Supplementary Material for

Two distinct ship emission profiles for organic-sulfate source apportionment of PM in sulfur emission control areas

Kirsten N. Fossum¹, Chunshui Lin¹²³, Niall O’Sullivan⁴, Lu Lei¹, Stig Hellebust⁴, Darius Ceburnis¹, Aqeel Afzal¹⁵, Anja Tremper⁶, David Green⁶⁷, Srishti Jain⁴, Steigvilė Byčenkienė⁸, Colin O’Dowd¹, John Wenger⁴, and Jurgita Ovadnevaite¹

¹School of Natural Sciences, Ryan Institute’s Centre for Climate & Air Pollution Studies, University of Galway, Galway, H91 CF50, Ireland
²State Key Laboratory of Loess and Quaternary Geology and Key Laboratory of Aerosol Chemistry and Physics, Chinese Academy of Sciences, 710061, Xi’an, China
³Department of Civil and Environmental Engineering, the Hong Kong Polytechnic University, Hong Kong, China
⁴School of Chemistry and Environmental Research Institute, University College Cork, Cork, Ireland
⁵Institute of Energy and Environmental Engineering, University of the Punjab, Lahore, Pakistan
⁶MRC Centre for Environment and Health, Environmental Research Group, Imperial College London, UK
⁷NIHR HPRU in Environmental Exposures and Health, Imperial College London, UK
⁸SRI Center for Physical Sciences and Technology, Lithuania

Correspondence to: Jurgita Ovadneviate (jurgita.ovadnevaite@universityofgalway.ie)
**S1 Supplementary Discussion**

**S1.1 Unconstrained PMF**

The PMF solution is a set of factor profiles represented by the corresponding mass spectra and time series. PMF is unconstrained when no *a priori* information about existing source profiles is used to obtain a mathematically reasonable solution. However, a mathematically reasonable solution is not necessarily physically reasonable (Canonaco et al., 2013) and unconstrained PMF can sometimes experience difficulties in separating aerosol sources with temporal covariations, resulting in unrealistic or highly mixed factors (Canonaco et al., 2013). Usually, interpretation of the factors (i.e., source types) is carried out with reference to the mass spectral profiles (e.g., biomass burning) or diurnal cycles (e.g., traffic emissions) of the known sources (Ulbrich et al., 2009) to conclude if the solution is physically reasonable.

When sea-salt aerosol is significant, a known fragmentation pattern of $m/z$ 38, 58, 60, and 83 in order of decreasing relative intensity (sea salt constituents, e.g., $^{23}\text{Na}^{35}\text{Cl}^+$) appears in the unconstrained PMF. However, no sea-salt fragmentation pattern appeared in the unconstrained factors (2-10) from the Dublin Port dataset. Using the high time resolution organic species, unconstrained PMF was attempted on the dataset. The solution of two – three unconstrained factors resulted in combined factors, including a hydrocarbon-like OA (HOA) factor, an aged or oxidised OA (OOA) factor, and another potentially split factor type of heavier ions (Figure S2a). The unconstrained PMF solutions resulted in mixed factors or splitting between factors such as HOA-like at after three factors (see Figure S2b for e.g. six factors). In this way, unconstrained PMF revealed what was expected, that there was an oil or petrol burning source (HOA) with a possible splitting of heavier ions, and a secondary OA (OOA) consistent with regional pollution found in Dublin (Lin et al., 2019; Lin et al., 2018; Ovadnevaite et al., 2021). However, the disparate yet overlapping primary sources of ship emissions, shipping related traffic, and shipping activities had not been successfully extracted, nor of the secondary formation of Dublin city OOA and port related OOA if any. The former lack of success with unconstrained PMF points to ship fuels having a chemical signature similar to HOA that are intrinsically linked, so the PMF cannot mathematically separate different fuel types (e.g. different types of ship fuels, diesel, or oil burning) using only UMR $m/z$ less than 120. However, the primary sources at the port were resolved by use of constrained profiles.

**S1.2 SO$_4^{2-}$ ions**

There was a remaining issue with separating the SO$_4^{2-}$ from ship plumes and from regional secondary formation. Within the PMF, the S-Ship factor is being apportioned this SO$_4^{2-}$ from regional secondary formation. The issue arises from the lack of substantial variation within the SO$_4^{2-}$ fragmentation profile (UMR). This lack of variation in the fragmentation profile exists even for degrees of neutralisation of the SO$_4^{2-}$ aerosol measured in controlled lab conditions (Chen et al., 2019). Over the PortAIR intensive campaign, SO$_4^{2-}$ during the exemplary S-Ship plumes (Table S1) was acidic. These SO$_4^{2-}$ profiles can be compared against those during six prominent regional secondary pollution episodes when most SO$_4^{2-}$ was in the form of neutralised ammonium sulfate (Figure S14). Overall, the variation at each $m/z$ can be explained by the sample standard deviation of the mean, except at $m/z$ 80, 81, and 98 (SO$_3$, HSO$_3$, and H$_2$SO$_4$, respectively). Of these three ions, only $m/z$ 80 has SNR $> 2$ (Figure S3). It is likely that the prominent SO$_4^{2-}$ portion of the mass spectrum in the constrained S-Ship profile caused the capture of regional pollution events. This capture of the regional pollution events occurred for all constrained PMF runs from up to 10 factor solutions. Even at higher factor numbers, no regional SO$_4^{2-}$ factor emerged, but rather at 9-10 factors a factor emerged that represented all SO$_4^{2-}$ and simply robbed contribution from the S-Ship factor.
The SO$_4^{2-}$ fragment ions included in the PMF were m/z 48 for SO$_3^+$, m/z 64 for SO$_2^+$, m/z 80 for SO$_4^+$, m/z 81 for HSO$_3^+$, and m/z 98 for H$_2$SO$_4^+$ (Sun et al., 2012), which account for about 54% of the measured SO$_4^{2-}$ (Figure S4a). The remaining SO$_4^{2-}$ was added back in later to the factors containing SO$_4^{2-}$, using the ion ratio to m/z 80. The S-Ship factor and OOA factor contained all significant fractions of the SO$_4^{2-}$ ions (Figure 3a), so these factors were affected by the re-addition of the non-measured SO$_4^{2-}$ fragments (see Methods). The S-Ship factor was scaled by a ratio of 1.42 and OOA was scaled by 1.18.

Supplementary Tables

Table S1. Characteristics of the exemplary plumes selected for determining the mean emission profile for both S-Ship and O-Ship types.

<table>
<thead>
<tr>
<th>Type</th>
<th>Start</th>
<th>End</th>
<th>Duration</th>
<th>SO$_2$ Mean (µg/m$^3$)</th>
<th>OA mean (µg/m$^3$)</th>
<th>SO$_4^{2-}$ mean (µg/m$^3$)</th>
<th>PM$_1$ mean (µg/m$^3$)</th>
<th>Wind speed (m/s)</th>
<th>Wind direction (˚)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-Ship</td>
<td>19/12/2022 23:20</td>
<td>19/12/2022 23:32</td>
<td>12 min</td>
<td>8.2 ±0.3</td>
<td>17 ±3</td>
<td>21 ±3</td>
<td>44 ±6</td>
<td>3.5 ±0.5</td>
<td>158 ±4</td>
</tr>
<tr>
<td></td>
<td>29/12/2022 20:53</td>
<td>29/12/2022 21:04</td>
<td>11 min</td>
<td>16.1 ±7.6</td>
<td>40 ±20</td>
<td>45 ±11</td>
<td>91 ±34</td>
<td>3.8 ±0.8</td>
<td>173 ±8</td>
</tr>
<tr>
<td></td>
<td>13/01/2023 18:18</td>
<td>13/01/2023 18:35</td>
<td>17 min</td>
<td>No data</td>
<td>22 ±4</td>
<td>29 ±3</td>
<td>53 ±3</td>
<td>4.0 ±0.6</td>
<td>174 ±1</td>
</tr>
<tr>
<td></td>
<td>21/01/2023 05:51</td>
<td>21/01/2023 05:57</td>
<td>6 min</td>
<td>87.9 ±0.3</td>
<td>47 ±8</td>
<td>62 ±4</td>
<td>113 ±12</td>
<td>4.6 ±0.5</td>
<td>169 ±14</td>
</tr>
<tr>
<td></td>
<td>24/01/2023 17:33</td>
<td>24/01/2023 17:44</td>
<td>11 min</td>
<td>5.5 ±1.6</td>
<td>7 ±2</td>
<td>11 ±5</td>
<td>23 ±8</td>
<td>0.2 ±0.3</td>
<td>192.77 ±0.08</td>
</tr>
<tr>
<td>O-Ship</td>
<td>23/12/2022 20:27</td>
<td>23/12/2022 20:33</td>
<td>6 min</td>
<td>7.0 ±2.1</td>
<td>95 ±14</td>
<td>2 ±1</td>
<td>105 ±16</td>
<td>2.6 ±0.4</td>
<td>252 ±22</td>
</tr>
<tr>
<td></td>
<td>01/01/2023 01:29</td>
<td>01/01/2023 01:35</td>
<td>6 min</td>
<td>6.2 ±0.7</td>
<td>89 ±32</td>
<td>2.1 ±0.9</td>
<td>95 ±32</td>
<td>3.1 ±0.5</td>
<td>235 ±8</td>
</tr>
<tr>
<td></td>
<td>06/01/2023 05:36</td>
<td>06/01/2023 05:43</td>
<td>7 min</td>
<td>9.8 ±1.8</td>
<td>87.4 ±0.8</td>
<td>3.7 ±0.3</td>
<td>98 ±1</td>
<td>3.7 ±0.8</td>
<td>230 ±18</td>
</tr>
<tr>
<td></td>
<td>08/01/2023 11:54</td>
<td>08/01/2023 12:06</td>
<td>12 min</td>
<td>8.0 ±1.0</td>
<td>138 ±23</td>
<td>2.5 ±0.4</td>
<td>145 ±24</td>
<td>4.4 ±0.4</td>
<td>222 ±6</td>
</tr>
<tr>
<td></td>
<td>08/01/2023 14:37</td>
<td>08/01/2023 14:43</td>
<td>6 min</td>
<td>8.2 ±0.3</td>
<td>101 ±6</td>
<td>2 ±1</td>
<td>112 ±5</td>
<td>4.0 ±0.9</td>
<td>221 ±2</td>
</tr>
</tbody>
</table>

Over the full campaign (Dec 2021 – Feb 2023), SO$_2$ had a median value of 0.921 µg/m$^3$, with a 25th – 75th percentile range of 0.457 – 1.564, and a 10th – 90th percentile range of 0.116 – 2.569 µg/m$^3$. The standard deviation is σ = 1.5116, and 3σ = 4.5348. Meaning that the values in Table S1 for all ship plume cases have peak SO$_2$ concentrations far outside the normal 3σ, and can be considered elevated concentrations. Over the intensive campaign Ni had a median value of 0.0017 µg m$^{-3}$, and V had a median value of 0.0012 µg m$^{-3}$ at hourly resolution.
Table S2. Mean characteristics of ship plumes associated with S-Ship (58 plumes) and O-Ship (190 plumes) source apportioned factors. Median values in blue.

<table>
<thead>
<tr>
<th></th>
<th>Plume number</th>
<th>Plume number PM$_1$ ≥ 50</th>
<th>PM$_1$ (µg/m$^3$)</th>
<th>N (nl/cm$^3$)</th>
<th>NO$_x$ (µg/m$^3$)</th>
<th>SO$_2$ (µg/m$^3$)</th>
<th>eBC (µg/m$^3$)</th>
<th>V/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S-Ship</strong></td>
<td>58</td>
<td>10</td>
<td>29 ± 22</td>
<td>1.52 ± 1.55 × 10$^4$</td>
<td>117.6 ± 118.0</td>
<td>3.5 ± 3.4</td>
<td>1.8 ± 1.4</td>
<td>3.41 ± 0.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21</td>
<td>21.09 × 10$^3$</td>
<td>83</td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>33</td>
<td>32 ± 26</td>
<td>3.75 ± 2.28 × 10$^4$</td>
<td>132.3 ± 108.7</td>
<td>3.9 ± 3.2</td>
<td>3.0 ± 1.8</td>
<td>0.74 ± 0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td>3.20 × 10$^3$</td>
<td>97</td>
<td></td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td><strong>O-Ship</strong></td>
<td>190</td>
<td>33</td>
<td>32 ± 26</td>
<td>3.75 ± 2.28 × 10$^4$</td>
<td>132.3 ± 108.7</td>
<td>3.9 ± 3.2</td>
<td>3.0 ± 1.8</td>
<td>0.74 ± 0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td>3.20 × 10$^3$</td>
<td>97</td>
<td></td>
<td></td>
<td>2.7</td>
</tr>
</tbody>
</table>
Figure S1. (a) Overview map of Dublin Port (satellite image credit: Imagery ©2024 Airbus, Landsat/Copernicus, Maxar Technologies, Map data ©2024 Google) (top) and (b) an image of the main container with the Xact container in-situ (bottom).
Figure S2. The factor profiles of the unconstrained OA PMF solution of six factors from PortAIR. Left axis is the relative ion fraction of the mass spectrum. Right axis is the relative ion fraction contained in that profile compared with the total (markers).

Figure S3. SNR plot of fragment OA and SO$_\text{4}^{2-}$ ions. Weak ions are considered $2 > \text{SNR} > 0.2$ (green band), while bad ions $\text{SNR} < 0.2$ (grey band).
Figure S4. Scatter plot of the mass concentration of the (a) input SO$_4^{2-}$ ions vs the SO$_4^{2-}$ measured, and (b) organic-sulfate factors (sum of factors) vs the input for PMF of the OA + SO$_4^{2-}$ mass concentration (line shows linear regression fit).

Figure S5. Excerpt time series of the high-resolution ambient measurements from PortAIR during the intensive month (December 22-24, 2022). From top to bottom panels, reconstructed PM$_1$ (NR-PM$_1$ species + eBC) displayed as species stacked on top of each other, the number concentration (N) of particles from 10-500 nm in dry electrical mobility diameter ($d_m$) from the SMPS, and the curtain plot of the SMPS data, right axis shows $d_m$ with the color indicating the number concentration ($dN$/dlog($d_m$)) of particles at that size.
Figure S6. PM$_1$ time series of the Dublin Port Q-ACSM and AE33 data (top panel) and of the established Dublin urban background site at UCD (bottom panel). Note that the vertical axis scales are different to make the UCD data viewable.

Figure S7. Scatter plots of relative intensities of OA ions of (a) O-Ship versus S-Ship mass spectrum, (b) X-Ship versus S-Ship, and (c) X-Ship versus O-Ship mass spectra. The 1:1 dashed line (grey), while the ions are shown as numbered markers representing the m/z (UMR) of each ion.
Figure S8. Scatter plot of the relative ion intensities of the classic Paris HOA Fraction (Crippa et al., 2013) compared to the HOA derived from the curb side in Dublin, Ireland (TCD HOA). This uses a different PM$_1$ Q-ACSM from the intensive campaign. The marker numbers are the m/z of the ions.

Figure S9. Correlation matrix of the time series of PMF factors and other (external) species at (a) native time resolution of the Q-ACSM, and (b) at hourly time resolution.
Figure S10. Number-size distributions showing mean (error bars show uncertainty) and 25th-75th percentiles of the exemplary (Table S1) pollution plumes for (a) S-Ship and (b) O-Ship emissions. The y-axis is average sum of the number concentration in log space (dN/dlog(dm)), and the x-axis is the particle dry electrical mobility diameter (dm) in nm. Percentiles are noisy due to low sample size (n=19 (S-Ship) and n=15 (O-Ship)).

Figure S11. Pie charts of the composition breakdown of the factors and other species contributing to PM1 data. Mean PM$_1$ is shown at the bottom of the pie (brackets show standard deviation of the mean).
Figure S12. Averaged number-size distributions of periods between the ‘bat ears’ in (a) during Marine Gas Oil (MGO) emissions. Data is shown as the lognormal particle concentration (dN/dlog(d_m)) vs dry electrical mobility diameter (d_m) in nm.

Figure S13. Scatter plot of the relative intensities of the OA ions of the O-Ship factor compared to the Dunkerque campaign Ship-like organic aerosol (ShOA) (Zhang, 2016). The marker numbers are the m/z of the ions.
Figure S14. Mean mass spectrum of the SO$_4^{2-}$ ion fragments for the regional ammonium sulfate (black) and for acidic sulfate plumes from the exemplary S-Ship cases (red). Standard deviation of the sample shown in error bars.

**Supplementary References**


Zhang, S., Dynamic analysis, in near field and with a finer temporal resolution, of a sub-micron aerosol in urban situation under industrial influence - Analyse dynamique, en champ proche et à résolution temporelle fine, de l’aérosol submicronique en situation urbaine sous influence industrielle. Université du Littoral Côte d’Opale (2016).