WP21- JRA4: D21.5 Report on mass closure experiments performed at six European sites.

Summary:
This report summarises the total observed organic carbon (TOOC) concentration performed at six different sites in Europe. TOOC includes the carbon from the gaseous phase as well as the carbon from the particle phase. The daily mean concentrations of TOOC for the two cities London and Paris are compared to each other in winter and summer. Additionally, the TOOC was calculated for three sites in Europe (from suburban to rural/remote) during summer. In general, the particle phase plays a minor role in the TOOC budgets compared to the gas phase. Cities have higher TOOC concentrations than more rural/remote regions. In winter the carbon concentrations at a particular site is higher compared to summer, which is due to additional anthropogenic emission sources typical of the winter season (e.g. biomass burning) and to meteorological conditions.

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1. Introduction to the concept of total observed organic carbon (TOOC)

Measurements of organic carbon compounds in both the gas and particle phases were combined to examine the total observed organic carbon (TOOC) in the atmosphere. Gas phase organic compounds are summarized under the term volatile organic compounds (VOCs), whereas organic particles are comprised of a wide range of organic aerosols.

This relatively new approach for the holistic consideration of the total organic carbon budget has been developed mainly in campaigns in the US (e.g. de Gouw et al., 2009; Heald et al., 2008; Roberts et al. 1998). The TOOC concept includes a large suite of gaseous compounds and particles. Therefore the combined analysis of gaseous compounds and particles, which play an important role in the chemistry of the troposphere and in the direct and indirect climate forcing, can provide new insights into the relative importance of these drivers. Figure 1 gives the conceptual framework of the total observed organic carbon (TOOC).

![Conceptual framework of the total observed organic carbon (TOOC); adapted from Heald et al., 2008.]

Similar calculation approaches are routinely used for nitrogen oxides and sulfur in the atmosphere. The TOOC calculation includes a large group of compounds, where many compounds which are likely to contribute have hardly been observed under real-world ambient conditions. Therefore, the combined analysis of gaseous compounds, which play an important role in the chemistry of the troposphere, and particles, which are a climate forcing agent, is an important issue. Methane is excluded from the TOOC as it is a long-lived compound (~9 years) and its life cycle is relatively well understood.

This mass calculation of atmospheric organic carbon is achieved by bringing together state-of-the-art equipment for both gaseous and particulate organic substances. In Europe such calculations were to date not performed. During intensive measurement campaigns in Europe (such as MEGAPOLI, ClearFlO, or EMEP intensive campaigns) data of volatile organic compounds (VOCs), oxygenated volatile organic compounds (OVOCs), and aerosols were measured and collected so that TOOC could be calculated for six European sites (Figure 2).
2. Methods

Sites:

The total observed organic carbon was calculated for the following sites in Europe: London (LON), Paris (PAR), SIRTA (SIR), Hohenpeissenberg (HPB), Revin (REV), and Cap Corsica (COR) (Figure 2).

The measurements in London (LON) were performed at North Kensington at the Sion Manning School courtyard area (51°31'15.18"N; 0°12'48.85"W). This site, classified as urban background site, is in a residential area with a main road in the West and a motorway (A40 Westway) in the South (70'000-100'000 vehicles per day) (Liu et al., 2014; Valach et al., 2014).

In Paris (PAR) the measurements were performed at LHVP (“Laboratoire d’Hygiène de la Ville de Paris”, 48°49'44.4"N; 2°12'25.2"E; Southern part of the city). The sampling site is located in a large public garden at approximately 150 m from a major road. Due to the low intensity of the surrounding traffic it is classified as Paris background pollution site (Ait-Helal et al., 2014; Favez et al., 2007; Gros et al., 2011; Sciare et al., 2010).

The second station in the greater Paris area is SIRTA (SIR; “Site Instrumental de Recherche par Télédétection Atmosphérique”; 48°42'46.8"N; 2°12'50.4"E). This suburban site at Palais eau is surrounded by fields, wooded areas, houses, and industries (Haefelin et al., 2005).

Two more French sites are running under the European Monitoring and Evaluation Programme (EMEP). In 2012 intensive summer campaigns took place at these two sites. Revin (REV) is located in the North-Eastern part of France, close to the Belgium boarder (49°54'0"N, 4°38'0"E). The air masses are mainly coming from the South-West but also by highly polluted air masses from the North of Europe. The site is classified as a background station.

The second EMEP site in France is located on the island Corsica. This site (533 m above sea level) is located in the extreme North of the island in the commune of Ersa (42°58'9.84"N; 9°22'49.08"E). This station is far from sources of anthropogenic pollution and surrounded by short vegetation typical of the Mediterranean.
scrubland. COR is influenced by long-range atmospheric transport, which includes timely air masses originating from the Sahara, the Rhone valley in France, and industrialized Po-area in Italy.

The German Global Atmosphere Watch and EMEP site Hohenpeissenberg (HPB) is located on top of the Hohenpeissenberg mountain (980 m above sea level, 47°48'0"N, 11°1'0"E, around 40 km North of the Alps) and about 300 m above the surrounding countryside. The nearest major city, Munich, is distant at around 70 km to the North-East. HPB is surrounded mainly by forests and agricultural pastures with coniferous trees and beeches growing on the slopes of the Hohenpeissenberg mountain in most directions. In the North-to-South foothills the village of Hohenpeissenberg is located with typical country road traffic. Main wind direction is South to South-West (Bartenbach et al., 2007; Birmili et al., 2003).

In Table 1 the site classification, the campaigns name, the season, and the time period of the campaign for the respective sites (used for TOOC calculation) are listed. In the time period considered for TOOC particulate as well as gaseous phase data were available. At the sites LON, PAR, and SIR winter and summer measurements were performed, whereas at HPB, REV, and COR only summer data were available. MEGAPOLI (Megacities: Emission, urban, regional and Global Atmospheric Pollution and climate effects, and integrated tools for assessment and mitigation) was a framework 7 project of the European Community and the measurements took place in 2009/2010, whereas all other data were collected in 2012. ClearfLo (Clean Air for London) was a Natural Environment Research Council (NERC)-funded scientific project. The other campaigns were under the European Monitoring and Evaluation Programme (EMEP).

<table>
<thead>
<tr>
<th>Site</th>
<th>Site classification</th>
<th>Campaign</th>
<th>Season</th>
<th>Time period</th>
</tr>
</thead>
<tbody>
<tr>
<td>London (LON)</td>
<td>urban background</td>
<td>ClearfLo</td>
<td>Winter</td>
<td>January 11 – February 7, 2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Summer</td>
<td>July 21 – August 28, 2012</td>
</tr>
<tr>
<td>Paris (PAR)</td>
<td>urban background</td>
<td>MEGAPOLI</td>
<td>Winter</td>
<td>January 15 – February 15, 2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Summer</td>
<td>July 7 – August 1, 2009</td>
</tr>
<tr>
<td>SIRTA (SIR)</td>
<td>Suburban background</td>
<td>MEGAPOLI</td>
<td>Winter</td>
<td>January 16 – February 12, 2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Summer</td>
<td>July 7 – 31, 2009</td>
</tr>
<tr>
<td>Hohenpeissenberg (HPB)</td>
<td>Rural background</td>
<td>EMEP</td>
<td>Summer</td>
<td>June 26 – July 14, 2012</td>
</tr>
<tr>
<td>Revin (REV)</td>
<td>Rural background</td>
<td>EMEP</td>
<td>Summer</td>
<td>July 7 – August 11, 2012</td>
</tr>
<tr>
<td>Cape Corsica (COR)</td>
<td>Mediterranean remote</td>
<td>EMEP</td>
<td>Summer</td>
<td>June 26 – July 04, 2012</td>
</tr>
</tbody>
</table>
Measurement techniques:

Organic aerosols concentrations were measured either with an aerosol mass spectrometer (AMS), a high resolution-time of flight-AMS (HR-Tof-AMS) or an aerosol chemical speciation monitor (ACSM). Aethalometers were used to analyse black carbon (BC) concentrations. Trace gas measurements (VOCs and OVOCs) were either performed with a gas chromatography-flame ionisation detector (GC-FID), a gas chromatography-mass spectrometer (GC-MS), a high performance liquid chromatography-UV-detector (HPLC-UV) (for OVOCs only), or a proton transfer reaction-mass spectrometer (PTR-MS) (Table 2). At all sites, ground based measurements were performed.

Organic matter measured in aerosols was converted to organic carbon by a constant factor of 0.5. Turpin and Lim (Turpin and Lim, 2001) reported converting factors for carbon weight to organic molecular weight between 0.48 and 0.63. Therefore, when using a constant factor, the variation in the results of the organic carbon particulate phase can go up to 25%. To compile the TOOC content, concentrations of each gaseous compound was converted to units of carbon mass concentrations (µg C/m³) at standard temperature and pressure conditions. To compare the different sites to each other, the particle and gas phase data were aggregated to daily mean concentrations.

Table 2: Instruments employed for the analysis of aerosols, black carbon (BC), VOCs, and OVOCs at the different investigated sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>instruments employed for the analysis of:</th>
<th>Aerosols</th>
<th>BC</th>
<th>VOCs</th>
<th>OVOCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>LON</td>
<td>AMS</td>
<td>aethalometer</td>
<td>GC-FID/FID (Agilent) (Hopkins et al., 2011; Hopkins et al., 2003)</td>
<td>GC-FID/FID (Agilent) (Hopkins et al., 2011; Hopkins et al., 2003)</td>
<td></td>
</tr>
<tr>
<td>PAR</td>
<td>HR-Tof-AMS (Aerodyne Research, Inc.) (Crippa et al., 2013; DeCarlo et al., 2006; Freutel et al., 2013)</td>
<td>aethalometer (Magee Scientific) (Freutel et al., 2013)</td>
<td>GC-FID (Chromatotec®) (Gros et al., 1999; Gros et al., 2011)</td>
<td>PTR-MS (Ionicon) (Gros et al., 2011)</td>
<td></td>
</tr>
<tr>
<td>SIR</td>
<td>HR-Tof-AMS (Aerodyne Research, Inc.) (Crippa et al., 2013; DeCarlo et al., 2006; Freutel et al., 2013)</td>
<td>aethalometer (Magee Scientific) (Freutel et al., 2013)</td>
<td>Charcoal cartridges, GC-FID (Chromatotec®) (Gros et al., 1999; Gros et al., 2011)</td>
<td>DNPH-cartridges, HPLC-UV (Bates et al., 2000; Detournay et al., 2011; Dettmer and Engewald, 2003; Kleindienst et al., 1998)</td>
<td></td>
</tr>
<tr>
<td>HPB</td>
<td>ACSM</td>
<td></td>
<td>GC-FID (Varian) (Plass-Dülmer et al., 2002)</td>
<td>ADS-GC-MS (Agilent) (Legreid et al., 2008; Legreid et al., 2007a; Legreid et al., 2007b)</td>
<td></td>
</tr>
<tr>
<td>REV</td>
<td>AMS</td>
<td>aethalometer</td>
<td>GC-FID/FID (Chrompack)</td>
<td>GC-FID/FID (Chrompack)</td>
<td></td>
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<tr>
<td>COR</td>
<td>ACSM</td>
<td>aethalometer</td>
<td>GC-FID/FID (Chrompack)</td>
<td>GC-FID/FID (Chrompack)</td>
<td></td>
</tr>
</tbody>
</table>

AMS: aerosol mass spectrometer
ACSM: aerosol chemical speciation monitor
HR-Tof-AMS: high resolution-time of flight-AMS
Table 3 summarises how many compounds were measured in the respective intensive campaigns. Note that the gaseous speciation can considerably differ from site to site depending on the measurement programme of the campaigns (e.g. no short-chained alkanes were measured at SIR).
### Table 3: Compounds investigated in the particulate and the gaseous phase. For gaseous phase the compounds investigated are indicated by the mentioned number. Note that not all stations investigated the same compounds. Depending on the scope of the intensive campaigns different compounds were measured.

<table>
<thead>
<tr>
<th>Compound group</th>
<th>LON</th>
<th>PAR</th>
<th>SIR</th>
<th>HPB</th>
<th>REV</th>
<th>COR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Winter</td>
<td>Summer</td>
<td>Winter</td>
<td>Summer</td>
<td>Winter</td>
<td>Summer</td>
</tr>
<tr>
<td><strong>Particulate phase</strong></td>
<td></td>
<td></td>
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<tr>
<td>C\textsubscript{org} aerosol</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>black carbon</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
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<tr>
<td><strong>Gaseous phase</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}-C\textsubscript{8} alkanes</td>
<td>12</td>
<td>12</td>
<td>10</td>
<td>14</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C\textsubscript{9}-C\textsubscript{16} alkanes</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>2</td>
<td>8</td>
<td>8</td>
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<tr>
<td>alkanes</td>
<td>11</td>
<td>11</td>
<td>7</td>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>alkynes</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>aromatics</td>
<td>18</td>
<td>18</td>
<td>11</td>
<td>11</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>terpenes</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>aldehydes</td>
<td>8</td>
<td>8</td>
<td>1</td>
<td>1</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>ketones</td>
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<td>7</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>alcohols</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
3. Results

In Figures 3-4 the TOOC (daily mean total observed organic carbon concentration) was calculated for different six sites. Figure 3 shows the TOOC of the cities London (LON) and Paris (two stations; PAR and SIR) in winter and summer. In Figure 4 the TOOC from urban to more remote or rural sites are depicted for the summer period. As already mentioned, not all stations measured the same compounds (Table 3). Therefore a comparison between the sites is difficult and this can only be done for measurement at the same site during winter and summer.

Generally, the TOOC at a specific site is higher in winter compared to summer (Figure 3). The TOOC mainly comes from the gaseous phase. For example, in London (LON) less than 10% are coming from the aerosol phase. This applies for winter as well as for summer. In LON the maximum concentration reached in winter was around 75 µg C/m³, whereas in summer TOOC reached 55 µg C/m³. One reason for this difference between the seasons is due to the meteorological conditions. In winter the boundary layer often remains stable and therefore an air exchange takes only partially place. Additionally, the photochemical reactivity is more elevated in summer than in winter. The main difference in the TOOC pattern between the two seasons is visible in the short and long chained alkanes. In winter 55% of the TOOC is attributed to them, whereas in summer only 38% of the TOOC is generated by them. The aromatics show the same tendency with higher values in winter (13%) and lower ones in summer (8%). The large contribution of (short lived) alkanes, alkenes, and aromatics to the TOOC at LON might be attributed to large vehicular and liquefied petroleum gas emissions. A similar observation was made in Mexico City (Blake and Rowland, 1995; de Gouw et al., 2009; Velasco et al., 2007). Elevated propane and n-butane concentrations are often attributed to nearby fuel and natural gas sources (Millet et al., 2005).

In contrast, the OVOC part (terpenes, aldehydes, ketones, and alcohols) of the TOOC is more dominant in summer (36%) compared to winter (19%), which is supported by the higher photochemical reaction activity in summer.

In Paris (PAR) around 45 µg C/m³ and 35 µg C/m³ TOOC were found in winter and summer, respectively. As in London, a similar TOOC pattern was observed in Paris, too. The aerosol part was small with around 9% for both winter and summer. The short chained alkanes and the alkenes were higher in winter (36% alkanes, 9% alkenes) and lower in summer (30% alkanes, 5% alkenes), whereas the aromatics slightly increased in summer (from 17% to 20%). Ketones (2% for both summer and winter), aldehydes (16% in winter, 15% in summer), and terpenes (4% in winter, 3% in summer) remained stable during the two seasons. In London an increase during summertime was observed. Alcohols increased substantially during summer (from 2% to 13%). Surprisingly, terpenes were not increasing during summertime, which would be expected with the higher biological activity of plants.

The TOOC values were smaller than 20 µg C/m³ in winter and slightly over 10 µg C/m³ in summer at SIRTA (SIR), the suburban Paris site. The trend with lower values in summer compared to winter was observed here, too. As less gaseous phase compounds were measured at SIR (e.g. no short chained alkanes (Table3)), the particulate phase was more dominant here with values of 24% and 16% of the TOOC in winter and summer, respectively. Aromatic compounds decreased from winter to summer from 23% to 13%, as observed in LON, too. Aldehydes decreased too from winter (43%) to summer (27%) at SIR, whereas the ketones increase from winter (9%) to summer (34%). Note that short chained alkanes, alkenes, alkynes and alcohols were not measured at this station.
Figure 3: Mean daily concentrations of organic carbon [µg C/m³] at London (LON), Paris (PAR), and SIRTA (SIR). Winter and summer data are shown.

Additionally to the three stations mentioned before (LON, PAR, and SIR) intensive measurement campaigns for particulate and gaseous phase took place at Hohenpeissenber (HPB; rural background, Germany), Revin (REV, rural background, France) and Corsica (COR, Mediterranean remote, France) in summer 2012 (Figure 4). At HPB around 12 µg C/m³ TOOC were calculated. The aerosol part was the minor fraction and corresponded to only 14% of the TOOC. 17% of the TOOC were attributed to short chained alkanes, whereas the alkenes, alkynes, and aromatics correspond together to 8%. The most relevant compounds at HPB in summer were the OVOCs. Together they generated 61% of the TOOC at this site. With 26% the ketones were the most important ones, followed by alcohols, terpenes (both 12%), and aldehydes (11%). As this station is surrounded from trees and the photochemical activity is elevated in summer, it is not surprising that the OVOCs are predominant here.

At REV the TOOC was only 5 µg C/m³. At this station the lowest TOOC summer concentration was found. With around 18% the aerosol part was relatively high compared to the other stations. The alkanes and aromatics corresponded to 27%. Terpenes, aldehydes, and ketones make 56% of the TOOC and were dominant in summer. Alkenes, alkynes, and alcohols were not measured at this site.

At the remote site in COR a relatively high TOOC was found with 30 µg C/m³. As for the majority of the stations the aerosol part is relatively small with 7% of the TOOC. Compared to the other stations, the long chained alkanes (9%) were more dominant as the short chained (0.2%). This is probably due to the amount of species measured; for the short ones only 2 compounds were analysed, for the long ones 7. Aromatics represented 4% of the TOOC. Aldehydes were predominant at this remote site with a value of 58%. As no other station has such a high value and also SIR measures the same compounds (20, Table 3) a local source must be the reason for this. Wind directions from Southern France or Northern Italy may also played an important role for this elevated value. Ketones, terpenes, and alcohols represent 11%, 8%, and 3% of the TOOC, respectively.
4. Conclusions

The TOOC give a good overview of the carbon composition at different sites and seasons (Figures 3-4). In the calculation of the TOOC, the gaseous phase is the predominant one compared to particles. Generally cities have higher organic carbon concentrations than more rural regions. In winter the carbon concentrations at a particular site is higher compared to summer, which is due to additional anthropogenic emission sources typical of the winter season (e.g. traffic) and to meteorological conditions. It is very difficult to compare stations to each other as the measured compounds differ largely depending on the objectives of the measurement campaigns or programmes.
5. Dissemination

Presentation

Hoerger, C.C.; Reimann, S. The total observed organic carbon (TOOC)-concept adapted for Europe, 14th Task Force on Measurement and Modelling Meeting, Zagreb (Croatia), May 6-8, 2013

Poster


6. References


near Mexico City in March 2006 during the MILAGRO study, Atmospheric Chemistry and Physics, 9, 3425-3442, 2009.


