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Organic and Elemental Carbon Aerosol Particulates at the Southern Great Plains Site Field Campaign Report

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Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement Climate Research Facility
CST	Central Standard Time
DOE	U.S. Department of Energy
EC	elemental carbon
EPA	Environmental Protection Agency
ft	foot
m	meter
nm	nanometer
OC	organic carbon
SGP	Southern Great Plains, an ARM megasite
TC	total carbon
UTC	Coordinated Universal Time

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1.0 Introduction

The purpose of this study was to measure the organic carbon (OC) and elemental carbon (EC) fractions of PM_{2.5} particulate matter at the U.S. Department of Energy (DOE)'s Atmospheric Radiation Measurement (ARM) Climate Research Facility Southern Great Plains (SGP) sampling site for a 6-month period during the summer of 2013. The site is in a rural location remote from any populated areas, so it would be expected to reflect carbon concentration over long-distance transport patterns. During the same period in 2012, a number of prairie fires in Oklahoma and Texas had produced large plumes of smoke particles, but OC and EC particles had not been quantified. In addition, during the summer months, other wild fires, such as forest fires in the Rocky Mountain states and other areas, can produce carbon aerosols that are transported over long distances. Both of these source types would be expected to contain mixtures of both OC and EC.

During the summer months, secondary organic aerosols also are produced that contribute to OC concentrations. If secondary organic aerosols were the exclusive source of particulate carbonaceous material, then only the OC fraction would be detected. If secondary organic aerosols were produced in air that already contained OC/EC mixtures, the EC/total carbon (TC) ratio within the mixture would decrease. In addition, the diurnal patterns of nighttime cooling could allow partitioning of gaseous OC vapors to the particulate phase, which also could modify EC/TC ratios.

2.0 Instrumentation and Method

The instrument used was a Model 4 Sunset Laboratory Semi-Continuous Organic Carbon/Elemental Carbon aerosol analyzer. This instrument has been tested as part of the U.S. Environmental Protection Agency (EPA)'s Environmental Technology Verification program for precision of multiple units, as well as comparison with the standard filter method (<http://www.epa.gov/etv/vt-ams.html#bcm>)

Because the actual concentrations were expected to be low, the instrument was operated on 2-hour cycles instead of the normal 1-hour cycle. For long-range transport, this was expected to provide sufficient resolution. The analysis method used on the collected samples was a modified NIOSH5040 method, which produces a result for OC and EC using the Thermal/Optical Method (referred to as "ThermOC" and "ThermEC"). This method generally has a detection limit on the order of 0.4 to 0.5 $\mu\text{gC}/\text{m}^3$ for the ThermEC as well as for TC obtained from a non-dispersive infrared detector. In addition to the above, the NIOSH5040 method of determining EC (ThermEC), an optically derived value for EC can also be obtained by monitoring the change of transmission of the 658-nm laser diode during sample collection on the filter. This technique is known as "OptEC."

Because the levels of EC were expected to be low, OptEC was the method used to measure EC in this study. The OpEC method has been found to be almost as accurate (i.e., within $\pm 10\%$) of the Thermal/Optical EC (ThermEC), and its limits of detection and precision are much better, being $< 0.1 \mu\text{gC}/\text{m}^3$ for a 2-hour cycle.

To obtain the OC values, the OptEC value is then subtracted from the TC measured by the non-dispersive infrared detector. This allows for an OC detection limit in the 0.2 to 0.3 $\mu\text{gC}/\text{m}^3$ range for the 2-hour cycles.

In addition to the 2-hour sampling/analysis of ambient air, an instrument blank was performed once per day for quality assurance purposes. An internal standard composed of a fixed-volume of 5% methane was used by the instrument with each cycle. This not only serves as an internal standard for quantification of the carbon collected, but also served as quality assurance for operation of the system during the duration of the program.

Several gases were needed to operate and calibrate the instrument. The size of cylinders used (i.e., 80 ft³) was sufficient for the entire project so no changing or maintenance was needed. The only routine maintenance required was changing the internal quartz fiber filter approximately once every two or three weeks. This maintenance was done by onsite technicians who were trained during initial installation of the instrument. The operational computer was connected to the Internet so remote checks could be made periodically on the operation of the instrument and data could be downloaded for review (see Figure 1).



Figure 1. Operational computer for the carbon sampling system at the Southern Great Plains site.

3.0 Sampling Site Description

The ARM SGP site is located approximately 7 miles southeast of Lamont, Oklahoma. The building in which the OC/EC aerosol analyzer was installed was the Guest Instrument Facilities, which is located about 310 meters to the southeast of the main offices at the site.

A sampling inlet made of $\frac{3}{8}$ -inch clean stainless steel tubing was installed so that, after exiting the side of the building at about 1.5 meters above ground level, it made a 90-degree bend vertically for a total distance of about 5 meters above the ground and about 2 meters above the roof of the building. The pipe was then secured to a metal platform. A PM_{2.5} cyclone was then added to the top of this sampling tube (see Figure 2).



Figure 2. Inlet tubing for carbon sampling at the SGP site. The PM_{2.5} input cyclone is installed at the top end of the tubing.

4.0 Sampling and Analysis Protocols

Sampling was done using a 2-hour cycle with the start of collection at the beginning of each even hour using Coordinated Universal Time (UTC). Ambient air then was sampled for 105 minutes. At the end of the sampling period, the pumps were shut off, the oven was sealed and purged of air, and the analysis was performed. This analysis period typically took about 12 minutes, which was sufficient time for the clean oven/filter to cool before the start of the next sampling cycle.

5.0 Quality Assurance Protocols

Initial calibration of the instrument for TC was done using externally applied organic carbon standards (i.e., sucrose), thereby ensuring that the internal 5% methane standard was quantified properly. During the length of the study, this internal standard was injected with each analysis cycle and served as an internal standard as well as quality assurance for proper operation of the instrument.

The instrument also recorded ambient temperature and pressure. These parameters had been calibrated at the factory as originally set up, but no check was made at the SGP site.

6.0 Results

N.B. Although all times were recorded as UTC and reported as such with the original data set, the times used in this report have been corrected to Central Standard Time (CST = UTC minus 6 hours) to more easily compare local events with possible local work schedules and diurnal daily cycles.

The length of the study from initial start until final shutdown was 176 days, 14 hours. With 2-hour cycles, this would potentially be a total of 2119 cycles. During 21 cycles, no data was collected for the following reasons: 6 due to filter changes; three due to poor internal calibration peak performance; and 12 due to skipped cycles consistent with slow cooling of the oven during very hot weather. The latter 12 missed cycles occurred during a 5-day period in July (i.e., July 16 to 21), and it was noted that there was a rapid increase and decrease of atmospheric pressure during this time, which may have had some effects that could explain the reason. Thus, the instrument provided data for 2098 of the potential 2119 cycle periods.

Analysis of instrument blanks consisted of 176 samples analyzed at 00:00 Universal Decimal Time (18:00 CST) each day. The results of these were an average TC instrument blank of 0.103 μgC with a standard deviation of 0.0705 μgC . Taking into account the 2-hour cycling period consisted of 0.86 m^3 of air, this would then be an instrument blank of 0.12 $\mu\text{gC}/\text{m}^3$ and standard deviation of 0.08 $\mu\text{gC}/\text{m}^3$. Because this value is low compared to the TC of this study (typically 2 to 5 $\mu\text{gC}/\text{m}^3$), this value was not subtracted from the reported results.

The OC values were generally in the range of 1 to 5 $\mu\text{gC}/\text{m}^3$ and the EC values were usually in the range of 0.1 to 0.4 $\mu\text{gC}/\text{m}^3$. These values are low compared with most urban areas of the United States, which typically are in the range of 3 to 20 $\mu\text{gC}/\text{m}^3$ range for OC and 1 to 8 $\mu\text{gC}/\text{m}^3$ for EC. The results for

the study can be seen in Figure 3 for both OC and EC; Figure 4 presents only the OC values; and Figure 5 presents only the EC values. Figure 6 shows data for both OC and EC and also the EC/TC ratio. It should be noted that anytime the EC/TC ratio is computed with values of OC and EC near the detection limit, this ratio will have more noticeable noise and uncertainty.

The ambient temperature and pressure for the period are provided in Figure 7 for the entire study. Figure 8 provides data for a 3-week period showing variations of daily temperatures as well as longer-term variations during this period.

Sampling was done at a constant flow rate determined by a mass-flow sensor using a VSO[®] control valve. The volume collected is 0.86 m³ except for a slightly shorter collection cycle following each instrument blank analysis, which is 0.74 m³. By incorporating the ambient pressure and temperature, the measured standard temperature and pressure volumes are corrected and reported in units of local-condition actual volume.

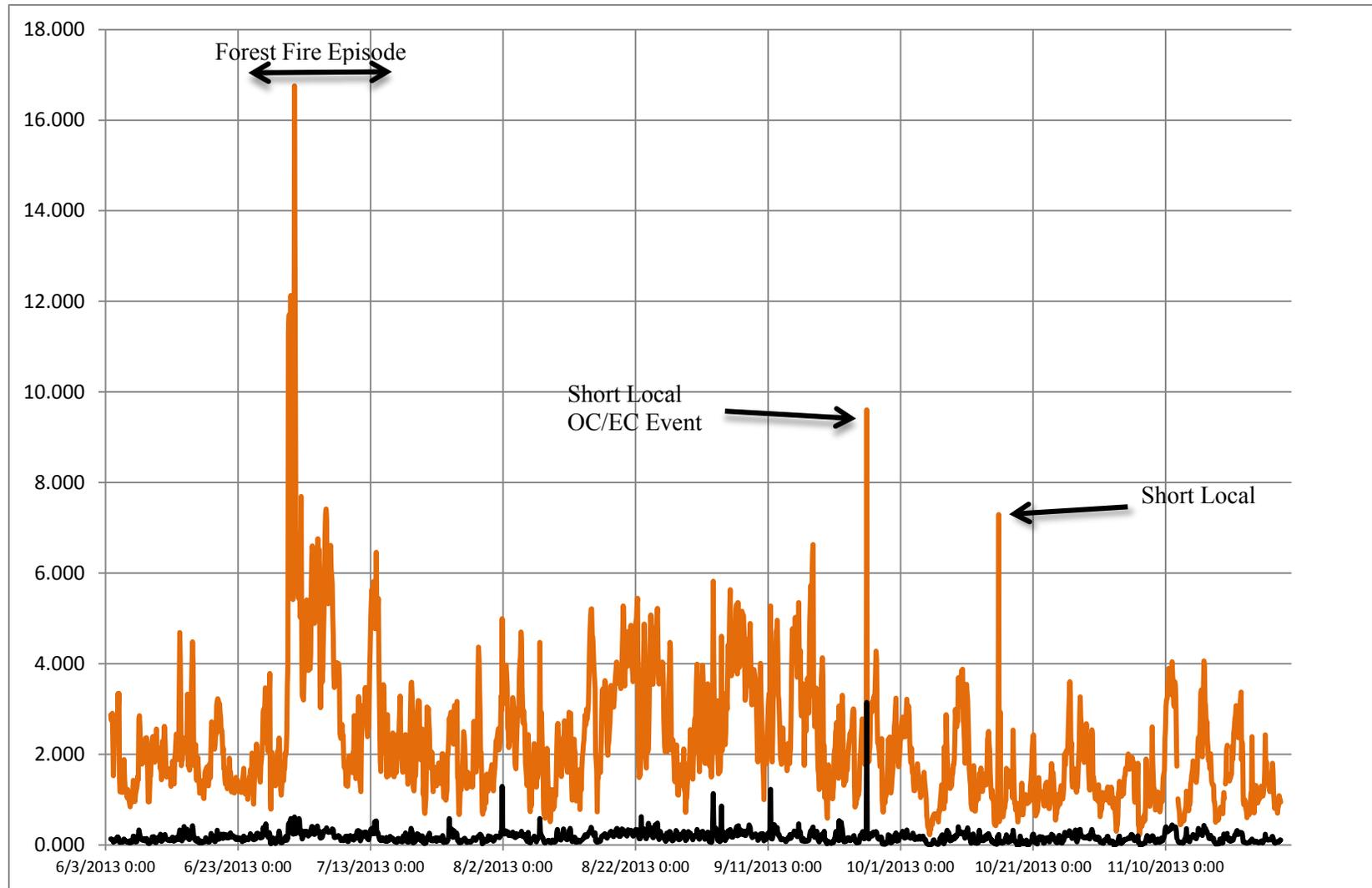


Figure 3. Data from full 6-month project (organic carbon [orange], elemental carbon [black], $\mu\text{gC}/\text{m}^3$).

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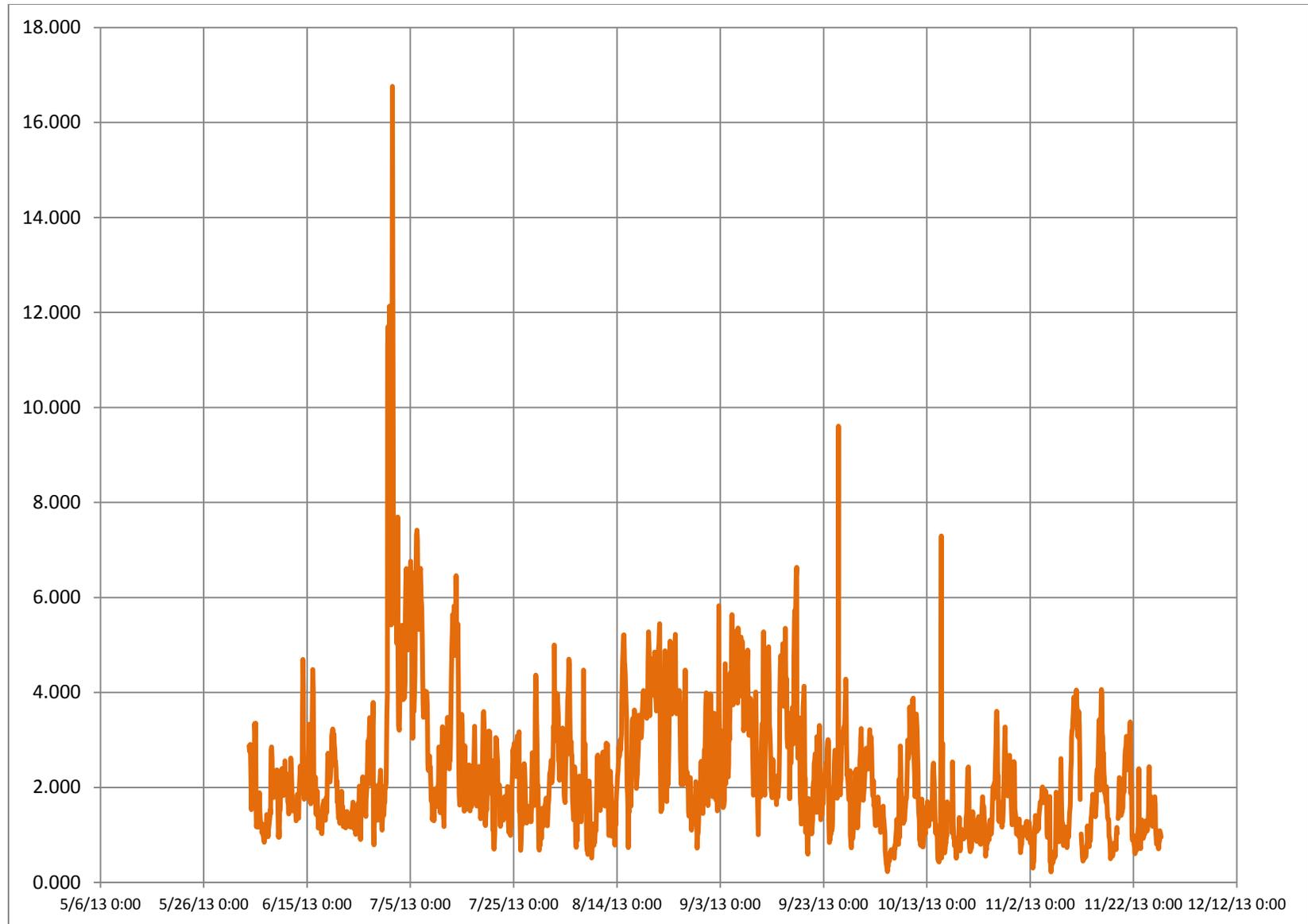


Figure 4. Organic carbon data for the entire project period ($\mu\text{gC}/\text{m}^3$).

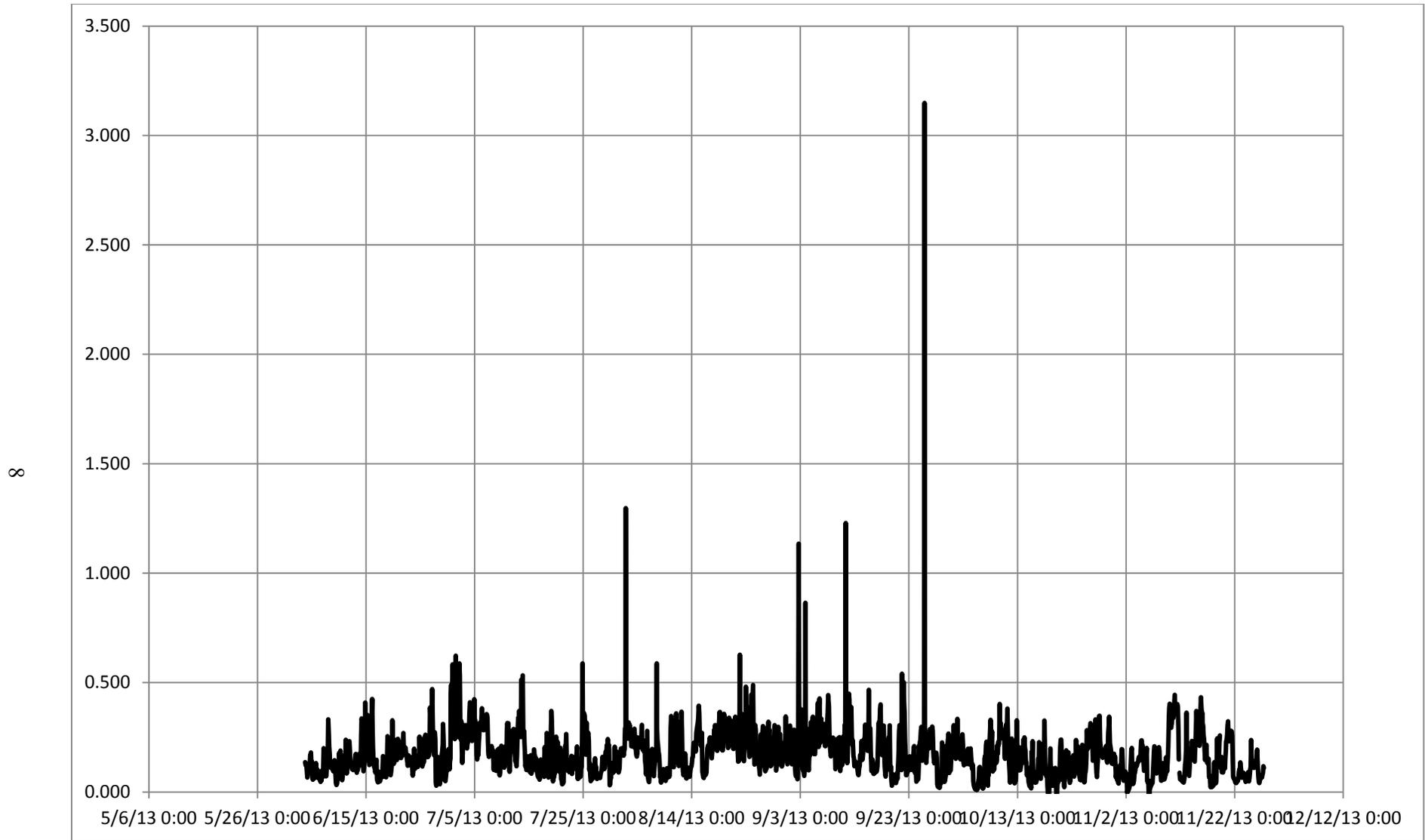


Figure 5. Elemental carbon data for the entire project period ($\mu\text{gC}/\text{m}^3$).

6

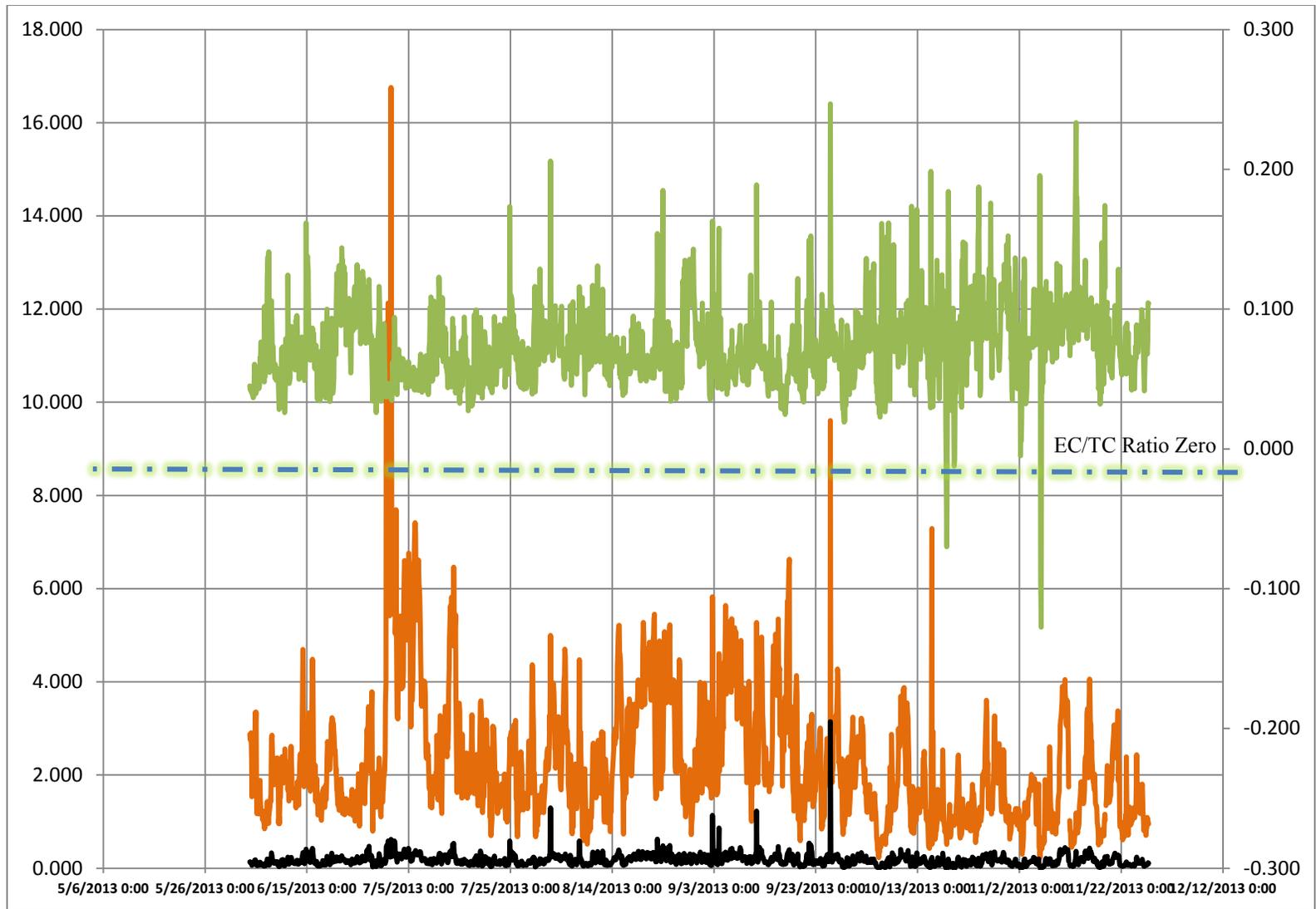


Figure 6. Organic carbon (orange line, left axis), elemental carbon (black line, left axis), elemental carbon to total carbon ratios (green line, right axis).

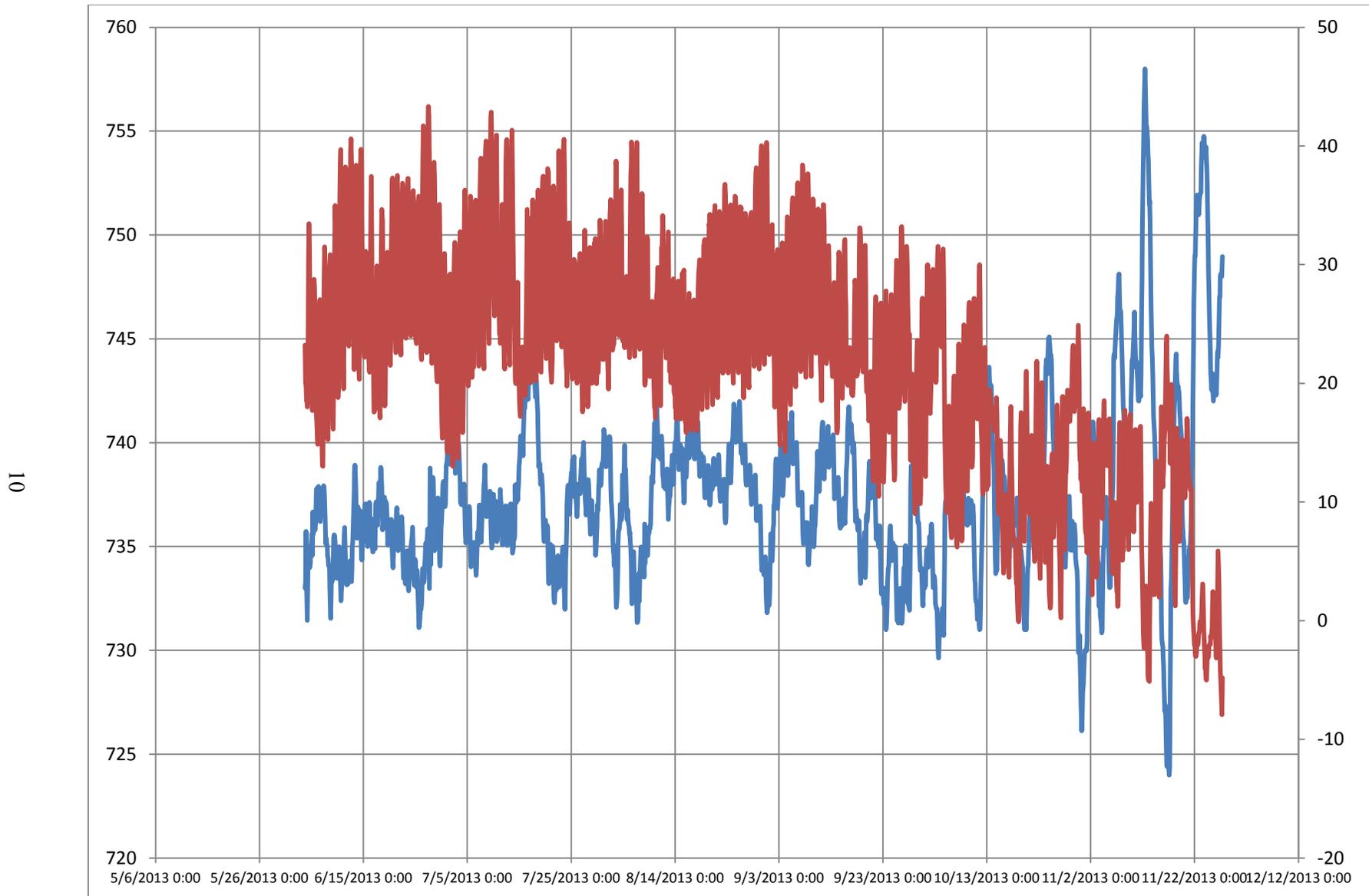


Figure 7. Atmospheric pressure (blue line, torr) and temperature (red line, °C) for the full sampling period.

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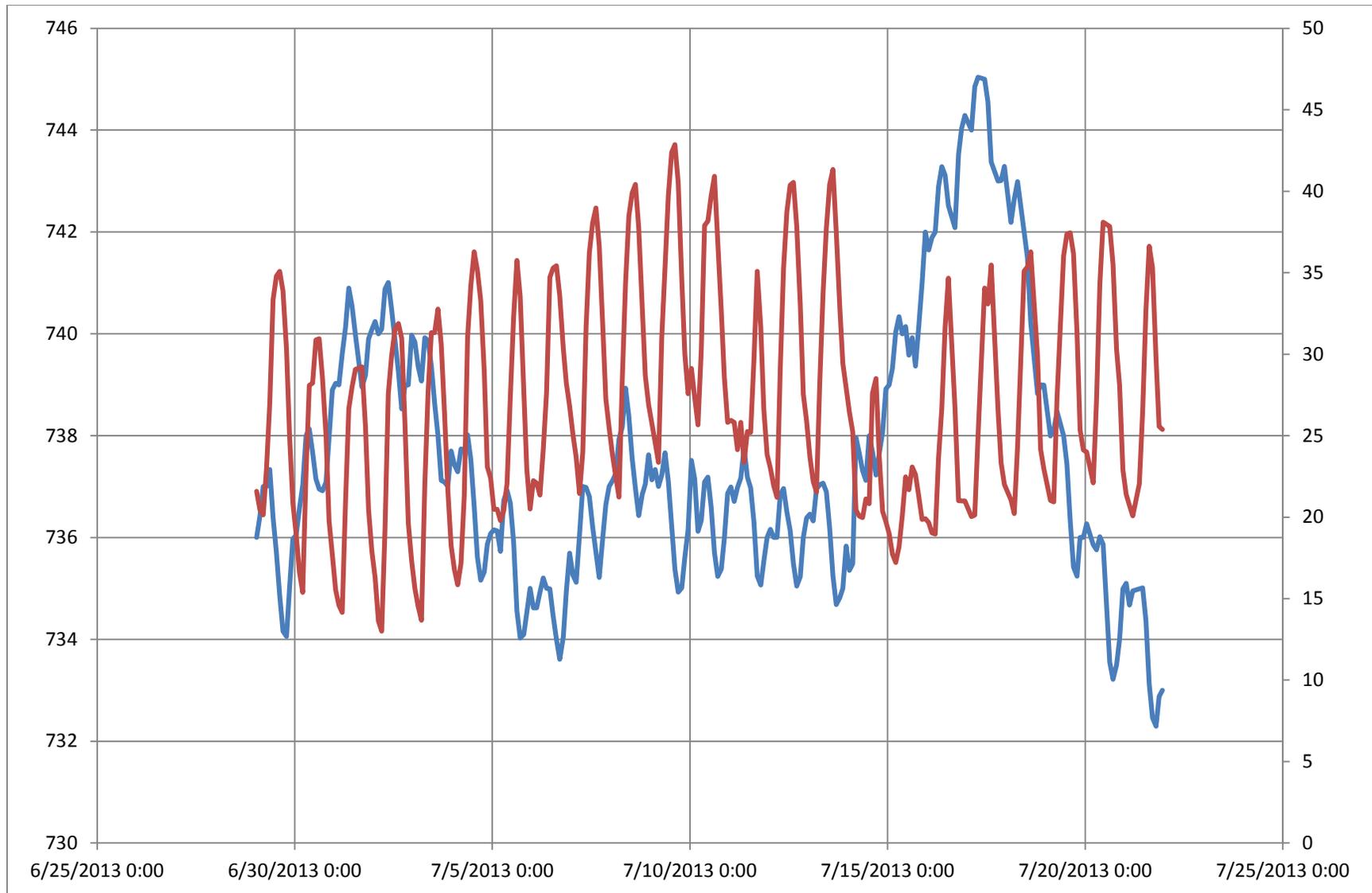


Figure 8. Atmospheric pressure (blue line, torr) and temperature (red line, °C) for the late June to late July sampling period.

7.0 Discussion

The OC, EC, and EC/TC ratios for the entire study are plotted in Figure 3, Figure 4, Figure 5, and Figure 6. Figure 7 and Figure 8 show the measured ambient temperatures and pressures. A small number of episodes are discussed below as well as in the accompanying figures. A complete discussion and understanding of these results would not only take into account the ambient temperatures and pressures, which were measured as part of this instrument, but also other meteorological conditions such as wind speed and direction.

There are some minor episodes that can be easily seen, as well as one moderate episode. Several of these episodes are quite short, on the scale of a few hours; and some are longer, over a week or more. The short episodes usually could be traced to extremely local sources, perhaps less than a few hundred meters, due to local activities. The longer episodes are explained by longer-range transport of events that happen many hundreds of kilometers away.

In addition to the variations shown in the previous figures, there are also obvious daily variations that can be explained by expansions and contractions of the day/night mixing layer. These can usually be noted, but are not always present because of meteorological conditions such as wind speed, which was not considered in this study.

Data for OC and EC, both in units of micrograms carbon per cubic meter and in **local CST**, are shown in the following figures. Several short periods that also contain the EC/TC ratio values are included. In addition, local ambient temperatures and pressures are shown.

7.1 Forest Fire Episode Plume: June 29 through July 14, 2013

There is an obvious episode that began around June 29, 2013, and lasted for nearly 2 weeks. This episode could be seen on photos of the GEOS-East satellite as a plume from several forest fires in Colorado. These fires produced an obvious plume that circulated in a clockwise direction as it moved east through the central states. It is likely the fires were part of either the West Fork Complex or the East Peak Fire in south-central Colorado during late June to early July 2013. See Figure 9, Figure 10, and Figure 11 for more details.

7.2 Short Local Event Plume

Data obtained during a local event can be seen in Figure 12, Figure 13, and Figure 14. This event occurred over only one of the two-hour sampling cycles from 20:00 to 21:45 in the evening. It can be seen that, for the previous several days, the EC/TC ratio had been in the 5 to 10% range; however, for this one cycle, the EC/TC ratio increased to 25%. Figure 15 shows the results for EC obtained at 1-minute intervals, showing two sharp plumes that occurred over a 20-to-25-minute period.

7.3 Two-Week OC/EC Buildup with Diurnal Cycles

Figure 16, Figure 17, and Figure 18 show a 16-day period during a hot period in August 2013. The OC measured during this period may be due to production of secondary organics that slowly increase in concentration. The strong diurnal cycle of EC and, to a lesser extent the EC/TC ratio, should be noted.

Figure 19 shows the ratios of elemental carbon and elemental carbon to total carbon over a one-week period in August 2013.

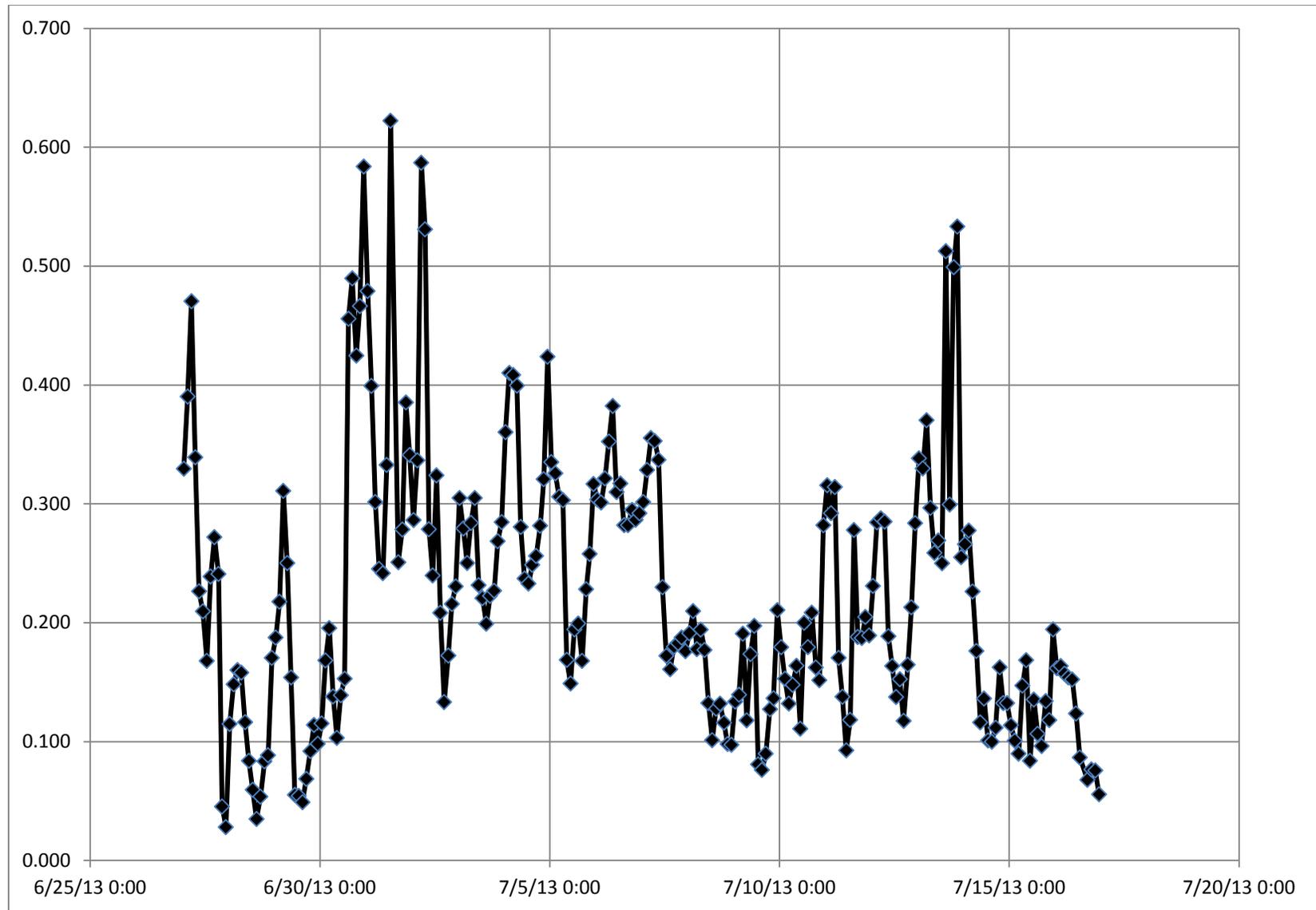


Figure 10. Elemental carbon data for the June-July 2013 forest fire episode ($\mu\text{gC/LCm}^3$).

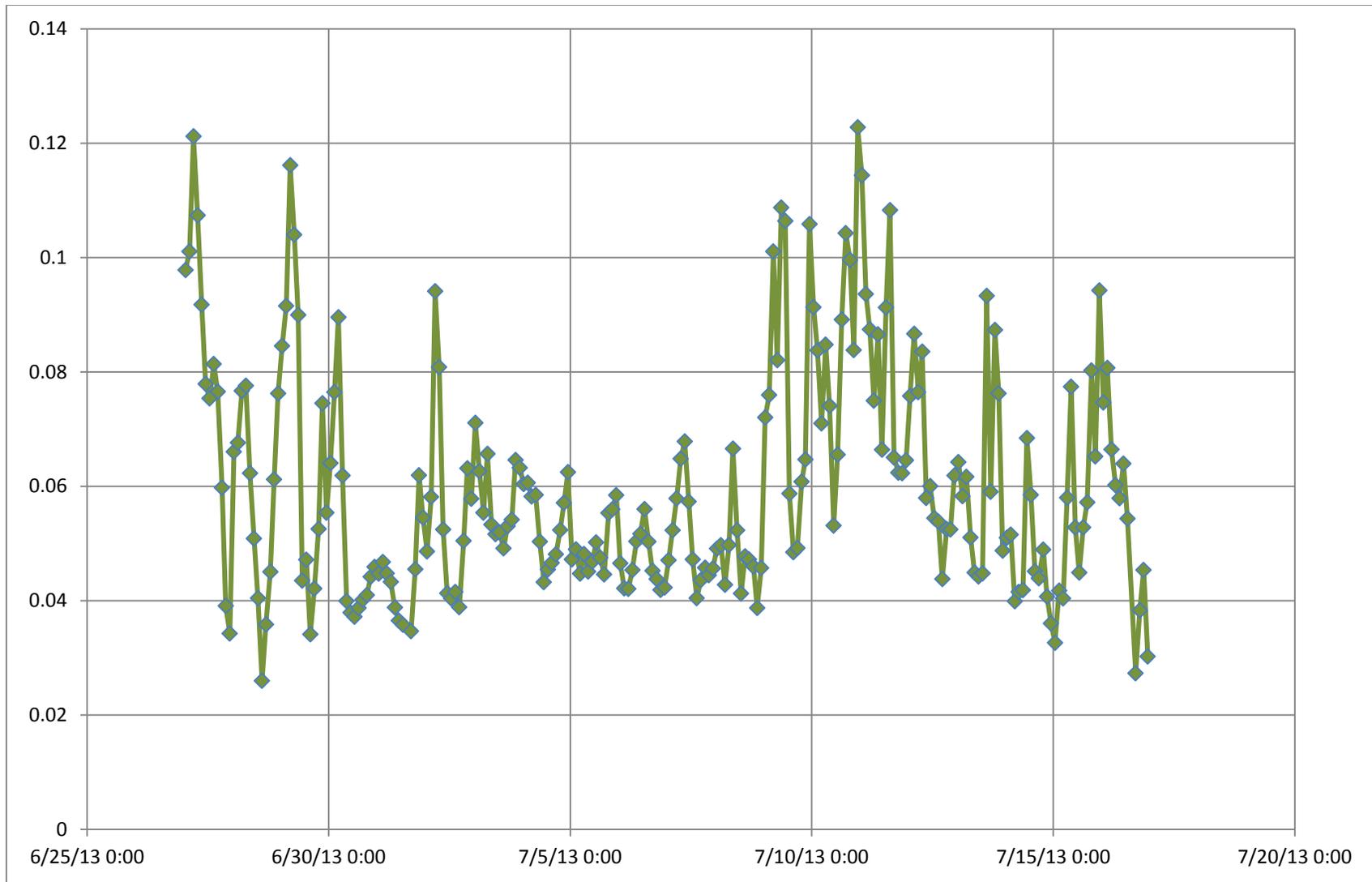


Figure 11. Elemental carbon to total carbon ratios for the June-July 2013 forest fire episode ($\mu\text{gC/LCm}^3$).

17

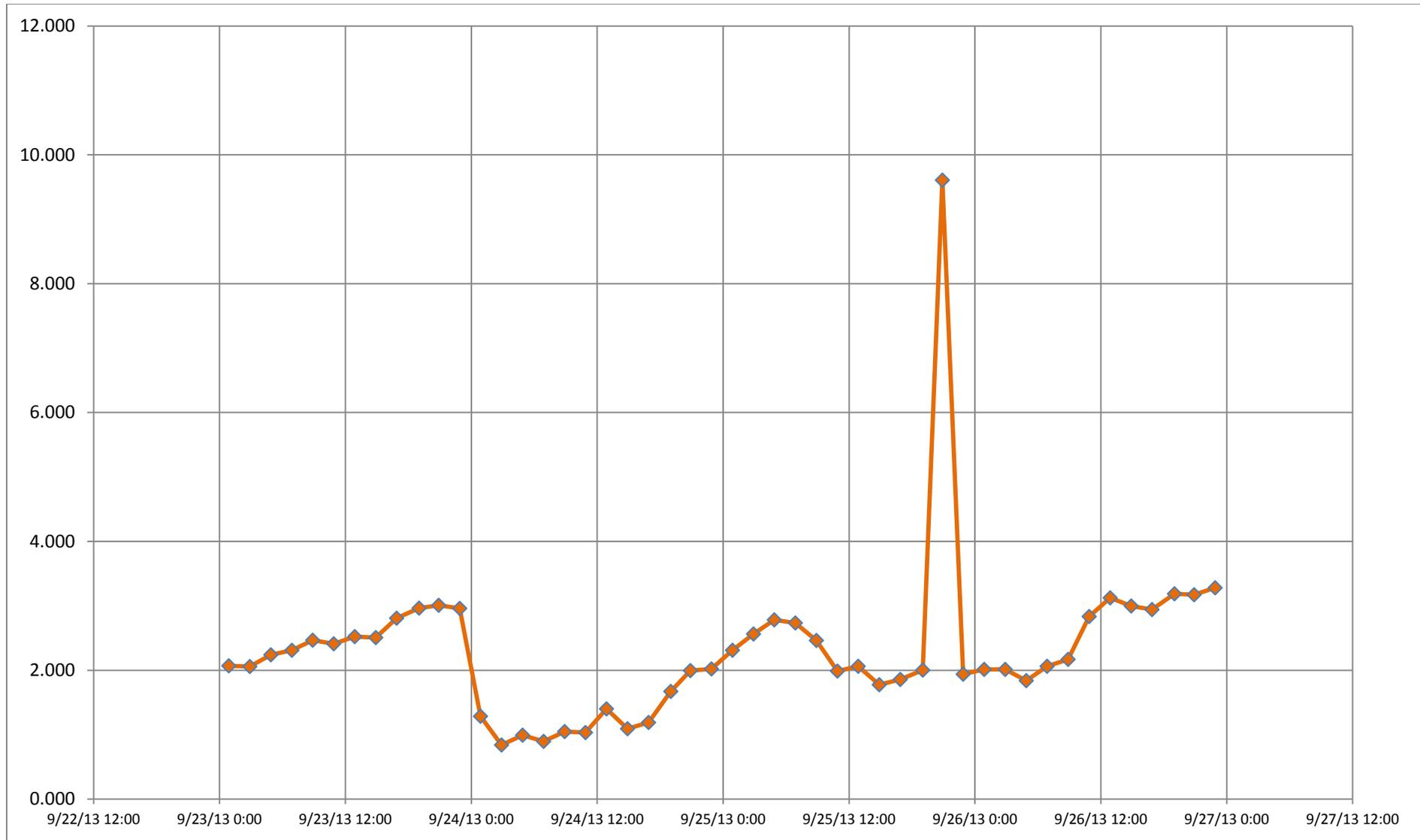


Figure 12. Organic carbon data for the August 23-26 local event ($\mu\text{gC}/\text{m}^3$).

18

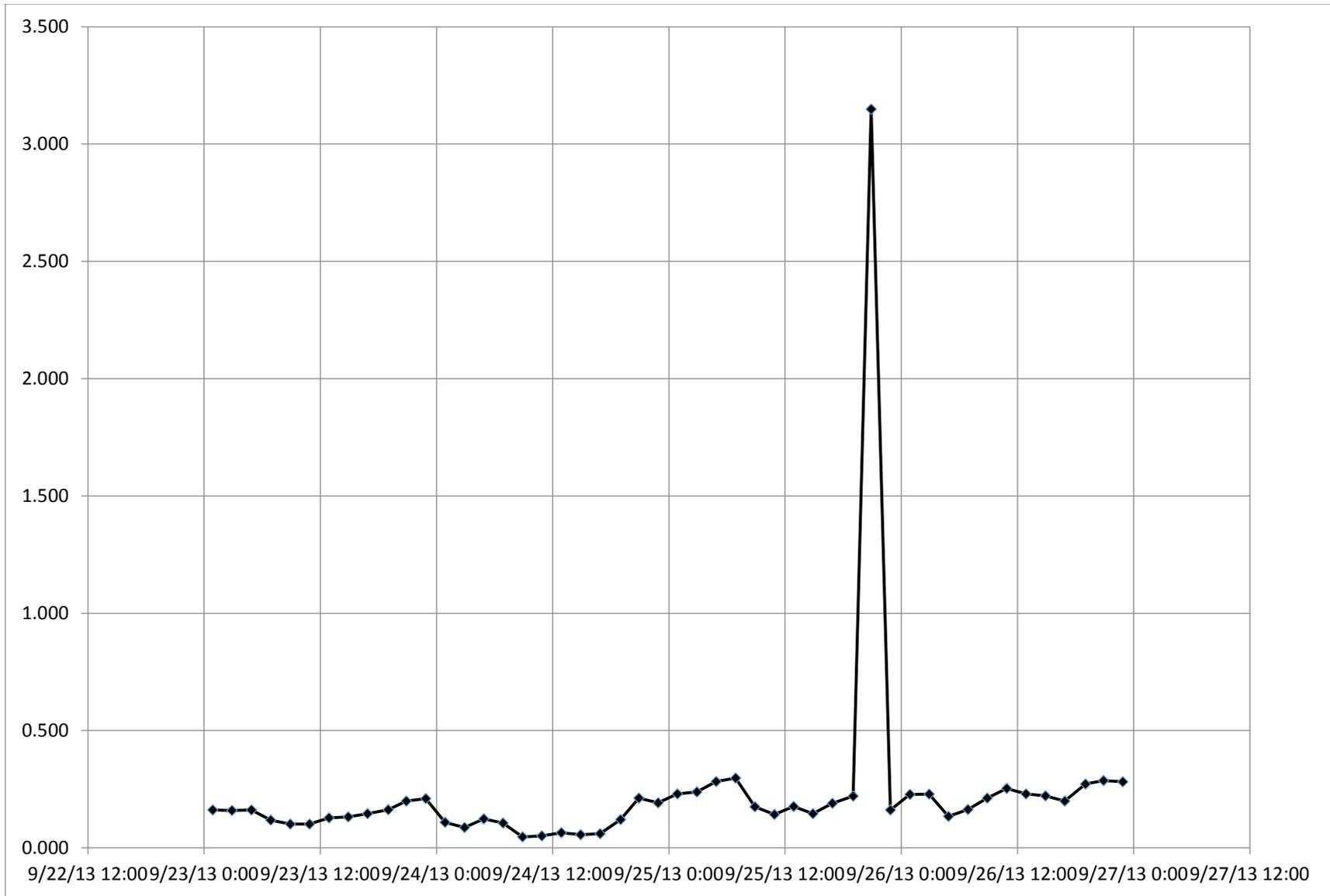


Figure 13. Elemental carbon data for the August 23-26 local event ($\mu\text{gC}/\text{m}^3$).

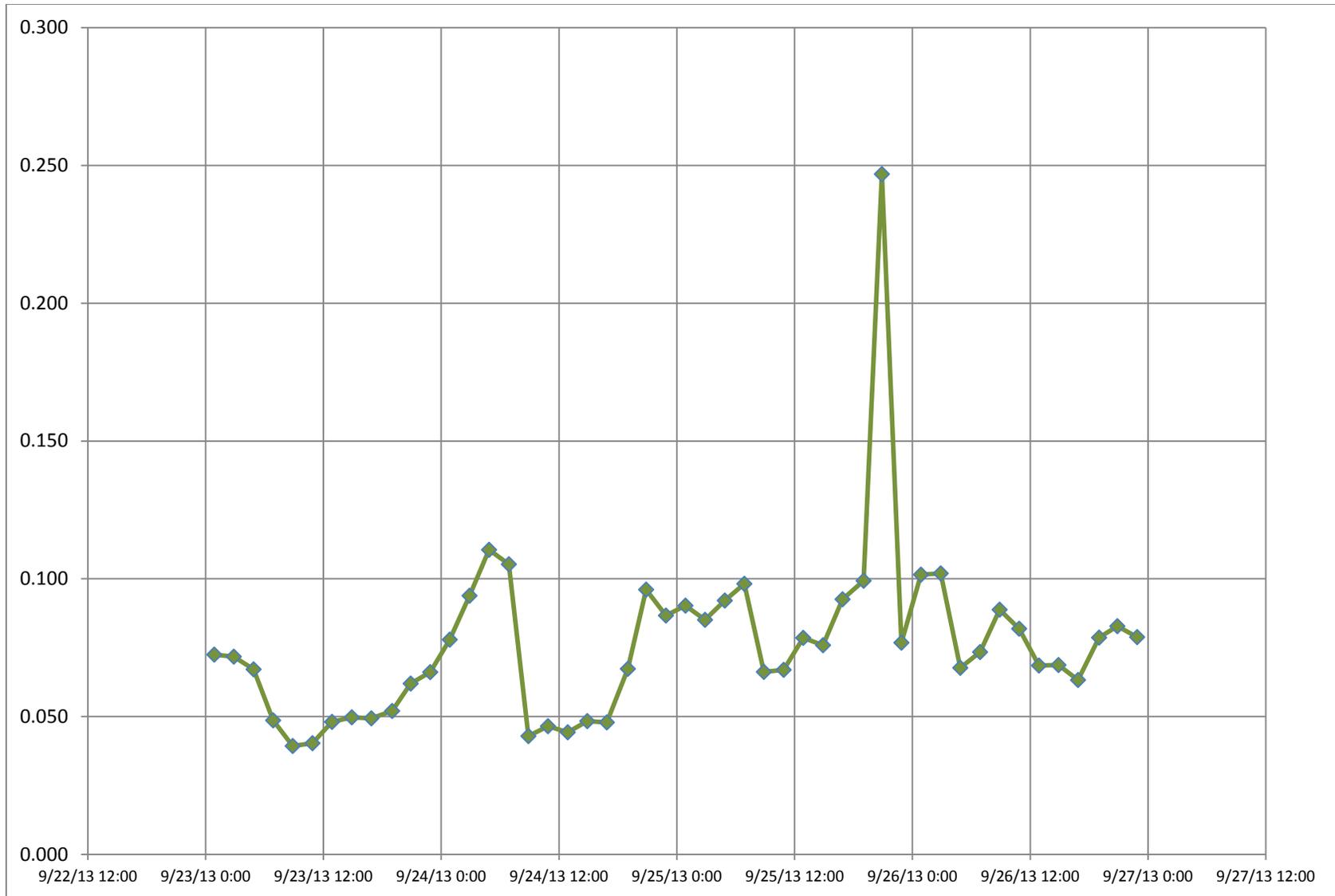


Figure 14. Elemental carbon to total carbon ratios for the August 23-26 local event.

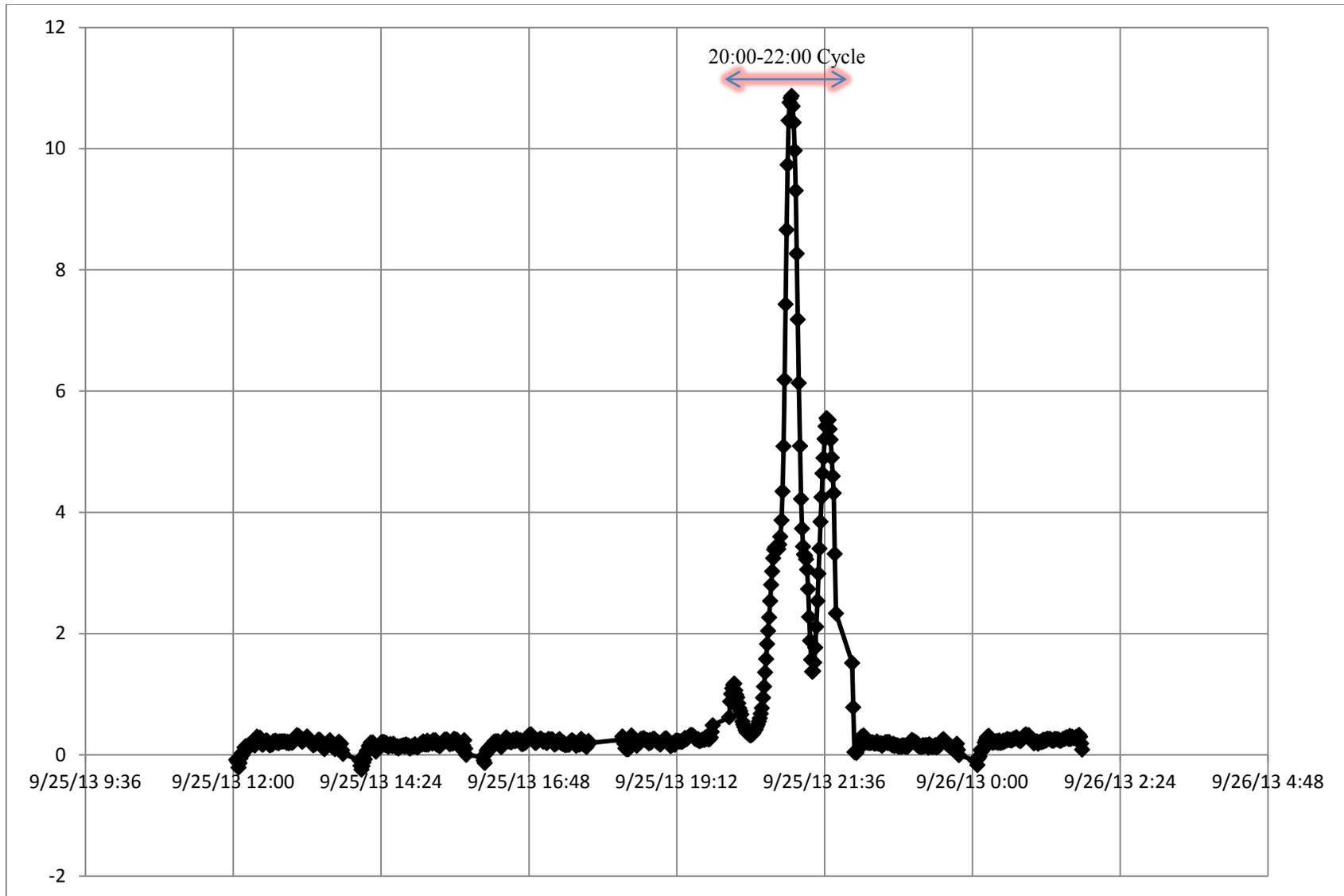


Figure 15. Elemental carbon data for October 25 ($\mu\text{gC}/\text{m}^3$).

21

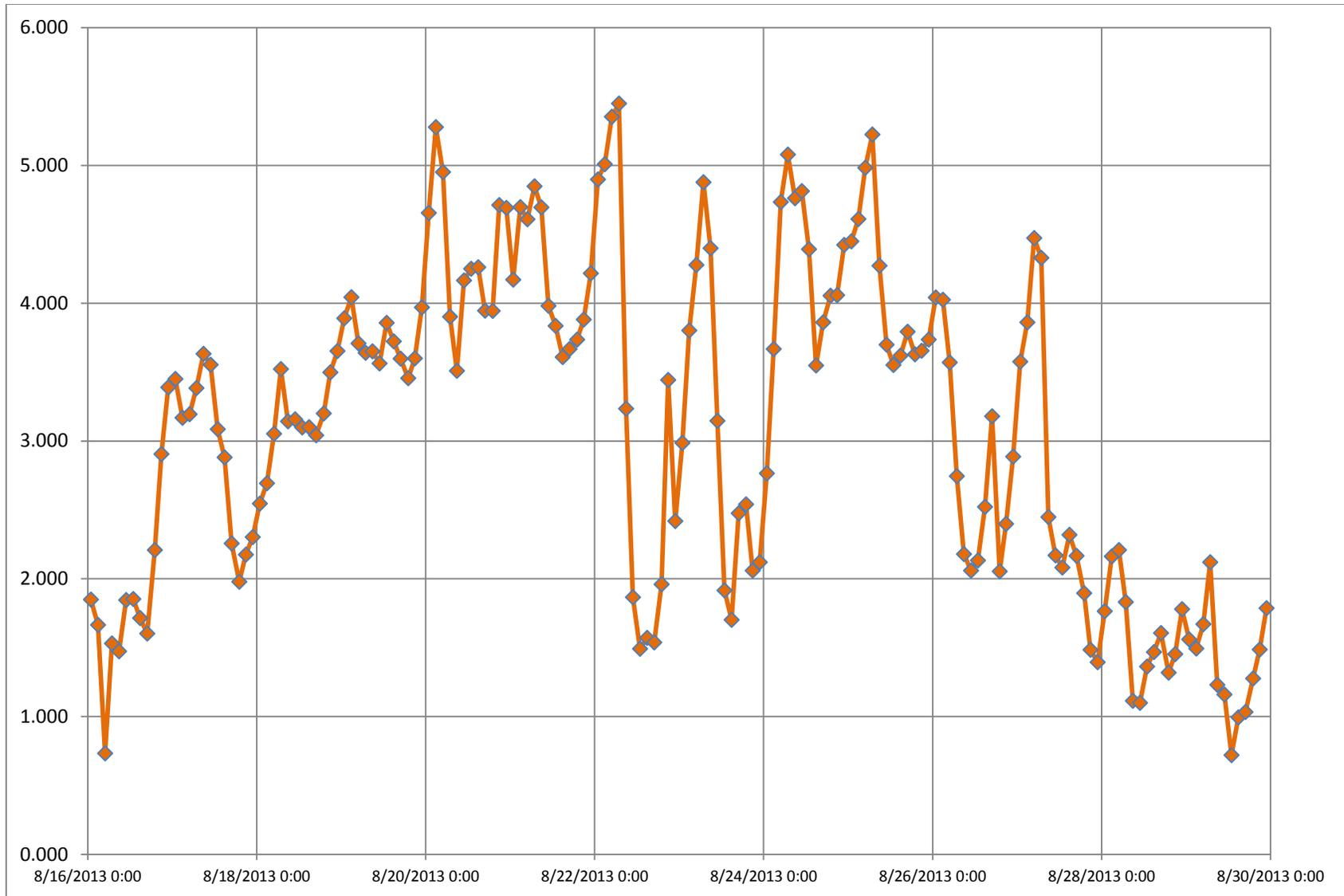


Figure 16. Organic carbon data for August 16-30 ($\mu\text{gC/LCm}^3$).

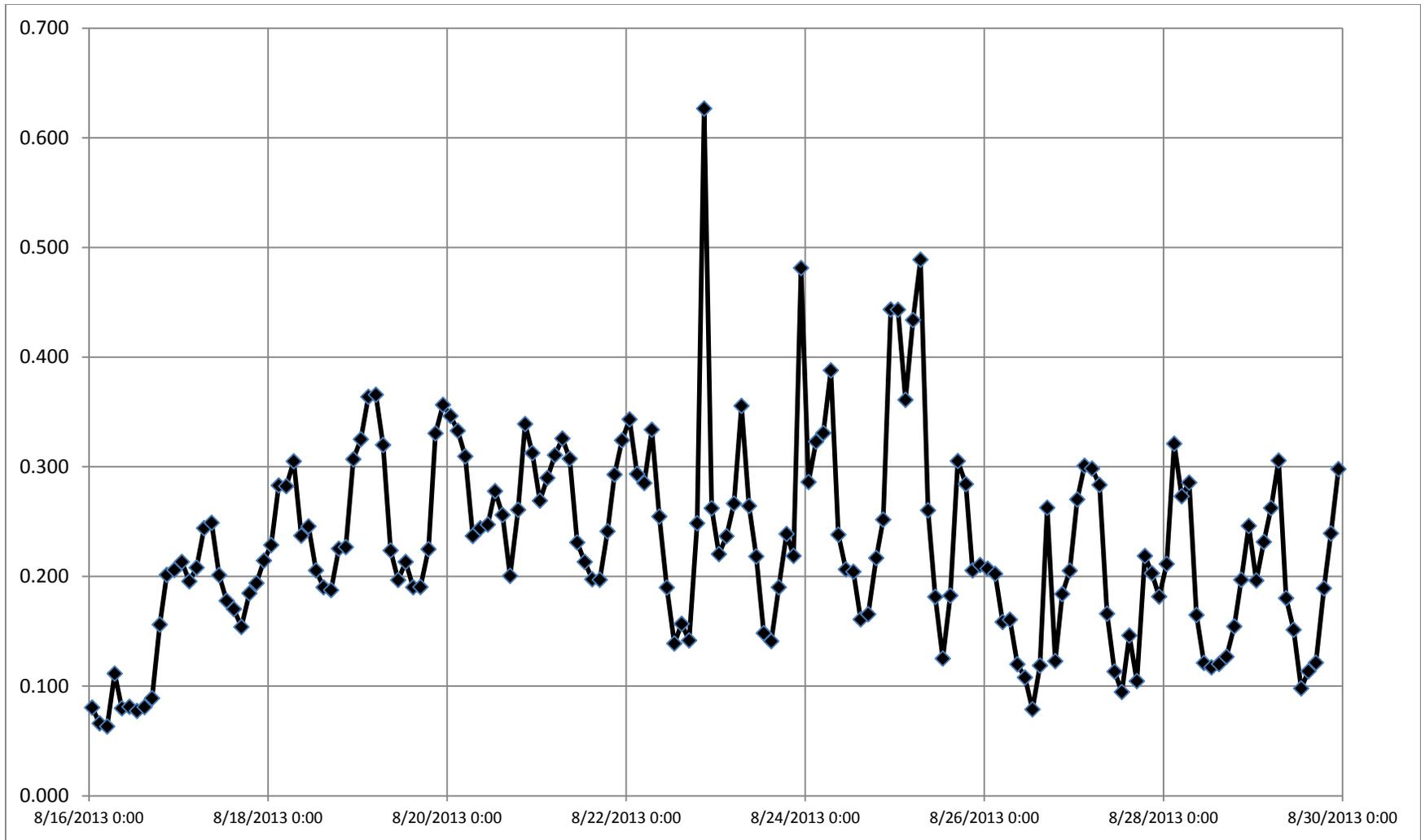


Figure 17. Elemental carbon data for August 16-30 ($\mu\text{gC/LCm}^3$).

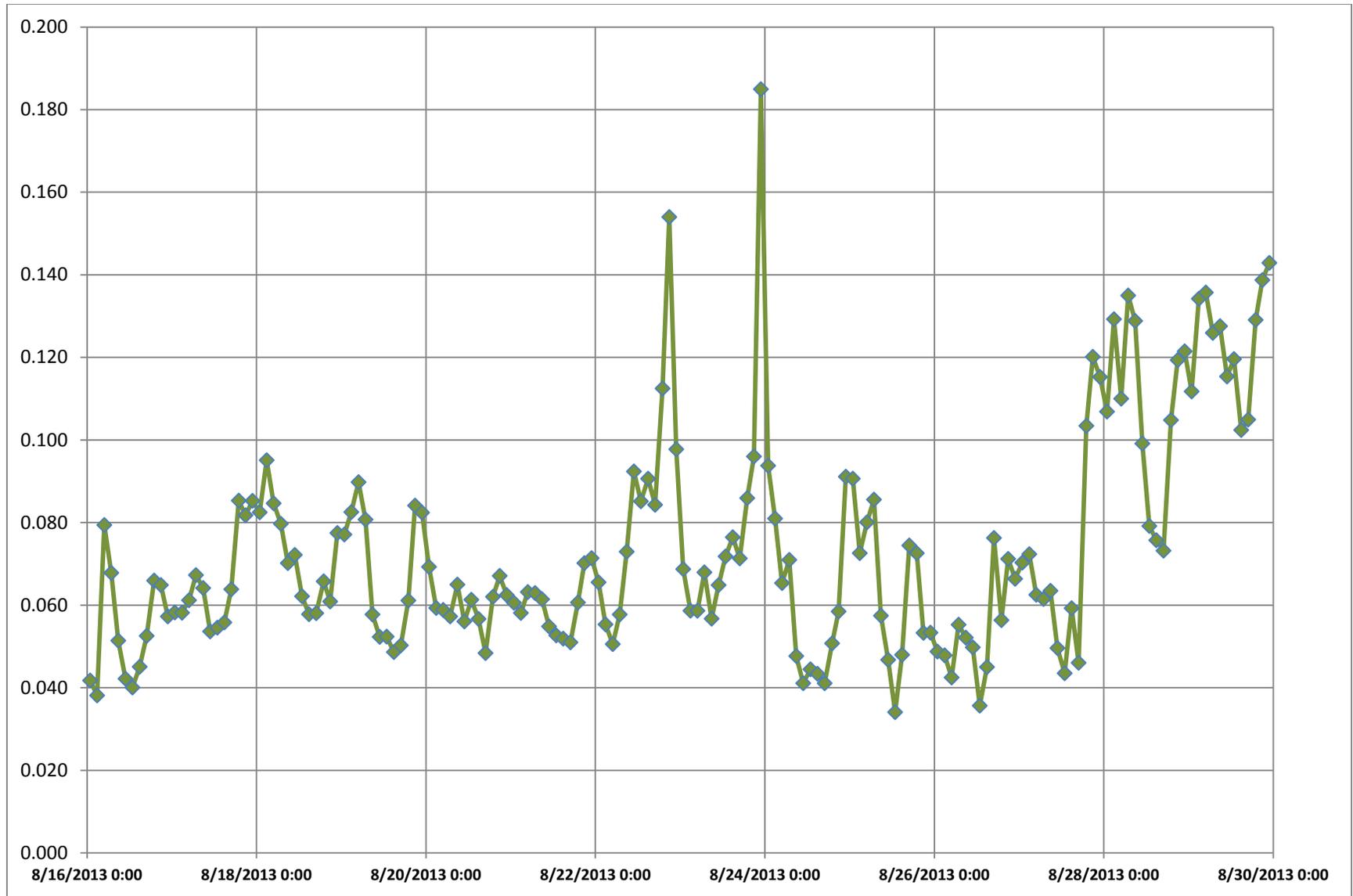


Figure 18. Elemental carbon to total carbon ratios for August 16-30.

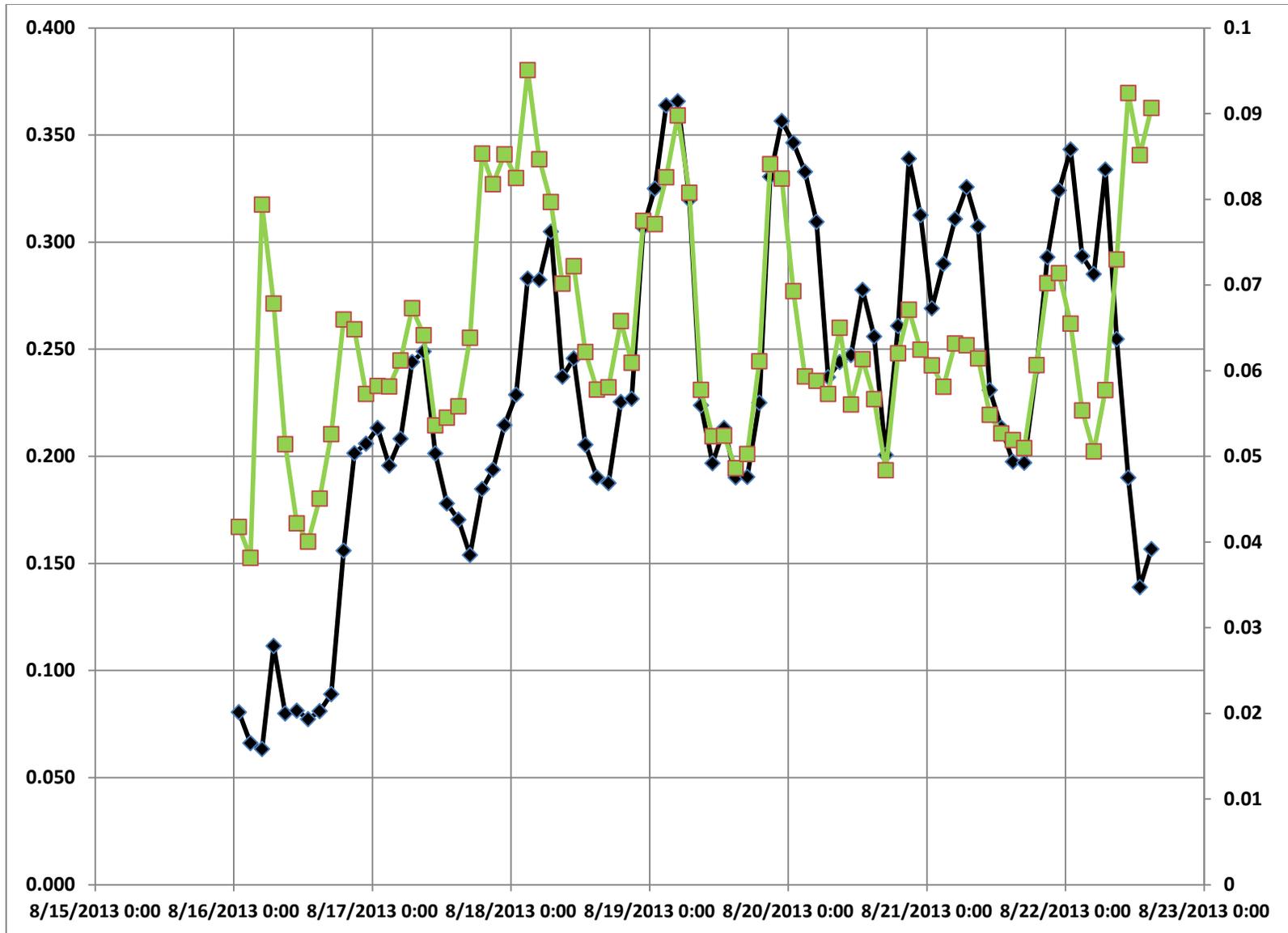


Figure 19. Elemental carbon (black line, left axis, $\mu\text{gC}/\text{m}^3$) and elemental carbon to total carbon ratios (green line, right axis).



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