Identifying Sources and Chemical Composition of Particulate Matter Using Single Particle Mass Spectrometry

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PARTICULATE MATTER (PM)

Collection of solid and/or liquid materials in various sizes, from a few nanometres (virus) to 100 micrometres (human hair)

PM$_{10}$: concentration of particles $\leq$ 10 $\mu$m diameter
PM$_{2.5}$: concentration of particles $\leq$ 2.5 $\mu$m diameter

EU limits

<table>
<thead>
<tr>
<th>PM$_{2.5}$</th>
<th>25 $\mu$g/m$^3$</th>
<th>1 year (averaged)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{10}$</td>
<td>40 $\mu$g/m$^3$</td>
<td>1 year (averaged)</td>
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<tr>
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<td>50 $\mu$g/m$^3$</td>
<td>24 hours (averaged)</td>
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**RECENT PM POLLUTION**

**March 2014**
Stagnant weather conditions → pollution accumulation
Air quality worse than many Asian cities
Traffic major contributor → attempt to reduce PM by alternating odd/even licence plates cars on roads

**Six years of PM data**
But Paris maximum still low compared to Beijing pollution!
Data from monitoring station on US embassy shows PM2.5 at unhealthy levels most of the time...WELL above EU limit.

http://www.theguardian.com/environment/2014/mar/17/paris-worse-air-pollution-beijing

SELECT CITY AIR QUALITY INDEX READINGS
FRIDAY MARCH 14, 2014

<table>
<thead>
<tr>
<th>City</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paris</td>
<td>185</td>
</tr>
<tr>
<td>Beijing</td>
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<td>Hong Kong</td>
<td>166</td>
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<td>Shenzhen</td>
<td>153</td>
</tr>
<tr>
<td>New Delhi</td>
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<tr>
<td>Lahore</td>
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<td>New York</td>
<td>51</td>
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<tr>
<td>LA</td>
<td>34</td>
</tr>
<tr>
<td>SF</td>
<td>24</td>
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<tr>
<td>Seattle</td>
<td>13</td>
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</tbody>
</table>

Beijing PM2.5 measure, highest value for every day 1,000 μg/m³

Since April 2008 there have been at least 1,812 days where air quality in Beijing has reached at least "unhealthy" levels. There have only been two days on which levels did not exceed "good."

Data from: US Department of State
Inhalation of PM can affect the respiratory tract

- Depends on *size* and *composition*

PM$_{10}$ & larger usually lodge in nose & throat
Irritation → hay fever

PM$_{2.5}$ → Combustion particles (solid fuel, traffic, etc.) reach alveoli aggravating asthma, chronic bronchitis, lung cancer, etc.
Viruses too → cold & flu

*International Agency for Research on Cancer* classified PM as carcinogenic to humans (Oct. 2013)
CLIMATE

DIRECT EFFECT

Scatter or absorb incoming solar radiation & re-radiated energy from earth’s surface

- Depends largely on particle chemical composition e.g. sulfates (cooling) vs. carbonaceous (warming)

INDIRECT EFFECT

Can act as cloud condensation nuclei → clouds scatter back solar radiation

*Intergovernmental Panel on Climate Change (IPCC), 5th Assessment Report, 2013*
**PARTICULATE MATTER SOURCES**

**PM<sub>2.5</sub>**
- Traffic exhaust
- Coal/peat/wood combustion (industrial/commercial/domestic)

**Components**
- Elemental carbon (soot)
- Organic carbon (e.g. PAHs $\rightarrow$ benzene $\rightarrow$ carcinogenic)
- Secondary species e.g. nitrate, sulfate $\rightarrow$ gas condensation onto particles

**PM<sub>10</sub>**
- Dust (road, quarrying, Saharan)
- Sea salt

**Components**
- Silicates, iron, calcium
- Sodium chloride, magnesium
- Secondary species e.g. nitrate, sulfate $\rightarrow$ gas condensation onto particles
PHD OBJECTIVE

Since health & climate effects dependent on chemical composition of PM:

Determine chemical composition of PM$_{2.5}$ at several locations and identify emission sources using source-specific chemical markers

Using single particle mass spectrometry
**Internal & external mixing state:**
- Elemental & organic carbon
- Metals
- Sodium chloride (sea salt)
- Nitrate
- Sulfate

**Particle Size Range (~PM2.5)**
- 100 nm → 3000 nm
Typical Mass Spectra

Wood Combustion (Combustion)

Elemental Carbon (Combustion)
Data Analysis

Several weeks at sampling location

A few hundred thousand mass spectra...

Algorithm
($K$-means)

Similar mass spectra grouped into particle classes

- Time series
- Size distributions
- Wind direction dependence

Source Identification
PARIS

How much of a city’s PM2.5 is local?

MEGAPOLI → European megacity study
(first international deployment of this ATOFMS)

RESULT → 20% combustion particles transported
→ contributes towards EU limit....

PhD Work Overview

Simplified ATOFMS Composition
Particle Types & Counts

Dunkerque

Industrial emissions

Particle Types & Counts:
- Sea salt: 38%
- K-containing: 33%
- Other metals: 2%
- OC: 1%
- PAH: 1%
- Fe-containing: 5%
- Ca-containing: 3%
- V-containing: 2%
- Min-containing: 1%

Haulbowline

Particle Types & Counts:
- Peat: 22%
- Coal: 15%
- Wood: 17%
- Traffic: 8%
- Sea Salt: 13%
- EC: 15%
- PAH: 2%

Wood burning & Dust

Corsica

Particle Types & Counts:
- EC: 54.1%
- Sea salt: 8.0%
- K-containing: 30.1%
- TMA-containing: 2.6%
- OC: 1.6%
- Others: 0.2%
- Ca-containing: 0.4%
- Shipping: 1.2%
- Fe-containing: 0.4%
Some ambient particles match chimney samples \( \rightarrow \) others from steel-manufacturing plant.

Metal-rich particle classes (Ca, Fe, Al, Mn, Zn)

Weather conditions good for transporting particles from GMF to site.
**Ambient vs Sample**

Internally mixed Mn, Fe, K, Al

**MATCH:** Ore sample & ambient

Ambient Mn particles accumulated nitrate during transport to site

Internally mixed Fe, K, Al, Na

**NO MATCH**

No Mn → neighbouring steel manufacturer
Differentiate between combustion & dust particles

Identify

- different sources (Europe vs. Sahara)
- different air masses & meteorological conditions

ChArMEx

CORSICA

WORK IN PROGRESS

Sea salt

Biomass burning event
NE. Italy

Transported dust
Sea salt

Small combustion particles
Large dust particles
Size Matters!

One particle class $\rightarrow$ based on composition = biomass burning

*BUT* different size distributions during different periods

= different sources
SUMMARY

Transported particles play large role in local air quality!

→ Paris impacted by emissions outside the city → industrial emissions from Benelux.

→ Confirmed presence & mixing states of particles in emission plume from industrial facility.
   (& which meteorological conditions required for transport to sampling site)

→ Distinguished particles coming from ferromanganese facility vs. steel manufacturing plant.
   (compared field measurements to chimney samples)

→ Identified transport of regional combustion & dust around the Mediterranean.
   (work in progress on probable sources e.g. Sahara, NE. Italy, PO Valley)
ACKNOWLEDGEMENTS