Seasonal Variations and Chemical Predictors of Oxidative Potential (OP) of Particulate Matter (PM), for Seven Urban French Sites

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Abstract: Epidemiological studies suggest that the main part of chronic effects from air pollution is likely to be linked with particulate matter (PM). Oxidative potential (OP) of PM is gaining strong interest as a promising health exposure metric. This study combined atmospheric detailed composition results obtained for seven different urban background environments over France to examine any possible common feature in OP seasonal variations obtained using two assays (acid ascorbic (AA) and dithiothreitol (DTT)) along a large set of samples ($N > 700$). A remarkable homogeneity in annual cycles was observed with a higher OP activity in wintertime at all investigated sites. Univariate correlations were used to link the concentrations of some major chemical components of PM and their OP. Four PM components were identified as OP predictors: OC, EC, monosaccharides and Cu. These species are notably emitted by road transport and biomass burning, targeting main sources probably responsible for the measured OP activity. The results obtained confirm that the relationship between OP and atmospheric pollutants is assay- and location-dependent and, thus, the strong need for a standardized test, or set of tests, for further regulation purposes.

Keywords: oxidative potential; urban background sites; OP tracers/predictors; chemical composition of PM

1. Introduction

Atmospheric pollution has been ranked as the fourth risk factor for premature mortality worldwide [1]. Epidemiological studies suggest that the largest part of chronic effects from air pollution can be linked to Particulate Matter (PM) [2–4] and its capacity to induce oxidative stress in vivo through the generation of excessive reactive oxygen species (ROS) and/or the inadequate antioxidant defences [5]. Cellular and acellular assays co-exist to assess endogenous and exogenous
ROS from PM, and acellular assays are gaining a strong interest for their quick and non-invasive character. In this context, Oxidative Potential (OP) of PM, an acellular metric based on the ability of particles to elicit oxidative reactions, is considered as a promising health exposure evaluation, as OP integrates particle size, surface properties and chemical composition of the PM [5–7]. OP most probably is a more representative metric of health impacts than PM mass concentrations, better reflecting the processes leading to impacts in the human body [8]. Regarding acellular assays, some cross-over studies between health and OP have led to positive correlations with toxicological markers of airway inflammation [9–12] or with health outcomes [7,13–18]. Nevertheless, further studies are still needed to establish proper links between OP and predictive health outcomes. Better understanding the correlations between oxidative effects and chemical composition of PM—and, further, their emission sources—is essential to possibly develop future regulations using OP.

The OP links with health outcomes and with specific chemical species and their emission sources may be the limiting steps to use OP acellular assays as a well-established metric, efficient in epidemiological studies and included in air quality measurements. Further, different OP methodologies co-exist, each of them displaying specific and assay-dependent associations with atmospheric pollutants. Thus far, no consensus has emerged towards a standard test or set of tests [7,19–21].

The widely used acellular DTT (dithiothreitol) assay is reported to be associated with some oxygenated Polycyclic Aromatic Hydrocarbons (PAHs) and notably quinones (1,4 naphthoquinone, 9,10 anthraquinone), transition metals (mainly Cu and Mn), Humic-Like Substances (HuLiS), and/or secondary organic aerosols (SOA) [22–27]. The acellular AA (Ascorbic Acid) assay is known to be correlated with elemental carbon (EC), organic carbon (OC), and many transition metals (Fe, Cu, Cr, Mn, Co, and Ni) [11,20,28–30]. The acellular DCFH (dichlorofluorescein) assay is known to be sensitive to organic compounds such as OC, PAHs [31], and also some metals or their oxides [6,31]. However, we must be aware that these correlations and linear analyses are not necessary exhibiting the proper causality between Reactive Oxygen Species (ROS) generation and active species from PM. In fact, some species display non-linear ROS generation [24,32] and many PM chemical species are co-emitted by different emissions sources inducing covariations and dependent variables. As an example, strong correlation is observed between PAHs and DTT depletion. However, PAHs are not redox-active and cannot oxidize the DTT, a reducing agent, but they are precursors of and/or co-emitted with redox active quinones [33–35].

OP determining factors have been settled by measuring the OP from reference compounds [24] or from ambient air samples from single sites or during time-limited field campaigns [17,36,37]. Larger time series and regional scale studies are needed to further connect oxidative potential to atmospheric pollutants.

The literature is still scarce about the comparison of different acellular OP measurements across cities [37,38]. Few studies have investigated several assays in the same cities over long time periods (>6 months) to better understand the OP seasonality and the links with PM chemical composition and emission sources [16,28,29]. Finally, there are also few studies relating the oxidative capacity of particulate pollution with a very detailed PM chemical characterization (>100 contaminants) [39].

This paper reports the seasonal OP variations, over a one-year period, obtained from two acellular assays (DTT and AA), and their correlations with PM chemical composition, for seven French urban background sites. Acellular OP measurements were performed using identical protocols on the large set of samples (N = 727 for DTT and N = 712 for AA assay). From 39 to 131 chemical species were analyzed for each PM sample. The objectives of this study were first to compare the seasonal evolutions of OP measurements for the different sampling sites and to identify the main PM chemical species—or predictors—that influence OP levels for the seven sites affected by different emission sources.
2. Experiments

2.1. Samplings

Filter samplings were achieved within different research programs, all conducted for the understanding of the diversity of the PM$_{10}$ chemistry in several areas of France, and gathered within the SOURCES [40] or DECOMBIO research projects [41]. For each site, about 100 samples, covering a one-year period, were chosen for OP assays along with chemical analyses. Locations of the sites are shown in Figure 1 and sampling details are reported in Table 1. All seven investigated sites are representative of urban background air quality. Among them, four sites are located in the Alps: Marnaz, Passy, Chamonix and Grenoble. The first three correspond to small cities (about 10,000 inhabitants) located in the Arve valley at elevated altitude (>500 m above sea level, m.a.s.l.) while Grenoble is more populated (150,000 inhabitants within a total of 680,000 inhabitants for the whole urban area) at about 200 m.a.s.l, standing as the gateway of the Alps. Note that these four sites are known to be strongly impacted by biomass burning emissions from residential heating in winter. In addition, adverse meteorological situations with low inversion layers in these mountainous areas are usually observed during winter [41–45]. Specific emission sources may influence each sampling sites; Chamonix and Passy are notably impacted by road traffic emissions, and industrial activities (transformation of carbonaceous materials and a waste incinerator) are located in the Passy area. Two other sites—Talence, included in the Bordeaux area and close to the Atlantic Ocean, and Nice, close to the Mediterranean Sea—are located in relatively large urban areas (1,200,000 inhabitants for the Bordeaux area, and 350,000 inhabitants in Nice). Finally, the site at Port-de-Bouc (PdB) is also located near the Mediterranean Sea and corresponds to a suburban site surrounded by industrial activities such as petrochemical activities (in Martigues, 6 km distance), steel, refinery and cement industries (in Fos-sur-Mer, 5 km distance) [46].

Figure 1. Location of the seven sampling sites.
Table 1. Sampling sites characteristics and sample details.

<table>
<thead>
<tr>
<th>Sites</th>
<th>Sampling Period</th>
<th>Coordinates</th>
<th>Altitude (m)</th>
<th>Typology</th>
<th>Climate</th>
<th>N a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marnaz</td>
<td>November 2013</td>
<td>46°32′27.78″ N, 6°30′0.29″ E</td>
<td>505</td>
<td>Urban background</td>
<td>Alpine</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>October 2014</td>
<td>46°32′27.78″ N, 6°30′0.29″ E</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Passy</td>
<td>November 2013</td>
<td>46°55′24.58″ N, 6°42′24.58″ E</td>
<td>583</td>
<td>Urban background</td>
<td>Alpine</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>October 2014</td>
<td>46°55′24.58″ N, 6°42′24.58″ E</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chamonix</td>
<td>November 2013</td>
<td>45°55′21.35″ N, 6°52′11.68″ E</td>
<td>1035</td>
<td>Urban background</td>
<td>Alpine</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>October 2014</td>
<td>45°55′21.35″ N, 6°52′11.68″ E</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grenoble</td>
<td>January 2014</td>
<td>45°9′42.24″ N, 5°44′8.16″ E</td>
<td>214</td>
<td>Urban background</td>
<td>Alpine</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>December 2014</td>
<td>45°9′42.24″ N, 5°44′8.16″ E</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Talence</td>
<td>March 2012</td>
<td>44°48′2.01″ N, 0°35′17.01″ W</td>
<td>20</td>
<td>Urban background</td>
<td>Oceanic</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>December 2012</td>
<td>44°48′2.01″ N, 0°35′17.01″ W</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nice</td>
<td>June 2014</td>
<td>43°42′7.48″ N, 7°17′10.49″ E</td>
<td>11</td>
<td>Urban background</td>
<td>Mediterranean</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>May 2015</td>
<td>43°42′7.48″ N, 7°17′10.49″ E</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Port-de-Bouc</td>
<td>June 2014</td>
<td>43°24′7.03″ N, 4°58′54.91″ E</td>
<td>3</td>
<td>Urban background</td>
<td>Mediterranean</td>
<td>113</td>
</tr>
<tr>
<td></td>
<td>May 2015</td>
<td>43°24′7.03″ N, 4°58′54.91″ E</td>
<td></td>
<td></td>
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</tbody>
</table>

[a] Total number of samples analyzed.

PM$_{10}$ filter samples were collected every third day (24 h sampling) using high-volume samplers (Digitel DA-80; 30 m$^3$ h$^{-1}$) loaded with quartz fibre filters (Pallflex Tissuquartz 150 mm).

Filters were pre-treated at 500 °C for 8 h to remove any organic contamination. Then, they were packed 5 by 5 into aluminium foil and then placed into Ziplock bags for transportation to the sampling site. After collection, they were downloaded from the filter holder, folded in half with the exposed surface inward inside a new aluminium foil, and individually put into a new Ziplock with their identification tags. About 10% of field blanks were collected in parallel to ambient air samples. All were kept at low temperature (−4 °C or below) from the sampling site until analysis. This procedure has been applied in our lab for the past 15 years and about 10,000 samples. PM$_{10}$ mass measurements were achieved at the sampling site using automated systems TEOM-FDMS (tapered element oscillating microbalance equipped with filter dynamics measurement system, Thermo) or beta gauges (MP101-RST or BAM 1020, manufactured by Environnement SA and MetOne, respectively) as part of the regulatory measurements maintained by the French air quality networks. The mass concentration of PM$_{10}$ on the filters was further reconstructed following chemical speciation analysis and compared to TEOM-FDMS measurements.

2.2. Chemical Composition of PM$_{10}$

The PM chemical characterization was performed in the same way for all samples with few exceptions listed in Table 2.

Organic and elemental carbon (OC and EC) were analyzed using a Sunset Lab. Instrument (Model 150C) following the EUSAAR2 protocol with a punch of 1.5 cm$^2$ [47]. Soluble anions and cations (NO$_3^-$, SO$_4^{2-}$, Cl$^-$ and NH$_4^+$, Mg$^{2+}$, Na$^+$, Ca$^{2+}$, K$^+$) were quantified by ionic chromatography [48]. Briefly, samples were soaked for 1 h in 10 mL of Milli-Q water with orbital shaking, and then filtered using 0.22 μm-porosity Acrodisc filters before analysis. AS/AG 17 and CS/CG 12A columns were used for anions and cations analyses, respectively. All inorganic elements, including trace metals (Al, Fe, Ti, As, Ba Cd, Ce, Cr, Cu, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, V, Zn, and Zr), were obtained by ICP-MS analysis [48]. Prior to ICP-MS analyses, each sub-sample was acid digested (HNO$_3$; HF; H$_2$O$_2$) with a microwave oven (Milestone ETHOS). Repeated measurements were performed on acid blanks, quality control standard solutions and standard reference material (SRM 1648a, urban particles). Sugar alcohols (arabitol, sorbitol, and mannitol, also called polyols) and anhydrous monosaccharides (levoglucosan, mannosan and galactosan) were quantified with an HPLC-PAD method [49]. For this analysis, extraction of filter samples was performed using ultra pure water under mechanical agitation for a period of 30 min, the extract being filtrated with 0.22 μm Nuclepore filters before injection [50]. Finally, polar and nonpolar organic species were extracted using an accelerated solvent extractor (ASE 200, Dionex), with two solvent mixtures (Acetone/dichloromethane 50:50 v/v and
dichloromethane/methanol 90:10 v/v). After reducing the extract to a volume of 1 mL under a gentle N₂ stream, 30 alkanes, 10 hopanes, 15 substituted (methyl-PAHs) and 7 sulfur PAHs (PASHs) were analyzed by GC-MS, while 16 PAHs were quantified by HPLC-fluorescence. Fourteen methoxyphenols were analyzed by GC-MS after derivatization step with BSTFA-TMCS (99:1). The extraction and analytical methods were validated by quantifying the concentrations of several organic compounds (PAHs, PASHs and hopanes) in certified standard material (SRM 1649b) [51].

In total, 8 to 10 field blank samples by location were also analyzed with the same techniques to determine the detection limits (DL) of the methods. The average blank values were subtracted from the values from the real samples to get atmospheric concentrations.

Table 2. Analysis of the PM chemical composition for each site.

<table>
<thead>
<tr>
<th></th>
<th>Marnaz</th>
<th>Passy</th>
<th>Chamonix</th>
<th>Grenoble</th>
<th>Talence</th>
<th>Nice</th>
<th>PdB</th>
</tr>
</thead>
<tbody>
<tr>
<td>∑10 Anions/Cations</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑33 Metals and trace elements</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>EC/OC</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑3 Polyols</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑3 Anhydrous monosaccharide</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑16 PAHs</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑30 Alkanes</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑15 Methyl-PAHs</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑7 PASHs</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑10 Hopanes</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>∑14 Methoxyphenols</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Ana: Analysis not available (not performed in the project that funded chemistry analysis).

2.3. OP Measurements of PM₁₀

All PM samples were submitted to the DTT and AA assays to assess their oxidative potential (Table 1). Prior to OP measurements, PM samples were extracted (vortexed) using a simulated lining fluid (Gamble solution with a surfactant) at 37°C in order to mimic lung bio-accessibility [24]. The extraction was performed at iso-concentration of 10 µg mL⁻¹ for all samples, in order to minimize the potential non-linear response of the DTT assay [52] and to get comparable conditions for every sites.

The methodology used for the DTT assay has been described into details previously [24]. Briefly, DTT depletion, when in contact with PM extracts, was determined by titrating the remaining amount of DTT with DTNB (dithionitrobenzoic acid) at different reaction times at 412 nm and with a 96-well plate spectrophotometer (Tecan, M200 and M1000). The AA assay is a simplified version of the synthetic respiratory tract lining fluid (RTFL) assay described by Kelly and Mudway [53] where only AA is used. AA depletion was read every 5 min for 30 min at 265 nm using UV-transparent 96-well plates. For both assays, the 96-well plate is auto shaken for 3 s before each measurement and kept at 37°C for the period of reaction. The results were normalized per cubic meter of air sampled since this metric is representative of human exposure. OPDTT corresponds to the consumption of DTT (nmol min⁻¹ m⁻³ of air) and OPAA corresponds to the consumption of AA (nmol min⁻¹ m⁻³ of air). Considering the large amount of data, unlikely to be presented in a limited number of illustrations, we made them accessible at https://pmall.univ-grenoble-alpes.fr/OP/.
2.4. Quality of the Data

Repeated measurements were performed on acid blanks (trace metal elements), water blanks (ions, sugars, and polyols), simulated lining fluid blanks (OP), solvents blanks (PAHs, PASHs, methoxyphenols, alkanes, and hopanes), quality control standard solutions and standard reference material (NIST SRM 1648b, urban dust). In total, 16 field blank samples and 16 laboratory blanks were also analyzed with the same techniques in order to determine the detection limits (DL) of the methods (OP measurements or chemical analysis). The average blank values were subtracted from the samples before calculation of atmospheric concentrations or OP levels (blank values and standard deviation of OP\textsuperscript{AA} 0.06 ± 0.01 nmol min\textsuperscript{−1} and OP\textsuperscript{DTT} 0.037 ± 0.005 nmol min\textsuperscript{−1}).

2.5. Data Treatment Procedures

Two seasonal periods were considered in this study: a warm period from April to September, and a cold period from October to March. Statistical analyses were performed using the software of Statistics R 3.4.0. Since the distribution of the data was non-normal, the non-parametric Mann–Whitney test was used to test the significance of the differences observed between sites or between seasonal periods in the OP, PM\textsubscript{10}, and chemical species concentrations. The non-parametric Spearman correlation (r\textsubscript{s}), based on the rank and not dependent on data distribution, was chosen for the regression analyses. Finally, the threshold of the p-value was set at 5% (p-value 0.05) for the statistical tests.

3. Results

3.1. OP and PM\textsubscript{10} Annual Average Concentrations

Overall, nearly all urban background French sites investigated present similar annual PM\textsubscript{10} mean concentrations despite different climate and meteorological conditions (about 17 ± 3 µg m\textsuperscript{−3}, see Figure 2). The annual OP\textsuperscript{DTT} mean of Passy and Nice present values significantly higher than that the ones observed for other sites. Among the three metrics (PM\textsubscript{10} mass, OP\textsuperscript{DTT}, and OP\textsuperscript{AA}, Figure 2), OP\textsuperscript{AA} gives the largest discrimination between the sites, providing the highest amplitude of values (ratio cold/warm season ranges between 1.5 (Nice) and 6.6 in Marnaz, in Table 3). In addition, annual OP\textsuperscript{AA} is significantly higher for Passy, Chamonix and Nice than for any other sites. Finally, we can assume that PM mass and OP\textsubscript{v} may be rather consistent across the French territory (at least for the southern part) on annual average, except for the Alpine sites.

3.2. OP and PM Seasonality

Temporal trends (daily and monthly means) for OP\textsubscript{v} are available at https://pmall.univ-grenoble-alpes.fr/OP/. Overall, higher PM\textsubscript{10} concentrations and OP\textsubscript{v} levels are observed during the cold period for all sites and this amplitude varies across the sites (Figure 3, PMall database). PM\textsubscript{10} and OP\textsubscript{v} levels are more variable during cold than warm periods, probably influenced by the atmospheric PM concentrations remaining relatively low and stable during warmer period (Figure 3, Supplementary Materials Figure S1 and S2). The ratios of the average values between cold and warm periods (Table 3) allow classifying such metrics: the OP\textsuperscript{DTT} ratio values are slightly lower than the PM\textsubscript{10} concentration ratios (except for Grenoble, Nice and Talence) and are lower than OP\textsuperscript{AA} ratio values. OP AA assay results present the highest amplitude between cold and warm periods (up to 6). Such seasonal variations highlight the importance of the different information brought by PM\textsubscript{10} and OP metrics.
Alpine sites (Grenoble, Passy, Marnaz and Chamonix) display the strongest seasonality for both PM$_{10}$ and OP$_v$. They exhibit the same range of ratios whatever the metric considered, which are significantly different from ratio values obtained for sites located closer to the sea coast (Nice and Port-de-Bouc). Similar climate or PM emission sources may account for OP annual means. For Talence, Nice and Port-de-Bouc ratios remain equal or under 3 for both PM$_{10}$ and OP$_v$. One hypothesis could be that the latter sites (Nice and Port-de-Bouc) have mild winters and do not experience strong impact of wood heating source during winter.

OP$_v$ seasonality has been highlighted by other studies but contrasted results had been observed among locations. Based on one-year sampling period, Abrams et al. [18] also found a significant increase of OP$_v^{\text{DTT}}$ activity during the cold season (November to January) in Atlanta. Similar trends have been reported in Thessaloniki (Greece) [54,55]. However, few studies displayed opposite trends with OP$_v^{\text{DTT}}$ higher activity in summer such as in Fresno (California, USA, urban site) [23] or Milan (Italy, traffic site) [31]. Here, OP$_v^{\text{AA}}$ exhibits seasonal variations that contrast with the available literature. Fang et al. [14] displayed an average ratio of summer to winter of $2.2 \pm 0.9$ for two urban sites in the south-eastern USA. Moreover, no significant seasonal variability in the activity for OP$_v^{\text{AA}}$ was found in

Figure 2. Representations in boxes and whiskers with two linear scales (blue line) to facilitate the reading for: (A) PM$_{10}$ concentrations ($\mu$g m$^{-3}$); (B) OP$_v^{\text{DTT}}$; and (C) OP$_v^{\text{AA}}$ for the seven sites. Solid lines in the boxes show the median value. PdB refers to Port-de-Bouc.
PM$_{2.5}$ in Budapest (Hungary) [29]—whereas OP$^{AA}$ normalized by µg presented a strong increase in summertime. However, OP$^{AA}$ seasonal variations studies are still very scarce (OP$^{DTT}$ temporal trends are more documented) and more studies are needed to compare and conclude about the seasonal trends for this OP assay. Nevertheless, OP$^{AA}$ and OP$^{DTT}$ do not stand alone among OP assays and some studies using other OP methodologies are also looking for seasonal trends. As an example, electron spin resonance can be used to quantify the radical hydroxyl OH•, while OP$^{ESR}$ is another assay relying on the physiological glutathione anti-oxidant. In a previous study performed with samples from 20 European cities, coefficients of temporal variance for OH• formation (0.26) showed less temporal variability within the six bimonthly measurements than did PM$_{2.5}$ mass (0.33), and GSH was more variable (0.71) [56,57]. Such trends were also observed in our study for the same relative assays (PM$_{10}$ instead of PM$_{2.5}$) for the urban background environment of the city of Chamonix where OH• formation (OP$^{ESR}$) did not display any seasonal pattern [28]. A one-year study in Tartu (Estonia) also led to different seasonal pattern between OH• formation and PM$_{2.5}$ mass concentrations [58]. Conversely to our study, oxidative potential represented by OH• formation exhibited relatively higher values in summer than winter in an urban background environment.

Overall, high OP$_{v}$ levels during cold period in European cities can be attributed to the common increase in PM concentrations due to additional emission sources and lower mixing rate in the cold period. Biomass burning contributes up to 70% of the PM mass in winter in alpine valleys [42,43,59] and is also likely to induce higher OP level through the chemical composition of the primary emissions and the biomass emissions ageing processes. Indeed, primary biomass emissions emit large quantity of PAHs that will lead to the formation of oxy-PAHs (and notably quinones) and nitro-PAHs, through homogeneous and heterogeneous oxidation reactions in the atmosphere [44,60–62], which are redox active species and of importance in oxidative potential contribution [22,24,63]. The cold period in Europe currently displays an increase for EC contents from traffic and biomass burning sources [64,65] both also direct emitters of PAH and PAH derivatives [35,65–67]. On the other hand, lower OP values during warmer period could be assigned to lower PM concentrations and the potential loss of volatile and semi-volatile organic compounds due to their evaporation with warmer temperatures and/or degradation by heterogeneous photochemical processes and/or different emission sources (no residential heating in summer). Alternatively, Fang et al. [14] explained their higher results for OP$^{AA}$ in summer by higher traffic emission at their site, traffic being a significant source for OP$^{AA}$. Finally, these discrepancies towards seasonal OP trends may also be assigned to differences in site typologies or experimental design. For example, Fang et al. [14] analyzed an extract from PM containing only water-soluble species whereas we considered total PM containing both insoluble and soluble species. All these assumptions could lead to the very different seasonal variations observed in OP$_{v}$. However, in this study, over the seven studied sites, whatever the climate or geography and the OP assay, a remarkable homogeneity in OP seasonal trends is observed for urban background sites.

| Table 3. Cold/warm ratios for PM$_{10}$, OP$^{DTT}_v$ and OP$^{AA}_v$. Values are given with first and third quartile in bracket ([first quartile, third quartile]). |
|-----------------|--------|-----------------|-----------------|
| Station         | PM$_{10}$ | OP$^{DTT}_v$ | OP$^{AA}_v$   |
| Marnaz          | 1.7 *** [1.3, 1.8] | 1.5 ** [1.2, 1.6] | 5.6 *** [4.1, 6.6] |
| Passy           | 2.8 *** [1.9, 3.2] | 2.1 *** [1.5, 2.4] | 4.6 *** [4.8, 5.4] |
| Chamonix        | 2.2 *** [1.7, 2.9] | 2.1 *** [1.5, 2.5] | 6.1 *** [5.4, 6.5] |
| Grenoble        | 1.6 *** [1.5, 1.7] | 2.1 *** [1.5, 2.6] | 3.9 *** [4.3, 2.6] |
| Talence         | 1.8 *** [1.3, 2.1] | 1.8 [1.1, 2.1] | 3.0 *** [2.3, 3.3] |
| Nice            | 1.1 [1.0, 1.2] | 1.2 ** [1.1, 1.4] | 1.8 *** [1.5, 1.9] |
| Port-de-Bouc    | 1.3 ** [1.2, 1.6] | 1.2 [0.9, 1.4] | 2.6 *** [2.1, 3.1] |

*** p-value < 0.001, ** p-value < 0.01, * p-value < 0.05 (non-parametric Mann–Whitney test).
3.3. OP and PM$_{10}$ Associations

Spearman correlations ($r_s$) for all sites, among OP$_v^{\text{DTT}}$, OP$_v^{\text{AA}}$ and PM$_{10}$ for the full year, cold and warm periods are reported in Table S1 and Table 4, respectively.

Whatever the OP$_v$ methodology (AA or DTT assays), OP$_v$ and PM$_{10}$ are always significantly correlated. However, the strength of the $r_s$ coefficient varies strongly according to the season and the city showing moderate relationships during the warm season and lower relationship for Mediterranean and Atlantic cities than for Alpine cities, preventing from any generalization. Over the sampling year, higher correlations are obtained between OP$_v^{\text{DTT}}$ and PM$_{10}$ with spearman values ranging $0.69 < r_s < 0.87$. Both OP assays are also significantly correlated for all sites, confirming similar seasonal trends. When comparing cold and warm periods, higher $r_s$ between OP$_v$ and PM$_{10}$ and inter-OP relations are found for the cold period. This observation is valid for all sites, and for both assays except for Talence, which presents better correlation between PM$_{10}$ and OP$_v^{\text{DTT}}$ ($0.77$ vs. $0.60$) during the warm period. Results observed for Talence might be due to a lack of observations for January and February period (cf. Figure S3 and Figure 4). Finally, with regards to $r_s$ values, OP$_v^{\text{DTT}}$ is more associated to PM$_{10}$ concentrations than OP$_v^{\text{AA}}$. Such observation was also reported in the city of Atlanta [14] and in the Netherlands [20]. The state of the art assigns PM concentration as a significant predictor of OP$_v^{\text{DTT}}$ in univariate models whereas OP$_v^{\text{AA}}$ is known to be more sensitive to some PM chemicals species [14]. However, correlations with chemical species is to be considered with caution (since correlation does not mean causation) given the significant covariations of many chemical species (including chemical species not analyzed) induced by emission sources. Nevertheless, it is still very useful to point out through emission tracers the main sources contributing to overall oxidative potential of PM. Interestingly, a seasonal evolution of the correlations between OP$_v$ values and PM$_{10}$ concentrations is observed, highlighting the importance of considering the whole sampling year to exhibit robust correlations for one site, since they are season-dependent.
Table 4. Spearman correlations \((r_s)\) between the \(OP_{\text{DTT}}^V\), \(OP_{\text{AA}}^V\) and the \(PM_{10}\) during the cold and warm period.

<table>
<thead>
<tr>
<th></th>
<th>Cold Period</th>
<th></th>
<th>Warm Period</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(OP_{\text{DTT}}^V)– (PM_{10})</td>
<td>(OP_{\text{AA}}^V)– (PM_{10})</td>
<td>(OP_{\text{DTT}}^V)– (OP_{\text{AA}}^V)</td>
<td>(OP_{\text{DTT}}^V)– (PM_{10})</td>
</tr>
<tr>
<td>Marnaz</td>
<td>0.86 ***</td>
<td>0.77 ***</td>
<td>0.65 ***</td>
<td>0.77 ***</td>
</tr>
<tr>
<td>Passy</td>
<td>0.84 ***</td>
<td>0.85 ***</td>
<td>0.70 ***</td>
<td>0.54 ***</td>
</tr>
<tr>
<td>Chamonix</td>
<td>0.90 ***</td>
<td>0.89 ***</td>
<td>0.87 ***</td>
<td>0.67 ***</td>
</tr>
<tr>
<td>Grenoble</td>
<td>0.88 ***</td>
<td>0.78 ***</td>
<td>0.84 ***</td>
<td>0.78 ***</td>
</tr>
<tr>
<td>Talence</td>
<td>0.60 ***</td>
<td>0.84 ***</td>
<td>0.66 ***</td>
<td>0.77 ***</td>
</tr>
<tr>
<td>Nice</td>
<td>0.91 ***</td>
<td>0.75 ***</td>
<td>0.82 ***</td>
<td>0.75 ***</td>
</tr>
<tr>
<td>PdB</td>
<td>0.75 ***</td>
<td>0.69 ***</td>
<td>0.89 ***</td>
<td>0.74 ***</td>
</tr>
</tbody>
</table>

*** \(p\)-value < 0.001, ** \(p\)-value < 0.01, * \(p\)-value < 0.05.

Figure 4. Spearman correlations between PM species and \(OP_v\) (DTT and AA) for each site considering the whole year datasets.

3.4. Correlations between OP and PM Chemistry

3.4.1. Contrasts between Sites

Figure 4 shows the \(r_s\) values obtained between the chemical species and \(OP_v\) and \(PM_{10}\) merging all sites datasets (detailed \(r_s\) coefficients are shown in Table S1, as well as for warm and cold periods in Tables S2 and S3, respectively).

\(OP_v\) and \(PM_{10}\) display some similar strong associations towards chemical compounds. However, they are not systematic and this underlies the difference between both metrics.

Ionic species are poorly correlated with \(OP_v\), whereas organics and metals show stronger correlations, with a few exceptions. In addition, OC and EC are highly correlated with both \(OP_v\) measurements for all sites \((r_s > 0.70)\). Interestingly, stronger correlations are observed during the cold period. Finally, for both periods (cold and warm), the significant correlations with the chemical species are more pronounced for \(OP_{\text{DTT}}^V\) than for \(OP_{\text{AA}}^V\), with a few exceptions as Talence (Table S3 and Figure 4). These observations are in good agreement with previous studies [14,39].

Correlation coefficients between chemical species and \(OP_v\) may be specific according to the environment (Alpine, Oceanic, and Mediterranean) (Table S1). Some biomass burning key species, such as potassium or rubidium, show higher \(r_s\) with both OP assays for Alpine sites (Marnaz, Passy,
Chamonix, and Grenoble) than for temperate climate sites (Talence and Nice where $r_s$ values are usually low or not-significant). In Passy, several organic species strongly correlate with both OP assays namely, anhydrous monosaccharides, alkanes, hopanes, PAHs, PASHs and methyl-HAPs, which are typically emitted by biomass burning, vehicular and/or industrial emission [68,69].

$Sb, Sn$ and $Zn$ show site-dependent correlations concerning the $OP^\text{DTT}_v$. These correlations are strong and significant for all sites and range from 0.50 (Marnaz) to 0.77 (Grenoble) for $Sn$, 0.53 (Passy) to 0.79 (Chamonix) for $Sb$ and 0.54 (Talence) to 0.84 (Chamonix) for $Zn$. These Nic, PdB, Talence, Grenoble and Chamonix display strong correlations along the whole year between both OP assays and Ba, $Sb$, and $Sn$. Previous trace elements are good proxy for non-exhaust emissions from traffic [70], and $Zn$ can be used as a traffic marker [71] as well as a marker for industrial activities—waste incineration and coal combustion [72]. Overall, $OP^\text{DTT}_v$ could be more specific to traffic source than $OP^\text{AA}_v$.

Interestingly, $Cl^-$ and $NO_3^-$, which are not redox-active, are associated to $OP_v$ along the year and during the cold period in the Arve Valley (Marnaz, Passy, Chamonix, with $r_s > 0.59$). In mountainous areas, the correlation with $Cl^-$ could originate from road salting during wintertime [73]. Salt resuspension may highly contribute to the PM mass, and it may only reflect the overall strong association between $OP_v$ and $PM_{10}$ in Arve Valley (Table 4). The association with $NO_3^-$, is much more surprising. Given that ammonium nitrate and ammonium sulphate do not exhibit any sensitivity towards both AA and DTT assays [28,74], this relation could be due to the redox organic pollutants (nitro-PAHs for instance) which can probably secondary be formed at the same time as $NO_3^-$ [44].

The number of strong correlations for $OP_v$ and $PM_{10}$ chemical species is lower during the warm period (Table S3) than during the cold period (Table S2) for all sites. The remaining associations in the warmer period, rely more to the DTT than the AA assay. The site of Port-de-Bouc (PdB) displays the lowest number of associations between $OP_v$ and chemical species. For Talence, associations between $PM_{10}$ composition and $OP_v$ are greater with the DTT assay during the warm period and the AA assay during the cold period. These differences show that the modulations of $OP_v$ levels are not only due to the variability of a few chemical species. $OP_v$ predictors are very likely variable depending on the emission sources—varying from sites and considered seasons.

### 3.4.2. OP Predictors

As EC and OC are strongly correlated with both OP assays and for all the sites; these chemical species seem good predictors to explain $OP_v$ values among the urban background sites investigated here (Figure 5). These results are also in agreement with the literature reported about the relation between the carbonaceous species and oxidative potential [7,34,75]. However, $OP^\text{AA}_v$ usually shows lower correlations with $OC$ than $EC$ [20,29,30,76,77]. $EC$ and $OC$ show pro-inflammatory effects in toxicological studies [21,78,79], highlighting the importance of such OP predictors even if several toxicological studies suggest that these effects are probably rather due to reactive compounds (metals, quinones, etc.) associated to carbonaceous particulate matter than from an intrinsic toxicity [8,79–81].

Univariate correlations over the seven sites also highlight the sum of anhydrous monosaccharides—named also monosaccharides—and methoxyphenols (when measured) (Figure 6 and Table S1). These molecular tracers of biomass burning (sum of anhydrous monosaccharides include levoglucosan) seem good $OP_v$ predictor candidates. Correlations between $OP^\text{AA}_v$ and monosaccharides range from 0.62 (Nice) to 0.94 (Chamonix) and 0.63 (Nice) to 0.93 (Chamonix) for methoxyphenols. Correlations are higher during cold period in agreement with the seasonality of wood combustion used for residential heating purposes (Table S2). Note that significant highest correlations are observed for Alpine sites for all biomass burning tracer species (monosaccharides, rubidium, potassium and methoxyphenols). This may be explained by larger primary emissions from residential heating as well as by the Alpine meteorological conditions and the influence of the geomorphology with the frequent formation of thermal inversion layers leading to the stagnation of pollutants. Figure 6 also shows that $OP^\text{AA}_v$ is strongly correlated with biomass burning tracers than $OP^\text{DTT}_v$. These findings are in
contradiction with those of Fang et al. [14] where their sampling site in Atlanta (USA) displayed higher correlations between biomass burning tracers and OP$_{DTT}$. The different site typologies (urban, coastal and mountainous sites) as well as the differences in the experimental design (simulated lining fluid used for extraction prior to OP measurements) may explain such differences.

Figure 5. Observed correlations between particulate OC (organic carbon), EC (elemental carbon) and OP$_{AA}$ or OP$_{DTT}$. All sites are combined. From top to bottom: OC and OP$_{DTT}$; EC and OP$_{DTT}$; OC and OP$_{AA}$; and EC and OP$_{AA}$.

Among the chemical components, Copper (Cu) was the only one showing very high correlation with both OP assays for all the sites. Correlation coefficients between Cu and OP$_{DTT}$ range from 0.68 (Talence) to 0.87 (Chamonix). For OP$_{AA}$, these correlations show significant differences among sites (0.45 (Marnaz) < $r_s$ < 0.89 (Nice)). For both assays, these correlations are strong and significant, whatever the season considered (Tables S2 and S3). These results are in agreement with several previous studies [7,20,30,34,82] highlighting Cu as a key predictor in the ROS budget. In the atmosphere, Cu largely originates from brake wear particles and is commonly used to identify traffic emission source [70]. Other metal(loid)s analyzed (Ba, Sb, and Sn), and used as tracer for non-exhaust traffic emissions [83,84], are not necessarily correlated with both OP assays for all the sites. The homogeneous Cu correlation with both OP assays is probably due to its high redox active properties (Sn, Sb, and Ba are not redox active), and/or should be due to its widespread use in European car brakes. In addition, the content of Cu in the disc brake pads is largely higher than other metal(loid)s [83]. Interestingly, when splitting sites according to their altitude (mountainous vs. non-mountainous (>500 m.a.s.l Marnaz, Passy and Chamonix vs. Talence, Grenoble, Nice and Port-de-Bouc)) correlations and slopes between Cu and OP$_{AA}$ are significantly different (see Figure 7). This result is also observed for Sn and Sb (Figure
S3 and Figure 4), as well as other trace elements associated with non-exhaust emissions (Ba, Cd, Pb, Zn, Ni, Cr and Mn). This surprising result highlights a different impact of non-exhaust vehicular emissions for OP$_{AA}$ in the Arve valley. One hypothesis should be a difference in the balance between heavy duty trucks and light vehicles running and thus affecting the PM chemical composition. A higher influence of heavy-duty truck is notably expected in the Arve Valley, ending by the “Mont Blanc tunnel”, and carrying a large part of the European freight transport. Moreover, mountainous locations, with steeper slopes, may require a higher use of brakes than in other regions.

![Figure 6](image_url)

**Figure 6.** Observed correlations between particulate monosaccharides concentrations and OP$_{AA}$ or OP$_{DTT}$. All sites are combined.

![Figure 7](image_url)

**Figure 7.** Observed correlations between particulate Cu concentrations and OP$_{AA}$ according the site typology (mountainous vs. non-mountainous).

### 3.5. Limitations of the Study

In this study, we performed measurements with two widely used acellular OP assays on PM samples from seven French sites to evaluate the main drivers of the oxidative potential of PM. While numerous compounds and PM source markers have been quantified here, the number of species analyzed cannot be exhaustive, covering all the relevant chemical species for the OP metric. As an example, some secondary organic aerosol (SOA) markers (MSA and oxalate) have been analyzed but several others are missing (biogenic or anthropogenic SOA markers, PAH derivatives such as...
oxygenated and nitrated ones). This has been done only for selected sites and not necessarily covering all the sampling periods presented here [43].

In addition, polyols have been quantified and used to trace primary biogenic emissions (PBOA), but additional and complementary markers such as cellulose were not included in this study, while their mass contribution to the PM [85,86] and their role on OP [87] can be significant. Thus, in summer and winter, with SOA from biomass burning emissions, the implication of SOA and PBOA on the measured OP levels cannot be ruled out. This is probably one of the main limitations of this study but the analysis of all these chemical species, and especially SOA markers and PAH derivatives, would be very time consuming and expensive and cannot be achieved on a such number of samples. Alternatively, the deconvolution of OP according to PM sources is probably more promising than simply connecting OP and ambient air concentrations of few chemical species [14,17,59,88]. Finally, note that, as all OP assays were obtained from PM$_{10}$ samples, results cannot be extrapolated to other PM size fractions.

Another major limitation of such studies relies on acellular assays. The biological system has many pathways that work together in living tissue to mitigate the toxicological response from PM exposure, and acellular OP assays only capture exogenous ROS from PM. Acellular assays cannot assess endogenous ROS released from the contact of PM with living tissues. Some studies have addressed the link between OP and markers of toxicological impacts [8,21,89,90] allowing the understanding of the involved cellular processes. In these studies, correlations were not systematic according to the assay or the atmospheric compound tested and toxicological markers [9,10,91]. Finally, and probably the most important when it comes to the ability of OP to represent a good “PM health impact metric”, the ability of OP to predict human endpoints is still necessary to test if OP is associated with increased mortality or morbidity independently from already known metrics such as PM$_{2.5}$ mass. Thus far, this is poorly documented in the literature [13,14,18] and no unifying OP assays have been identified to predict the induction of toxic response from PM. Thus, this study contributes to evaluate if ambient air OP measurements show significance, coherence, stability and repeatability, and could be used in the future to improve air quality policies.

4. Conclusions

This study reported the seasonal variations of acellular oxidative potential along a large set of samples (N > 700) corresponding to seven different urban background environments. A remarkable homogeneity in the OP$_{v}$ seasonal trends was observed with higher levels in wintertime for all the studied sites. Univariate correlations were used to understand the influence of the chemical composition of PM$_{10}$ on OP$_{v}$ variations. Among the many quantified particulate species, four of them were identified as OP predictors: OC, EC, anhydrous monosaccharides (in association with methoxyphenols when measured) and Cu. The specific targeting of these species could allow decreasing OP levels and by them the harmfulness of the PM. These species are mainly emitted by traffic and biomass burning sources. However, the formal assignment between emission sources and OP$_{v}$, as measured here, is difficult to achieve due to some species co-emissions and will be further resolved through inversion methodologies. For other species, associations with OP were strongly influenced by the season. In summer, OP$_{v}$ values were mainly associated with tracers of vehicular and industrial sources. For the OP$_{v}$ seasonality, it is recommended to be careful when assessing oxidative potential within punctual campaign (seasonal dependence) and, overall, consider yearly sampling as a more robust method in assessing oxidative potential. In addition, this study focused only on urban background locations. Investigations in other environments (e.g., rural background and roadside) would be required to generalize the observations made here and to determine OP$_{v}$ predictors over France and Europe. Finally, the results obtained confirm that the relationship between oxidative potential and PM composition is assay, season and location dependent and, thus, there is a strong need for a standardized test, or set of tests, for further regulation purposes.
Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/10/11/698/s1, together with online visualization at https://pmall.univ-grenoble-alpes.fr/OP/.

Author Contributions: G.U. and J.-L.J. conceived, designed, acquired funding and supervised the study. A.C. (Aurelie Charron) performed OP assays and data curation. J.-L.B. and A.C. (Aude Calas) performed chemistry analysis. G.U. and A.C. (Aude Calas) analyzed the data and wrote the manuscript. J.M.F.M., J.-L.J. and G.U. are supervising the PhDs of A.C. (Aude Calas) and/or S.W.; S.W. settled OP web application and some plots (visualization + software). F.C., G.B. and B.M. are coordinating the filter sample collection for Atmo Nouvelle-Aquitaine, Atmo Auvergne-Rhône-Alpes and Atmo Sud, respectively. O.F. and A.A. are in charge of the CARA program coordination and aerosol health effect topics, respectively, for the French reference laboratory for air quality monitoring (LCSQA). All authors reviewed and commented on the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations
The following abbreviations are used in this manuscript:

- PM$_{10}$ Particulate matter with aerodynamic diameter lower than 10 µm.
- OP$^{\text{DTT}}$ Oxidative potential of PM measured by the dithiothreitol, normalized by cubic meter of air.
- OP$^{\text{AA}}$ Oxidative potential of PM measured by the ascorbic acid, normalized by cubic meter of air.
- AASQA Agence Agréée de Surveillance de la Qualité de l’Air.

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