WMO	World Meteorological Organization

Thermal-Optical Analysis / Thermal Evolution Analysis

During the analysis of both thermal-optical analysis (TOA) and thermal evolution analysis (TEA), a small punch of the filter is placed either inside the Desert Research Institute (DRI) carbon analyzer (https://www.dri.edu/) or the Sunset laboratory-based carbon analyzer (http://www.sunlab.com) and subjected to a step-wise heating protocol.

IMPROVE_A (referred to as IMPROVE_A TOR in the manuscript) is a TOA protocol. The heating is in successive steps of 140°C (OC1), 280°C (OC2), 480°C (OC3), and 580°C (OC4) in helium (He) flow and 580°C (EC1), 740°C (EC2), and 840°C (EC3) in 2% O_2 and 98% He environment (Figure S1a; Table S1) (Chow et al, 2007). The evolved carbon is first oxidized to CO_2 then reduced to CH_4 and be determined by a flame ionization detector (FID)~~ via using an internal standard of CH_4~~. During the heating under a non-oxidative atmosphere, much of the OC will be combusted and leave the filter, some OC including the oxygenated compounds, char and turn to pyrolyzed organic carbon (POC) which would be combusted under an oxidative environment with EC. The POC mass defined in the IMPROVE_A TOR method is estimated by monitoring the reflectance (i.e., thermal optical reflectance; TOR) of a 633-650 nm laser beam within the oxidative environment. The combustion of POC result in an increased laser reflectance signal. When the reflectance signal returns to its initial intensity at the start of the analysis (i.e., prior to the formation of POC), it is assumed all POC is combusted and the remaining carbon mass in the analysis belongs to EC. The IMPROVE_A TOR protocol defines OC as OC1+OC2+OC3+OC4+POC while EC is defined as EC1+EC2+EC3-POC.

The IMPROVE (referred to as DRI-TOR in the manuscript) protocol is similar to the IMPROVE_A TOR protocol, and the heating steps in this TOA protocol includes 120°C (OC1), 250°C (OC2), 450°C (OC3), and 550°C (OC4) in He flow and 550°C (EC1), 700°C (EC2), and 800°C (EC3) in 2% O_2/98% He atmosphere (Figure S1b; Table S1) (Chow et al., 1993). OC is defined as OC1+OC2+OC3+OC4+POC while EC is defined as EC1+EC2+EC3-POC.

The EnCan-Total-900 (ECT9) is a TEA protocol that utilizes higher temperature set point and longer retention time (compared to ~~IMPROVE~~ DRI-TOR and IMPROVE_A TOR) for baseline separation of OC, POC, and EC (Huang et al., 2006; Chan et al., 2010). The ECT9 method consists of three temperature settings. First, two 600 s heating stages at 550°C and 870°C under pure He stream for OC and POC including carbonate carbon (CC) determination, respectively; then followed by EC determination over a 420 s heating at 900°C under 2% O_2 and 98% He atmosphere (Figure S1c; Table S1). Different from the ~~IMPROVE~~ DRI-TOR and IMPROVE_A TOR protocols, POC defined in ECT9 method is not a charring correction but represent different groups of organic compounds, as well as some calcium carbonate ($CaCO_3$) that does not combust under 550°C. The total OC in ECT9 method is defined as OC+POC.

Figure S1 Comparison of the (a) IMPROVE_A TOR, (b) ~~IMPROVE~~DRI-TOR, and (c) EnCan-Total-900 (ECT9) protocols used in the different networks. Note that the time scale (i.e., x-axis scale) for ~~IMPROVE~~ DRI-TOR and IMPROVE_A TOR are for illustration purposes as ~~IMPROVE and IMPROVE_A~~both protocols are event driving depending on the particle loading on the filter punch.

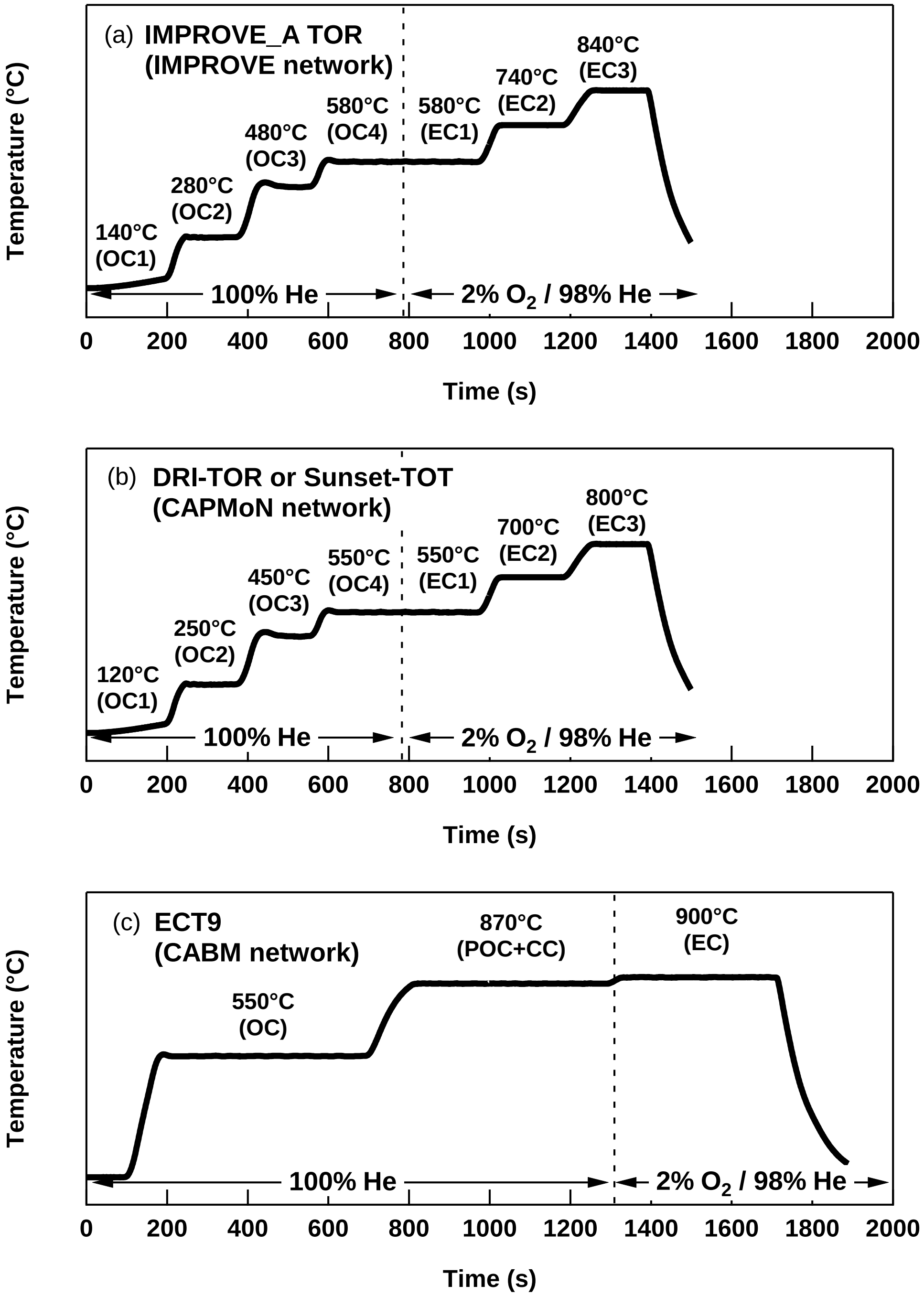


Table S1 Experimental parameters of the three TOA/TEA protocols used in this study.

Methods Carrier gas	Carbon fraction	IMPROVE_A TOR Temp (°C), Time (s)	~~IMPROVE~~DRI-TOR / Sunset-TOT Temp (°C), Time (s)	ECT9 Temp (°C), Time (s)
He-purge		30, 90	30, 90	90
He	OC1	140, 150-580	120, 150-600	-
He	OC2	280, 150-580	250, 150-600	-
He	OC3	480, 150-580	450, 150-600	-
He	OC4	580, 150-580	550, 150-600	-
He	OC	-	-	550, 600
He	POC	-	-	870, 600
O_2/He	EC1	580, 150-580	550, 150-600	-
O_2/He	EC2	740, 150-580	700, 150-600	-
O_2/He	EC3	840, 150-580	800, 150-600	-
O_2/He	EC	-	-	900, 420

Note: OC in IMPROVE_A TOR and ~~IMPROVE~~ DRI-TOR are defined as OC1+OC2+OC3+OC4+POC
EC in IMPROVE_A TOR and ~~IMPROVE~~ DRI-TOR are defined as EC1+EC2+EC3-POC
For ECT9, total OC is defined as OC+POC. For consistency purpose, the “ECT9 OC” discussed in this work refers to OC+POC.

Radiocarbon analysis

The $^{14}C/^{12}C$ abundances associated to the individual mass fractions of TC, OC and EC were determined using accelerator mass spectrometry (AMS) at the Keck Carbon Cycle AMS (KCCAMS) Facility at University of California Irvine (UCI). The KCCAMS/UCI runs an inhouse modified AMS compact instrument (0.5MV 1.5SDH-2) purchased from National Electrostatic Corporation (Beverly et al., 2010). Optimizations to the spectrometer couple with ultra-small sample capabilities (Santos et al., 2007) allowed for the measurement of single OC and/or EC fractions, besides TC samples. Mass fractions of TC, OC and EC isolated by the ECT9 protocol using a Sunset Laboratory instrument (Huang et al., 2006) was shipped to KCCAMS/UCI as cryogenically trapped CO_2 in sealed ampules followed by a separated set of reference materials. Isolated CO_2 samples were then converted to filamentous graphite following specific protocols (Santos and Xu, 2017) and analyzed for their carbon isotopes. Radiocarbon results as FM (fraction modern carbon) were corrected for background effects and isotopic fractionation with $\delta^{13}C$ of prepared graphite measured directly at the spectrometer, as described by Santos et al. (2007).

Figure S2 Box plots summarizing the magnitude of the gaseous adsorption, in (a) absolute value and (b) percentage, on CAPMoN TC, OC, POC, and EC mass measurements. Measurements prior to 2008 were obtained using the Sunset-TOT method while measurements from 2008-2015 were obtained using the DRI-TOR method. Each individual box represents the 25th, 50th, and 75th percentiles of the measurement values while the 10th and 90th percentiles are represented by the bottom and top whiskers, respectively.

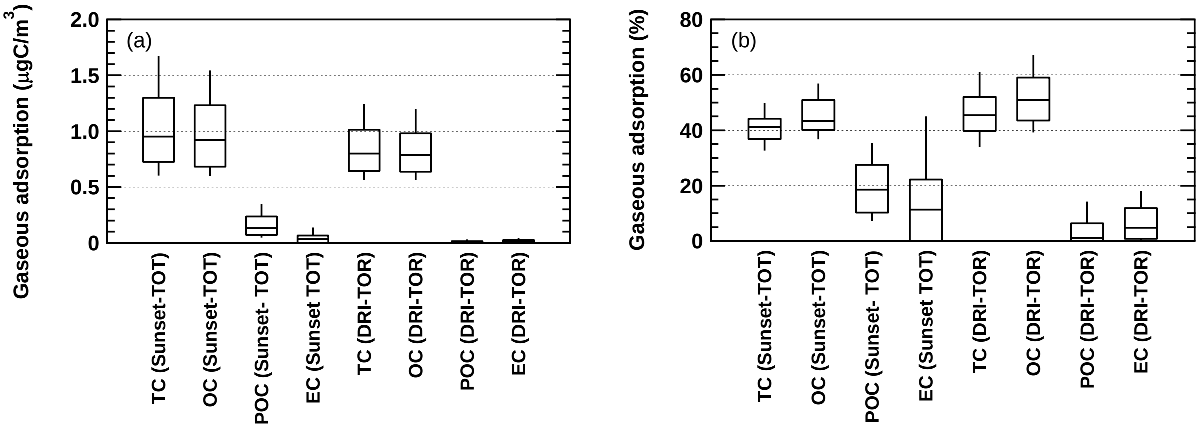


Figure S3 Monthly averaged ECT9 EC and IMPROVE_A TOR EC concentrations time series.

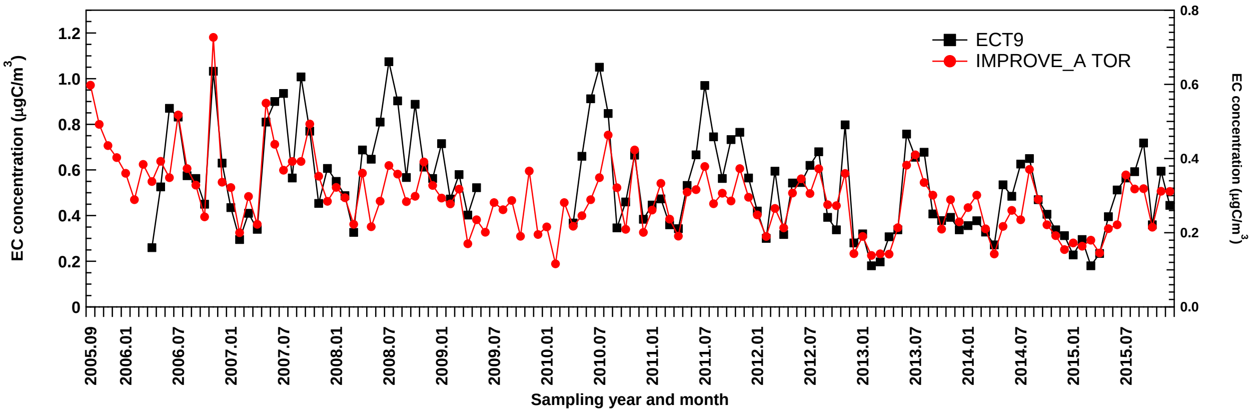


Table S2~~3~~ Correlation coefficients (r) of various monthly averaged carbonaceous mass measurements among different networks (IMPROVE, CAPMoN and CABM). All measurements cover the period from 2008 to 2015.

		IMPROVE_A TOR				DRI-TOR				ECT9			
		TC	OC	EC	POC	TC	OC	EC	POC	TC	OC	EC	POC
IMPROVE_A TOR	TC	1	0.99	0.79	0.90	0.91	0.91	0.68	0.87	0.88	0.87	0.77	0.60
	OC		1	0.69	0.90	0.90	0.90	0.63	0.87	0.86	0.87	0.74	0.56
	EC			1	0.68	0.76	0.70	0.81	0.69	0.73	0.63	0.74	0.61
	POC				1	0.82	0.81	0.62	0.85	0.83	0.83	0.73	0.59
DRI-TOR	TC					1	0.99	0.74	0.92	0.79	0.78	0.71	0.41
	OC						1	0.63	0.92	0.77	0.77	0.67	0.40
	EC							1	0.63	0.63	0.56	0.69	0.31
	POC								1	0.77	0.75	0.70	0.44
ECT9	TC									1	0.98	0.91	0.70
	OC										1	0.82	0.75
	EC											1	0.50
	POC												1

Seasonality in Carbon Concentration and Possible Origination

To determine the air mass origins, a Lagrangian particle dispersion transport model (FLEXible PARTicle dispersion model; FLEXPART) (Stohl et al., 2005) was applied to obtain daily five-day back-trajectories from Egbert from 2006 to 2015. Figure S6 summarizes the average FLEXPART footprints for summer (May-Oct) and winter (Nov-Apr) seasons, showing the probability of air masses originating from various regions. These results indicate regional contributions from boreal forest in the northern part of Ontario and Quebec, as well as anthropogenic emissions from the northern U.S. Five-day trajectories show larger concentrations from the N and NW, consistent with wind roses shown in Figure S4.

At low ambient temperatures, primary emissions (e.g., local transportation, residential heating, and industrial activities) account for most of the ambient OC and EC (Ding et al., 2014). Increased human activities (e.g., traveling by car and barbecuing) during warmer weather could lead to increased emissions. High ambient temperature also leads to increased biogenic emissions (e.g., monoterpenes) from the boreal forest and increased SOA formation (Chan et al., 2010; Leaitch et al., 2011; Passonen et al., 2013; Tunved et al., 2006). The central and eastern boreal forest fire season typically occurs from May to August when ambient air is dry and hot, resulting in generally increased OC and EC emissions (Lavoué et al 2000). Transboundary transport of biomass burning emissions from the U.S. could also contribute to the higher concentrations in southern Ontario (Healy et al. 2017). Increasing ambient temperature from 10 °C to 20 °C leads to higher OC concentrations from 0.84 to 1.61 µgC/m^3 (91.7% increase) and EC concentration from 0.31 to 0.45 µgC/m^3 (45.2% increase). The temperature dependency of OC and EC suggests a potential climate feedback mechanism consistent with the observations from Leaitch at al. (2011) and Passonen et al. (2013).

Figure S4 Wind rose analysis (by month) based on the local wind speed and direction data for various months obtained at Egbert over the period from 2006 to 2015.

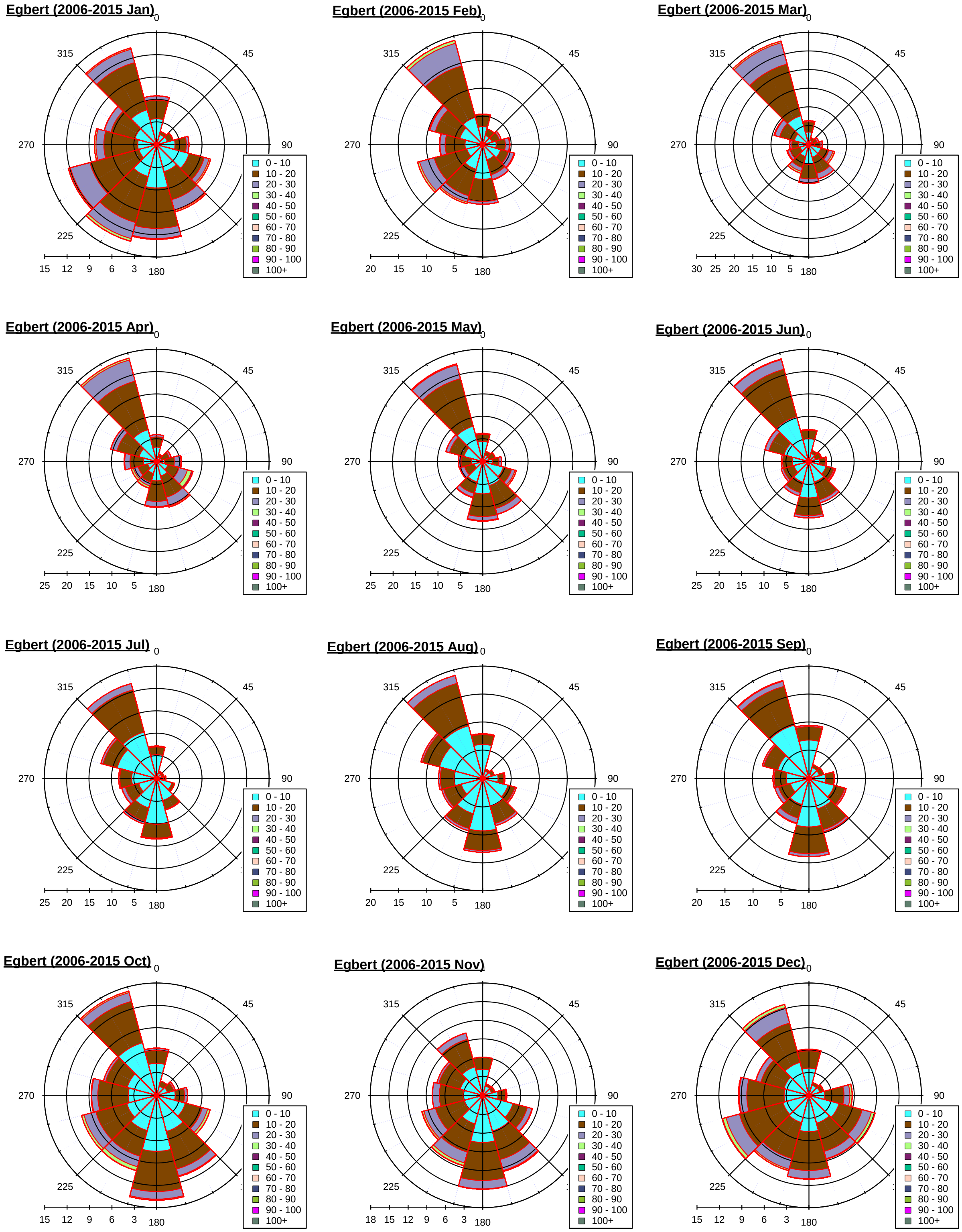


Figure S5 Figure shows the relationship of (a) TC, (b) OC, and (c) EC as a function of ambient temperature. IMPROVE, CAPMoN, and CABM measurements are represented by the black, orange, and blue markers, respectively. The red trace represents the best-fitted Sigmoid function on all measurement while the red dashed lines cover the 95% confidence interval of the best-fit function.

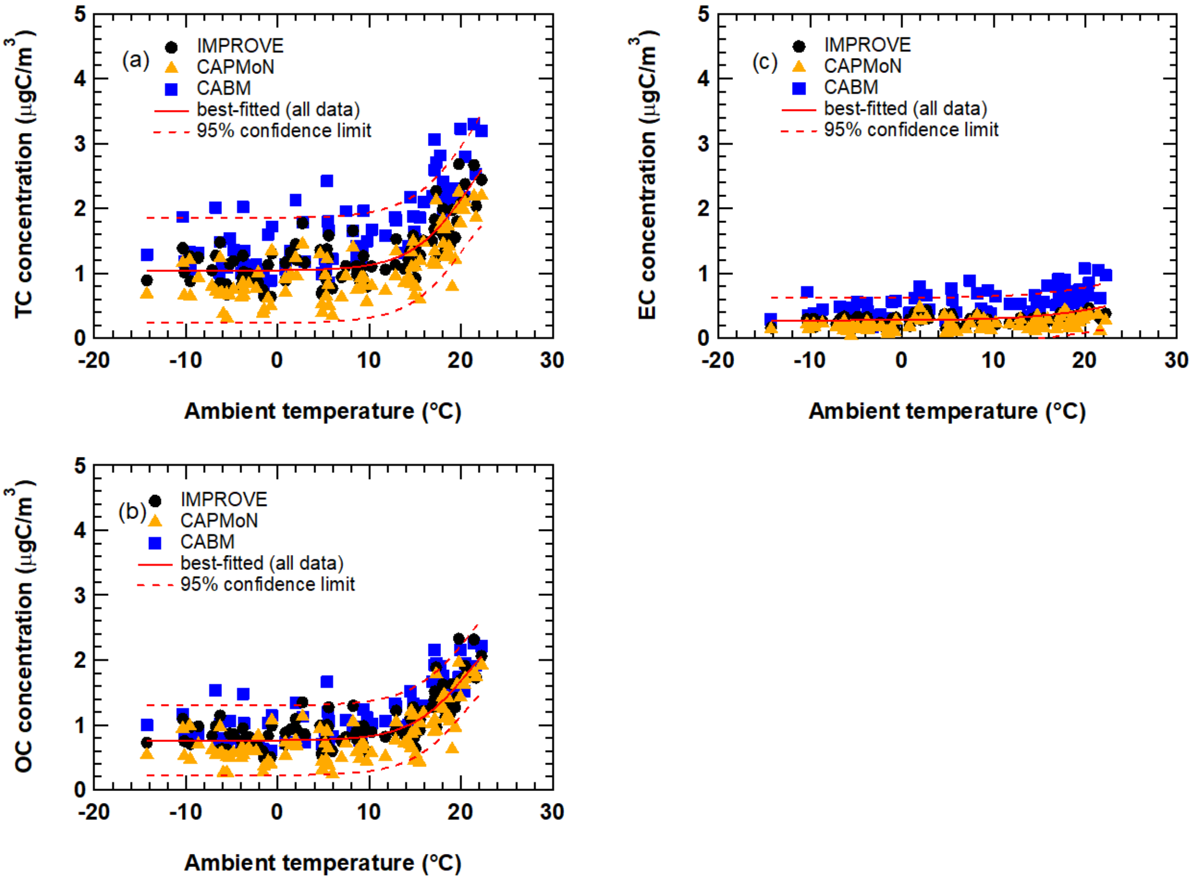
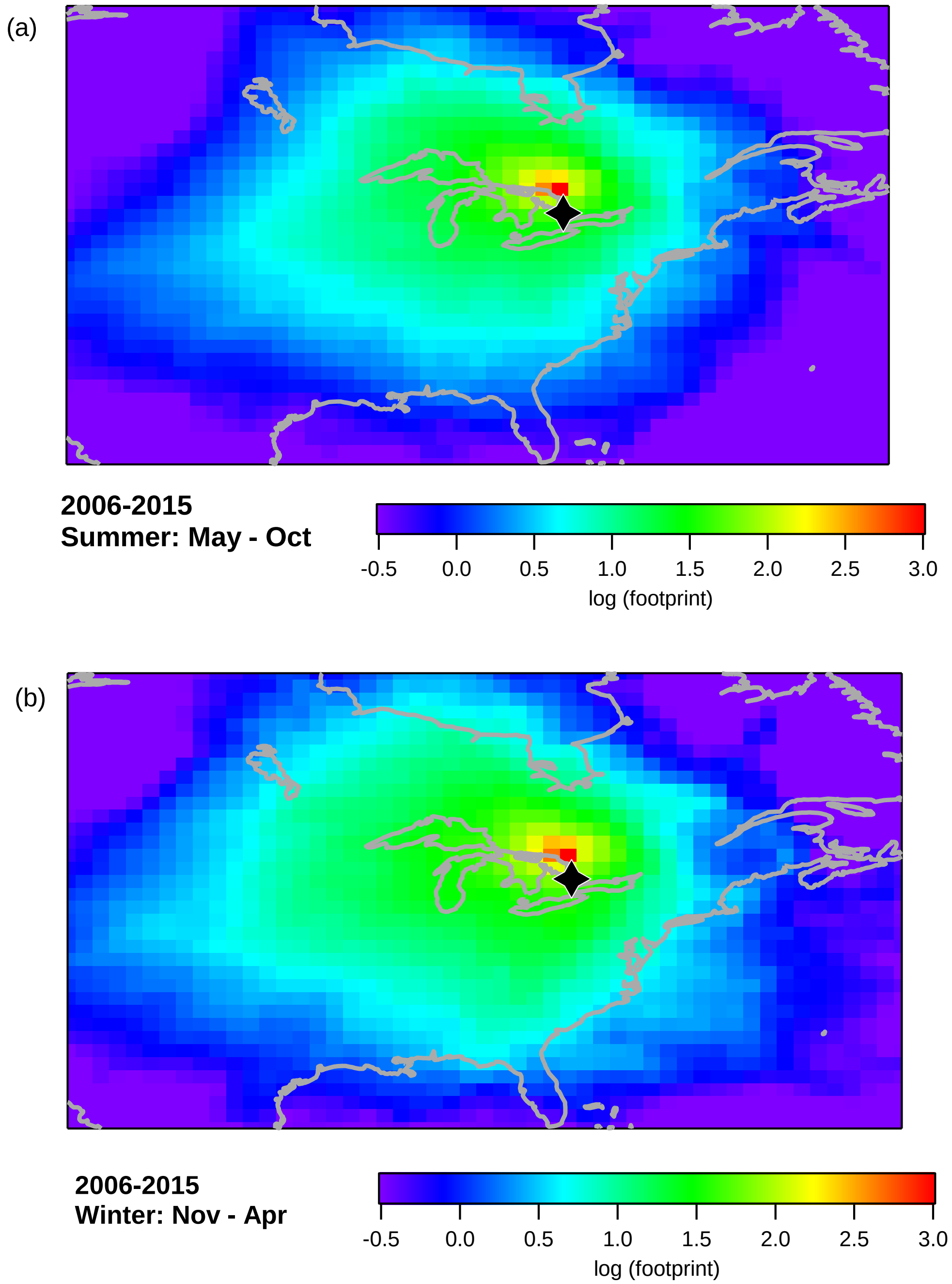


Figure S6 Figure showing the average air masses footprint reaching Egbert derived from FLEXPART. Results are derived from daily footprint over the period from 2006 to 2015, from (a) May to October and (b) November to April. Red, green, and purple colors represent the relative probability of the air masses origin in decreasing likelihood. To improve the visibility, results are plotted on log scale.



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Referee #1 comments:

Comments:
This paper describes organic and elemental carbon concentration measured at one site using different sampling devices and flows and using different temperature protocols for analyzing TC, OC and EC. It tries to evaluate how well results are comparable, which is important as it is known that at least the used temperature protocol and used optical correction method have affect to the OC and EC concentrations. Also, different ways of correcting/uncorrecting gaseous artefact were studies.
The paper has clear structure and objective and it is worth of publishing after revision. Detailed comments are described below. In addition to these comments, clarify much more clearly, which results are new and not presented before. Occasionally, it was not clear whose results were presented. Also, check that same tense are mainly used when presented your results. Consider to retitle the subtitles in Results and discussion chapter, some of them were not informative if the names of the network are known.
>> The authors appreciate the useful comments and suggestions from the referee, and we address all the comments accordingly.

Abstract:
Based on the suggested correction, modify the abstract.
>> This is addressed.

Lines 23-30: OK
Lines 30-32: Why not compared without normalizing the concentrations? Check comment further below. Otherwise this kind of information belongs here.
>> After some consideration and discussions among the co-authors, we agree to remove this section and focus on the absolute data inter-comparison section.

Lines 32-36: this is not the objective of this paper and not actually studied here. The discussion of the sources of OC and EC is presented in lines 417-425 and are based on other studies. No proves for forest fires occurrence were presented although speculated. Anyway this is not the scope of this study, if I understood correctly. Remove.
>> The authors have conducted some preliminary analysis and results suggested that forest fire could potentially influence the Egbert site and result in elevated EC concentration during summer time. Additional research is currently on going and the results are expected to be included in a separate manuscript. Considering this is preliminary results, we have now removed such content to the supporting material.

Lines 38-41: these lines are more like a conclusions not belong into the abstract.
>> These sentences are removed.

Introduction
Line 43. Modify the sentence to remove double parentheses e.g…carbonaceous aerosol, including elemental carbon (EC), often referred to black carbon (BC) and organic carbon (OC) make up a large fraction…
>> This is addressed.

Line 43-44: reference needed
>> A reference has been added.

Lines 120-127, Objective:

- be more specific of how many sites are compared in this study (in line 120-121). Now I got the feeling that multiple sites were compared (line 125)
- remove the names of the networks or write them open

>> This is addressed. We have made it clear that the comparison was not for multiple sites.

Sampling and Measurements

General comments: overall it is slightly difficult to remember the name of the different networks and the used protocols. I need to check them constantly. In the Results and discussion, use other subtitles than the name of the network vs other network.

>> The authors apologize for the confusion. The protocol names throughout the paper have now been verified and modified to ensure they are consistent. The subtitles have also been revised to avoid confusion.

Line 151-153: Modify the sentence by replacing "The IMPROVE measurements… to Results of/from the IMPROVE measurements

>> We have improved the sentence.

Lines 140-155: Add information if they are sampled at the same day as at the IMPROVE network and add sample amount into Table 1.

>> The CAPMoN samples were indeed collected on the same day as the IMPROVE samples and this information is now mentioned in the manuscript. We have also included the total number of samples used in the analysis in Table 1.

Line 155. I do not understand the reference of IMPROVE. Is it a book, paper or internet page? Specify.

>> We have removed this reference.

Line 166: Re-locate the manufacture info of the quartz filters directly after quartz filters were mentioned.

>> This is addressed.

Lines 163-170: Add information of the sample amount for Sunset-TOT and DRI-TOR and both into table 1.

>> The number of samples are now added.

Line 171-172 Use reference not internet pages for Sunset instrument. Add also, information of the manufactory, and country.

>> Manufactory is Sunset Laboratory Inc. from the USA. This info is now added.

Line 176-178. This sentence is slightly confusing. Are you referring to results presented in Chow et al paper? Modify this sentence more clearly. Inform also what "small difference" means e.g. how much TC mass differs between IMPROVE_A TOR and Sunset-TOT/ DRI-TOR.

>> Yes, we are referring to the results discussed in Chow et al. (2007) and the sentence is revised for clarity. The "small difference" refers to the temperature difference discussed in the previous sentence, which is the typical temperature difference between each ramping temperature used in the two protocol.

Line 179: the subtitle “the ECCC Canadian Aerosol Baseline Network” is slightly confusing as you used name of the CABM network later. Replace to CABM.
>> This is addressed.

Lines 189-191. Add the amount of the filters.
>> The total number of samples has been included in Table 1.

Differences in Sampling and Analysis among Networks
Line 213: Modify the sentence so that network is added e.g. cyclones were used in IMPROVE and CABM networks whereas an impactor was used in CAPMoN network.
>> This information is included.

Line 215: bounce or bounce off. Check, which is correct?
>> We mean bounce off. When hit the impactor surface, some large solid particles may bounce and not be collected by the impactor plate and then re-enter the airstream and be collected by the filter downstream.

Line 225: Re-order the list so that IMPROVE is before CAPMoN, as it was first introduced in the manuscript.
>> This is addressed.

Lines 225-228: Specify how CAPMoN results (TC, OC, EC) are calculated especially when monthly mean values are presented. Did you use monthly mean value for vapor artifact or did you subtract vapor artifact for individual sample and then calculate the average.
>> For CAPMoN measurements, vapor adsorption artifact was applied to each individual 24-h samples. Then, all the artifact corrected samples within each month were used to compute the monthly average measurement. For IMPROVE measurements, the monthly median OC artifact derived from 13 sites were subtracted from all individual OC measurements in the same month before monthly averaged were derived. The above information is now added to the manuscript.

Line 229: References needed after the statement “multiple studies”
>> The “multiple studies” here were indeed referring to the references in line 231 (i.e., Chow et al., 2004; 2005; Watson et al., 2005). The sentence is now revised to include references.

NIST urban dust standard comparison (SRM 8785 & 1649a)
Remove the NIST and (SRM 8785 and 1649a) from the subtitle
>> This is addressed.

This chapter need to be reorganized and clarified. I did not understand if the intercomparison is the same as the analysis of four replicates.
>> The word “inter-comparison” was used because this is a comparison exercise conducted by two labs even though there were just four replicates. It was realized that using “replicates” was not proper in description of those SRM 8785 filters since they are not the same in mass loading. This has been addressed in the revised version.

Reorganize:
Paragraph 1:

Start with the introduction of the urban dust sample (SRM 1649a) then describe how SRM 8785 is done and continue with the reference. After those, describe the intercomparison/analysis of four replicates. Line 237: “OCEC measurements” is not right way to describe OC and EC analysis. Modify the sentence e.g. consistency between the ECT9 and the IMPROVE_A TOR analytical methods were assessed by measuring four replicates of …….
>> This is addressed and the paragraph is now rearranged.

Line 239: replace IMPROVE_A to IMPROVE_A TOR
>> This is addressed.

Line 240: replace “measuring” to analysing
>> This is addressed.

Line 246-247: ECCC and DRI laboratory has not been presented. Could this information be added under the network presentation e.g. in line 151. Once sampled, filters were stored in freezer until they were ready to be analysed in the DRI laboratory in xx. Similarly the ECCC laboratory.
>> This is addressed.

Paragraph 2: Show first the results based on Figure 2, where analyzed results were compared to the reported one. Change then the numbering of the figures, if Fig. 2 is presented before Fig. 1.
>> This is addressed and Fig 1 and 2 are now in reversed order.

Paragraph 3: Compare TC, OC and EC results analyzed with ECT9 and IMPROVE_A TOR protocols. Were there any test solution that were analyzed during the intercomparison that could indicate the reason of discrepancy (instrumental, inhomogeneous sample etc) of TC between two different protocols and instruments?
>> Unfortunately, no such solution was analyzed by both labs in this inter-comparison effort. The current analysis was not able to determine the reason for causing the difference observed during the inter-comparison. During the analysis, both labs analyzed the filters using their own standard operation procedure and therefore the regression results reflect any difference that would be caused by all reasons in combined.

Specify whether linear or orthogonal regressions were used in Fig 1. Orthogonal is better if either of the instrument is reference one (and concentrations are known).
>> We have specify the type of regressions to use in the revised version.

Line 251: ….Use correct protocol name “IMPROVE_A TOR” and remove by DRI
>> This is corrected.

Line 251: “compared well” does not inform if the concentration is the same. Modify the sentence. Paragraph 4
>> “Compared well” means the average values were within uncertainties and therefore they are not statistically different. The sentence is now modified by stating this explicitly.

Line 257: clarify what multiple SRM 1649a samples mean. Was it three samples as mentioned in line 266?

>> We literally means a few. In here, SRM 1649a (which is dust powder) were weighted and analyzed by the OCEC analyzer for TC, and then separately for OC and EC. The word “multiple” is removed to avoid confusion.

Line 267-269: EC to TC ratio of 0.425 measured with carbon isotopes should also compared to the value analyzed with ECT9 protocol. Now it has been compared only for reference value and result derived from the IMPROVE_A TOR protocol.
>> This is addressed.

Line 261: refer that the method is presented in the Supplement material section. You can also consider to present the calculation (Eq 1) and text describing it in the Supplement material section.
>> We prefer to leave a brief discussion of the method in the main text while all the technical details of the methodology will remain in the supplement material section.

Results and discussion
Add one paragraph where you have presented how you have compared different samples having different sampling times. If you compare weekly samples to 24h-samples collected every third day, have you calculated average of 2-3 samples and how you have weighted the sampling times to match to the weekly samples as well as possible or have you only compared monthly values. Also, inform if exactly same days were sampled for IMPROVE and CAPMoN networks. Remind readers that Aug 16, 2006 – Oct 24, 2008 24h-sampling had different sampling times in IMPROVE network than after that.
After this, you can continue with PSAP measurement, but maybe without any subtitle, which is confusing as you have compared PSAP results here. If subtitle is needed, maybe something about “comparability”
>> The corresponding paragraph is revised to include more information regarding how the comparison is done.

PSAP measurement need to be explain under the Sampling and Measurements chapter.
>> This is addressed.

Lines 272-276: Are these results and interpretation presented by Yang et al. or are they interpreted by the writers? Clarify.
>> The results (comparison between the integrated weekly and once every third day samples) are conclusions from Yang et al. This is clarified in the revised version.

Line 279-280: How have the correlation plot in Figure 3c done where weekly and every third day samples were compared? Are the third day samples averaged over 2-3 samples to cover the week samples or are they monthly averages? Clarify.
>> Results in Fig 3c represent the comparison between the two sets of monthly averages derived from the integrated weekly and once every third day samples. This is clarified in the revised version.

Vapor adsorption corrections
Line 284-286: Why monthly averaged results were presented and not daily? If I understood correctly, artifact correction was made for daily samples. I do understand that it is difficult to present data over long-time period, but clarify how the monthly averages have been calculated. Were artifact subtraction made individually for each sample, which were then averaged over month or calculated first monthly averages of OC and monthly average of gaseous OC and then subtracted. Specify here or in the beginning of the “Results and discussion” chapter.

>> For the CAPMoN measurements, artifact correction was applied to the 24-hour samples. Then the artifact corrected data were averaged over the month to get the monthly average. For downloaded IMPROVE measurements were already artifact corrected. Average vapor adsorption in a monthly basis was first determined from measurements from 13 sites (exclude Egbert). Then, such value was applied to all individual measurements before the monthly average is computed.

Monthly data is used here to assess the comparability among three networks. The original measurements from various networks have different sampling frequencies (every three day vs. weekly integrated) and it could cause complications. Thus, monthly averages are used to be consistent through the entire manuscript. In addition, monthly means are often considered as a reliable time resolution in comparisons between climate models and observations, due to the limitation of reported emission inventories (usually as annual values). Therefore, the analysis obtained here could be directly relevant to those comparisons . We have included a statement about how the measurements presented in this section were obtained.

Lines 285-286: Throughout the paper POC is discussed separately, although it is already included to OC. It is slightly confusing. If not presented/published before, I recommend that one section/paragraph is added where the contribution of POC (monthly averages) from TC for all protocols are presented and discussed. In addition, POC comparison between 24h TOT (Sunset-TOT) and TOR samples (IMPROVE_A TOR) and between DRI-TOR and IMPROVE_A TOR samples should be done. POC discussion, plots and statistics can be removed elsewhere in the Results and Discussion chapter.

>> POC from IMPROVE_A TOR and DRI-TOR are simply a charring correction and this analysis also show that it is always proportional to OC. On the other hand, ECT9 POC is not a charring correction but appear to represent a different class of organics, likely the oxygenated organics. For the ECT9 method, POC is considered as a separate carbonaceous fraction from the measured OC although reported as part of “total OC”. To a certain extent, the POC from various method were compared through the use of correlation coefficient.

Line 293-294: This sentence is quite loose if the readers have not information of the gaseous artefact of IMPROVE samples. Remove the information presented in lines 309-313 after the information of the CAPMoN samples (line 293). Explain to the readers what anchor IMPROVE sites are (Line 312). It may also be reasonable to remove the blank concentration discussion here after the gaseous artefact discussion.

>> The reason to include the artifact information for the IMPROVE samples is to verify the statement mentioned earlier that the lower filter face velocity of the CAPMoN measurements leads to higher filter artifact. We believe the content here provides readers a perspective of the relative magnitude of the artifact when dealing with the different measurements. Also, IMPROVE has changed their SOP and use blank correction to address the artifact correction for new measurements. Although this does not impact the measurements used in this manuscript, we thought it was a good idea to include such information. This paragraph is revised to avoid confusion. The filter blank concentration discussion is now removed.

Add field blank contribution for uncorrected OC values for all three networks. Now, only results of IMPROVE measurements were presented.

>> We decided to leave out the discussion of filter blank because this is not handled the same across different networks.

Line 296: add detection limit in the unit of ugC/cm2 in parentheses

>> This is addressed.

Line 299: Clarify, why vapor adsorption affects POC correction.
>> As seen in Figure 4 and Figure S2, the backup filter also possesses a small amount of POC and therefore artifact lowers the POC concentration slightly, however, the magnitude of the POC artifact has never come close to the artifact for OC.

Line 302: remove information in the parentheses (red open circles)
>> This is addressed.

Line 306: add reference after the sentence mentioned of POC to EC ratio. Correct also the mark EC/POC ratio as EC/POC already means a ratio of EC and POC. Discuss of the POC/EC using different protocols and their differences (shortly).
>> This is addressed. The authors did not intend to introduce another parameter (POC/EC). Although this was used in the reference Chen et al. (2004). What the authors intended to say here is that an optical correction using reflectance is a more consistent method than the optical correction using transmission under the situation when POC concentration is large compared to EC. We have revised the content here accordingly to avoid the confusion.

Figure 4: Rescale the y-axis for EC. Remove the POC plot as OC includes the POC.
>> Figure 4b has been rescaled. Although POC is part of OC (which is now mentioned in the text), the authors would like to retain Figure 4c in the text. This is to illustrate the point that although artifact influence the POC concentration and therefore impact EC concentration indirectly, the influence is small hand artifact affects only OC primarily.

Figure 5: In this plot, all data points (daily) can be easily presented instead of monthly (, if exactly the same days are sampled). Use daily data and add regression lines and equations for both data sets (DRI-TOR and Sunset-TOT). Use the same color for dots and line for DRI-TOR and another one for Sunset-TOT or color-coded the marks based on the time (or season) for DRI-TOR and Sunset-TOT. Use e.g. gray scale for Sunset-TOT and rainbow scale for DRI-TOR. If too messy, remove one of them to supplement (or make two plots). Also, specify why the linear regression should be go through the zero.
>> We have addressed this in the previous comment.

CAPMoN vs.IMPROVE measurements

Line 318: Instead of the used subtitle, could it be “comparison of daily sampling methods” or something which describes more illustratively what is compared, if the networks are not familiar for the readers.
>> The authors agree that this title may not be as appropriate. We have now combine the section “CAPMoN vs. IMPROVE measurements” and “CABM vs. IMPROVE measurements” to one paragraph titled “Comparison among IMPROVE, CAPMoN, and CABM Measurements”.

Lines 319-321: The discussion of summer peak should be removed to the chapter Seasonality in Carbon.
>> This is removed.

Lines 321-326: the correlation coefficients have been presented in the table 2, do not repeat the values in the text. Concise these lines e.g. better correlations of TC, EC and OC were found between the protocols that use same POC correction method (DRI-TOR and IMPROVE_A TOR) than between Sunset-TOT, which use transmittance for POC correction and IMPROVE_A TOR (Table 2). Especially correlation

of EC between Sunset-TOT and IMPROVE_A TOR was poor. Note, that Sunset-TOT and IMPROVE_A TOR had slightly different sampling time.
>> We accept the suggestion and this has been addressed.

Figure 6: CAPMoN time series have been already presented in Fig 4. Remove this figure and plot correlation plot between IMPROVE and CAPMoN 24h-measurements (, if exactly the same days are sampled) instead of monthly mean. Color-code the marks based on season/time/or something else.
>> Figure 4 was create to explain the gas adsorption artifact. The CAPMoN time series were also included in Figure 6 as a direct visual comparison with IMPROVE and CABM measurements. The reason why using monthly means throughout the entire paper has been addressed in the previous comment.

Lines 327-331 and Table 2: Clarify what kind of regression (linear, orthogonal) has been used. Prefer orthogonal. Clarify also, are the regression calculated from monthly mean values? Remove slopes, which are already presented in Table2. Explain why Regression 1 was used. Is it correct to force through the zero?
>> The information on the type of regression fit has been included. Fitted parameters are included in a few places just to provide a quick reference to the readers. Even though all fitted parameters are included in Table 2, having to look up values during reading can take some time. The choice of linear regression fit is totally subject to the reader what method the reader may prefer. Fitting the data through the zero is physically reasonable in many cases when we know an offset should not be present and the slope gives the best estimate of the relationship between the two sets of measurements. In some situations, a non-zero intercept may also make sense as it may be physically be explained by over or under correction, or having a systematic bias. That's why here we provide both sets of linear regression fit results so that readers can obtain the information they needed depending on what the reader may prefer to look for.

Lines 332-336: remove this paragraph to the new POC section.
>> We do not think a separate paragraph for POC is suitable. As the reviewer suggested, POC is part of OC and we prefer to include POC discussion with other carbonaceous measurements. In addition, POC is a charring correction under the IMPROVE or IMPROVE_A methods. The ECT9 POC however is not a charring correction. So we prefer not to directly compare the POC concentration from different protocol but just to point out their differences from the analysis.

CABM vs. IMPROVE measurements
Line 337: Change the subtitle e.g. Monthly comparison or something else
>> The subtitle has been removed as this section has been combined with the previous section.

As CABM measurements does not subtract the gaseous artefact, the writers may consider to plot figures 6 and 7 with uncorrected data.
>> The purpose of this analysis is to understand the difference in measurements among the various networks despite the unique differences in their sampling and analysis, which artifact correction is considered one of them. By plotting the CABM measurements with the uncorrected CAPMoN measurements will only provide the relationship between the two data set. But it does not provide the information how the CABM measurements are compared with other measurements.

Figure 6: remove 6a-c to Supplement and delete 6d. Modify Fig 6a-c so that common x-axis is used to save space. Refer also to Figure 7 that should be presented against (x-axis) to CABM network that has the different sampling time compared to other networks.

>> Although it seems that the CAPMoN results are being shown twice (in Figure 4 and 6), the presence of the CAPMoN data are for different objectives. In Figure 4 the data is shown for illustrating the magnitude of the gas adsorption artifact, whereas in Figure 6, we include the CAPMoN data for the completeness because that will give the reader a direct visual comparison of all the data from different network. We have considered the suggestion to modify the x-axis of these time series graphs to save space but the results were not ideal. We have adjusted the size of the graph and try our best to make the graph clear.

Line 340-341: after "comparable" should be present correlation coefficient. The percentage shows the similarity of the concentrations. Also, if it is said that concentrations are higher, the writers should said where to compare "higher than". Modify this sentence.
>> The word "comparable" is removed and the sentence is modified.

Lines 342-346: Again, I do not understand why both regressions are presented. Why fits are forced through the origin? I recommend to use only regression with intercept unless there is a clear reason for forcing through the zero. Again if comparative is used, there have to be the other party.
>> The type of linear regression fit to use is really subjected to the reader preference. The authors believe the regression fit results forcing through zero is a good start of the analysis assuming there is no systematic bias or offset among the various data sets. In a few cases, we also extend our analysis to discuss results when not forcing the fit through zero. Tables 2 and 4 summarize all the linear regression fit results by forcing through zero and allowing an intercept.

Lines 351-352: CABM network did not see any short-term variation as it has week-long sampling time. Anyway the Fig. S3 shows monthly mean values that is even longer time than week. Modify the sentence.
>> The sentence is modified. Short-term variations are replaced by seasonal variations.

Line 353-359: POC discussion should be remove to its own section/paragraph. In line 356, Table 3 has not been presented yet. Why not use table 2? Remove the regression discussion with forced intercept
>> Table 3 summarizes the correlation coefficients among different variables (e.g., OC, EC, TC, etc.) and results have been used in various locations although we may not have explicitly mentioned in the manuscript. There are more discussion of the results summarized in Table 3 in the "normalized time series" section. However, since we are removing the normalized data analysis section, we moved Table 3 to the supplementary information.

Comparison of the Normalized Time Series
I do not understand this chapter. Why the data should be normalized to Jan 2008 data? This can be removed or explained better the meaning of this chapter.
>> We have removed the normalized analysis section and recombine some of the analysis to the ordinary inter-comparison section. Because of this, Figure 8 and 9 are also removed from the manuscript.

Seasonality in Carbon
Although this chapter if very interesting, it is not part of the objective. To stay with the objective, it would be interesting to see how the gaseous artefact correction varies between the season/temperature for DRI-TOR, Sunset-TOT and IMPROVE_A TOR. The writers can use the Sigmoid function if wanted but concentrate on the contribution of gaseous artefact. Also comparison of TC, OC

and EC during different season between different networks is interesting. Is there any differences between different networks based on the season?
>> The authors think that the observed seasonality in carbon is an important observation that is result from the inter-comparison analysis. Therefore, the authors prefer to keep this section but has shorten it slightly. The authors have done separate analysis and it was observed that the POC from IMPROVE_A TOR and DRI-TOR are always proportional to the OC because POC defined in this protocol is a charred OC correction. Therefore, the seasonality observation for the IMPROVE_A TOR POC does not mean much as this, to certain extent, resemble the relationship seen in IMPROVE_A TOR OC. The ECT9 POC, however, is different because our analysis and past research have shown that ECT9 POC represents separate category of OC compounds and therefore the seasonality relationship of the ECT9 POC actually provide additional insight that do not provide by OC and EC observations.

In the beginning of the Results and Discussion, the writers can present general overview of the results (yearly concentrations of TC, OC and EC). In addition, wind roses and footprints, if wanted, can be presented shortly here and put the plots in the Supplement.
>> The authors have removed the majority content regarding the wind rose and transport model results to the supporting materials.

Conclusions:
Based on the modification and comments, modify this chapter. In addition
Line 443-444: the filter face velocity does not affect for the field blank concentration. Now the readers may get wrong message. Modify. Add also information of the other field blanks e.g. field blanks accounted xx-xx% (xx-xx ugC/cm2) of the measured OC.
>> The sentence is modified to avoid confusion.

Lines 445-446: I am not sure if this statement was proved in this manuscript, although true. Modify this sentence e.g. Start with the information that CABM network did not correct gaseous artefact and its OC has xx% higher concentration than with two other networks that had the correction done.
>> This is addressed.

Lines 446-448: I do not understand this statement or its purpose. Too long story and too much details (like values of r). Describe the contribution of POC of TC /OC.
>> This is addressed.

Lines 451-452: SRM 8785 samples demonstrate the consistency of the different protocols not long-term carbon measurements. Correct.
>> This is addressed.

Line 457: "North American harmonized carbonaceous concentration map" is new for me and may be to other readers. Clarify shortly
>> The authors apologize for the confusion. We have modified the sentence to better represent our true meaning.

Supplement:
Line 69-70. Actually internal signal is used to correct slight variation during each analysis. TC, OC and EC concentrations are calculated based on the calibration value calculated from external calibration.
>> The sentence is modified to improve clarity.

Correct. Line 79: There were no IMPROVE protocol. It was named to DRI-TOR and Sunset-TOT. Correct Table S1: Use the protocols names you have chosen to use (Sunset-TOT and DRI-TOR). First column IMPROVE_A TOR, second column both Sunset-TOT and DRI-TOR and third column ECT9
>> The name "IMPROVE" and "IMPROVE_A" are the original name of the two protocols. In this manuscript we have The paragraph has been modified to improve clarity. Table S1 has also been updated to avoid confusion.

FigureS1: protocol name IMPROVE has been used, although not mentioned in the manuscript. Either rename that or add to the manuscript that the temperature steps used in analyzing particulate carbon in CAPMoN network are called IMPROVE although different optical correction used.
>> Figure S1 captions and figure content have been modified to be consistent with the rest of the manuscript.

Table S1 and Figure S1: Replace IMPROVE_A to IMPROVE_A TOR
>> This is addressed.

Figure S3: Add information that results are monthly averages.

>> This is addressed.

Referee #2 comments:

Review of “Inter-comparison of the elemental and organic carbon mass measurements from three North American national long-term monitoring networks” by Chan et al. This paper summarizes collocated organic and elemental concentrations from three different types of analysis and sampling protocol. The results are useful in furthering our understanding of thermal optical analyses and resulting biases from sampling artifacts as well as temperature protocols. The paper is fairly well organized and written but could benefit from some clarification. I recommend publication after the authors address comments below.
>> The authors appreciate the useful comments and suggestions from the referee, and we address all the comments accordingly.

Line 1: The title, as well as some description in the text is somewhat misleading because it implies that large geographic scale comparisons are made when in fact the comparisons only exist at one site. Perhaps changing or including something regarding different analytical protocols would help clarify this point.
>> The authors have modified the title to reflect the fact that the inter-comparison was done in one “co-located” site. Corresponding sections, including abstract and introduction have also been modified to reflect this information.

Line 23: Please state years.
>> This coverage information (2005-2015) has been included.

Line 23-26: Again, similar to the title, point out that collocated samplers only exist at one site, so really what is being compared here are the impacts from different sampling and analytical protocols, not a large scale geographic comparison.
>> This is addressed.

Line 29: More on this later, but I don’t understand the value of the normalized comparison. The agreement depends on what you have normalized each time series to. Over what time periods where these comparisons made?
>> In the original study, each time series is normalized to its corresponding concentration measured on Jan 2008. This converts all concentration time series to a percentage change with respect to the measured concentration on Jan 2008. The comparisons for normalized concentration were made from 2008 to 2015.

After some consideration and discussions among the co-authors, we agree to remove the normalized comparison section and focus on the comparison on the absolute data.

Line 35: Is there any evidence for linkages to forest fire emissions and increased vehicular emissions? Did the authors include analysis of these emissions or is this conjecture?
>> Due to the length limit, it is not possible to include all the analyses in this manuscript. A separate analysis that involved the investigation of the 10 years BC emission trends at a number of CABM sites, including a boreal forest site, has suggested that the elevated BC emissions during summer at Egbert could be contributed by the forest fire emissions. The analysis is still currently on going and the full results is expected to be given in a separate manuscript.

Line 36-37: This may be true depending on artifact corrections and how they are applied across a network.

>> The abstract has been modified and this does not apply anymore as the original sentence was removed.

Line 38: Again, extrapolating data and comparisons from one site to "regional to continental-scale-harmonized maps" hasn't been shown here and may not necessarily be true, especially given different sampling times and sources.
>> The main idea of mentioning a "regional to continental-scale concentration map" is trying to express the effort of evaluating the consistency and compatibility from difference datasets by different networks when using atmospheric OC and EC measurements to constrain their emission changes at regional and continental scales. The "regional to continental-scale concentration map" is not proper and concise expression. It has been removed from the revised version.

The authors have included additional text in the introduction of the revised manuscript to explain the rational accordingly.

Line 23-41: I think it would be helpful if the abstract more closely reflected the comparison work rather than sources which was a rather minor part of the work and mostly based on previously published work (e.g., secondary aerosol formation in summer, smoke in summer, higher OC and EC in summer, etc.).
>> The abstract has been modified.

Line 52: OC can also absorb solar radiation.
>> The word "primarily" is now added.

Line 52,53,56,57: I would suggest using either BC or EC and keeping the same nomen-clature throughout the paper, unless the authors are actually referring to different measurements, then clarify and define.
>> BC and EC share lots of similarity in describing the physical appearance of the aerosol. In some cases, the word BC and EC can be inter-changed but not in all. We do not agree that all the term "BC" in the manuscript can be replaced by "EC" without changing the original meaning. The usage of BC and EC has been addressed in "introduction" of the revised version, and the authors have clearly defined the definition according to Petzold et al (2013).

Line 58: Include "impacts of" changing emissions since OC and EC measurements don't directly determine emissions.
>> This is addressed.

Line 61: The first sentence is unclear. Wouldn't long term measurements just depend on making the same measurement over time and doesn't really depend on a universal definition?
>> In fact, it is challenging to make ambient BC measurements. The word "long-term" is used in this manuscript because the main focus of this work is on long-term measurements. The corresponding sentence has been modified to avoid confusion.

Line 67: The sentence starting with "BC is a generic term" would be a better starting sentence for this paragraph and the authors could remove the current first sentence.
>> This is addressed.

Line 71: Replace "being" with "is"
>> This is addressed.

Line 72: Include “as” after “EC is referred to”
>> This is addressed.

Line 75: Can the authors clarify what they mean by “EC and BC resembled each other”?
>> We meant the trends in long-term time series of EC and BC concentration resembled each other. The sentence is now revised.

Line 80: I am not sure what the authors mean by “direct measurement of carbon mass as part of gravimetric mass”?
>> We meant the carbon mass measured by TOA or TEA is part of the particulate matter mass. This sentence is revised.

Line 97: I’m not sure what is meant by “resulting EC method”?
>> This sentence is revised.

Line 111: Can the authors provide a reference for the OC overestimation?
>> A reference is added.

Line 120: The acronyms for the various networks should be spelled out at first usage.
>> The acronyms of the three networks were first spelled out in the abstract. They are spelled out again in the revised version when it first appear after the abstract.

Line 122: Again, this is somewhat misleading. Add that these collocated measurements occurred at one site.
>> This is addressed.

Line 123: I might have missed this later, but what are the solutions for improving the compatibility?
>> The authors thank the referee for pointing this out and the word “solution” should not be used in here. Instead, the authors have replaced this by “suggestions”. Based on the current work, two suggestions are: (1) ensure maintaining the same SOP for sampling and analytical procedure for any lab to ensure internal consistency, (2) to establish or include the use of a reference material or calibration materials (as suggested by World Meteorological Organization scientific advisory group) during the inter-comparison study. These information has now be included in the revised manuscript.

Line 124: I am not sure the results from one site have been demonstrated to create a regional and continental scale harmonized carbon concentration data set.
>> The authors realized we may not be expressing ourselves clearly and led to misunderstanding. The abstract has now been modified to remove those sentences. The corresponding content in the introduction has also been modified to clearly express our meaning when we meant to create a combined data set.

Line 138: What is meant by “regional-scale monitors”? Do the authors mean that many samplers operate across the United States?
>> We refer this to regional-scale monitoring stations. This is corrected in the revised version.

Line 139: replace “understanding long-range transport” with “understanding long-term trends”.
>> This is addressed.

Line 139-140: I suggest replacing the Malm 1989 reference with the Malm 1994 reference (Malm, W. C., J. F. Sisler, D. Huffman, R. A. Eldred, and T. A. Cahill (1994), Spatial and seasonal trends in particle concentration and optical extinction in the United States, J. Geophys. Res., 99(D1), 1347-1370)
>> This reference is added.

Line 143-144: The IMPROVE samplers typically sample midnight to midnight, was the sampler at Egbert running on a different schedule?
>> Yes, the IMPROVE samplers at Egbert was run on a different schedule and this has been confirmed by DRI.

Line 148: Are the filters shipped cold?
>> Yes, they are shipped in coolers with ice pack.

Line 155: Spell out CAPMoN.
>> This is addressed.

Line 159: Do the measurements include carbon at all of these sites as well?
>> Historically there have been a number of sites that carry carbon analysis. However, they have been slowly shut down and Egbert is the only site with the longest collection history. This information is included in the revised version.

Line 176: Also see Malm et al. (2001) for a discussion of sampling biases on OC and EC concentrations (Malm, W. C., B. A. Schichtel, and M. L. Pitchford (2011), Uncertainties in PM2.5 gravimetric and speciation measurements and what we can learn from them, J. Air & Waste Manage. Assoc., 61, 1131-1149, doi:10.1080/10473289.2011.603998.)
>> The reference Malm et al., 2011 is now included.

Line 179: Spell ECCC- Also, please choose notation, either CABM or ECCC. Both are used interchangeably throughout the paper and it is confusing.
>> ECCC is removed from the subtitle.

Line 184: replace “costal” with “coastal”
>> This is addressed.

Line 207: replace “measurements is” with “measurements are”
>> This is addressed.

Line 211: Include “an” between “uses” and “impactor”
>> This is addressed.

Line 212: Replace “Impactor” with “Impactors”
>> This is addressed.

Line 218-222: See the Malm et al., 2011 paper mentioned earlier.
>> The reference Malm et al., 2011 is now included.

Line 228: Can the authors provide some references for the multiple studies?
>> References are now included.

Line 232: Change “introduce” to “introduces”

>> This is addressed.

Line 236: I think you can remove “SRM 8785 & 1649a” from the section header.
>> This is addressed.

Line 246: No correlations are given in Figure 1. Also include figure parts in the text and include OC.
>> Correlations are now included in the figure as well as the text.

Line 248-9: Need figure parts for Figure 2 in the text too (e.g., Figure 2(a)-(d) shows TC, EC, OC, and EC/TC, respectively)
>> This is addressed.

Line 249-250: It is unclear what the authors mean by “Irrespective of data disparity”?
>> This is now removed.

Line 270: I am not sure this is clear: Do the authors just resample the high resolution data for different averaging times? When they say different data sets do they mean the same measurement just with different averaging times? Wouldn’t you expect these to compare well? Or do they compare EC to the PSAP measurement? The figures have units of Mm-1, so it suggests that they either converted EC to absorption coefficient (if so, what absorption efficiency was used?). Please clarify, including figure caption 3 when “comparison of different sets of measurements” from (c) because it is misleading.
>> In this section, we use the 1 min resolution PSAP data (measuring aerosol absorption, assumed dominantly by BC) as a common data set. We then average this data set to the once every third day resolution to simulate IMPROVE and CAPMoN data. We also average the 1 min PSAP data to weekly integrated values to simulate the CABM data. The reason we do not directly compare IMPROVE or CAPMoN data with CABM is because these measurements were not in same sampling frequency and therefore when converting these data to monthly averages, there is no way to know if any difference in monthly means was caused by the natural data variations in the original measurements or it was due to the difference in sampling frequency (it could be caused by both factors). In addition, this analysis was done by Yang et al (2011) and therefore it is not repeated in this manuscript. To ensure no obvious bias caused by the difference in sampling frequency, two different monthly means of PSAP (by every three days vs. by weekly integrated) are directly compared. We have clarify the paragraph in the revised version.

Line 255: Which EC/TC value was further verified? Also, replace “sample” with “samples”
>> In Figure 2d (the original Figure 1d), the three blue bars represent the EC/TC ratio reported by the certificate and also determined from the inter-comparison from the TEA and TOA methods. The green bar represent the EC/TC value calculated from an independent method based on carbon isotope. Here we mean to verify the EC/TC values determined from the TEA/TOA method by carbon isotope method.

Line 283: Over what time period?
>> This is addressed.

Line 288: Can the authors comment on the offset (nonzero intercept) and what it implies in terms of sampling artifacts or biases?
>> A linear regression fit forcing through the origin was applied to Figure 5. The authors believe a fit through zero makes more sense because any non-zero intercept would imply that the

artifact correction obtained from the backup filter was either too much or not enough compared to the actual artifact. The fact that the intercepts were insignificant suggests this is a reasonable assumption and the artifact correction was reasonable.

Line 298: Yes, the POC correction directly influences EC concentrations. Can the authors comment on this vapor adsorption issue with respect to the PSAP weekly comparisons?
>> PSAP in an in-situ instrument that continuously measures the changes in the amount of light transmitted through a quartz filter when particles are deposited onto the filter inside the PSAP. Even though filter media is involved in PSAP measurements, vapor adsorption is not expected to be an issue for PSAP measurements because there is no heating involved, so the adsorbed materials do not char and contribute to absorption.

Line 303: Add a period and start "An optical correction" as a new sentence.
>> This is addressed.

Line 317: Include "monthly mean" before DRI-TOR CAPMon measurements and "comparable to the concentrations derived from the IMPROVE_A: : :."
>> This is addressed.

Line 320: What are considered "good correlations"?
>> We consider measurements with correlations above 0.8 to be a good correlation.

Line 351-352: Can the authors describe Figures 7a-c before 7d to keep them in order?
>> This is addressed.

Line 355: At what level of significance?
>> Here the significant correlation is a relative comparison based on the correlation coefficient. We have corrected the wording in the sentence to avoid confusion.

Line 358: I am not convinced the normalized analysis is necessary and adds to the paper. The comparisons between samplers would change depending on what the data are normalized to (choose a different month or an annual mean for example). The comparisons already discussed are more useful because they show the true biases. The diurnal wind cycles on the timelines could be added to the earlier timelines if the authors want to include that analysis.
>> We agree with the referee and we have removed the normalized analysis section and combine some of the information into the section where inter-comparison of the absolute measurements. Because of this, Figure 8 and 9 are now removed from the manuscript.

Line 393: I think elevated carbon concentrations in summer are better shown in Figure 6 given the averaging times.
>> We have modified the sentence to reference this.

Line 413: When are the concentration in the N and NW higher?
>> For OC, elevated concentration could occur during SOA formation when air mass is originated from the N and NW. For EC, elevated concentration could potentially be related to forest fire emissions although more research is needed to verify this.

Line 414: Do the authors mean residential instead of residual?
>> Thank you, and this is addressed.

Line 431: How appropriate is the comparison with ECT9 POC since this is a nonlinear relationship?
>> The authors do not totally understand this comment. However, the corresponding text has been revised to avoid confusion.

Line 447: Also include longer sampling time.
>> This is addressed.

Line 452: What are typical measurement uncertainties? Are these greater?
>> Typical uncertainties could be about 15% for individual OC and EC measurements. The monthly averages should be higher than 20%.

Line 452: Note that others have performed similar comparisons across networks (CSN and IMPROVE) for continental scale integration. Biases for both OC and EC between networks were less than 10% (similar sampling and analytical procedures). Hand, J. L., B. A. Schichtel, M. Pitchford, W. C. Malm, and N. H. Frank (2012a), Seasonal composi-tion of remote and urban fine particulate matter in the United States, J. Geophys. Res., 117, D05209, doi:10.1029/2011JD017122. Hand, J. L., B. A. Schichtel, W. C. Malm, and N. H. Frank (2013), Spatial and temporal trends in PM2.5 organic and elemental carbon across the United States, Advances in Meteor., 2013, Article ID 367674.
>> The reference has been included accordingly.

Line 504: This link did not work, it needs to be updated: http://vista.cira.colostate.edu/Improve/improve-data/
>> The authors cannot locate the above link. We believe there was a mistake for not copying the proper link. The authors have checked the link (http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm) in the acknowledgement section and ensure it is working.

Line 699: Table 1. Can the authors clarify: Is "IMPROVE" under CAPMoN consistent with lines 170-171 that lists IMPROVE-TOT for 2005-2007 and IMPROVE_TOR protocol? It is challenging to keep these different protocols straight and so careful attention to how they are referred to in the paper and the tables would help.
>> The authors understand the concern from the referee. We have modified the names of the protocols throughout the paper to ensure they are consistent.

Line 702: Table 2: Similar comment, here it is referred to as "Sunset-TOT". The number of significant digits included in this table seem unnecessary.
>> The protocol name has been verified to be consistent with other parts of the manuscript. We keep the additional significant digits to ensure no round off error when those information will be used by the readers.

Line 710, 713: I don't think these tables are necessary, see earlier comment.
>> This table has now been removed from the main paper and be included in the supplementary information.

Line 718: Figure 1: Again, please be consistent with ECCC and CABM
>> CABM (Canadian Aerosol Basement Measurement) is our network name whereas ECCC (Environment and Climate Change Canada) is our institution name. We believe ECCC is more appropriate in Figure 1 (now become Figure 2) caption.

Line 725: Figure 2, Same comment as previous figure. What is ICP? Please relate x-axis labels to the caption description.
>> This is addressed.

Line 732: Figure 3: See earlier comment- this comparisons is unclear.
>> The corresponding paragraphs have been modified to provide additional information to explain these figures.

Line 740: Figure 4: It would help to see the comparisons in (b) and (c) if the scales were reduced. Again, note the data description in the figures do not match the discussions or tables (e.g., “Sunset-TOT”)
>> We have modified the names of the protocols throughout the paper to ensure they are consistent with the description in the Figure caption.

Line 757: Figure 6: Please include location in this figure caption so it is clear that the three different networks are collocated at one site.
>> This is addressed.

Line 766: Figure 7: Which “IMPROVE” are the comparisons made against? Please be clear in the caption to match the axis labels.
>> This is addressed.

Figures 8 and 9: Are unnecessary and do not lend to a better understanding of the comparisons.
>> These figures are now removed.