OVERVIEW OF THE CESAPO PROJECT
RESULTS IN BRINDISI

D. Contini
Istituto di Scienze dell’Atmosfera e del Clima, ISAC-CNR, Lecce, Italy

Agenzia Regionale per la Prevenzione e la Protezione dell’Ambiente

Istituto di Scienze dell’Atmosfera e del Clima, ISAC-CNR, Lecce

Dipartimento DISTEBA, Università del Salento, Lecce

Istituto per la Dinamica dei Processi Ambientali, IDPA-CNR

CESAPo Workshop
Air quality, monitoring strategies and models use for particulate pollution
Patras, 7 April 2014
Objective

The objective of this presentation is to give an overview of the results obtained by the Italian partners regarding the **characterisation of pollution sources** and of the **role of the harbour emissions** in the Brindisi area during the activities of CESAPO.

Outline

Description of the Brindisi area and of the main pollution sources acting on the area and of the emission inventory.

Source apportionment in Brindisi and impact of the ships and harbour-related emissions to PM2.5, PAHs and particle number concentrations.

Large-scale (regional) and local-scale simulation of the impact of ships and harbour-related emissions to gaseous and particulate pollution in the Brindisi area.
The Brindisi area is characterised by a quite complicated scheme of emission sources including:

**Urban emissions (88,500 inhabitants).**

**Harbour-related emissions** (harbour traffic accounted yearly for more than 9.5 million tons, over 520,000 passengers and over 175,000 vehicles).

**Airport emissions.**

**Industrial emissions.**

**Petrochemical emissions.**
The study is based on an integrated approach measurements/simulations of pollution dispersal to characterise the sources acting on the area.

**Meteorology and analysis of the main emissions in Brindisi**
- (emission inventories and chemical profiles)

**Model simulations**
- **Large scale** (regional) BOLCHEM model.
- **Local scale**, ADMS-Urban.
In both cases models have been used to investigate the ships and harbour contributions to atmospheric pollution.

**Analysis of experimental data**
- **Low temporal resolution** using the receptor model Positive Matrix Factorization (PMF) to evaluate the contribution of the different sources to PM2.5 concentrations.
- **High temporal, resolution** to investigate the harbour contribution to atmospheric aerosol.

**Evaluation of air quality and of the role of the harbour.**

**Information for guidelines on harbour environmental management and for analysis of future scenarios.**
The emission inventory has been performed by ARPA Puglia. It is based on INEMAR (a database developed by a consortium of Italian regions). The resolution is at the municipality level.

During the CESAPO project it has been done the update of the emission inventory from 2007 to 2010 with specific focus on harbours.

Shipping and harbour compared with the other emissions in Brindisi municipality YEAR 2010

- **CO2**: Maritime traffic 2010 0.4% | Other emission total 2010 99.6%
- **COV**: Maritime traffic 2010 3% | Other emission total 2010 97%
- **NOx**: Maritime traffic 2010 9% | Other emission total 2010 91%
- **PTS**: Maritime traffic 2010 16% | Other emission total 2010 84%
- **SO2**: Maritime traffic 2010 12% | Other emission total 2010 88%
An Intensive Observation Period (IOP) was performed between June and October 2012.
The minimum and maximum average concentrations were observed inside the harbour areas.

Limited correlations (coefficients lower than 0.7) were observed between the measuring stations located inside the harbour area.
SOURCE APPORTIONMENT OF PM2.5 USING POSITIVE MATRIX FACTORIZATION (PMF)
The site was devoted to the collection of daily PM2.5 samples for source apportionment object of another presentation.

Two high volume samplers (one with wind selection capability) were used for collection of 48-72 hours samples for the determination of PHAs concentrations. Samples were collected on PUF and quartz filters. Fifteen of the EPA priority PAHs were determined in gas and particulate phase on the two samplers. Characterisation of PAHs was conducted with a quadrupole mass-spectrometer.
The 102 samples were analysed using the Positive Matrix Factorisation receptor model (EPA 3.0) to characterise the contribution to PM2.5 of the different sources.

**Two crustal contributions.** One characterised by **Al, Fe and Mn** (16.4% of PM2.5) and the other associated to **crustal carbonates** (7.7% of PM2.5 - the area is characterised by limestone).

**Biomass burning/fires contribution,** characterised by **K⁺** (11.7% of PM2.5) and presents especially in the first three weeks of July.

**Two industrial contributions.** One characterised by **Ni and V** (15.3 % of PM2.5) and the other by **Sb and Cr** (0.4 % of PM2.5).

**Marine contribution** (15.3 % of PM2.5)

**Road traffic** (16.4 % of PM2.5)

**Ammonium sulphate** (27.3% of PM2.5)

The PMF reasonably reconstruct 97.8% of measured concentrations.

\[
y = 0.97 \pm 0.04 x + 10 \pm 600 \\
R^2 = 0.87
\]
The V/Ni ratio is higher in the wind directions mainly influenced by ship traffic with respect to wind direction influenced by urban/industrial area. This likely indicates a mixed source.

A method to estimate ship contribution is the formula:

\[ PM_a = \frac{<r> \cdot V_a}{<F_{V, HFO}>} \]

\[ 8205.8^* \quad 65 \pm 20 \]

PRIMARY CONTRIBUTION OF SHIP TRAFFIC TO PM\(_{2.5}\): 2.8%
The “edge” is a measure of the maximum amount of oil combustion particles which are expected per unit contribution of nss-SO$_4^{2-}$. There appears to be 0.55 μg/m$^3$ of sulphate for every 1 μg/m$^3$ of primary oil combustion particles.

Using the slope of this edge it is possible to estimate that oil combustion contributes for 1.3 μg/m$^3$ to nss-SO$_4^{2-}$ (about 40% of total nss-SO$_4^{2-}$). This correspond to about 11% of PM2.5.
INFLUENCE OF HARBOUR-INDUSTRIAL AREA ON PAHs CONCENTRATIONS
### Sampling Phase Average (ng/m$^3$) Partitioning

<table>
<thead>
<tr>
<th>Sampling</th>
<th>Phase</th>
<th>Average (ng/m$^3$)</th>
<th>Partitioning</th>
</tr>
</thead>
<tbody>
<tr>
<td>All directions (360°)</td>
<td>Gas phase</td>
<td>3.49 (0.57 – 10.98)</td>
<td>18% GAS, 82% PARTICULATE</td>
</tr>
<tr>
<td></td>
<td>Particulate phase</td>
<td>0.78 (0.23 – 1.65)</td>
<td>82% GAS, 18% PARTICULATE</td>
</tr>
<tr>
<td>Harbour-industrial area</td>
<td>Gas phase</td>
<td>3.98 (0.66 – 7.82)</td>
<td>30% GAS, 70% PARTICULATE</td>
</tr>
<tr>
<td></td>
<td>Particulate phase</td>
<td>1.74 (0.14 – 4.24)</td>
<td>70% GAS, 30% PARTICULATE</td>
</tr>
</tbody>
</table>

ΣPAHs from 360° sampling (Q$_{360}$ for h$_{360}$ hours)

**Evaluation of general effect of harbour-industrial area on PHAs concentrations**

\[ \chi = \frac{Q_{P,h}}{Q_{P,h} + Q_{A,h}} = \frac{Q_P}{h_P} + \frac{Q_{360} - Q_P}{h_{360} - h_P} \]

ΣPAHs from harbour sampling (Q$_p$ for h$_p$ hours)
<table>
<thead>
<tr>
<th>PAH</th>
<th>Average (%)</th>
<th>Range (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphtylene</td>
<td>81.6</td>
<td>(9.5 – 100.0)</td>
</tr>
<tr>
<td>Acenaphtene</td>
<td>97.9</td>
<td>(80.7 – 100.0)</td>
</tr>
<tr>
<td>Fluorene</td>
<td>92.9</td>
<td>(52.9 – 100.0)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>46.4</td>
<td>(10.9 – 100.0)</td>
</tr>
<tr>
<td>Anthracene</td>
<td>41.4</td>
<td>(0.0 – 100.0)</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>16.3</td>
<td>(5.0 – 23.6)</td>
</tr>
<tr>
<td>Pyrene</td>
<td>25.1</td>
<td>(7.1 – 45.5)</td>
</tr>
<tr>
<td>Benzo[a]Anthracene</td>
<td>6.9</td>
<td>(0.5 – 16.8)</td>
</tr>
<tr>
<td>Chrysene</td>
<td>10.4</td>
<td>(2.9 – 21.9)</td>
</tr>
<tr>
<td>Benzo[b]Fluoranthene</td>
<td>9.0</td>
<td>(1.1 – 19.8)</td>
</tr>
<tr>
<td>Benzo[k]Fluoranthene</td>
<td>10.7</td>
<td>(1.3 – 32.4)</td>
</tr>
<tr>
<td>Benzo[a]Pyrene</td>
<td>30.2</td>
<td>(14.0 – 46.8)</td>
</tr>
<tr>
<td>Benzo[ghi]Perylene</td>
<td>11.9</td>
<td>(0.4 – 27.8)</td>
</tr>
<tr>
<td>Indeno[1,2,3-c,d]Pyrene</td>
<td>32.2</td>
<td>(0.0 – 100.0)</td>
</tr>
<tr>
<td>Dibenzo[a,h]Anthracene</td>
<td>10.2</td>
<td>(0.0 – 100.0)</td>
</tr>
<tr>
<td><strong>ΣPAHs</strong></td>
<td><strong>55</strong></td>
<td><strong>(29 – 87)</strong></td>
</tr>
</tbody>
</table>

The concentration of Benzo[a]Pyrene is within the legislation level both at ASI site and and the Terminal Passeggeri in the harbour area.

Total PAHs (particulate+gas).

The direct effect of the harbour-industrial area is quite variable and depending on the congener studied.
INFLUENCE OF SHIP EMISSIONS ON PM2.5 AND PARTICLE NUMBER CONCENTRATIONS
SITE 2 (HARBOUR) - DESCRIPTION

This site was a Mobile Laboratory devoted to high temporal resolution measurements for the analysis of harbour pollution sources.

- A **micrometeorological station** based on a 3D ultrasonic anemometer (Gill R3 AT 100Hz);
- A pDR-1200 photometer was used to measure **PM2.5 concentration** (at 1Hz).
- A condensation particle counter CPC Grimm 5.403 was used to measure **(at 1 Hz) the number concentration of particles** with radius between 10 nm and 1000 nm. The air inlet of the CPC was dried using a device specifically built.
- A DOAS remote-sensing system used for the evaluation of **NO₂ and SO₂ emissions** associated to ship traffic.
- A network video-camera (Axis 221) used to monitor the ships moving in the area and to **synchronise data with ship traffic**.
In several periods the wind direction was compatible (WNW-ENE) with a possible contribution to measured concentrations.

<table>
<thead>
<tr>
<th>PM2.5</th>
<th>Number concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(µg/m³)</td>
<td>(part / cm³)</td>
</tr>
<tr>
<td>16.6</td>
<td>14400 (9060 std. dev.)</td>
</tr>
</tbody>
</table>
The diurnal pattern of particle number concentrations shows two peaks correlated with ship traffic.

The contribution of ship-related emissions appears often between arrival and departure and often are superimposed to emissions during hostelling and loading/unloading activities.
CONTRIBUTION OF SHIP TRAFFIC AND HARBOUR-RELATED EMISSIONS

\[ \Delta_P = C_{DP} - C_{DSP} \]

Average concentration associated to wind direction in the sector WNW-ENE with simultaneous presence of ship emission influence.

Average concentration associated to the wind direction in the sector WNW-ENE without influence of ship emissions.

\[ F_P \quad \text{Frequency of the 30-mins periods influenced by ship.} \]

\[ C_D \quad \text{Average concentration associated to winds from the WNW-ENE sector.} \]

\[ \epsilon = \frac{(C_{DP} - C_{DSP})F_P}{C_D} = \frac{\Delta_P F_P}{C_D} \]

Direct average contribution of ship emissions to atmospheric concentrations in relative. Contini et al., J. Environmental Management, 92, 2119-2129, 2011.

<table>
<thead>
<tr>
<th>PM2.5</th>
<th>Particle number conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only ship traffic</td>
<td>7.4% (± 0.4%)</td>
</tr>
<tr>
<td>Ship traffic + hostelling and loading/unloading periods</td>
<td>9.3% (± 0.5%)</td>
</tr>
</tbody>
</table>

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MODELS USED

Large scale model

BOLCHEM that includes the meteorological model BOLAM, SAPRAC90 for chemical and AERO3 for aerosol.

Nested grids. One grid (resolution 0.25°x0.25°) covering all Italy and a second grid (0.06° x 0.06°) covering all the Apulia region. About 6 km resolution.

Two runs. One including all sources and the second eliminating the emissions associated to the harbour. This allows the determination of harbour primary and secondary contributions to atmospheric concentrations in the area studied.

Local scale model

ADMS-Urban.

Emissions. It include the emissions of ships in the harbour during the manoeuvring and hotelling phases and the output is compared with measured data from the monitoring stations.

The output area is 13 km x 7 km with a spatial resolution of 130m x 70m (100x100 grid points).

No chemical reactions. This allows the determination of harbour primary contributions to atmospheric concentrations in the area studied.
LARGE SCALE MODEL RESULTS

monthly average (July)

spatial resolution: ~6km x 6km

Average relative contribution to concentrations in the Brindisi area:

- NO\textsubscript{X} ~ 40\%-45\%
- PM\textsubscript{10} ~ 10\%-15\%
- PM\textsubscript{2.5} ~ 15\%-20\%

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RESULTS OF LOCAL SCALE MODEL

**spatial resolution:** ~130m x 70m

<table>
<thead>
<tr>
<th></th>
<th>%</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NOx</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Via Taranto</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Casale</td>
<td>9</td>
<td>16</td>
</tr>
<tr>
<td>Via dei Mille</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Terminal</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>Perrino</td>
<td>34</td>
<td>42</td>
</tr>
<tr>
<td>Average</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td><strong>PM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Via Taranto</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Casale</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Via dei Mille</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Terminal</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Perrino</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Average</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

- Larger contributions in the monitoring stations closer or within the port area.
- Average contributions of shipping emissions to mean concentrations are in the range **11-20% for NOx**.
- Primary contributions are in the range **5-6% of PM** in the harbour and decreasing rapidly at distances of a few km.
<table>
<thead>
<tr>
<th>Sito</th>
<th>PM2.5 or PM10</th>
<th>Particle Number</th>
<th>Fonte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brindisi</td>
<td>7.4% (± 0.4%)</td>
<td>26.5% (± 0.5%)</td>
<td>Risultati CESAPO</td>
</tr>
<tr>
<td>Venezia (3 sites)</td>
<td>1- 8 %</td>
<td>-</td>
<td>Contini et al., J. Environmental Management, 92, 2119-2129, 2011</td>
</tr>
<tr>
<td>Venezia (Sacca Fisola)</td>
<td>3.5% (± 1%)</td>
<td>6% (± 1%)</td>
<td>Report for Venice port authority – Season 2012</td>
</tr>
<tr>
<td>Halifax (Canada)</td>
<td>3.4 %</td>
<td>-</td>
<td>Gibson et al., Atmos. Chem. Phys. Discuss., 13, 4491–4533, 2013</td>
</tr>
<tr>
<td>Cork (Irland)</td>
<td>1.5 %</td>
<td>18%</td>
<td>Healy et al., Atmos. Chem. Phys. 10, 9593-9613, 2010</td>
</tr>
<tr>
<td>Melilla (Spain)</td>
<td>2%</td>
<td>-</td>
<td>Viana et al., Environmental Science and Technology 43, 7472-7477, 2009</td>
</tr>
<tr>
<td>Algeciras (Spain)</td>
<td>3 - 7 %</td>
<td>-</td>
<td>Pandolfi et al., Environmental Science and Pollution Research, 18, 260-269, 2011</td>
</tr>
<tr>
<td>California (10 sites)</td>
<td>1.4 - 8.8 %</td>
<td>-</td>
<td>Agrawal et al., Environ. Sci. Technol. 43, 5398-5402, 2009.</td>
</tr>
<tr>
<td>England, Italy and Portugal</td>
<td>5 - 10 %</td>
<td>-</td>
<td>Simulations. Fagerli e Tarrason (2001). Preliminary estimate from EMEP/MSC-W, requested by DG Environment</td>
</tr>
</tbody>
</table>
PMF source apportionment of PM2.5 at ASI site (1.4 km from the harbour) indicated the presence of eight factors/sources (2 of industrial origin). The primary contribution of shipping was 2.8%. The secondary contribution of oil combustion to nss-sulphate was about 40% corresponding to 11% of PM2.5.

Inside the harbour the primary contribution of ship traffic to PM2.5 was 7.4 ± 0.4% (becoming 9.3 ± 0.5% if hostelling and loading/unloading phases are included).

The average direct contribution of ship traffic to particle number was 26.5 ± 0.5% (becoming 39 ± 1% if hostelling and loading/unloading phases are included).

Large and local scale models showed that harbour and ships contribution to NOx and SO₂ is larger with respect to the contribution to aerosol. Primary contribution to PM2.5 is relevant near the harbour area and it is quickly decreasing with distance but secondary contributions appears to interest a much larger area.

At ASI site (1.4 km from harbour) the direct effect of harbour-industrial area to total (gas+particle) PHAs concentrations was 55% and presents a strong dependence on the congener studied.
THANKS FOR YOUR KIND ATTENTION

Acknowledgements

I wish to thank all the members of the research groups at ISAC-CNR, University of Salento and ARPA Puglia that worked at this work.

Many thanks to Dr. Aldo Tanzarella and his staff at Brindisi Port Authority for the data of ship traffic in Brindisi and the help in the logistic of the measurement campaign.

Many thank to Dr. G. Savoia and his staff at Consorzio ASI for logistic support and for hosting some of the instruments.

Many thanks to MarineTraffic.com for the information on ship traffic and typologies in Brindisi.
Il metodo per la valutazione del FRE è descritto in Premuda et al. 2011 (Atmospheric Environment 45, 5212-5219) e si basa sull’equazione:

\[ F_j = \sum_i (CL)_{i,j} \cdot \Delta z_i \cdot \bar{u}_j \cdot \text{sen} \beta_j \cdot \cos \vartheta_i \]

- **\( F_j \)**: flow rate del gas attraverso la j-sezione verticale esaminata;
- \((CL)_{i,j}\) è il valore del i-esimo spessore ottico del gas nel piano j-esimo;
- \(\Delta z_i\) è l’incremento verticale tra la i- e la i-1 misura;
- \(\bar{u}_j\) è la velocità media del vento alla j-esima sezione;
- \(\beta_j\) è l’angolo azimutale tra il j-piano e l’asse del pennacchio;
- \(\theta_i\) è l’angolo tra la direzione della i,j-misura ed il piano di terra.
05/08/2012

**Arrivi**
- 7:00 Blue ferry
- 7:30 Red ferry
- 19:00 Yellow ferry
- 19:00 black ferry

**Partenze**
- 1:15 Black ferry
- 2:15 yellow ferry
- 12:00 red ferry
- 18:15 blue ferry

<table>
<thead>
<tr>
<th>FRE giornaliero</th>
<th>SO₂ (kg)</th>
<th>NO₂ (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dati misurati diurni</td>
<td>62.1</td>
<td>165.1</td>
</tr>
<tr>
<td>Stima sulle 24 ore</td>
<td>115</td>
<td>326</td>
</tr>
</tbody>
</table>

Emissione giornaliera media dei traghetti nel periodo di misura