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2	SUPPORTING INFORMATION
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4	Characterization of Urban Aerosol in Cork City (Ireland)
5	using aerosol mass spectrometry
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2 Map of the study area



4 Fig. S1 Map of the measurement site

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1 PM time trends

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- 5 Fig. S2. PM mass during the field study (all measurements in μ g m⁻³)
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7 Meteorology

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9 Back trajectories of the air masses arriving at the measurement site were calculated 10 for 00:00 and 12:00 for each day of the campaign, depicting the path taken by the air 11 mass reaching the sampling site over the previous five days. The back trajectories 12 were run using the on-line HYSPLIT model developed by the National Oceanic and 13 Atmospheric Administration (NOAA) (Draxler and Rolph, 2003).

Three predominant origins of air masses arriving at the receptor were classified. Marine Polar (mP) described air masses emerging from polar regions around southern Greenland and advecting south-east over the North Atlantic, marine Arctic (mA) air coming mainly form the north Scandanavian Arctic regions and Continental marine polar (cmP) for air stagnated as a pressure gradually strengthened and centred over Mace Head and anti-cyclonic conditions were observed for most of the time during this period.

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Days (February 2009)	Air mass type	Air mass trajectory plot	P. Marine	P. Stagnant
1 st	cmP	BOALHOFFI EXCEL DEALED AND AND AND AND AND AND AND AND AND AN		Yes
2 nd , 3 rd	сР	Education of the second		Yes
4 th	cmP			Yes
5 th – 8 th	mA	TRANSPORT TOOLS TRANSPORT TOOLS TOO	Yes	
9 th -15 th	mP	Extension from the constraint of the constraint	Yes	
16 th -19 th	cmP	Monte de la construcción de la c		Yes
20 th -22 nd	mP	Basessi Facilitations and any discretional of the second s	Yes	

2 Table S1. Air mass back trajectories.



1 Correlation table for AMS (Table S2) and ATOFMS (Table S3) between aerosol

2 categories and selected m/z peaks

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ATOFMS	OC-EC-SUL	OC-EC-NIT	OC-EC-CH	Na-K-OC-NIT	Ca-EC
m/z 113	0.52	<0.1	0.65	0.30	0.11
m/z 37	0.94	0.30	0.74	0.48	0.14
m/z 55	0.76	<0.1	0.70	<0.1	0.14

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6 Table S2. Correlation table between selected ATOFMS peaks (m/z 37, 55 and 113)

7 and organic main ATOFMS particle types. Correlations were obtained by temporal

8 series of ATOFMS clusters and ATOFMS peaks queries from the dataset.

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				AMS Factor	•	
m/z	Species	1	2	3	4	5
		LV-OOA	COA	НОА	PCOA	BBOA
29	C_2H_5	0.21	0.65	0.50	0.58	0.82
39	C ₃ H ₃	0.2	0.65	0.38	0.61	0.89
41	C₃H₅	0.26	0.68	0.48	0.55	0.80
43	C ₃H ₇	0.11	0.55	0.56	0.59	0.72
43	$C_{3}H_{2}O_{2}$	0.41	0.63	0.28	0.35	0.92
44	CO ₂	0.64	0.43	0.35	0.25	0.50
55	C₃H₃O	0.37	0.70	0.26	0.45	0.96
55	C₄H ₇	0.16	0.60	0.59	0.55	0.73
57	C₄H ₉	0.11	0.47	0.58	0.57	0.63
57	C₃H₅O	0.34	0.67	0.2	0.43	0.99
60	$C_2H_4O_2$	0.24	0.68	0.27	0.5	0.99

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Table S3: Correlation table between selected AMS peaks (high resolution m/z) and
 organic main AMS particle types. Correlations were obtained by temporal series of
 AMS factor and AMS peaks queries from the dataset.







- 12 OM:OC of 1.4 was assumed for converting the AMS organic mass.

1 AMS PMF solution description

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The PMF analysis on the HR organic matrix of the AMS data was performed for 1 to 6 factors, and summary of diagnostics and results from the different factor solutions is shown in Table S4. PMF solutions with factor numbers greater than 5 provided no new distinct factors and instead displayed splitting behaviour of the existing factors.

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N Factors	Factors	Note
2	HOA/LV-OOA	HOA has a strong m/z 60
3	HOA/LV-OOA/BBOA	BBOA has a number of peaks not commonly seen in reference spectra, Large residuals at key m/z's and time periods.
4	HOA/LV-OOA/BBOA/PCOA	A new factor PCOA is found.
5	HOA/LV- OOA/BBOA/PCOA/COA	A new factor COA is found. Distinctive diurnal cycles
		for Factors and MS that compare well with database MS. Better correlation with concomitant measurements (Table S5) than with the 4 factor solution (increase average R ² , see Fig. S5)
>5	Splitting	HOA and LV-OOA begin to split

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10 Table S4. Summary of the AMS PMF results

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12 Rotational ambiguity

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Different 30 seed solutions converged to nearly identical solutions with the lowest value of Q/Qexp (Fig. S5 a). The total range of Q/Qexp varied by only 1% and there were not substantial differences across the 30 solutions (Fig. S5 b). With FPEAK varying from -1 to 0.5 in increment of 0.25 (seed=0), the lowest Q/Qexp was obtained at -0.25 (Q/Qexp = 4.775; (Fig. S5 c-e)) and the total R2 (Table S5) were

- 1 higher and similar for FPEAK≥-0.25. Therefore, FPEAK=-0.25 was chosen as the
- 2 best solution.
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In addition, higher correlation values (R²) between the assigned factors in a PMF solution and their corresponding tracers (in this case gaseous, ATOFMS and off-line filter techniques measurements), were used as additional criterion. Table S5 shows correlation between the 4 and 5 PMF factor solutions and a number of satellite measurements.

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Solution type		4	factor	solutio	n	5 factor solution				
		(not chosen) (this study)								
N Fa	ctor	1	2	3	4	1	5	3	4	2
Factor	r name	LV- OOA	BBOA	HOA	PCOA	LV- OOA	BBOA	HOA	PCOA	COA
AMS (1	AMS org	0.22	0.86	0.53	0.77	0.24	0.9	0.43	0.65	0.6
hour)	AMS nit	<u>0.75</u>	0.34	0.16	0.1	<u>0.79</u>	0.34	0.14	0	0.24
	AMS amm	<u>0.69</u>	0.5	0.18	0.23	<u>0.77</u>	0.52	0.15	0.17	0.27
	AMS sul	<u>0.72</u>	0.22	0.01	0	<u>0.75</u>	0.22	0	0	0.15
	AMS Chl	0.29	<u>0.83</u>	0.25	0.53	0.38	<u>0.87</u>	0.2	0.41	0.4
gas (1 hour)	NOx	0	0	<u>0.31</u>	0	0	0	<u>0.39</u>	0	0
ATOFMS	OC-EC-SUL	0	0.23	0.15	0.3	0	0.21	0	<u>0.35</u>	0.22
(1 hour)	OC-EC-NIT	<u>0.19</u>	0	0	0	<u>0.25</u>	0	0	0	0
	OC-EC-CH	0	0	0	0.25	0	0	0	0.29	0
	Na-K-OC-NIT	<u>0.57</u>	0.27	0	0	<u>0.65</u>	0.27	0	0	0.33
	Ca-EC	0	0	<u>0.25</u>	0	0	0	<u>0.35</u>	0	0
Off –Line	Levoglucosan	0	<u>0.75</u>	0.31	<u>0.9</u>	0.16	<u>0.8</u>	0.23	<u>0.84</u>	0.34
(6 hours)	F	0.15	0.65	0.32	0.7	0.23	0.7	0.25	0.66	0.35
	CI	0	<u>0.60</u>	0.2	<u>0.77</u>	0.15	<u>0.72</u>	0.17	<u>0.70</u>	0.18
	Br	0	<u>0.66</u>	0.35	<u>0.70</u>	0.12	<u>0.61</u>	0.28	<u>0.75</u>	0.29
	ĸ	0.21	0.56	0.17	<u>0.59</u>	0.3	<u>0.65</u>	0.11	0.50	0.25
	EC	0	0.68	0.38	0.87	0.1	0.72	0.32	0.80	0.35
Sun set (2	ос	0.12	0.53	0.5	0.63	0.15	0.56	0.48	0.58	0.27
hours)	тс	0.1	0.66	0.4	0.8	0.15	0.8	0.37	0.78	0.33

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8 Table S5. Correlation table for the four and five PMF solution of the AMS organic

9 matrix and a number of external variables.

All R² discussed below are significantly different (at 95% confidence) and the five
factor solutions presents, relative to the four factor one:

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5 - HOA increases its correlation with NO_x from 0.31 to 0.39.

6 - HOA increases its correlation with ATOFMS Ca-EC from 0.25 to 0.35.

BBOA increases its correlation with AMS Chloride from 0.83 to 0.87, and worse with
Br.

9 - BBOA was found better correlated with levoglucosan, K and Cl at 6 hours10 resolution.

LV-OOA shows better correlations between secondary species. Specifically: from
0.75 to 0.79, from 0.69 to 0.77, and from 0.71 to 0.75 for ammonium, sulphate and
nitrate, respectively.

PCOA increases its correlation from 0.3 to 0.35 and from 0.25 to 0.29 of two
 specific ATOFMS clusters: EC-OC-SUL and EC-OC-CH, respectively. The
 correlation between these two specific ATOFMS clusters and AMS factor PCOA is
 unique of this factor.

PCOA reduced the correlation with biomass markers with a five factor solution, and
improve the Br correlation from 0.70 to 0.75.

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7 PMF solution

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PMF Solution	AMS 5 factor								
	Factors	LV-OOA	COA	HOA	PCOA	BBOA			
AMS	LV-OOA	0.95	0.25	0.00	0.00	0.25			
4 factor	BBOA	0.29	0.65	0.22	0.42	0.99			
	HOA	0.00	0.46	0.95	0.23	0.30			
	PCOA	0.1	0.26	0.22	0.98	0.61			

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Table S6. Temporal correlation (as R²) between four and five factor PMF solutions. PMF factors were found to conserve the temporal trends. The correlation table points out a correlation between BBOA and COA (0.65), as reported in recent laboratory experiments (He et al. 2010).

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7 Bootstrapping analysis.

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9 The difficult issue of the uncertainty was also quantitatively addressed with 10 bootstrapping with replacement of MS (Ulbrich et al. 2009, Allan et al. 2010). Fig. S8 11 shows the mean and standard deviations from bootstrapping along with the base 12 solution. Whilst peak standard deviation of the total signal can be seen for HOA 13 (3.3%) and LV-OOA (7.3%), the other three factors show higher variations: BBOA 14 (20%), PCOA (18%) and COA (21%).

Key peaks for LV-OOA (m/z 28 and m/z 44) as well as for HOA (m/z 43 and 57) shows very low (<2%) peak standard deviations (SD). BBOA shows low peak SD for key marker at m/z 60, but high SD for m/z 57 (29%, tracer for HOA). PCOA shows high SD for peaks at m/z 55 and 57, but lower for key markers such as m/z 39, 41, 44, 77, 91, 113. Finally, COA shows a high SD for m/z 60 (marker for BBOA) and



1 oxidized fraction (m/z 28 and 44), but low SD for key ions (m/z 41, 5%; C₄H₇, 3% and

2 Other supporting data







Fig. S9. OA components of the five factor solution separated by the three main ion families: (a) Family CHO_2 as expected is dominated by LV-OOA with m/z 44. Interestingly the second most abundant peak is found at m/z 60 and attributed to BBOA. (b) Family CHO₁ shows again as expected strong signal by LV-OOA at m/z 28 and 43. The peak at m/z 57 (C_3H_5O) is again unique for BBOA. (c) Family CH shows strong signature for HOA. Factor COA shows a different CH patterns with signals at m/z 27, 39, 41 and 55. Finally, m/z 91 for family CH is mainly represented by factor PCOA.





Fig. S10. Diurnal variation of specific HR peaks for the whole period of study. Please note interesting features of m/z 55 (C_3H_3O) and m/z 57 (C_3H_5O) spiking during lunch times but not during traffic conditions, which is capture by the PMF analysis as COA.

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1 Other supporting plots

Aerosol type	Wind rose	Polar plot
BBOA		-43 -34 -35 -38 -22 -15 -15 -15 -15 -15 -15 -15 -15 -15 -15
PCOA		
HOA		
COA		



Figure S11. The wind roses depict the trend in scores with wind direction and time for
a typical day. Figures were generated with Openair software (Carslaw, D.C. and
Ropkins, K. Openair - an R package for air quality data analysis, Environ. Modell.
Soft. 27-28, 52-61, 2012)

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2 Figure S12. AMS aerosol mass size distributions for (a) Organics, (b) Sulphate, (c)

- 1 [µg m⁻³] versus D (vacuum aerodynamic diameter, [nm]), Figures on the right are in
- $2 \quad dM/d \log (D) [\mu g m^{-3}]$ versus local time.