MeSmarT – Measurements of Shipping Emissions in the Marine Troposphere
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• Outline of the project “MeSmarT”
• Measurement techniques and sites
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## Motivation

### What is air pollution?

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Sources</th>
<th>Health Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO, NO₂ (Nitrogen Oxides)</td>
<td>Fuel combustion, wood burning</td>
<td>Lung diseases, respiratory symptoms</td>
</tr>
<tr>
<td>SO₂ (Sulfur Dioxide)</td>
<td>Fuel combustion (especially high-sulfur fuel), industrial processes, volcanoes</td>
<td>Aggravates asthma, respiratory symptoms</td>
</tr>
<tr>
<td>PM (Particulate Matter)</td>
<td>Emitted directly or formed through chemical reactions, fuel combustions, industrial processes</td>
<td>Heart and lung diseases, potentially carcinogenic, premature mortality</td>
</tr>
<tr>
<td>O₃ (Ozone)</td>
<td>Formed by chemical reaction</td>
<td>Aggravates lung diseases and asthma, premature death</td>
</tr>
<tr>
<td>CO (Carbon Monoxide)</td>
<td>Fuel combustion</td>
<td>Reduces amount of oxygen in body’s organs and tissues, aggravates heart diseases</td>
</tr>
</tbody>
</table>
Motivation

Air pollution caused by shipping emissions:

• Increase of international trade volume and shipping
• Concentration of shipping emissions in coastal areas and harbor cities (20 % within 12 nm – Zone)
• Considerable contribution to local air pollution with severe health effects
Motivation

Shipping emission NO$_2$ - measurements by satellite

Motivation

Political measures:

Sulfur fuel content regulation

Nitrogen oxides emission regulation

SECA zones Europe and worldwide

MeSmarT – Measurements of Shipping Emissions in the marine Troposphere
• How is the actual situation of air pollution over the North and Baltic Sea and what is the contribution of shipping emissions?
• How do the political regulations influence the air quality?
• How can we assure the quality of our measurements?
• Is it possible to reproduce measured data with state-of-the-art modelling?
Outline of the project MeSmarT

- How is the actual situation of air pollution over the North and Baltic Sea and what is the contribution of shipping emissions?
- How do the political regulations influence the air quality?
- How can we assure the quality of our measurements?
- Is it possible to reproduce measured data with state-of-the-art modelling?

- How can we observe and control the compliance of the shipping emission regulations?
- Which measurement methods are suitable for this?
Remote sensing: MAX-DOAS

**Multi-Axis Differential Optical Absorption Spectroscopy**

- Detection of column densities of trace gases for different optical paths
- Vis spectrometer (400 – 570 nm) for NO₂ measurements
- UV spectrometer (315 – 385 nm) for SO₂ measurements
## Measurement methods

### In-situ-measurements: Airpointer (MLU)

<table>
<thead>
<tr>
<th></th>
<th>SO$_2$</th>
<th>NO, NO$_2$, NO$_x$</th>
<th>O$_3$</th>
<th>CO$_2$</th>
<th>Non-Dispersive IR-Spectroscopy LI-COR LI820</th>
</tr>
</thead>
<tbody>
<tr>
<td>Messprinzip:</td>
<td>UV-Fluoreszenz (EN 14212)</td>
<td>Chemiluminesz von NO (EN 14211)</td>
<td>UV-Absorption (EN 14625)</td>
<td>Non-Dispersive IR-Spectroscopy LI-COR LI820</td>
<td></td>
</tr>
<tr>
<td>Detection limit</td>
<td>0.25 ppb</td>
<td>0.4 ppb</td>
<td>0.5 ppb</td>
<td>1 ppm</td>
<td></td>
</tr>
<tr>
<td>Measuring range</td>
<td>&lt; 10 ppm</td>
<td>&lt; 20 ppm</td>
<td>&lt; 200 ppm</td>
<td>&lt; 20000 ppm</td>
<td></td>
</tr>
<tr>
<td>Time period</td>
<td>&lt; 90 s</td>
<td>&lt; 60 s</td>
<td>&lt; 30 s</td>
<td>1 s</td>
<td></td>
</tr>
</tbody>
</table>
Measurement sites

MeSmarT – Measurements of Shipping Emissions in the marine Troposphere
Resarch vessel cruises


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Resarch vessel cruises


NO$_2$ in situ

NO$_2$ DOAS

commons.wikimedia.org

B. Mathieu-Üffing

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Research vessel cruises


MeSmarT – Measurements of Shipping Emissions in the marine Troposphere
Research vessel cruises

Unique data set:
- Different seasons
- Different weather conditions
- Different air mass origins

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Measurements in Wedel

29.4.2013 – 3.7.2013

MeSmarT – Measurements of Shipping Emissions in the marine Troposphere
Measurements in Wedel


MeSmarT – Measurements of Shipping Emissions in the marine Troposphere
Analysis of sulfur content in fuel

Formula for Sulphur content in fuel:

\[
\% S_{in\ fuel} = \frac{\Delta SO_2}{\Delta CO_2} \cdot 0,232
\]

Tuttle et. al., 1995
Williams et. al., 2006
Moldanova et. al., 2009

Example:
For first ship emission peak shown:

\[
\% S_{in\ fuel} = \frac{12 \text{ ppb}}{3,5 \text{ ppm}} \cdot 0,232 = 0,79 \pm 0,11\%
\]

(Caution: Measurement uncertainty : 15% according to Berg et. al. 2012)
Analysis of sulfur content in fuel

Example for 4 Peaks shown in graph:
1.): \((0.79 \pm 0.11)\) %S in fuel
2.): \((0.56 \pm 0.08)\) %S in fuel
3.): \((0.92 \pm 0.13)\) %S in fuel
4.): \((0.29 \pm 0.04)\) %S in fuel

Example for 23 Peaks of 2 days:
Measurements on the island Neuwerk

Since 5.7.2013

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Measurements on the island Neuwerk

Since 5.7.2013

Ship Emissions

Konzentration in ppb

CO2-Konzentration in ppm
Measurements on the island Neuwerk

Lisa Kattner
Filter analysis

- Gravimetric analysis of PM10
- Ion chromatography for anions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$) and cations (NH$_4^+$, Na$^+$, K$^+$, Ca$^{++}$, Mg$^{++}$)
- ICP-MS (Inductively Coupled Plasma Mass Spectrometry) for elemental analysis, especially V, Ni, Fe (tracer for shipping emissions)
- Organic carbon (TOC) and elemental carbon (EC)
- GC-MS (gas chromatography mass spectroscopy) for Polycyclic aromatic hydrocarbons (PAH)
Outlook

- Aircraft measurements Uni Bremen:

- Modelling (Volker Matthias, HZG Geesthacht)

- comparison with Satellite data
• MeSmarT project objectives:
  • Examine the influence of shipping emissions on the marine atmosphere over the North and Baltic Sea
  • Find a way to controll the emission regulations
• Two methods: remote sensing and in-situ measurements
• First results of research cruises: mapping air pollution
• Measurements in Wedel: Investigating single ship plumes and determining sulfur content in ship fuel
• Measurements in Neuwerk: Combining measurements of clean marine background air and single ship plumes
Thank you!

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