European Aerosol Conference 2011 – 5-9 sep 2011 – Manchester, UK

$PM_{2.5}$, PM_1 and $PM_{0.4}$ acidity during spring and summer at one Po Valley site

G. Sangiorgi[1], L. Ferrero[1], M.G. Perrone[1] and E. Bolzacchini[1]

[1]POLARIS Research Centre, Department of Environmental Sciences, University of Milan - Bicocca, Milan, I-20126, Italy

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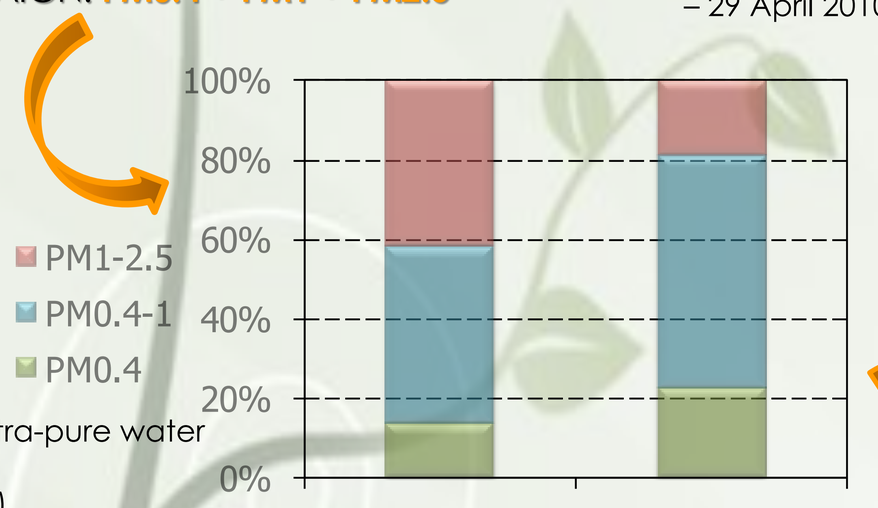
✓ SAMPLING SITE: **SANNAZARO DE' BURGONDI** (PAVIA) typical rural site in the middle of the Po Valley, Italy

✓ SAMPLING CAMPAIGN: **PM0.4 + PM1 + PM2.5**

SPRING: 10 June – 2 July 2010

SUMMER: 24 March – 29 April 2010



✓ ANALYSIS

PTFE filters extracted in ultra-pure water by ultrasonic bath and analyzed by IC (Dionex®)

water soluble inorganic ions

Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}

mono-/dicarboxylic acids

acetic, propionic, formic, glutarric, succinic, malonic, maleic, oxalic acids

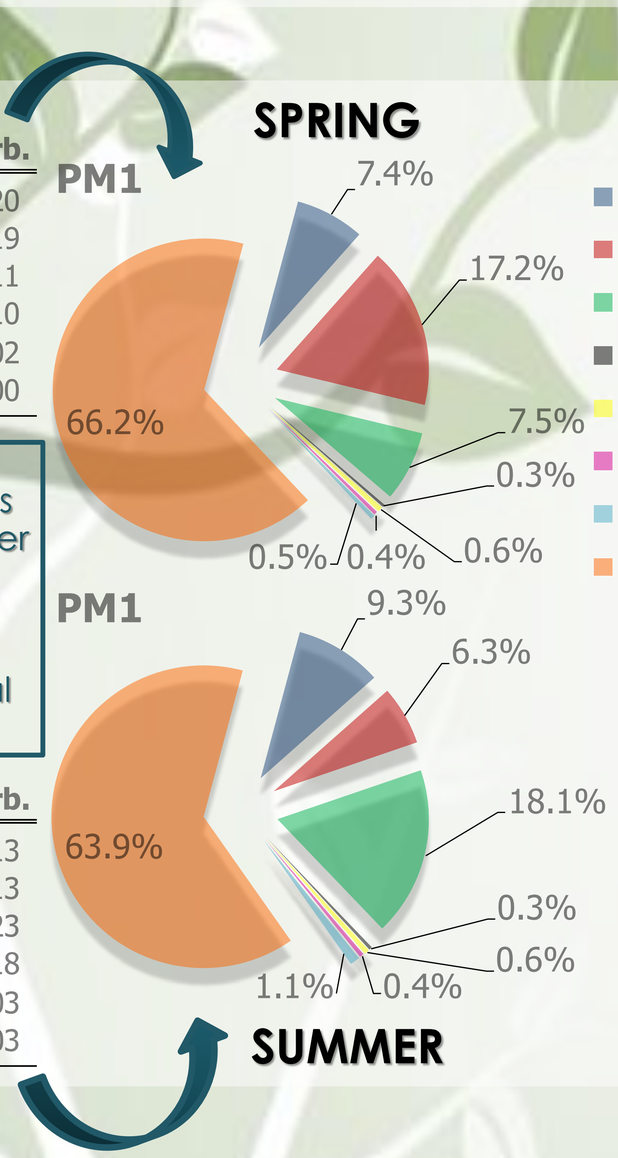
µg/m³		SPRING PM2.5	SPRING PM1	SPRING PM0.4	SUMMER PM2.5	SUMMER PM1	SUMMER PM0.4
MEAN		21	12	3	13	12	5
DEV.ST.		14	8	1	8	7	1
MIN		3	3	2	2	1	3
MAX		59	32	4	49	26	7

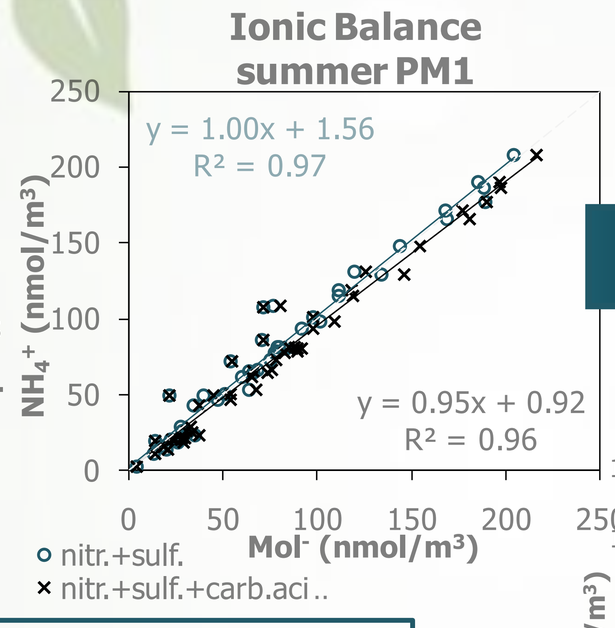
High daily variations of PMx concentrations, low seasonal variation of average PMx concentrations. General low PM2.5 concentrations, typical of a rural site of the Po Valley.

µg/m³		NH_4^+	NO_3^-	SO_4^{2-}	Carb.
MEAN	PM2.5	2.02	5.75	1.24	0.20
DEV.ST.	PM2.5	2.01	5.75	1.32	0.19
MEAN	PM1	1.17	2.94	0.99	0.11
DEV.ST.	PM1	1.10	3.18	0.84	0.10
MEAN	PM0.4	0.07	0.14	0.14	0.02
DEV.ST.	PM0.4	0.04	0.05	0.08	0.00

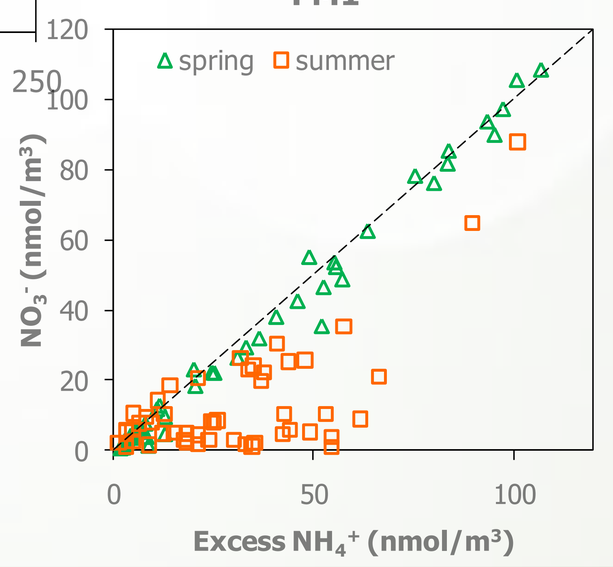
Seasonality of the ions of secondary origin: NO_3^- decreases dramatically from spring to summer (**volatility of NH_4NO_3**), SO_4^{2-} and carboxylic acids increases (**photoreactivity of gaseous precursors**). Very typical trend for the Po Valley.

µg/m³		NH_4^+	NO_3^-	SO_4^{2-}	Carb.
MEAN	PM2.5	0.86	0.88	2.04	0.13
DEV.ST.	PM2.5	0.88	1.76	1.62	0.13
MEAN	PM1	1.37	0.80	2.95	0.23
DEV.ST.	PM1	0.97	0.99	2.34	0.18
MEAN	PM0.4	0.32	0.12	0.87	0.03
DEV.ST.	PM0.4	0.17	0.08	0.48	0.03





Very similar pattern of ionic balance for both the seasons and all the PMx: R^2 very high (**$R^2 \geq 0.96$**); slope very close to 1 (**slope ≥ 0.85**) and slightly lower by adding carboxylic acids as negative ions.

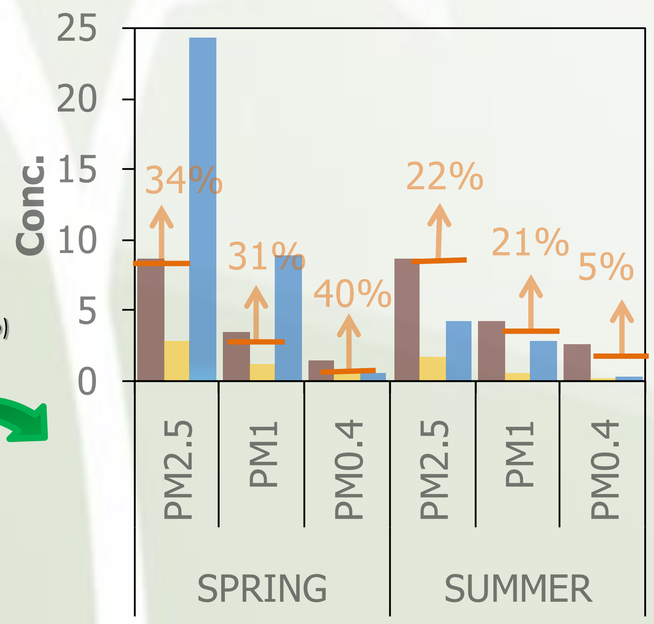


SPRING: the excess NH_4^+ neutralizes NO_3^-.
SUMMER: NO_3^- is too low concentrated to explain excess NH_4^+. Likely, NH_4^+ is present in PM to neutralize organic acids.
The same trends were result for all the PMx

Aerosol Inorganic Model (E-AIM):

It is a state-of-the-art aerosol **thermodynamic model** that can simulate free acidity (free H^+), aerosol water content, and activities of ionic species in aqueous aerosols and the solid- and liquid-phase compositions

(Clegg et al., 1998; http://www.aim.env.uea.ac.uk/aim/aim.php)



	SPRING T (°C)	SPRING RH %	SUMMER T (°C)	SUMMER RH %
PM2.5	12±5	72±19	21±5	72±17
PM1	12±4	72±18	23±5	69±15
PM0.4	12±1	77±9	26±1	61±3

All the samples of PMx in spring and summer are **AMMONIUM RICH** ($NH_4^+/SO_4^{2-}>1.5$).

Low levels of **total H^+** and **free H^+** (< 10 nmol/m³ on average).

Free H^+ and **H_2O** average concentrations decrease in summer.

Lower % of **free H^+-to-tot H+** in summer (~20%) than in spring (30%).

✓ **Total H^+**: total amount of H^+ contributed by the strong acids, such as sulfuric and nitric acids, in the aqueous extract of the aerosols.

► **$H^+tot=2\times[SO_4^{2-}]+[NO_3^-]-[NH_4^+]$**

✓ **Free H^+**: moles of free hydrogen ions in the aqueous phase of aerosols per unit of air (nmol/m³).

► **H+free = output of E-AIM model-II**

CONCLUSION

Seasonality trend of inorganic ions and carboxylic acids in a rural site of Po Valley was showed.

The **ionic balance** was very close to **neutrality** (all the samples were ammonium rich and tot H^+ and free H^+ concentrations were very low).

In **summer** there was a higher level of **excess NH_4^+** and **carboxylic acids**. Even if the tot H^+ concentration was higher, the free H^+ was lower.

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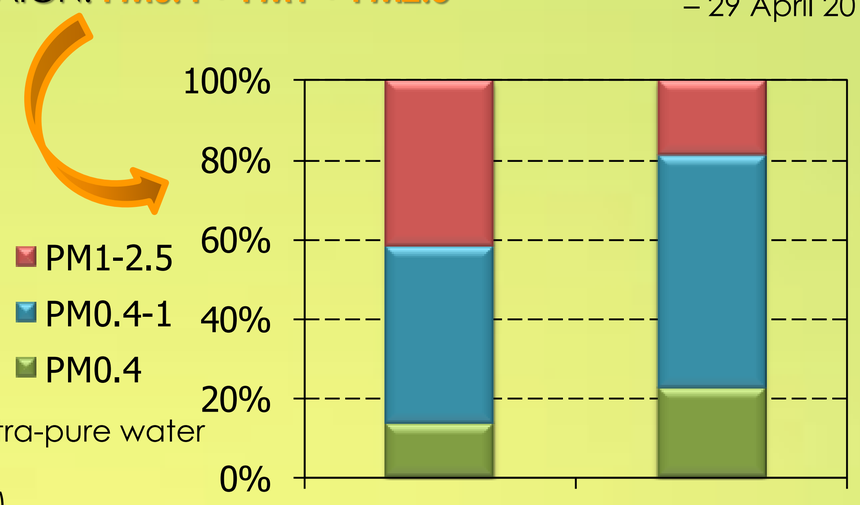

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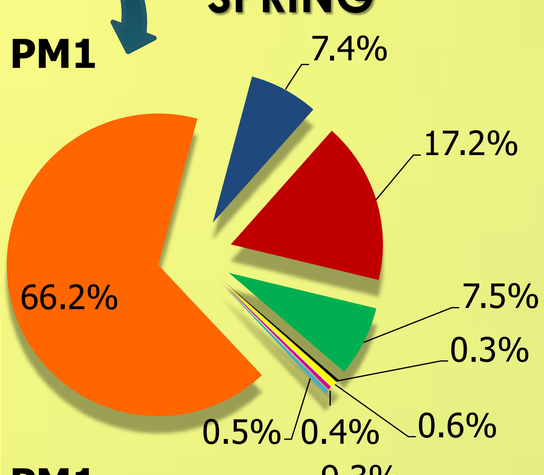
SPRING

PM1



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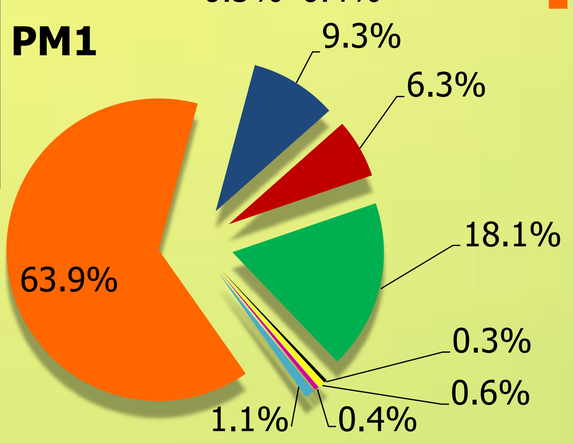
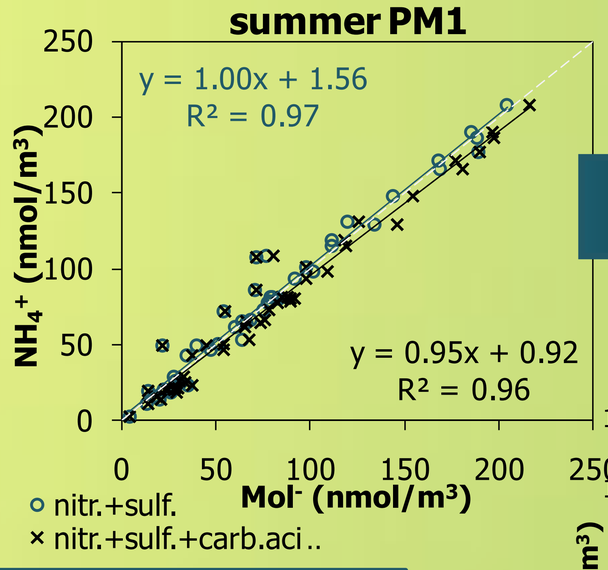


SUMMER

Ionic Balance summer PM1



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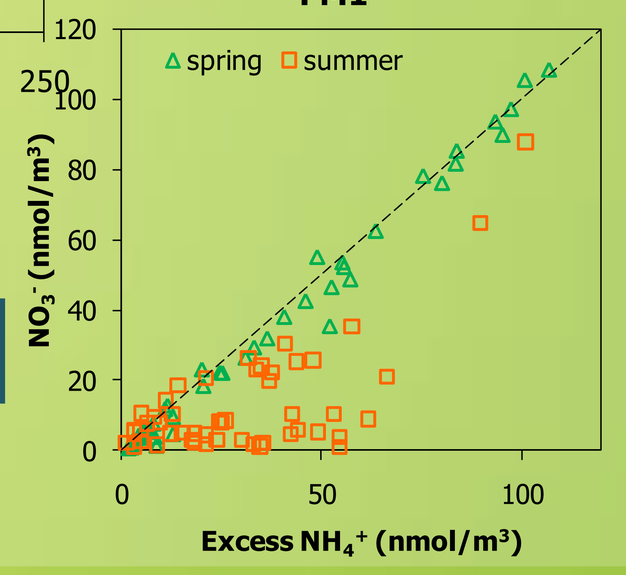

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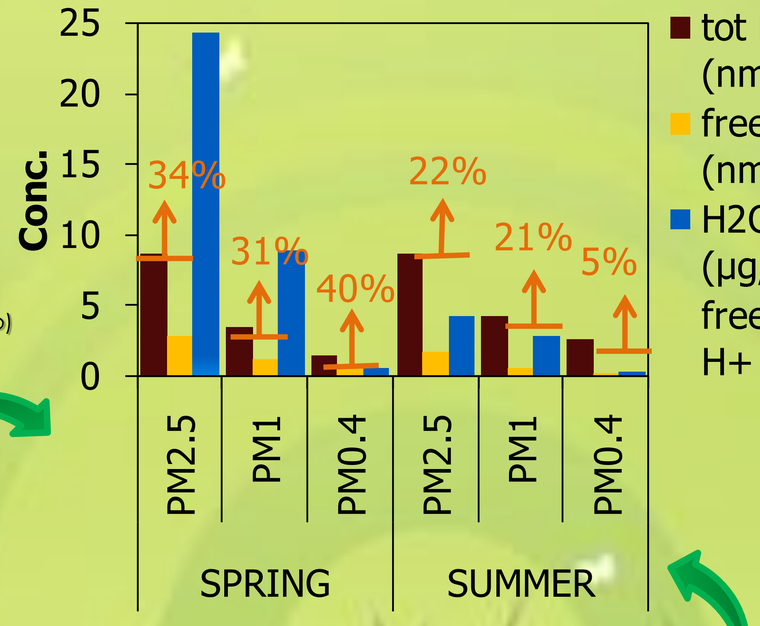

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