

Source apportionment of the oxidative potential of aerosols at 15 French sites for yearly time series of observations

Abstract

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The reactive oxygen species (ROS) carried or induced by particulate matter (PM) are suspected to induce oxidative stress in vivo, leading to health impacts in Human populations. The oxidative potential (OP) of PM, displaying the ability of PM to oxidize the lung environment is gaining a strong interest to examine health risks associated to PM exposure. In this study, OP was measured by two different acellular assays (dithiothreitol, DTT and ascorbic acid, AA) on samples from yearly time series of filters collected in 15 different sites in France between 2013 and 2016, including urban, traffic and valley typologies. The same filters were characterized with an advanced chemical speciation allowing source-apportionment of PM_{10} using positive matrix factorization PMF method for each series, for a total above 1700 samples. This study provides therefore a nation-wide synthesis on the source-apportionment of OP using coupled PMF and multiple linear regression model. The road traffic, biomass burning, dust, MSA-rich, and primary biogenic sources have distinct positive redox-activity towards the OP^{DTT} assay. The OP^{AA} assay only presents significant activity for the biomass burning and road traffic sources. The daily median source contribution to the total OP_{DTT} highlights the dominant influence of the road traffic source. Both the biomass burning and the road traffic sources contribute evenly to the observed OP^{AA} . Would the OP being a good proxy of Human health impact, it appears that domestic biomass burning and road traffic are the two main sources to target in order to decrease significantly the OP over the French territory and to lower the health risks from PM exposure.

Introduction

Air quality has become a major public health issue, being the fourth global cause of mortality with 7 million premature deaths worldwide per year due to both indoor and outdoor exposure (World Health Organization, 2016). Driving 90 % of this health impact (Lelieveld et al., 2015), particulate matter (PM) is one of the key pollutants in the air linked to health outcomes, although the exact mechanism leading to toxicity is not yet fully understood (Barraza-Villarreal et al., 2008; Beck-Speier et al., 2012; Brauer et al., 2012; Goix et al., 2014;

Goldberg, 2011; Saleh et al., 2019). Many urbanized areas, mainly located in low- or middle-income countries, are exposed to PM concentration far higher than the recommendation guideline of the WHO.

Although PM are now monitored in many countries and large efforts are observed to document ambient concentrations, the underlying processes leading to the observed concentrations in the atmosphere, and particularly the understanding of emissions sources, are still an active field of research (Diémoz et al., 2019; El Haddad et al., 2011; Golly et al., 2019; Hodshire et al., 2019; Jaffrezo et al., 2005; Jiang et al., 2019; Marconi et al., 2014; Moreno et al., 2010; Piot et al., 2012; Salameh et al., 2015; Samaké et al., 2019a; Waked et al., 2014). In recent years, strong focus has been put worldwide on source-apportionment methods in order to better understand the processes leading to the airborne concentrations and the accumulation of PM in the atmosphere. This includes direct modeling approaches such as Chemistry Transport Model using tagged species (Brandt et al., 2013; Kranenburg et al., 2013; Mircea et al., 2020; Wagstrom et al., 2008; Wang et al., 2009) or field studies coupled with receptor models (RM) (Belis et al., 2020; Pernigotti et al., 2016; Simon et al., 2010), notably Positive Matrix Factorization (PMF). PMF can be based either on AMS time resolve spectrum (Bozzetti et al., 2017; Petit et al., 2014, 2015) or on filter analysis (Amato et al., 2016; Bressi et al., 2014; Fang et al., 2015; Jain et al., 2018; Liu et al., 2016; Petit et al., 2019; Salameh et al., 2018; Srivastava et al., 2018; Waked et al., 2014) or a mix of these different measurement techniques (Costabile et al., 2017; Vlachou et al., 2018, 2019). Score of results indicate that PM originate from a wide variety of sources, not only from natural (volcano, sea spray, soil dust, vegetation, bacteria, pollen...) or anthropogenic (road traffic, residential heating, industry...) sources, but also is formed as secondary product and condensed from the gaseous phase (ammonium-nitrate and -sulfate...). As a result, the chemistry, size distribution or reactivity of PM widely vary from location to location and season to season, which induces large changes in the health impacts depending on all of these parameters (Kelly and Fussell, 2012).

Faced with this diversity, it is understandable that epidemiological studies have difficulty in finding clear links between the atmospheric mass concentration of PM and the associated short-term health impacts. Indeed, the mass of PM may not be the relevant metric when dealing with health impacts of airborne particles since major properties (chemistry, shape, size distribution, solubility, speciation) driving PM toxicity are not taken into account within the mass. It is now believed that the measurement of the reactive oxygen species (ROS) should be more closely linked to the potential adverse health effects of atmospheric PM, since oxidative stress is a key factor in the inflammatory response of the organism, leading for instance to respiratory diseases or when exposed for a long period of time, cardiovascular diseases or even cancer (Lelieveld et al., 2015; Li et al., 2003). Therefore, the oxidizing potential (OP) of PM being an indirect measure of the ability of the particles to induce ROS in a biological medium (Ayres et al., 2008; Cho et al., 2005; Li et al., 2009; Sauvain et al., 2008) has been proposed as a potential proxy of the health impacts of atmospheric

exposure. Indeed, some recent studies already established associations between OP and different possible health outcomes (Costabile et al., 2019; Karavalakis et al., 2017; Steenhof et al., 2011; Strak et al., 2017b; Tuet et al., 2017; Weichenthal et al., 2016b, 2016a).

The demonstration of the OP to be a good proxy of health impact is still needed. At this point, there is also no clear consensus toward a standardized method to measure the OP of PM, and many assays and protocols co-exist (DTT, GSH, AA, ESR, $^{\circ}\text{OH}$ or H_2O_2 , among others), with samples extracted with different methods (water, simulated lung fluid (SLF), etc.), and not always with a constant mass of PM. However, the dithiothreitol (DTT) and ascorbic-acid (AA) assay are widely used in associations with health endpoints (Abrams et al., 2017; Atkinson et al., 2016; Bates et al., 2015; Canova et al., 2014; Fang et al., 2016; Janssen et al., 2015; Strak et al., 2017a; Weichenthal et al., 2016a; Yang et al., 2016; Zhang et al., 2016) even if the exact methodologies differ from one study to the other. The same is true for the seasonality of OP based on these two assays (Bates et al., 2015; Calas et al., 2019; Cesari et al., 2019; Fang et al., 2016; Ma et al., 2018; Paraskevopoulou et al., 2019; Perrone et al., 2016; Pietrogrande et al., 2018b; Verma et al., 2014, 2015a; Weber et al., 2018; Zhou et al., 2019). Finally, several studies also linked OP variabilities with the contributions of emission sources of PM (references). Several studies have already shown that different sources of PM have different reactivity to OP tests (Bates et al., 2015; Cesari et al., 2019; Fang et al., 2016; Paraskevopoulou et al., 2019; Verma et al., 2014; Weber et al., 2018; Zhou et al., 2019). In particular, sources with high concentrations of transition metals, such as road traffic, appear to have a higher intrinsic oxidizing potential than other sources of PM., even if the exact methodologies differ from one study to the other.

Thus, it is now necessary to know if this new parameter of PM (oxidizing potential) complements the usual metric (mass concentration per cubic meter).

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In order to address these questions, we gathered in this study an extensive database of about 1 700 samples from 15 yearly time-series of observations over continental France, collected during many research programs conducted between 2013 and 2018. On each of these samples, we concurrently measured the OP with the DTT and AA assays, together with an extensive chemical characterization allowing PM source apportionment using a harmonized PMF (Positive Matrix

Factorization) approach (Weber et al., 2019). Then, we apportioned the OP measured by the DTT and AA assay to the emission sources using a multilinear regression approach, following Weber et al. (2018). In this way, we can estimate the oxidizing capacity of each microgram of PM from the different identified emission sources but also the relative contribution of the different sources to the OP^{DTT} and OP^{AA} on seasonal and daily basis.

Material and method

Sites description

The selected sites had to fulfill three conditions: 1) a yearly sampling period, 2) the required chemical analysis to perform a standardized PMF study and 3) enough filter surface left to assess the OP measurements. A total of 14 sites were included in this study (one being sampled 2 times at 5 years interval) taken from different research programs. The chosen sites reflect the diversity of typology we could encounter in the western Europe: urban (NGT, TAL, AIX, MRS-5av), urban traffic (NIC), urban alpine valley (GRE-cb, GRE-fr, VIF, CHAM, MNZ, PAS), industrial (PdB) and traffic (RBX & STG-ce) and are details in Table [tab:tab1] and cover different area of France (Figure [fig:fig1]). All these sites are monitored by the local AASQA (Atmo Sud, Atmo AURA, Atmo Aquitaine and Atmo HdF). We note, however, the absence of remote or rural sites in our current dataset.

Figure 1. Location of the 15 sampling sites. Color codes denote the typology of the site: red, urban; orange, urban valley; magenta, industrial; blue, traffic.

Table 1. Sampling sites meta-data.

Ville	Abbreviation	Typology	Coordinate	Elevation	# sample	Date
Marseille	MRS-5av	Urban bgd	43.3060 °N, 5.3957 °E	64 m	72	2015-01-1
Port-de-Bouc	PdB	Industrial	43.4019 °N, 4.9819 °E	1 m	113	2014-06-0
Aix-en-provence	AIX	Urban bgd	43.5302 °N, 5.4413 °E	188 m	56	2013-08-0
Nice	NIC	Urban traffic	43.7020 °N, 7.2862 °E	1 m	105	2014-07-1
Talence	TAL	Urban bgd	44.8004 °N, 0.5880 °W	20 m	120	2012-03-0
Nogent	NGT	Urban bgd	49.2763 °N, 2.4821 °E	28 m	135	2013-01-0
Grenoble	GRE-fr_2013	Urban bgd	45.1618 °N, 5.7356 °E	214 m	225	2013-01-0
Grenoble	GRE-fr_2017	Urban bgd	45.1618 °N, 5.7356 °E	214 m	122	2017-02-2
Grenoble	GRE-cb	Urban bgd	45.1833 °N, 5.7251 °E	212 m	124	2017-02-2
Vif	VIF	Urban bgd	45.0580 °N, 5.6768 °E	310 m	125	2017-02-2
Chamonix	CHAM	Urban valley	45.9225 °N, 6.8699 °E	1038 m	93	2013-11-0
Marnaz	MNZ	Urban valley	46.0577 °N, 6.5334 °E	504 m	89	2013-11-0
Passy	PAS	Urban valley	45.9235 °N, 6.7136 °E	588 m	88	2013-11-0
Roubaix	RBX	Traffic	50.7065 °N, 3.1806 °E	10 m	157	2013-01-2

Sample analysis

Chemical speciation

The PM₁₀ concentration was measured at each site by means of an automatic analyzer, according to EN 16450:2017 (CEN, 2017a), and daily (24 hours) filter samples were collected every third day by employees of the corresponding regional air quality monitoring network. Samplings were achieved on pre-heated quartz fiber filters using high-volume sampler (DA80, Digitel), following EN 12341:2014 procedures (CEN, 2014). Off-line chemical analysis performed on these filters are fully described in the respective papers. Briefly, the elemental and organic carbon fractions (EC and OC) were measured via thermo-optical analysis (Sunset Lab. Analyzer (Birch and Cary, 1996)) using the EUSAAR-2 protocol (Cavalli et al., 2010; CEN, 2017b). Major water-soluble inorganic contents (Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺) and methane-sulfonic acid (MSA) were determined using ion chromatography (CEN, 2017c; Jaffrezou et al., 2005). Many metals or trace elements (e.g., Al, Ca, Fe, K, As, Ba, Cd, Co, Cu, La, Mn, Mo, Ni, Pb, Rb, Sb, Sr, V, and Zn) were measured by ICP-AES or ICP-MS (Alleman et al., 2010; CEN, 2005; Mbengue et al., 2014). Finally, various anhydrosugars (including levoglucosan, mannosan, arabitol, sorbitol, and mannitol) were analyzed using High Performance Liquid Chromatography followed by pulsed amperometric detection (HPLC-PAD) (Waked et al., 2014).

OP assays

The same methodology was applied for all the OP measurements of the collected filters (Calas et al., 2017, 2018, 2019). Shortly, we performed the extraction of PM into a simulated lung fluid (SLF) to simulate the bio-accessibility of PM and to closely simulate exposure conditions. In order to take into account the non-linearity of the OP with the mass and to have comparable results between them, the extraction takes place at iso-mass (10 or 25 of PM, depending on the site), by adjusting the area of filter extracted. The filter extraction method includes both water soluble and insoluble species. After the SLF extraction, particles removed from filter are not filtrated, the whole extract is injected in the multi-wall plate. Samples were processed using the AA and DTT assays. DTT depletion when in contact with PM extracts was determined by dosing the remaining amount of DTT with DTNB (dithionitrobenzoic acid) at different reaction times (0, 15, 30 minutes) and absorbency was measured at 412 using a plate spectrophotometer (Tecan, M200 Infinite). The AA assay is a simplified version of the synthetic respiratory tract lining fluid (RTFL) assay (Kelly and Mudway, 2003), where only AA is used. AA depletion is read continuously for 30 minutes by absorbency at 265 nm (TECAN, M1000 Infinite). The maximum depletion rate of AA is

determined by linear regression of the linear section data. For both assays, the 96-wells plate is auto shaken for 3 seconds before each measurement and kept at 37° C . Three filter blanks (laboratory blanks) and three positive controls (1,4 Napthoquinone, 24,7 μM) are included in every plate (OP^{AA} and OP^{DTT}) of the protocol. The average values of these blanks are then subtracted from the sample measurement of this plate. Detection limit (DL) value is defined as three times of the standard deviation of laboratory blanks measurements (blank filters in Gamble+DPPC solution).

The samples were stored from 1 to 4 years before they were analyzed for the DECOMBIO and SOURCES sites. The MobilAir samples were analyzed in the months following their collection. As mentioned in (Verma et al., 2015), the OP activity may be impacted by such storage time. However, in a previous program (ANSES ExPOSURE, 2017), still ongoing, we have been measuring the same filter over time. Over one year (about one measurement per month), OP results for DTT and AA assays display respectively a coefficient of variation of 18 and 12 %. Hereafter, the OP^{DTT} and OP^{AA} normalized by air volume are noted OP_v^{DTT} and OP_v^{AA} , respectively, with unit .

Source apportionment

The source apportionment of the OP can be performed in two main ways: 1) include the OP as an input variable for receptor-model (RM) (Cesari et al., 2019; Fang et al., 2016; Ma et al., 2018; Verma et al., 2014) or 2) conduct source attribution to the PM mass and then, using a multiple linear regression (MLR) model, assign OP to each of the sources from the source-receptor model (Bates et al., 2015; Cesari et al., 2019; Paraskevopoulou et al., 2019; Verma et al., 2015b; Weber et al., 2018; Zhou et al., 2019). We decided to use the second approach because the inclusion of OP in the PMF could potentially destabilize the results but also forces the OP to positive values (see below).

PM mass apportionment: Positive Matrix Factorization

Methodological background The source apportionment at the 15 sites was conducted thanks to a Positive Matrix Factorization (PMF), using the EPA PMF 5.0 software (US EPA, 2017) that makes use of the ME-2 solver from Paatero (1999). Briefly, the PMF was introduced by Paatero and Tapper (1994) and is now a common tool for source-apportionment study. It aims at solving the receptor model equation

$$X = G \cdot F,$$

where X is the $n \times m$ observation matrix, G is the $n \times p$ contribution matrix and F is the $p \times m$ factor profile (or *source*, but some factor are not a proper emission *source* but may reflect secondary processes), with n the number of sample, m the number of measured chemical specie and p the number of profile. Hereafter, the G matrix will be in and the F matrix in of PM.

PMF set up Some of the PMFs were run during previous campaign, namely SOURCES (Favez et al., 2017; Weber et al., 2019), DECOMBIO (Chevrier, 2016; Chevrier et al., 2016), MobilAir (<https://mobilair.univ-grenoble-alpes.fr/>, Borlaza et al. (n.d.)). For the aims of this study, all PMF have been rerun according to a harmonized methodology, following the SOURCES program, in order to have a common set of input species and constraints in the model and to have comparable sources’ profiles.

The input species are slightly site-dependent, but include carbonaceous compound (OC & EC), ions (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}), organic compounds (levoglucosan, mannosan, arabinol, manitol (summed and referred to polyols) and MSA) and metals for a total of about 30 species. The list of metals is not exactly the same for each of the sites, due to too low concentrations on some filters. The uncertainties were estimated thanks to the method proposed by Gianini et al. (2012) and was tripled if the signal over noise ratio was below 2 (classified as “weak” in the PMF software). Between 8 to 10 factors were identified for at the different sites and are summarized in Table SI REF. On each of the PMF, the possibility of adding constraints to the factors was used to better disentangle possible mixing between factors and reduce the rotational ambiguity, based on *a priori* expert knowledge of the sources geochemistry. A PMF solution was considered valid if it followed the recommendation of the European guide on air pollution source apportionment with receptor models (Belis et al., 2019) as well as the geochemical identification of the various factors. Estimation of the precision of the PMF was obtained on both the base and constrained runs thanks the both the bootstrap (BS) and displacement (DISP) functions of the EPA PMF5.0.

Similarity assessment of the PMF factors

Since PMF resolves sites-specific factor of PM, we may question if a factor named by the user “Primary traffic” at CHAM display indeed a similar chemistry as a “Primary traffic” at NGT for instance. In order to identify the the chemical similarity of the PMF profiles, a similarity assessment of all PMF factor profiles was run following the DeltaTool approach (Pernigotti and Belis, 2018), similarly to what we presented recently in (Weber et al., 2019). Shortly, the DeltaTool approach compares a pair of factor profile based on it mass-normalized chemical compounds thanks to 2 different metrics, the Pearson distance (PD) and the standardized identity distance (SID) (see Belis et al. (2015)) for a detailed explanation of theses 2 metrics). The first one is 1 minus the Pearson correlation coefficient ($\text{PD} = 1 - r^2$) and so is strongly influenced by individual extreme points (namely OC or EC in our dataset) whereas the second one, SID, is more sensitive to every specie since it includes a normalization term, expressed as follows

$$\text{SID} = \frac{\sqrt{2}}{m} \sum_{j=1}^m \frac{|x_j - y_j|}{x_j + y_j},$$

where x and y are two different factors profile in relative mass and m the number

of common specie in x and y .

OP apportionment

Multiple linear inversion

Similar to Weber et al. (2018), a multiple linear regression (MLR) was conducted independently at each sites with the two OP (DDT and AA) being the dependent variables and the sources contribution obtained from the PMF being the explanatory variables, following the equation:

$$OP_{obs} = G \times \beta + \varepsilon,$$

with OP_{obs} a vector of size $n \times 1$ of the observed OP_v^{DDT} or OP_v^{AA} in , G is the matrix ($n \times (p+1)$) of the mass contribution of PM sources determined from the PMF in and a constant unit term for the intercept (no unit), the coefficients (i.e. intrinsic OP of the source and the intercept) of size $((p+1) \times 1)$ in for the intrinsic OP and for the intercept. The residual term ($n \times 1$) accounts for the misfit between the observation and the model. We expressively did not fix the intercept to zero. Indeed, if the system is well constrained the intercept should be close to zero and conversely a non-zero intercept would point out missing explanatory variables. A weighted least square (WLS) were used in order to take into account the uncertainties of the OP measurements.

In our previous study (Weber et al., 2018), we used a stepwise backward elimination of negative coefficients. The assumption was that air is an oxidative environment, thus the PM oxidative potential cannot be negative. However, the application of this method to our enlarged dataset led, at some sites, to unrealistic exclusion of almost all sources together with a bad reconstruction of OP. This observation tends in favor of possible coating effect of some oxidative species in presence of other chemical components or non-linear effects, seen in our model as “negative” OP. We then decided to remove the positivity constraint in this study. Moreover, the removal of this constraint lead to more homogeneous intrinsic OP for the main PM sources.

A careful data-treatment was performed in order to remove from the dataset highly specific samples (e.g. firework) since we focus in this study to the dominant sources and processes leading to the population exposure of OP.

The uncertainties of the coefficients given by the MLR were estimated by bootstrapping (BS) the solutions 500 times with randomly selected 70 % of the samples in order to account for possible extremes events or seasonal variations of the intrinsic OP per source. The uncertainty of the PMF result G is not taken into account.

The computation was done thanks to the WLS method of the *statsmodels* package of python (Seabold and Perktold, 2010).

Contribution of the sources to the OP

The contribution G^{OP} in of the sources to the OP is computed at each site independently and is simply the product of the intrinsic OP in from the MLR times the source contribution of the PMF G in :

$$G_k^{\text{OP}} = G_k \times \beta_k$$

where k is the source considered. The uncertainties of G^{OP} is computed thanks to the uncertainties of β estimated from the BS. The uncertainties of the PMF G_k is not taken into account.

Results

Due to the amount of results, unlikely to be summarized into single graph, we also present an interactive visualization of all the results at <http://getopstandop.u-ga.fr> where the reader can find all the details per station of the results presented hereafter.

PMF results

A deep discussion on the PM mass source-apportionment results are given in the respective document (Borlaza et al., n.d.; Chevrier, 2016; Weber et al., 2019). However, the PMF of these studies were rerun for the present study to include a common set of species and validation criteria, following the SOURCES methodology (Favez et al., 2017; Weber et al., 2019) in order to have comparable data across sites. Shortly, we observed PMF factors from biomass burning (from residential heating, mainly traced by levoglucosan), primary road traffic (identified by EC, Cu, Fe, Sn and Ca^{2+}), mineral dust (thanks to Ti, Ca^{2+} , and others crustal elements), secondary inorganic (nitrate-rich (NO_3^- and NH_4^+) and sulfate-rich (SO_4^{2-} and NH_4^+ , together with some OC and Se), salt (fresh (Cl^- and Na^+) and aged (Na^+ , Mg^{2+}) sea salt) as well as primary biogenic (traced by the polyols) and MSA-rich (traced MSA). Some other local sources were also identified at some sites, targeting either some local heavy loaded metals sources with a very low contribution to the total PM mass —supposedly linked to industrial process— or factor related to shipping emission (namely heavy fuel oil, HFO) at some coastal sites. The list of the identified factors at each sites is given in SI REF.

Figure 2. Similarity profile in the PD-SID space for all the pairs of PMF profile identified at all sites (see text for explanation). The mean (dot) and standard deviation (lines) are reported in the figure. The values in parenthesis indicate the number of pairs of profile considered : with (N 2) the number of site where the profile is identified.

To assess if PMF factors identically named are indeed similar in terms of

geochemistry, we reported similarity metrics (PD: Pearson distance and SID: standardized identity distance defined in (Pernigotti and Belis, 2018)) in Figure [fig:fig2] for all the identified profiles. The figure reports the mean and standard deviation of the PD and SID for all possible pairs of profile but the details for each given pair of profile may be found in the website. According to Pernigotti and Belis (2018), two profiles are considered similar if their PD and SID fall down the green rectangle delineating the area with $PD < 0.4$ and $SID < 1$. We do observe a good similarity (i.e. $PD < 0.4$ and $SID < 1$) for the main sources of PM, namely biomass burning, nitrate-rich, primary biogenic, road traffic, sulfate-rich. The dust, aged salt and MSA rich are often identified and present acceptable SID, but do present important value for the PD metric. As the PD is sensitive to "extreme points" that can strongly affect the pearson correlation, this translates in our case into the species contributing most to the PM mass (mainly OC and EC). Then these profiles show differences in concentrations mainly for OC and EC. The MSA-rich is found to be the most variable factor and a detail analysis of the chemistry profile (see the website) indicates a lot of differences for the concentration of EC but also NO_3^- and NH_4^+ from site to site, where some sites present contribution of theses species to the total PM mass whereas other don't. Since it includes secondary organic species, its variability may be explained by different formation or evolution pathways (humidity, temperature, solar irradiation, etc.). We also point out that the industrial source has a very diverse chemistry since it gathers different local industrial processes. Nevertheless, the geochemical stability of the majority of PMF factors on a regional scale seems to us sufficient to consider that these emission sources have a similar chemistry throughout France.

It is also interesting to note that the species contributing to oxidizing potential have low concentration variability in the source profiles emitting them. Indeed, previous studies pointed out the role of transition metals in the OP of PM (Calas et al., 2018; Verma et al., 2015a). In our source-apportionment, most of the copper is apportioned by the road traffic source, which is then suspected to play a key role in the observed OP^{DTT} and moreover to the OP^{AA} value since the copper (Cu) is apportioned between 34 % to 54 % (first and third quantile) by the road traffic factor, with a concentration ranging from 1.7 to 3.1 of PM from this source. We also note that the concentration uncertainties of Cu into the road traffic is rather low (see website) as well as the concentration variation across sites, suggesting that the intrinsic OP of this source may be similar at the regional scale. Also, the levoglucosan, which shows strong correlation to the OP^{DTT} and OP^{AA} , is quasi-exclusively apportioned by the biomass-burning source. Moreover, a lot of OC is contributing to the PM of this factor and some metals (notably the copper) are apportioned by this factor (10 % of the total copper). The biomass burning is then also strongly suspected to contribute to both OP in wintertime.

OP seasonality

The 15 time-series for both the OPDTT and OPAA at each site are presented in SI and the website. A monthly aggregated view is given in Figure [fig:fig3], for both the OP_v^{DTT} and OP_v^{AA} . It is noted that the dataset covers complete seasonality and is, in this sense, representative of a regional climatology of the OP since it includes different sources with different seasonal activities. Similar to the previous work of Calas et al. (2018, 2019), extended by new yearly time-series, we observed a seasonality of both the OP_v^{DTT} and OP_v^{AA} , with higher values of OP during the cold months compared to the warm months. We also note that during the winter, the statistical distribution of OP values does not follow a normal distribution and significant variability is observed. Notably, and as shown in SI XX and already pointed out in Calas et al. (2019), the alpine sites present stronger seasonality compare to the others (GRE-fr, GRE-cb, VIF, CHAM, MNZ, PAS). Also, some sites do not present this seasonality, notably the traffic sites (RBX and STG-cle), the urban traffic (NIC) or the industrial one (PdB). This seasonality could be explained by the source of biomass combustion, which also exhibits this type of seasonality, especially in the Alpine valleys, being the major source of PM in these regions in winter. Also, as presented in the SI XX and in Calas et al. (2019), some rapid variation of the OP^{DTT} and OP^{AA} are observed, with drastic increase or decrease within the frame of few days, similarly to the PM10 mass, suspected to be linked with atmospheric circulation and vertical mixing of the boundary layer, notably due to inversion layer that traps the pollutants in the valley.

Figure 3. Boxenplot of OPvDTT and OPvAA seasonal value. The numbers in the x-axis indicate the number of observation. Each box represents one decile and the black line indicates the median of the distribution. Some values greater than $15.5 \text{ nmol min}^{-1} \text{ m}^{-3}$ are not displayed for graphical purpose.

Correlation OP – sources

This study focuses on the main drivers of OP at the regional scale. For this reason, we decided to include in the main discussion only the PMF factor identified at least two-thirds of the sites (i.e. 10 out of 15 sites), namely the aged salt, biomass burning, dust, MSA rich, nitrate-rich, primary biogenic, primary road traffic and sulfate-rich sources. The other local sources barely contributed to the total PM mass and important uncertainties were often attached to them. The only notable exception is the HFO profile identified at some coastal sites, discussed hereafter in it’s own section. We invite the reader to explore the website to have the full view of the results.

In order to have a first estimate of the sources that can be associated with the OP, the Spearman correlation between the source mass apportionment from the PMF and the measured OP_v^{DTT} and OP_v^{AA} are presented in Figure [fig:fig4]. This figure takes into account all samples from all sites. First of

all, the two OP shows good correlation but do not carry the exact same signal ($r_{\text{OP DTT-OPAA}}=0.61$). Secondly, the only source that strongly correlates to one OP ($r>0.6$) is the biomass burning to the OP_v^{AA} . Some mild correlation ($0.3<r<0.6$) are found for the OP_v^{DTT} vs. road traffic, biomass burning, nitrate-rich and dust and for the OP_v^{AA} vs. nitrate rich and road traffic. This result is in line with previous study, either with the source correlation (Weber et al., 2018) or with the proxy of sources (namely, levoglucosan for biomass burning and EC, iron, copper or PAH for road traffic) (Calas et al., 2019, 2018; Charrier and Anastasio, 2012; Cho et al., 2005; Hu et al., 2008; Janssen et al., 2014; Künzli et al., 2006; Ntziachristos et al., 2007; Pietrogrande et al., 2018a; Verma et al., 2014, 2009). However, the nitrate rich source, mildly correlated to both OP, doesn't present any atmospheric compound that are known to be redox-active (to our knowledge). This correlation may then not reflect any causality and the multilinear regression should disentangle possible co-variation of the nitrate-rich source and other redox-active one.

Figure 4. Spearman correlation coefficient between the OP_vDTT and the OP_vAA to the 8 PM sources identified at at least two third of the sites. All sites are grouped together in this figure, taking into account the whole time-series of measurement (number of observation days: Aged salt 1430; Biomass burning 1700, Dust 1489, MSA rich 1595, Nitrate rich 1700, Primary biogenic 1700, Road traffic 1587, Sulfate rich 1524).

Accuracy of the MLR model

The MLR statistical validation was carried out by a residual analysis between the OP observed and the OP reconstructed by the model. For this evaluation, the intrinsic OP of the sources was set to the mean of the 500 bootstrap values. Table [tab:tab2] presents the fitted line between the modeled and observed OP_v^{DTT} and OP_v^{AA} together with the Pearson correlation coefficient. Details and individual scatter plot are given the SI XX. All but two sites present a very good correlation between observed and reconstructed OP ($r^2>0.7$) and a regression line close to unity. We note that two models (STG-cle for AA and VIF for DTT) present a clear lower correlation ($r^2=0.46$ and 0.49 , respectively) together with the fitted line the farthest than the $y=x$ line. However, an in-depth analysis highlights that such a correlation is driven by few days of observation on this regression (see SI XX). We therefore consider our models valid for the rest of this study and each intrinsic OP (i.e. coefficient of the regression) may be explored individually to geochemically explain the observed OP.

Limit of the linear model

Despite our models being able to reproduce most of the observations, we can also see in figure SI XX that even if the MLR produces normally distributed residuals (observation minus model), it also tends to underestimate the highest values

and the residuals are often heteroscedastics (i.e. the higher values, the higher the uncertainties). Then, the underlying hypothesis of linearity between endogenous variables (source PM concentration) and exogenous variables (OP) may be deemed invalid. The reader should keep in mind that non-linear processes are strongly suspected for the source-apportionment of OP, as already noted by Calas et al. (2018) or Charrier et al. (2016). As a result, future developments on OP apportionment models should focus on this suspected non-linearity, either with co-variations terms or even non-linear model such as neural-network for instance.

Observed vs reconstructed OP equation and Pearson correlation, taking the mean value of the 500 bootstraps, for all the sites.

	DTTv	AAv
MRS-5av	0.77x+0.60 $r^2=0.72$	0.69x+0.10 $r^2=0.72$
PdB	0.87x+0.24 $r^2=0.84$	0.91x+0.07 $r^2=0.87$
AIX	0.91x+0.18 $r^2=0.82$	1.01x+0.04 $r^2=0.92$
NIC	0.76x+0.52 $r^2=0.79$	0.88x+0.12 $r^2=0.83$
TAL	0.76x+0.34 $r^2=0.77$	0.83x+0.07 $r^2=0.86$
NGT	0.81x+0.43 $r^2=0.75$	0.97x+0.05 $r^2=0.87$
GRE-fr_2013	0.97x-0.14 $r^2=0.79$	0.69x+0.20 $r^2=0.79$
GRE-fr_2017	0.77x+0.20 $r^2=0.81$	1.02x+0.01 $r^2=0.94$
GRE-cb	0.70x+0.35 $r^2=0.72$	0.81x+0.20 $r^2=0.86$
VIF	0.62x+0.47 $r^2=0.49$	0.78x+0.20 $r^2=0.93$
CHAM	0.87x+0.21 $r^2=0.90$	0.85x+0.14 $r^2=0.93$
MNZ	0.87x+0.19 $r^2=0.95$	0.90x-0.01 $r^2=0.96$
PAS	0.76x+0.72 $r^2=0.90$	0.96x-0.06 $r^2=0.82$
RBX	0.75x+0.49 $r^2=0.72$	0.86x+0.31 $r^2=0.75$
STG-cle	0.75x+0.57 $r^2=0.73$	0.55x+0.64 $r^2=0.46$

Intrinsic OP per sources

Even if the models reproduce the observations correctly, this does not guarantee that the geochemical meaning extracted is the same for each of the models, i.e. the intrinsic OP of the sources may completely differ from site to site. The question is then to identify if a given source contributes similarly to the OP at all sites. In other words, does all model extract any geochemical general information relative to the OP? Figure 5 presents the intrinsic OP^{DTT} **A**) and OP^{AA} **B**) for the selected subset of sources. The values of all the N bootstraps for all the n stations where the sources were identified (i.e. between $500 \times 15 = 7500$ and $500 \times 10 = 5000$ values) are represented by the boxenplot to display the value distribution, together with the mean and standard deviation in white dots and lines, respectively. The exact values of mean and standard deviation are also reported in Table [tab:tab3] and details per station for all sources are given in Table SI4.

Figure 5. Intrinsic OP A) DTT and B) AA for the sources identified at at least two third of the site (i.e. 10 sites). The graphic displays the $n \times N$ intrinsic OP in parenthesis (with n the number of site where the source was identified and $N = 500$ bootstraps) and their statistical distribution via boxenplot: each box delimit a decile. The mean and standard deviation are also given in white dots and lines, respectively.

First of all, the mean values of the intrinsic OP are almost always found positive when considering the whole dataset. The only case where a small negative mean intrinsic OP found is for the MSA rich factor for the AA assay (-0.018(152)), but strong variance is attached to this result. It then confirms, if still needed, that airborne particles are an oxidant material.

We also observe a net distinction of the intrinsic OP for the different sources of PM, with intrinsic OP ranging from 0.044(64) to 0.223(85) for the DTT and -0.018(152) to 0.197(104) for the AA. We confirm the previous studies that also found different reactivity (or intrinsic OP) for different sources based on RM techniques (Ayres et al., 2008; Bates et al., 2015; Cesari et al., 2019; Costabile et al., 2019; Fang et al., 2016; Paraskevopoulou et al., 2019; Perrone et al., 2019; Verma et al., 2014; Weber et al., 2018; Zhou et al., 2019). Notably, the road traffic source is the most reactive source toward the OP^{DTT} , with a value of 0.223(85) which is almost twice the value of the other group of reactive source, namely 0.132(410), 0.129(65), 0.121(114) and 0.112(113) for the MSA rich, biomass burning, dust and primary biogenic sources, respectively. Interestingly, the nitrate-rich factor is the second most correlated to the OP^{DTT} but is the one associated with the lowest intrinsic OP^{DTT} (0.044(65)). Concerning the intrinsic OP^{AA} , less sources present redox activity. Notably, only the biomass burning and road traffic present an intrinsic OP easily distinguishable from 0, with respect to the uncertainties with intrinsic OP^{AA} of 0.197(103) and 0.161(108), respectively. Overall, it appears that the intrinsic OP of the different sources (except the MSA-rich) are similar at a regional level, paving the road to the implementation of OP in CTM.

Overall, the OP^{DTT} is more balanced than the OP^{AA} as already pointed by Fang et al. (2016) and Weber et al. (2018) and seems to target all the sources containing either metals and organic species but is not sensitive to ammonium nitrate source. OP^{AA} mainly target biomass burning and primary road traffic factor, as already pointed out in previous studies (Bates et al., 2019 and references therein). We then confirm what previous studies found either by direct OP measurement at the source or by source -apportionment. It is however hard to directly compare the absolute value of our result to the literature since all protocols vary from one group to another. The coefficient of variation (CV, standard deviation over mean) of the intrinsic OP are the lowest for the **biomass burning** and primary **road traffic** for the DTT assay with values of 0.5 and 0.38, respectively, as well as for the AA assay with value of 0.52 and 0.67, respectively. The variability of the biomass burning intrinsic OP is more site dependent, with a low

uncertainty at any given site, but with slightly different intrinsic OP between sites. It then suggests that the variability is not linked to uncertainties of the model but from local variation of the chemistry of this profile. However, the biomass burning is the most geochemically stable profile in our dataset, with a $PD < 0.1$ and $SID < 0.7$. Hence, the variability should come from species not measured in our dataset. Namely, no PAH, oxy-PAH, OH-PAH nor quinone are measured, although they are known to contribute to the OP (Charrier and Anastasio, 2012) and have short live time and being heavily influenced by the climatic condition (Miersch et al., 2019). The road traffic chemical profile is also similar at all sites (with the exception of RBX and VIF where mixing effects are observed) with our given set of species. Moreover, the uncertainty of the road traffic intrinsic OP at each site lies in the uncertainties of the other sites. Hence, the low variability for the OP^{DTT} indicates that the observed species, similar at each sites, are the one that influence OP^{DTT} . However, for the OP^{AA} the variability is higher with some important difference from site to site, without clear distinction by typology or groups of sites. Then, some species that are not measured here may influence the OP^{AA} , but not the OP^{DTT} .

The inorganic factor (**sulfate-rich** and **nitrate-rich**) presents a high CV. However, the CV may not be an accurate measure for some sources with near 0 mean intrinsic OP. The standard deviation is similar to the one of the biomass burning and road traffic for the OP DTT, and are among the lowest variability for the OP^{AA} (see table REF). The two inorganic factor are also very similar at each site in term of chemical composition, as presented in the SID-PD space in Figure [fig:fig2].

The **dust** source presents an important variability when taking into account the whole sites, but a deeper analysis shows 2 groups of sites: AIX-RBX-VIF and the others. The first group presents high intrinsic OP for both assays, whereas the others display half (OP^{DTT}) or almost null (OP^{AA}) intrinsic OP (see table XXX). Then, the first conclusion is that 80 % of the sites agree on a common intrinsic OP for the dust source. The high variability for VIF may be explained by different chemistry. Indeed, the dust factor at VIF highly differs from the other dust factors with a $PD > 0.75$ when compared to the other sites (see SUP INFO). We don't have clear hypothesis yet for the two others sites.

Despite the different PMF (and so number of sources) solution at each site and the different OP signal, the rather low variability of the intrinsic OP for a given source suggests that a given source of PM behave similarly at each site with regards to the OP. It then supports the idea that, at the national scale, the sources described above have a determined and stable intrinsic OP. This result achieved the very first requirement before a potential implementation of the OP in deterministic chemistry transport model (CTM).

Variability of the biogenic and organic sources

High variability is found for the **MSA rich** source with high variability between sites but also at a given site, with a CV of 3.1 and 7.8 for the DTT and AA assay, respectively.

The secondary organic source appears to be the most variable source in term of intrinsic OP, notably for the DTT assay. The MSA rich factor is the one among the 8 major sources of PM that contributes the less to the total PM mass and the PMF bootstrap result presents important variability for the PM₁₀ apportioned by this source. In our study, the secondary organic factor (SOA) is mainly traced by the MSA, but its remaining composition is yet unknown. This PMF factor is still not yet fully understood and few studies reported it so far. As a result, we don't know for instance the loading of HULIS, quinone or isoprene derived compounds in this factor, nor the amount of aging this factor encountered at each site. Such unknown is reflected in the MSA rich factor being the less similar factor between sites (see previous similarity assessment section). Such uncertainties on the chemistry of this factor may explain the diversity of intrinsic OP observed. Indeed, it has been shown that SOA species may contribute to the OP^{DTT} in the early stage of aging (McWhinney et al., 2013) or to the OP^{DCFH} (Zhou et al., 2018), but due to aging processes and photochemical degradation, aged SOA species may contribute to a lesser extent to it (Jiang and Jang, 2018; Wang et al., 2017). But Verma et al. (2009, 2015a) pointed that aging of SOA may increase the OP. Moreover, Tuet et al. (2019) shown that humidity and seed particles have also an effect on SOA OP^{DTT}. Since all these parameters vary in our study, it may explain the diversity of chemistry and thus intrinsic OP^{DTT} we observed for SOA. To a lesser extent, this variability is also found for the AA assay, suggesting that the same phenomena affects the SOA OP^{AA}. The sulfate-rich factor is also suspected to account for some SOA since OC are present in non-negligible amounts. Then, the variability of the sulfate-rich, and similarly for the **aged sea-salt**, intrinsic OP may be explained by the same phenomena.

Also the **primary biogenic source**, mainly traced by polyols, presents some variability for the OP^{DTT}. Samaké et al. (2017) highlighted that spore or bacteria does contribute to the OP^{DTT} and OPAA activity, even if the microbial cells are dead. However, the authors also present the inhibition of the DTT loss rate in presence of metals and 1,4-naphtoquinone or Cu. Since both results are observed, depending on which microbiota are living on the sampled PM, intrinsic OP^{DTT} may be enhanced or decreased. The variability of intrinsic OP^{DTT} observed in Figure 5 may then reflect the local different microbiology living in the PM or covariation of the primary biogenic source with another metal or 1,4-naphtoquinone rich source for instance. Also, Samaké et al. (2019b) pointed that some secondary species may be incorporated in this factor at some site, making it a mix of primary biogenic and SOA, another hypothesis is the "aging" of this factor. It is then possible that the SOA mixed in the primary biogenic may influence the intrinsic OP in different way, similarly to the MSA

rich factor.

OP type	station	Aged salt	Biomass burning	Dust	MSA rich	Nitrate
DTT	All stations and BS	0.038(113)	0.129(65)	0.121(114)	0.132(410)	0.044(65)
	AIX	-0.134(55)	0.107(28)	0.224(58)	0.051(63)	0.015(70)
	CHAM	-	0.092(6)	0.087(18)	0.240(49)	0.065(28)
	GRE-cb	0.018(46)	0.105(26)	0.122(21)	0.779(210)	0.053(21)
	GRE-fr_2013	0.181(69)	0.261(22)	0.131(32)	0.080(136)	-0.021(60)
	GRE-fr_2017	-0.083(163)	0.102(47)	0.094(39)	-0.173(323)	0.008(18)
	MRS-5av	0.110(44)	0.114(68)	0.025(22)	0.168(224)	0.088(102)
	MNZ	-	0.116(5)	0.069(15)	0.095(31)	0.053(7)
	NIC	0.120(26)	0.117(13)	0.110(27)	-	0.081(46)
	NGT	0.116(43)	0.191(35)	-	0.533(298)	0.023(35)
	PAS	-	0.129(11)	0.109(15)	0.161(75)	0.161(55)
	PdB	0.032(32)	0.179(14)	0.140(19)	0.123(80)	0.017(22)
	RBX	-0.006(50)	-0.018(43)	0.251(16)	-0.096(72)	0.066(9)
	STG-cle	0.137(37)	0.155(17)	-	0.370(71)	0.084(18)
	TAL	-0.044(30)	0.147(19)	0.103(21)	0.063(43)	-0.036(32)
	VIF	0.004(68)	0.144(28)	0.105(344)	-0.540(870)	0.002(19)
AA	All stations and BS	0.024(54)	0.197(103)	0.037(86)	-0.020(156)	0.010(56)
	AIX	-0.049(46)	0.194(18)	0.157(27)	0.051(58)	0.118(82)
	CHAM	-	0.174(12)	-0.048(15)	0.001(37)	-0.032(39)
	GRE-cb	-0.007(27)	0.169(36)	-0.015(16)	-0.169(103)	0.030(12)
	GRE-fr_2013	0.037(19)	0.183(11)	0.012(11)	-0.036(32)	-0.004(14)
	GRE-fr_2017	0.103(83)	0.368(26)	0.017(8)	-0.016(100)	-0.036(17)
	MRS-5av	0.016(7)	0.101(12)	0.004(7)	-0.029(34)	0.004(9)
	MNZ	-	0.266(12)	0.006(11)	0.082(16)	-0.084(30)
	NIC	0.034(22)	0.112(11)	-0.001(16)	-	-0.018(17)
	NGT	0.069(31)	0.428(60)	-	-0.078(234)	0.063(35)
	PAS	-	0.161(13)	-0.002(7)	-0.013(35)	0.040(58)
	PdB	0.011(14)	0.138(7)	0.034(8)	-0.003(26)	-0.011(15)
	RBX	0.069(26)	0.223(42)	0.167(23)	0.090(63)	0.019(12)
	STG-cle	-0.023(30)	0.026(25)	-	0.080(20)	0.044(12)
	TAL	0.008(17)	0.134(15)	0.006(9)	-0.015(30)	0.004(10)
	VIF	0.021(41)	0.284(23)	0.150(181)	-0.221(385)	0.015(20)

Contribution of the sources to the OP

Since the intrinsic OP of the 8 sources may be considered as stable (except the MSA-rich), we can estimate the sources contribution to the OP, similarly to the sources contribution to the PM concentration. In this part, we estimate the contribution of the sources to the OP and PM concentration at each sites, then present an aggregated view of the seasonal contribution in Figure 6, and the daily contribution in Figure 7 and 8, taking into account all the sites. Since our dataset included an important proportion of alpine sites and given the fact that

all sites are urbanized, the extrapolation to the whole France or other region should be done cautiously. Also, only the contributions of the 8 previously selected sources are reported here. The full results with details per site are presented in the website mentioned above.

Seasonality of the contribution

Figure 6. Mean monthly contribution of the main 8 sources to the (a) PM₁₀ mass, (b) OP_vDTT and (c) OP_vAA taken into account each sources contribution of every sits; and there respective normalized contribution in (d) PM₁₀ mass, (e) OP_vDTT and (f) OP_vAA (taking into account only these 8 sources).

It is already known and well documented that PM₁₀ mass concentration presents a seasonality, notably in alpine valley due to the biomass burning source and meteorological effects. By construction, the contribution to OP_vDTT and OP_vAA from each source is proportional to the mass contribution of the source in question. However, the relative importance of the contributions of the sources is altered by the fact that they have different intrinsic OPs. The question, therefore, is what are the sources of PM that contribute the most to the OP. The mean monthly contribution of the 8 sources from all sites to the PM₁₀ mass, OP_v^{DTT} and OP_v^{AA} are presented in Figure [fig:fig6] (a), (b) and (c), respectively.

As already shown by previous study in France (Favez et al., 2017; Petit et al., 2019; Srivastava et al., 2018; Waked et al., 2014; Weber et al., 2019), the seasonal mean contribution to the PM₁₀ mass show the importance of the biomass burning source, followed by the secondary inorganic (sulfate-rich and nitrate-rich), the dust and road traffic. But as a direct consequence of the different intrinsic OP, we do observe a redistribution of the relative importance of the sources. Namely, the nitrate-rich source that may contribute to a significant amount to the PM₁₀ mass, notably in spring, barely contribute to the OP_v^{DTT} nor to the OP_v^{AA}. Conversely, the road traffic contributes to about 15 % during summer to the mean PM₁₀ mass but is more than 50 % of the mean OP_v^{AA} in the same period of time (Figure [fig:fig6] (d), (e) and (f)). However, the biomass burning sources is still a major contributor to both the OP_v^{DTT} and OP_v^{AA} during winter months. We note that the primary biogenic source still contributes to the OP_v^{DTT} but to a lesser extent to the OP_v^{AA}. Also the dust source continues to be an important contributor to the OP_v^{DTT} but not to the OP_v^{AA}. These results tend to confirm what previous studies already found. With regard to the seasonality of OP, regulations should target the biomass burning emission in order to decrease the PM₁₀ OP during winter by a large amount, but also the road traffic that contributes homogeneously to both OP all around the year.

Daily mean and median contribution

Figure 7. Averaged daily contribution of the sources to (a) the PM₁₀ mass, (b) the OPvDTT and (c) the OPvAA. The bars represent the mean and the error bars the 95 % confidence interval of the mean.

Figure 8. Median daily contribution of the sources to (a) the PM mass, (b) the OPvDTT and (c) the OPvAA. The bars represent the mean and the error bars the 95 % confidence interval of the median.

The seasonal mean contribution of the source may not take into account the rapid day-to-day variability of the OP observed in SI XXX. Moreover, most epidemiological studies average the yearly exposition to a “daily averaged” or “daily median” exposure (World Health Organization, 2016). In this part, we try to express the population exposition to the sources to both the mass and OP metric on a daily basis.

The daily contribution is shown in Figure [fig:fig7] and Figure [fig:fig8], for the mean and median daily contribution, respectively. The results highly differ if considering the mean or the median contribution, and the two statistical indicators do not answer the same question. In particular, mean contribution is determined by the sum of individual measurements making it highly sensitive to outliers. On the other hand, median contribution is the middle value when the measurements in the actual dataset are arranged in ascending order. The skewness of the distribution is not surprising as some high PM₁₀ events (i.e., outliers in the dataset) were present in our measurements. This is also specifically anticipated in alpine areas (XX out of 15 sites) where the development of atmospheric inversions causing increased pollutant concentrations are highly favorable.

Therefore, the mean contribution is more related to the question “*What Which sources contribute the most to the PM₁₀ OP or mass?*” whereas the median contribution addresses the question “*What is the chronic population exposure to the PM₁₀ OP or mass?*”. Since there is strong seasonality, day-to-day variability and non- normally distributed contribution of the source to the PM₁₀ mass, notably for the biomass burning, we do observe important differences when looking at the mean or median contribution. Therefore, we decided to report both statistics in this study. Here again, we want to remind the reader that our dataset includes several alpine site strongly affected by the residential biomass burning heating, then the result might not reflect the overall regional exposure.

We do observe (Figure [fig:fig7]) a redistribution of the daily **mean** contribution sources’ rank between the PM₁₀ mass, OP_v^{DTT} and OP_v^{AA} similarly to the monthly mean contribution shown above. Since the biomass burning source is an important contributor to the PM₁₀ mass, it contributes also significantly to both

OP and is ranked as the first contributor to both OP_v^{DTT} and OP_v^{AA} mean daily contribution (mean 0.51 and 0.72, respectively). The road traffic source contribution, due to its highest intrinsic OP in both assays, has almost the same daily mean contribution than the biomass burning for the OP_v^{DTT} , and is the second contributor to the daily mean OP_v^{AA} , with half the contribution of the biomass burning (mean 0.50 and 0.34, respectively). The other source barely not contribute to the OP_v^{AA} (<0.1). For the OP_v^{DTT} , the dust is the third contributor (mean 0.34), followed by the sulfate rich and primary biogenic (0.23 and 0.16, respectively). The nitrate-rich, aged seasalt and MSA-rich present a low contribution (mean <0.1), due either to their low intrinsic OP or to their low contribution to the PM mass.

However, for the daily **median** contribution, due to the high seasonality of the biomass burning source and the consistent contribution throughout the year of the road traffic, sulfate-rich and dust sources, the ranks of the sources is even more drastically redistributed between all the considered metric (Figure [fig:fig8]) A) mass, B) OP_v^{DTT} and C) OP_v^{AA}). Moreover, the absolute value of the contribution is also lowered compare to the mean daily contribution, due to low frequencies of highly loaded PM events. The major source contributing to the OP_v^{DTT} is now the road traffic (median 0.36) and contributes more than twice as much as the second source, namely the dust one (median 0.16), followed by the sulfate-rich (median 0.13) and then the biomass burning (median 0.11). For the OP_v^{AA} , the two dominant sources are the road-traffic (median 0.29) and the biomass burning (median 0.19). The others sources being negligible in front of them (aged seasalt 0.016, primary biogenic 0.015 and the others contributes less than 0.01).

The high differences between the mean and median contribution has strong implication for air quality policy. Indeed, as previously shown, the biomass burning may contribute to more than 50 % of the high OP during winter, and even more for some days. However, such events do not represent the daily exposure of the population. Even if the regulation should target those events to prevent acute exposure, we should also take into account the long term exposure to a lower but constant level of pollutant. With this respect, the biomass burning source impact is drastically lowered but the road traffic emission become a major concern. Moreover, our dataset includes several site in alpine valley that bias our result toward a more important contribution of the biomass burning source compare to the actual urbanized French cities. Then, our conclusion strongly supports that at the regional scale, the important source to target in order to decrease the chronic exposure to PM pollutant is the road traffic one. However, site specific typologies (notably alpine valley, or “hot spot” with specific sources) may also target other sources, notably the biomass burning source in alpine valley, to prevent acute exposure of the population.

Other PMF factors

So far, we have focused on sources with regional impact. However, we would like to discuss the case of 2 sources that are often controversial for political decision-makers or inhabitants but are less representative of the urban background of French cities.

Heavy fuel oil

Among the others sources, not present at at least 2 third of the site, the Heavy fuel oil (HFO) identified at MRS-5av and PdB, present an intrinsic OP^{DTT} of 0.51(14) and 0.21(4), respectively, and an intrinsic OP^{AA} of 0.04(2) and 0.11(3), respectively. The intrinsic OP^{DTT} is then in average higher than the road traffic one, making the HFO the second contributor of the daily mean and median source contribution at MRS-5av for the OP^{DTT} contribution and the fourth one for the OP_v^{AA} contribution (see website <http://getopstandop.u-ga.fr>). For PdB, an important contribution, but lower than for MRS-5av is found, for both the DTT and AA. Although only 2 sites presented an HFO factor, it suggests that the PM originated from this source may significantly contribute to the total OP around harbor cities.

Industrial

An industrial factor was identified at 6 sites. However, the “industrial” name for this factor cover a wide variety of chemistry, as denoted in the similarity Figure [fig:fig2]. They share a common set of metal (Al, As, Cd, Mn, Mo, Pb, Rb, Zn), in different concentration levels. Since we are not aware of any emission source releasing these metals jointly into the atmosphere, we have named this factor “Industrial”, although the exact type of industry is not yet known. This factor also barely contributes to the PM_{10} mass, with a mean concentration of around 1. The intrinsic OP^{DTT} is high for GRE-cb and GRE-fr_2017 (0.52(30) and 0.37(27), respectively) as well as the intrinsic OP^{AA} (0.82(29) and 0.61(17), respectively), but is close to 0 for the other sites and both OP. The high intrinsic OP seems to indicate again the role of metals in the OP of PM, however since this factor has strong uncertainties associated with the PMF results, and then to the intrinsic OP, is hard to go into further conclusion at this point.

Limitations of the study

In this study, we focused on major sources and trends, hence limit our study to some aspect. Notably the PMF standardized approach allows common source identification at the national scale but may also “polish” some site specificity. Also, the choice to focus on the main sources of PM and to discuss the aggregated results allows discussion on some local specificity, notably potential local sources that contribute to the OP (for instance HFO or industry).

One main limitation is also the use of linear regression tools whereas it has been shown that OP does not respond linearly with mass. The residual analysis seems to agree with this experimental finding since the highest OP samples is underestimated by the MLR model. The addition of co-variation term or even the use of non-linear regression may be the next step to better explain the OP of the sources and provide more accurate policy for air quality.

Moreover, if the intrinsic OP results from the MLR can be extrapolated to any given site with similar regional background of the urbanized area used in this study, the source' contributions extrapolation should be taken cautiously since our dataset displays an over-representation of the alpine sites with regard to the whole France.

Conclusion

To our knowledge, this study gathers the most important database of OP samples with concomitant observations of chemistry analysis, source-apportionment through PMF and the measure of two OP assays (DTT and AA) for 15 yearly time series over France spanning between 2012 to 2016 for a total of >1700 samples.

- We demonstrate that source apportionment of OP through a “simple” multi linear regression without any constraint on the coefficient show good statistical result and is able to explain the observed OP_v^{DTT} and OP_v^{AA} .
- The associated uncertainties of the MLR coefficient estimated thanks to bootstrapping the solution highlight the importance of the yearly representativeness of the input dataset.
- The intrinsic OP of the main regional sources presents values that are in the same range at each site, especially for the primary traffic, biomass burning, nitrate rich, dust & sulfate rich PMF factor. Biogenic and MSA rich factors present higher discrepancy according to the site but also present the highest uncertainties at each site.
- Different sensitivity for the 2 OP assays toward the given source is highlighted. The DTT appears to be the most balanced test, whereas the AA targets mainly the biomass burning and primary traffic factor.
- In accordance with previous studies the primary road traffic and biomass burning factor has been shown as the main absolute OP contributors. On the opposite, the secondary inorganic sources (nitrate and sulfate rich) barely contribute to OP.
- In order to assess the chronicle population exposure, the median contribution of sources to the OP_v^{DTT} and OP_v^{AA} are also reported and present important discrepancy with regard to the mean contribution. The importance of the road traffic source drastically increases, notably for the OP_v^{DTT} , whereas the biomass burning contribution is lowered. Barely only the road traffic and biomass burning sources contribute to the daily

median of the OP_v^{AA} . Moreover, since there is no consensus toward the “best” OP assay for epidemiological or toxicological assessment, the sources that react to both OP should be of the first importance for regulation purposes. Then, the biomass burning and road traffic sources could be targeted to decrease the regional OP exposure.

- Finally, the relatively stable intrinsic OP at a large geographical scale for the main PM sources paves the road to the implementation of the OP into regional chemistry transport model. This step would allow a quantitative estimation of the french population exposure OP, expending potential cross-over studies with epidemiology (today limited to this dataset sites)

Fundings

This work was partially funded by ANSES for OP measurements (ExPOSURE program, grant 2016-CRD-31), IDEX UGA grant for innovation 2017 ROS-ONLINE and CDP IDEX UGA MOBILAIR (ANR-15-IDEX-02) Atmo Sud for the chemical analyses of the samples from NIC, MRS-5av and PdB, Atmo AuRA for the chemical analysis of the samples from GRE-fr, GRE-cb, VIF, CHAM, PAS and MNZ, and the French Ministry of Environment, as part of the National reference laboratory for air quality (LCSQA), for the samples from GRE-fr, TAL and NIC. The study in CHAM, MNZ and PAS was funded by ADEME. The PhD of Samuël Weber was funded by a grant from ENS Paris. This study was also supported by direct funding by IGE (technician salary), the LEFE CHAT (program 863353: “Le PO comme proxy de l’impact sanitaire”), and LABEX OSUG@2020 (ANR-10-LABX-56) (both for funding analytical instruments).

The authors wish to thanks all the peoples from the different AASQA or laboratories who gathered the filter and analyzed them (long list of name).

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