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Supplement of

AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in five southern European cities

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Supplementary material

For each AIRUSE station, the following conclusions can be drawn on the chemical speciation:

- Barcelona urban background: PM10 is made up of OM+EC, SIA and mineral dust+sea salt in similar proportions reflecting a mix of high traffic density and regional pollution as main causes of the PM pollution in the city. In PM2.5 the mineral dust + sea salt contribution is reduced to 1/6 of the mass, the OM+EC contribution increases to around 2/3 with the remaining part being made by SIA, slightly reduced with respect to PM10 because 50% of nitrate has a coarse mode of occurrence.
- Athens suburban background: for PM10 the average composition is similar to that described for BCN, but with slightly higher mineral dust (25%) + sea salt (9%) contribution and much higher sulphate load (19%). This differentiation may arise from the higher African dust influence and the higher coal or S-rich heavy oil combustion emissions in this region of the EU or from the influence of Eastern/Southeastern European countries and Turkey. In PM2.5 the influence of ammonium sulphate is very large (sulphate alone is the 26% of the PM2.5 mass) indicating the high influence from coal combustion or other S-bearing fuels. The remaining PM2.5 mass is dominated by OM+EC (another 45%). Levels of SIA are slightly reduced with respect to PM10 because 85% of nitrate has a coarse mode of occurrence.
- Florence urban background: PM10 has a predominant OM component (52%), probably due to a high contribution from biomass burning from the domestic sector, 18% of SIA and around 15% of mineral dust (12%) and sea salt (3%). The dominant secondary origin of PM10 (56%) is partially favoured by the high emissions, with a relevant contribution from biomass burning, and the specific stagnant conditions and reduced boundary layer depths. The OM contribution is in even higher in PM2.5 (OM+EC, 69%) and the other contributions are relatively reduced with respect to PM10. Again 50% of the PM10 nitrate is not present in PM2.5 due to the occurrence of coarse nitrate.
- Milan urban background: PM10 is also dominated by OM (around 40%), but with a very high contribution of ammonium nitrate (22%) and relatively low mineral dust (10%) and sea salt (2%) contributions. The high concentrations of secondary components in PM10 (71%) are partially favoured by the high emissions and the specific stagnant conditions and reduced boundary layer depths induced by the typical meteorology of the Po Valley. The composition of PM2.5 is similar to PM10 but with higher loads of OM+EC (45%) and ammonium nitrate (23%), but reduced sea salt and mineral loads (1 and 4%). In this case most of the nitrate in PM10 is present in PM2.5 (94%) pointing to the predominance of fine ammonium nitrate over coarse nitrate as described in the other sites.
- Porto traffic site: OM+EC represents 37% of PM10 (14% EC), while SIA and dust are about 12-15% each and sea salt 13%. High proportion of sea salt, EC and OM are higher are due to the Atlantic location of Porto and to the higher influence of fuel (both fossil and biomass) combustion. In PM2.5 the composition is similar but with an increased proportion of OM+EC (29+19%) and reduced of mineral dust and sea

salt (8 and 5%). SIA levels are slightly reduced with respect to PM10 because 40% of nitrate has a coarse mode of occurrence.

Table S1: Summary of the number of samples collected for each city and analytical technique in colours.

			BCN-UB	FI-UB	MLN-UB	POR-TR	ATH-SUB
		Start date	01/01/2013	05/01/2013	15 /01/2013	05/01/2013	02/02/2013
		End date	31/12/2013	03/01/2014	14/01/2014	31/12/2013	30/01/2014
Daily samples	PM10	**Mass**	**113**	**222**	**370**	**123**	**193**
		Elements	113^{I}	222^{P}	$241^{P/X}$	$123^{P/I}$	$193^{P/I}$
		Ions	113	222	337	123	193
		EC/OC	113	222	348	123	193
		CC	113	222	89	123	193
	PM2.5	**Mass**	**117**	**239**	**369**	**126**	**239**
		Elements	117^{I}	239^{P}	361^{X}	$126^{P/I}$	$239^{P/I}$
		Ions	117	239	374	126	239
		EC/OC	117	239	370	126	239
		Levoglucosan	117	239	356	126	239

^{P}: PIXE, ^{I}: ICP, ^{X}: XRF

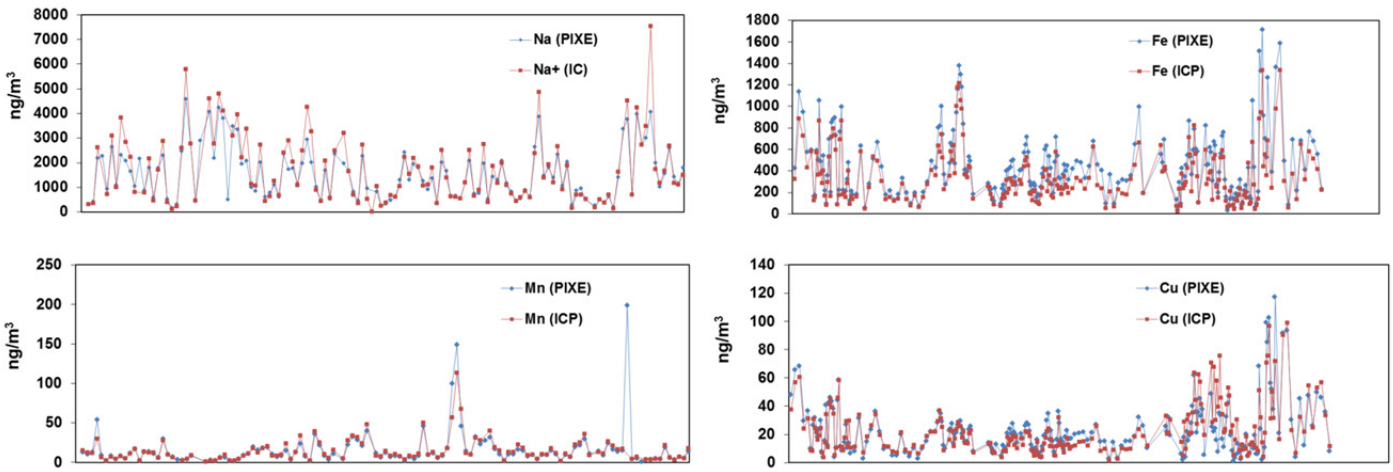


Figure S1. Comparison of results obtained with different analytical techniques in Porto (left panels) and Florence (right panels).

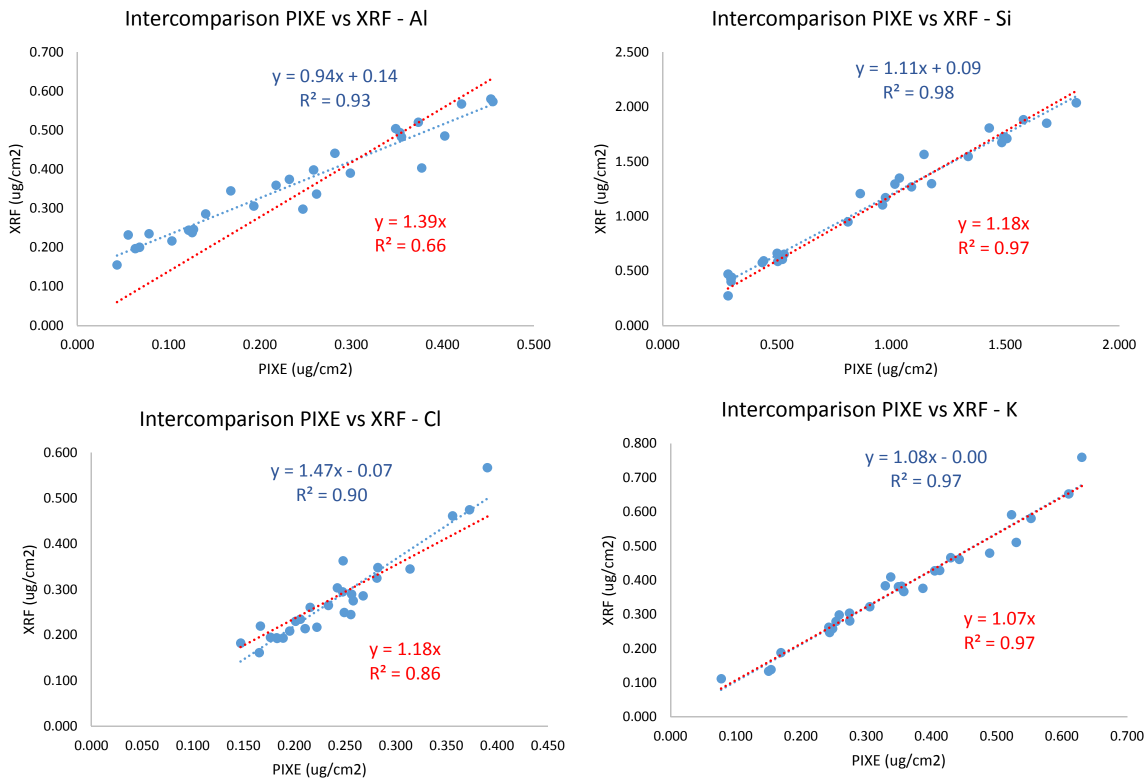
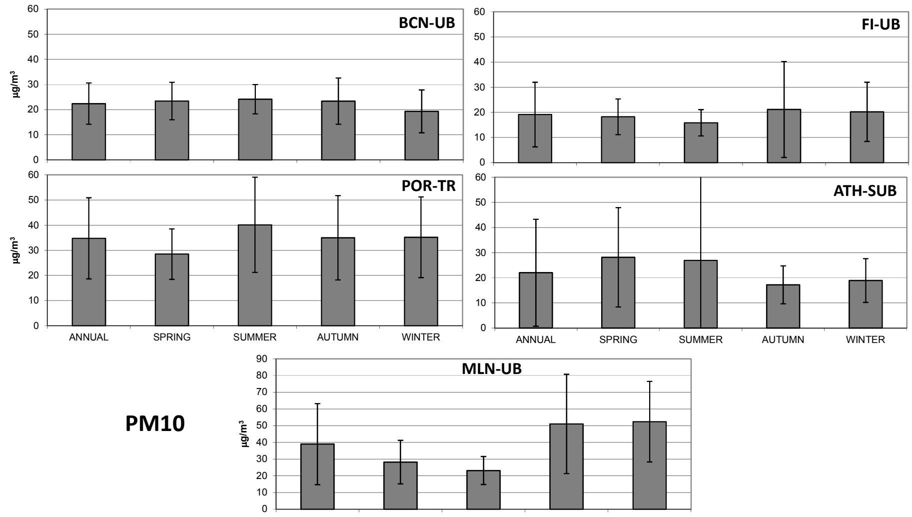


Figure S2. Comparison of results obtained with PIXE and XRF techniques in Milan for Al, Si, Cl and K. Red fits are constrained to the origin.



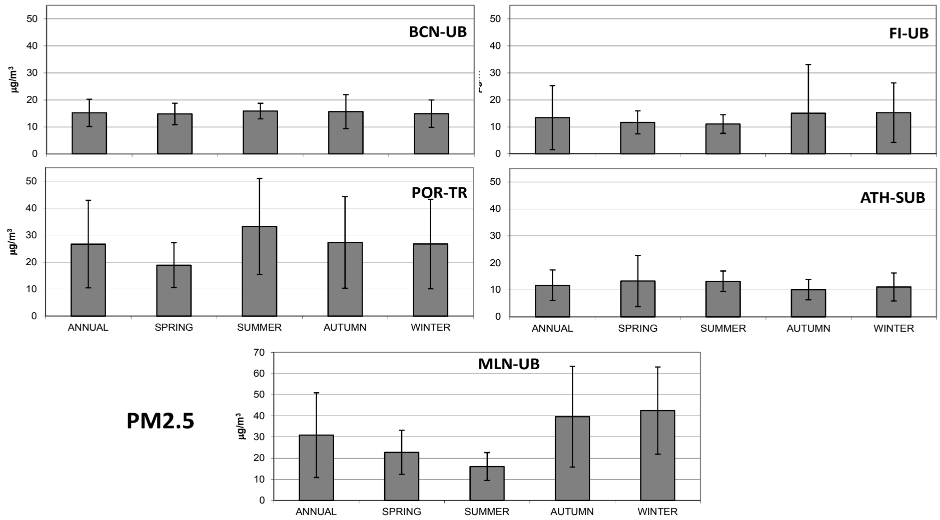


Figure S3. Seasonal variation of mean levels (± standard deviation) of PM10 and PM2.5 levels for the study period at the five AIRUSE cities.

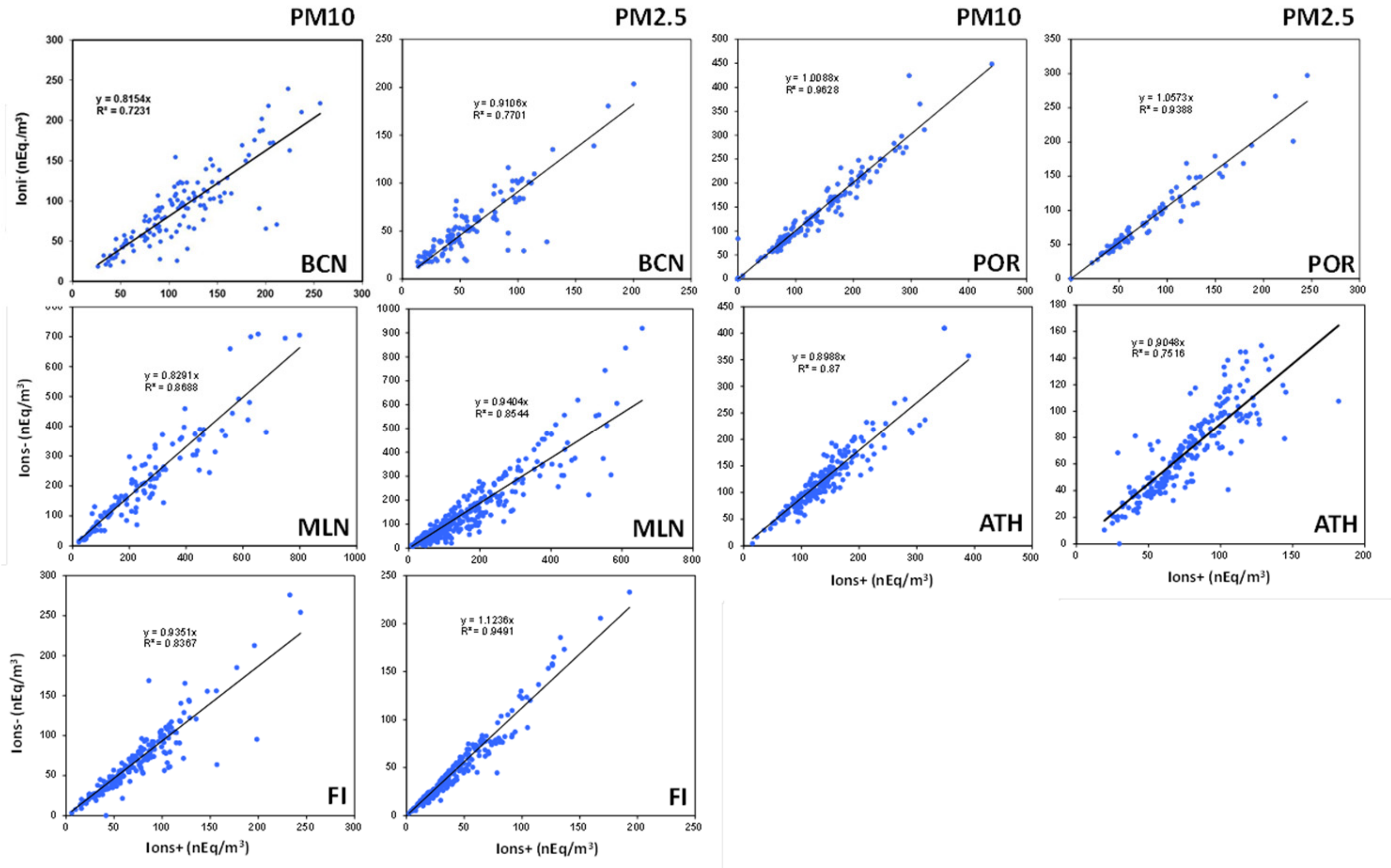
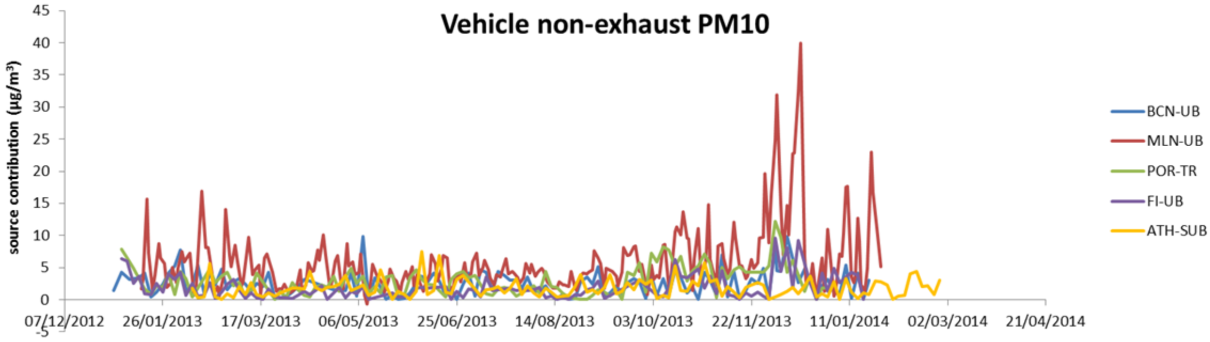
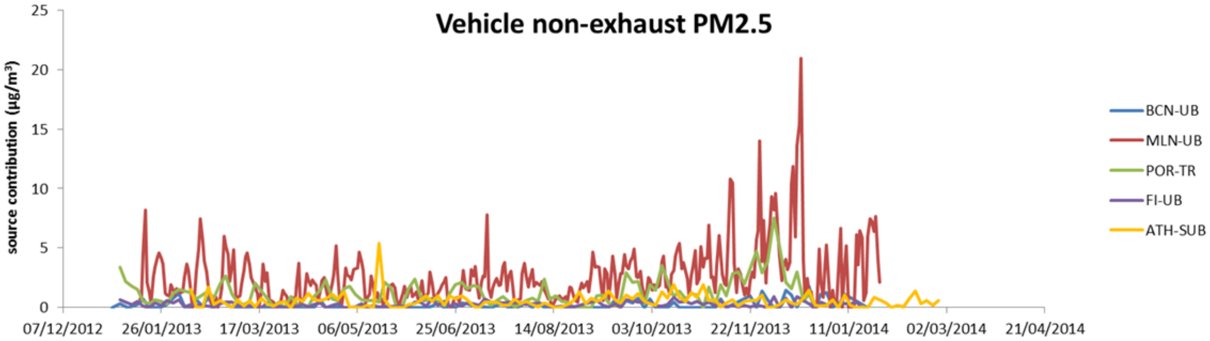
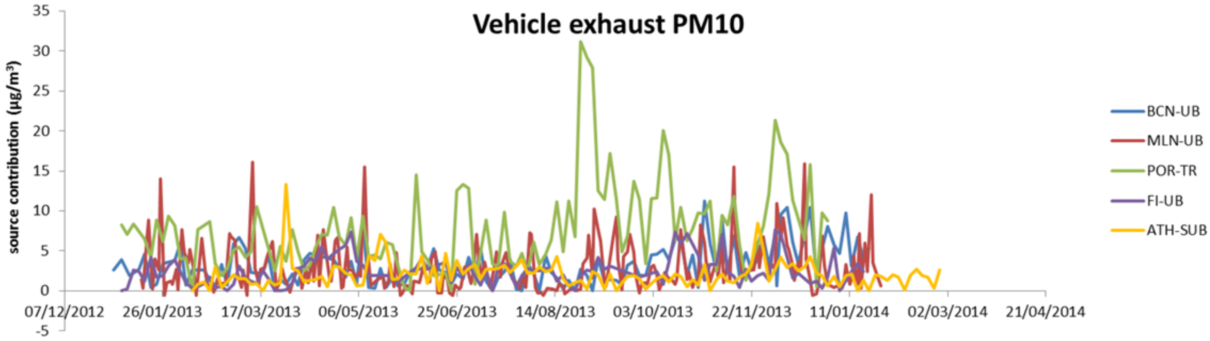
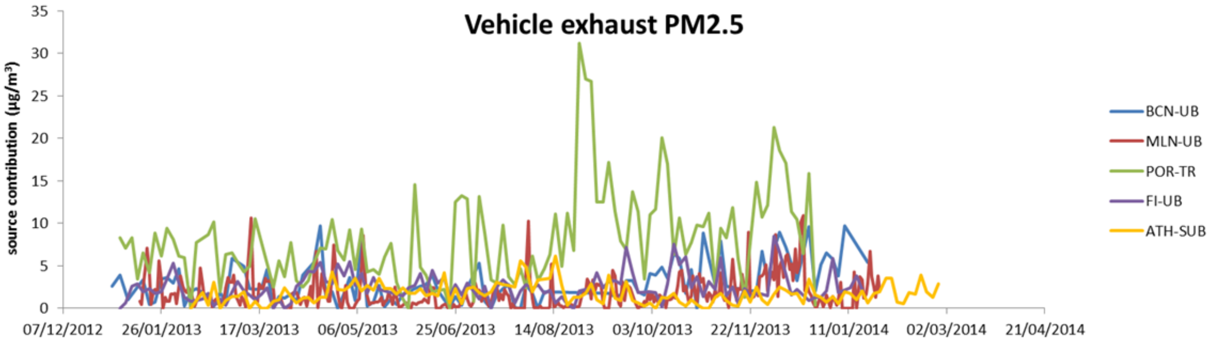


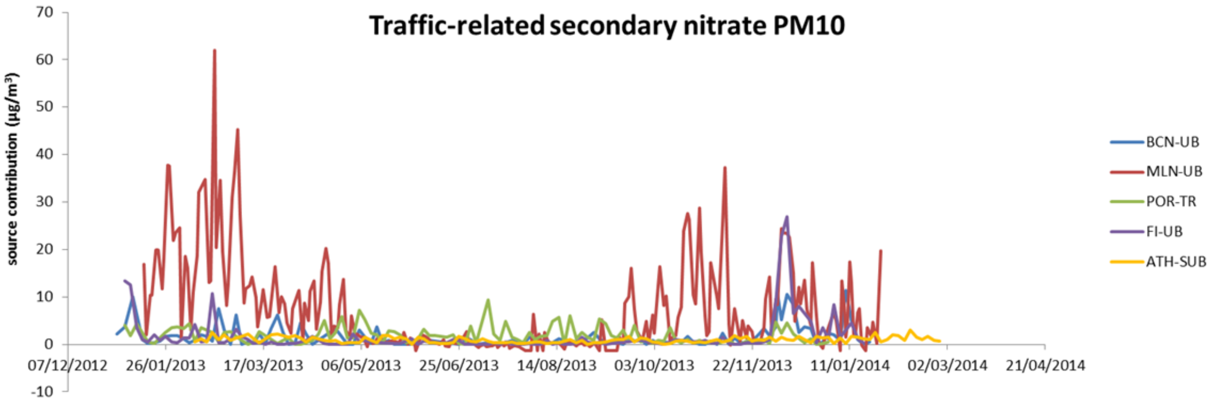
Figure S4. Ion balance of anionic (ions-: Cl^-, NO_3^- and SO_4^{2-}) and cationic (ions+: NH_4^+. Na^+, K^+, Ca^{2+}, Mg^{2+}) species in daily samples of PM10 and PM2.5 from the five AIRUSE cities.

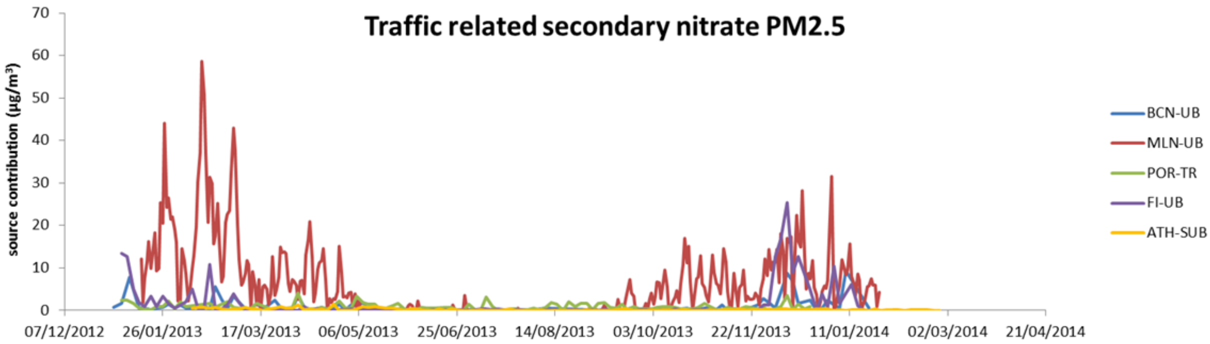

Vehicle non-exhaust PM10
source contribution (µg/m³)
45
40
35
30
25
20
15
10
5
0
-5
07/12/2012
26/01/2013
17/03/2013
06/05/2013
25/06/2013
14/08/2013
03/10/2013
22/11/2013
11/01/2014
02/03/2014
21/04/2014
BCN-UB
MLN-UB
POR-TR
FI-UB
ATH-SUB

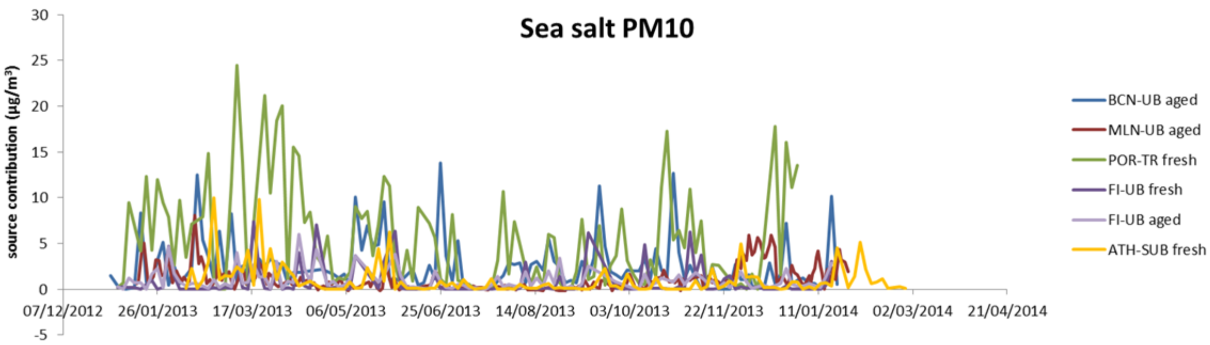

Vehicle non-exhaust PM2.5
source contribution (µg/m³)
25
20
15
10
5
0
07/12/2012
26/01/2013
17/03/2013
06/05/2013
25/06/2013
14/08/2013
03/10/2013
22/11/2013
11/01/2014
02/03/2014
21/04/2014
BCN-UB
MLN-UB
POR-TR
FI-UB
ATH-SUB

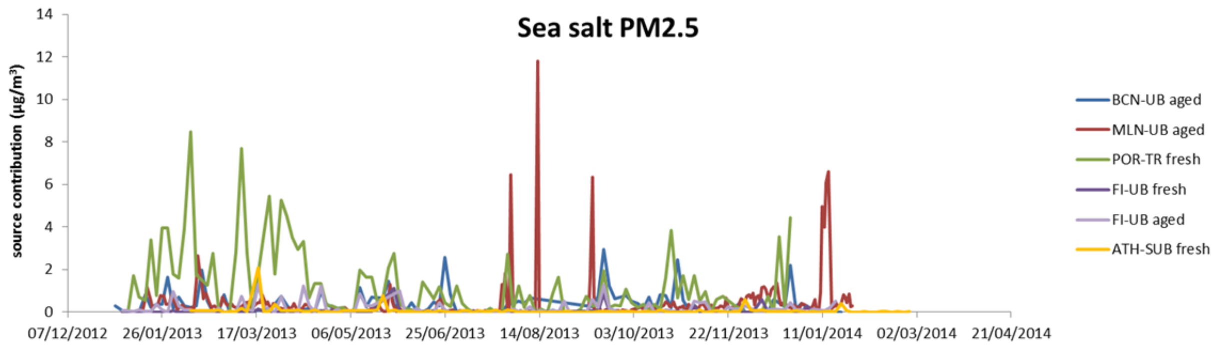

Vehicle exhaust PM10
source contribution (µg/m³)
35
30
25
20
15
10
5
0
-5
07/12/2012
26/01/2013
17/03/2013
06/05/2013
25/06/2013
14/08/2013
03/10/2013
22/11/2013
11/01/2014
02/03/2014
21/04/2014
BCN-UB
MLN-UB
POR-TR
FI-UB
ATH-SUB

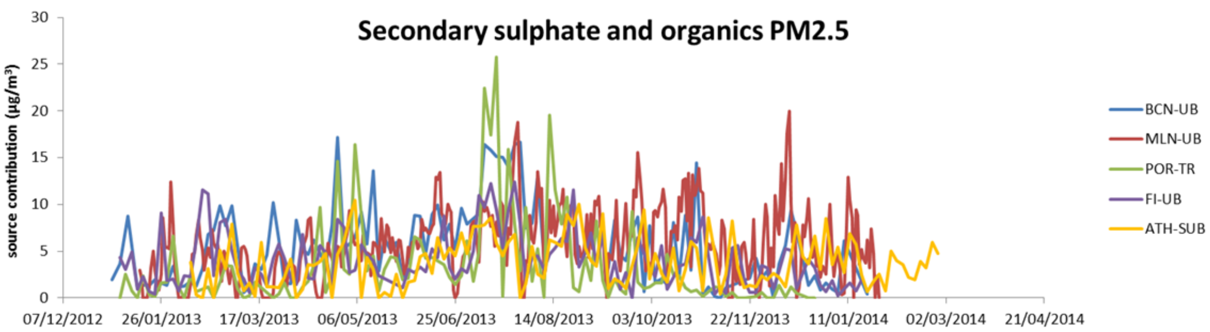

Vehicle exhaust PM2.5
source contribution (µg/m³)
35
30
25
20
15
10
5
0
07/12/2012
26/01/2013
17/03/2013
06/05/2013
25/06/2013
14/08/2013
03/10/2013
22/11/2013
11/01/2014
02/03/2014
21/04/2014
BCN-UB
MLN-UB
POR-TR
FI-UB
ATH-SUB


Traffic-related secondary nitrate PM10
source contribution (µg/m³)
BCN-UB
MLN-UB
POR-TR
FI-UB
ATH-SUB


Traffic related secondary nitrate PM2.5
source contribution (µg/m³)
BCN-UB
MLN-UB
POR-TR
FI-UB
ATH-SUB


Sea salt PM10
source contribution (µg/m³)
BCN-UB aged
MLN-UB aged
POR-TR fresh
FI-UB fresh
FI-UB aged
ATH-SUB fresh


Sea salt PM2.5
source contribution (µg/m³)
BCN-UB aged
MLN-UB aged
POR-TR fresh
FI-UB fresh
FI-UB aged
ATH-SUB fresh


Secondary sulphate and organics PM2.5
source contribution (µg/m³)
BCN-UB
MLN-UB
POR-TR
FI-UB
ATH-SUB

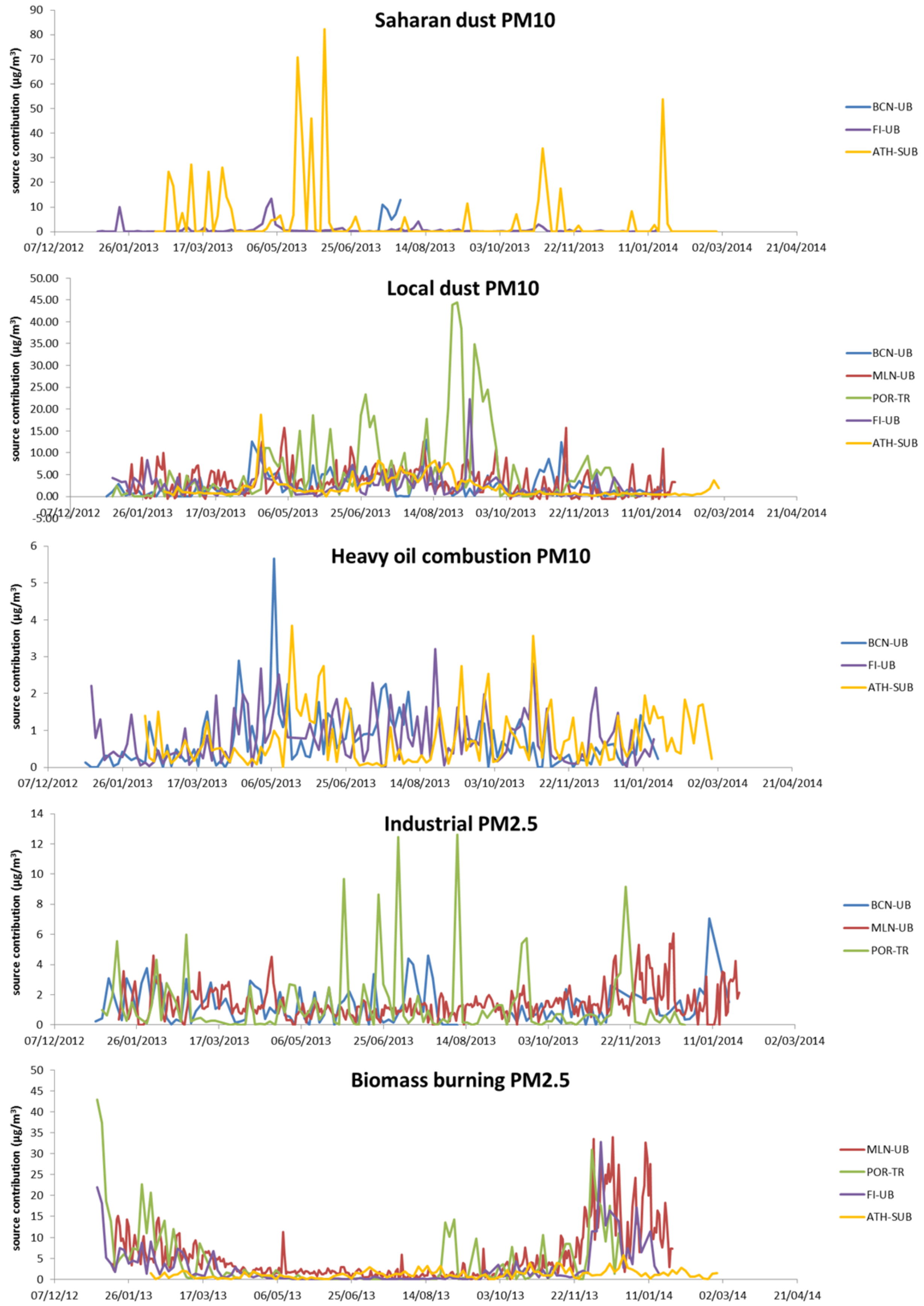


Figure S5. Daily source contributions to PM10 or PM2.5 levels for the study period at the five AIRUSE cities.

Table S2: Explained variation (%) of species in PM10 and PM2.5 (BCN-UB)

BCN-UB	Heavy oil combustion	Vehicle non-exhaust	Mineral	Industrial	Aged sea salt	Vehicle exhaust	Secondary nitrate	Secondary sulphate and organics
EC	5	3	0	0	0	58	3	26
OC	0	3	5	5	0	42	8	33
NH_4^+	0	0	0	0	0	0	34	44
Cl^-	0	2	1	10	70	4	2	0
NO_3^-	0	0	10	0	18	0	68	0
Al	0	29	62	0	0	0	0	7
Ca	0	36	51	2	3	0	3	0
Fe	2	32	23	9	5	14	4	4
K	0	11	25	7	8	22	13	10
Mg	0	14	35	1	35	5	0	7
Na	1	1	12	0	65	5	1	8
S	13	1	0	1	4	8	0	70
Li	3	20	46	7	4	4	3	11
Ti	1	33	48	3	0	0	0	14
V	69	0	10	0	0	0	4	17
Cr	9	18	8	22	6	23	7	5
Mn	5	12	20	36	3	11	4	1
Ni	58	5	3	7	3	2	7	10
Cu	5	33	4	22	8	16	6	1
Zn	13	4	7	71	1	0	3	0
Ga	8	17	35	22	0	1	0	14
As	9	4	5	29	2	17	8	22
Se	13	4	7	1	14	19	5	19
Rb	0	23	41	5	0	7	5	18
Sr	3	22	43	3	16	0	1	9
Cd	3	1	0	57	1	7	6	19
Sn	22	24	1	11	6	17	9	0
Sb	3	30	0	14	8	17	11	5
Ba	11	22	15	14	6	19	13	0
La	10	16	35	4	1	13	0	18
Ce	3	17	32	5	2	21	0	17
Pb	6	5	1	67	1	2	4	12

Table S3: Explained variation (%) of species in PM10 and PM2.5 (FI-UB)

FI-UB	Heavy oil combustion	Vehicle non-exhaust	Mineral	Fresh sea salt	Aged sea salt	Vehicle exhaust	Secondary nitrate	Secondary sulphate and organics	Saharan dust	Biomass burning
EC	8	15	0	0	0	36	3	0	0	30
OC	1	5	3	0	2	26	7	15	0	36
Levo	0	0	1	1	0	0	0	0	1	84
Na	1	3	1	29	56	2	0	5	2	0
Mg	0	7	22	14	28	0	0	6	20	0
Al	1	7	35	0	0	1	0	6	44	1
Si	3	9	45	1	0	0	0	8	34	1
S	2	3	3	0	5	0	0	76	2	6
Cl	0	1	0	89	0	0	5	0	0	4
K	2	1	8	1	2	13	9	11	7	38
Ca	2	10	69	2	2	0	0	7	6	0
Ti	4	10	41	1	0	1	2	6	33	0
Mn	0	28	33	0	3	9	4	13	7	1
Fe	3	52	19	0	6	0	4	3	12	0
Ni	40	6	8	1	3	8	4	11	1	12
Cu	5	65	10	0	6	1	6	0	3	0
Zn	0	25	7	0	4	15	12	17	0	12
As	0	7	7	0	3	19	4	21	1	11
Se	26	0	7	0	6	17	7	26	0	3
Br	9	0	0	3	12	33	1	16	0	19
Rb	0	31	18	0	3	0	5	7	12	13
Sr	0	0	35	5	4	13	0	12	11	2
NH_4^+	0	0	0	0	0	0	24	72	0	0
NO_3^-	0	0	6	0	22	0	66	0	0	2
V	97	0	0	0	0	0	0	0	3	0
Ba	5	45	10	0	4	7	1	1	6	3
Pb	11	0	0	0	2	19	7	10	0	20
Cr	3	36	9	0	7	14	0	9	3	8
Cd	4	3	5	0	4	8	18	13	0	16

Table S4: Explained variation (%) of species in PM10 and PM2.5 (ATH-SUB)

ATH-SUB	Heavy oil combustion	Secondary sulphate and organics	Vehicle non-exhaust	Biomass burning	Vehicle exhaust	Mineral	Secondary Nitrate	Sea salt
EC	22	0	13	15	27	0	11	0
OC	8	27	0	5	55	2	0	0
Na	0	6	0	0	0	0	52	35
Mg	0	1	2	0	0	44	24	19
Al	0	0	0	1	0	85	2	0
Si	0	1	1	1	0	86	1	0
Cl	0	0	1	0	0	0	0	87
K	2	17	3	12	7	31	15	3
Ca	0	0	20	0	4	53	4	4
Ti	2	5	0	1	3	77	0	1
Mn	0	7	18	5	4	53	3	0
Fe	2	1	25	1	2	53	3	0
Ni	27	10	36	1	0	6	2	1
Cu	8	1	58	0	8	3	10	0
Zn	0	16	40	26	0	4	0	0
Br	7	31	0	12	6	0	24	12
NH_4^+	4	79	10	4	0	0	0	0
NO_3^-	0	0	3	0	0	6	76	1
SO_4^{2-}	2	70	9	0	0	5	5	2
V	85	4	0	0	0	12	0	0
As	19	0	0	69	0	4	3	0
Sr	27	0	0	12	0	38	0	6
Cd	12	9	8	50	8	0	5	0
Sb	22	8	34	13	7	1	0	1
Pb	22	0	5	67	2	1	0	0

Table S5: Explained variation (%) of species in PM10 and PM2.5 (POR-TR)

POR-TR	Biomass burning	Secondary nitrate	Heavy oil and Secondary sulphate	Mineral	Sea salt	Industrial	Vehicle non-exhaust	Vehicle exhaust
EC	13	0	0	0	0	11	12	60
OC	29	4	9	4	0	8	0	38
levo	84	0	0	0	0	2	0	6
Na	0	5	3	4	78	3	3	3
Mg	0	8	3	19	59	0	3	0
Al	1	12	2	68	0	0	7	3
Si	1	14	2	70	0	1	9	2
S	3	4	58	5	9	4	0	13
Cl	9	0	2	0	82	0	0	0
K	17	6	5	31	7	3	3	24
Ca	0	15	0	50	13	2	15	1
Ti	1	12	3	64	0	2	12	2
V	2	8	56	4	9	2	0	7
Cr	1	13	0	23	3	9	45	1
Mn	0	8	0	32	1	19	21	5
Fe	0	16	0	32	3	4	41	0
Ni	5	3	42	4	6	10	0	11
Cu	1	14	0	12	4	6	47	7
Zn	0	6	0	7	2	70	14	0
Br	11	6	13	4	25	5	0	24
NH_4^+	13	16	50	0	0	0	1	0
NO_3^-	14	58	3	0	4	0	16	1
Li	1	0	7	62	5	3	7	16
As	11	0	6	9	2	9	16	41
Rb	14	0	5	51	1	3	7	17
Cd	12	0	8	0	0	37	28	14
Sn	8	0	4	0	1	2	63	0
Sb	6	2	3	5	2	3	53	0
Ba	0	4	2	28	2	0	61	0
La	0	1	10	54	10	3	9	16
Ce	1	3	4	48	3	3	13	20
Pb	11	0	7	0	0	34	23	3

Table S6: Explained variation (%) of species in PM10 and PM2.5 (MLN-UB)

MLN-UB	Vehicle exhaust	Vehicle non exhaust	Secondary nitrate	Heavy oil & secondary sulphate	Mineral dust	Indust rial	Aged sea salt	Biomass burning
EC	18	12	12	7	0	21	0	24
OC	5	17	11	9	5	14	4	13
Levo	0	7	0	0	0	0	0	88
Al	0	12	2	4	49	4	0	1
Si	1	27	0	6	60	0	0	0
S	0	0	3	67	0	24	0	0
Cl	0	0	0	0	0	20	67	0
K	1	0	7	1	23	9	0	44
Ca	1	23	3	0	44	4	2	0
Ti	2	25	3	3	53	3	1	2
V	0	0	0	79	1	32	0	0
Cr	11	31	0	11	2	15	0	5
Mn	14	24	7	2	17	3	4	4
Fe	3	50	2	2	8	4	1	4
Ni	8	21	0	23	4	23	0	3
Cu	5	42	7	0	4	21	0	0
Zn	46	12	8	3	4	0	5	2
Br	21	0	11	16	0	16	18	5
Rb	0	7	3	4	31	12	0	31
Ba	2	16	0	8	14	25	4	9
Pb	22	9	8	0	4	13	17	11
Sn	4	5	2	19	15	32	8	17
Na^+	0	12	19	0	0	0	35	0
NH_4^+	0	0	50	23	1	0	5	3
Mg^+	2	22	3	0	19	2	0	2
NO_3^-	2	1	60	1	1	0	5	7