Supporting Information

Levels and Sources of Atmospheric Particle-Bound Mercury in Atmospheric Particulate Matter (PM_{10}) at Several Sites of an Atlantic Coastal European Region

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Major ions and trace metals extraction and quantification

Major cations (Na^+, K^+, Ca^{2+}, NH_4^+ and Mg^{2+}) and anions (Cl^-, NO_3^- and SO_4^{2-}) were extracted with ultrapure water by ultra-sonication and quantified by zone capillary electrophoresis (HP3DCE, Agilent, Palo Alto, CA, USA) according to the Blanco-Heras et al. procedure [1]. Trace metals were extracted by acid digestion and quantified by inductively coupled mass spectrometry (ICP-MS) as described in previous papers [2]. Trueness of the methods offers good results after SRM 1648a urban particulate matter reference material analysis. Statistical summary for the concentrations of major ions and metals are shown in Table S1. Average relative abundances of anions follow the sequence $Cl^- > SO_4^{2-} > NO_3^-$ with Cl^- (2.4-9.9 μg m^{-3}) and SO_4^{2-} (4.4-8.4 μg m^{-3}) dominating the anion budget (Table S1). Na^+ (1.4-7.1 μg m^{-3}) dominates the cation budget at all sites (US, SS and IS) with the sequence $Na^+ > Ca^{2+} > NH_4^+ > Mg^{2+} > K^+$. High concentrations were observed for Al (0.23-0.64 μg m^{-3}) and Fe (0.25-1.1 μg m^{-3}) at all sites, while low values were achieved for Bi (0.08-0.18 ng m^{-3}), Cd (0.19-0.23 ng m^{-3}), As (0.70-1.5 ng m^{-3}) and Sb (0.88-3.3 ng m^{-3}) (Table S1).

Equivalent black carbon and UV-absorbing particulate matter quantification

After gravimetric determination of the PM_{10}, filter sample portions were analyzed for equivalent black carbon (eBC) and UV-absorbing particulate matter (UVPM) by using a Magee Sootscan™ OT-21 (Berkeley, CA, USA) transmissometer. The OT-21 measures the absorption of light (in ATN units) by particles collected on a filter at two wavelengths. The measurements at 880 nm (in the infrared spectrum) are interpreted as a measure of light-absorbing carbon analogous to black carbon present on the filter. eBC should be used instead of black carbon for data derived from optical absorption methods, together with a suitable mass absorption cross-section (MAC) for the conversion of light absorption coefficient into mass concentration [3].

The measurements at 370 nm (in the UV spectrum) are designated as UVPM indicator of aromatic organic compounds. The attenuation was estimated as follows:

$$ATN = -100\ x\ ln\frac{I}{I_0}$$

where I and I_0 are the respective transmission intensities through the loaded and unloaded filter (blank filter). Statistical summary are shown in Table S1. High values of eBC and UVPM (3.3 and

2.3 µg m^{-3} for eBC and UVPM, respectively) were achieved at US. However, several samples at US (two samples) and IS (three samples) exceeds the maximum value for the measurement of the attenuation at 780 nm (filter too dark). Also, the maximum value for the measurement of the attenuation at 370 nm was exceeded by seventeen samples at US, four samples at SS and eight samples at IS.

Backward Trajectory Analysis

Backward trajectories using the NOAA Hybrid Single- Particle Lagrangian Integrated Trajectory Model (HYSPLIT) model [4] was run in this study to track the transport pathways and source regions of target sites. Backward trajectories were calculated at 2500, 1500 and 500 m above mean sea level (AMSL) 120 h before the time of the arrival to study sites. Conclusions derived from backward trajectories shows that air masses were mainly transported from Atlantic Ocean during the study period. The semi-permanent presence of Azores high pressure and the Icelandic low pressure systems over the North Atlantic Ocean explained the high Atlantic Ocean influence at studied sites [4].

Seasonal variation of major ions, trace metals, equivalent black carbon and UV-absorbing particulate matter levels in PM_{10}

Table S2 gives the statistical summary of several major ions and metals measured at three sites during the study period. Concentrations of Ca^{2+}, NO_3^-, eBC, As, Cd, Pb and Sb were high during winter as compared to summer season at several sites. Meteorological conditions, during winter time (characterised by high wind speed) would enhance the re-suspension of crustal elements, which could explain the high Ca^{2+} mass. Also, during winter time the increase of fossil fuel combustion could explain the high levels of NO_3^-, eBC and several metals such as As, Cd, Pb and Sb linked to anthropogenic activities.

Table S1. Average, RSD, range and minimum and maximum values of major ions, metals, eBC and UVPM in PM_{10} samples at urban site (US) N=44, suburban site (SS) N=38 and industrial site (IS) N=41.

Site	Average (ng m^{-3})	Max (ng m^{-3})	Min (ng m^{-3})	Range (ng m^{-3})	RSD (%)
PM_{10} mass[a]					
US	49.6	128.5	25.1	103.4	41.8
SS	31.4	82.8	13.2	69.6	45.3
IS	62.2	334.0	14.3	319.7	83.0
NH_4^+					
US	851.4	3812	<3.8	3809	91.6
SS	885.1	3754	42.3	3712	86.2
IS	1268	5496	3.8	5492	93.6
K^+					
US	200.0	1044	28.7	1015	92.3
SS	166.9	1139	53.5	1086	108.7
IS	592.0	4783	50.9	4731.6	137.5
Na^+					
US	2201	9026	341.4	8684	84.0
SS	1377	4034	56.6	3978	64.3

IS	7046	42755	546.2	42209	139.0

Table S1. *Cont.*

Ca^{2+}					
US	479.0	1592	103.8	1489	62.6
SS	284.0	2251	77.8	2173	122.0
IS	1482	5865	159.7	5706	90.3
Mg^{2+}					
US	531.1	5583	54.0	5529	205.4
SS	165.5	481.6	11.4	470.3	58.0
IS	1994	14857	56.7	14800	195.2
Cl^{-}					
US	4660	21478	339.9	21138	100.2
SS	2366	12012	47.3	11965	107.2
IS	9853	80015	9.3	80006	142.1
SO_4^{2-}					
US	5332	18238	1080	17158	73.9
SS	4425	13879	923.2	12955	76.7
IS	8428	23324	932.7	22392	63.2
NO_3^{-}					
US	1636	7200	71.3	7129	89.1
SS	1409	5974	151.6	5823	92.7
IS	2840	16303	223.2	16080	117.0
Al[a]					
US	0.64	3.1	0.04	3.1	103.0
SS	0.23	0.72	0.03	0.69	82.9
IS	0.58	2.1	0.001	2.1	85.6
As					
US	0.70	2.0	0.15	1.9	65.6
SS	0.74	2.7	0.08	2.6	78.5
IS	1.5	4.4	0.19	4.2	71.5
Bi					
US	0.18	0.74	0.02	0.72	88.6
SS	0.08	0.41	0.003	0.41	101.0
IS	0.17	0.92	0.004	0.92	127.4
Cd					
US	0.23	1.4	0.05	1.3	99.9
SS	0.19	1.4	0.02	1.4	121.8
IS	0.21	0.85	0.01	0.84	89.7
Cr					
US	4.6	16.3	<0.12	16.2	87.5
SS	2.1	7.1	<0.12	7.0	96.5
IS	6.8	38.9	<0.12	38.8	113.9
Cu					
US	32.2	98.1	5.6	92.5	63.3
SS	17.9	56.2	3.0	53.2	52.4
IS	34.4	87.2	1.1	86.1	56.3

Table S1. *Cont.*

Fe[a]					
US	0.70	2.1	0.10	2.0	77.2
SS	0.25	0.70	0.01	0.69	68.6
IS	1.1	5.5	0.01	5.4	115.0
Mn[a]					
US	0.02	0.05	<0.001	0.05	78.3
SS	0.01	0.03	<0.001	0.03	83.8
IS	0.04	0.15	0.002	0.15	98.2
Ni					
US	4.9	12.9	0.69	12.2	65.9
SS	3.7	20.7	<0.09	20.6	102.4
IS	6.7	23.6	0.26	23.3	86.9
Pb					
US	10.1	30.2	0.93	29.3	72.3
SS	6.3	19.5	0.40	19.1	73.1
IS	7.2	24.9	0.47	24.5	77.8
Sb					
US	3.3	12.8	0.42	12.3	85.6
SS	0.88	3.5	0.06	3.4	68.8
IS	1.2	5.2	0.03	5.2	95.8
Si					
US	1.7	8.2	0.11	8.1	103.0
SS	0.62	1.9	0.09	1.8	82.9
IS	1.5	5.6	0.002	5.6	85.6
Sr					
US	4.9	14.4	1.6	12.7	49.6
SS	2.4	4.2	0.80	3.4	35.6
IS	5.8	23.9	1.7	22.2	66.5
V					
US	8.8	22.1	0.50	21.6	61.0
SS	6.4	19.4	0.52	18.9	69.2
IS	8.8	27.3	1.3	26.0	64.5
Zn					
US	36.9	108.7	7.3	101.4	73.5
SS	25.9	57.0	3.6	53.4	60.3
IS	43.9	137.3	7.9	129.3	67.4
eBC					
US	3348[b]	7481[b]	1308[b]	6174[b]	42.3[b]
SS	1552	2984	137.3	2846	43.2
IS	1779[c]	5693[c]	175.3[c]	5518[c]	74.8[c]
UVPM					
US	2245[d]	3059[d]	1373[d]	1687[d]	24.1[d]
SS	1552[e]	2984[e]	137.3[e]	2846[e]	43.2[e]
IS	1444[f]	3170[f]	170.5[f]	2999[f]	53.8[f]

[a]Results expressed as μg m^{-3}

[b]N=42, the concentration of two samples exceeds the maximum value for the measurement of the attenuation at 880 nm (filter too dark)

[c]N=39, the concentration of thee samples exceeds the maximum value for the measurement of the attenuation at 880 nm (filter too dark)
[d]N=27, the concentration of 17 samples exceeds the maximum value for the measurement of the attenuation at 370 nm (filter too dark)
[e]N=34, the concentration of four samples exceeds the maximum value for the measurement of the attenuation at 370 nm (filter too dark)
[f]N=33, the concentration of eight samples exceeds the maximum value for the measurement of the attenuation at 370 nm (filter too dark)

Table S2. Seasonal variation of major ions, metals, eBC and UVPM in PM_{10} samples at urban site US (summer season N=22, winter season N=22), suburban site SS (summer season N=17, winter season N=21) and industrial site IS (summer season N=18, winter season N=23).

	Summer			Winter		
Site	**Max (ng m^{-3})**	**Min (ng m^{-3})**	**Average±SD (ng m^{-3})**	**Max (ng m^{-3})**	**Min (ng m^{-3})**	**Average±SD (ng m^{-3})**
PM10 mass[a]						
US	70.3	25.1	41.7±11.6	128.5	26.9	56.9±25.2
SS	57.9	13.2	28.3±11.8	82.8	17.2	33.9±15.8
IS	74.5	14.3	41.4±15.8	334.0	24.7	78.4±63.3
NH_4^+						
US	2488	<3.8	755.7±575.9	3812	58.8	947.1±945.3
SS	1747	166.3	653.4±445.8	3754	42.3	1084±905.0
IS	2495	3.8	889.3±688.5	5496	3.8	1564±1409
K^+						
US	1044	28.7	203.9±228.5	685.6	75.5	196.1±132.2
SS	198.3	53.5	113.2±45.5	1139	81.9	213.1±233.0
IS	4782.5	51.0	749.9±1136	1628	84.9	468.5±414.2
Na^+						
US	7564	341.4	1936±1585	9026	430.7	2466±2083
SS	2700	493.9	1333±631.6	4034	56.6	1415±1051
IS	32789	546.2	5277±7153	42755	560.5	8431±11419
Ca^{2+}						
US	1593	103.9	476.2±352.7	1036	166.5	481.9±244.7
SS	359.4	113.1	223.8±83.4	2251	77.9	335.5±458.5
IS	4908	300.6	1446±1295	5865	159.7	1511±1401
Mg^{2+}						
US	5583	54.0	723.2±1518	1003	64.7	339.1±232.0
SS	301.7	53.2	155.6±69.9	481.6	11.4	174.1±112.9
IS	14857	56.7	3323±5503	5098	75.5	953.5±1254
Cl^-						
US	15676	340.0	3679±4126	21478	541.2	5640±5056
SS	6839	47.3	2213±1937	12012	103.3	2497±2946
IS	22205	9.3	6113±6054	80015	630.9	12779±17540
SO_4^{2-}						
US	16133	2215	5813±3931	18238	1080	4850±3984
SS	13649	1469	4664±3561	13879	923.2	4220±3227
IS	23324	1322	7976±6094	20108	932.7	8782±4759

Table S2. *Cont.*

NO_3^-						
US	4192	205.7	1373±1162	7200	71.3	1899±1690
SS	3358	448.1	1029±717.2	5974	151.6	1736±1574
IS	6016	375.1	1983±1533	16303	223.2	3511±4146
Al[a]						
US	2.2	0.14	0.58±0.48	3.1	0.04	0.69±0.80
SS	0.72	0.05	0.27±0.23	0.51	0.03	0.20±0.14
IS	1.5	0.08	0.51±0.39	2.12	0.001	0.63±0.56
As						
US	1.2	0.17	0.59±0.25	2.0	0.15	0.81±0.58
SS	2.7	0.17	0.66±0.59	2.4	0.08	0.80±0.56
IS	2.6	0.19	1.1±0.71	4.4	0.35	1.8±1.2
Bi						
US	0.59	0.07	0.16±0.11	0.74	0.02	0.20±0.20
SS	0.25	0.02	0.07±0.07	0.41	0.003	0.08±0.08
IS	0.29	0.01	0.10±0.08	0.92	0.004	0.22±0.27
Cd						
US	0.44	0.06	0.15±0.09	1.4	0.05	0.32±0.29
SS	0.38	0.02	0.13±0.11	1.4	0.05	0.24±0.29
IS	0.85	0.01	0.16±0.19	0.84	0.05	0.24±0.18
Cr						
US	14.0	<0.12	4.3±3.0	16.3	<0.12	4.9±4.9
SS	5.1	<0.12	2.1±1.5	7.1	<0.12	2.0±2.3
IS	9.0	<0.12	3.8±2.7	38.9	<0.12	9.1±9.4
Cu						
US	58.8	5.6	26.7±12.4	98.1	9.1	37.7±25.2
SS	29.9	7.6	14.7±6.2	56.2	3.03	20.6±10.6
IS	61.0	7.6	31.6±12.7	87.2	1.1	36.6±23.3
Fe[a]						
US	1.6	0.16	0.61±0.37	2.1	0.10	0.79±0.67
SS	0.62	0.05	0.27±0.18	0.70	<0.01	0.23±0.16
IS	1.7	0.06	0.57±0.47	5.5	<0.01	1.5±1.5
Mn[a]						
US	0.03	<0.001	0.01±0.01	0.05	0.003	0.02±0.01
SS	0.03	0.003	0.01±0.008	0.03	<0.001	0.01±0.008
IS	0.05	0.002	0.022±0.02	0.15	0.003	0.05±0.04
Ni						
US	12.9	0.74	5.2±3.3	12.9	0.69	4.6±3.2
SS	8.0	<0.09	2.9±2.0	20.7	<0.09	4.3±4.7
IS	15.0	0.56	4.9±4.4	23.6	0.26	8.2±6.5
Pb						
US	27.3	2.4	8.2±6.1	30.2	0.93	12.1±8.1
SS	17.3	0.94	5.4±4.8	19.5	0.40	7.2±4.3
IS	13.6	0.47	5.7±4.5	24.9	0.52	8.4±6.2

Table S2. *Cont.*

Sb						
US	7.1	0.74	2.6±1.5	12.8	0.42	4.0±3.6
SS	1.6	0.25	0.73±0.41	3.5	0.06	1.0±0.71
IS	5.2	0.14	1.0±1.2	4.1	0.03	1.3±1.1
Si						
US	5.8	0.37	1.5±1.3	8.2	0.11	1.8±2.1
SS	1.9	0.13	0.71±0.62	1.4	0.09	0.53±0.38
IS	4.1	0.20	1.3±1.0	5.6	0.002	1.7±1.5
Sr						
US	14.4	1.6	4.7±2.8	8.2	2.1	5.1±2.0
SS	4.2	0.80	2.5±1.1	4.2	1.4	2.3±0.60
IS	11.5	1.7	5.0±2.5	23.9	2.1	6.5±4.7
V						
US	22.1	2.6	9.6±5.2	20.4	0.50	8.0±5.6
SS	19.4	2.2	6.4±4.4	16.3	0.52	6.3±4.4
IS	21.0	1.9	8.6±5.5	27.3	1.3	9.0±5.9
Zn						
US	100.2	7.3	25.0±20.5	108.7	12.02	48.8±28.2
SS	57.0	3.8	20.5±14.8	53.2	3.57	30.6±14.9
IS	71.6	7.9	30.0±17.8	137.3	12.7	54.8±32.7
eBC						
US	5629	1308	3304±1181	7482[b]	1631[b]	3396±1668[b]
SS	2468	353.8	1221±610.8	4423	109.2	1769±999.0
IS	2980	331.6	1443±738.4	5694[c]	175.3[c]	2082±1660[c]
UVPM						
US	3059[d]	1373[d]	2384±564.8[d]	2865[e]	1427[e]	2072±475.3[e]
SS	2637	477.9	1371±610.2	2984[f]	137.4[f]	1733±674.9[f]
IS	3170	455.7	1541±751.9	2553[g]	170.6[g]	1327±815.3[g]

[a]Results expressed as μg m^{-3}

[b]N=20, the concentration of two samples exceeds the maximum value for the measurement of the attenuation at 880 nm (filter too dark)

[c]N=20, the concentration of three samples exceeds the maximum value for the measurement of the attenuation at 880 nm (filter too dark)

[d]N=15, the concentration of seven samples exceeds the maximum value for the measurement of the attenuation at 370 nm (filter too dark)

[e]N=12, the concentration of 10 samples exceeds the maximum value for the measurement of the attenuation at 370 nm (filter too dark)

[f]N=18, the concentration of three samples exceeds the maximum value for the measurement of the attenuation at 370 nm (filter too dark)

[g]N=16, the concentration of seven samples exceeds the maximum value for the measurement of the attenuation at 370 nm (filter too dark)

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