Sources contribution to the oxidative potential of PM$_{10}$ at 15 French sites

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Introduction – air quality and OP

Aerosols are highly diverse

What proxy(ies) for air quality?
- Mass,
- Number,
- Size,
- Shape,
- Chemistry,
- ...

Integrative one:
The **oxidative potential (OP)** of PM
~ability of PM to generate ROS

Adapted from Pinazo-Durán et al. (2013)

Micrographies from USGS, UMBC (Chere Petty) & Arizona State University (Peter Buseck). Credit: NASA earthobservatory [https://earthobservatory.nasa.gov/Features/Aerosols/](https://earthobservatory.nasa.gov/Features/Aerosols/)
Motivation & objectives

**Univariate correlation OP vs chemistry is not causality**

**Inversion by sources (road traffic, BB, ...)**

→ explanatory variables: concentration in $\mu$g m$^{-3}$ of source per day.

- « Aggregate » chemistry informations (~species covariation).
  Few proxies allow identifying main PM sources

- More relevant for regulation and epidemiological studies.

- Need pre-treatment (e.g. PMF), so adding uncertainties.

- Need an inter-comparaison of a "similar" source at different sites
Simultaneous measurement of OP and chemistry

- Numerous research programs through (inter-)national collaborations
- Unique database
  - 16000 filters samples
  - 82 stations
  - Between 2011 and 2019
  - Up to >130 species
- OP measurements
  - DTT, AA, DCFH
  - SLF: Gamble + DPPC
  - Isomass
  - >5800 samples.
How to proceed?

**STEP 1: PM SOURCES (PMF)**
- Aggregate chemistry (quinone, etc)
- ~10 explanatory variables
- Regulation purposes

**OP** \(_{\text{obs}}\) = \(\sum_i \text{OP}_i \times \text{PM}_i\)

**STEP2: OP SOURCES**
- Linear mixing model (adapted WLS)
- Bootstrapping \(\rightarrow\) uncertainties
- Intrinsic OP of a source
  (=OP per \(\mu g/m^3\) of PM source)

**Let applicate it in Chamonix**
- PMF: 8 sources
- Year: 2013-2014 (~120 samples)
- OP: DTT & AA

**Method & application in Chamonix:** Weber et al 2018, ACP
https://doi.org/10.5194/acp-18-9617-2018
Introduction

OP source-apportionment in Chamonix

Synthesis 15 sites

Example in Chamonix, France – model validation

Model close to observations

8 sources explain 94% of the OP variance

Method & application in Chamonix: Weber et al 2018, ACP
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**Introduction**

**OP source-apportionment in Chamonix**

**Synthesis 15 sites**

**Example in Chamonix, France – model results**

Err. bars: std 1000 bootstraps

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**Coefficient β of the regression**

![Graph showing coefficient β for different sources]

**Different coefficients → different “intrinsics” OP**

β × [source]

**Redistribution of the sources weight → novel view of the aerosol**

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**Method & application in Chamonix:** Weber et al 2018, ACP

[https://doi.org/10.5194/acp-18-9617-2018](https://doi.org/10.5194/acp-18-9617-2018)
Generalization – the SOURCES program

SOURCES project
- PMF at 15 sites
- Between 2013 to 2016
- Min 1 year, 1 every 3rd day
- 2148 samples
- Advance chemical speciation
- Similarity assessment (deltaTool)
  + other programs

Results → [http://pmsources.u-ga.fr/](http://pmsources.u-ga.fr/)

Are sources’ intrinsic OPs stable at regional scale? What are the sources’ contributions to OPs?

15 PMF, comparison, uncertainties, similarity assessment: Weber et al 2019, Atmosphere
[https://doi.org/10.3390/atmos10060310](https://doi.org/10.3390/atmos10060310)
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Generalization – synthesis of intrinsic OP (OPI)

**Intrinsic OP** (= OP/µg of PM) → “toxicity” of the source

- 3 tests with different reactivities
- OP DTTv: more homogeneous.
- OP AAv: BB & traffic.
- OP DCFHv ???

- Low dispersion within a given source (most of the time).
- **Geochemical sens**
- ≠ to investigate (chemistry?)

At a national scale, aerosols sources present different reactivities.

*Weber et al, 2019. in prep...*
High variability of intrinsic OP for the road traffic. Why?

Hypothesis:
Traffic = wide chemistry...
→ direct/indirect emissions
→ strong & fast reactivity: f(d, hv, ...)
→ fine & coarse
→ ...

Road traffic
≠ chemistry ↔ ≠ OP
Ok

Nitrate rich
= chemistry ↔ = OP
Ok

Biomass burning
= chemistry ↔ ≠ OP
?
3 tests – 3 results: DTT ~homogeneous, AA BB++ (& traffic), DCFH BB (& industrial / Ø traffic)

Some local sources contribute significantly to OP (HFO, Industrial)

OP\textsuperscript{DTT}: Importance of PBOA & SOA / Nitrate rich barely contribute

Important differences. Which one is “the best”??
Conclusion & perspectives

- Unique database of **coupled** advanced chemistry and OP measurements
  - >130 species (carbonaceous, ions, metals, organics…)
  - 3 OP assays (DTT, AA, DCFH), isomass, using simulated lung fluid
  
  [Calas, 2017]  
  [Calas et al, 2019, submitted]

- Detailed **source-apportionment study** (15 sites, still ongoing)
  - SOURCES program: [http://pmsources.u-ga.fr](http://pmsources.u-ga.fr)

  [Weber et al, 2019, atmosphere]

- Development of **OP source-apportionment** based on PMF results

  [Weber et al, 2018, ACP]
  [Weber et al, 2019, in prep]

- Application at the national scale
  - Novel view of aerosols
  - **Redistribution of the sources contribution**

What’s next?

- Need to understand intrinsic OP variability for some sources
- What OP assays is “the best”? → Epidemiology & toxicology
- Toward OP in CTM
Thank you for your attention!

...and to all the people who made it possible.
Introduction

OP source-apportionment in Chamonix

Synthesis 15 sites

State of the art

- Different a-cellular OP measurements (mostly DTT, AA, DCFH)
- Univariate statistic (correlation)
  - DTT: balanced between metals & organics
  - AA sensible to metals & OC
  - But correlation is not causality (levo, NO₃…).
    We need multivariate approaches.
- Multivariate statistic (ACP, k-means, MLR…)
  - Few studies with source-apportionment (see review Bates et al, 2019)
  - Rapid increase in past few years (Verma et al, 2014 ; Bates et al, 2015 ; Fang et al, 2016 ; Ma et al, 2017…)
  - Mostly focused on BB and traffic: chamber measurement & field sampling

However:

There is a need of long time monitoring together with assessment of the diversity of sources and investigation the spatial variability.
Toward spatio-temporal model and prediction

- WIP: Use of source-tracking CTM (LOTOS-EUROS)
- Confrontation CTM / PMF
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