



## Black Carbon and Organic Components in the Atmosphere of Southern Italy: Comparing Emissions from Different Sources and Production Processes of Carbonaceous Particles

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### ABSTRACT

Initial measurements of black carbon (BC) content at both 880 and 370 nm, obtained in two sites in southern Italy by an aethalometer, have been analyzed. The sites are located in the same region (Basilicata), but are affected by different emission sources. In one case the main source of BC is related to vehicular traffic from a nearby freeway. Data were collected, although not continuously, during 2008, 2009 and 2010. In the second case, a fresh crude-oil pre-treatment plant continuously burns petroleum-derived products, thus contributing to emissions of both carbonaceous matter and its organic component. The corresponding data-set was collected in the period January–April 2011. At the first site, two daily peaks were found for the BC content, typical of vehicles emissions, with maximum values ranging from 2000 ng/m<sup>3</sup> to 4700 ng/m<sup>3</sup> found during weekdays. This behavior disappears at the weekend or when polluted air-masses from north-east Europe are transported over the measurement site. At the second site, two daily peaks were never found, suggesting that crude oil chemical processes were the main source of the emissions. In this case, the maximum BC values ranged between 1000–8000 ng/m<sup>3</sup>, depending on the processes occurring at the fresh crude-oil pre-treatment plant. Moreover, the estimated level of BC at 370 nm was higher than that of BC at 880 nm in all months, except for April, indicating a clear organic component in atmospheric aerosols. Finally, based on a best-fit procedure applied to the seven wavelengths' absorption coefficients, aerosols with different spectroscopic properties have been detected at these two sites.

**Keywords:** Black carbon; Organic fraction; Aethalometer; Atmospheric aerosol.

### INTRODUCTION

Black Carbon (hereafter BC) or dark soot is a carbonaceous aerosol emitted in the atmosphere as the residual of incomplete combustion processes in industrial flames, car combustion engine, domestic heating systems, natural fires.

The term “Black Carbon” is commonly used to indicate light-absorbing aerosols being BC defined by the optical method used to measure it. Elemental carbon is another frequently used term to identify almost the same fraction of carbonaceous aerosols but operationally defined by the thermo-optical methods which are TOR (Thermal Optical Reflectance) or TOT (Thermal Optical Transmittance), as in Chow *et al.* (2009). BC is characterized to be the main absorber of visible light in the atmosphere. In some cases, carbonaceous particles show a strong absorption at UV wavelengths which is characteristic of many organic

compounds, such as Polycyclic Aromatic Hydrocarbons (PAHs). In these cases the organic fraction of BC is a part of Organic Carbon (OC).

During last years interest on BC and OC role in atmospheric aerosols has been strongly increasing due to several reasons.

First of all the fine-submicrometer nature of BC particles make them able to be inhaled into human respiratory system causing adverse health effects as in Laden *et al.* (2006). At the same time, as a result of some combustion processes such as residential wood burning or biomass burning, other organic compounds considered toxic and carcinogenic for human health as such as PAHs, furans, Polychlorinated Biphenyl (PCBs), Polybrominated Diphenyl Ethers (PBDEs) and dioxins (Shresta *et al.*, 2010) can be produced. They can be sorbed to BC surface or can undergo a gas-to-particle conversion process and thus easily carried into the lungs.

Secondly, BC has been recognized by IPCC (2007) to be one of the main responsible of global warming due to light absorption. This is still a relevant aspect because, being BC an indicator of anthropogenic activities, the understanding of its role in positive radiative forcing can be directly related to anthropogenic influence on climate change.

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Another important feature is BC chemical inertia, which causes it to have long lifetime in the atmosphere, with wet deposition as the main removal mechanism, and to be easily transported over long distances: Eleftheriadis *et al.* (2009) have analysed long-time series (1998–2007) of BC content at the Zeppelin station (Svalbard Islands), carried at the North Pole just by air circulation. The possibility that carbonaceous aerosol can diffuse very far from production areas forces scientists to study how long-range transport of BC affects air quality, in comparison with local produced BC, so that competent authorities can be addressed towards effective actions, to improve strategies for pollution control.

The biggest part of studies on BC measurements comes mainly from India and China, since these high populated nations have experienced, during last years, a strong and rapid industrialization, along with a massive diffusion of vehicles. These intense activities have put as urgent the problem to study how BC production have effects on air quality in tropical and semi-arid regions, in megacities and on meteorology. On this subject the following papers have to be mentioned: Madhavi Latha and Badarinath (2005), Badarinath *et al.* (2007), Cao *et al.* (2009a, b), Zhou *et al.* (2009), Raghavendra Kumar *et al.* (2011), Raju *et al.* (2011).

Although the crucial role that fine carbonaceous particles play on both global warming and human health, although the “brown cloud” well visible over Po Valley when landing with an airplane, few data on BC content are available from Italian sites and, more specifically, from South Italy. Invernizzi *et al.* (2011) have recently considered BC content as an indicator of air quality in Milan, but particular attention should be concentrated on the knowledge of BC sources and on the capability in characterizing their different combustion products, on the base of different combustion processes.

The aim of this work is to show the very first measurements in South Italy of BC content in  $PM_{2.5}$  at the ground obtained by means of an aethalometer and to analyse its variations in atmospheric particulate. Measurements have been collected in two sites located in Basilicata region (South Italy) and affected by very different BC production and/or transport processes. This strong difference will allow, in one site, to identify vehicular emissions from a freeway as the principal component of BC content in atmospheric particulate. Moreover, during some summer days, the BC amount exceeding the locally produced fraction will be identified as a trans-boundary transport effect.

The second site is characterized by emissions coming from incomplete combustion of torched crude oil which undergoes some pre-treatment processes, before being carried to the refinery. Although the possible impact on human health and air quality, very few are the studies dealing with emissions caused by crude oil extraction activities, because the major interest is usually addressed to dramatic events suddenly worsening air quality and, for this reason, having strong and immediate implications on human health. For example, offshore oil-spill ignition events have been described in Lighty *et al.* (2000), or oil fields fires such as during the 1991 Gulf War have been studied by Fowler *et al.* (1993).

In the past, Yassaa and Cecinato (2005) have realised a short measurements campaign during November 1999 to

estimate the absolute contents and relative distributions of organic aerosols in torched gases emitted during crude oil extraction in Hassi-Messaoud city (Algeria), focusing their attention on the chemical composition of the emitted organic aerosols, detected by means of the mass spectrometry technique and characterised by specific fingerprints.

In situations in which it is important to quickly evaluate air quality, also in a qualitative way, the use of an aethalometer for the estimation of both BC and its organic component would represent an useful, low-cost and easy-to-use instrument.

## INSTRUMENT AND MEASUREMENTS SITES

The instrument used in this study to estimate BC content and to detect its organic fraction in  $PM_{2.5}$ , is a Rack-Mount Aethalometer Model AE31 from MAGEE Scientific, deeply described by A. D. A. Hansen (2003), equipped with 7 wavelengths lamps to measure radiation attenuation due to carbonaceous particles deposition. In fact, thanks to an appropriate cyclone set on the top of the inlet tube, atmospheric  $PM_{2.5}$  is forced to impinge on a quartz filter tape, alternatively illuminated by 7 wavelengths lamps (370, 470, 520, 590, 660, 880, 950 nm) whose attenuation is mainly due to the light absorption by BC aerosols. The presence of an UV lamp allows measuring only qualitatively the organic component of BC: in cases in which an organic component in BC content is present, the BC estimated at UV wavelength (370 nm) will be higher than BC measured at 880 nm. The aethalometer has been operating with a flow-rate of 4 L/min and a time-resolution of 5 minutes. This kind of instruments (MAGEE aethalometer series) has been widely used in different studies for air pollution evaluation such as Madhavi Latha and Badarinath (2005), Cao *et al.* (2009a, b), Das *et al.* (2009), Dutkiewicz *et al.* (2009), Invernizzi *et al.* (2011), highlighting carbonaceous particles properties, mainly in urban areas.

In this work five-minutes averaged data, collected in two sites in South Italy, in a region named Basilicata, are analysed. Their locations are shown, respectively, in Figs. 1(a) and 1(b).

The first one is Tito Scalo (40.60°N, 15.72°E, 750 m a.s.l.), a wide rural area with few factories producing scarce emissions. Private homes and some small villages contribute, in winter time, to BC emissions along with its organic fraction, due to the common use of stoves for house heating. In this area, the most important source of BC is represented by a freeway connecting the Eastern and Western sides of South Italy and, for this reason, strongly affected by working days traffic. This road is far about 1 km from the measurements site. As verified by HYSPLIT (<http://ready.arl.noaa.gov/hysplit-bin/trajasrcm.pl>) back-trajectories calculated over five days and deeply described in a previous study by Esposito *et al.* (2004), this site can be affected by sea-salt aerosols if the air masses were travelling over Atlantic Ocean or Mediterranean Sea, or by anthropic particles in case of air trajectories coming from North-East Europe, or by Saharan dust load. In this site the instrument has been located at the ground, in the area of the Institute of Methodologies for Environmental Analysis.



**Fig. 1.** Google maps of the measurements sites: a) CNR-IMAA, b) Hotel Park Grumentum.

The second site is still a rural one, it is in a valley named Agri Valley ( $40.33^{\circ}\text{N}$ ,  $15.92^{\circ}\text{E}$ , 582 m a.s.l.), where small towns located over both ridges and cultivated areas have been the main peculiarities till 1996, when intensive extraction activities of crude oil started. This area contribute to about 25% of Italian oil production by Ente Nazionale Idrocarburi (ENI) and till April/May 2011, the oil wells here located have been producing about 86000 Barrel of Oil Equivalent (BOE) per day ([http://www.eni.com/it\\_IT/eni-nel-mondo/italia/attivita-eni/attivita-eni.shtml](http://www.eni.com/it_IT/eni-nel-mondo/italia/attivita-eni/attivita-eni.shtml)). The measurement site is far about 2 km from the area where crude oil undergoes a pre-treatment process, before reaching the pipeline directed to the refinery. These processes imply continuous

emissions from three visible control flames continuously burning. Moreover, this site is very close to a main road which is less busy than the freeway in Tito Scalo. During the measurements period under examination, the low-levels HYSPLIT back-trajectories (ending points 500–1500 m a.g.l.) show different origins: Atlantic Ocean, Mediterranean Sea, North-Africa and North-East Europe. In this second case the instrument has been located on the roof of the Grumentum Park Hotel, about 12 m a.g.l., in such a position to be downwind respect to the oil pre-treatment centre, according to the prevailing wind blowing directions, as recorded by ALSIA (Agenzia Lucana di Sviluppo ed Innovazione in Agricoltura, Lucana Agency for Development

and Innovation in Agriculture).

The data set considered for Tito Scalo discontinuously covers the period May 2008–November 2010, while measurements at Hotel Park Grumentum have been continuously collected from 12 January 2011 until 30 April 2011. The few instrument stops occurred in Agri Valley have been caused by electricity network problems.

## RESULTS AND DISCUSSION

### Measurements in Tito Scalo

Measurements in Tito Scalo have been discontinuously carried out because, in the past, the aethalometer was used in conjunction with a high resolution radiometer and a DEKATI impactor. In fact, as reported in Calvello *et al.* (2010), to widely describe and compare aerosol optical and physical properties with the above mentioned instruments, both at the ground and over the atmospheric column, cloudless atmospheric conditions are requested. For this reason, the biggest part of data has been collected during spring-summer seasons of years 2008, 2009, 2010.

In Table 1, total measurement days number, BC mean value and the corresponding standard deviations for each year and month are reported. The lowest mean value ( $843.7 \pm 475.6 \text{ ng/m}^3$ ) has been obtained during September 2010, while the highest has been found on August 2008 ( $2404.1 \pm 654.1 \text{ ng/m}^3$ ). Apart from these extreme values, the mean value of BC content, in spring/summer seasons, oscillates between 1000 and  $1500 \text{ ng/m}^3$ . Considering past papers on BC content variations in different sites, the values obtained in Tito Scalo are well below those found in January by Madhavi Latha and Badarinath (2005) in an urban site close to two freeways: in this case, on a daily base, the BC content was varying between  $1471 \text{ ng/m}^3$  and  $11175 \text{ ng/m}^3$ .

The urban site considered by Raghavendra *et al.* (2011) was characterized by the lowest mean values of BC during the monsoon season ( $1040 \pm 470 \text{ ng/m}^3$ ) and the highest ones during winter time ( $3310 \pm 610 \text{ ng/m}^3$ ).

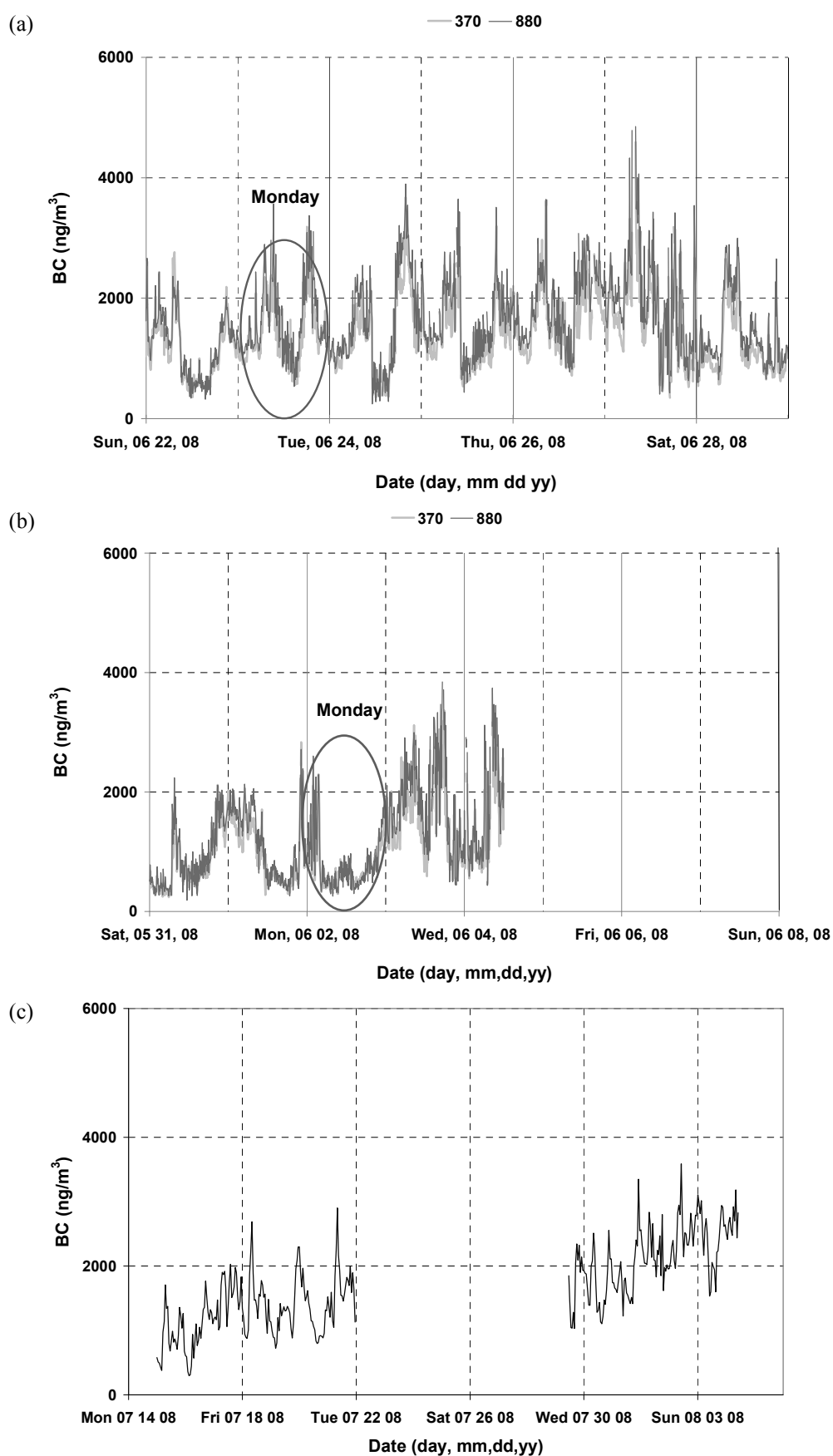
As said before, the main source locally producing BC is the road close to the site, where emissions from vehicles exhausts can diffuse over the area of interest. During summer season, some biomass burning caused by agricultural activities in the neighbourhood or forest fires simply due to carelessness can occur.

In Fig. 2(a) a typical BC content time behaviour (estimated at 370 and 880 nm, 5 minutes time resolution) during a summer working week (June, 22<sup>nd</sup>–June, 28<sup>th</sup> 2008) is reported. Among the seven days of this week, an ellipse emphasizes BC variation during Monday, because it clearly shows the rush-hour two peaks feature as the main characteristic of a working day. These peaks are roughly spread, respectively, from about 5:00 to 11:00 GMT and from 15:00 to 21:00 GMT and centred, respectively, at about 7:00 and 19:00 GMT, with maxima below  $4000 \text{ ng/m}^3$ . Moreover, it has to be noticed that measurements of BC content do not differ depending on the wavelength considered for light attenuation by aerosol absorption (370 nm or 880 nm).

The systematic nature of this behaviour indicates, as in Zhou *et al.* (2009) and Cao *et al.* (2009), the vehicular traffic as the main source of BC in the measurement site. It must to be noted that, day by day, these peaks can obviously change the ratios of their intensity, or their duration, as can be verified looking at working days other than Monday. The BC content variation during Saturday and Sunday, when the two peaks structure disappears and the mean BC content drops below  $1000 \text{ ng/m}^3$ , confirms emissions from vehicles to be the main source of combustion products. As a further confirmation, in Fig. 2(b) four days of measurements,

**Table 1.** BC data-set in Tito Scalo: for each year, measurements period along with number measurement days, mean BC contents and corresponding standard deviations are reported.

Year, Month	N. Meas. days	<BC> ( $\text{ng/m}^3$ )	Stand. Dev.
May 2008	17	1079	672
June 2008	14	1467	796
July 2008	16	1341	635
August 2008	4	2404	654
September 2008	3	1406	880
<b>Total meas. days num.</b>	<b>54</b>		
April 2009	8	1240	812
May 2009	18	1240	784
June 2009	4	1437	1469
October 2009	2	1576	538
<b>Total meas. days num.</b>	<b>32</b>		
March 2010	2	996	426
April 2010	11	1109	608
May 2010	6	1066	428
June 2010	4	1016	522
July 2010	5	1416	722
August 2010	6	1055	603
September 2010	8	844	476
November 2010	1	1321	643
<b>Total meas. days num.</b>	<b>43</b>		



**Fig. 2.** Time dependence of BC content in Tito Scalo estimated at 370 nm and 880 nm for the periods a) June, 22<sup>nd</sup> 2008–June, 28<sup>th</sup> 2008; b) May, 31<sup>st</sup> 2008–June, 4<sup>th</sup> 2008; c) July, 29<sup>th</sup> 2008–August, 4<sup>th</sup> 2008.

from May, 31<sup>st</sup> 2008 (Saturday), to the first hours of June, 4<sup>th</sup> 2008 (Wednesday) are reported. This case is interesting because, considering June, 2<sup>nd</sup> (Monday), the two peaks behaviour of a usual working day is lost, since in Italy June, 2<sup>nd</sup> is the national holiday to celebrate Italian Republic. Moreover, a flat maximum extending from Saturday at 21:00 to Sunday at 8:00 is observed, with BC slightly below 2000 ng/m<sup>3</sup>, while a narrower peak extending from Sunday at 21:00 to Monday at 4:00 is found. On June, 2<sup>nd</sup> (Monday) there is a minimum in BC content, whose highest value is lower than 1000 ng/m<sup>3</sup>, during both daytime and night-time hours.

Typical features of BC content in this measurements site can also be lost, for example, when trans-boundary sources add their contribution to the local ones. To illustrate this case, hourly averaged measurements collected in the periods July, 15<sup>th</sup> (Tuesday)–July, 21<sup>st</sup> (Monday) and July, 29<sup>th</sup> (Tuesday)–August, 4<sup>th</sup> (Monday) of BC estimated at 880 nm are considered in Fig. 2(c). Starting from July, 31<sup>st</sup>, the second measurements sequence highlights, compared to the first one, a trend with an increasing BC content, and a time behaviour without any particular structure, during both working and no working days. The mean BC content in the first period was  $1287 \pm 560$  ng/m<sup>3</sup>, while in the second one was  $2404 \pm 654$  ng/m<sup>3</sup>.

Since no local smoke or, in general, no BC extra source during the measurements period has been identified, this variation could be explained by the advection of air masses with a high carbonaceous particles loading. Both five-days air masses back trajectories computed by the HYSPLIT model and the smokes NAAPS maps ([http://www.nrlmry.navy.mil/flambe-bin/aerosol/display\\_directory\\_aer2?DIR=/web/aerosol/public\\_html/global/ops\\_01/europe/](http://www.nrlmry.navy.mil/flambe-bin/aerosol/display_directory_aer2?DIR=/web/aerosol/public_html/global/ops_01/europe/)) confirm this hypothesis.

In Fig. 3(a) the low-level back trajectories (ending point 500, 1000, 1500 m) are reported for July, 31<sup>st</sup> at 12:00 GMT. They are found moving close to the ground and coming from North-East Europe, more specifically from Ukraine, Byelorussia, Romania, where both obsolete industrial activities and vehicular traffic emissions are poorly controlled, such as fine carbonaceous particles. The NAAPS map estimated for July, 27<sup>th</sup> at 12:00 GMT and reported in Fig. 3b suggests also the presence of smoke particles over Ukraine and Romania that could have been carried to the measurements site.

In Fig. 3(c) the air masses paths found for August, 2<sup>nd</sup> come from East Europe (Croatia and Slovenia) but are more localised than before, probably due to a high pressure system. This would contribute to trap particles in the mixing layer both produced in the neighbourhood of the measures site, or therein transported by other sites. In fact, in Fig. 3(d) the corresponding NAAPS map (on August, 2<sup>nd</sup> at 12:00 GMT) shows two smoke spots over the Italian area crossed by the air masses.

### Measurements in Agri Valley

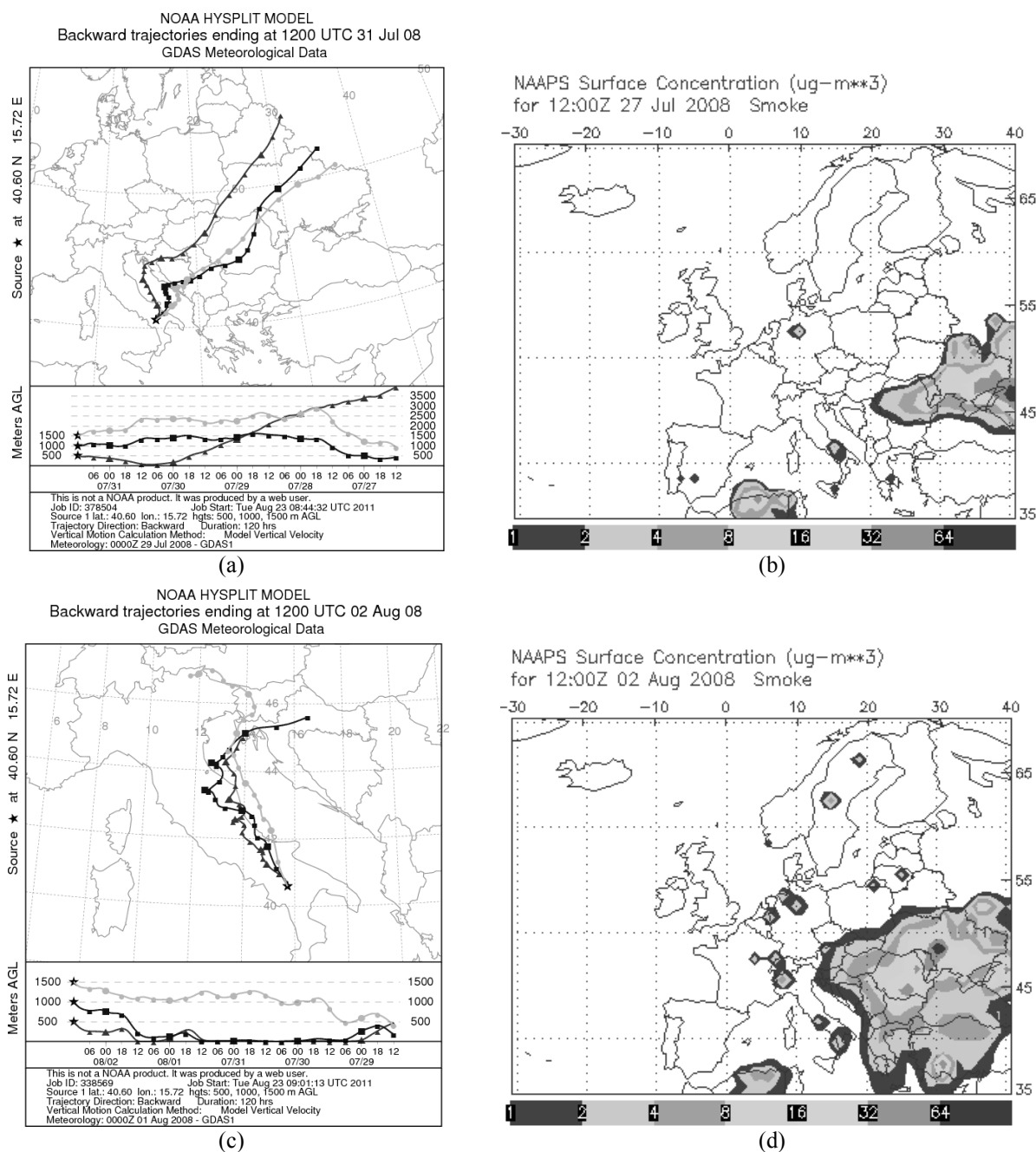
From January, 12<sup>th</sup> 2011 until the end of April 2011, the AE31 aethalometer has been installed in Agri Valley to study variations of atmospheric particulate properties

caused by the different chemical pre-treatment processes of crude oil extracted in that area. Due to this particular activity insisting over the site, a well distinct contribution of Organic Carbon to the carbonaceous particulate loading was expected, while no information was available on the specific industrial processes occurring over there.

In Figs. 4(a)–4(d) time behaviour of BC estimated both at 880 nm and 370 nm (5 minutes time resolution) is reported for each measurements month. During both March and April some problem at the electricity network caused two instrument stopping, with a consequent lack of data. Firstly, it must be noted that the BC values detected at 370 nm were often higher than BC detected at 880 nm, meaning that, as explained by the aethalometer manufacturer in Hansen (2003), Organic Carbon is one of the components of carbonaceous particles. This feature has been found independently of the measurements period (winter or late springtime), implying that the organic component comes from crude oil chemical processes taking place in Agri Valley, instead of residential wood burning or farming fires that could contribute to organic particles production. In fact, the organic fraction produced by wood stoves should follow a regular 24 hours time dependence, contrary to the obtained results, while farming fires should be concentrated in very short periods (few days) of the year. Neither daily two peaks structure related to vehicular traffic emissions has been detected. Generally, BC measured both at 880 nm and 370 nm follows, day by day, the same time dependence, suggesting a single production process of carbonaceous aerosol containing a significant organic component.

In Table 2, for each measurement month, total measurement days, mean BC content and related standard deviations are reported: a very first observation of these data highlights monthly averaged values of BC content lower than those measured in Tito, but with associated standard deviations of the same order of mean values, implying great variations during the days.

Furthermore, variation of both BC components shows a different time dependence on a monthly scale, probably due not only to the changing meteorological conditions, but also to the processes variation that took place in the oil pre-treatment centre, as verified by Yassaa and Cecinato (2005). In fact, looking at Figs. 4(a)–4(d), different structures on different time scales can be identified: some peaks spread over only 2 days such as January, 25<sup>th</sup>–27<sup>th</sup> or for longer periods such as March, 9<sup>th</sup>–13<sup>th</sup> or even much longer, such as in February, 7<sup>th</sup>–14<sup>th</sup>. Overlapped to these wide-spread peaks other structures much more regular than previous ones can be identified. For example, considering measurements obtained from February, 6<sup>th</sup> to February, 11<sup>th</sup> six peaks of similar duration with maximum value ranging from more than 2000 ng/m<sup>3</sup> to about 6000 ng/m<sup>3</sup> have been detected, quite often over the maximum BC content found in Tito ( $\approx 3000$  ng/m<sup>3</sup>). The values of minima, instead, are comparable ( $\approx 400$  ng/m<sup>3</sup> in both sites). Similar structures with peaks of lower intensity, but with 24 hours duration are found in the periods March 1<sup>st</sup> - March 6<sup>th</sup>, April 20<sup>th</sup>–April 24<sup>th</sup>. In January this behaviour is less evident but still present, for example, from January 17<sup>th</sup> until January 19<sup>th</sup>.



**Fig. 3.** a) HYSPLIT five-days back-trajectories for July, 31<sup>st</sup> 2008, b) NAAPS map for July, 27<sup>th</sup> 2008; c) HYSPLIT five-days back-trajectories for August, 2<sup>nd</sup> 2008 and d) NAAPS map for August, 2<sup>nd</sup> 2008.

Since the time duration of these peaks is about 24 hours, from about 14:00 GMT of one day until about 14:00 GMT of the following day, it can be supposed the influence of the daily cycle of the Mixed Layer Depth.

### SPECTROSCOPIC PROPERTIES OF CARBONACEOUS AEROSOL

Carbonaceous particles are usually considered as absorbing atmospheric component whose absorption coefficient  $\sigma_a(\lambda)$ , as computed by Moosmuller *et al.* (2009) is inversely proportional to the wavelength  $\lambda$ :

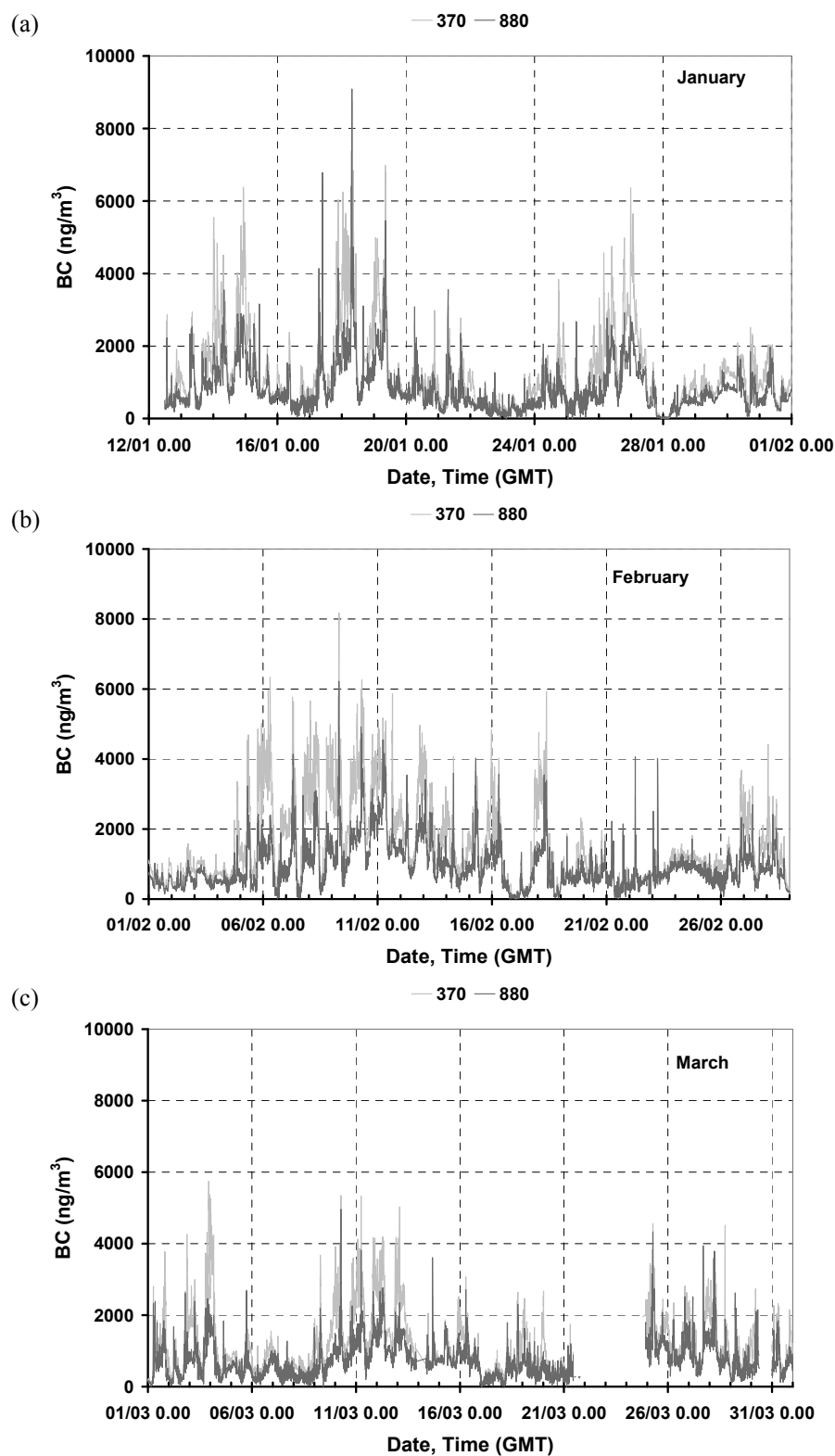
$$\sigma_a(\lambda) \propto 1/\lambda. \quad (1)$$

There are cases in which combustion products are characterized by absorption coefficients where wavelength exponent is higher than 1 and, in order to reduce the uncertainty on BC estimation, a procedure to calculate this exponent is requested. The seven-wavelengths absorption coefficient measured by the aethalometer allows to apply a best-fit procedure in order to correctly detect the organic component of BC. In fact, as widely described in Esposito *et al.* (2012), the absorption coefficient can follow, more generally, the Ångström turbidity formula:

$$\sigma_a(\lambda) = \beta(\lambda/\lambda)^{-\alpha}. \quad (2)$$

Since at the UV wavelength there could be some organic compound strongly absorbing, thus leading to an

overestimation of the  $\alpha$  parameter, the wavelength range 470–950 nm has been considered for the best-fit technique application and  $\alpha$  parameter estimation. In Fig. 5(a) the normalized histograms of the alpha parameter derived from



**Fig. 4.** Time dependence of BC content in Agri Valley estimated at 370 nm and 880 nm for a) January, b) February, c) March, d) April 2011.



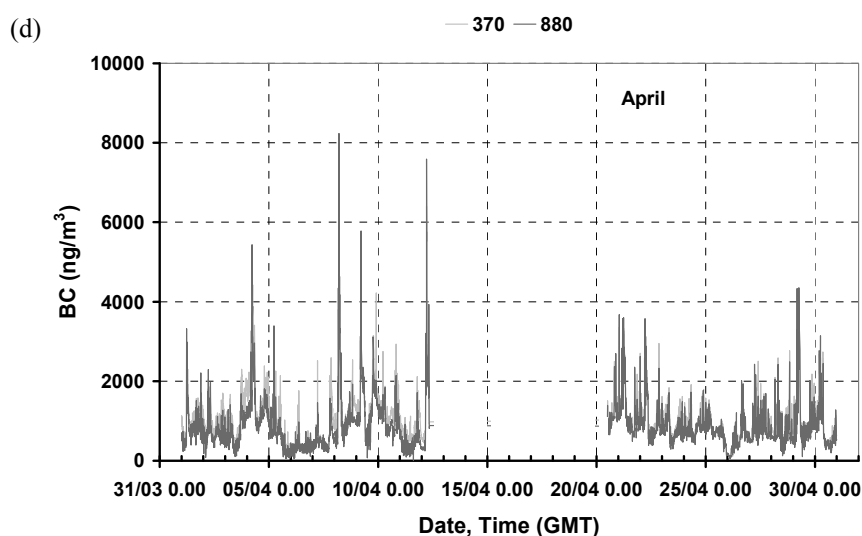


Fig. 4. (continued).

**Table 2.** BC data-set in Agri Valley in 2011: for each month number measurement days, mean BC contents and corresponding standard deviations are reported.

Month	N. Meas. days	<BC> (ng/m <sup>3</sup> )	Stand. Dev.
January	20	822	653
February	28	494	171
March	28	735	495
April	23	858	589

measurements in Tito for the periods May 2008, June 2008 and May 2009 are shown. All the data-sets are characterized by a mode value of 0.9, while the corresponding mean values are, respectively,  $0.89 \pm 0.08$ ,  $0.87 \pm 0.05$ ,  $0.88 \pm 0.07$ . The high concentration of data in a such short range ( $0.9 < \alpha < 1.0$ ) with very few data out of this interval suggests, independently of the period, the presence of the same type of combustion product in the measurement site.

In Fig. 5(b) the normalized histogram of alpha values obtained in Agri Valley during April 2011 are reported. In this case the mode value corresponds to  $\alpha = 1$  with mean value  $0.99 \pm 0.10$ . Data corresponding to  $\alpha = 1$  represents 41% of the entire data-set, while the sum of data corresponding to  $\alpha = 1.1$  and  $\alpha = 1.2$  represents 37% of the data. These results imply that there were some days during which combustion products have changed their spectroscopic properties and it has been verified it happened on April, 10<sup>th</sup> until April 12<sup>th</sup>. In fact the second histogram corresponding to these days shows a mode at  $\alpha = 1.2$ , mean value  $1.11 \pm 0.11$  and the 72% of data in the range 1.1–1.2.

## CONCLUSIONS

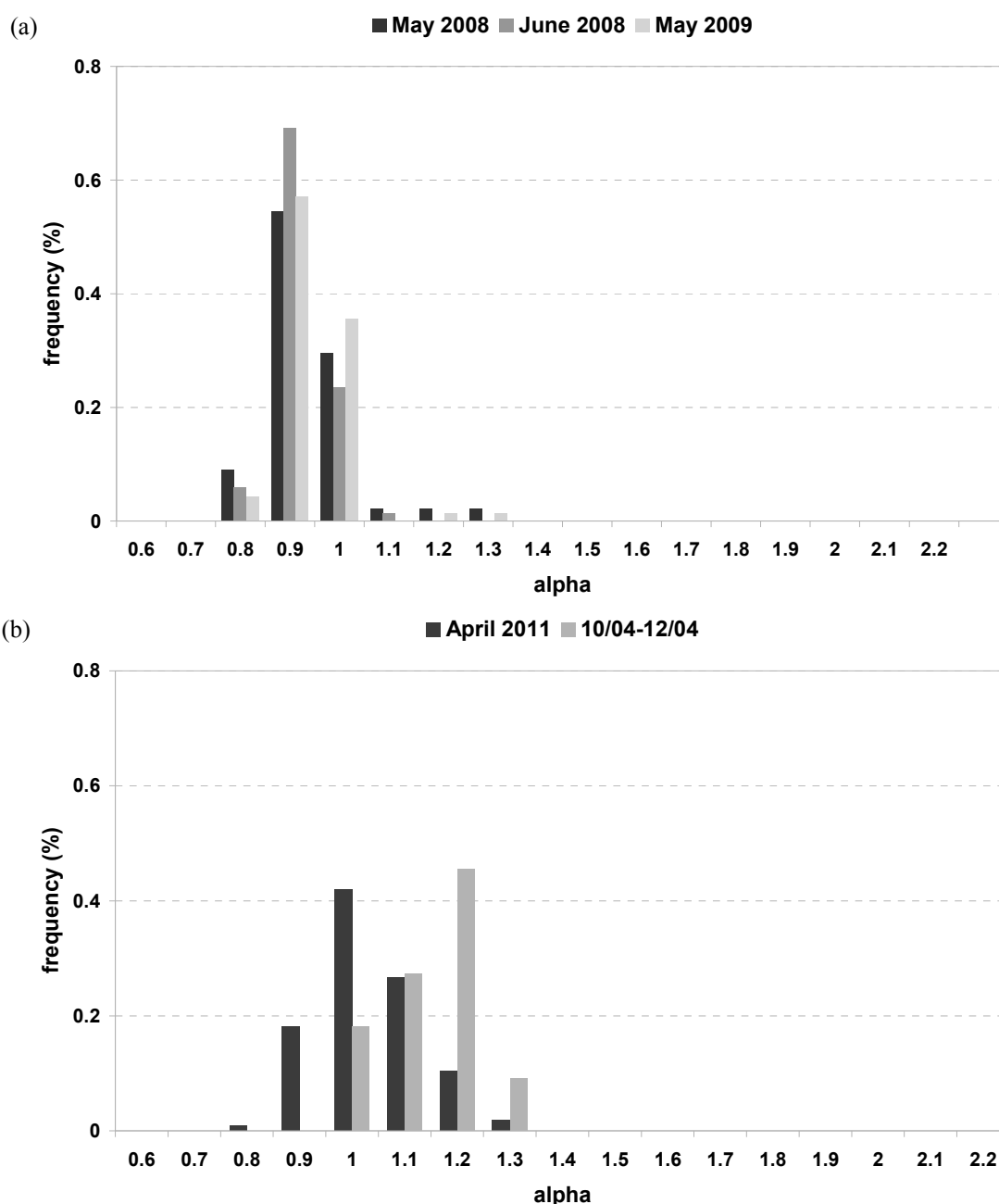
This study has shown BC data collected in two sites located in Basilicata (South-Italy) affected by different sources of carbonaceous particles: in one case a freeway close to the measurements site is the major BC source, in the other a fresh-oil pre-treatment plant produces BC together with an organic component. In fact, 24 hours-long chemical

processes involve continuous emissions from incomplete combustion of torched crude oil.

As it would be expected, the first site, Tito Scalo, is characterised by a typical BC two peaks daily behaviour, with maximum value ranging from  $2000 \text{ ng/m}^3$  to  $4700 \text{ ng/m}^3$ , strictly related to the rush-hours commuters. Week and week-end days with massive contribution of trans-boundary air masses coming from North-East Europe have been found. In these cases, the usual two peaks behaviour is lost and an increased BC content over the whole period is highlighted. These results suggest the importance to take into account not only local production sources of carbonaceous aerosols, but also the displacement of air masses carrying combustion products that affect air quality. At the moment, organic component of BC in this site has been detected only during very few winter days, probably due to the usage of house heating stoves.

The second site, Agri Valley, is characterised by BC estimated at 370 nm quite often higher than BC estimated at 880 nm, probably related to the chemical processes taking place there. BC maximum values (at 880 nm), depending on the period, was varying between  $1000\text{--}8000 \text{ ng/m}^3$ . Both components follow a quite similar time behaviour, indicating they are originated by the same processes, with a 24 hours structure superimposed to peaks structures spreading over many days. During April 2011 the time dependence of BC content shows variations, probably connected to changes in chemical pre-treatment processes of crude oil.

Finally, the seven wavelength set-up of the aethalometer has been exploited in order to have information on spectroscopic properties variation of carbonaceous particles. By applying a best-fit technique on the absorption coefficients, different values of the Angstrom exponent have been found, depending on the measurement site. In Tito, mean alpha values collected in May and June 2008 and May 2009 have been found ranging between  $0.87 \pm 0.05$  and  $0.89 \pm 0.08$ . Measurements collected in Agri Valley during April 2011 give mean alpha value  $0.99 \pm 0.10$  with a short period with mean alpha value  $1.11 \pm 0.11$ . These results



**Fig. 5.** Histogram of  $\alpha$  parameter a) in Tito Scalco for May 2008, June 2008 and May 2008, b) in Agri Valley for April 2011 and for the period April, 10<sup>th</sup>–April, 12<sup>th</sup>.

indicate, site by site, different combustion products or, in the same site but on different days, a variation in production processes.

Although aethalometer does not allow to a-priori discriminate which kind of process produces BC, this instrument gives the possibility to follow carbonaceous aerosol properties variation and easily characterize air quality even if, specially for the organic component, in a qualitative way.

#### ACKNOWLEDGMENTS

The authors are grateful to the Director of Hotel Park

Grumentum and his staff for their kindness and their support. This work has been partially supported by Osservatorio Ambientale della Val d'Agri.

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Received for review, December 21, 2011

Accepted, August 24, 2012