Air Quality and impact of road salting

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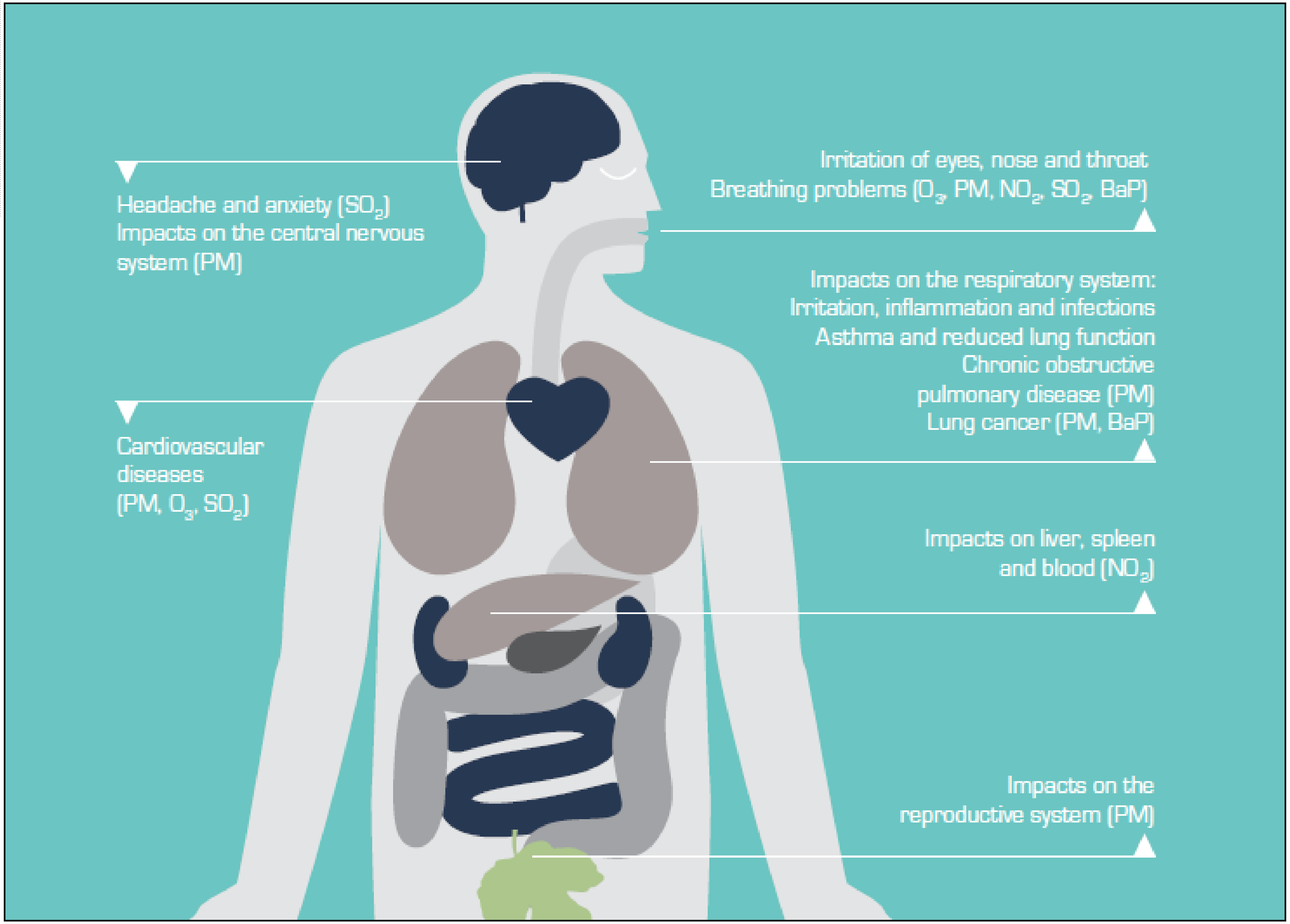
Spanish Research Council (CSIC)

CLEAN ROADS, Trento, 6 Febbraio 2015

Outline

- **Air Quality**
- **Legislation**
- **Impact of road salting**
  - **Methods and results**
  - **Alternatives**
- **The AIRUSE LIFE project**

Air Quality: impact on health



Source: EEA, 2013f.

430,000 premature deaths in EU are attributed to air pollution (WHO, 2013)

Legislation

Policies \ Pollutants		PM	O_3	NO_2 NO_x NH_3	SO_2 SO_x S	CO	Heavy metals	BaP PAH	VOCs
Directives regulating ambient air quality	2008/50/EC	PM	O_3	NO_2	SO_2	CO	Pb		C_6H_6
	2004/107/EC						As, Cd, Hg, Ni	BaP	
Directives regulating emissions of air pollutants	2001/81/EC **IPPC**	([a])	([b])	NO_x, NH_3	SO_2				NMVOC
	2010/75/EU **NEC**	PM	([b])	NO_x, NH_3	SO_2	CO	Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V		VOC
	Euro standards on road vehicle emissions **EUROx**	PM	([b])	NO_x		CO			HC (hydrocarbons), NMHC (non-methane hydrocarbons)
	94/63/EC	([a])	([b])						VOC
	2009/126/EC	([a])	([b])						VOC
	1999/13/EC	([a])	([b])						VOC
	91/676/EEC			NH_3					
Directives regulating fuel quality	1999/32/EC	([a])			S				
	2003/17/EC	([a])	([b])		S		Pb	PAH	C_6H_6, HC (hydrocarbons), VOCs
International conventions	MARPOL 73/78	PM	([b])	NO_x	SO_x				VOC
	LRTAP	PM ([a])	([b])	NO_2, NH_3	SO_2	CO	Cd, Hg, Pb	BaP	NMVOC

Air Quality standards

Contaminante	Valor límite/objetivo /Umbral de Alerta	Concentración	Nº superaciones máximas	Año de aplicación
PM_{10}	Media anual Media diaria	40 µg/m^3 50 µg/m^3	>35 días/año	2005
$PM_{2,5}$	Media anual	25 µg/m^3		2010 (objetivo) 2015 (límite)
SO_2	Media diaria Media horaria Umbral de alerta (3 horas consecutivas en área representativa de 100 km o zona o aglomeración entera)	125 µg/m^3 350 µg/m^3 500 µg/m^3	>3 días/año >24 horas/año	2005
NO_2	Media anual Media horaria Umbral de alerta (3 horas consecutivas en área representativa de 100 km o zona o aglomeración entera)	40 µg/m^3 200 µg/m^3 400 µg/m^3	>18 horas/año	2010
Pb	Media anual	0,5 µg/m^3		2005
CO	Media máxima octohoraria diaria	10 mg/m^3		2005
C_6H_6	Media anual	5 µg/m^3		2010
O_3	Media máxima octohoraria diaria Umbral de información Umbral de alerta	120 µg/m^3 180 µg/m^3 240 µg/m^3	>25 días/año	2010 En vigor En vigor
As	Media anual	6 ng/m^3		2013
Cd	Media anual	5 ng/m^3		2013
Ni	Media anual	20 ng/m^3		2013
B(a)p	Media anual	1 ng/m^3		2013

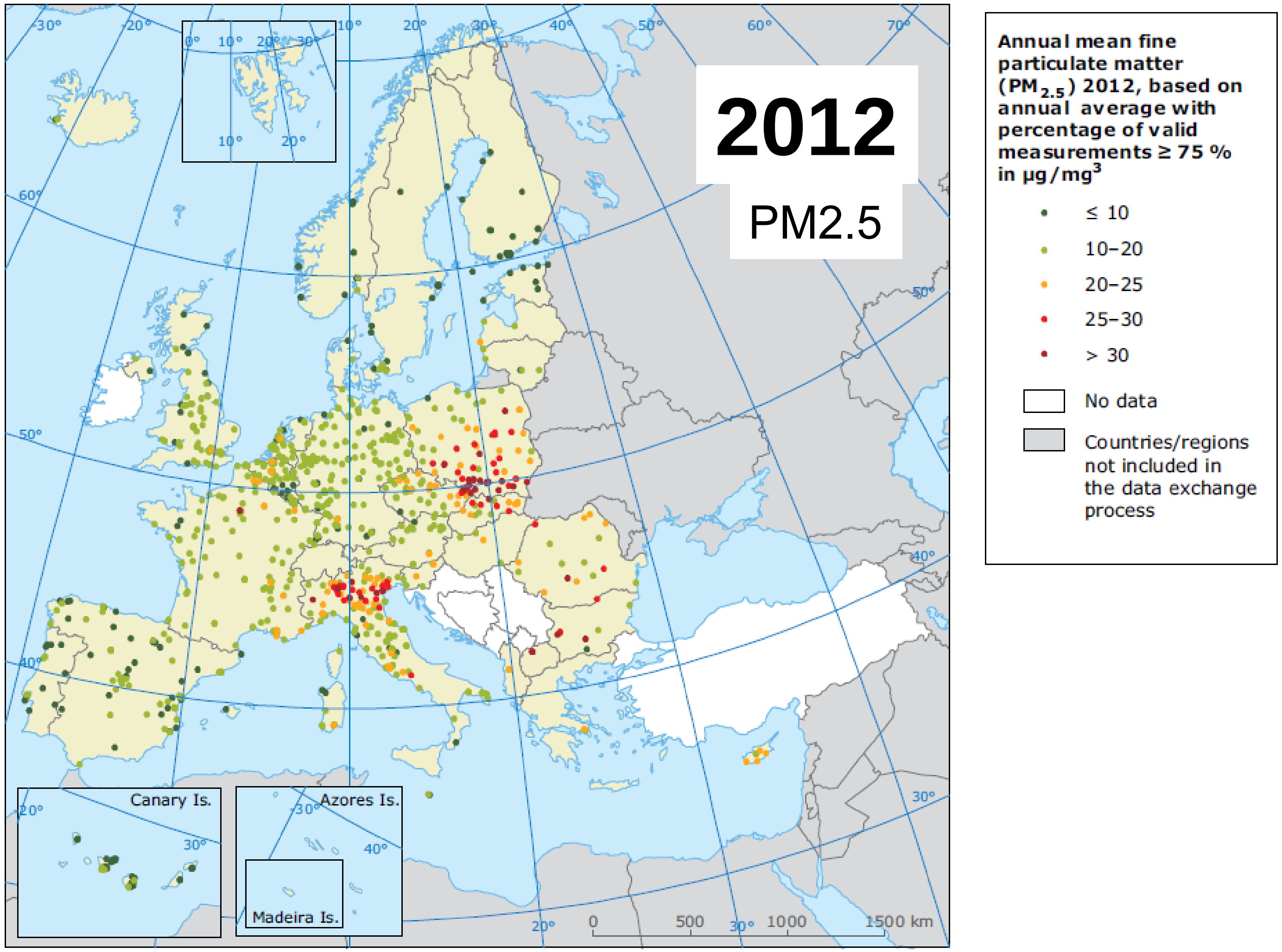
WHO guidelines

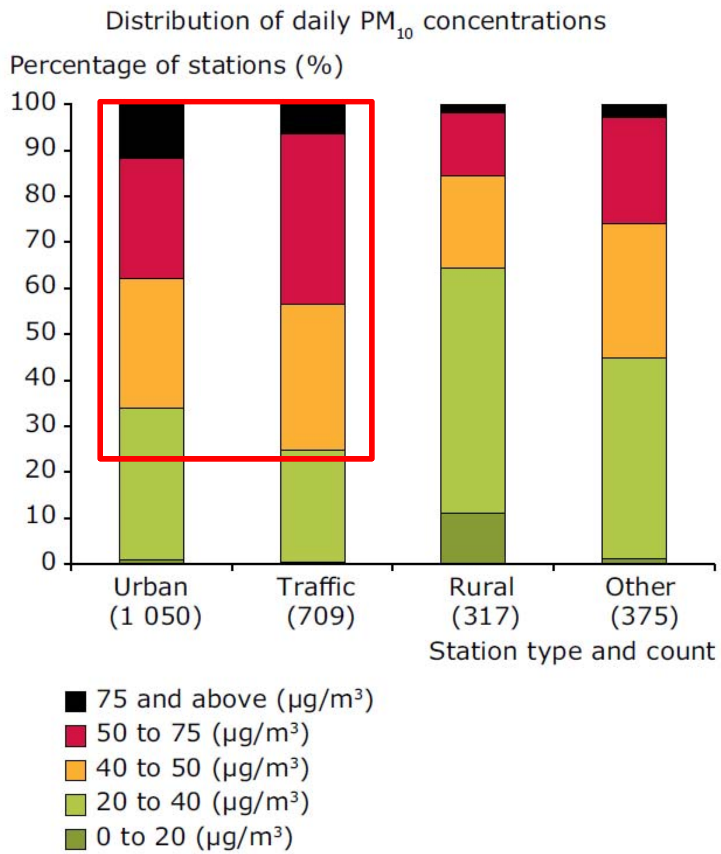
Table ES.1 Percentage of the urban population in the EU-28 exposed to air pollutant concentrations above EU and WHO reference levels (2010–2012)

Pollutant	EU reference value	Exposure estimate (%)	WHO AQG	Exposure estimate (%)
$PM_{2.5}$	Year (25)	10–14	Year (10)	91–93
PM_{10}	Day (50)	21–30	Year (20)	64–83
O_3	8-hour (120)	14–17	8-hour (100)	95–98
BaP	Year (1 ng/m^3)	24–28	Year (0.12 ng/m^3)	85–89
NO_2	Year (40)	8–13	Year (40)	8–13
SO_2	Day (125)	< 1	Day (20)	36–43
CO	8-hour (10)	< 2	8-hour (10)	< 2
Pb	Year (0.5)	< 1	Year (0.5)	< 1
Benzene	Year (5)	< 1	Year (1.7)	10–12

EEA, 2014

Particulate matter: attainment





European Environment Agency

October 2013

Air Quality in Europe- 2013 report

Particulate matter: formation

Origin

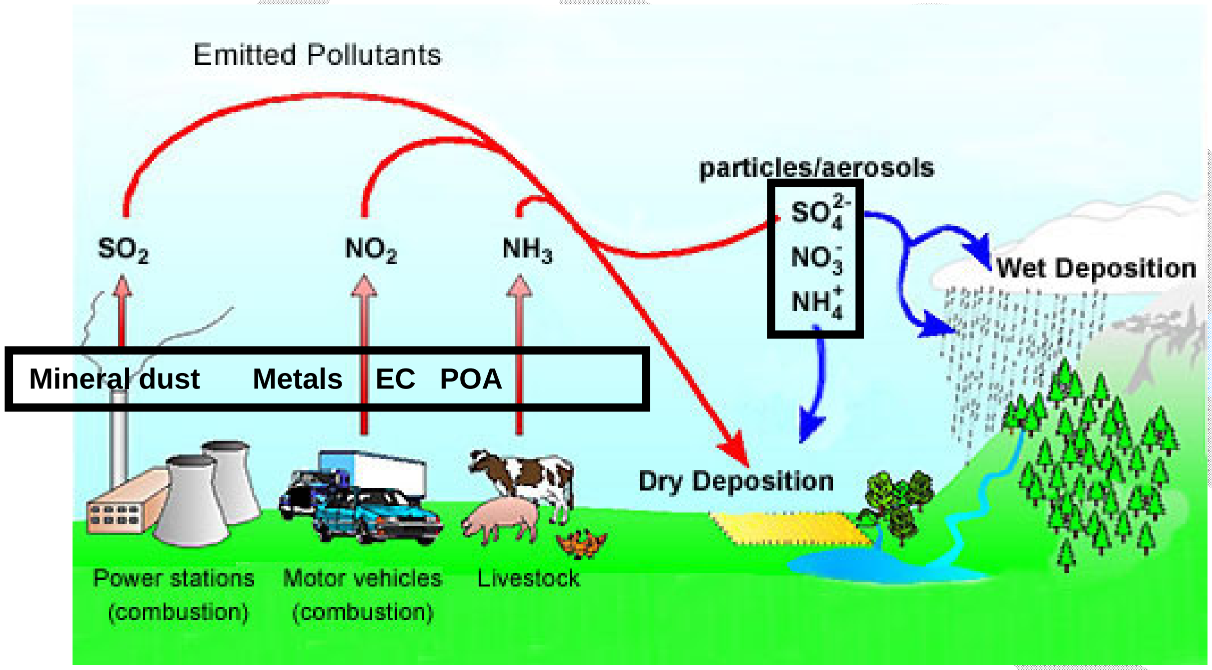
•Natural

•Anthropogenic

Formation mechanism

•Primary: direct emissions

•Secondary: formation in atmosphere from gas precursors



Particulate matter: composition

Mineral Matter:

Al_2O_3, Mg,
Ti, Fe, K, SiO_2
CO_3^{2-}, P, Ca,

Marine Aerosol:

Cl^-, Na^+,
SO_4^{2-},
DMS

Trace Elements:

As, Ba, Bi, Cd, Ce, Co, Cr, Cs,
Cu, Dy, Er, Ga, Gd, Ge, Hf, La,
Li, Mn, Mo, Nd, Ni, Pb, Pr, Rb,
Sb, Sc, Se, Sm, Sn, Sr, Ta, Th,
Ti, Tl, U, V, W, Yb, Zn, Zr

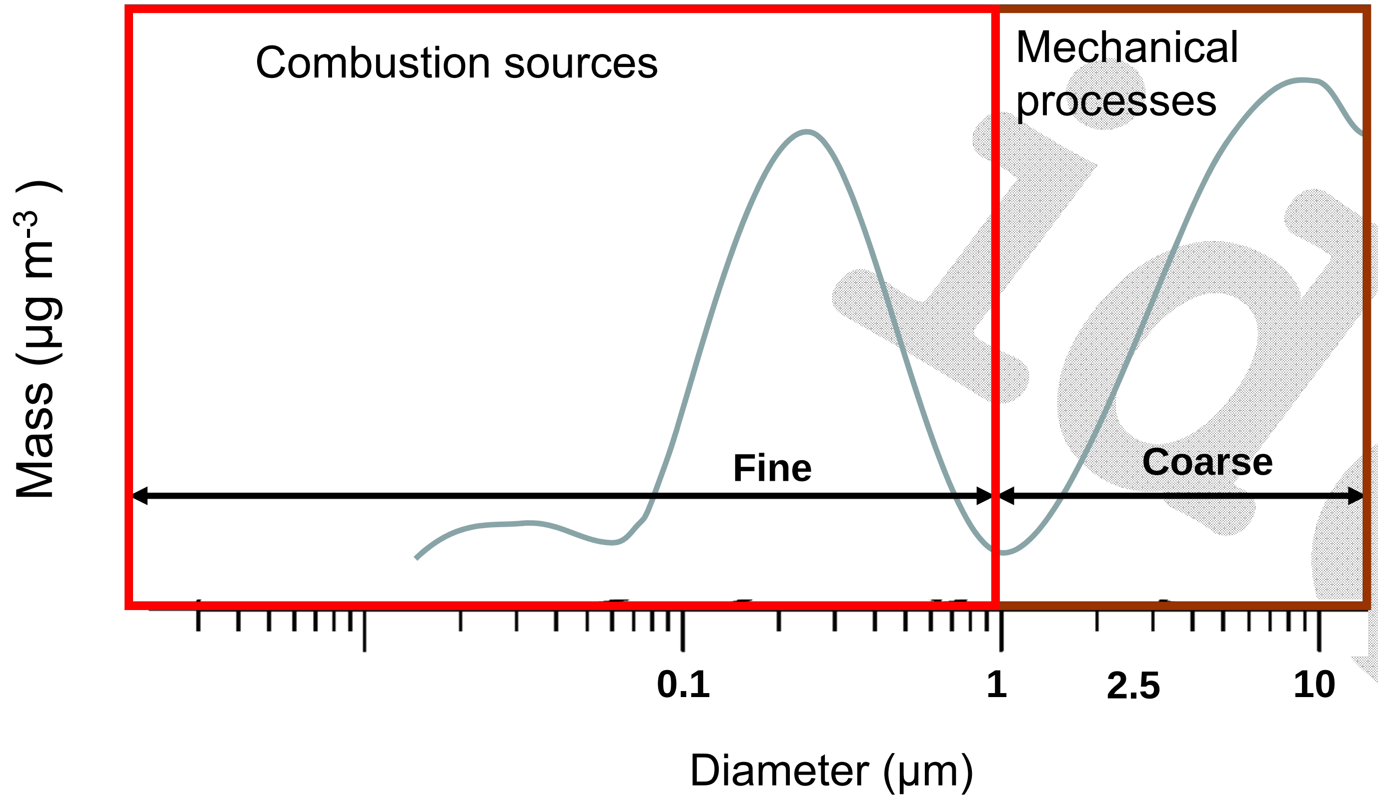
Carbonaceous compounds:

Organic Matter +
Elemental Carbon

Secondary Inorganic Aerosol:

$SO_4^{2-}NO_3^-$
NH_4^+

Particulate matter: size



Coarse:

Mechanical /evaporation processes

Primary

Fine:

Combustion processes

Primary & secondary

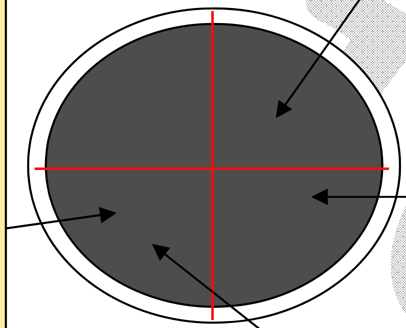
Sample characterization of daily PM_{10} filters

Crustal-mineral

Al_2O_3	ICP-AES
Ca	ICP-AES
K	ICP-AES
Mg	ICP-AES
Fe	ICP-AES
Ti	ICP-AES
P	ICP-AES
CO_3^{2-}	ind. from Ca
SiO_2	ind. from Al_2O_3

Sea salt

Na^+	ICP-AES
Cl^-	Ion Cromat.



Carbonaceous compounds

Organic Carbon (OC)
Elemental carbon (EC)
thermal-optical (Sunset)

Secondary inorganics

NH_4^+	specific electrode
SO_4^{2-}	Ion Cromat.
NO_3^-	Ion Cromat.

40 trace elements (ICP-MS)

As, Ba, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Ga, Gd, Ge, Hf, La, Li, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Yb, Zn, Zr

Determining:
80% of PM mass

Source apportionment

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{jk} + e_{ij} \qquad i=1,2,\ldots,m \quad j=1,2,\ldots,n$$

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \frac{\left(x_{ij} - \sum_{k=1}^{p} g_{ik} f_{jk} \right)^2}{\sigma_{ij}^2}$$

Factor analysis techniques (PCA, PMF)

No information about rces is needed

Difficult to distinguish be e si ilar sources

Chemical Mass Balance (CMB, COPREM)

Resolving higher n ber of sources

All emissio profi must be known

Hybrid model

by means of the **Multilinear Engine** scripting language

Multilinear Engine (ME-2)

Differences with customary PMF

- A priori and partial information about sources can be implemented (source fingerprints, emission profiles, physical constraints..)
- Does not solve only well-defined tasks, but any action defined in the script file
- Different algorithm and non-negativity constraints

$$Q_{enh} = Q + Q_{aux}$$

1st step of ME-2

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \frac{\left(x_{ij} - \sum_{k=1}^{p} g_{ik} f_{jk} \right)^2}{\sigma_{ij}^2}$$

Base solution (equivalent to standard PMF)

2nd step of ME-2

$$Q_{aux} = \frac{\left(f_{jk} - a_{jk} \right)^2}{\sigma_{jk}^{aux\,2}}$$

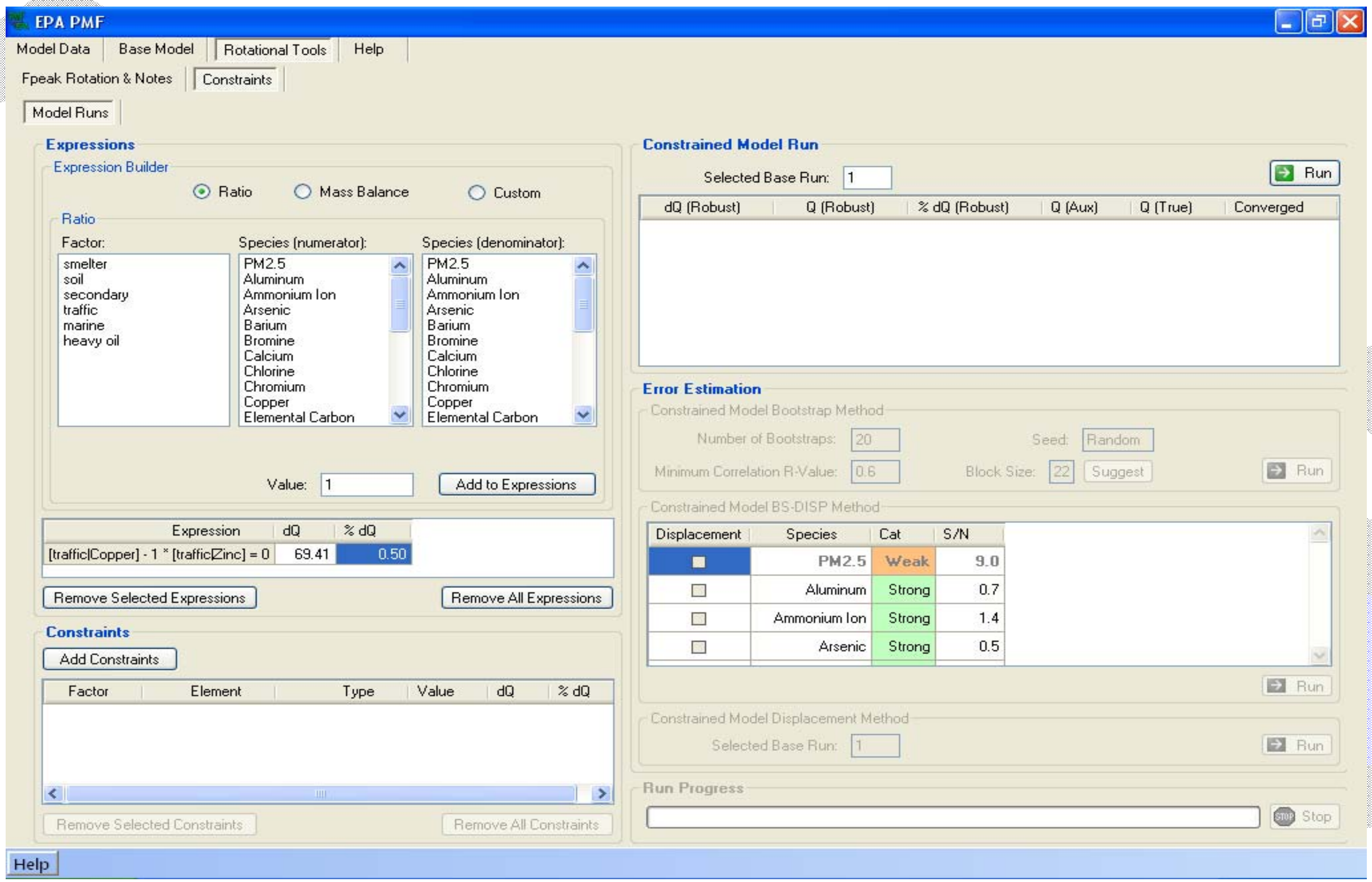
Implementing target emission profiles

f_{jk} **raw** specie concentrations

a_{jk} experimental **target** specie concentrations

σ_{jk}^{aux} uncertainty of the equations

ME-2 is implemented in EPA PMF v5



Road salting contribution estimate

Hyphotesis	Method	References
Road salt is the only source of Cl	Cl or Cl^- determination in PM10 samples (IC, XRF, PIXE)	EC Guildeline
Road salt is NOT the only source of Cl (sea salt, coal burning, waste burning, industries)	Full chemical characteization of PM10 samples	Richard et al., 2011 and many others
No chemistry available	Generalized Additive Modelling	Aldrin et al., 2008 Steiermark, 2008
	Emission module + numerical dispersion modelling	Denby et al., 2012

EC Guideline
http://ec.europa.eu/environment/air/quality/legislation/pdf/sec_2011_0207.pdf

Impact of road salting

The PARIS case-study

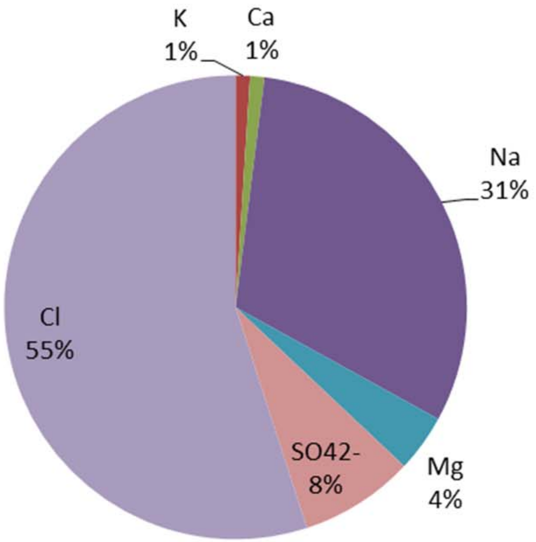
Illustration 1: Localisation de la station de mesure de proximité trafic à Porte d'Auteuil

Methods:

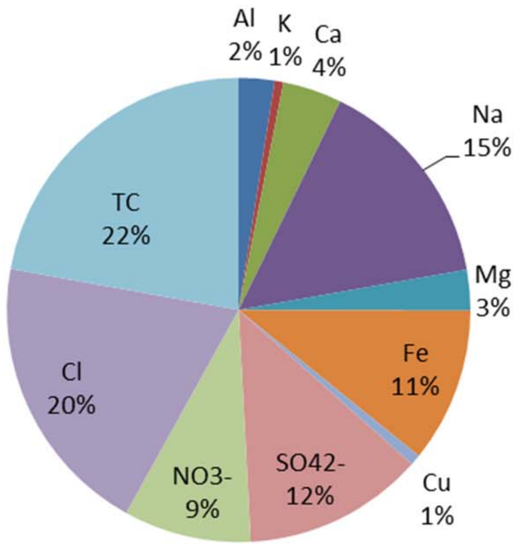
1. One year PM10 sampling and chemical speciation:
   - 60 elements
   - Total carbon
   - Water soluble ions
2. Multilinear Engine source apportionment

A priori information

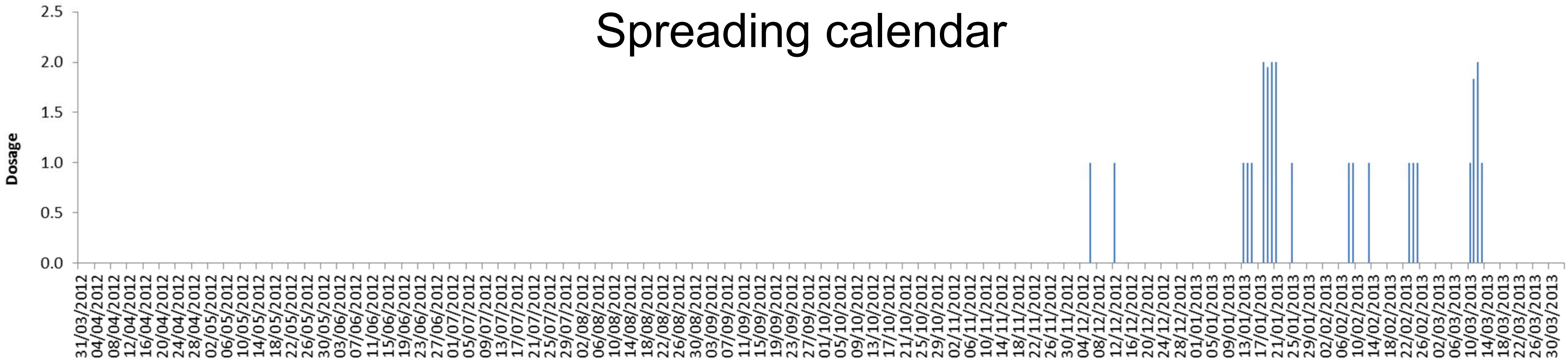
Road salt composition



Aged sea spray

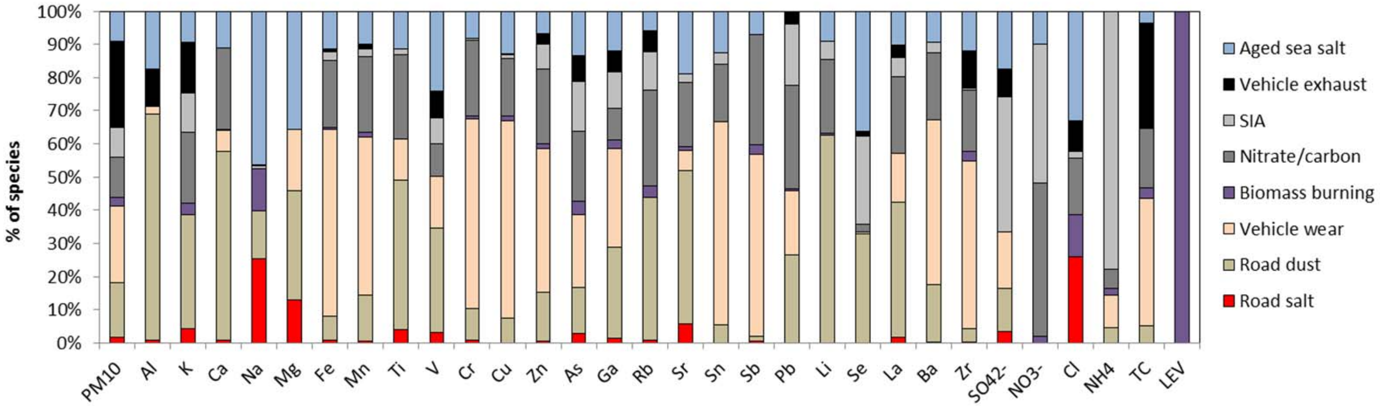


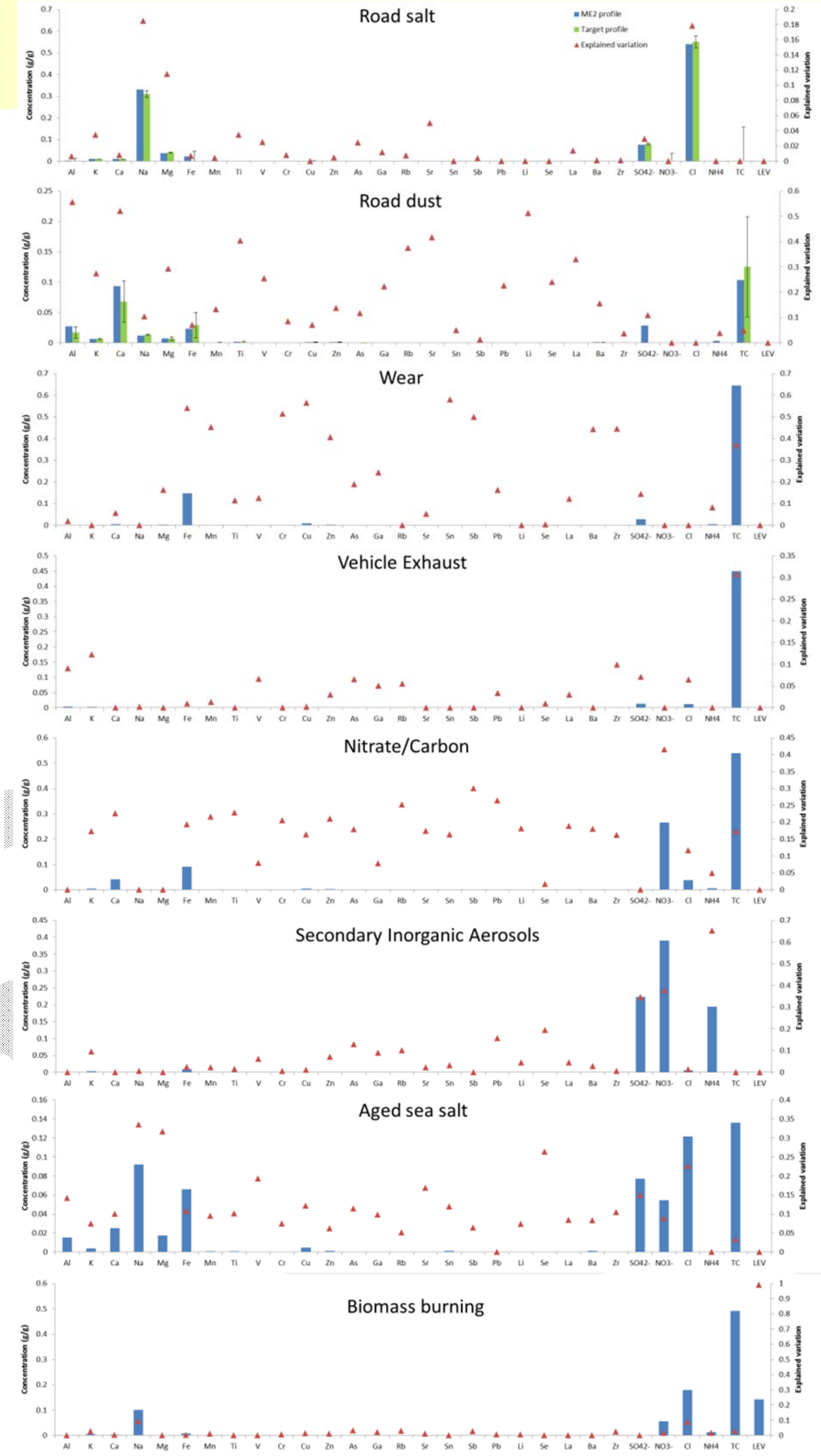
Spreading calendar



Impact of road salting

Results: Source profiles



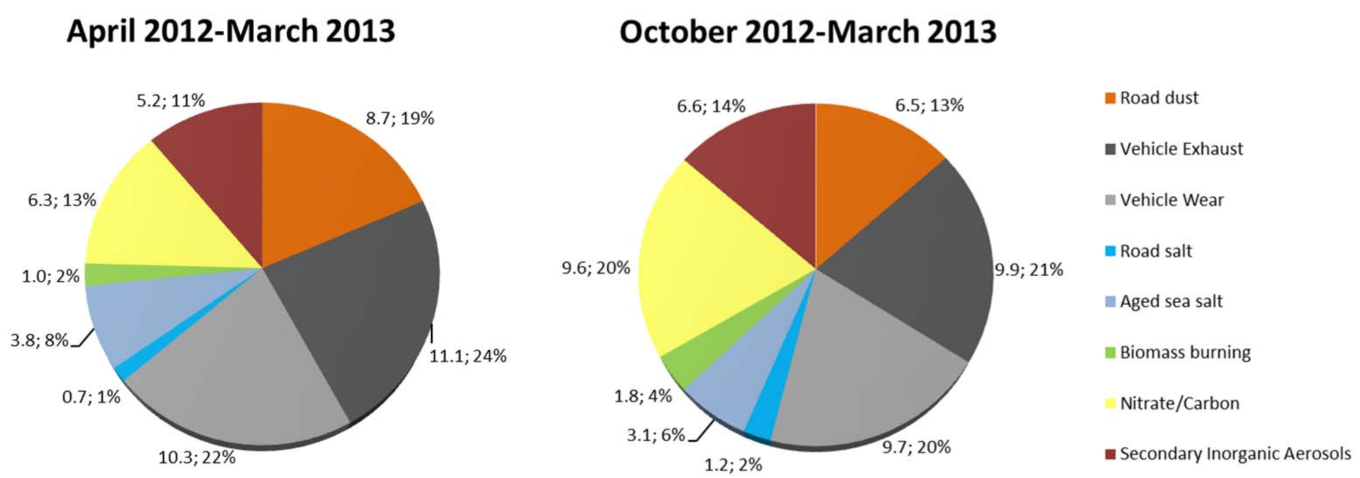


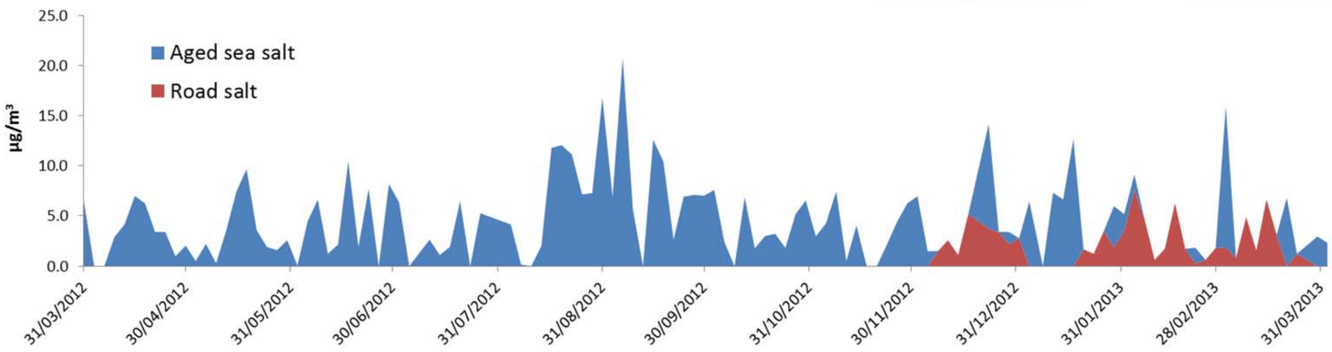
Amato et al., in prep.

INERIS AIRPARIF LSCE CSIC Consejo Superior de Investigaciones Científicas

Impact of road salting

Results. Source contributions



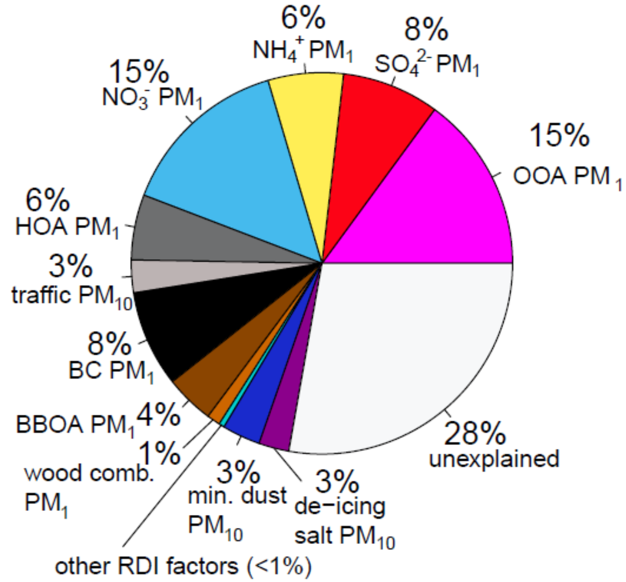


Amato et al., in prep.

Alpine environment

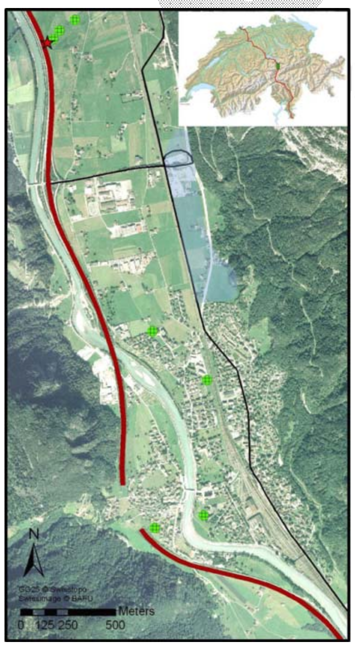
Zurich urban background

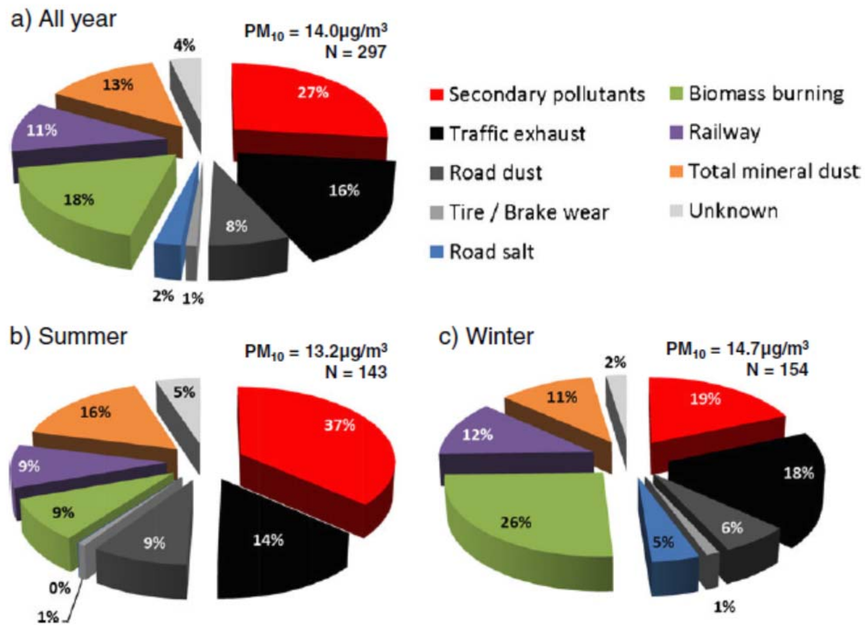
Richard et al., 2011



Swiss transit highway A2

Ducret-Stich et al., 2013





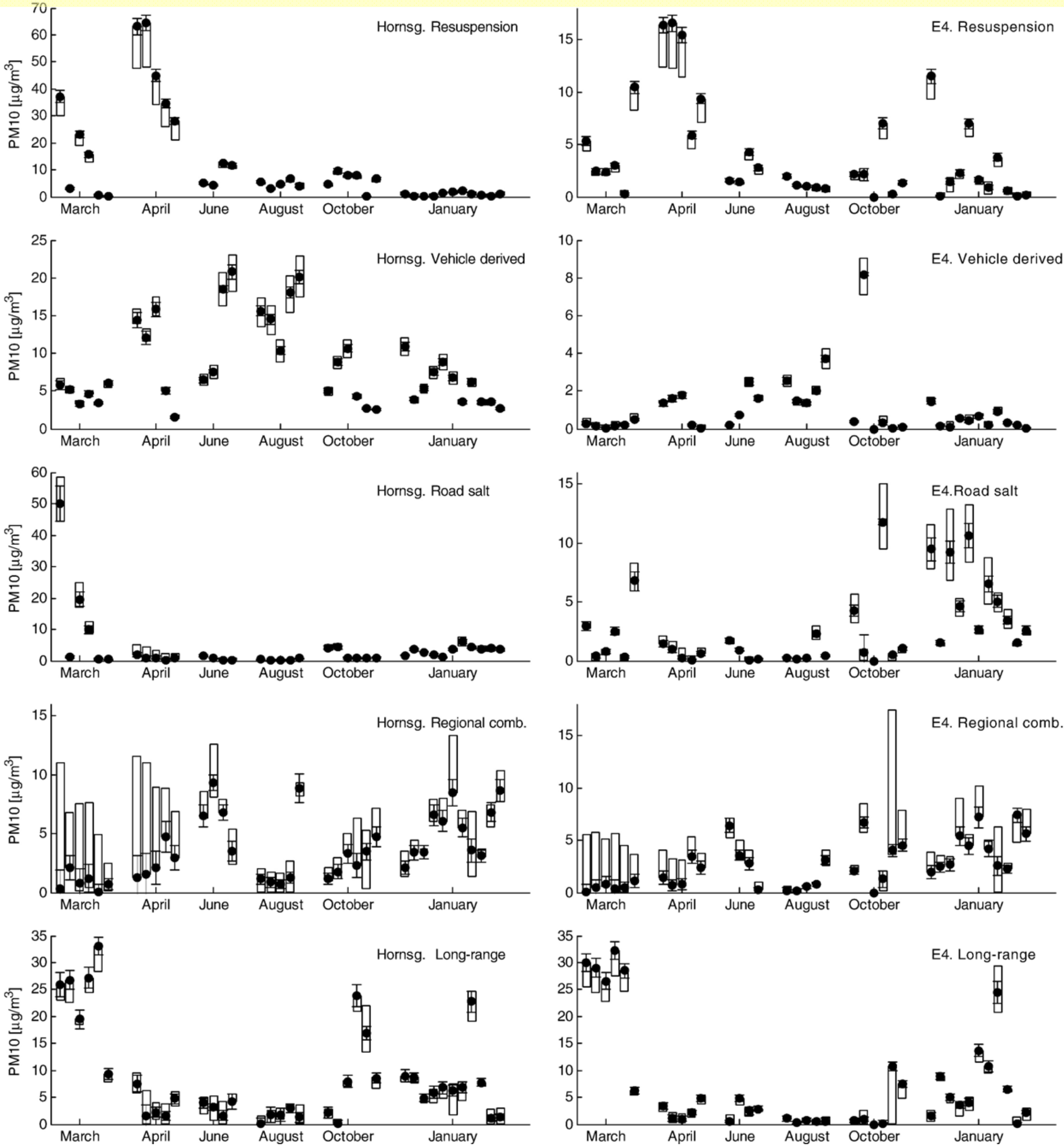
Impact of road salting

SWEDEN
2% of PM10

may lead to levels above 50 µg m^{-3} on a daily levels

Furusjo et al., 2007

City center | Highway

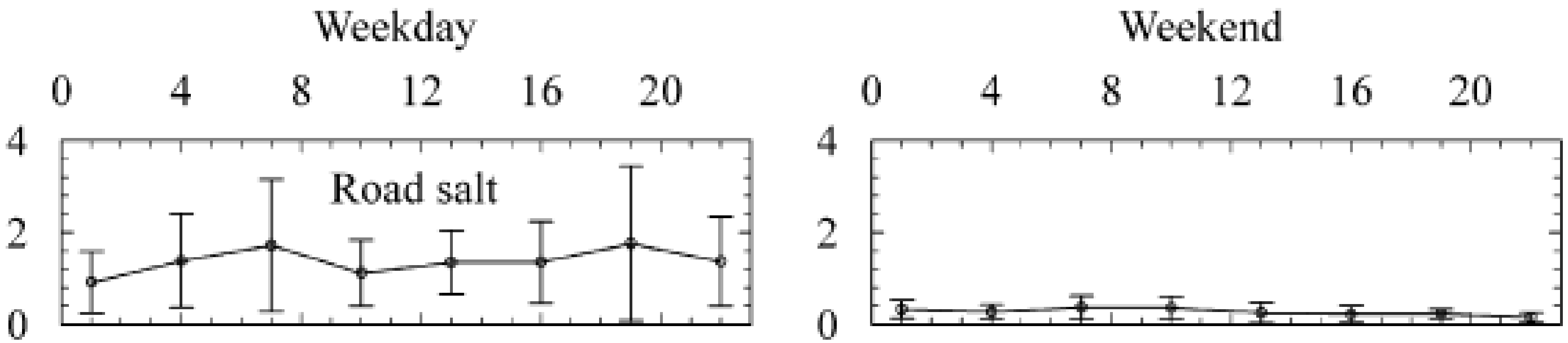


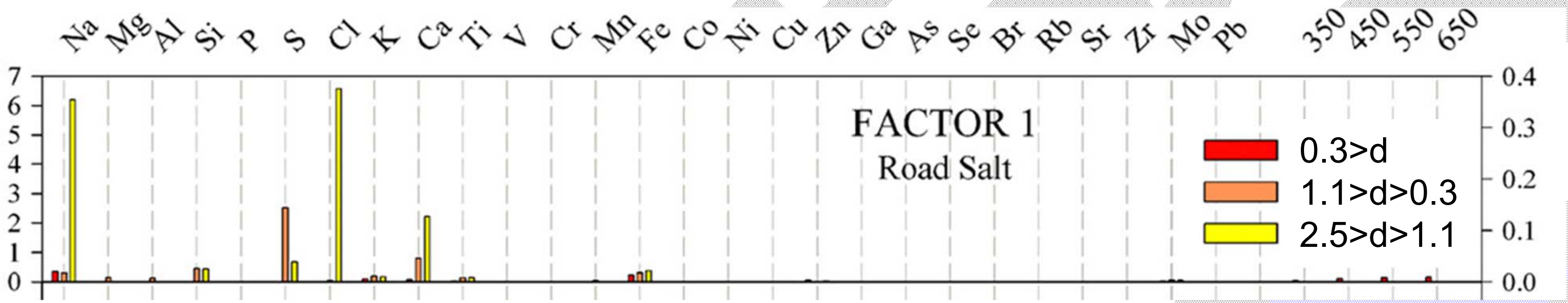
Other studies

Reference	Country	Parameter	Increase
Gertler et al., 2006	USA	Emission factor	30% (traction sand 100%)
Ketzel et al., 2007	USA	Emission factor	5-45% (salt + sand)
Cheng et al., 1998	Canada	PM2.5-10	1-2% in winter
Clements et al., 2014	Colorado	PM2.5-10	19-26%
Kumar et al., 2012	Syracuse (NY)	PM2.5-10	< 1 ug/m3
Peng et al., 2010	Austria	PM10	3-4%

Impact of road salting

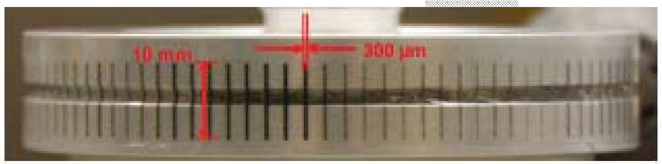
3h size-segregated road salt in PM





Peré-Trepat et al., 2007

Davis Rotating drum
Universal-size-cut Monitoring (DRUM)



Alternatives to NaCl

Deicers:

- $MgCl_2 \cdot 6H_2O$ (20% in water)
- Calcium Magnesium Acetate (CMA, 25% in water)
- $CaCl_2$
- $CHKO_2$

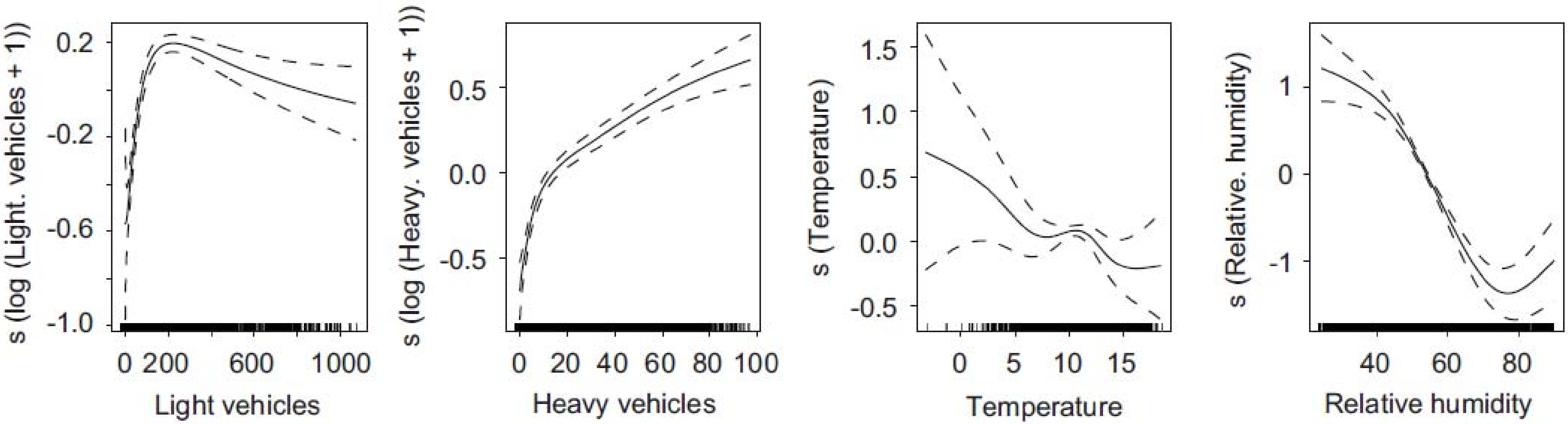
Less corrosive and some studies show also their efficiency as dust binders

According to Bohner et al. (2011) a prerequisite for this is that the air humidity is at least 35 %, otherwise the use of water is more effective

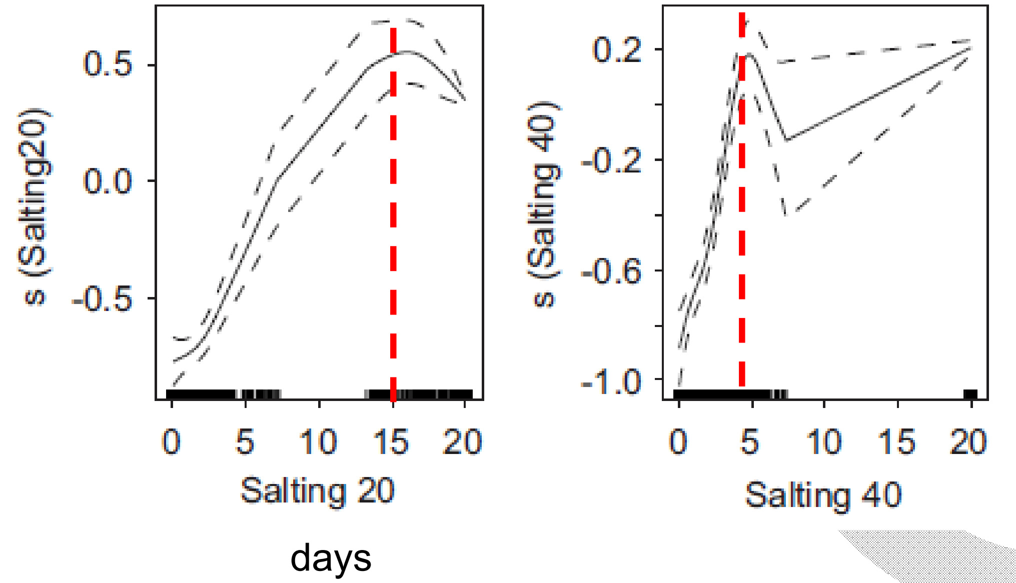
Alternatives to NaCl

$MgCl_2$

In Norway similar results with 20 or 40 g/m^2 dosage

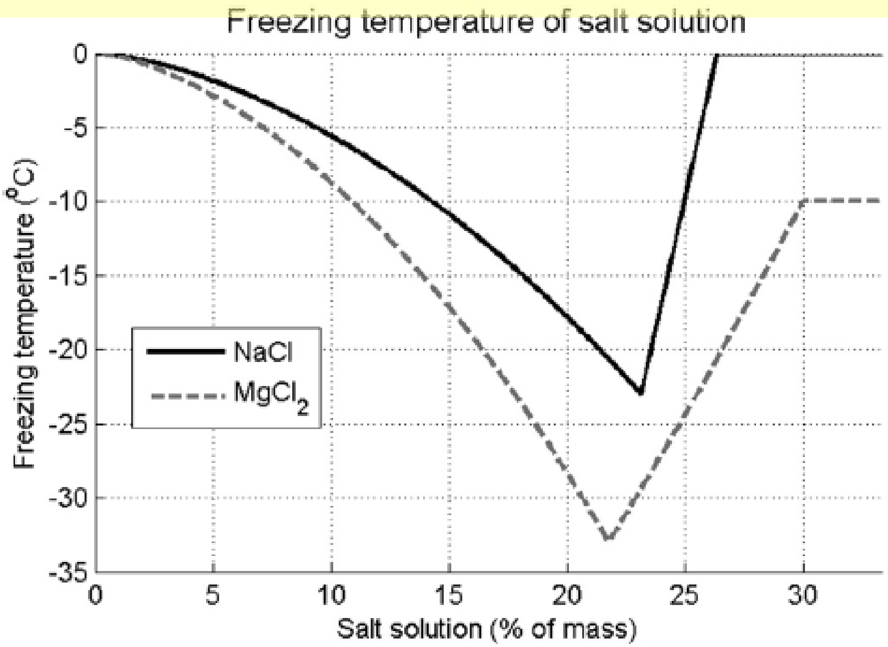


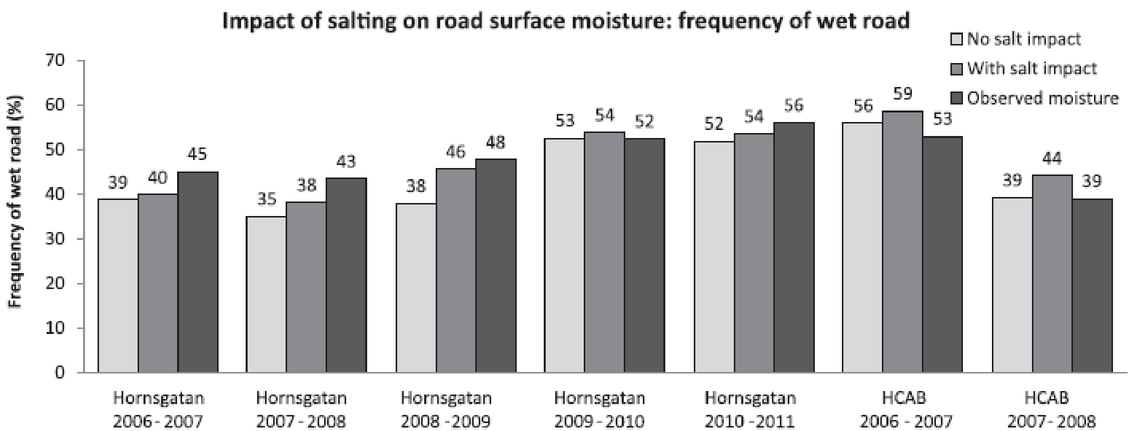
30% reduction of PM2.5-10 levels

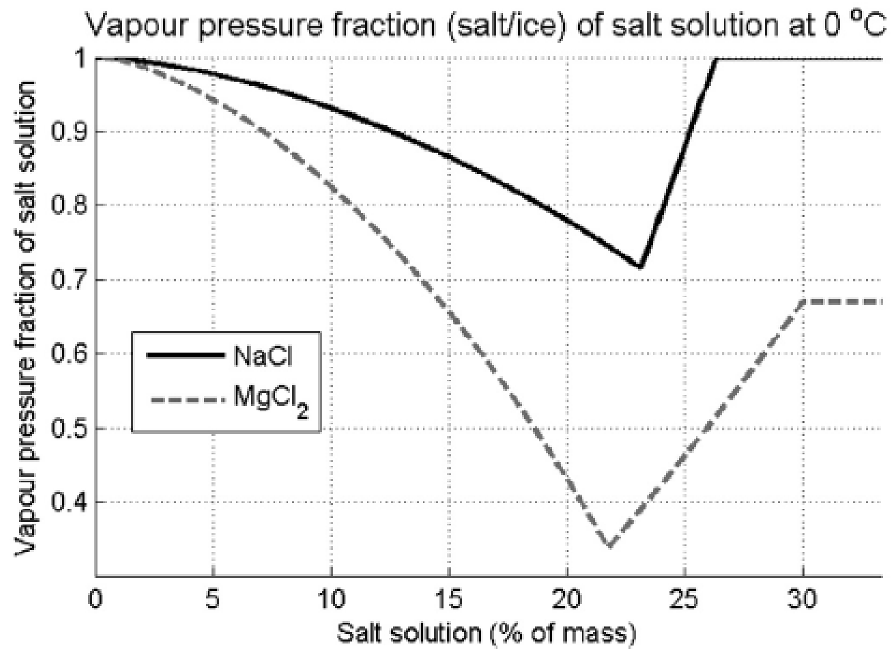


Aldrin et al., 2008.

Alternatives to NaCl







Denby et al., 2012

Calcium Magnesium Acetate (CMA)

- Sweden: 35% daily reduction (Norman and Johansson, 2006).
- Austria: 20-30% daily reduction (10% annual)

  www.life-cma.at

Studded tires

Sanding/salting

- Stuttgart, no reduction
- London:
  - No significant reduction in urban corridors
  - Reduction up to 40% at industrial sites

CSIC

Are dust-binders efficient also in the Mediterranean climate?

LIFE11 ENV/ES/000584

AIRUSE

Testing and Development of air quality mitigation measures in Southern Europe

www.airuse.eu

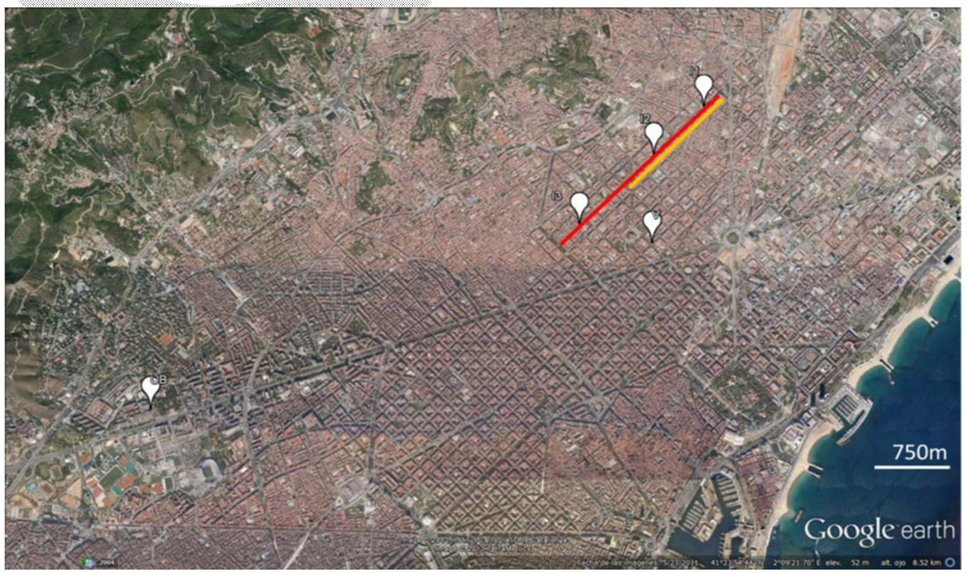
AIRUSE test on dust binders

$MgCl_2$ tested at urban road

CMA tested at:

- urban road
- industrial road
- unpaved road

Urban road test (Barcelona)



- Dust Track, TEOM and GRIMM;
- High volume samplers PM10 (daily)
- High volume samplers PM2.5 (every third day).
- PM chemical characterization (ions, elements, OC and EC);
- Streaker for PM2.5 and PM2.5-10;
- Black Carbon (MAAP and mini-aeth);
- NOx, O_3 and SO_2 and meteo.

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CMA and $MgCl_2$

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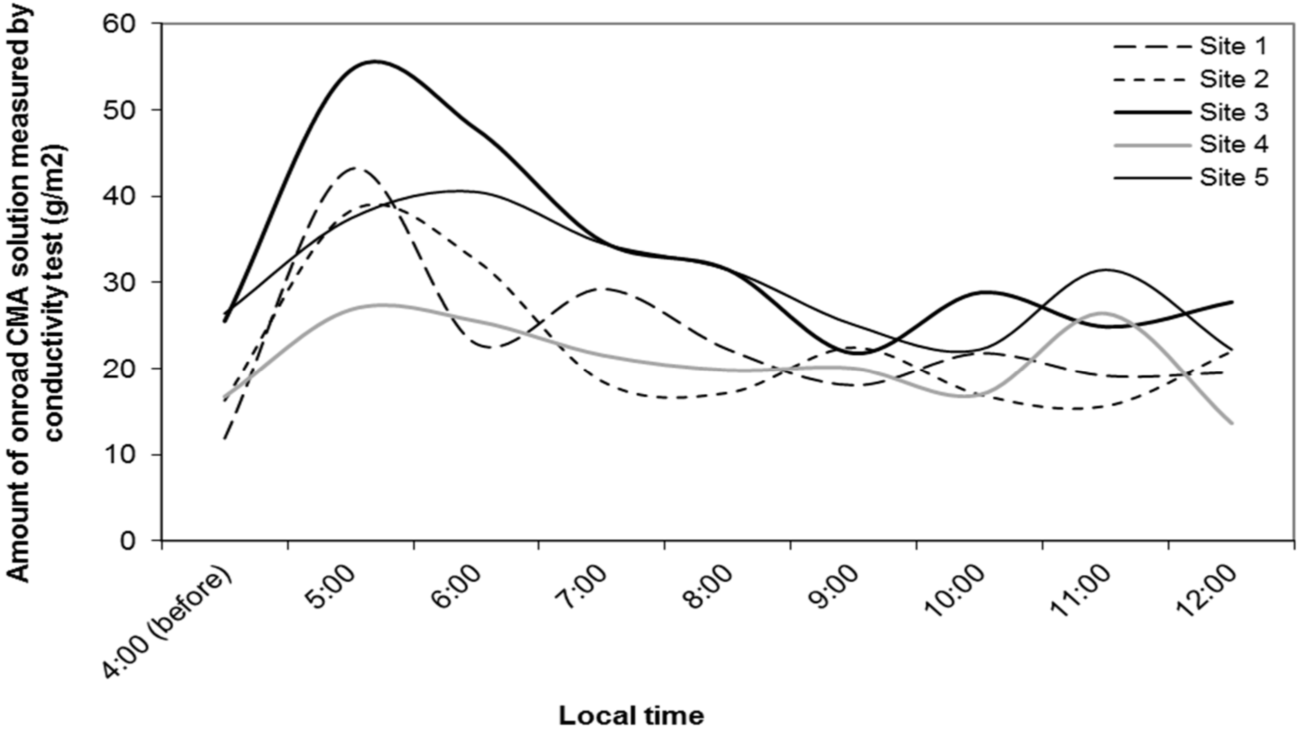
Results

Amount of CMA solution on road surface



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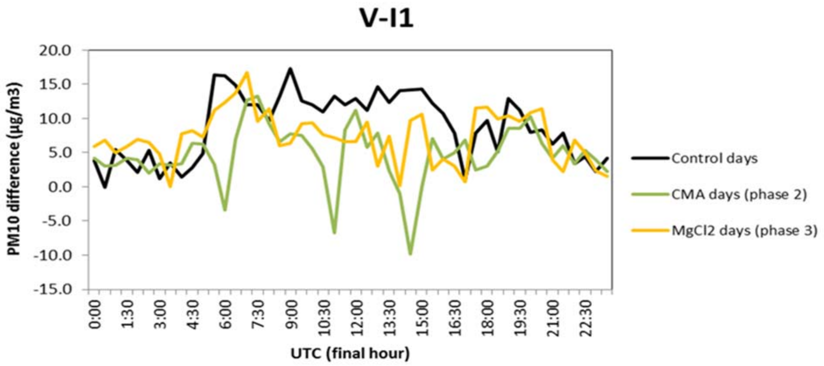
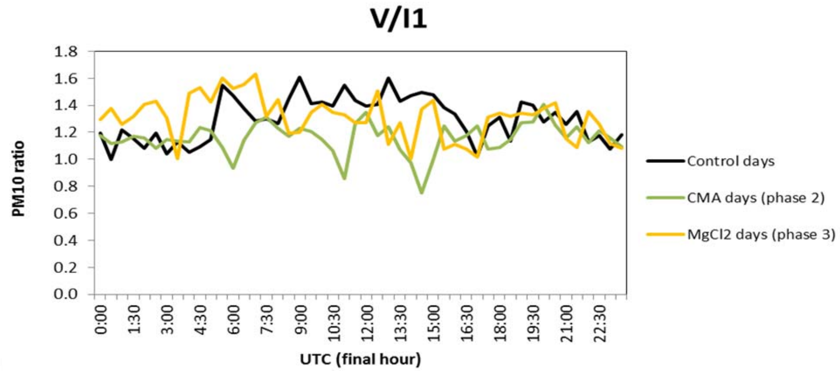
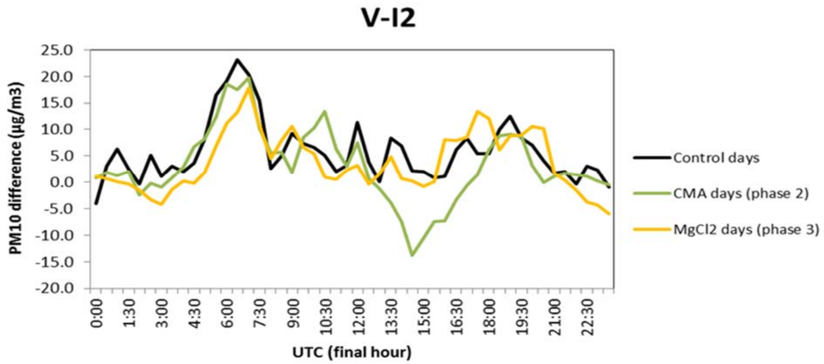
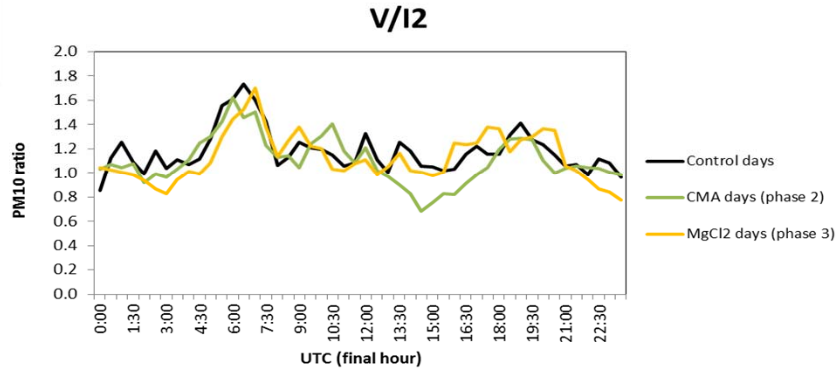
Effect on hourly PM

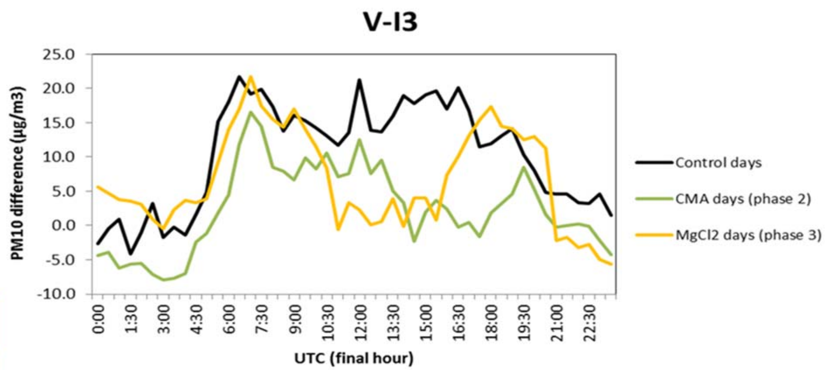
No statistically significant reduction

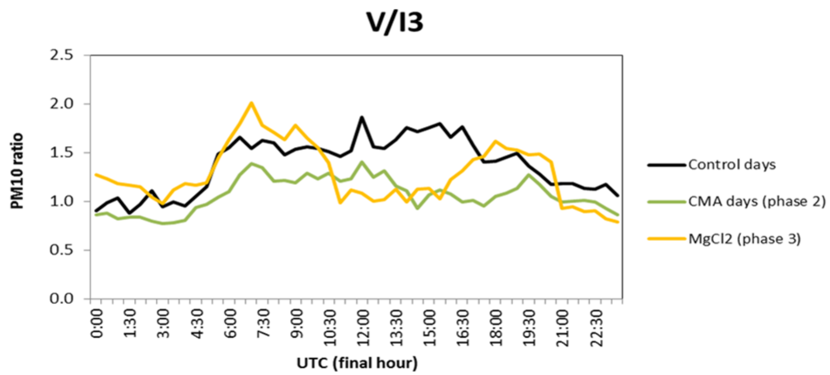




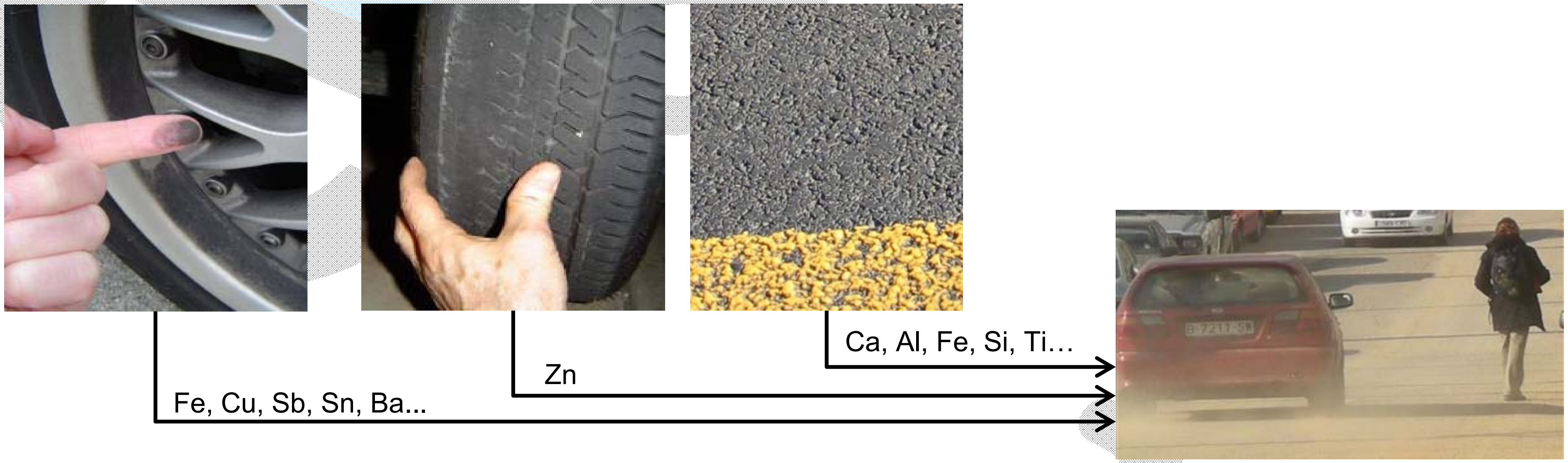








Effect on tracers (% of reduction)



	phase 1	phase 1	phase 1	phase 1	phase 2	phase 2	phase 2	phase 2 - 48h	phase 2 - 48h	phase 2 - 48h	phase 3	phase 3	phase 3
	V-I2	V-I1	I3-I2	I3-I1	V-I3	V-I2	V-I1	V-I3	V-I2	V-I1	V-I3	V-I2	V-I1
Mineral	-	-	-	-	-	-	-	-	-	-	-	-	-
Al	-	-	-	-	-	1	-	2	0	-	9	5	-
Ca	-	-	-	-	-	-	-	-	-	-	-	-	-
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-
K	5	-	7	-	-	5	-	5	4	3	-	6	3
Mg	-	-	-	-	-	-	1	-	-	8	19	-	29
Li	-	-	-	-	-	4	-	8	7	9	4	-	-
Ti	-	-	-	-	-	-	-	1	-	1	-	-	-
Cr	5	26	-	-	10	7	-	30	12	-	16	12	24
Mn	-	-	-	-	-	-	-	8	-	1	-	-	-
Cu	22	45	-	9	8	2	-	5	-	-	-	-	-
Zn	-	-	-	-	2	-	3	24	1	17	25	-	11
Ga	-	-	-	2	0	-	6	18	-	11	2	2	-
Rb	-	-	4	-	-	-	-	-	-	-	1	-	-
Sr	-	-	-	-	-	-	-	1	-	-	-	-	-
Sn	-	-	-	11	-	-	-	-	-	-	-	-	-
Sb	12	53	7	43	8	31	8	-	24	14	-	-	-
Ba	-	-	-	-	-	-	-	-	-	-	-	-	-
La	-	-	5	14	-	-	0	8	-	13	-	9	-
Ce	-	-	8	25	-	-	-	-	-	1	-	4	-
Pb	8	6	5	2	-	-	-	17	-	5	6	-	-
Bi	-	31	15	49	-	-	-	5	-	-	-	-	12

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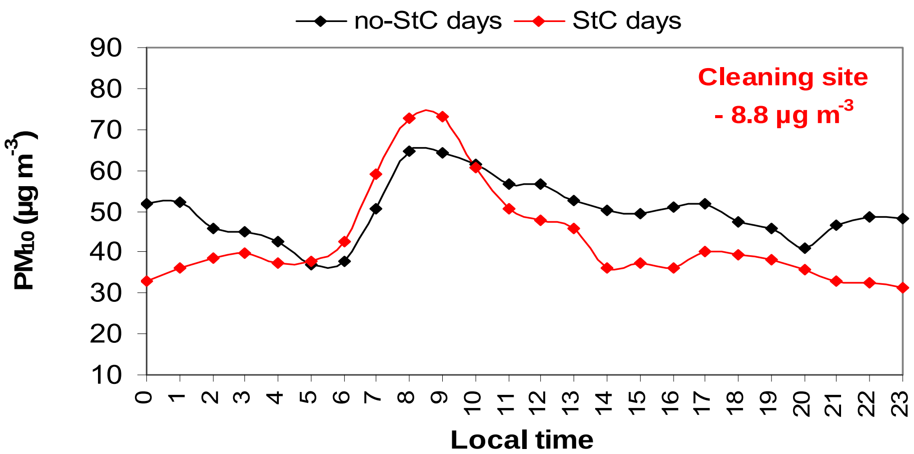
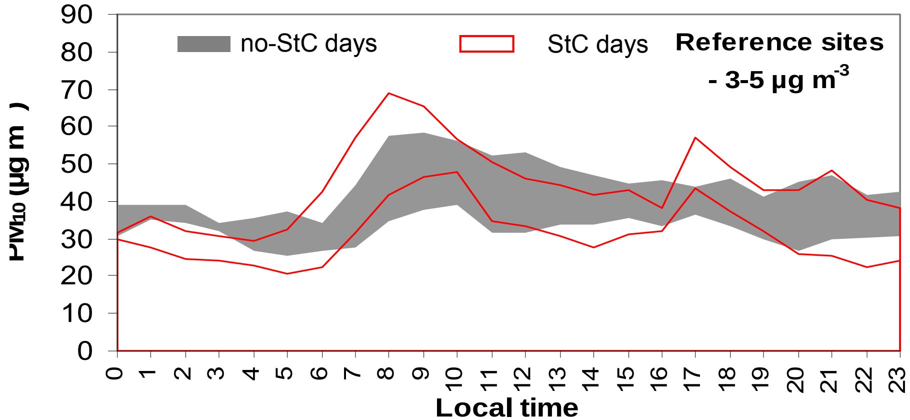
Street washing





Amato et al., ATM ENV 2009

Reduction: 4-5 µg m^{-3} (7-10%)

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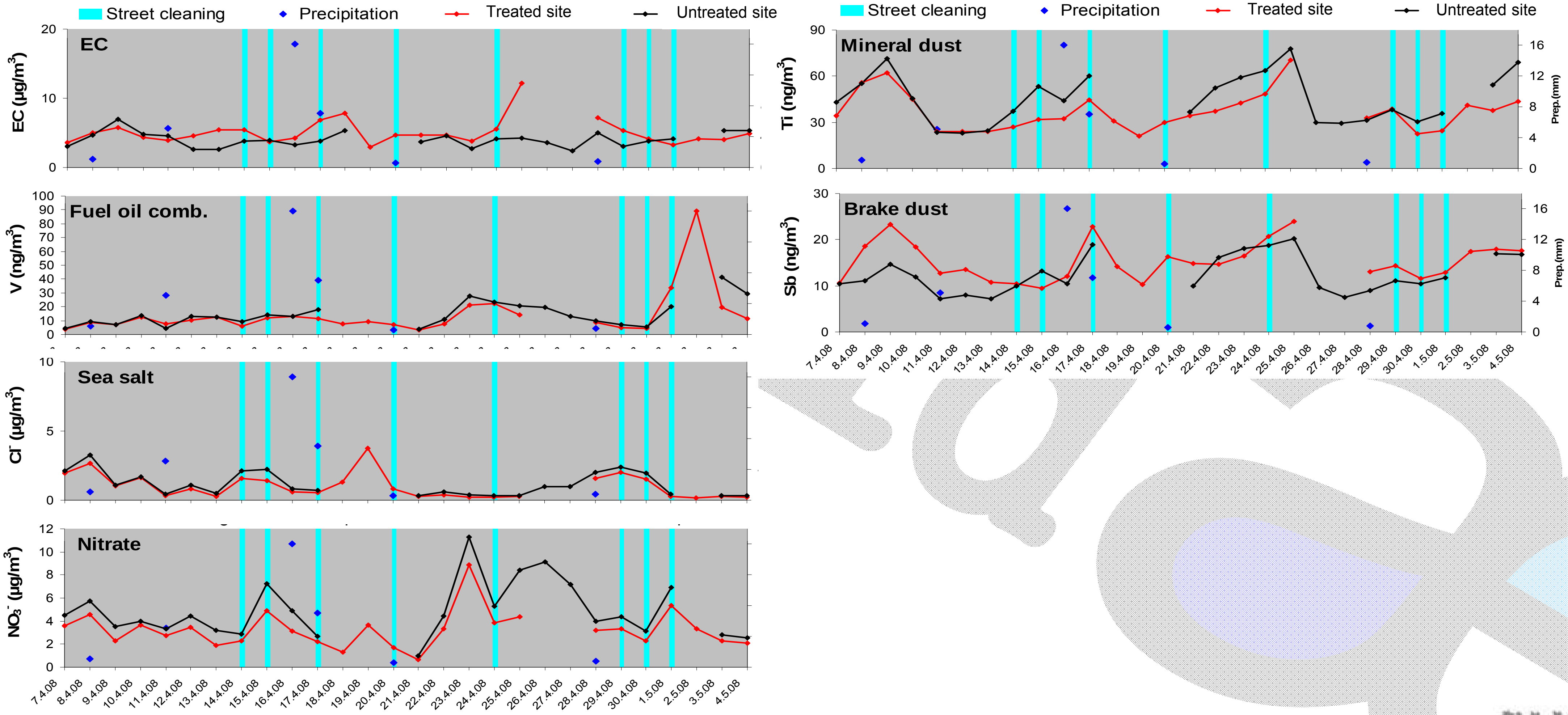
Street washing



Amato et al., ATM ENV 2009

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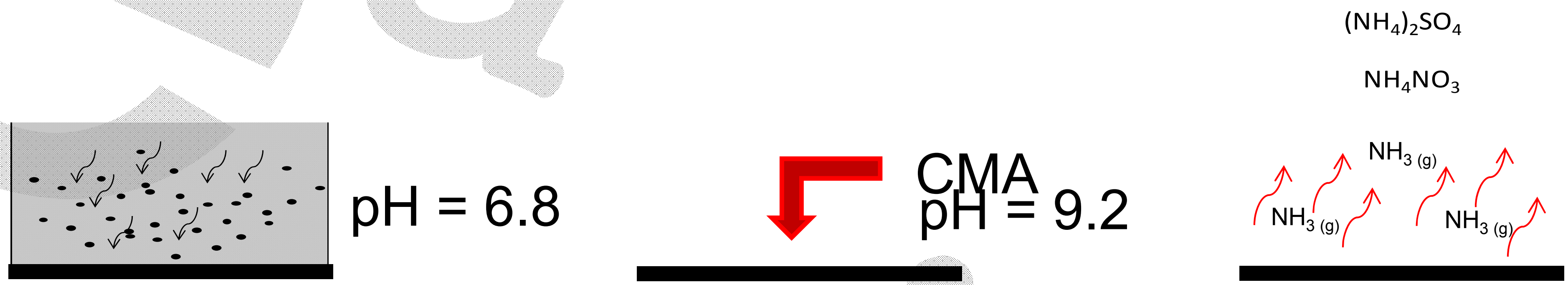
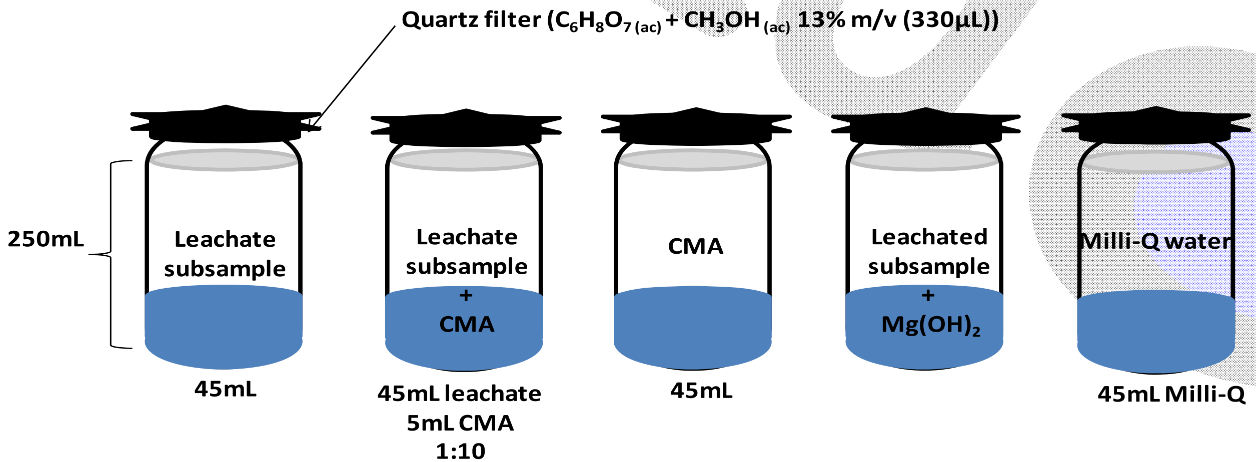
Possible NH_3 stripping



$(NH_4)_2SO_{4\,(ac)} \leftrightarrow NH_4^+{}_{(ac)} + SO_4^{2-}{}_{(ac)}$

$NH_4NO_{3\,(ac)} \leftrightarrow NH_4^+{}_{(ac)} + NO_3^-{}_{(ac)}$

$NH_{3\,(ac)} + H_2O \leftrightarrow NH_4^+{}_{(ac)} + OH^-{}_{(ac)}$



97% NH_3 stripping

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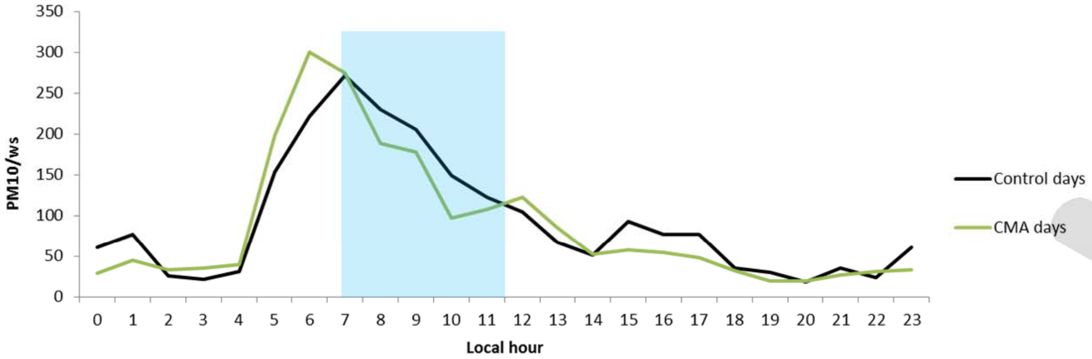
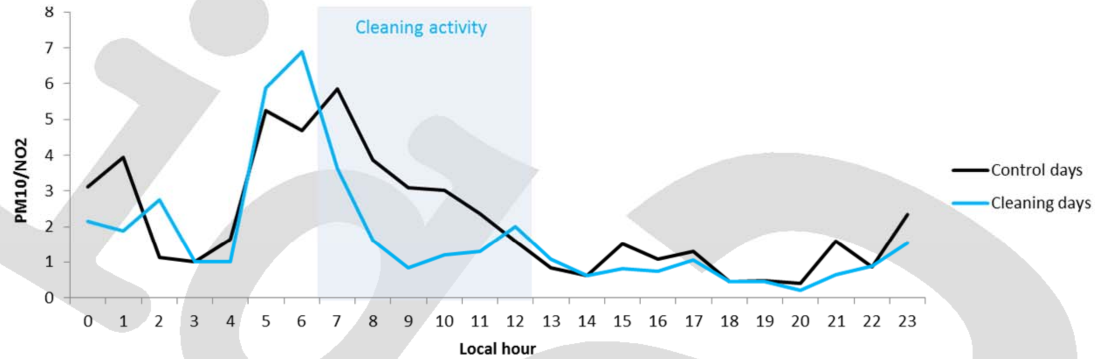
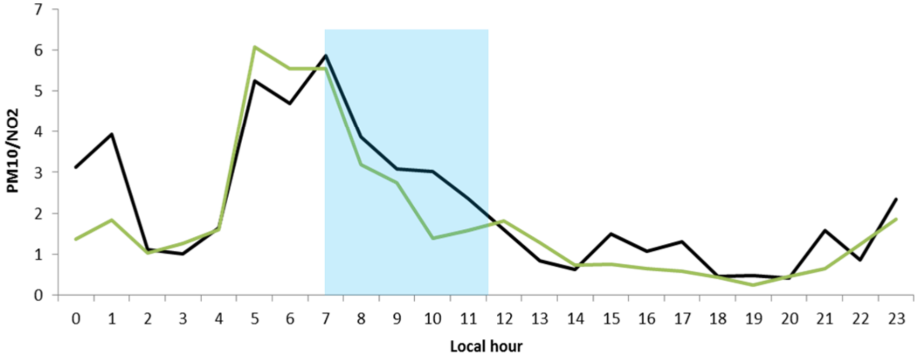
Industrial paved road

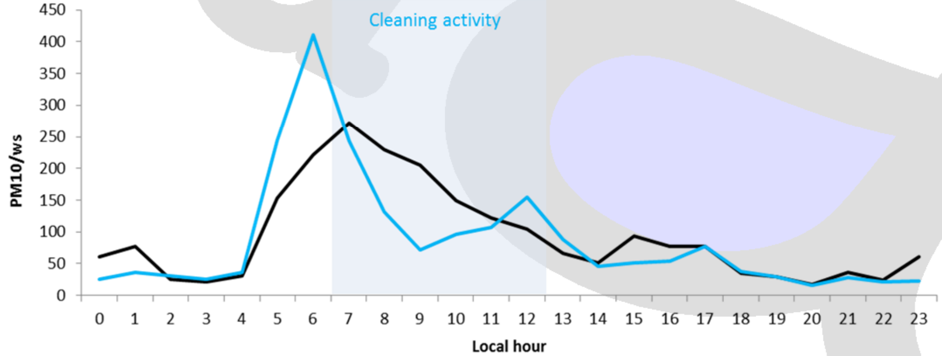
CMA

Water-only





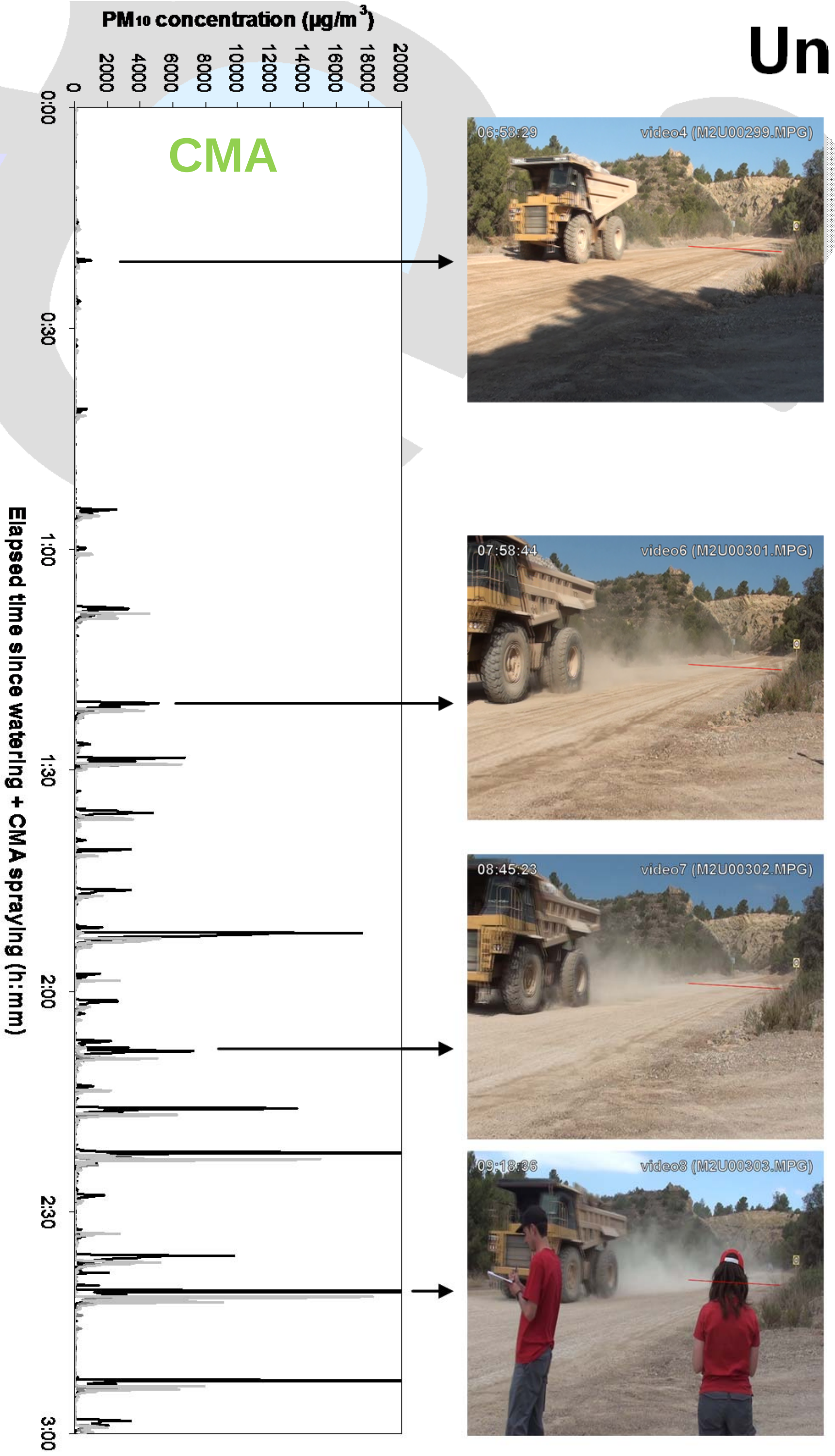


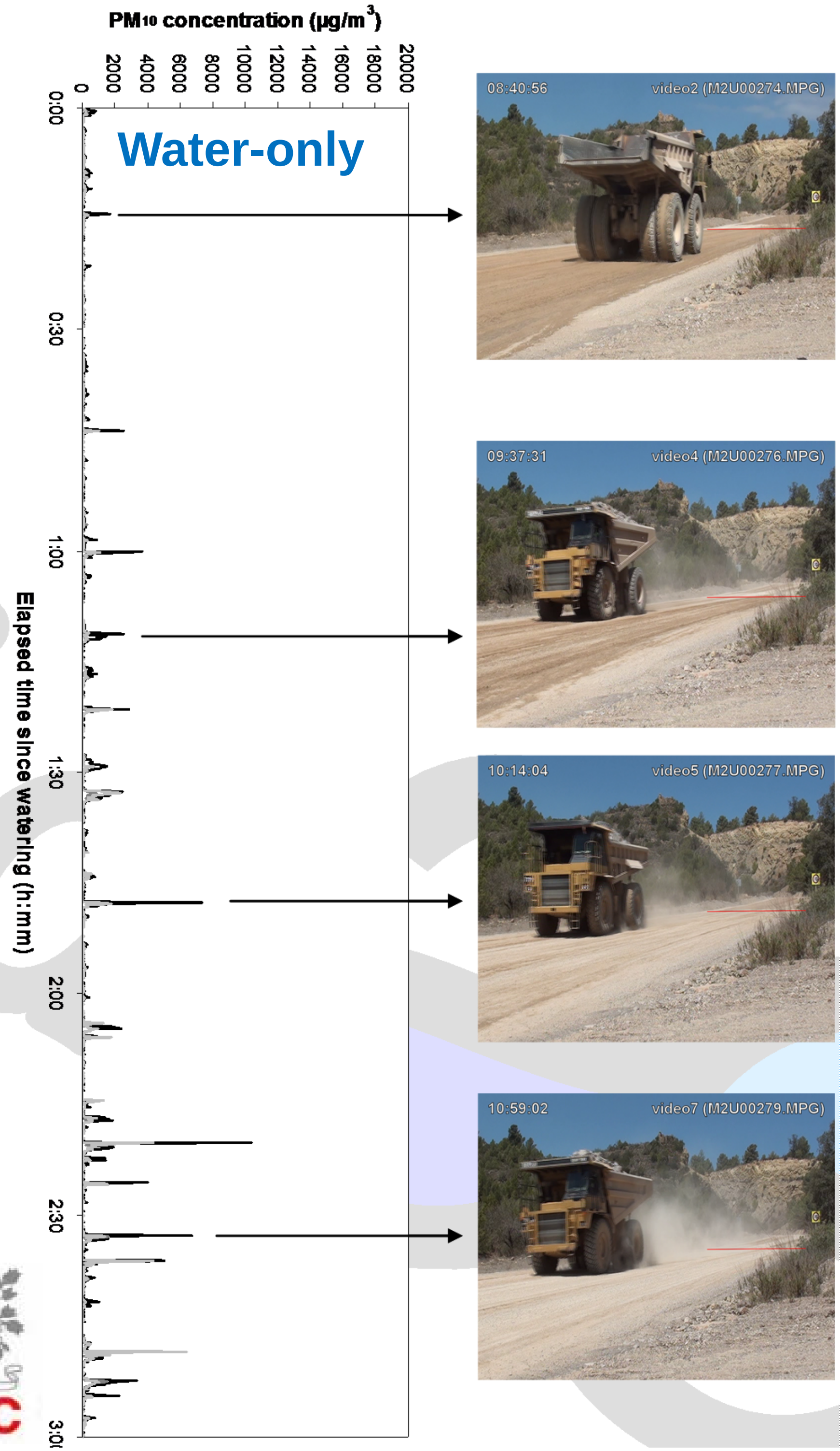


8% reduction

18% reduction

Unpaved road





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Source	Location	Dust loading	Measure	Dosage	PM10 reduction	Monitoring site
Road dust	Urban paved road	3-6 mg/m^2	Street washing	1 L/m^2	7-10% on a daily mean	kerbside
			CMA	15-20 g/m^2	Negligible	kerbside
			$MgCl_2$	15-20 g/m^2	Negligible	kerbside
	Industrial paved road	20-40 mg/m^2	Street washing	27 L/m^2	18% on a daily mean	kerbside
			CMA	30-60 g/m^2	8% on a daily mean	kerbside
	Industrial unpaved road		Street washing	3.5 L/m^2	>90% up to 1 h	downwind
			CMA	100 g/m^2	Not observed	downwind

Conclusions

- The EC provides the Member States with the possibility to subtract the contribution of road sanding/salting from the number of exceedances
- Importance of quantifying road salt contribution to PM
- Methods include PM chemical speciation and source apportionment, GAM modelling
- Road salting increase PM levels by 1-4% on a annual mean, but up to 50 µg/m^3 on a daily basis
- Impact of traction sand is larger
- Alternative deicers exist ($MgCl_2$ and CMA) which may act also as dust binders
- No effectiveness of dust binders has been found in the Mediterranean region, being water more effective

Acknowledgements:

Instituto de Tecnología Cerámica jtc

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CLEAN ROADS

AXA Research Fund

LIFE AIRUSE

Ajuntament de Barcelona

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Grazie per la vostra attenzione

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