



Intercomparison between NIOSH, IMPROVE_A, and EUSAAR_2 protocols: Finding an optimal thermal–optical protocol for Philippines OC/EC samples

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ABSTRACT

Thermal–optical analysis is one of the most widely–recognized methods for measuring organic carbon (OC) and elemental carbon (EC) in atmospheric particulates. Up to date however, there is no standard protocol of analysis and different protocols give varying OC/EC apportionments. This study aims to find an optimal thermal–optical analysis protocol for Philippine OC/EC samples by comparing three widely–used protocols: NIOSH, IMPROVE_A and EUSAAR_2. Philippines is particularly interesting because it has one of the highest EC concentration and lowest OC/EC ratio in the region. In terms of total OC and EC quantification, NIOSH and IMPROVE_A show negative and positive EC bias, respectively – NIOSH exhibits premature EC evolution in the OC4 pure He phase, while IMPROVE_A OC4 temperature step (580 °C) is not sufficiently high, causing some OC to be carried over to He/O₂ phase to be measured mainly as EC2. EUSAAR_2 minimizes both effects and may be most accurate in this aspect. However, IMPROVE_A is the only method that is capable of properly resolving individual OC and Philippines's particularly abundant EC fractions owing to the protocol's variable step durations. Concurrently, IMPROVE_A and EUSAAR_2 yield lowest pyrolyzed carbon (PC) formation for urban and rural site, respectively. Minimal PC formation is desired to minimize errors associated with its correction. Finally, transmittance laser correction is preferred over reflectance as it is capable of accounting for char formed within filter. The study thus recommends a modified IMPROVE_A, with increased OC4 temperature step (650 °C, adopted from EUSAAR_2) and transmittance laser correction, as optimal. This protocol is expected to give proper OC and EC evolution, fractionation, and measurement with minimized PC formation and proper correction, leading to more accurate results. Preliminary testing shows that recommended protocol meets those expectations. Application to larger number and wider variety of samples is needed to more properly assert these findings.

Keywords: Thermal–optical analysis, NIOSH, IMPROVE_A, EUSAAR_2, OC/EC

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1. Introduction

Thermal–optical analysis is one of the most widely used methods for measuring organic carbon (OC) and elemental carbon (EC) in atmospheric particulates. These particles have great significance due to their profound effects on human health, climate change, and visibility (Japar et al., 1986; Ramanathan and Carmichael, 2008; Baron et al., 2009; Janssen et al., 2011; Anenberg et al., 2012). The technique was originally proposed by Birch and Cary (1996) and it takes advantage of the distinct properties of OC and EC, differentiating between the two by controlling the analysis atmosphere and temperature.

First phase of the analysis occurs in pure helium atmosphere where temperature is raised between 550 °C to 870 °C, depending on protocol used. Thermally unstable OC volatilizes and is subsequently measured though some OC may also undergo pyrolysis during this phase. EC meanwhile, remains bound to filter since without any oxidants or reactions, it volatilizes only through sublimation at temperatures about 3 650 °C (Peterson and Richards, 2002). Since pyrolysis of OC produces char, which is EC and thus light–absorbing, transmittance/reflectance of the sample decreases from its baseline value as pure He phase progresses. These changes

are continuously monitored by a He–Ne laser, allowing corrections to be made later. Second phase of analysis occurs in 2% O₂ in He atmosphere. O₂ oxidizes both pyrolytically formed char and native EC content of the sample, releasing these from the filter and making their quantification possible. Consequently, transmittance/reflectance values of filter increase during this phase. When laser signal returns to baseline value, the instrument automatically sets this as the “split point” which is used to correct for char generated during first phase of the analysis. It treats EC detected from start of He/O₂ phase up to this point as pyrolytic and it is added to the total OC amount. EC detected after this “split point” are then treated as native EC content of the sample.

Different protocols having their own temperature ramps and step durations are used in thermal–optical analysis. While yielding virtually equal total carbon concentrations (TC, equal to the sum of OC and EC), different protocols give varying OC/EC splits or apportionment leading to wide variation in resulting concentrations (Chow et al., 2001; Reisinger et al., 2008). Up to present, different organizations use different thermal–optical protocols. Three of the most widely–recognized protocols are summarized in Table 1. The first protocol, NIOSH (National Institute for Occupational Safety and Health), was derived from Birch and Cary (1996)

and was originally intended to measure EC as tracer of diesel exhaust for occupant exposure control of workers, such as those in the mining industry. It was also one of the first to be widely-used for ambient monitoring, particularly in US EPA's (Environmental Protection Agency) Speciation Trends Network urban sites, until its substitution with IMPROVE_A protocol in April 2006 (U.S. EPA, 2006).

Table 1. Temperature steps and durations of NIOSH, IMPROVE_A (Chow et al., 2007), and EUSAAR_2 (Cavalli et al., 2010) protocols

STEP	NIOSH T (°C), duration (s)	IMPROVE_A ^a T (°C), duration (s)	EUSAAR_2 T (°C), duration (s)
OC1	310, 80	140, 150-580	200, 120
OC2	475, 60	280, 150-580	300, 150
OC3	615, 60	480, 150-580	450, 180
OC4	870, 90	580, 150-580	650, 180
EC1	550, 45	580, 150-580	500, 120
EC2	625, 45	740, 150-580	550, 120
EC3	700, 45	840, 150-580	700, 70
EC4	775, 45		850, 80
EC5	850, 120		
EC6	870, 120		

^a Residence time at each temperature step depends on when the FID signal returns to the baseline.

The second protocol, currently most widely used in US, is IMPROVE_A (Interagency Monitoring of Protected Visual Environments). Proposed by Chow et al. (2007), it is originally used in all US IMPROVE network sampling sites. It differs from NIOSH on the following: highest temperature in pure He phase of analysis (OC4) is lowered from 870 °C of NIOSH to 580 °C since it was found that often, the laser signal already increases at 870 °C pure He step. This indicates that light-absorbing substances are prematurely evolving at this temperature step when supposedly it should not, leading to inaccurate OC-EC split. Fung et al. (2004) suggested that similar to the mechanism of carbon oxidation of MnO₂, metal oxides present in sample may cause this premature oxidation. To avoid this, IMPROVE_A's highest temperature step in pure Helium (He) is lowered to 580 °C; IMPROVE_A protocol uses laser reflectance for pyrolysis corrections, in lieu to NIOSH's laser transmittance correction. Rationale is that reflectance is more influenced by near-surface char (where ~80% of deposit is located), which appears to evolve first in He/O₂ phase, while transmittance is more affected by within-filter char resulting in longer return-to-baseline laser signal times and thus, more delayed OC-EC split. Reflectance corrections were also found to agree more closely with optical methods that are based on EC light absorption (Chow et al., 2004).

Third and most recent protocol is EUSAAR_2 (European Supersites for Atmospheric Aerosol Research). Proposed by Cavalli et al. (2010) with the purpose of having a standardized method for European sites, it builds on NIOSH and IMPROVE_A protocols through the following: Longer OC1 and OC2 step times – the two assumptions for accurate optical correction of pyrolytic char (designation of OC-EC split) is that either char formed from pyrolysis of OC evolves first in He/O₂ step, or it has equivalent light attenuation with native EC. But in reality, both assumptions may not be always true and therefore biases in the OC-EC splits occur. EUSAAR_2 protocol minimizes this error by favoring volatilization of OC over pyrolysis by prolonging steps in lower temperatures, OC1 and OC2; Laser transmittance correction – since this corrects for pyrolytic carbon formed within filter, which is still part of total carbon; 650 °C maximum He phase step – while 580 °C in pure He of IMPROVE_A protocol does limit premature evolution of light absorbing substances, Cavalli et al. (2010) found that this temperature was too low, leading to significant amounts of OC

being carried over to the He/O₂ phase. 650 °C was identified to be the optimum maximum temperature for He phase since 91–98% of most OC evolve at this temperature without premature evolution of light absorbing substances. Thus, 650 °C is adopted as maximum temperature step in pure He phase for EUSAAR_2; Lastly, like in IMPROVE_A, durations of the temperature steps in the EUSAAR_2 protocol, though defined, are all prolonged enough such that the carbon peaks are properly resolved most of the time and no overlaps will occur.

This study aims to find an optimal thermal-optical analysis protocol for Philippine OC/EC samples by comparing NIOSH, IMPROVE_A and EUSAAR_2. Philippines is particularly interesting because it has one of the highest EC concentration and lowest OC/EC ratio in the region. Samples used represent both rural and urban setting and their detailed OC/EC characterization has been previously published (Bautista et al., 2014). Criteria used for comparison include laser correction method (transmittance vs. reflectance); minimization of pyrolyzed carbon formation to reduce associated errors; correct evolution and quantification of total OC and EC; proper fractionation of different OC and EC fractions; and analysis times. Consequently, the study proceeds to recommend and test an optimal protocol for the observed Philippine setting.

2. Methodology

For succeeding parts of this paper, we use the following convention for different protocols and their corresponding laser correction method: NT-NIOSH Transmittance; NR-NIOSH Reflectance; IT-IMPROVE_A Transmittance; IR-IMPROVE_A Reflectance; ET-EUSAAR_2 Transmittance; and ER-EUSAAR_2 Reflectance. Note that standard correction mode for both NIOSH and EUSAAR_2 is Transmittance while IMPROVE_A uses Reflectance, but both correction methods were performed for each of the three protocols so as to obtain more insights regarding their comparisons.

2.1. NIOSH, IMPROVE_A, and EUSAAR_2 comparison

Eighty four urban (Valenzuela City, Metro Manila) and 35 rural (Angat, Bulacan) ambient 24-hours air particulate samples were analyzed for protocol comparison. Sampling was done over a one-year period from September 2011 to August 2012 (twice a week – Wednesdays and Sundays) using Pallflex quartz-fiber filters pre-baked at 900 °C for three hours (to remove adsorbed carbonaceous material). Sampling was done in PM_{2.5} range using Gent sampler with PM₁₀ impactor installed on top of the sampling head assembly. Nucleopore coarse filter (8 µm pore size) placed before actual quartz filter removed particles in the PM_{2.5-10} range.

Analyses for OC and EC concentrations were done using Sunset Laboratory OC-EC Aerosol Analyzer. The method used is thermal-optical analysis wherein three (3) separate 1.5 cm² punches were obtained from the same filter per sample then analyzed subsequently using NIOSH, IMPROVE_A, and EUSAAR_2 protocols (See Table 1). Calculations for both transmittance and reflectance corrections were then performed for each protocol using the software bundled with Sunset Analyzer to obtain carbonaceous aerosol concentrations.

Analyses yield four OC fractions (OC1 to OC4, evolving during the pure He atmosphere phase of the analysis), a pyrolyzed carbon fraction (PC, portion of the OC that has undergone pyrolysis and transformed into EC during the analysis – co-evolves with EC and corrected with laser transmittance/reflectance) and three to six EC fractions, depending on the protocol used (EC1 to EC6, evolving during the 2% oxygen/98% helium atmosphere phase of the analysis). From these, total OC=OC1+OC2+OC3+OC4+PC and total EC=EC1+EC2+...+EC[n]-PC (where [n] is number of resulting EC fractions of protocol used). Corrections for EC fractions are as follows: EC1_{corrected}=EC1_{original}, as given by instrument-PC; If PC is greater than EC1_{original}, then EC1_{corrected}=0 and EC2 would be subsequently

corrected as $EC2_{corrected} = EC2_{original} - (PC - EC1_{original})$; the same is done for EC3 if $(PC - EC1_{original})$ is still greater than $EC2_{original}$. $EC1_{corrected}$, $EC2_{corrected}$, ..., $EC[n]_{corrected}$ will be simply referred to as EC1, EC2, ..., EC[n] for the remaining parts of this paper.

Typical measurement errors as calculated by the instrument are in the range of 6.0%–7.8% and 6.5%–10% for OC and EC, respectively. However, as discussed in the latter parts of this paper, there are inherent systematic errors to take into account, highly dependent on which protocol is used.

Quality assurance/quality control procedures are summarized in Bautista et al. (2014).

2.2. Recommended protocol testing

From the results of protocol comparison, a recommended thermal–optical analysis protocol (modified version of IMPROVE_A with increased OC4 temperature step to 650 °C and laser transmittance correction) was formulated and subsequently tested on sixteen (16) urban samples from the same site in Valenzuela. These were collected in October–December 2012 and analyzed using same methods, except that three (3) separate 1.5 cm² filter punches were analyzed using recommended protocol, IMPROVE_A, and EUSAAR_2.

3. Results and Discussion

3.1. OC and EC measurement comparisons between temperature protocols

Shown in Table 2 are averages of OC, EC, and TC in $\mu\text{g m}^{-3}$ and their percent contribution to whole $\text{PM}_{2.5}$ mass for both sites for the one-year sampling duration. All protocols yield almost equivalent TC values of about $14.5 \pm 0.1 \mu\text{g m}^{-3}$ for urban Valenzuela site and $6.2 \pm 0.2 \mu\text{g m}^{-3}$ for rural Angat site. Additionally, this indicates fairly uniform particulate matter deposition on filter samples since protocol comparisons were done by analyzing three (3) 1.5 cm² punches from the same filter. While this is the case for TC, varying OC and EC apportionment were observed across different protocols, being consistent with reports of Chow et al. (2001) and Reisinger et al. (2008). Valenzuela OC concentrations were in the range of 8.00–9.56 $\mu\text{g m}^{-3}$ while EC were at about 4.85–6.63 $\mu\text{g m}^{-3}$. Angat, meanwhile, has OC values ranging from 4.08–5.32 $\mu\text{g m}^{-3}$ and EC values of about 0.94–2.29 $\mu\text{g m}^{-3}$. These data are graphically represented in box plots in Figure 1a and 1b. In general, IR consistently gives the lowest OC and highest EC in both sites and vice versa for NT. The relationship between the other protocols, however, is less defined and appears to be site-specific (i.e., different for urban and for rural).

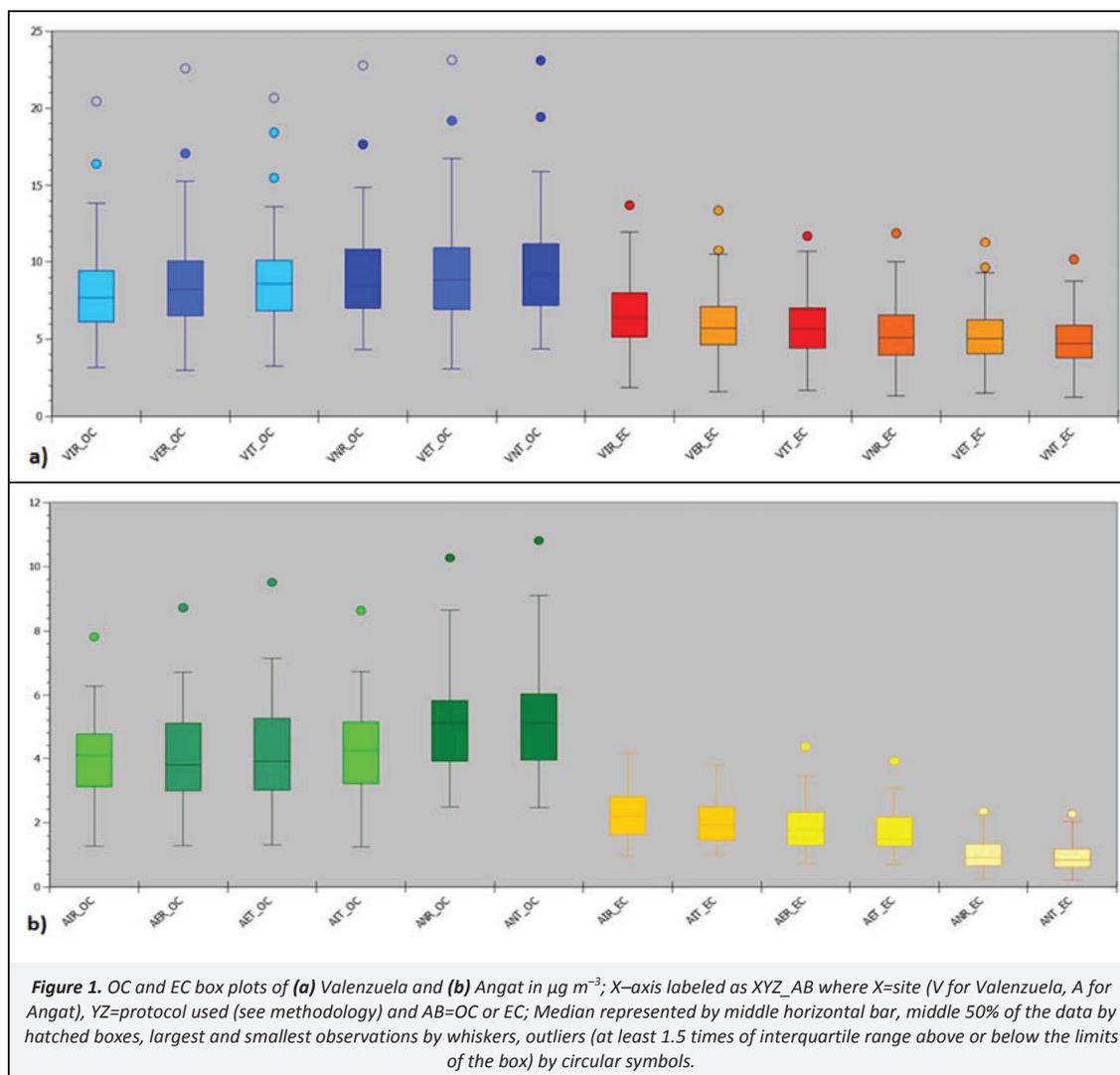


Table 2. Averages of OC, EC and TC concentrations in $\mu\text{g m}^{-3}$ for urban Valenzuela, Metro Manila and rural Angat, Bulacan from September 2011–August 2012, using NIOSH, IMPROVE_A, and EUSAAR_2 protocols with both transmittance and reflectance corrections

	Valenzuela			Angat		
	OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	TC ($\mu\text{g m}^{-3}$)	OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	TC ($\mu\text{g m}^{-3}$)
NT	9.56	4.85	14.41	5.32	0.94	6.26
NR	9.13	5.30	14.44	5.23	1.05	6.28
IT	8.79	5.87	14.66	4.29	2.10	6.39
IR	8.00	6.63	14.64	4.08	2.29	6.37
ET	9.20	5.21	14.41	4.27	1.75	6.02
ER	8.52	5.89	14.41	4.12	1.90	6.02

To be more statistically adequate and with the aim of looking at more general relationships, scatter plots (see the Supporting Material, SM, Figures S1 and S2) comparing OC and EC values given by different protocols were done for the whole dataset (i.e., pooled data of both sites). The linear parameters of the plots (slope, intercept, and R^2) are summarized in Tables 3a and 3b. These comparisons show that OC and EC values of all protocols are highly correlated with one another with R^2 values greater than 0.94. Linear equations generated by these comparisons (given by Tables 3a and 3b) thus provide the means to “interconvert” OC and EC concentrations between protocols. At the very least, this provides Philippine OC/EC data great flexibility since comparisons can be made with any other past or future data obtained using any of these protocols. The other implication of this observation is that since there are definite relationships across protocols, the main reasons driving differences between them must be constant and systematic. If so, two most probable reasons for differences are (1) method of laser correction (i.e., transmittance vs. reflectance) and (2) differences between individual temperature steps of the protocols.

3.2. Transmittance vs. reflectance

To investigate difference between transmittance and reflectance corrections, we focus on comparisons between same temperature protocol but with different laser correction methods (i.e., NT vs. NR, IT vs. IR, and ET vs. ER) in Tables 3a and 3b (represented graphically in Figures S1 and S2, see the SM). Results show that for all three protocols transmittance tends to result in higher OC and lower EC value. Moreover, magnitude of the effect of this trend is almost same for all protocols with reflectance vs. transmittance slopes of about 0.9 and 1.1 and intercepts of about 0.2 and -0.06 for OC and EC, respectively. This suggests that effect of laser correction method is independent of temperature protocol. For all protocols, this trend is highly linear with concentration within the range of samples obtained, having R^2 values greater than 0.99. Near-zero intercept, slopes greater than 1, and highly linear results indicate that using the same temperature protocol, transmittance and reflectance will consistently give almost equal values at lower concentrations but will increasingly deviate from each other as higher loadings are analyzed (seen graphically in the SM, Figures S1 and S2). This is probably the main reason for site-specific differences in trends between Valenzuela and Angat (as seen in Table 2 and Figure 1a and 1b) wherein NR–NT, IT–IR, and ET–ER have closer average values and box plot distributions for rural Angat but less so in urban Valenzuela, where heavier filter loadings are observed.

Cause of the transmittance vs. reflectance difference, as Chow et al. (2004) have reported, is char formed within the filter during sample analysis. Eighty percent of the deposit is initially located near or on the filter surface, but as analysis progresses, pyrolyzed carbon (PC) formation occurs throughout the filter (particularly during He phase). The disparity however, is introduced during He/O₂ phase wherein reflectance signal goes back to baseline earlier than transmittance since reflectance detects only PC at filter surface while transmittance monitors whole filter cross-

section. This suggests that when O₂ is introduced, surface PC together with native EC evolves first and evolution of PC formed within (or at the back side) the filter is more delayed.

Relating to observed trends, it is likely that for lightly loaded filters, PC formed within filter are negligible thus giving roughly same reflectance and transmittance results. Heavily loaded filters however have more significant internal PC contribution, resulting in divergence between transmittance and reflectance corrections.

3.3. Pyrolyzed carbon formation and correct evolution

As noted by Cavalli et al. (2010), underlying assumptions for pyrolyzed carbon (PC) correction (i.e., either char formed from pyrolysis of OC evolves first in He/O₂ step, or it has equivalent light attenuation with native EC) may not always hold true. Therefore, to minimize errors associated with this, minimal pyrolyzed carbon (PC) formation is desired. To investigate protocol performances regarding this, Figure 2a and 2b summarize average percentages of individual carbon fractions to TC for Valenzuela and Angat. Comparing between protocols within same laser correction method, NIOSH appears to give lowest PC formation for both transmittance and reflectance in Angat (Figure 2b, 10.39% and 8.88%, respectively) as well as for transmittance in Valenzuela (Figure 2a, 8.76%), while IMPROVE_A results in lowest PC formation for Valenzuela using reflectance correction (Figure 2a, 4.87%). Low PC formation for NIOSH is however misleading and the reason may be seen by looking at individual thermograms.

As summarized in Table 4, visual inspection of thermograms show increase in both transmittance and reflectance signal in pure He phase (e.g., see the SM, Figure S3) occurring frequently for NIOSH protocol (and almost not at all for IMPROVE_A and EUSAAR_2). As Chow et al. (2001) and Fung et al. (2004) reported, probable reason is that 870 °C step in He phase, which is only present in NIOSH, is too high leading to premature oxidation of light-absorbing carbon by metal oxides within the sample. Thus, it is not valid to say that NIOSH has lowest percent PC since it may already have evolved as early as in OC4 stage. In Figure 2b, percent OC4 of NIOSH protocol is much greater compared to other two protocols and looking at Figure 1b, it can also be said that Angat OC values of NIOSH are significantly higher than those given by IMPROVE_A and EUSAAR_2. This premature evolution is the reason for relatively higher OC and lower EC results of NIOSH protocol.

Another important factor to be taken into account is that as Cavalli et al. (2010) reported, highest He step of IMPROVE_A protocol (580 °C), is not sufficiently high and that some OC carry over to He/O₂ phase and detected alongside either PC or native EC. This is also observed for Philippine samples as seen in Figure 2a and 2b where on average cumulative percentage up to OC4 of EUSAAR_2 protocol (which has a highest He step of 650 °C) is slightly greater than that of IMPROVE_A (about 2.3% difference in Valenzuela and 4.9% in Angat). Again, this is more evident in Angat since it is more OC-dominated and has lower EC values. However, going back to comparisons, it appears that the magnitude and

resulting bias of this effect is significantly less than that of premature evolution in NIOSH protocol. Still, this may be the primary cause of slightly lower OC and higher EC values of IMPROVE_A measurements.

Taking these observations into account, the following may be concluded for PC formation: IMPROVE_A protocol results in lowest PC contribution in Valenzuela for both transmittance and reflectance corrections even with possible positive bias due to OC that carries over to He/O₂ phase being detected as PC. EUSAAR_2, on the other hand, yields lowest PC value in Angat for both laser correction methods, slightly lower than that of IMPROVE_A.

3.4. Fractionation and analysis times

Another important consideration for protocol selection is proper carbon fractionation, that is respective fractions evolve completely during each temperature step and are not carried over to the next. This is important for proper characterization of carbonaceous aerosol since separate fractions may provide clues to

different sources. IMPROVE_A protocol does this inherently since it does not move on to next temperature step without the FID signal going back to baseline. Therefore, resolutions of NIOSH and EUSAAR_2 are investigated with IMPROVE_A as reference.

Looking at Figure 2a and 2b, it is evident that NIOSH does not resolve properly for both OC and EC. OC1 NT and NR (10.3% in Valenzuela and 11.5% in Angat, only one value is given for this and all succeeding comparisons since transmittance and reflectance gives approximately equal percentages), which evolves at 310 °C, should be more than or equal to OC2 IT and IR (20.2% in Valenzuela and 17.4% in Angat) which evolves only at 280 °C. Instead, OC1 NT and NR are significantly lower for both sites. This shows that there is not enough time for OC1 NIOSH to evolve completely before proceeding to next temperature step, and thus is carried over to next fractions and not accounted for properly. Same is observed when comparing cumulative percentages of OC2 NT and NR (evolves at 475 °C; 24.6% in Valenzuela and 23.0% in Angat) to OC3 IT and IR (evolves at 480 °C; 46.0% in Valenzuela and 44.4% in Angat).

Table 3. Linear slope, intercept, and R^2 values of (a) OC and (b) EC comparisons of NIOSH, IMPROVE_A, and EUSAAR_2 protocols. Parameters at top and left edge of the tables correspond to y-axis and x-axis variables, respectively

(a) OC Line Eqns.		NT	NR	IT	IR	ET	ER
	Slope		0.925	0.940	0.843	1.025	0.928
NT	Intercept		0.291	-0.350	-0.162	-0.778	-0.492
	R^2		0.995	0.953	0.950	0.946	0.941
	Slope	1.076		1.011	0.910	1.103	1.002
NR	Intercept	-0.275		-0.607	-0.416	-1.059	-0.773
	R^2	0.995		0.949	0.952	0.942	0.943
	Slope	1.014	0.939		0.896	1.084	0.982
IT	Intercept	0.745	0.980		0.166	-0.343	-0.097
	R^2	0.953	0.949		0.993	0.980	0.975
	Slope	1.127	1.046	1.109		1.203	1.093
IR	Intercept	0.596	0.820	-0.131		-0.490	-0.261
	R^2	0.950	0.952	0.993		0.974	0.977
	Slope	0.923	0.854	0.904	0.810		0.906
ET	Intercept	1.166	1.369	0.460	0.574		0.208
	R^2	0.946	0.942	0.980	0.974		0.996
	Slope	1.014	0.941	0.993	0.893	1.099	
ER	Intercept	0.986	1.182	0.286	0.392	-0.199	
	R^2	0.941	0.943	0.975	0.977	0.996	

(b) EC Line Eqns.		NT	NR	IT	IR	ET	ER
	Slope		1.101	1.036	1.183	0.948	1.091
NT	Intercept		-0.020	0.933	0.982	0.687	0.681
	R^2		0.993	0.959	0.962	0.965	0.961
	Slope	0.043		0.935	1.073	0.858	0.992
NR	Intercept	0.046		0.976	1.009	0.718	0.696
	R^2	0.993		0.954	0.967	0.964	0.970
	Slope	0.044	1.021		1.135	0.902	1.034
IT	Intercept	-0.713	-0.811		-0.053	-0.104	-0.213
	R^2	0.959	0.954		0.992	0.977	0.967
	Slope	0.039	0.901	0.874		0.792	0.913
IR	Intercept	-0.660	-0.777	0.083		-0.046	-0.175
	R^2	0.962	0.967	0.992		0.977	0.978
	Slope	0.049	1.124	1.082	0.053		1.149
ET	Intercept	-0.568	-0.662	0.224	0.179		-0.104
	R^2	0.965	0.964	0.977	0.977		0.994
	Slope	0.042	0.978	0.935	0.047	0.865	
ER	Intercept	-0.455	-0.561	0.357	0.304	0.116	
	R^2	0.961	0.970	0.967	0.978	0.994	

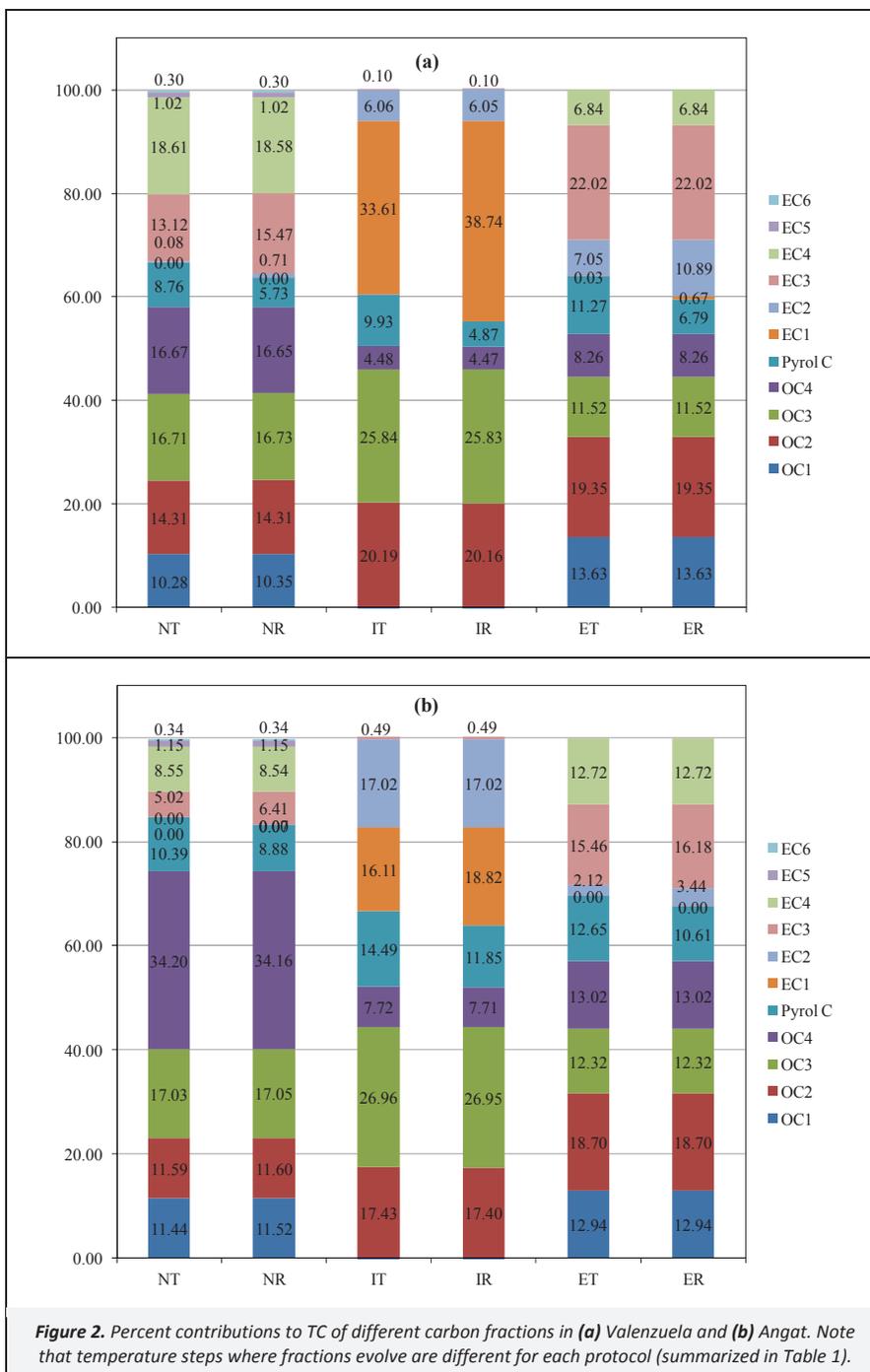


Table 4. Frequency of early laser signal increase during pure He phase (see the SM, Figure S3) for Valenzuela and Angat samples

	NIOSH		IMPROVE_A		EUSAAR_2	
	Trans.	Reflec.	Trans.	Reflec.	Trans.	Reflec.
Valenzuela	40	30	0	0	3	3
Angat	21	13	1	0	3	2

84 Valenzuela, 35 Angat samples

Proper fractionation of EC is equally as important, especially since Philippines have such high concentrations, particularly of IMPROVE_A EC1 fraction. Looking at results, EC1 NT and NR (550 °C) should be close to EC1 IT and IR values (580 °C; 34–39% in

Valenzuela and 16–19% in Angat) but since time intervals for NIOSH EC steps are likewise too fast, laser correction still has not returned to baseline when it shifts to next temperature step. As a result, entire NIOSH EC1 (and also EC2) peaks were often counted as all PC resulting to null values, and this is incorrect. This does not happen for IMPROVE_A since for almost all samples, laser signals already attain baseline value during EC1 step (580 °C) and thus, PC and EC1 are almost always on the same signal peak and are properly distinguished from each other. NIOSH’s poor peak resolution is visually easy to observe in its thermograms (as is shown by the example in Figure S3, see the SM).

EUSAAR_2, on the other hand, seems to resolve OC properly as shown by almost equal cumulative OC3 IT and IR (480 °C; 46.0%

in Valenzuela and 44.4% in Angat) and OC3 ET and ER (450 °C; 44.5% in Valenzuela and 44.0% in Angat) percentages for both Valenzuela and Angat (Figure 2a and 2b). The slight differences between protocol results also imply that very few material (about 1.5% in Valenzuela and 0.4% in Angat) evolve between 450 °C and 480 °C. In contrast, there is a large disparity between cumulative OC2 IT and IR (280 °C; 20.2% in Valenzuela and 17.4% in Angat) and OC2 ET and ER (300 °C; 33.0% in Valenzuela and 31.6% in Angat) indicating considerable amounts of OC evolving between 280 °C and 300 °C. However, same as observed in NIOSH, EC resolution of EUSAAR_2 was also poor. Particularly evident is virtually null EC1 (500 °C) and low EC2 in ET and ER (550 °C; 7–11% in Valenzuela and 2.1–3.4% in Angat) compared to very high EC1 values in IT and IR (580 °C; 34–39% in Valenzuela and 16–19% in Angat). Thus while EUSAAR_2 performs well in other criteria, it falls short with regards to proper fractionation of heavily EC-loaded samples, such as from the Philippines.

In general for Philippine OC/EC samples, IMPROVE_A solely provides good OC and EC fraction resolutions owing to its variable step times; EUSAAR_2 resolves OC properly but not EC; while NIOSH does not have good carbon fractionation for both.

One resulting disadvantage for IMPROVE_A however is that since it waits for FID signal to go back to baseline, analysis times are variable and generally longer. Analyses using IMPROVE_A take about 1 360–1 800 s for Valenzuela (average of 1 662 seconds) and 1 223–1 712 s (average of 1 386 seconds) for Angat. NIOSH and EUSAAR_2, on the other hand, have constant 804 and 1 169 s analysis times, respectively.

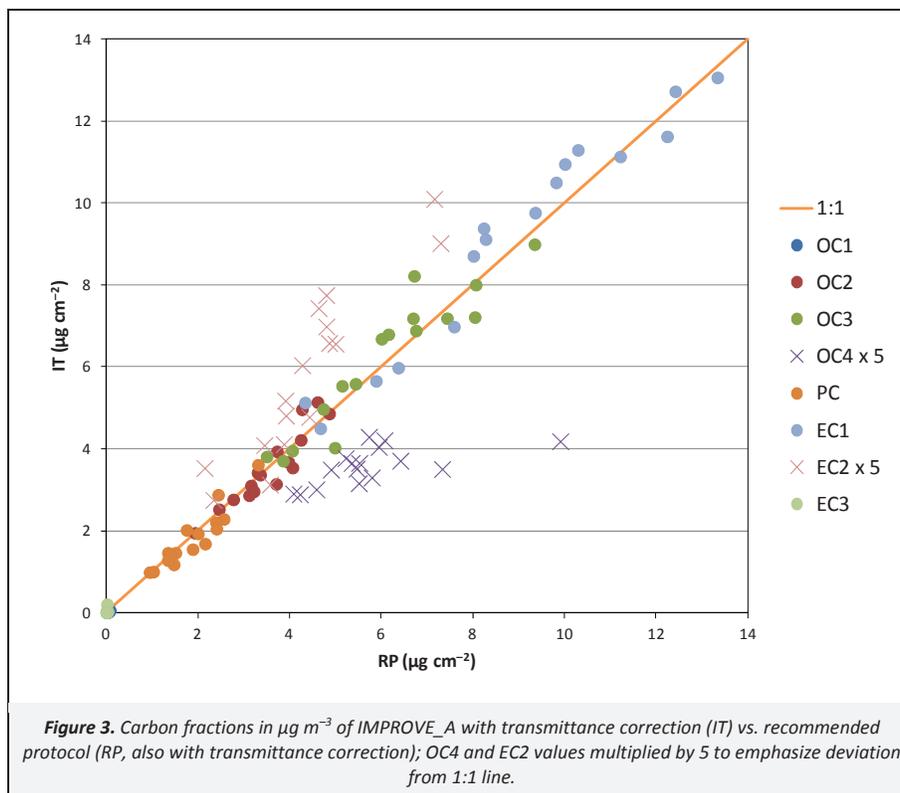
3.5. Recommended protocol for Philippine OC/EC samples and its preliminary results

Integrating all these findings, the following protocol is recommended for improved analysis accuracy as applied to Philippine

OC/EC samples: a modified version of IMPROVE_A with increased OC4 temperature step (650 °C from 580 °C, adopted from EUSAAR_2 protocol) and transmittance as laser correction method. The proposed protocol is expected to give (1) minimized unevolved OC in the He phase (due to increased OC4 temperature) leading to more accurate OC/EC quantification, as seen in EUSAAR_2; (2) proper resolution of OC and EC fractions as observed in IMPROVE_A; (3) minimal PC formation leading to minimized errors associated with its correction; and (4) OC laser correction by transmittance which takes into account PC formed within filter.

Recommended protocol (RP) was tested against IMPROVE_A (both IT and IR) and EUSAAR_2 (ET) on a new batch of sixteen (16) samples collected in Valenzuela from October–December 2012. Comparison of RP and IT carbon fractions (Figure 3) shows increased OC4 and decreased EC2 for RP, while all other fractions remain virtually equivalent. These results indicate (a) unevolved OC in pure He phase has been minimized in RP due to increased OC4 temperature step (650 °C), leading to more accurate OC quantification; (b) unevolved OC4 in IT is majorly detected as EC2, showing that IMPROVE_A has inherent negative OC/positive EC bias; and (c) RP maintains the same controlled pyrolyzed carbon (PC) formation as IT, demonstrated by equivalent PC contributions between protocols. Same exact trends are observed when comparing RP and IMPROVE_A both using reflectance laser correction (not shown).

Concurrently, comparisons of total OC and EC of RP vs. IR and ET (Figure 4a and 4b; IR and ET are standard laser correction modes of IMPROVE_A and EUSAAR_2, respectively) show that RP and ET expectedly yield equivalent OC and EC concentrations, demonstrating that RP is as accurate as EUSAAR_2 in this aspect. RP however, has advantage in terms of proper OC and EC fractionation due to its variable step times, while EUSAAR_2 cannot properly resolve individual EC fractions in such heavily EC-loaded samples as seen in Figure 5.



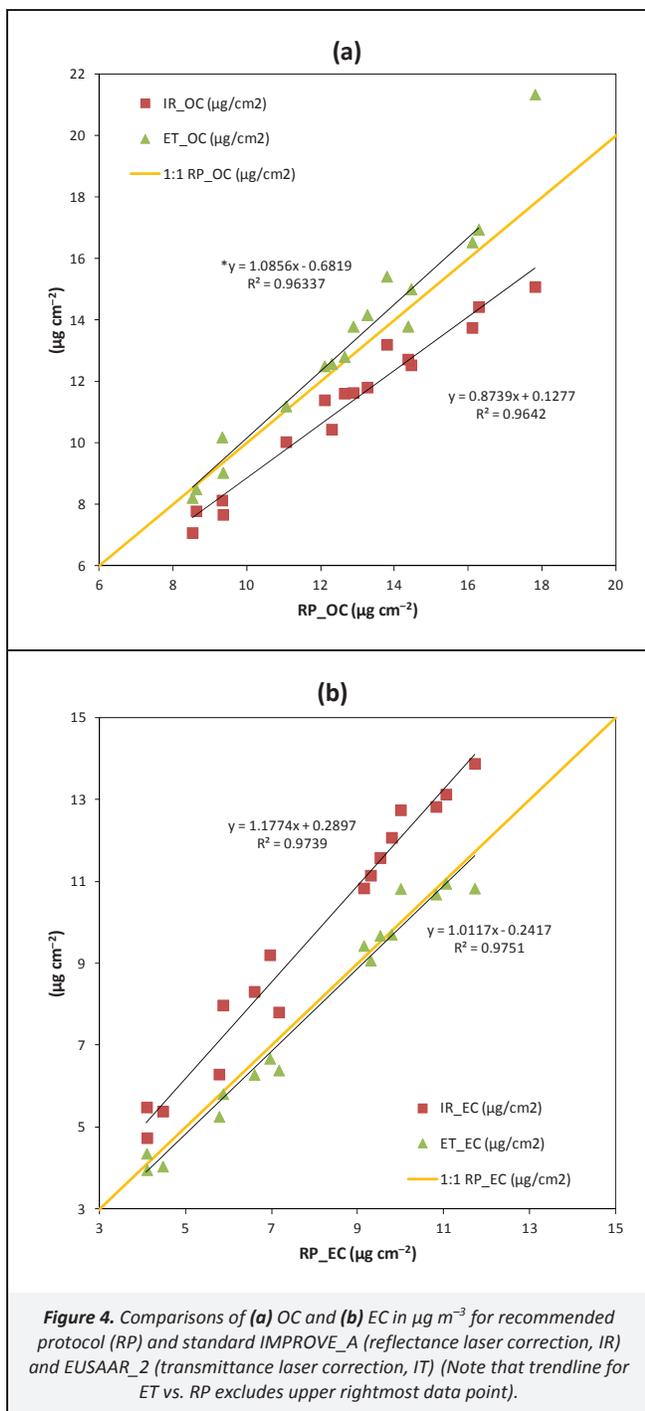


Figure 4. Comparisons of (a) OC and (b) EC in $\mu\text{g m}^{-3}$ for recommended protocol (RP) and standard IMPROVE_A (reflectance laser correction, IR) and EUSAAR_2 (transmittance laser correction, IT) (Note that trendline for ET vs. RP excludes upper rightmost data point).

These results show the effectiveness of the recommended protocol for OC/EC analysis of Philippine samples, which are again characterized by heavy EC (particularly IMPROVE_A EC1 fraction) loadings. It minimizes disadvantages observed in established protocols, while maintaining desired performance criteria. It can thus be said that recommended protocol meets aforementioned performance objectives and expectations for samples analyzed. Moreover, it is also expected to perform as well for lightly-loaded samples. Thus, recommended protocol is envisioned to have better general applicability than established protocols due to its better accuracy and non-sensitivity towards degree of filter loading. However, application to larger number and wider variety (both in degree of filter loading and OC/EC composition) of samples is still needed to more properly assert these findings.

4. Conclusions

In summary, this study compares NIOSH, IMPROVE_A, and EUSAAR_2 protocols with the aim of finding an optimal thermal-optical analysis method for Philippine OC/EC air particulate samples. Comparisons show all three protocols give equivalent total carbon (TC) concentrations but differ in their OC and EC apportionments. Main reasons for disparity are differences in laser correction method and protocol step temperatures and durations.

Divergence between laser correction methods is mainly associated with their ability to account for PC formed within filter (i.e., transmittance is capable and reflectance is not). As a result, reflectance yields lower OC and higher EC concentrations. This disparity increases with concentration or filter loading. In terms of total OC and EC quantification, NIOSH exhibits premature EC evolution in the OC4 pure He phase, while IMPROVE_A OC4 temperature step (580 °C) is insufficiently high, causing some OC to be carried over to He/O₂ phase to be measured mainly as EC2. , NIOSH and IMPROVE_A thus show negative and positive EC bias, respectively. EUSAAR_2 minimizes both effects and may be most accurate in this aspect. Concurrently, IMPROVE_A and EUSAAR_2 yield lowest pyrolyzed carbon (PC) formation for urban and rural site, respectively. Minimal PC formation is desired to minimize errors associated with its correction. Finally, IMPROVE_A is solely capable of properly resolving individual OC and Philippines’s particularly abundant EC fractions owing to the protocol’s variable step durations.

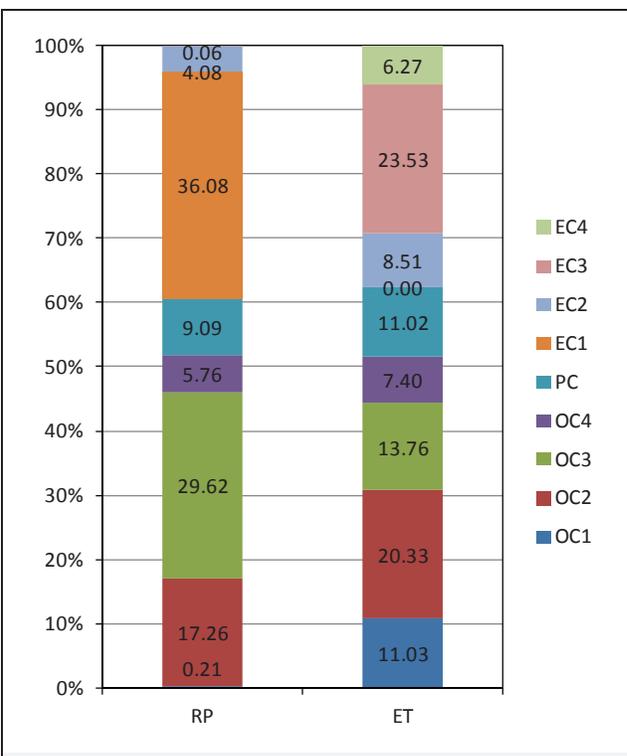


Figure 5. Percent contributions to TC of recommended protocol (RP) vs. EUSAAR_2 (ET), both with transmittance correction.

Integrating these findings, a modified version of IMPROVE_A protocol with increased OC4 temperature step (650 °C, adopted from the EUSAAR_2 protocol) using transmittance laser correction method is recommended as optimal for Philippine OC/EC sample analysis. The protocol is expected to result in proper OC and EC evolution, detection, and fractionation despite high EC loadings in Philippine samples. Further, minimized PC formation and accounting of within-filter-PC is expected to lead to more accurate results.

Preliminary testing of recommended protocol show good results, meeting said expectations. However, application to larger number and wider variety of samples is still needed to more properly assert these findings.

Acknowledgments

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Supporting Material Available

OC and EC protocol comparison scatter plots (Figures S1 and S2) and Typical NIOSH thermogram showing premature increase of laser and overlap of carbon fraction peaks (Figure S3). This information is available free of charge via the internet at <http://www.atmospolres.com>

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