Sources of Oxidative Potential (OP) in atmospheric PM_{10}, $PM_{2.5}$, and PM_1

A study discovering and identifying the different drivers of OP in North-Eastern Spain

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INTRODUCTION
Particulate Matter

Particulate Matter (PM)

"PM are microscopic particles of solid or liquid matter suspended in the air."

4.5 million premature deaths around the world (7.6% of all deaths) was attributed to high levels of PM in 2016 (WHO, 2018)

PM also has an ecological effect. This includes direct deposition into the soil, which **affect the nutrient cycling**, and its acidic and alkaline content can cause leaf surface injury in plants (Grantz et al., 2003).

These are major concerns as the impact of **PM might increase with climate change**, increasing the impact of PM on the environment and human health (Dias et al., 2012; Ministerio para la Transición Ecológica, 2018).

The WHO has established new guidelines for ambient PM levels, citing PM as the **"single biggest environmental treat to human health"**.

INTRODUCTION
Challenges

Particulate Matter (PM)

"PM are microscopic particles of solid or liquid matter suspended in the air."

The PM has diverse range of source, both Primary and Secondary, and Biogenic and Anthropogenic.

Correlating chemical composition with hazardous human health effects is a challenge.

INTRODUCTION
Oxidative Potential

Measures intrinsic capacity of PM to generate Reactive Oxygen Species (ROS) that can oxidize the lungs.

Good indicator, as studies linked respiratory diseases with ROS.

AA
DTT

Different assays have different sensitivity

DTT (Dithiothreitol) is a balanced assay between transition metals and organic species.
AA (Ascorbic Acid) is more sensitive to specific transition metals (like Cu)

METHODOLOGY
Chemical Speciation

Samples take:
January 2018 – March 2019

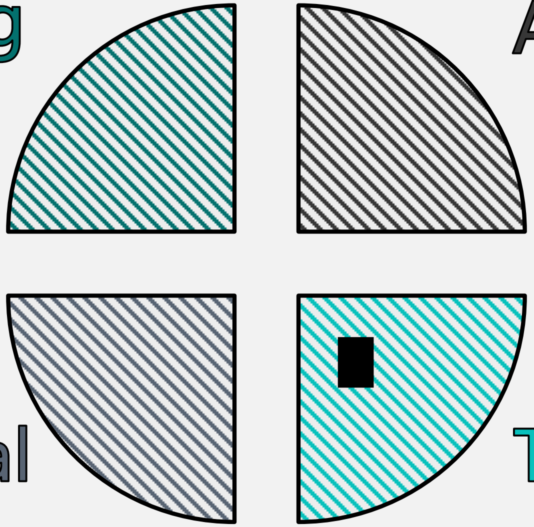
Filter sample take roughly
once every 4 days

Montseny Rural Background Station
41°46'45.63''N, 02°21'28.92''E, 720 m a.s.l

Barcelona Urban Background Station
41°23'14.50"N, 02°06'55.60"E, 68 m a.s.l.

METHODOLOGY
Chemical Speciation

PM Filter



Leaching

NO_3^-, Cl^-, SO_4^{2-} :*Ion Chromatography*

NH_4^+ :*Selective electrode*

Acid Digestion

ICP-AES: Al, Ca, K, Na, Mg, Fe, Ti, P

ICP-MS: Li, Ti, V, Cr, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Cd, Sn, Cs, Ba, La, Ce, Pr, Nd, Hf, Tl, Pb, Bi, Th, U

Oxidative Potential

AA Assay *(Ascorbic Acid)* *DTT Assay* *(Dithiothreitol)*

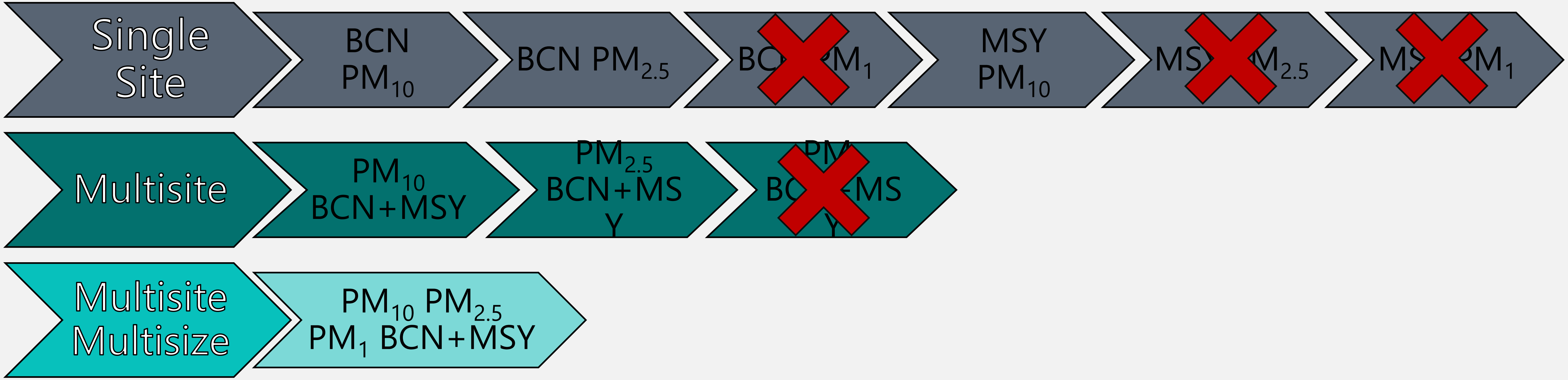
Thermal-Optical Analyzer

OC & EC

METHODOLOGY

Source Apportionment

To obtain the source Positive Matrix Factorization (PMF) was applied



METHODOLOGY

Source Apportionment

OC	**OC-rich source**	Traced by OC
	Mineral	Traced by Al, Ti, Ga, Rb, Li
	Road Dust	Traced by Fe, Cr, Cu, Sn
SO_4	**Secondary SO_4^{2-}**	Traced by SO_4^{2-}, NH_4^+
	Combustion	Traced by EC
	Heavy Oil	Traced by V, Ni
NO_3	**Secondary NO_3^-**	Traced by NO_3^-, NH_4^+
	Sea Spray	Traced by Na, Mg
	Industry	Traced by Pb, Zn, Cd

METHODOLOGY
Source Apportionment

SOURCE	PM_{10} PD	PM_{10} SID	$PM_{2.5}$ PD	$PM_{2.5}$ SID
OC-rich	0.16	0.74	0.08	0.67
Secondary SO_4^{2-}	0.05	0.57	0.05	0.64
Secondary NO_3^-	0.06	0.06	0.02	0.47
Mineral	0.02	0.51	0.03	0.47
Combustion	-	-	0.16	0.70
Sea Spray	0.05	0.65	0.05	0.67
Road Dust	-	-	0.14	0.51
Heavy Oil	0.03	0.67	0.04	0.68
Industry	0.14	0.66	0.09	0.58

PD = Pearson Distance
SID = Similarity Identity Distance

PD — A PD < 0.4 is considered acceptable.

SID — SID < 1 as an acceptable criteria.

Perrone, M.R., Bertoli, I., Romano, S., Russo, M., Rispoli, G., Pietrogrande, M.C., 2019. PM2.5 and PM10 oxidative potential at a Central Mediterranean Site: Contrasts between dithiothreitol- and ascorbic acid-measured values in relation with particle size and chemical composition. Atmos. Environ. 210, 143–155. https://doi.org/10.1016/j.atmosenv.2019.04.047

METHODOLOGY
OP Apportionment

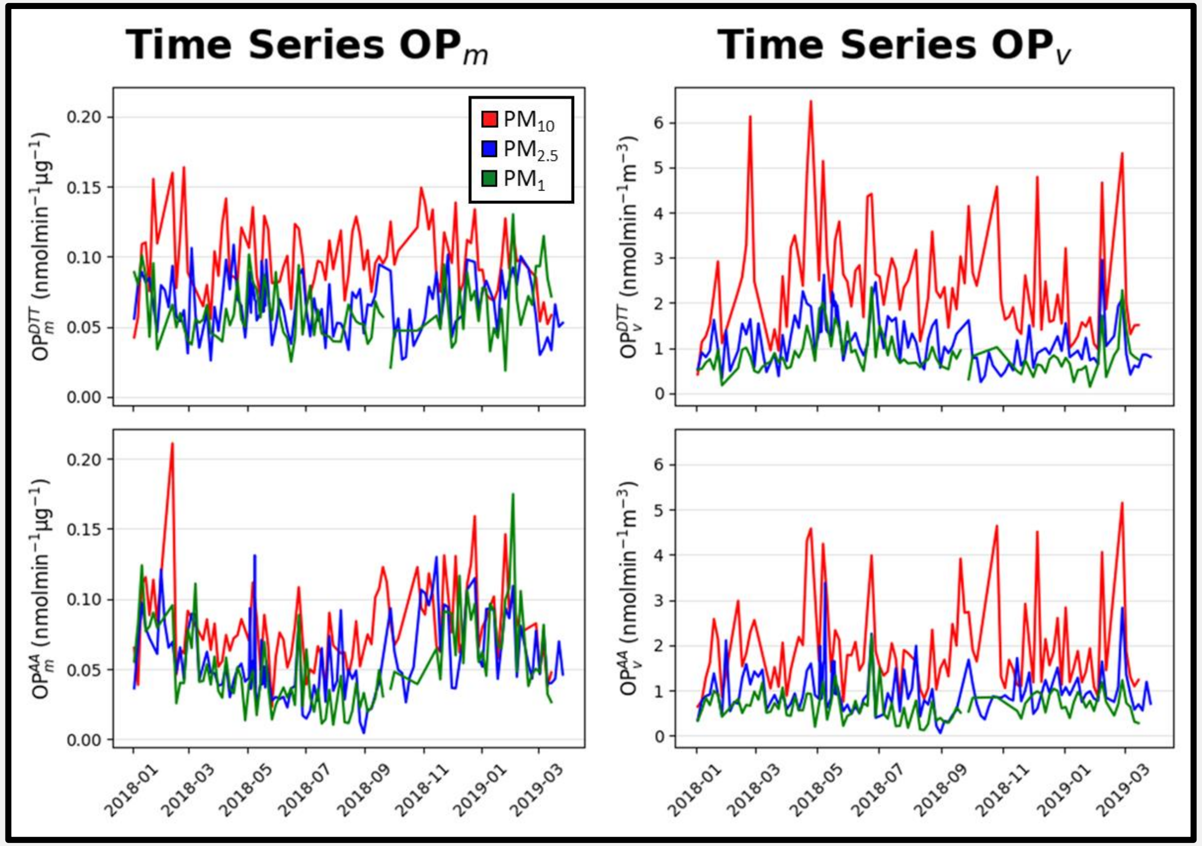
The OP apportionment was done using a **Multiple Linear Regression** (MLR) model, applying **Weighted Least Squared** (WLS)

$$OP_{obs} = \beta_0 + (G_i * \beta_i) + \varepsilon$$

Model was bootstrapped a **1000 times**, randomly selecting **70%** of the samples

Multiplying the **Intrinsic OP** with the **median mass contribution** will determine **the median human exposure**.

RESULTS
Barcelona OP Time Series



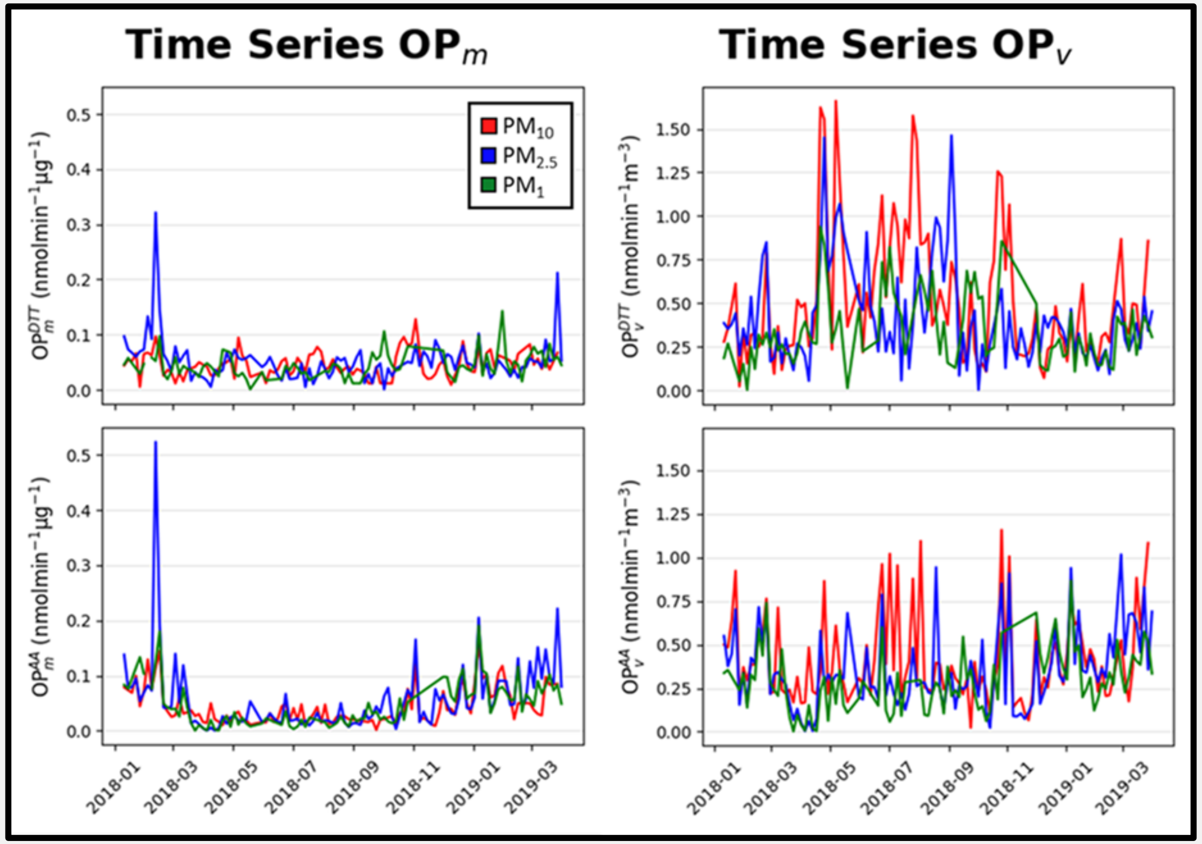
01 No seasonal pattern in either OP_m or OP_v implies that the sources of OP are stable yearlong.

02 The **PM_{10}** levels are significantly higher than **$PM_{2.5}$** and **PM_1**, which were in the same range.

03 This indicated that main drivers in **PM_{10}** and **PM_1**.

RESULTS

Montseny OP Time Series



01 Increase in seasonality

02 The levels of **PM_{10}**, **$PM_{2.5}$**, and **PM_1** are all in the same range.

03 This indicated that main drivers is **PM_1**.

04 The lack of an increase in **PM_{10}** means the **Barcelona PM_{10}** increase is due to **local emission**.

RESULTS

OP Comparison

Site	Country	Type	Year	Reference
Barcelona	ES	Urban Background	Jan 2018 – Mar 2019	This study
Montseny	ES	Rural Background	Jan 2018 – Mar 2019	This study
Passy	FR	Urban Valley	Nov 2013 – Oct 2014	(Weber et al., 2021)
Grenoble	FR	Urban Background	Mar 2017 – Mar 2018	(Weber et al., 2021)
Nogent	FR	Urban Background	Jan 2013 – May 2014	(Weber et al., 2021)
Roubaix	FR	Traffic	Jan 2013 – May 2014	(Weber et al., 2021)
Marseille	FR	Urban Background	Jan 2015 – Dec 2015	(Weber et al., 2021)
Strasbourg	FR	Traffic	April 2013 – April 2014	(Weber et al., 2021)
Chamoix	FR	Urban valley	Nov 2013 – Nov 2014	(Weber et al., 2021)
Nice	FR	Urban traffic	Jul 2014 – May 2015	(Weber et al., 2021)
Aix-en-provence	FR	Urban background	Aug 2013 – Jul 2014	(Weber et al., 2021)
Talence	FR	Urban background	Mar 2012 – Mar 2013	(Weber et al., 2021)
Marnaz	FR	Urban valley	Nov 2013 – Oct 2014	(Weber et al., 2021)
Port-de-bouc	FR	Industrial	Jun 2014 – May 2015	(Weber et al., 2021)
Vif	FR	Urban background	Mar 2017 – Mar 2018	(Weber et al., 2021)
Bern	CH	Urban-Traffic	June 2018 – May 2019	(Grange et al., 2022)
Zürich	CH	Urban	June 2018 – May 2019	(Grange et al., 2022)

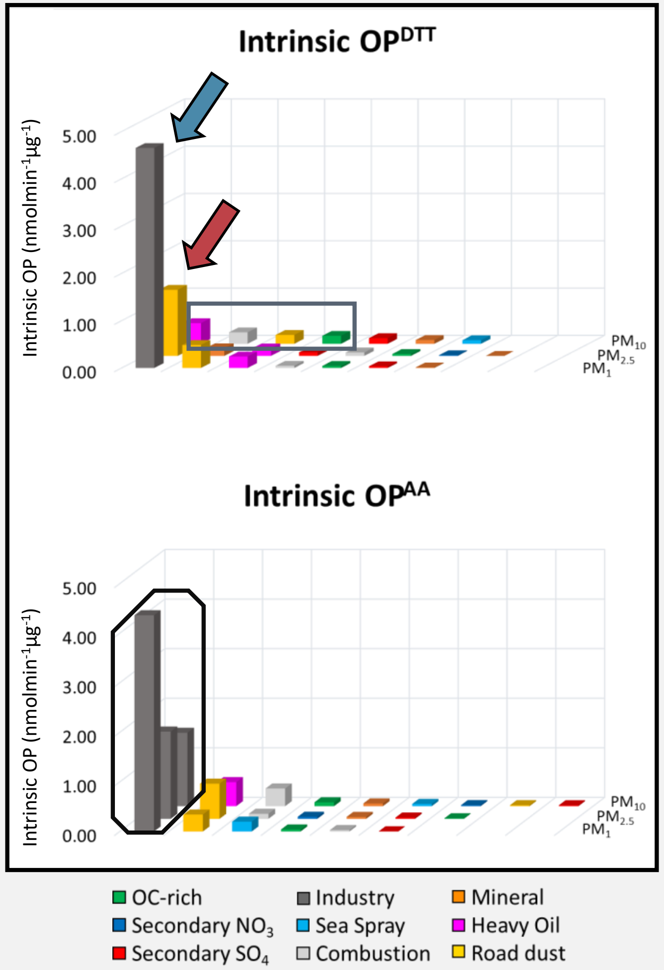
OP_v^{DTT}

Site	Country	PM_{10}	$PM_{2.5}$
Passy	FR	4.4	-
Bern	CH	2.9	1.1
Nogent	FR	2.7	-
Roubaix	FR	2.6	-
Marseille	FR	2.6	-
Barcelona	ES	2.5	1.2
Strasbourg	FR	2.4	-
Chamoix	FR	2.3	-
Nice	FR	2.2	-
Aix-en-provence	FR	1.9	-
Talence	FR	1.8	-
Marnaz	FR	1.8	-
Port-de-bouc	FR	1.8	-
Grenoble	FR	1.5	-
Vif	FR	1.3	-
Zürich	CH	1.3	0.8
Cadenazzo	CH	1.0	0.7

OP_v^{AA}

Site	Country	PM_{10}	$PM_{2.5}$
Bern	CH	4.1	1.6
Chamoix	FR	2.6	-
Passy	FR	2.2	-
Nogent	FR	2.2	-
Roubaix	FR	2.1	-
Barcelona	ES	1.9	1.0
Aix-en-provence	FR	1.7	-
Zürich	CH	1.7	0.8
Cadenazzo	CH	1.7	1.2
Marnaz	FR	1.6	-
Grenoble	FR	1.5	-
Vif	FR	1.5	-
Strasbourg	FR	1.3	-
Basel	CH	1.2	0.7
Nice	FR	1.0	-
Talence	FR	1.0	-
Payerne	FR	0.7	0.4

RESULTS
Barcelona Intrinsic OP



PM$_{10}$ — PM$_{10}$ has anthropogenic drivers, with Heavy Oil, Combustion, Road Dust, and OC-rich.

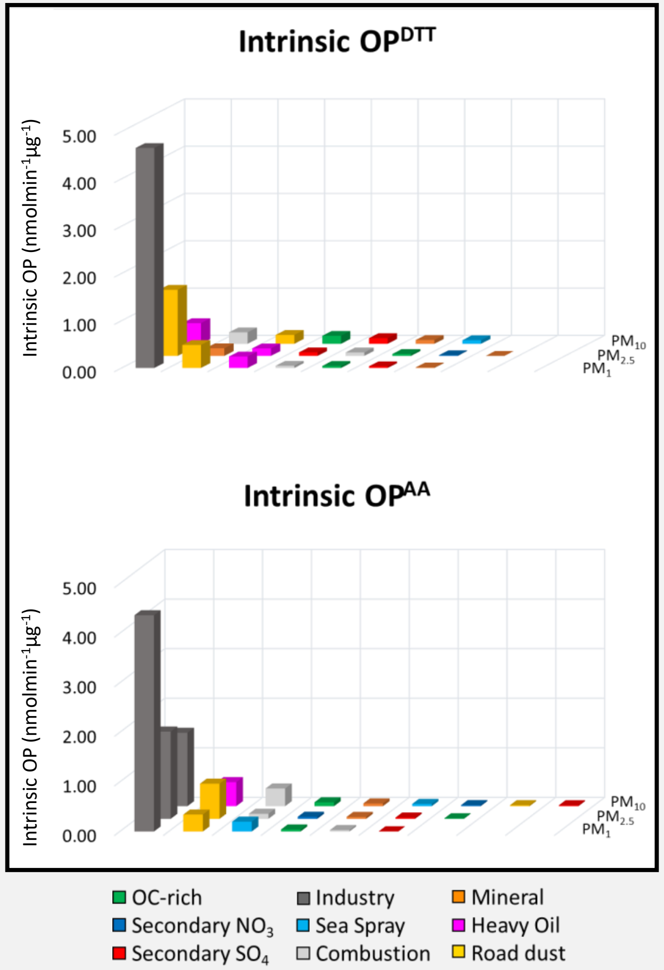
PM$_{2.5}$ — PM$_{2.5}$ is driven by Road Dust.

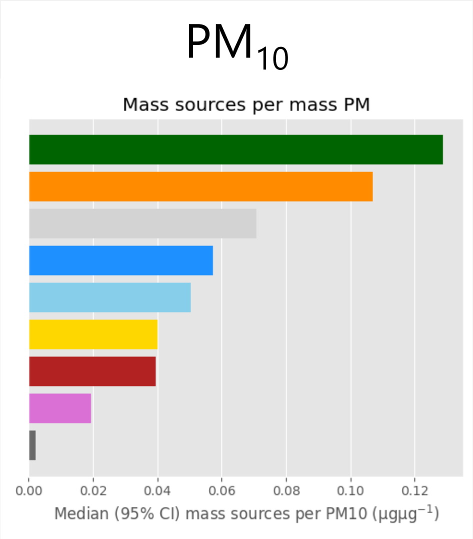
PM$_1$ — PM$_1$ is driven by Industry.

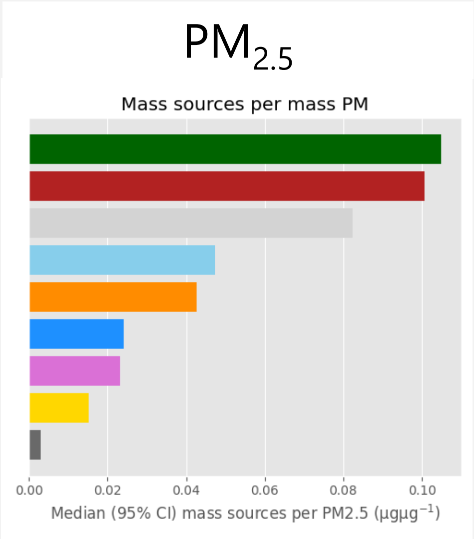
OP^{AA} — Intrinsic OP^{AA} is driven by the Industry source in all PM sizes

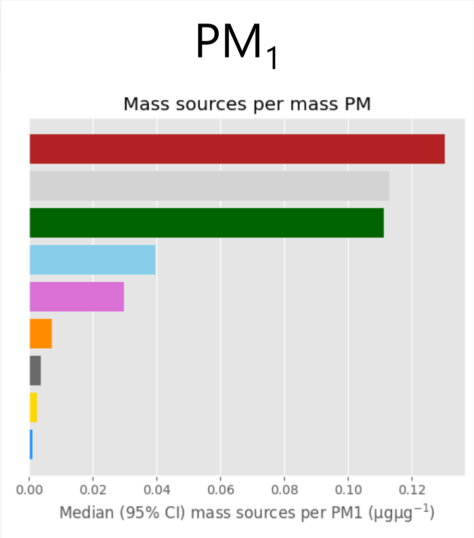
RESULTS

Barcelona Intrinsic OP



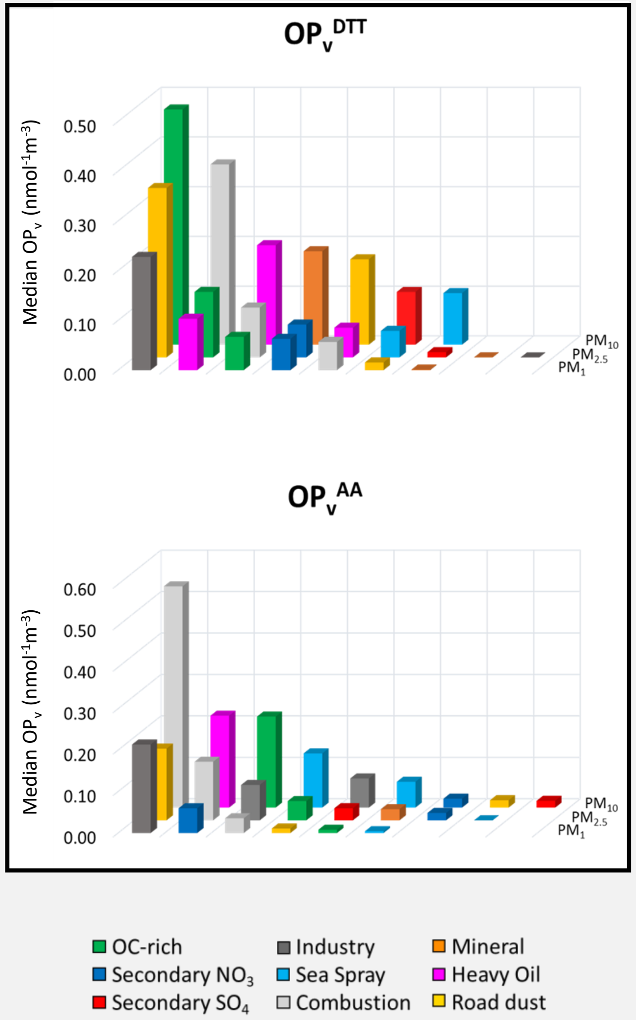






RESULTS

Barcelona Human Exposure OP



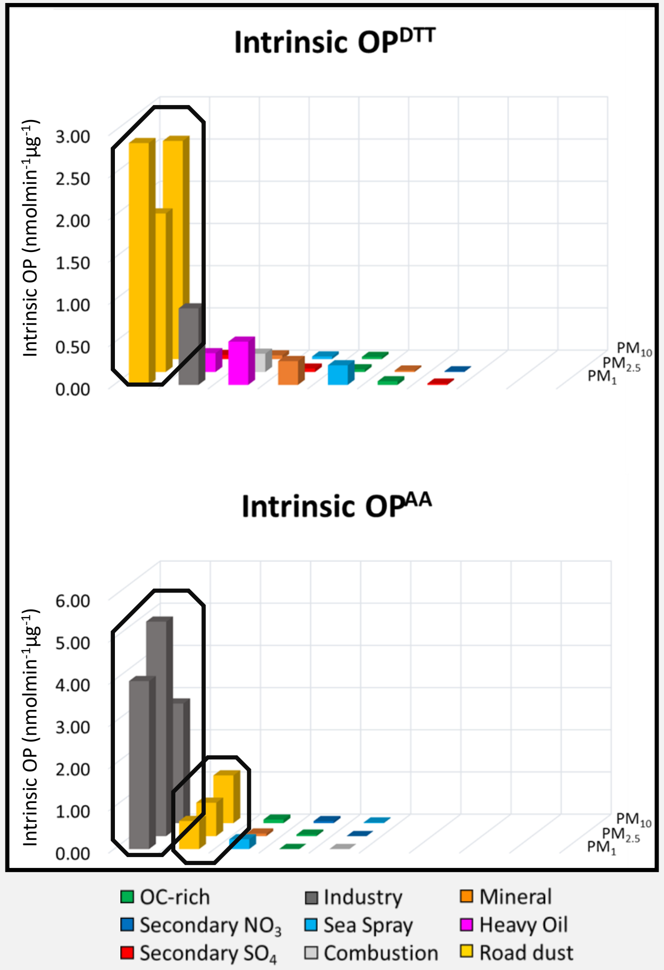
PM_{10} — PM_{10} has anthropogenic drivers, with OC-rich, Combustion, Road Dust, and Heavy Oil.

$PM_{2.5}$ — $PM_{2.5}$ is driven by Road Dust and Combustion.

PM_1 — PM_1 is driven by Industry.

RESULTS

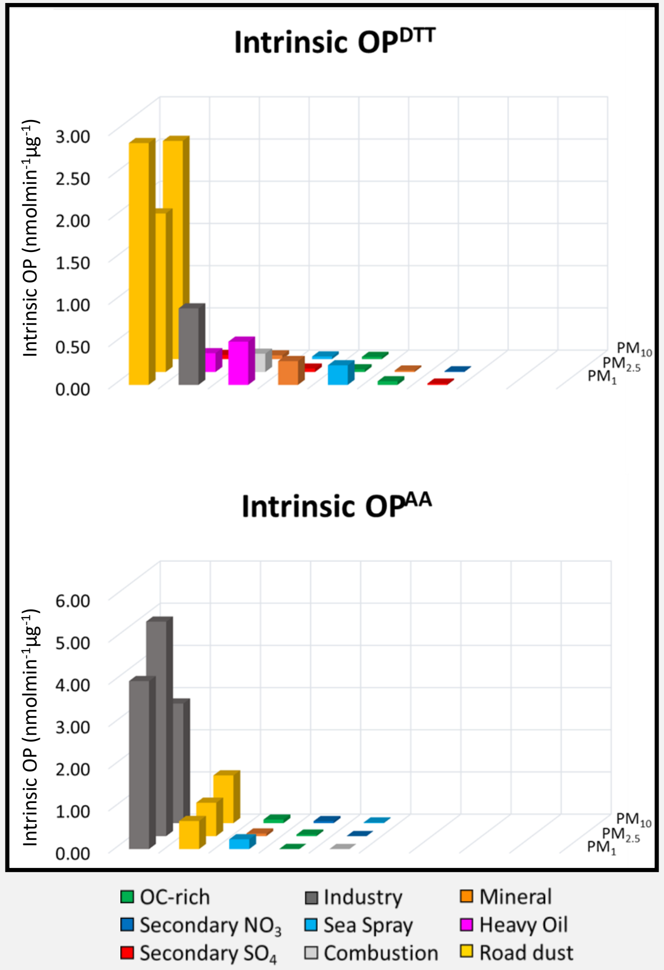
Montseny Intrinsic OP

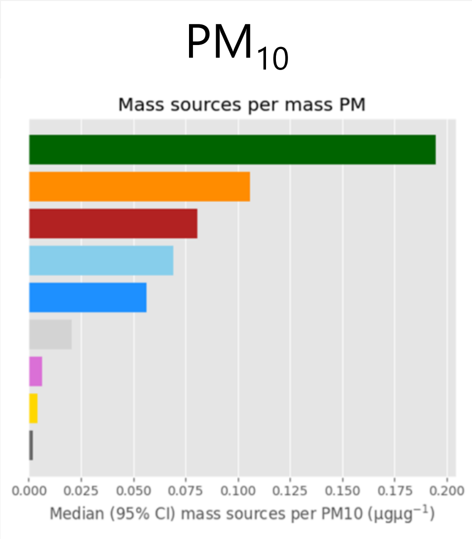


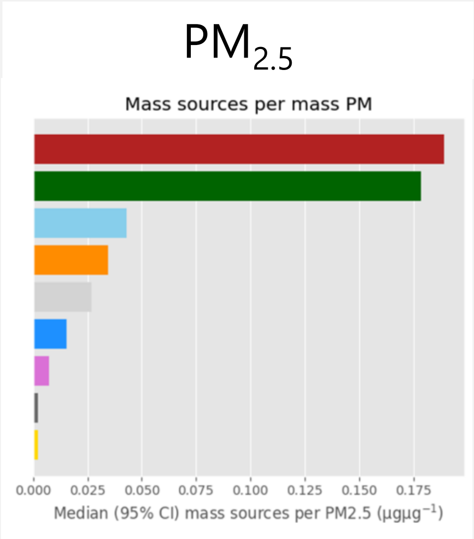
OP^{DTT} — OP^{DTT} was driven by **Road Dust**.

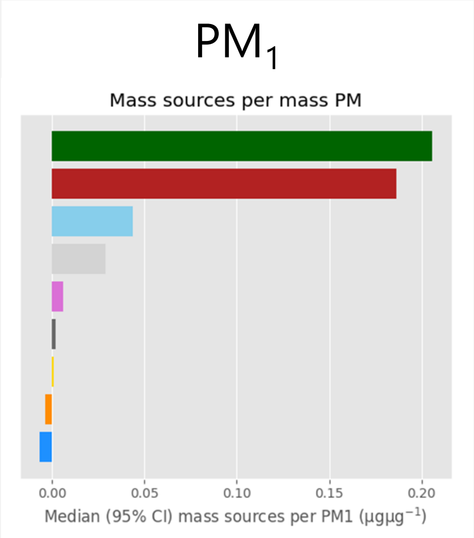
OP^{AA} — OP^{AA} was driven by **Industry**, followed by **Road Dust**.

RESULTS
Montseny Intrinsic OP

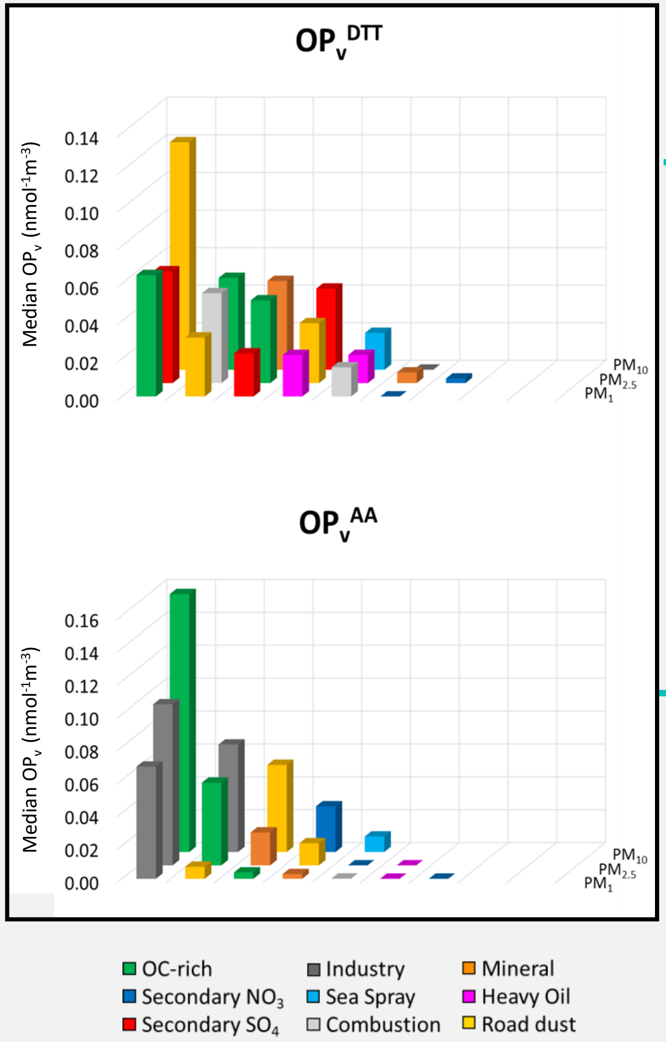








RESULTS
Montseny Human Exposure OP



OP_v^{DTT}

- PM_{10} — PM_{10} has various drivers, led by Road Dust.
- $PM_{2.5}$ — $PM_{2.5}$ has various drivers.
- PM_1 — PM_1 is driven by OC-rich.

OP_v^{AA}

- PM_{10} — PM_{10} has various drivers, led by OC-rich.
- $PM_{2.5}$ — $PM_{2.5}$ is driven by Industry and OC-rich.
- PM_1 — PM_1 is driven by Industry.

CONCLUSIONS

This research is, to the authors knowledge, the first paper to be published regarding the simultaneous OP measurement in PM_{10}, $PM_{2.5}$, and PM_1.

Main drivers of OP are in PM_{10} and PM_1 in Barcelona.
Only in PM_1 in Montseny.

The OP was driven mostly by local anthropogenic sources in Barcelona such as Shipping and Traffic in PM_{10}

PM_{10} and $PM_{2.5}$ had similar drivers in Barcelona but PM_1 was different and driven by PM_1. This shows the important of PM_1 OP measurements

THANK YOU FOR YOUR ATTENTION