ASSESSMENT OF THE $PM_{2.5}$ OXIDATIVE POTENTIAL IN NORTHERN FRANCE-RELATIONSHIPS WITH CHEMICAL COMPOSITION AND SOURCE CONTRIBUTION

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Introduction

Air pollution caused by particulate matter (PM), has been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC). Toxicological studies proved that PM induced oxidative stress, DNA damage, heart diseases and inflammation in the lung. Northern France is one of the regions that shows exceedance in $PM_{2.5}$ daily concentrations, recommended by the world health organization (25µg/m^3). Oxidative Potential (OP) is known as a health effect potency indicator of the airborne PM, as it estimates the capacity of PM to generate reactive oxygen species (ROS). Compared to cellular tests, a-cellular studies have the advantages of their low cost and simplicity. Ascorbic acid (AA), and Dithiothreitol assay (DTT), are two of the most used tests. The aims of this study were to :
- Estimate the oxidative potential of $PM_{2.5}$ collected in Dunkerque (2010-2011), an industrial site in Northern France, using DTT and AA tests.
- Compare information given by both AA and DTT tests, and study the relationships between OP, $PM_{2.5}$ chemical composition, and contributing sources (local and regional).

Methodology

Sampling site

- Dunkerque (51.0362060N; 2.3794091E).
- Digitel DA80, 30m³/h, 12h.
- 57 selected samples.

- Coastal city in Northern France.
- 210 000 inhabitants.
- Strongly affected by **industrial emissions.**

Chemical characterization

- Water soluble ions: ion chromatography.
- Major and Trace elements: ICP-MS and ICP-AES.
- Total carbon: CHNS/O microanalysis.

OP measurements

a. Extraction solvent

Gamble's solution (pH=7.4)

- Simulates real conditions of bioaccessibility in human lungs.
- Represents the interstitial fluid in the deep lung.

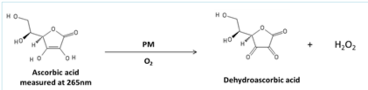
b. Sample preparation

- 1/10 of cellulose filter :1-1.5mg of $PM_{2.5}$
- 14 mL of Gamble's solution (1/50000 <S/L< 1/500) (g/mL).
- Extraction tubes shaken at 37°C for 24 h, 250 rpm.
- Suspensions filtered using 0.45 µm nylon syringe filters before OP measurement.

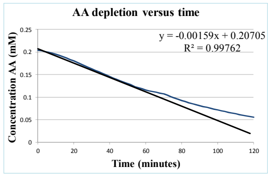
c. OP tests

- **AA :** antioxidant that simulated the respiratory tract lining fluid RTLF.
- **DTT:** simulates reductant species in the cells like NADH.
- Protocols developed in microplates, 96 wells.

AA Depletion

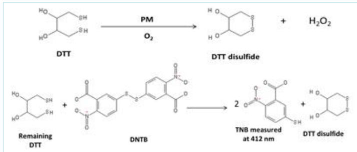


- The redox active species in the particles oxidize AA to dehydroascorbic acid and catalyze the formation of ROS by transferring an electron to oxygen molecules.
- 2h measurement of the AA depletion.
- Slope of the linear part = depletion rate of AA (mM/min).

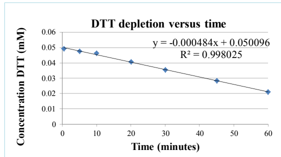


- Oxidative potential expressed considering the depletion rate and the mass of $PM_{2.5}$ (OP-AAm, pmol/min/µg) or air volume (OP-AAv, nmol/min/m^3).

DTT Depletion



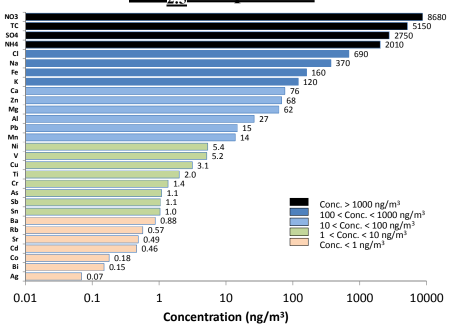
- Redox-active species in PM oxidize DTT to DTT-Disulfide, and catalyze the reduction of oxygen species to ROS like O_2^- and H_2O_2. Remaining DTT reacts with added DTNB, generating DTT-disulphide, and 2-nitro-5- thiobenzoic acid (TNB).



- Remaining DTT is quantified at 7 different times.
- OP-DTTv , OP-DTTm calculated same as AA.

Results

$PM_{2.5}$ composition



NO_3^-, TC, SO_4^{2-}, NH_4^+, Cl^-, and Na consist together 97% of the total analyzed species, and 67.4% of $PM_{2.5}$ mass concentration.

$PM_{2.5}$ Contributing Sources *(Kfoury et al,2016)*

11 emission sources were identified using the constrained weighted-non-negative matrix factorization (CW-NMF).

- Sea salts
- Aged sea salts
- Traffic non exhaust
- Crustal
- Secondary sulfate
- Secondary nitrate
- Heavy fuel oil combustion
- Combustion
- Electric Steel Plant
- Integrated steel work (ISW)-Sintering Stack
- ISW-Fugitive

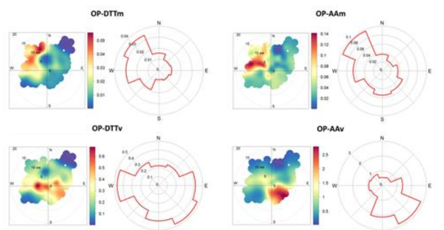
OP values in Dunkerque

OP-DDTv nmol/min/m^3	OP-DTTm pmol/min/µg	OP-AAv nmol/min/m^3	OP-AAm pmol/min/µg	$PM_{2.5}$ µg/m^3
0.36	17.7	1.12	50	29.2

Values are similar to those found in other studies, performed in urban sites in Europe.

OP values and source contribution (local scale)

(Polar plots and concentration roses drawn using R software, Openair package (Carslaw and Ropkins, 2012)).



OP-DTT and OP-AA:

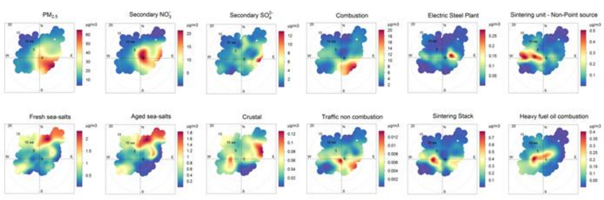
- Different polar plots patterns => not affected by the same sources/species.

Industrial park located in the NW sector:

- **high OP-DDTm and OP-AAm, and low OP-AAv and OP-DDTv values** : =>1 µg of PM coming from the industrial park, has a higher Oxidative Potential than 1 µg of PM coming from other origins, **but 1 m^3 of air coming from the industrial park, has a lower OP than 1 m^3 of air from the urban sector (SE),** especially when considering AA values.

OP-AAv, OP-DTTv, $PM_{2.5}$ and sources polar plots:

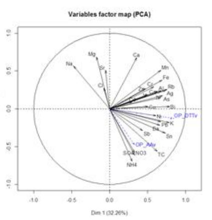
- **OP-AAv**: polar plot pattern similar to $PM_{2.5}$, combustion and traffic non combustion sources.
- **OP-DTTv:**
  - Linked to a higher number of sources.
  - High values in the SE sector, like traffic and combustion's polar plots.
  - High values also in the W sector, similarly to the **ISW sintering stack, sintering unit non-point source**, and **heavy fuel oil combustion** (HFO).



OP values and PM chemical compounds

Principal Component Analysis (variables= analyzed chemical species and supplementary variables =OP values).

	Dim.1	Dim.2	Dim.3	Dim.4	Dim.5
% of variance	32.3	14.8	9.7	8.5	6.4
Cumulative % of variance	32.3	**47.1**	56.7	65.3	71.7
OP-DTTv	**0.84**	-0.13	-0.09	-0.02	0.03
OP-AAv	0.33	**-0.48**	0.17	-0.01	0.02

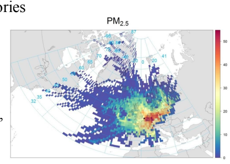


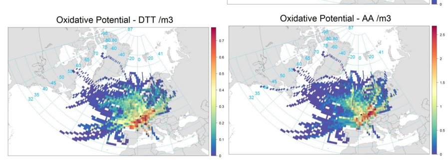
First 2 axes (47% of variance) :
- ✓ **OP-DTTv**: highly associated with the metals (Ni, Pb, Ba, Sn, Bi, Cu mainly).
- ✓ **OP-AAv**: associated with NO_3^-, TC, SO_4^{2-}, NH_4^+, that contribute the most to PM mass.
- ✓ Na, Mg, Cl and Sr (sea salts): no influence on OP values.

OP origin using CWT (regional scale)

Concentration Weighted Trajectories (CWT) parameters :

- Hysplit air mass back-trajectory, final 100m.
- 72h, 1 trajectory every 3h.
- R software, Openair package, Trajlevels.





- OP sources maps slightly different.
- Common sources: France, Belgium, Netherlands, Central Europe.

Conclusion

OP measured using Ascorbic Acid (AA) and Dithiothreitol depletion do not respond to the same species/sources: OP-AA response has been related to the $PM_{2.5}$ major components, as well as $PM_{2.5}$ concentration. Combustion sources, and traffic brake-wear could also play a role in the observed values of OP-AA. OP-DTTv was found to be mainly associated with metal concentrations. As a consequence, OP-DTT and OP-AA do not show similar patterns when considering the wind sector. OP-DTT has been linked to integrated steel works, heavy fuel oil combustion, and traffic non combustion sources. Expressing OP in both mass related and volume related units allows to give complementary information. OP expressed in pmol/min/µg allows to compare the intrinsic oxidative potential of PM emitted by different sources. From a health effect point of view, pmol/min/m^3 is more appropriate. Finally, AA and DTT OP tests appeared to be complementary.

References

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