Carbonaceous aerosol: where is it coming from?

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Contents

Summary

Chemical composition as well as physical properties of organic and elemental carbon fractions (OC and EC, respectively) as well as black carbon (BC) reflect specific emission sources (combustion of fossil fuel by vehicular traffic and shipping, biomass burning in electricity plants and wood stoves, and biogenic contribution). In this report a number of these features are described. For political decision-making, an essential question is the following: when emissions of one source (traffic) go down in the near-future, will the (associated) health risk also be lower? At this time, any answer to this question is highly speculative as current knowledge is incomplete and debatable. We therefore focus on a more basic question, i.e., can we discriminate between contributions of the various sources by looking at the OC and EC concentrations? And, equivalently, does the ratio OC/EC change for different sources?

The work presented here is the starting point for a more extended review to be produced at a later stage. Chapter 3 interprets concentration data from in-situ measurements, while Chapter 4 primarily describes emission characteristics based on (global-scale) modelling studies. Some interesting observations from this study are:

- Usually organic carbon concentrations exhibit a poor correlation with elementary carbon indicating a different origin for their presence in PM. Also, average concentrations of OC are higher than those of EC.
- EC originates from primary sources, i.e. transport, biomass burning, and energy production (using coal). The highest levels are measured near busy roads and inside tunnels. EC accounts for approximately 30% of the total carbon at urban sites. At rural sites, this is 10% (PM2.5) to 20% (PM10).
- Similar levels of EC are observed in PM2.5 and PM10 indicating that EC is mainly associated to PM2.5. In contrast, OC levels measured in PM2.5 are clearly lower than in PM10. Its presence in the coarse fraction is some 20-40% of total OC and probably caused by large biogenic particles.
- 30% of the organic carbon comes from fossil fuel combustion, even in the city centres. Biomass burning and natural emissions (mainly of gaseous precursors such as terpenes) dominate the emissions of OC.
- The OC/EC ratio is higher than 1 for all examined datasets. This indicates that most of the OC in PM2.5 and PM10 is of a secondary origin (SOA), possibly owing to various chemical reactions of volatile gaseous compounds and their subsequent condensation in the atmosphere. EC is entirely related to primary aerosol (POA).

- EC and OC levels observed in Asian cities are higher than in US and EU. This is believed to be caused by specific sources like fuel combustion by traffic and wood burning for residential cooking.
- The study of the various experimental data sets show that OC/EC ratios vary between around 1 (along busy traffic streets and within tunnels) and 15 (shipping). Ratios for urban background sites and biomass burning are between 4 and 5. The data from ships exhausts were characterized with a (very) low (and rather unexpected) EC content.
- The data from modelling studies give a somewhat different perspective. Here, the burning of fossil fuel (traffic, power generation, industry) leads to lower OC/EC ratios (up to 1) compared to biomass burning (near 6), both in agreement with observational data. For residential activity (mainly cooking) it is 3. Shipping emissions have an OC/EC ratio varying between 2 and 7, much lower than concluded from the measurement. Part of these discrepancies can be understood by considering the effect of dilution and SOA formation on concentration levels: EC-rich exhaust becomes mixed with less EC-rich ambient air, increasing the OC/EC ratio. Modelling studies often include emission inventories, which do not take into account the effect of mixing of air masses. Further examination is needed here.

1

Introduction

Burning carbon containing material, such as biomass or fossil fuel, results in the emission of (precursors to) carbonaceous aerosol. The material burnt and the burning conditions influence the chemical characteristics of the resulting carbonaceous aerosol. Incomplete burning (i.e., oxygen limited and/or low temperature) results in a higher fraction of so-called black or elemental carbon (BC or EC, with a high carbon content), whereas complete burning results relatively in more organic carbon (OC, with a lower carbon content and relatively more hydrogen and oxygen). The terms BC and EC are operationally defined, meaning that their quantifications (and definition) depend on the observational method.

Another distinction to make is between primary and secondary (organic) aerosol: The former refers to direct emission of aerosol to the atmosphere, whereas the latter refers to the emission of gaseous precursors (volatile organic compounds or VOC's) which are subsequently oxidized to semi-volatile vapors, which will in turn partition between the gas phase and the particulate phase, leading to secondary organic aerosol (SOA). Both primary and secondary organic aerosol can be biogenic or anthropogenic in origin. The majority of semi-volatile organic vapor originates from terpene emissions from plants and trees, rendering the majority of SOA of biogenic origin. These emissions could in turn be influenced by (anthropogenic) pollution and climate change (e.g. Guenther et al., 2006), blurring the distinction between natural and human caused aerosol. Aerosol resulting from human induced biomass burning is considered anthropogenic. See e.g. Kanakidou et al (2005) or Hallquist et al (2008) for a review of organic aerosol (the former focusing on the link with global climate change, the latter focusing on chemical transformation of the aerosol).

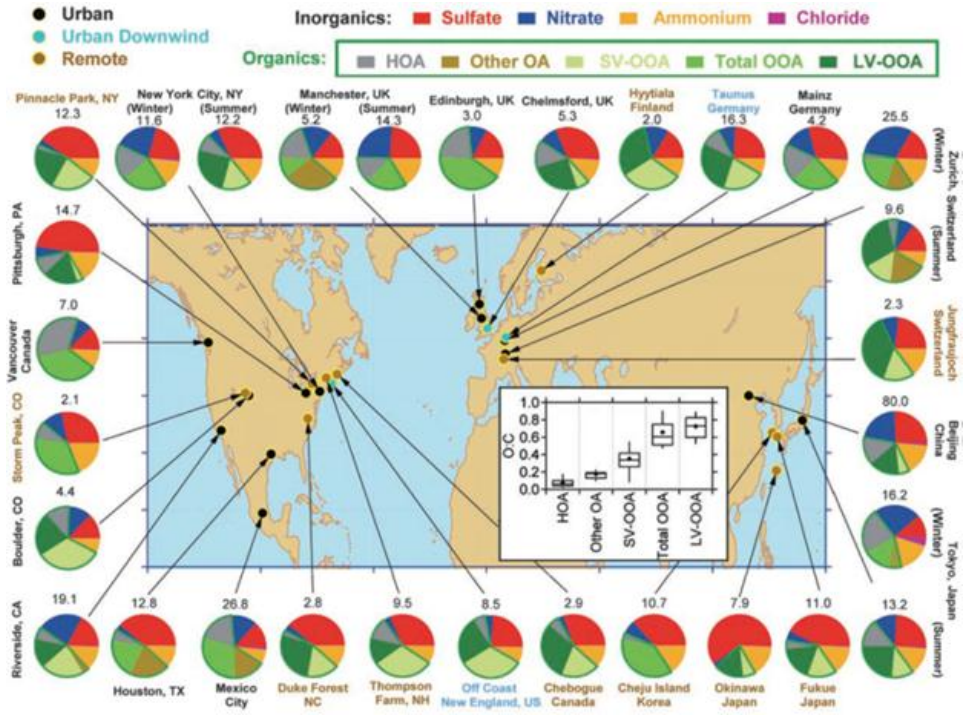
Once in the atmosphere, all aerosol particles undergo chemical and physical transformation processes, such as oxidation, polymerization, condensation, evaporation, coagulation etc. Collectively, the effect of these processes is termed atmospheric aging, referring to the resulting changed composition. The aerosol will become more internally mixed as a result, meaning that the composition will become more homogeneous amongst the aerosol population. A secondary result is that typical source characteristics will gradually become blurred by these aging processes, besides being affected by dilution. As a result of oxidation, aged organic aerosol typically has a

lower H:C ratio and a higher O:C ratio than freshly emitted or recently formed organic aerosol (Heald et al., 2010).

Organic aerosol makes up a quarter to a half of the fine aerosol mass at continental mid-latitudes (e.g. Putaud et al, 2004) and an even larger fraction in forested areas. Due to the multitude of compounds and potential reactions involved, the exact chemical composition of organic aerosol is poorly characterized (Jimenez et al, 2009). Hallquist et al (2008), drawing on several earlier studies, mention selected markers for the identification of anthropogenic and biogenic sources of SOA, e.g. furandione, nonanal and oxygenated PAH for the former, and methyl tetrols, pinonaldehyde and pinonic acid for the latter. In addition, other chemical markers have been suggested as indicative of specific sources. The combined analysis of 14C content and OC/EC ratios showed that the EC fraction in Central Europe is generally dominated by fossil fuel, whereas only ~30% of OC is derived from fossil fuel combustion, even in the city centre (Szidat et al., 2006).

Figure 1 shows the chemical composition at a number of sites in the Northern Hemisphere (Jimenez et al., 2009). The organic fraction is sub-divided into 5 source-specific components. Black carbon is excluded from this figure, since the observational method used cannot observe refractory material.

Figure 1: Total mass concentration (in micrograms per cubic meter) and mass fractions of non-refractory inorganic species and organic components in sub-micrometer aerosols measured with the Aerosol Mass Spectrometer (AMS) at multiple surface locations in the Northern Hemisphere (this excludes black or elemental carbon). HOA = hydrocarbon-like organic aerosol (mostly primary emissions from fossil fuel combustion); SV-OOA = semi-volatile oxygenated organic aerosol; LV-OOA = low-volatility oxygenated organic aerosol; If this distinction was absent, only total oxygenated organic aerosol (OOA) is given; Other OA includes primary organic aerosol other than HOA that have been identified in several studies, including from biomass burning. The inset shows the O:C ratio typical for the different types of organic aerosol, showing the effect of atmospheric aging processes.



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Motivation

Since the beginning of 2012 the experimental determination of black carbon (BC) in particulate matter (PM) has been included in the Dutch monitoring network (LML). The reason is that BC is believed to have stronger relation with observed health effects than the regulated metrics PM10 and PM2.5. In addition, BC (or EC) might be a better indicator to estimate the results of emission reduction measures in cities.
The incorporation of new instruments in LML will result in new datasets that become available for interpretation as well as modelling. For example, in future these data can be used in the large-scale air quality concentration maps for the Netherlands published annually (GCN maps). In anticipation, the urge for more knowledge was felt regarding sources, presence and composition of black and/or elemental carbon. The same kind of questions were raised concerning the organic carbon fraction in PM.
Chemical composition as well as physical properties of these carbon fractions are believed to reflect the respective emission sources like traffic and shipping (combustion of fuel) and wood stoves (biomass burning). With this in mind, some questions of interest are:

1. Can we discriminate between the contributions of the various sources to EC and OC? Does the ratio EC/OC change for different sources?
2. When measuring EC and OC can we assess how much originates from traffic, wood burning and shipping? Is this representative for the Netherlands? And how does this compare to the natural (biogenic) contribution?
3. When emissions of one source (traffic) go down in the near-future, will the (associated) health risk also be lower?
4. What is the influence of artefacts and experimental methods?
5. What is the chemical composition of EC and OC in general terms? Is it possible to define a “characteristic” chemical emission profile for each of the sources? If so, how do they compare to each other?

The study here focusses on some of these questions. It will be the basis for a more extended review to be produced at a later stage. Chapter 3 studies concentration data from in-situ measurements, Chapter 4 primarily deals describes emission characteristics based on global-scale observations and modelling.

3 Concentrations

This chapter presents organic carbon (OC) and elemental carbon (EC) concentrations for both the fine and coarse size fractions of particulate matter (PM2.5 and PM10). In particular, detailed analyses of atmospheric OC and EC in terms of sources, sampling and analytical methods determined in recently published field studies of the Asian, American (USA) and European (EU) cities are reported here.

In most cases, literature data showed that ambient PM samples were collected by means of pre-baked quartz fiber filters or even samplers containing teflon/nylon filters. Besides, in many previous studies it was found that the use of thermal analysis coupled with optical transmission/reflectance (TOT/TOR) techniques or, alternatively, oxidation methods (TOM) provided adequate estimates of particle mass, OC and EC. Ambient carbonaceous components were further detected by the non-dispersive infrared (NDIR) analysis in a few studies.

Among the extensive inventories of the (multi-year) experimental data, measurement locations are often divided into urban and rural sites. Carbonaceous aerosol concentrations observed during specific summer/winter time sampling campaigns are also reported here. Detailed information on the examined US, Asian and EU datasets may be found in the Supporting Information (Appendix A).

3.1 Correlations between OC and EC

Figures 2 and 3 show the correlation that may be found between atmospheric OC and EC concentrations, based on the results of studies carried out in different cities of the US, Asia and EU regarding carbonaceous particulate emissions (PM2.5 and PM10). Data are given here as mean values on a monthly or annual time scale. These results are used as a starting point to select the various sources that could potentially contribute to both OC and EC (in PM2.5 and PM10).

From a first analysis of the data displayed in Figures 2 and 3, it can be noted that OC concentrations exhibit a poor correlation with EC concentrations indicating a different origin for OC and EC in PM. A (strong) correlation between OC and EC is usually considered as indicative of a common emission source(s) for both compounds (see e.g. Duan et al. (2005), and references therein).

In most cases, average concentrations of OC are higher than those of EC in both PM2.5 and PM10 (see Figures 2 and 3). Atmospheric EC is expected mainly to originate from primary sources, i.e. incomplete combustion emissions of vehicle exhaust (diesel or gasoline based engines), biomass burning and coal combustion (e.g. Viana et al., 2007; Pio et al., 2008; Li and Bai, 2009). On the other hand, OC emissions can most probably be ascribed to the above cited primary sources and in addition to secondary processes occurring in the atmosphere, such as many (complex) oxidation processes of volatile organic compounds (VOC) (e.g. Guor-Chen Fang et al., 2008, and references therein).

Figure 2: Correlation between OC and EC concentrations (µg/m^3) at the US, Asian and EU sampling sites for PM2.5.

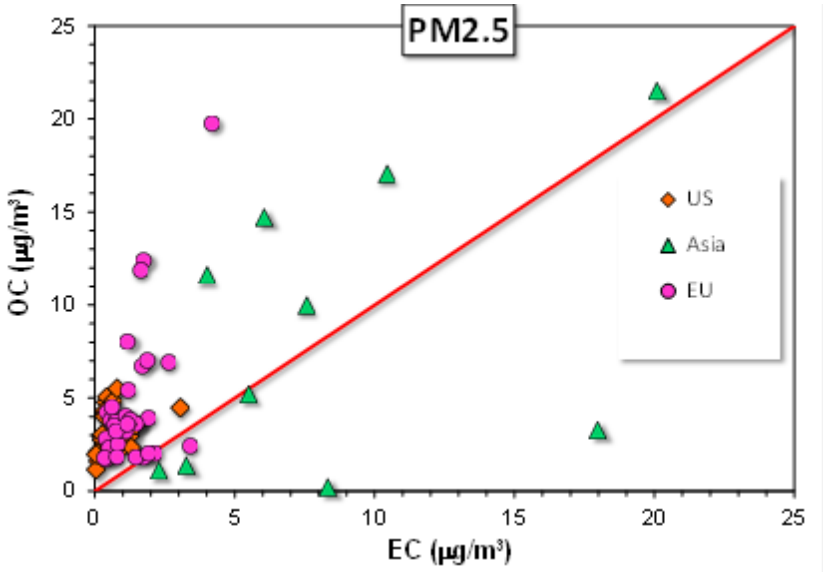
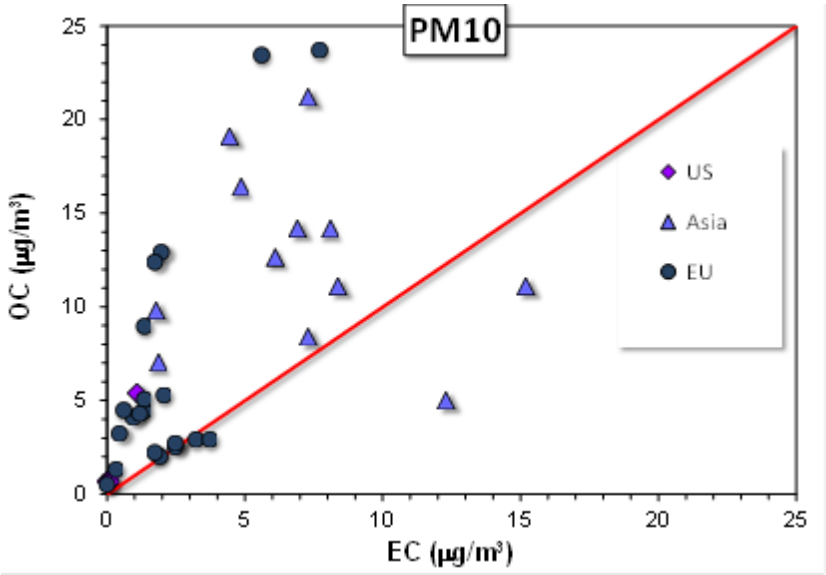


Figure 3: Correlation between OC and EC concentrations (μg/m^3) at the US, Asian and EU sampling sites for PM10.



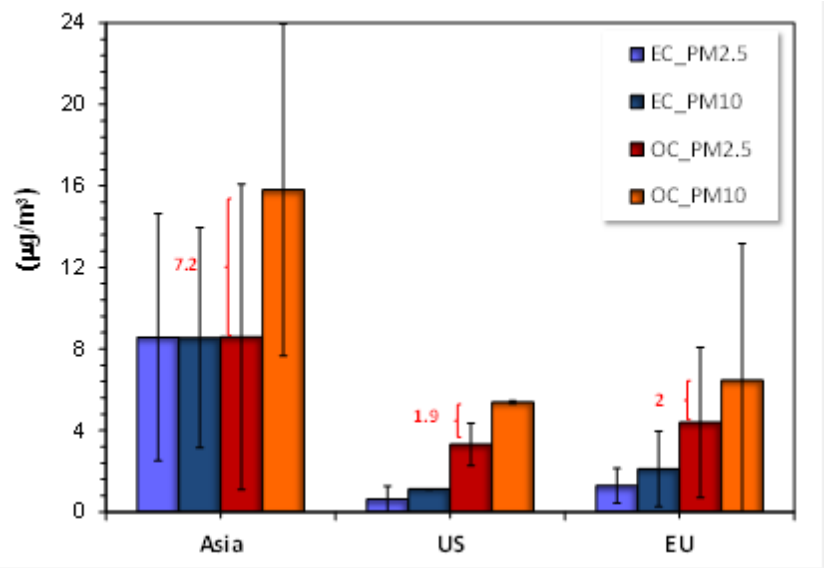
3.2 Average OC and EC concentrations in PM10 and PM2.5

As depicted in Figure 4, the EC and OC contents of both PM2.5 and PM10 detected in Asian cities are significantly higher compared to US and EU sampling sites. In addition, Asian sites also exhibit a lower OC/EC ratio. The higher percentages observed in Asian areas can likely be explained by a dominant contribution from (local) primary emission sources like fuel combustion, wood burning for residential cooking, and the biogenic contribution from vegetation (next to possible differences in sampling and analytical methods).

Results further indicate that, to some extent, similar levels of EC can be found in both PM2.5 and PM10 in the Asian, US and EU datasets. Subsequently, it might be hypothesized that EC is predominantly associated to PM2.5 particles, in spite of previous observations reported in literature on different mass fractions of PM (Hueglin et al., 2005; Duarte et al., 2008).

On the other hand, from Figure 4 it can be seen that, on average, the measured OC concentrations of PM2.5 are clearly lower than those of PM10, with differences in values ranging from 2 to 7 μg/m^3, approximately corresponding to 20-40% of the mean OC value. This implies that diverse primary/secondary emission sources provided a larger contribution to OC that is contained in the coarse mass fraction of aerosols, i.e. PM10, compared to that one observed in the fine mass fraction, i.e. PM2.5.

Figure 4: Average concentrations of EC and OC for PM2.5 and PM10 at the Asian (n= 10-15), US (n= 5-49) and EU (n= 20-36) sampling sites, according to the results of prior studies reported in the literature. The error bars indicate the standard deviations (absolute values) calculated based on the measurements of each sampling campaign



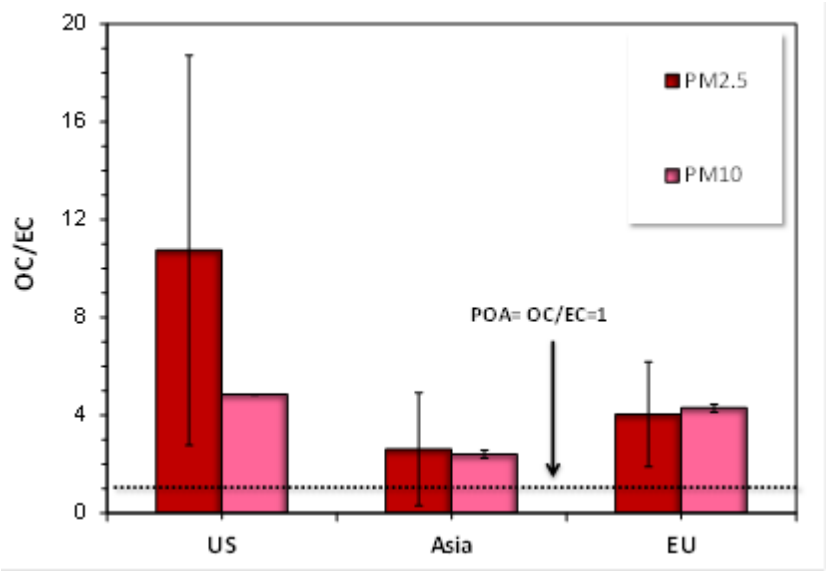
The variation in the OC/EC ratio obtained for the PM2.5 and PM10 fractions at the different sites in US, Asia and EU is shown in Figure 5. On average, the OC/EC values estimated for the PM2.5 in the US areas resulted from 2 up to 4 times higher compared to all the other values obtained for PM10 in the US, as well as for the PM2.5/PM10 at any locations.

With regards to the high OC/EC ratios measured in PM2.5 during the US sampling campaign, it can be noted that relatively larger OC values were detected compared to EC, as a possible result of the significant contribution of primary and secondary sources to the total OC in aerosols, such as biomass burning, fossil fuel combustion processes, biogenic sources, chemical reactions of gas-phase compounds in the atmosphere.

There is also evidence from Figure 5 that each OC/EC ratio was higher than 1 for all the examined datasets. These results indicate that most of the OC in PM2.5 and PM10 is of a secondary origin, possibly owing to various chemical reactions of volatile gaseous compounds and their subsequent condensation in the atmosphere. In fact, the OC/EC ratio has usually been used as indirect tracer method to distinguish primary organic aerosol (POA) from secondary organic aerosol (SOA) in PM samples (Hoffmann and Warnke, 2007).

The expected high SOA formation might be related to different emission sources of both anthropogenic and biogenic origin, such as biomass burning, fossil fuel combustion, diesel engines, gasoline engines, solar radiation, photochemical smog (e.g. Hoffmann and Warnke, 2007; Viana et al., 2007; Duarte et al., 2008).

Figure 5: Average concentrations of the OC/EC ratio for PM2.5 and PM10 at the US (n= 5-25), Asian (n= 10-15) and EU (n= 21-36) sampling sites, according to the results of prior studies reported in the literature. The error bars indicate the standard deviations (absolute values) calculated based on the measurements of each sampling campaign. Dashed horizontal line indicates OC/EC ratio equal to 1 as a tracer of primary organic aerosol (POA) emissions.



3.3 Spatial variation of OC and EC

The EC and OC concentrations, with respect to the total carbon (TC) content, estimated for different urban and rural environments during various EU sampling campaigns are shown in Figures 6 and 7, respectively. These results show that EC account for approximately 30% of TC at urban sites in both PM2.5 and PM10. With regards to the results derived from sampling campaigns conducted at the rural sites, EC concentrations correspond to about 20% of TC for PM2.5 and to about 10% of TC for PM10.

As expected, EC measured at the urban sites is higher than found at rural sites. These data confirm that EC mostly derived from urban traffic emissions. In fact, low EC values have been mainly associated to rural background sites (Duan et al., 2005). Furthermore, EC was found to provide the largest contribution to the fine mass fractions (i.e. PM2.5) of carbonaceous aerosols (e.g. Duarte et al., 2008; Zhu et al., 2010; Ancelet et al., 2011).

Figure 6: Average concentrations of EC/TC and OC/TC ratios for PM2.5 found at the urban and rural EU sites.

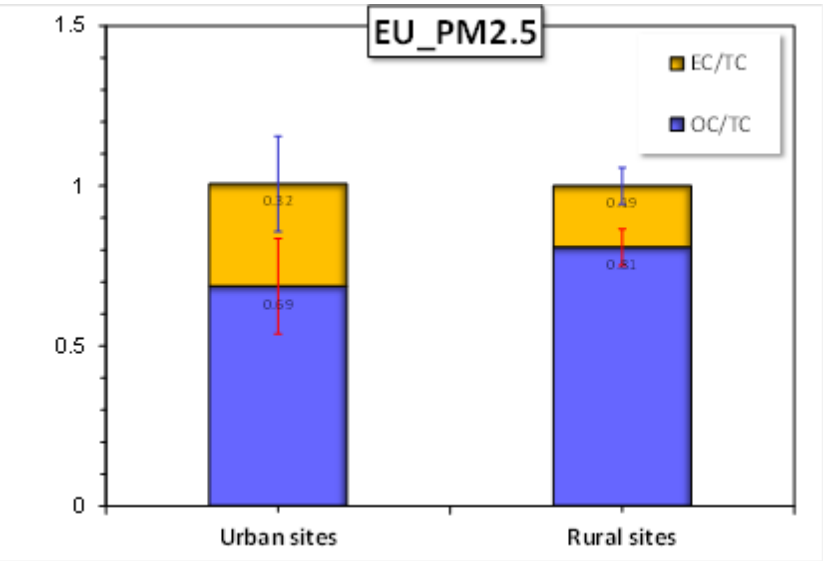
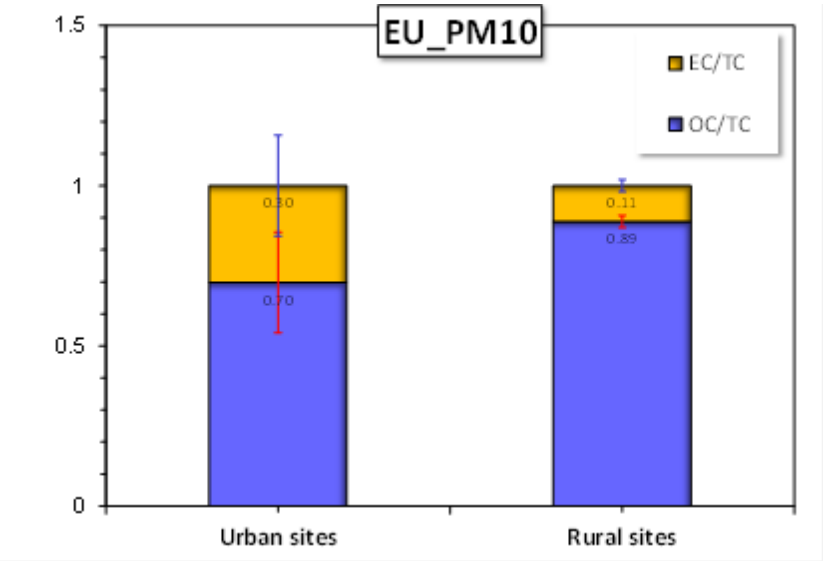


Figure 7: Average concentrations of EC/TC and OC/TC ratios for PM10 found at the urban and rural EU sites.



3.4 Seasonal variation of OC and EC

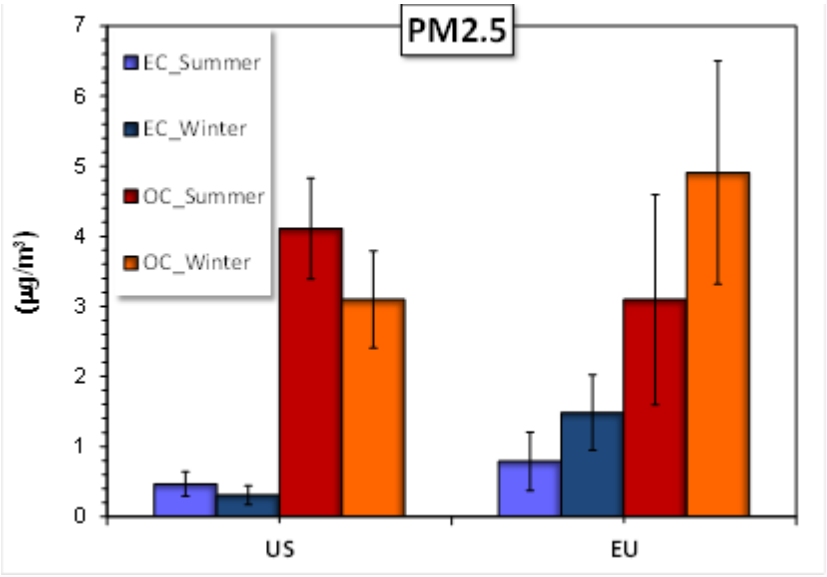
The average concentrations of EC and OC measured in PM2.5 during distinct summer and winter sampling campaigns at the US and EU sites are depicted in Figure 8. These results indicate that both EC and OC in the US areas are higher in summer than in winter. In contrast, the EU datasets exhibit increased concentrations of EC and OC from the summer to the winter.

In particular, with regard to the results of the US studies, it can be suggested that the high temperature conditions occurring in summer might possibly increase the photochemical activity of the atmosphere, leading to an increased secondary OC formation, probably in combination with wild bush fires.

On the other hand, the results found at the EU sites are consistent with those reported in literature, indicating an increased OC content in the winter compared to the summer, most probably due to the enhanced emissions from coal combustion, biomass or (domestic) wood burning in combination with more stable atmospheric conditions (Duan et al., 2005; Viana et al., 2007; Duarte et al., 2008).

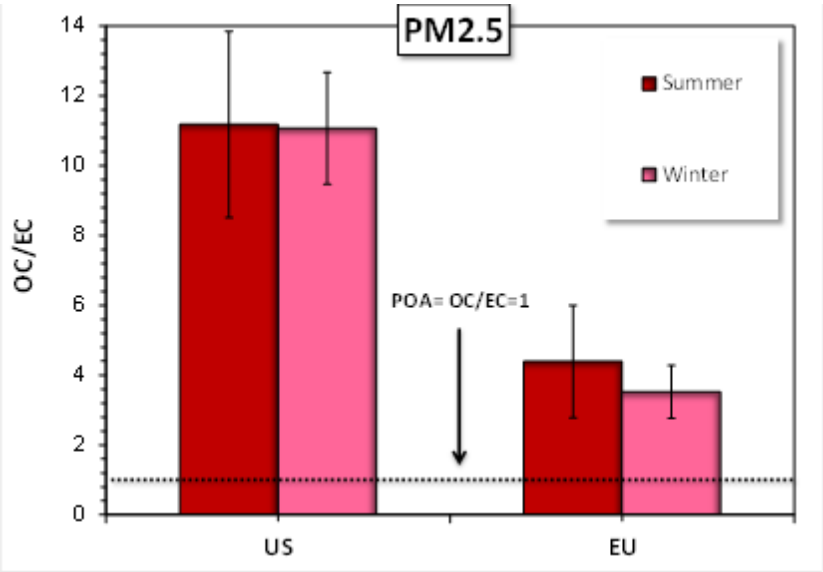
Overall, these differences in EC and OC contents in PM, in relation to the summer or winter sampling campaigns, might be attributed to the different contributions from the specific emission sources of the aerosol products.

Figure 8: Average concentrations of EC and OC for PM2.5 observed in summer and winter at the US (n= 19) and EU (n= 9-20) sampling sites, according to the results of prior studies reported in the literature. The error bars indicate the standard deviations (absolute values) calculated based on the measurements of each sampling campaign.



The seasonal variation of the OC/EC ratios obtained for the PM2.5 at the US and EU sites are reported in Figure 9. A decreasing trend in OC/EC concentrations as a function of the seasonal variation was clearly found only when comparing the results derived from the EU datasets. In addition, as can be seen from Figure 8, OC/EC ratios were much higher than 1, at which value the OC content can be considered as originating from primary emission sources, i.e. POA, with average concentrations ranging from 5 to 11 for the whole examined datasets. These finding would imply that SOA significantly contributes to the total OC content that has been found in aerosols, both in summer and in winter suggesting that this parameter is not necessarily indicative for the seasonal variation.

Figure 9: Average concentrations of the OC/EC ratio for PM2.5 observed in summer and winter at the US (n= 7-10) and EU (n= 8-21) sampling sites, according to the results of prior studies reported in the literature. The error bars indicate the standard deviations (absolute values) calculated based on the measurements of each sampling campaign. Dashed horizontal line indicates OC/EC ratio equal to 1 as a tracer of primary organic aerosol (POA) emissions.

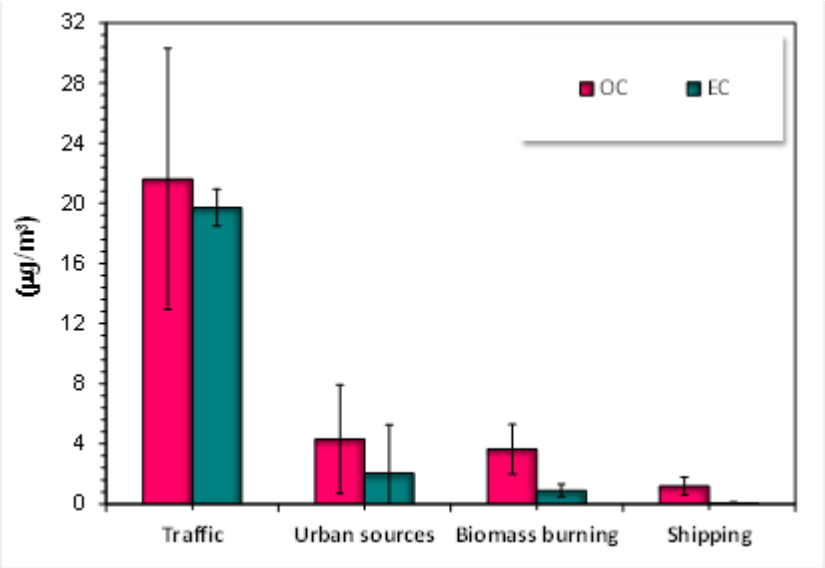


3.5 Sources

The average OC and EC concentrations of PM2.5 originating from different carbonaceous particulate emissions sources, i.e. traffic (from urban tunnels), urban sources (background urban locations), biomass burning and shipping are presented in Figure 10, according to the data that may be found in previous studies.

The results showed that the highest OC and EC values and the resulting OC/EC ratios (above 20) were determined for traffic, in particular for roadsides or in urban road tunnels related PM emissions sources. Measurements of PM composition in the exhaust emissions from urban sources and biomass burning indicated that similar OC and EC concentrations were determined for the examined datasets, as shown in Figure 10. In addition, in the same Figure 10 there is evidence that the emissions from the exhaust gases of ships were composed of negligible EC concentrations compared to emissions from the other analysed sources.

Figure 10: Average concentrations (in μg/m^3) of the OC and EC derived from different PM2.5 aerosols emission sources at various sampling sites. Traffic sites include tunnel measurements. The error bars indicate the standard deviations (absolute values) calculated based on the measurements of each sampling campaign

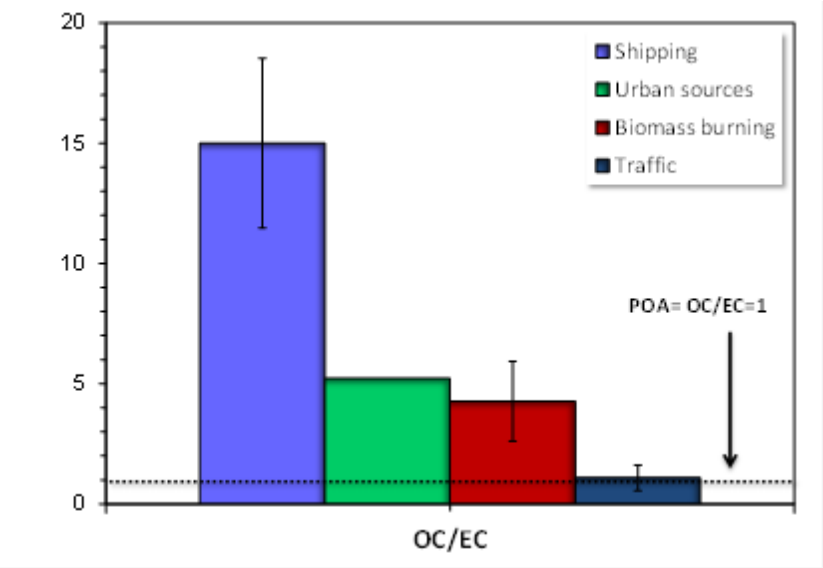


As a consequence, the highest OC/EC ratios of about 15 were determined for the gaseous ship-emitted aerosols, similar OC/EC results ranging from 4 to 5 were observed in the emissions caused by urban and biomass burning sources, whereas the lowest OC/EC value of near 1 was associated to the exhausts from traffic PM sources (which include tunnel measurements (see Figure 11).

As such, the results suggest that the composition of PM emitted by ships, urban sources and biomass burning was dominated by SOA, indicating that OC might have both primary and, especially, secondary origins. On the other hand, total PM mass concentrations from traffic sources are predominantly released into the atmosphere as POA, being mainly related to EC particles (i.e. “soot” or “black carbon”), directly emitted during incomplete combustion from motor vehicles exhausts.

In the next chapter emissions of OC and EC will be considered in more detail.

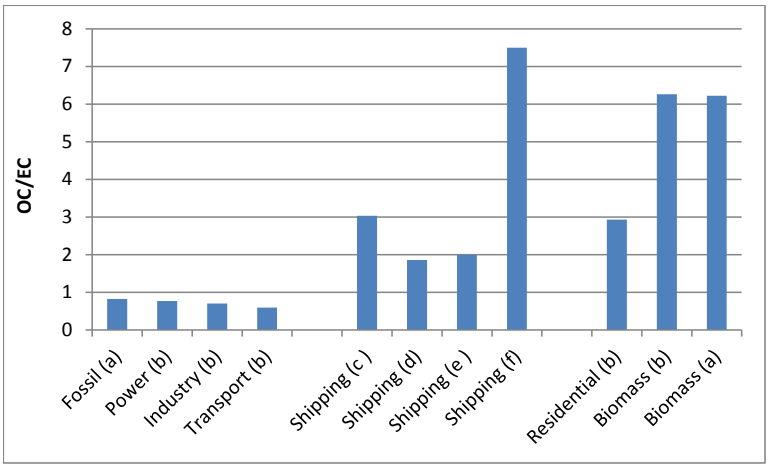
Figure 11: Average concentrations of the OC/EC ratios derived from different PM2.5 aerosols emission sources at various sampling sites. The error bars indicate the standard deviations (absolute values) calculated based on the measurements of each sampling campaign. Dashed horizontal line indicates OC/EC ratio equal to 1 as a tracer of primary organic aerosol (POA) emissions.



4
Emissions

Different source materials lead to different OC/EC ratios when burnt. This is partly a reflection of the material characteristics, but is also influenced by the burning conditions which may be typical for the material in question. See figure 12 for a more detailed overview of this ratio in sector-specific emissions as reported in several research articles involving modelling and/or observations. Note that the distinction between model-based or observation-based estimates is somewhat arbitrary, since emission inventories may be based on extrapolating measured quantities, while direct observations may be extrapolated to provide a global assessment. The estimates are visually distinguished in: specific fossil fuel burning, emissions from shipping, residential activity (e.g. cooking) and biomass burning emissions.

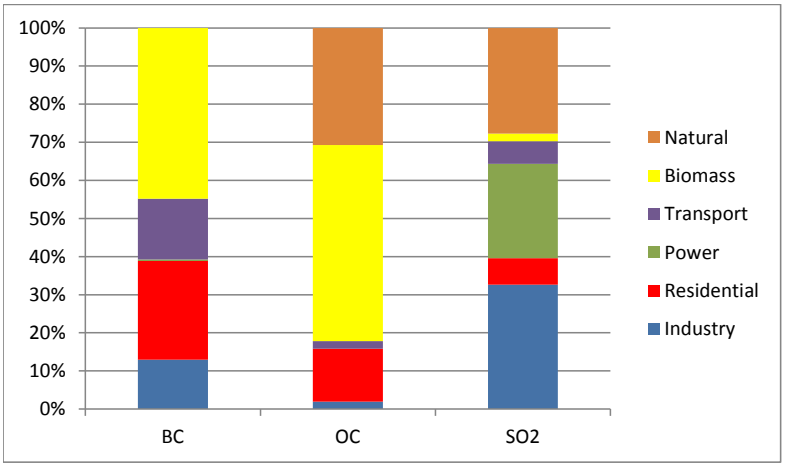
Figure 12: OC/EC ratios for different sectors, assembled from sources, based on observations or models. Sources: (a) Huneeus et al (2012); (b) Koch et al (2007); (c) Corbett et al (2010); (d) Lack et al (2009); (e) Eyring et al (2005); (f) Wang et al (2008). Numbers taken from reference a are the average of several studies. References b, e and f are based on global emission inventories used in global modeling. References c and d are based on observations.



Fossil fuel burning typically leads to lower OC/EC ratios than biomass burning. With the exception of the results reported by Wang et al. (2008), shipping emissions have an OC/EC ratio (~2 to 3) in between those that are characteristic for other fossil fuel burning (<1) and for biomass burning (>5).

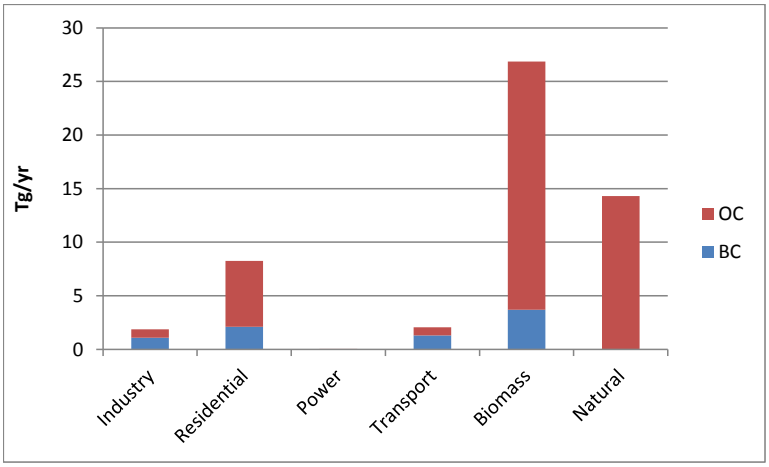
Sector-specific emissions as reported by Koch et al (2007) using the NASA Goddard global climate model are shown in figure 13. These are expressed as the percentage contribution of each sector to each of the classes BC (black carbon), OC (organic carbon) and SO_2 (the most important anthropogenic precursor to sulfate aerosol).

Figure 13: Relative contribution of different sectors to global emissions of black carbon (BC), organic carbon (OC) and sulfur dioxide (SO_2, a precursor to sulfate aerosol). Based on data in Koch et al (2007).



Zooming in on the carbonaceous aerosol emissions by sector, figure 14 shows the absolute emissions of both BC and OC of each of these sectors. In absolute amounts, biomass burning and natural emissions (mainly of gaseous precursors such as terpenes) dominate emissions of OC. Even though fossil fuel burning has a much lower OC/EC ratio (see figure 12), in absolute terms biomass burning causes most BC emissions, according to this global climate model. There are large regional differences in carbonaceous aerosol emissions. In Europe BC emissions are dominated by fossil fuel combustion, whereas in the Southern Hemisphere biomass burning is relatively more important (Bice et al., 2009).

Figure 14: Global emissions in Tg/yr (1 Tg = 10^{12} g or 1 megaton).



Extrapolating observations of ship emissions to the global scale, Lack et al. (2008) calculated that shipping contributes 1.7% of global BC emissions (amounting to 133 Gg/yr). Near ports this contribution could be much higher (up to 40%), reaching up to 50 ng/m^3. Judging from their figure 3, the North Sea, the Californian coast, the Gibraltar area, the Persian Gulf and South-East Asia are examples of such 'hotspots' of substantial BC emissions from commercial shipping.

Eyring et al. (2005) report on emissions from road traffic, aviation and shipping. The relative emission of particulate matter is largest for shipping (for which PM10 emissions are equivalent to 0.61% of fuel consumption), less so for road traffic (0.16%) and negligible –in a relative sense- for aviation (0.0005%). Global fuel consumption is similar for shipping and aviation (280 and 207 Tg/yr, respectively) and approximately ~5 times higher for road traffic (1320 Tg/yr). This can be compared with the approximately 5 times higher OC/EC ratio for shipping compared to road traffic (see figure 12).

While the BC fraction in Central Europe is predominantly of fossil origin, only ~30% of OC comes from fossil fuel combustion, even in the city centre of Zurich (Szidat et al., 2006). In wintertime, the non-fossil OC fraction is thought to mainly originate from biomass burning, whereas in summertime the formation of secondary organic aerosol from biogenic precursors is thought to be dominant. These results were obtained by ^{14}C analysis coupled with the OC/EC ratio (see also Sandradewi et al., 2008). Other tracers for biomass burning, such as levoglucosan and mannosan, were also utilized (ten Brink et al., 2010).

Viana et al (2009) tested the applicability of several tracers of particulate emissions from shipping. They found that, for 24 hour averaged PM10 and PM2.5 samples, a ratio of V/Ni of ~4 to 5 was indicative of ship emissions, as were ratios of V/EC <2. A ratio of the latter exceeding 8 excluded ship emissions from having impacted the PM composition. The OC/EC ratio did not correlate with ship emissions, as could also be deduced from the fact that this ratio is in between those from other prevalent sources (cf. figure 12).

5

Summary and Conclusions

- Organic carbon in air arises from combustion processes as well as from secondary chemical reactions such as the oxidation of volatile organic compounds. Elementary carbon mainly originates from primary sources, i.e. transport, biomass burning, and energy production (using coal).
  The highest OC and EC concentrations are measured near busy roads or inside tunnels. In general, concentrations of OC are higher than those of EC. EC accounts for approximately 30% of the total carbon at urban sites. At rural sites, this is 10% (PM2.5) to 20% (PM10). Mostly, OC concentrations are higher that EC concentrations. Usually, OC correlates poorly with EC indicating a different origin for their present in PM.
  Similar levels of EC are observed in PM2.5 and PM10 indicating that EC is mainly associated to PM2.5. In contrast, OC levels measured in PM2.5 are clearly lower than in PM10. Its presence in the coarse fraction is some 20-40% of total OC and probably caused by large biogenic particles.
  The OC/EC ratio can be used to distinguish primary organic aerosol (POA) from the secondary fraction (SOA). On average, this ratio is well above 1 in the examined datasets indicating that most of the OC is of a secondary origin. A substantial part of OC (20-40%) is found in the coarse fraction and probably related to the biogenic contribution.
- In Asian cities EC and OC are significantly higher than at US and EU sampling sites. This can be explained by local sources like specific combustion, intensified wood burning for residential cooking, and the biogenic contribution from vegetation.
  In the US both EC and OC are higher in summer than in winter. It can be understood that the higher temperatures in summer increase the photochemical activity of the atmosphere, leading to more secondary OC formation, probably in combination with wild bush fires resulting in more EC. Results at the EU sites are more consistent with those reported in literature, i.e., an increased OC content in the winter compared to the summer, probably due to the enhanced emissions from coal combustion and/or (domestic) wood burning in combination with more stable atmospheric conditions.
- In Europe BC emissions are dominated by fossil fuel combustion, whereas in the Southern Hemisphere biomass burning is relatively more important.
  In absolute amounts, biomass burning and natural emissions (mainly of gaseous precursors such as terpenes) dominate emissions of OC in Europe. Some 30% of OC

comes from fossil fuel combustion, even in city centres. In wintertime, the non-fossil OC fraction is thought to mainly originate from biomass burning, whereas in summertime the formation of secondary organic aerosol from biogenic precursors is thought to be dominant.

- The study of the various experimental data sets show that OC/EC ratios vary between around 1 (along busy traffic streets and within tunnels) and 15 (shipping). Ratios for urban background sites and biomass burning are between 4 and 5. The data from ships exhausts were characterized with a (very) low (and rather unexpected) EC content.
- The data from modelling studies give a somewhat different outlook. Here, the burning of fossil fuel (traffic, power generation, industry) leads to lower OC/EC ratios (up to 1) compared to biomass burning (near 6), both in agreement with observational data. For residential activity (mainly cooking) it is 3. Shipping emissions have an OC/EC ratio varying between 2 and 7, much lower than concluded from the measurement. Part of these discrepancies can be understood by considering the effect of dilution and SOA formation on concentration levels: EC-rich exhaust becomes mixed with less EC-rich ambient air, increasing the OC/EC ratio. Modelling studies often include emission inventories, which do not take into account the effect of mixing of air masses. Further examination is needed here.

6

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Appendix A. Supporting Information

Table 1: Concentrations of OC, EC, OC/EC and TC in PM samples from previous studies conducted in US areas (n.a.= not available; TC= Total Carbon; TOM= thermal optical method; GC-MS= gas chromatography interfaced to mass spectrometry).

Reference	Site	Source	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
Snyder et al. 2010	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	3.03	n.a.	n.a.	n.a.	Summer	July 2007
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	3.85	n.a.	n.a.	n.a.	Summer	July 2007
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	4.07	n.a.	n.a.	n.a.	Summer	July 2007
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	3.37	n.a.	n.a.	n.a.	Summer	July 2007
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	3.38	n.a.	n.a.	n.a.	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3.66	n.a.	n.a.	n.a.	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3.99	n.a.	n.a.	n.a.	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3.85	n.a.	n.a.	n.a.	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	4.39	n.a.	n.a.	n.a.	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	4.1	n.a.	n.a.	n.a.	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3.24	n.a.	n.a.	n.a.	Summer	July 2007
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	2.18	n.a.	n.a.	n.a.	Winter	January-February 2008
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	2.54	n.a.	n.a.	n.a.	Winter	January-February 2008
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	2.82	n.a.	n.a.	n.a.	Winter	January-February 2008
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	2.81	n.a.	n.a.	n.a.	Winter	January-February 2008
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	2.91	n.a.	n.a.	n.a.	Winter	January-February 2008

Reference	Site	Source	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	2.7	n.a.	n.a.	n.a.	Winter	January-February 2008
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3.49	n.a.	n.a.	n.a.	Winter	January-February 2008
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3.05	n.a.	n.a.	n.a.	Winter	January-February 2008
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3.29	n.a.	n.a.	n.a.	Winter	January-February 2008
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	4.5	n.a.	n.a.	n.a.	Winter	January-February 2008
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3	n.a.	n.a.	n.a.	Winter	January-February 2008
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	4.23	0.3	14.1	4.53	Summer	July 2007
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	5.05	0.55	9.2	5.60	Summer	July 2007
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	4.76	0.41	11.6	5.17	Summer	July 2007
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	2.17	0.16	13.6	2.33	Winter	January-February 2008
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	2.74	0.26	10.5	3.00	Winter	January-February 2008
	Cleveland	urban site	quartz fiber filters	TOM	PM2.5	2.92	0.27	10.8	3.19	Winter	January-February 2008
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	5.07	0.52	9.8	5.59	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	5.05	0.38	13.3	5.43	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	4.30	0.32	13.4	4.62	Summer	July 2007
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	2.75	0.26	10.6	3.01	Winter	January-February 2008
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	4.00	0.33	12.1	4.33	Winter	January-February 2008
	Detroit	urban site	quartz fiber filters	TOM	PM2.5	3.03	0.26	11.7	3.29	Winter	January-February 2008
Min Li, 2006	Philadelphia	urban site	quartz fiber filters	GC-MS	PM10	5.38	1.11	4.8	6.49	Annual value	January-November 2000
	Los Angeles	urban site	quartz fiber filters	GC-MS	PM2.5	4.46	3.03	1.5	7.49	Annual value	January-November 2000
	Los Angeles	urban site	quartz fiber filters	GC-MS	PM2.5	6.23	4.87	1.3	11.10	Annual value	January-November 2000
Zhang, 2009	4 cities	urban site	quartz fiber filters	TOM	PM2.5	1	n.a.	n.a.	n.a.	Averagel value	March 2004-February 2005
Qin, 2006	New York	urban site	teflon, nylon, quartz filter	n.a.	PM2.5	2.93	1.28	2.3	4.2	Averagel value	February 2000-December 2003

Reference	Site	Source	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
Qin, 2006	New York	urban site	teflon, nylon, quartz filter	n.a.	PM2.5	2.4	1	2.3	3.4	Averagel value	January 2001-December 2003
	New York	urban site	teflon, nylon, quartz filter	n.a.	PM2.5	2.32	0.74	3.1	3.06	Averagel value	January 2001-December 2003
	New York	urban site	teflon, nylon, quartz filter	n.a.	PM2.5	3.51	1.493	2.4	5.00	Averagel value	January 2001-December 2003
	New York	urban site	teflon, nylon, quartz filter	n.a.	PM2.5	2.33	1.361	1.7	3.69	Averagel value	January 2001-December 2003
Miguel, 2004	Los Angeles	urban site	quartz fiber filters	n.a.	PM2.5	4.83	0.59	8.2	5.42	Winter	October 2001-December 2002
	Los Angeles	urban site	quartz fiber filters	n.a.	PM2.5	5.49	0.80	6.9	6.29	Summer	March 2002-Juy 2002

Table 2: Concentrations of OC, EC, OC/EC and TC in PM samples from previous studies conducted in Asian areas (n.a.= not available; TC= Total Carbon; TOR= thermal optical reflectance; TMO= thermal manganese dioxide oxidation technique; TOM= thermal optical method; CA= combustion analysis; EA= Elemental analysis; NDIR= non dispersive infrared).

Reference	Site	Source	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
Fang et al., 2008	China	urban site	pre-fired quartz filters	TOR	PM2.5	14.7	6.1	2.4	20.80	n.a.	n.a.
	China	urban site	pre-fired quartz filters	TOR	PM 10	19.7	7.8	2.5	27.50	n.a.	n.a.
	China	urban site	hi-vol air samplers	TMO	PM 2.5	1.36	3.32	0.4	4.68	n.a.	1994-2002
	China	urban site	hi-vol air samplers	TMO	PM 2.5	21.5	20.16	1.1	41.66	n.a.	1994-2002
	China	urban site	hi-vol air samplers	TMO	PM 10	7.02	1.85	3.8	8.87	n.a.	1994-2002
	China	urban site	hi-vol air samplers	TMO	PM 10	29.1	10.1	2.9	39.20	n.a.	1994-2002
	China	urban site	hi-vol air samplers	TMO	PM 10	14.16	8.08	1.8	22.24	Winter	Nov 2000-Febr 2001
	China	urban site	hi-vol air samplers	TMO	PM 10	14.17	6.96	2.0	21.13	Winter	Nov 2000-Febr 2001
	Japan	urban site	low-vol air samplers	TOR, TOM, A	PM 2.5	1.1	2.3	0.5	3.40	n.a.	1991-1996
	Japan	urban site	low-vol air samplers	TOR, TOM, CA	PM 2.5	5.2	5.51	0.9	10.71	n.a.	1991-1996
	Japan	urban site	low-vol air samplers	TOR, TOM, CA	PM 10	5	12.3	0.4	17.30	n.a.	1991-1996
	Korea (Sihwa)	urban/suburban site	pre-fired quartz filters	TOR, TMO	PM 10	9.8	1.8	5.4	11.60	n.a.	1994-2001
	Korea (Seoul)	urban/suburban site	pre-fired quartz filters	TOR, TMO	PM 2.5	9.97	7.57	1.3	17.54	n.a.	1994-2001
	Korea (Seoul)	urban/suburban site	pre-fired quartz filters	TOR, TMO	PM 10	11.1	8.39	1.3	19.49	n.a.	1994-2001
	Korea (Seoul)	urban/suburban site	pre-fired quartz filters	TOR	PM 2.5	3.27	18	0.2	21.27	n.a.	1994-2001
	Korea (Seoul)	urban/suburban site	pre-fired quartz filters	TOR	PM 2.5	0.19	8.39	0.0	8.58	n.a.	1994-2001
	Korea (Seoul)	urban/suburban site	pre-fired quartz filters	TOR	PM 10	11.1	15.2	0.7	26.30	n.a.	1994-2001
	Korea (Seoul)	urban/suburban site	pre-fired quartz filters	TOR	PM 10	8.39	7.3	1.1	15.69	n.a.	1994-2001
	Taiwan	urban/suburban site	dichomotus sampler	EA	PM 2.5	17.04	10.4	1.6	27.44	Winter	Nov 1998-April 1999
	Taiwan	urban/suburban site	dichomotus sampler	EA	PM 2.5	11.59	4	2.9	15.59	Winter	Nov 1998-April 1999

Reference	Site	Source	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
	Taiwan	urban/suburban site	dichomotus sampler	EA	PM 10	12.63	6.1	2.1	18.73	Winter	Nov 1998-April 1999
	Taiwan	urban/suburban site	dichomotus sampler	EA	PM 10	32.25	23.06	1.4	55.31	Winter	Nov 1998-April 1999
Quin and Xie, 2011	China	suburban site	Statistical analysis, GIS	n.a.	PM 2.5	n.a.	n.a.	4.0	n.a.	n.a.	n.a.
	China	suburban site	Statistical analysis, GIS	n.a.	PM 2.5	n.a.	n.a.	6.7	n.a.	n.a.	n.a.
	China	suburban site	Statistical analysis, GIS	n.a.	PM 2.5	n.a.	n.a.	7.7	n.a.	n.a.	n.a.
	China	suburban site	Statistical analysis, GIS	n.a.	PM 2.5	n.a.	n.a.	4.1	n.a.	n.a.	n.a.
	China	suburban site	Statistical analysis, GIS	n.a.	PM 2.5	n.a.	n.a.	4.1	n.a.	n.a.	n.a.
	China	suburban site	Statistical analysis, GIS	n.a.	PM 2.5	n.a.	n.a.	3.9	n.a.	n.a.	n.a.
Duan, 2005	China	urban/suburban site	quartz fiber filters	NDIR	PM 10	21.2	7.3	2.9	n.a.	Winter	n.a.
	China	urban/suburban site	quartz fiber filters	NDIR	PM 10	16.4	4.8	3.4	21.20	Fall	September 2002
	China	urban/suburban site	quartz fiber filters	NDIR	PM 10	19.1	4.5	4.2	23.60	Winter	October 2002
	China	urban/suburban site	quartz fiber filters	NDIR	PM 10	25.6	10.5	2.4	36.00	Winter	November 2002

Table 3: Concentrations of OC, EC, OC/EC and TC in PM samples from previous studies conducted in EU areas (n.a.= not available; TC= Total Carbon; TOT= thermal optical transmission technique; TOC= thermal optical carbon; TOM= thermal optical method; VDI= 1996, in German).

Reference	Site	Source	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
Reche et al. 2012	Barcelona	biomass burning	quartz fiber filters	TOT	PM 2.5	3.6	1.5	2.4	5.10	Winter	February-March 2009
Saarikoski, 2008	Helsinki (Fin)	urban site	quartz fiber filters	TOC	PM 1	2.5	0.89	2.8	3.39	Annual value	March 2006-February 2007
	Helsinki (Fin)	urban site	quartz fiber filters	TOC	PM 1	n.a.	n.a.	3.3	n.a.	Annual value	March 2006-February 2007
	Helsinki (Fin)	biomass combustion	quartz fiber filters	TOC	PM 1	n.a.	n.a.	6.6	n.a.	Annual value	March 2006-February 2007
	Helsinki (Fin)	traffic	quartz fiber filters	TOC	PM 1	n.a.	n.a.	0.7	n.a.	Annual value	March 2006-February 2007
Iinuma, 2007	Helsinki (Fin)	biomass burning	quartz fiber filters	TOT	PM 2.5	n.a.	n.a.	1.7	n.a.	Annual value	n.a.
Viana, 2007	Amsterdam	urban site	quartz fiber filters	TOT	PM 2.5	6.7	1.7	4.7	8.40	Winter	2005
	Barcelona	urban site	quartz fiber filters	TOT	PM 2.5	6.9	2.6	3.1	9.50	Winter	2004
	Ghent	urban site	quartz fiber filters	TOT	PM 2.5	5.4	1.2	4.4	6.60	Winter	2004
	Amsterdam	urban site	quartz fiber filters	TOT	PM 2.5	3.9	1.9	2.8	5.80	Summer	2006
	Barcelona	urban site	quartz fiber filters	TOT	PM 2.5	3.6	1.5	2.6	5.10	Summer	2004
	Ghent	urban site	quartz fiber filters	TOT	PM 2.5	2.7	0.8	3.5	3.50	Summer	2005
Dutch Report	NL	urban site	quartz fiber filters	n.a.	PM 10	3.21	0.47	6.8	3.68	Annual value	2006-2007
	NL	urban site	quartz fiber filters	n.a.	PM 10	4.43	1.31	3.4	5.74	Annual value	2006-2007
	NL	urban site	quartz fiber filters	n.a.	PM 10	5.05	1.3	3.9	6.35	Annual value	2006-2007
	NL	urban site	quartz fiber filters	n.a.	PM 10	5.27	2.04	2.6	7.31	Annual value	2006-2007
	NL	urban site	quartz fiber filters	n.a.	PM 10	4.07	0.98	4.2	5.05	Annual value	2006-2007
	NL	urban site	quartz fiber filters	n.a.	PM 10	4.28	1.18	3.6	5.46	Annual value	2006-2007
BOP Report, 2010	Breda	urban site	quartz fiber filters	TOT	PM 10	2.9	3.2	0.9	6.10	Annual value	n.a.

Reference	Site	Source	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
	Hellendoorn	urban site	quartz fiber filters	TOT	PM 10	2.2	1.8	1.2	4.00	Annual value	n.a.
	Rotterdam	urban site	quartz fiber filters	TOT	PM 10	2.9	3.7	0.8	6.60	Annual value	n.a.
	Schiedam	urban site	quartz fiber filters	TOT	PM 10	2.5	2.5	1.0	5.00	Annual value	n.a.
	Vredepeel	urban site	quartz fiber filters	TOT	PM 10	2.7	2.5	1.1	5.20	Annual value	n.a.
	Cabauw	urban site	quartz fiber filters	TOT	PM 2.5	1.8	1.8	1.0	3.60	Annual value	n.a.
	Hellendoorn	urban site	quartz fiber filters	TOT	PM 2.5	1.8	1.5	1.2	3.30	Annual value	n.a.
	Rotterdam	urban site	quartz fiber filters	TOT	PM 2.5	2.4	3.4	0.7	5.80	Annual value	n.a.
	Schiedam	urban site	quartz fiber filters	TOT	PM 2.5	2	2.1	1.0	4.10	Annual value	n.a.
	Vredepeel	urban site	quartz fiber filters	TOT	PM 2.5	2	1.9	1.1	3.90	Annual value	n.a.
Duarte et al., 2008	Oporto	urban site	quartz fiber filters	TOM	PM 10	1.3	0.3	4.3	1.60	Summer	2004
	Moitinhos	rural site	quartz fiber filters	TOM	PM 10	0.5	0.05	10.0	0.55	Summer	2004
	Oporto	urban site	quartz fiber filters	TOM	PM 10	n.a.	n.a.	2.5	n.a.	Summer	2004
	Moitinhos	rural site	quartz fiber filters	TOM	PM 10	n.a.	n.a.	10.3	n.a.	Summer	2004
Hueglin, 2005	Bern	urban site	Filter Method	VDI	PM 2.5	19.7	4.2	4.7	23.94	Annual value	April 1998-March-1999
	Bern	urban site	Filter Method	VDI	PM 10	23.4	5.6	4.2	29.02	Annual value	April 1998-March-1999
	Zurich	urban site	Filter Method	VDI	PM 10	23.7	7.7	3.1	31.38	Annual value	April 1998-March-1999
	Zurich	urban site	Filter Method	VDI	PM 2.5	12.4	1.8	6.9	14.17	Annual value	April 1998-March-1999
	Zurich	urban site	Filter Method	VDI	PM 10	12.9	2	6.4	14.89	Annual value	April 1998-March-1999
Hueglin, 2005	Basel	suburban site	Filter Method	VDI	PM 2.5	11.8	1.6	7.4	13.44	Annual value	April 1998-March-1999
	Basel	suburban site	Filter Method	VDI	PM 10	12.4	1.8	6.9	14.17	Annual value	April 1998-March-1999
	Payerne	rural site	Filter Method	VDI	PM 10	8.9	1.3	6.9	10.25	Annual value	April 1998-March-1999
	Chaumont	rural site	Filter Method	VDI	PM 2.5	4.2	0.4	10.5	4.61	Annual value	April 1998-March-1999
	Chaumont	rural site	Filter Method	VDI	PM 10	4.5	0.6	7.5	5.07	Annual value	April 1998-March-1999

Reference	Site	Source	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
Pio et al., 2008	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	3.8	0.54	7.0	4.34	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	3.7	0.74	5.0	4.44	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	1.9	0.40	4.8	2.30	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	3.5	0.70	5.0	4.20	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	2	0.65	3.1	2.65	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	2.1	0.70	3.0	2.80	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	2.8	0.42	6.6	3.22	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	8	1.23	6.5	9.23	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	4.5	0.64	7.0	5.14	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	2.3	0.46	5.0	2.76	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	2.5	0.86	2.9	3.36	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	3.2	1.14	2.8	4.34	Summer	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	3.2	0.78	4.1	3.98	Winter	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	7	1.94	3.6	8.94	Winter	2003
	Portugal	rural site	quartz fiber filters	TOM	PM 2.5	4	1.14	3.5	5.14	Winter	2003
Malaguti et al., 2012	Trisaia, Italy	rural site	quartz fiber filters	TOM	PM 2.5	1.69	0.44	3.8	2.13	Spring/Summer	May-June 2010
	Trisaia, Italy	rural site	quartz fiber filters	TOM	PM 2.5	1.76	0.34	5.2	2.10	Spring/Summer	May-June 2010
Hellebust, 2010	Cork port, Ireland	urban site	microbalance	n.a.	PM 2.5	3.6	1.2	2.9	4.81	Winter	October-February 2008
	Cork port, Ireland	urban site	microbalance	n.a.	PM 2.5	1.8	0.7	2.4	2.57	Summer	April-September 2008

Table 4: Concentrations of OC, EC, OC/EC and TC in PM samples measured from biomass burning (n.a.= not available; TC= Total Carbon; TOT= thermal optical transmission technique; TOM= thermal optical method).

Reference	Site	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
Reche et al. 2012	Barcelona	quartz fiber filters	TOT	PM 2.5	3.6	1.5	2.4	5.10	Winter	February-March 2009
Iinuma, 2007	Helsinki (Fin)	quartz fiber filters	TOT	PM 2.5	n.a.	n.a.	1.7	n.a.	Annual value	n.a.
Pio et al. 2008	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	3.8	0.54	7.0	4.34	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	3.8	0.54	7.0	4.34	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	3.7	0.74	5.0	4.44	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	1.9	0.40	4.8	2.30	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	3.5	0.70	5.0	4.20	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	2	0.65	3.1	2.65	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	2.1	0.70	3.0	2.80	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	2.8	0.42	6.6	3.22	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	8	1.23	6.5	9.23	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	4.5	0.64	7.0	5.14	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	2.3	0.46	5.0	2.76	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	2.5	0.86	2.9	3.36	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	3.2	1.14	2.8	4.34	Summer	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	3.2	0.78	4.1	3.98	Winter	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	7	1.94	3.6	8.94	Winter	2003
	Portugal	(pre-fired) quartz fiber filters	TOM	PM 2.5	4	1.14	3.5	5.14	Winter	2003

Table 5: Concentrations of OC, EC, OC/EC and TC in PM samples measured from traffic (urban tunnels) (n.a.= not available; TC= Total Carbon; TOM= thermal optical method; TOR= thermal optical reflectance; TG-R= thermogravimetric and reflectance analysis).

Reference	Site	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
Ancelet, 2011	Wellington, New Zealand	quartz fiber filters	TOM	PM 2.5	21.7	21.3	1.4	43.00	Winter	Dec 2008-March 2009
	Wellington, New Zealand	quartz fiber filters	TOM	PM 2.5	30.9	18.6	1.7	49.50	Winter	Dec 2008-March 2009
Zhu, 2010	Taiwan	quartz fiber filters	TOR	PM 2.5	10	20	0.5	30.00	Spring/Summer	n.a.
	Taiwan	quartz fiber filters	TOR	PM 2.5	23.9	18.9	1.3	42.80	Spring/Summer	n.a.
Hung-Lung, 2009	China	quartz fiber filters	TOR	PM 2.5	53	94	0.6	147.00	Winter	n.a.
Guor-Chen Fang et al., 2008	China	quartz fiber filters	TOM	PM 10	14.16	8.08	1.8	22.24	Winter	Nov 2000-Febr 2001
Suvendrini Lena et al., 2007	New York	quartz fiber filters	TG-R	PM 2.5	n.a.	5.86	n.a.	n.a.	Summer	1999
	New York	quartz fiber filters	TG-R	PM 2.5	n.a.	2.62	n.a.	n.a.	Summer	1999
	New York	quartz fiber filters	TG-R	PM 2.5	n.a.	2.6	n.a.	n.a.	Summer	1999
	New York	quartz fiber filters	TG-R	PM 2.5	n.a.	7.34	n.a.	n.a.	Summer	1999
	New York	quartz fiber filters	TG-R	PM 2.5	n.a.	3.8	n.a.	n.a.	Summer	1999
	New York	quartz fiber filters	TG-R	PM 2.5	n.a.	2.57	n.a.	n.a.	Summer	1999

Table 6: Concentrations of OC, EC, OC/EC and TC in PM samples measured from shipping (urban tunnels) (n.a.= not available; TC= Total Carbon; TOM= thermal optical method; TOT= thermal optical transmission technique).

Reference	Site	Method	Analysis	Mass Fraction	OC	EC	OC/EC	TC	Campaign	Period
Moldanova´, 2009	Celtic sea	quartz fiber filters	TOM	PM 7	n.a.	n.a.	12.0	n.a.	Summer	June 2007
Krudysz, 2008	Long beach_Pacific ocean	quartz fiber filters	TOT, TOM	PM 2.5	1.6	0.12	13.3	1.72	Winter	2005
	Long beach_Pacific ocean	quartz fiber filters	TOT, TOM	PM 2.5	1.14	0.05	22.8	1.19	Winter	2005
	Long beach_Pacific ocean	quartz fiber filters	TOT, TOM	PM 2.5	2.07	0.15	13.8	2.22	Winter	2005
	Long beach_Pacific ocean	quartz fiber filters	TOT, TOM	PM 2.5	1.95	0.05	39.0	2.00	Winter	2005
	Long beach_Pacific ocean	quartz fiber filters	TOT, TOM	PM 10	0.65	0.05	13.0	0.70	Winter	2005
	Long beach_Pacific ocean	quartz fiber filters	TOT, TOM	PM 10	0.66	0.04	16.5	0.70	Winter	2005
	Long beach_Pacific ocean	quartz fiber filters	TOT, TOM	PM 10	0.8	0.05	16.0	0.85	Winter	2005
	Long beach_Pacific ocean	quartz fiber filters	TOT, TOM	PM 10	0.63	0.05	12.6	0.68	Winter	2005

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