Methods used in Barcelona to evaluate the effectiveness of CMA and MgCl2 in reducing road dust emissions

Action B7

Coordinated by:
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1. INTRODUCTION

Calcium-Magnesium Acetate (CMA) has been proposed as dust binder and its application on paved roads was recently tested in Sweden, Austria, Germany and UK in order to mitigate road dust emissions (Norman and Johansson, 2006; www.life-cma.at; Barratt et al., 2012). These previous studies showed that in most cases a reduction of kerbside PM10 concentrations was reached, even if short lived (few hours). The effectiveness of CMA in binding deposited particles seems to be closely related to the degree of road moisture (Gustafsson et al., 2010). This is a crucial aspect, mostly when evaluating the potential effectiveness in South European environments, where the higher solar radiation might further reduce the life-time of the air quality benefit. MgCl2 has been also proposed and tested in Norway as a possible dust suppressant due its high hygroscopic and deliquescent properties. This is the first study evaluating CMA and MgCl2 in a South European city, characterized by a relatively dry climate.

2. STUDY AREA

The city of Barcelona (NE of Spain) lies on the western coast of Mediterranean basin, surrounded westerly by the Collserola range (512 m a.s.l.), and by two river basins at north and south. The city is characterized by hot summers and mild winters, with low and infrequent precipitations (520 mm annual mean for the period 2003-2009). Beside the adverse climatic conditions, the city of Barcelona suffers air pollution also due to the high vehicle density (5,900 veh. km\(^{-2}\), one of the largest in Europe), with high share of diesel-powered and 2-wheelers and due to the urban architecture with relatively high buildings and narrow streets. Beside road traffic (the main source of PM in Barcelona), other local (shipping, urban works and metallurgy) and regional sources have been identified in the area, being there also indications of non-fossil combustion processes (Amato et al., 2009a; Minguillón et al., 2011; Reche et al., 2012a; van Drooge et al., 2013).

In this scenario, emissions of road dust were estimated to increase PM10 and PM2.5 background levels by 16-17% and 6-8% respectively, as annual average (2003-2009), though still lower than carbonaceous emissions from motor exhausts (14-23% and 22-33%) (Amato et al., 2009a, Reche et al., 2012a and 2012b). Road cleaning activities have been recently tested in one of the commercial district of Barcelona (Eixample), resulting in a daily reduction of PM10 measured at traffic site by 7-10% (Amato et al., 2009b) and larger decrease for specific tracers od mineral and brake dust (Amato et al., 2010).

The present study was set-up in the same commercial district, selecting Industria road (between 15000 and 18000 vehicles per day) for the evaluation of dust suppressant effectiveness since it consists of 2.5 km of trafficked road, with constant traffic flow and building height. Other requirements were related to the orientation of the road (parallel to
the coastline) and absence of biking lanes. *Industria road* is oriented 45º-225º, traffic is one way heading north and distributed on three lanes, with the rightest lane exclusive for buses and taxi and a parking lane on the left side. The orientation of the road and the 7-store buildings may generate street canyon effect during first afternoon hours, as shown by Amato et al., (2011). Ordinary road cleaning activities were suspended during the whole period.

Pavement of *Industria road* is asphalt concrete with density within 2.21-2.42 t/m3, with a proportion of 3-5% of binder, ratio filler/binder of 1.1-1.5 and aggregate size distribution as shown in Fig. S1.

### 3. DUST SUPPRESSANTS

During April and May 2013 the full width of *Industria road* (9 m) was spread only during dry and working days according to the following calendar:

- Phase 1: 25% CMA aqueous solution (ICE & DUST-AWAY, Nordisk Aluminat) was spread on a 1400 m stretch in the morning of 16th, 17th and 18th April;
- Phase 2: 25% CMA aqueous solution was spread on a 2300 m stretch in the morning of 22nd, 23rd, 24th April and 2nd, 6th, 8th, 13th May;
- Phase 3: 20% MgCl2 aqueous solution was spread on a 2300 m stretch on 21st and 23rd May.

Both solutions were sprayed by means of a Springer SD210 spreader vehicle at a rate of 20 g/m2 (Fig. 2). The spreader covers a 2.7 m wide area and it adjusts the flow according to the speed of tractor in order to assure an even and constant application on road surface. The amount of CMA solution on road was monitored hourly at five spots, from 1 hour up to 7 hours after its application by means of the conductivity sensor (SOBO, Boschung) which was previously calibrated for the 25% CMA aqueous solution.

![Figure 2. Spreader used for CMA and MgCl2 solutions](image)

Spreading calendar was based on weather forecast (no rain, temperatures above 0ºC) and traffic activity (only working days). Given that the air quality benefit is expected to be short
lived (www.life-cma.at; Barratt et al., 2012; Gustafsson et al., 2010), CMA and MgCl₂ solutions were spread around between 5 and 9 am local time, in order to maximize its effectiveness during the most-polluted hours due to traffic emissions (7-9 am). Totally the duration of spreading was around 1 hour.

In order to avoid build-up of CMA on road surface, after each test a vacuum-assisted sweeping vehicle cleaned road surface starting from 23:00 of the same day or of the day after, so that the effectiveness of dust suppressant can be evaluated only on the first-day or of the first-2-days.

At high dosage, CMA solution may reduce friction between road pavement and tires (www.life-cma.at). For traffic safety a number of measures were taken: speed limit was decreased from 50 to 30 km/h, road signals were warned drivers of possible slippery conditions, friction tests were performed before and after the CMA application following the UNE-EN 13036-4:2012 protocol. This protocol allowed, providing fast information on slip resistance, the possibility of withdraw immediately the application of CMA.

4. MEASUREMENTS

Five monitoring sites were used for this study, divided as:

- Three mobile laboratory vans (I1, I2 and I3) installed at the parking lane of Industria road (Fig.1). During phase 1, only stations I1 and I2 were inside the road stretch treated with CMA; during phase 2, also station I3 was inside the stretch.
- One reference kerbside (western side) mobile laboratory van (V) installed at a parallel untreated road (Valencia road) at a perpendicular distance of 650 m away from Industria road (Fig.1). To avoid confounding factors such as road cleaning activities, the 500m stretch around measuring point were never cleaned during the whole period.
- One reference urban background monitoring station (UB), located 5.5 km away from Industria road (Fig.1).

![Figure 1. Map of Barcelona and location of the five monitoring sites](image-url)
The monitoring sites (Fig. 3) were equipped with the following instruments:

- High volume samplers for 24-hours samples of PM10 and PM2.5 (DIGITEL and MCV) at I2, V and UB. At I2 and V, PM10 and PM2.5 were collected every day and every third day respectively, while at UB both fraction were collected every third day. PM samples were collected onto quartz fiber filters (Pallflex Ø15 cm) after drying at 205 °C during 5 h and conditioned for 48 h at 20 °C and 50% of relative humidity. Weights of blank filters were measured three times every 24 h by means of a Sartorius LA 130 S-F microbalance (1 μg sensitivity). After sampling, filters were brought back to laboratory to be weighted two more times every 24 hours of conditioning at the same T and HR conditions of first weighing. Once the weights of samples were determined, filters were destined to several analytical (destructive) treatments:
  - A quarter of each filter was acid digested (5 ml HF, 2.5 ml HNO3, 2.5 ml HClO4) for the determination of major and trace elements and analyzed respectively by inductively coupled plasma mass spectrometry and atomic emission spectrometry (ICP-MS and ICPAES) (Querol et al., 2001).
  - A quarter of each filter was leached in 20 ml of bi-distilled water for the extraction of water-soluble ions and subsequent analysis by ion chromatography (IC) for sulfate, nitrate and chloride and by specific electrode for ammonium.
  - A section of 1.5 cm² from the remaining half filter was used for the determination of OC and EC by a thermal-optical transmission technique (Birch and Cary, 1996) using a Sunset Laboratory OCEC Analyzer with the NIOSH 5040 temperature program. Total carbon (TC) was determined as the sum of OC and EC.

In every case blank concentrations were subtracted for determining final concentrations in samples.

- PM monitors (TSI Dust Track, Tapered Element Oscillating Microbalance (TEOM) and GRIMM optical counters) measuring every 30 minutes basis concentrations of PM10, PM2.5 and PM1. PM10 and PM2.5 mass concentrations from each instrument were corrected through inter-comparison with 24-hours average gravimetric mass from high volume samplers, where available. PM2.5-10 concentrations were calculated as PM10–PM2.5 where available.

- Two STREAKER samplers at I2 and V which permit to obtain the elemental characterization of PM (PM2.5 and PM2.5-10) with resolution of 1 hour. Full details of the sampler, its cut-off diameters, control unit, etc. can be found in Formenti et al. (1996). Briefly, particles are separated on different stages: an impactor deposits the aerosol coarse fraction (aerodynamic diameter between 2.5-10 μm) on a Kapton foil while the fine fraction (<2.5 μm) is collected on a Nuclepore filter having 0.4 μm pores. Sampling flux is 1 l min⁻¹. The two collecting plates (Kapton and Nuclepore) are paired on a cartridge which rotates at constant speed for a week: this produces a circular continuous deposition of particulate matter (streak) on both stages. The stages collected were analyzed by Particle Induced X-Ray Emission (PIXE) at the LABEC-INFN facility in Florence (based on a 3 MV Tandetron accelerator) where an external beam set-up is fully
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(dedicated to atmospheric aerosol studies (Calzolai et al., 2006; Chiari et al., 2005) (Fig.2.6). For this analysis, the beam (3 MeV protons) was collimated to a rectangular spot (width: 1mm, height: 2mm) and it was moved along the streak in steps corresponding to 1 hour of aerosol sampling. X-ray spectra have been fitted for 25 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo and Pb) using the GUPIX software package (Maxwell et al., 1995) and the elemental concentrations were obtained via a calibration obtained with a set of thin standards certified within 5% (Micromatter Inc.).

- Hourly EBC concentrations (at λ = 637 nm) were measured by means of a multi-angle absorption photometer (MAAP, model 5012 Thermo Scientific) at I3 and UB and by means of Magee AE51 Mini-Aethalometer (at λ = 880 nm) at I2 and V.
- NOx, O₃, CO and SO₂ monitors and meteorological towers (temperature, pressure, solar radiation, wind speed and direction).

Figure 3. Industria road with traffic signals and air pollution monitoring stations