Impact of Air Pollution on heritage sites

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Cultural Heritage at Risk

Black crust on Marble
Milan Cathedral

Flood – Troja,
Prague

Pluvial
Flooding -
Ferrara
Cathedral

Megalithic
Temples,
Malta
Cultural Heritage at Risk

AEOLIAN ISLANDS
WORLD HERITAGE SITE
Safeguarding Cultural Heritage at Risk

• To encourage the **sharing and appreciation** of Europe's cultural heritage as a **shared resource**;
• To raise awareness of **common history and values**;
• To reinforce a sense of belonging to **Europe**; and
• To better **protect, safeguard, reuse, enhance, valorise and promote** Europe's cultural heritage.
## Air Pollution impact on Heritage

<table>
<thead>
<tr>
<th>DAMAGE PROCESS</th>
<th>OUTDOOR MATERIALS MAINLY AFFECTED</th>
<th>CLIMATE PARAMETERS</th>
<th>POLLUTANTS</th>
</tr>
</thead>
</table>
| SOILING, BLACK CRUST FORMATION | • Marble  
• Limestone  
• Sandstone with carbonate matrix  
• Air-setting and hydraulic mortar  
• Cement mortar and concrete  
• Glass | • Rain amount  
• Time of wetness (T, RH)  
• Light | • Soluble salt fraction of PM (SO$_{4}^{2-}$, SO$_{3}^{2-}$, NO$_{3}^{−}$, NO$_{2}^{−}$, Br$^{-}$, HPO$_{4}^{2−}$, Cl$^{−}$, CHO$_{2}$, C$_{2}$H$_{5}$O$_{2}$ AND C$_{2}$O$_{4}^{2−}$)  
• VOC |

Black crust formation on surfaces partially sheltered from rain wash-out

- **Rain and Humidity**
- **Gas and aerosol deposition**
- **SO$_{2}$ oxidation**
- **H$_{2}$SO$_{4}$**
- **Gypsum formation**

- **Microscopic aspect**
- **Black crust**
- **Marble/limestone**

Carbonaceous particles
# Air Pollution impact on Heritage

<table>
<thead>
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<th>POLLUTANTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marble</td>
<td>Marble</td>
<td>Rain amount</td>
<td>SO\textsubscript{2}</td>
</tr>
<tr>
<td>Limestone</td>
<td>Limestone</td>
<td>Rain pH</td>
<td>HNO\textsubscript{3}</td>
</tr>
<tr>
<td>Sandstone</td>
<td>Sandstone with carbonate matrix</td>
<td>Time of wetness (T, RH)</td>
<td>CO\textsubscript{2}</td>
</tr>
<tr>
<td>Air-setting and hydraulic mortar</td>
<td>Cement mortar and concrete</td>
<td></td>
<td>PM, PM\textsubscript{10}, PM\textsubscript{2.5}</td>
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<tr>
<td></td>
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<td>SO\textsubscript{2}</td>
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<td>NO\textsubscript{2}</td>
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<td>PM, PM\textsubscript{10}, PM\textsubscript{2.5}</td>
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<tr>
<td></td>
<td>Marble</td>
<td>Light</td>
<td>HNO\textsubscript{3}</td>
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<td></td>
<td>Limestone</td>
<td></td>
<td>CO\textsubscript{2}</td>
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<td></td>
<td>Sandstone with carbonate matrix</td>
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<td>PM, PM\textsubscript{10}, PM\textsubscript{2.5}</td>
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<td></td>
<td>Air-setting and hydraulic mortar</td>
<td></td>
<td>Soluble salt fraction of PM (SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-}, Br\textsuperscript{-}, HPO\textsubscript{4}\textsuperscript{2-}, Cl\textsuperscript{-}, CHO\textsubscript{2}, C\textsubscript{2}H\textsubscript{3}O\textsubscript{2} AND C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-})</td>
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<tr>
<td></td>
<td>Cement mortar and concrete</td>
<td></td>
<td>VOC</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td></td>
<td>VOC</td>
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<tr>
<td></td>
<td>Carbonate and silicate stones</td>
<td></td>
<td>VOC</td>
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<tr>
<td></td>
<td>Air-setting and hydraulic mortar</td>
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<td>VOC</td>
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<tr>
<td></td>
<td>Cement mortar and concrete</td>
<td></td>
<td>VOC</td>
</tr>
<tr>
<td></td>
<td>Wood</td>
<td></td>
<td>VOC</td>
</tr>
<tr>
<td>Metals: steel, zinc, copper, bronze, lead</td>
<td></td>
<td></td>
<td>VOC</td>
</tr>
<tr>
<td>Sandstone</td>
<td>Sandstone</td>
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<td>VOC</td>
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<tr>
<td>Limestone</td>
<td>Limestone</td>
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<td>VOC</td>
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<tr>
<td>Air setting and hydraulic mortar</td>
<td>Cement mortar and concrete</td>
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<td>VOC</td>
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<tr>
<td>Brick</td>
<td>Brick</td>
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<td>VOC</td>
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</tbody>
</table>

Rain amount, Rain pH, Time of wetness (T, RH), Light, PM, PM\textsubscript{10}, PM\textsubscript{2.5} mean that they are dependent on the weather conditions and the pollutants in the air.
SURFACE RECESSION OF CARBONATE STONES

Material dissolution due to the chemical attack induced by:

1. **Clean rain** (rain at pH 5.6 in equilibrium with 330 ppm CO$_2$ – karst effect)

2. **Acid Rain** (additional acidity due to anionic components, such as SO$_4^{2-}$, NO$_3^{-}$……)

3. **Dry deposition** (gaseous pollutants occurring between precipitation events)

Material surface erosion due to the mechanical effect of rain

\[ \text{Acid Rain} \]

\[ \text{HNO}_3 \]

\[ \text{H}_2\text{SO}_4 \]

Dry deposition

\[ \text{SO}_2 \]

\[ \text{NO}_x \]

“Gutta cavat lapidem”
Surface recession is expected to be higher in the areas that will be more affected by precipitation, that are the mountain chains (Alps, Carpathians, Pyrenees) and the westerlies exposed areas, reaching values higher than 30 µm/year.

Bonazza et al. 2009. STOTEN
Coastal areas of Mediterranean Basin

Coastal areas are complex and fragile eco-cultural-systems that need specific consideration for their best preservation.

Observing the UNESCO World Heritage Map is noticeable the abundance of cultural heritage sites (in orange) that raise on the littoral zones.
Heritage in Coastal areas of Mediterranean Basin

COASTAL AREAS (monuments, landscapes, etc.)

Siracusa (Italy)

Tourism and commercial sectors

UNDERWATER HERITAGE (monuments/ecosystems)

Christ of the Abyss – San Fruttuoso (Genoa, Italy)

Baia (Naples, Italy)
Global ship emissions for various chemical species ($SO_2$, $SO_4^{2-}$, CO, NO$_x$, EC, CO$_2$, OC, NMVOCs, ash)
SO$_2$ emissions of transport sector in Italy (from ISPRA report)

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<tbody>
<tr>
<td>Cars</td>
<td>61.375</td>
<td>26.233</td>
<td>4.953</td>
<td>1.296</td>
<td>225</td>
<td>223</td>
<td>227</td>
<td>235</td>
<td>244</td>
<td>215</td>
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<tr>
<td>Light duty vehicles</td>
<td>16.518</td>
<td>11.720</td>
<td>2.529</td>
<td>450</td>
<td>84</td>
<td>88</td>
<td>82</td>
<td>70</td>
<td>72</td>
<td>53</td>
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<tr>
<td>Heavy duty vehicles &amp; bus</td>
<td>50.006</td>
<td>32.798</td>
<td>4.342</td>
<td>611</td>
<td>107</td>
<td>113</td>
<td>104</td>
<td>105</td>
<td>96</td>
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<tr>
<td>Mopeds and motorcycles</td>
<td>2.404</td>
<td>890</td>
<td>163</td>
<td>57</td>
<td>9</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>10</td>
<td>8</td>
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<tr>
<td>Trains</td>
<td>846</td>
<td>545</td>
<td>69</td>
<td>7.3</td>
<td>0.9</td>
<td>0.7</td>
<td>0.8</td>
<td>0.6</td>
<td>0.3</td>
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<tr>
<td>Inland navigation</td>
<td>119</td>
<td>91</td>
<td>11</td>
<td>1.9</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
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<tr>
<td>Aviation (LTO)</td>
<td>243</td>
<td>291</td>
<td>448</td>
<td>345</td>
<td>524</td>
<td>497</td>
<td>478</td>
<td>453</td>
<td>490</td>
<td>497</td>
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<tr>
<td>TOT</td>
<td>211.651</td>
<td>143.940</td>
<td>100.102</td>
<td>52.513</td>
<td>29.332</td>
<td>27.472</td>
<td>24.826</td>
<td>23.372</td>
<td>23.325</td>
<td>21.942</td>
</tr>
</tbody>
</table>

Fonte: ISPRA

[Bernetti, Contaldi and Sestili, 2017]
SO\textsubscript{2} emissions in port-cities

According to POSEIDON Project, which monitored ship emission in four port-cities, Brindisi and Venice (Italy), Patras (Greece) and Rijeka (Croatia), it was highlighted that the road traffic and maritime sector had comparable emissions especially for NO\textsubscript{x} and PM\textsubscript{2.5}, while shipping was noticed as the transport sector mainly responsible for SO\textsubscript{2} emissions.

Comparison of relative emissions associated to maritime and road transport in four port cities

[E. Merico et al. 2017]
Pollution in coastal cities

- Concentration of air pollutants monitored by the Regional Agency for Environmental Protection of Italy:

Legend:
UT = urban traffic-oriented monitoring stations
UB = urban background monitoring stations
How can naval traffic affect Cultural Heritage?

Materials carbonate based:
- Limestone
- Marble
- Sandstone with carbonate matrix
- Air-setting and hydraulic mortar, etc.

- **Sulfation by** $\text{SO}_2$ → **BLACK CRUSTS FORMATION**
  - Limestone to gypsum
  - Deposition of soot
  - Rain partially sheltered

- **SURFACE RECESSION**
  - Rainwashed areas
  - May be white

- **SALTS CRYSTALLIZATION**
Different approaches to study the impact of pollution on Cultural Heritage in coastal areas

- **LAB SIMULATION STUDY**
  - FIELD EXPOSURE TESTS
  - CASE STUDY

On sandstone in Belfast (UK)

«...the mobility of gypsum may have been enhanced by the presence of NaCl...»

- **SAMPLES FROM HISTORICAL BUILDING** → e.g. Bilbao

«...Nitrate is the major soluble compound of the analysed subsamples...are supposed to come from harbour traffic (combustion of fuels) as well as from fuels used in industrial processes...»

- **FIELD EXPOSURE TESTS**
  - e.g. ARQUEOMONITOR Project –ES → field exposure tests of metallic and stone samples underwater in Cadiz Bay

[http://arqueologianauticaysubacuatica.uca.es/arqueomonitor/; Camara et al., 2017]
FINAL REMARKS

- Need of enhancing the consciousness regarding the importance of protection of coastal natural & cultural heritage

- Ship emissions can affect the state of conservation of the materials belonging to cultural heritage, in particular buildings and outdoor monuments

- Need of mitigation strategies aiming at reducing emissions (Mediterranean ECA)

- Still lack of studies regarding the naval impact on underwater heritage
Thank you for your attention
What kind of emissions can be produced by ships?

**AIR EMISSIONS**

- **Macropollutants:**
  - $SO_2$, $NO_x$, CO, $CO_2$ and $O_3$
  - Particulate matter (PM) — ! Black Carbon (BC)
  - Non-Methane Volatile Organic Compounds (NMVOCs)

- **Micropollutants:**
  - Metals
  - Organic species

- **Other**
  - Incineration of waste
  - Noise
  - Visual pollution

**DISCHARGE TO SEA**

- Sewage (black water)
- Grey water
- Oil and oily mixtures
- Wash water from scrubbers
- Garbage
- Ballast water

Recent and Relevant EU Projects on ship emissions

Financed by the European program for territorial Cooperation MED 2007/2013:

- **APICE 2010 – 2013 - Common Mediterranean strategy and local practical Actions for the mitigation of Port, Industries and Cities Emissions**
  The aim of the project was to develop a knowledge-based approach for air pollution mitigation and sustainable development of port activities, managed by spatial planning policies at local level, which included the territory around the ports.
  [http://www.apice-project.eu/](http://www.apice-project.eu/)

- **CAIMANs 2014-2015 - Cruise and passenger ship Air quality Impact Mitigation ActioNs**
  The project studies the impact of passenger maritime traffic on air quality in five important port cities in the northern Mediterranean: Barcelona, Marseilles, Genoa, Venice and Thessaloniki.
  [http://www.medmaritimeprojects.eu/section/caimans](http://www.medmaritimeprojects.eu/section/caimans)

- **POSEIDON 2014-2015 - Pollution monitoring of ship emissions: an integrated approach for harbours of the Adriatic basin**
  The POSEIDON project aimed at investigating the impact on air quality of four major harbours in the Adriatic/Ionian Seas (Brindisi, Patras, Rijeka and Venice), using a common state-of-the-art methodology based on emission inventories, numerical modelling and experimental results in order to produce comparable information useful to plan future actions and controls of emissions in the Adriatic/Ionian macroregion.
  [http://www.medmaritimeprojects.eu/section/poseidon](http://www.medmaritimeprojects.eu/section/poseidon)