Oxidative Potential of PM_{10} in the Arve Valley (France) – comparison of different acellular assays.

Nanosafe2016

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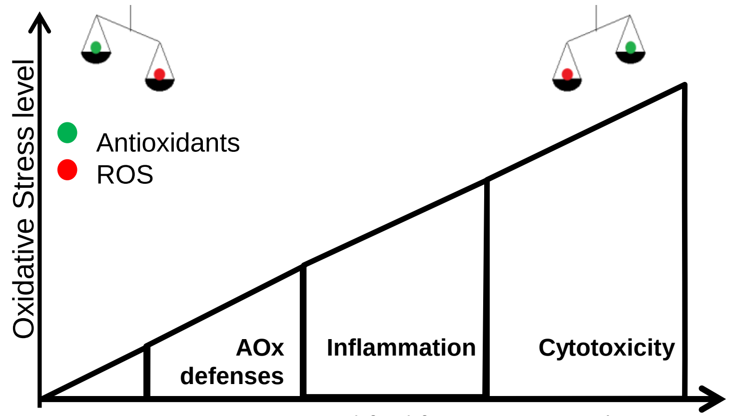
Exposure to PM:

- Adverse health effects (cardiovascular/respiratory diseases, asthma…)

Hypothesis : PM induce or carry Reactive Oxygen Species (ROS) → Oxidative Stress.

- PM have an Oxidative Potential (OP).



Modified from Baeza et al. 2007

PM regulation metric : based on PM concentrations (PM_{10} , $PM_{2,5}$ …)

- Not ideal : most of PM mass consists of low toxicity components (sea salt, crustal dust…) and conversely for trace elements.
- OP, metric for PM toxicity?

Several OP assays exist:

- *In vivo* assays
- *In vitro* cellular assays
- ***In vitro* acellular assays.**

1- Respiratory Tract Lining Fluid assay (RTLF): King's College London

- Monitoring depletions (simultaneous) of real lung anti-Ox : Glutathione (GSH), Ascorbic acid (Asc.), urea (UA)
- Multiple Anti-Ox - % consumption

2- DTT (Dithiothreitol) assay: IGE – Grenoble

- Depletion of an Anti-Ox surrogate
- + Bioaccessibility (Simulated Lung Fluid)
- Single Anti-Ox – kinetic measurement

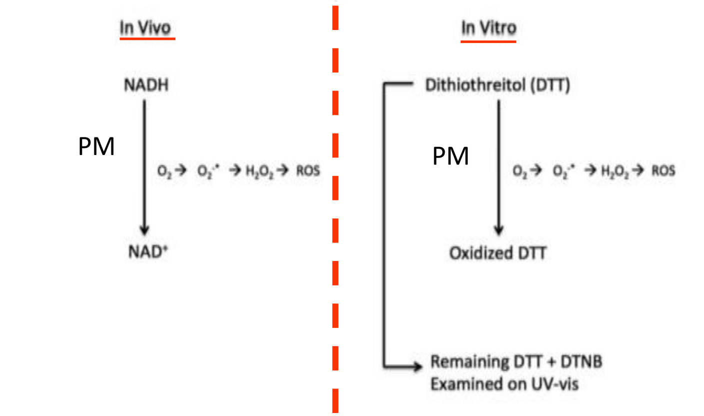
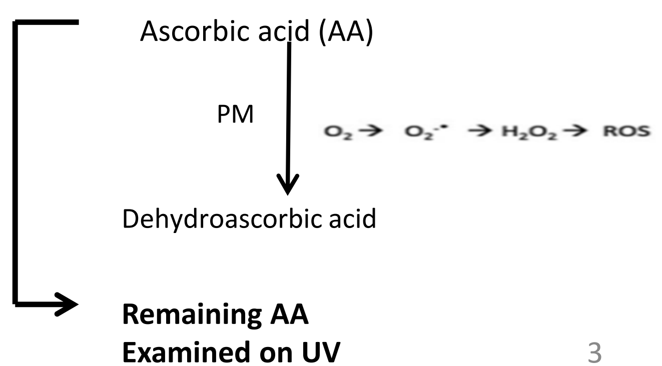


Fig. 1 DTT reaction mechanism and its resemblance to the NADH transformation in cells to generate ROS.

Modified from Nicolas et al. 2015

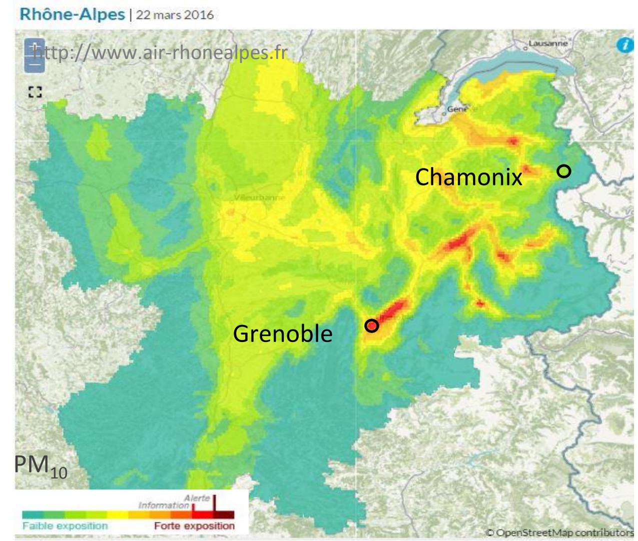
3- AA (Ascorbic Acid) assay: IGE - Grenoble

- Depletion of a single lung Anti-Ox
- + Bioaccessibility (Simulated Lung Fluid)
- Single Anti-Ox – kinetic measurement

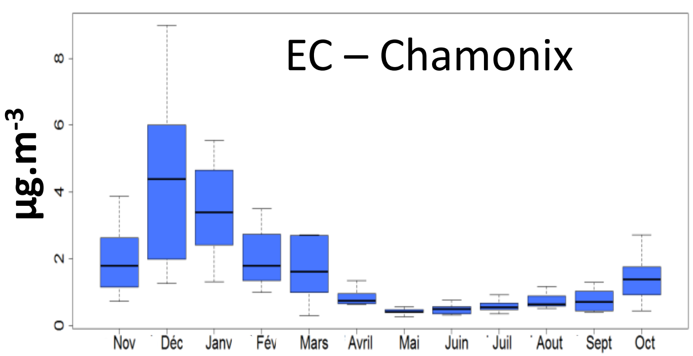


PM samples from the Arve Valley (Chamonix Valley) :

French Alpine Valley, which frequently presents high PM concentrations



Strong seasonality of the chemical composition of PM (monthly average – 1 sample every three days):



- 1 year sampling (Nov 2013 - Oct 2014)

Three locations (Chamonix, Passy, Marnaz)

- On each PM sample (1 every 3 days):

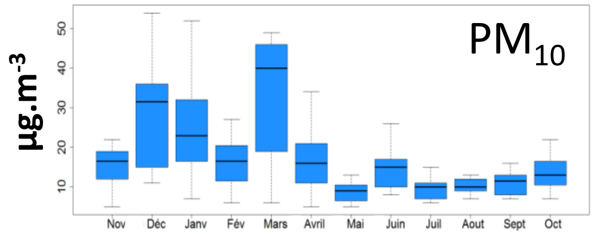
Large chemical speciation of the PM (160 species analyzed)
3 acellular assays tested

OP seasonal dynamics (Chamonix)?

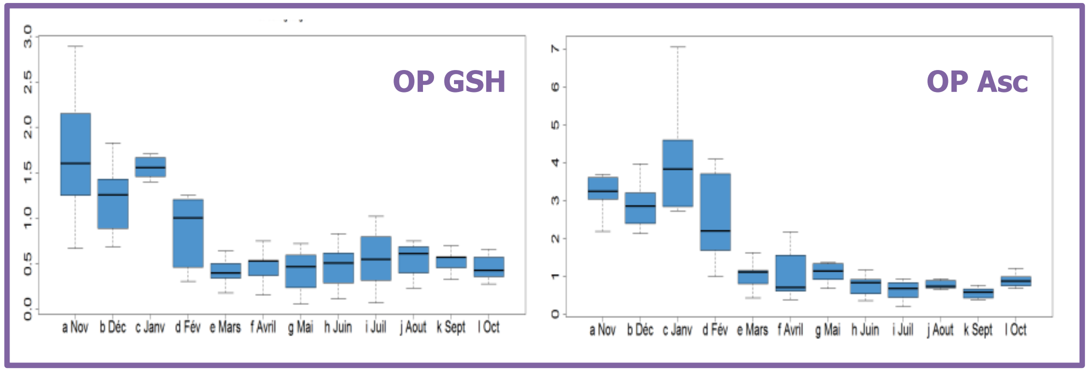
1- Respiratory Tract Lining Fluid assay (RTLF): King's college London

2- DTT (Dithiothreitol) assay: IGE - Grenoble

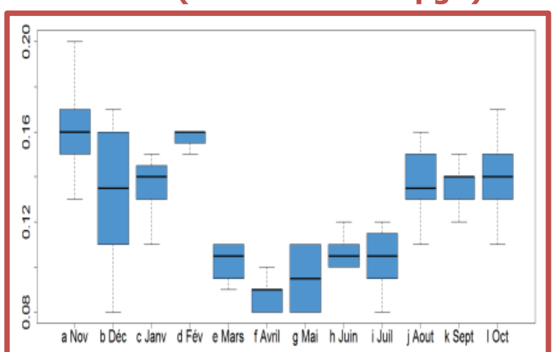
3- AA (Ascorbic Acid) assay: IGE - Grenoble



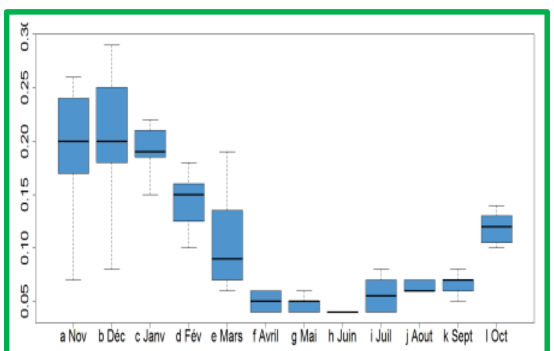
OP RTLF (% Antioxidant consumption.µg^{-1})



OP DTT (nmol DTT.min^{-1}.µg^{-1})



OP AA (nmol DTT.min^{-1}.µg^{-1})



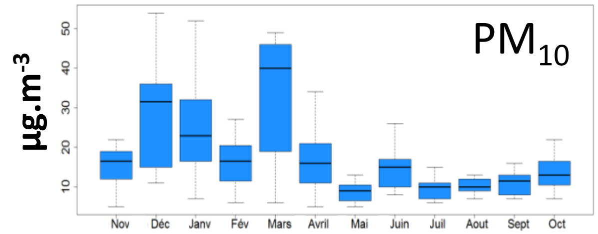
OP normalized by PM mass (µg^{-1}): Representative of PM chemical composition

Seasonal dynamics of the OPs
Chemical composition?

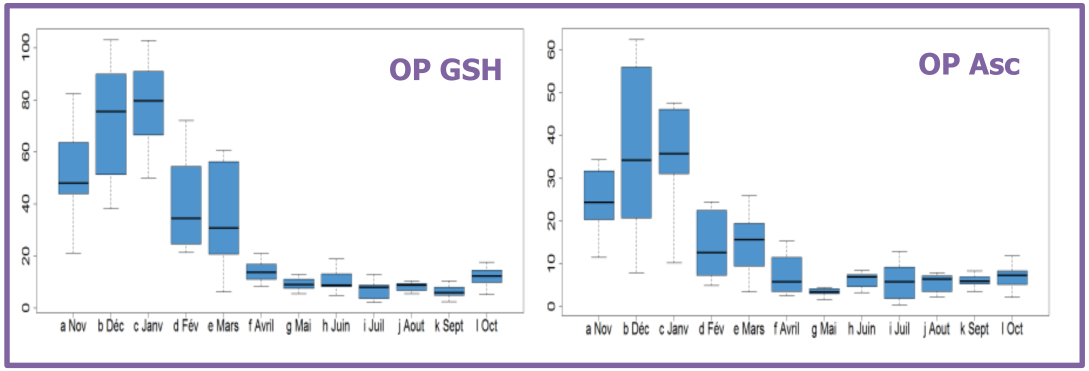
+ differences in function of the assay (DTT vs the other) :
Assay specificity?

OP seasonal dynamics (Chamonix)?

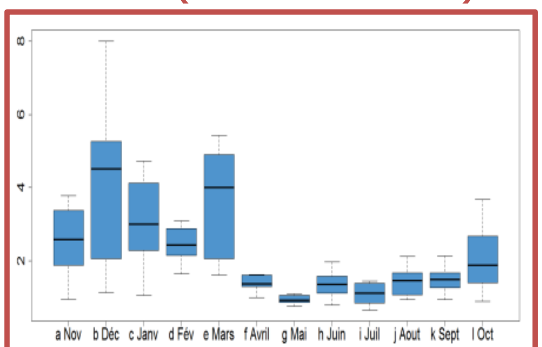
1- Respiratory Tract Lining Fluid assay (RTLF): King's college London
2- DTT (Dithiothreitol) assay: IGE - Grenoble
3- AA (Ascorbic Acid) assay: IGE - Grenoble



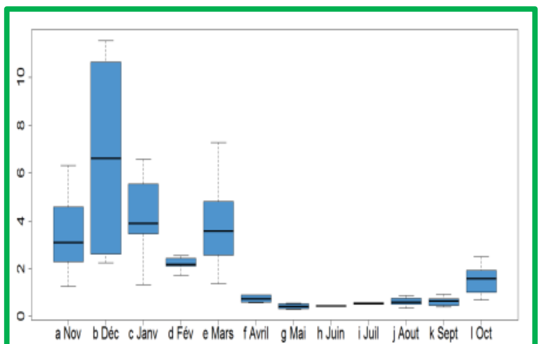
OP RTLF (% Antioxidant consumption.m^{-3})



OP DTT (nmol DTT.min^{-1}.m^{-3})



OP AA (nmol DTT.min^{-1}.m^{-3})



OP normalized by air volume (m-^{3}):
Representative of human exposure

- Significant seasonal dynamics of the OP (as for some chemical species)
- Large evolutions over the year (higher for OP than for PM_{10})

Related to PM chemical composition ?

OP more pertinent than PM_{10} regarding PM toxicity?

Spearman correlation OPs, PM_{10} and chemical composition (Chamonix).

Spearman correlation coefficients (* p-value<0.02) (DJF)

r	OP_{GSH} m^{-3}	OP_{Asc} m^{-3}	OP_{DTT} m^{-3}	OP_{AA} m^{-3}	PM_{10}
OP GSH m-3					
OP Asc m-3	0.92*				
OP DTT m-3	0.85*	0.74*			
OP AA m-3	0.92*	0.82*	0.88*		
PM10	0.80*	0.76*	0.93*	0.86*	
EC	0.90*	0.85*	0.91*	0.89*	0.91*
OC	0.91*	0.92*	0.89*	0.92*	0.92*
Cl	0.72*	0.54*	0.80*	0.80*	0.71*
NO3	0.45*	0.53*	0.56*	0.45*	0.67*
SO4	0.73*	0.78*	0.81*	0.73*	0.86*
NH4	0.32	0.46*	0.45*	0.34	0.56*
Cu	0.80*	0.71*	0.88*	0.80*	0.81*
Cr	0.55*	0.51*	0.57*	0.50*	0.51*
Fe	0.56*	0.60*	0.61*	0.57*	0.71*
Mn	0.56*	0.51*	0.70*	0.57*	0.63*
Ni	0.38	0.36	0.59*	0.45	0.54*
Zn	0.81*	0.80*	0.84*	0.80*	0.88*
Levoglucosan	0.92*	0.92*	0.89*	0.93*	0.91*
Sum PAH	0.79*	0.85*	0.84*	0.81*	0.93*
Sum Alkanes	0.47*	0.68*	0.42	0.48*	0.54*
Sum methylPAH	0.42	0.60*	0.47*	0.44*	0.51*
Sum Hopanes	0.44*	0.60*	0.45*	0.46*	0.53*

Cold period: December January February

- Correlations driven by cold period (high PM_{10} concentrations)
- Correlations with not redox active species like PAH, levoglucosan, SO4… → correlations with redox active quinones and metals.
- Good correlation between OP assays during the cold period → high atmospheric concentrations.
- Correlations with biomass burning tracers (PAH, Levoglucosan)

Spearman correlation OPs, PM_{10} and chemical composition (Chamonix).

Spearman correlation coefficients (* p-value<0.02) (JJA)					
r	OP_{GSH} m^{-3}	OP_{Asc} m^{-3}	OP_{DTT} m^{-3}	OP_{AA} m^{-3}	PM_{10}
OP GSH m-3					
OP Asc m-3	0.28				
OP DTT m-3	0.34	0.53*			
OP AA m-3	0.49	0.28	0.82*		
PM10	0.43	0.60*	0.71*	0.53	
EC	0.24	0.31	0.47*	0.64*	0.26
OC	0.49*	0.48*	0.81*	0.64*	0.73*
Cl	-0.43	0.082	-0.56	-0.64	-0.32
NO3	0.23	0.36	0.66*	0.53	0.73*
SO4	0.11	0.12	0.15	-0.41	0.58*
NH4	0.120	0.035	0.13	-0.34	0.41
Cu	0.55*	0.52*	0.79*	0.77*	0.71*
Cr	0.46	0.51*	0.61*	0.64*	0.48*
Fe	0.40	0.090	0.60*	0.63*	0.81*
Mn	0.37	0.57*	0.75*	0.58*	0.90*
Ni	0.40	0.038	-0.025	-0.40	0.54
Zn	0.40	0.41	0.79*	0.66*	0.69*
Levoglucosan	0.26	0.16	0.34	0.52	-0.016
Sum PAH	0.060	0.36	0.51*	0.63*	0.17
Sum Alkanes	0.15	0.42	0.48*	0.39	0.52*
Sum methylPAH	0.0430	0.019	0.30	0.69*	-0.14
Sum Hopanes	0.340	0.52	0.59*	0.55	0.57*

Warm period: June July August

- Different correlations between cold and warm periods:

Lower correlations between OP assays during the warm period
Less correlations between chemical species and OPs
Correlations with traffic tracers (Cu, Hopanes, EC).

- Comparison of the assays:

Correlation differences between the OP_{ASC} (RTLF – King's College London) and OP_{AA} (Single Anti-Ox – Grenoble).
Correlation differences between OP_{GSH} (RTLF) and OP_{DTT} (Grenoble)
→ Because bioaccessibility is taking into account?

Take home message:

- Seasonal dynamics of the OP assays
- Correlations of the OP assays with specific chemical species → source?
- Correlations between the assays when high PM concentrations.
- Strong correlation differences between cold and warm period.
- Contribution of taking bioaccessibility into account?

Work to do :

- Descriptive statistics of OP *vs* Chemistry of PM
- OP *vs* source appointment
- For the different locations

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AO interne LTHE LGGE 2014/Labex

And thank you for your attention