Article

Important Contribution to Aerosol Oxidative Potential from Residential Solid Fuel Burning in Central Ireland

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Abstract: Numerous studies have shown negative health effects related to exposure to ambient particulate matter (PM), likely due to induced oxidative stress. In this study, we have examined ambient PM samples from Birr, a small (~5000 inhabitants) town in central Ireland, for their water-soluble DTT-based oxidative potential (OP_DTT) with a resolution of 6 h, together with online chemical characterization measurements, to assess the OP of organic aerosols, in particular from residential solid fuel burning. The OP_DTT normalized by the volume of sampled air shows a high variability, ranging from <0.1 to 3.8 nmol min^{-1} m^{-3}, and a high correlation with PM mass. A lower variability was associated with the mass-normalized OP. Nevertheless, both tended to present higher values during night-time pollution episodes. Simple and multivariate linear regression approaches linked OP_DTT to residential solid fuel burning, and in particular to wood (~87%) and peat (~13%) combustion. The results of the present study show how residential solid fuel burning can have a severe impact on air quality, even in small towns, with potential negative health effects on the exposed population.

Keywords: oxidative potential; organic aerosol; biomass burning aerosol; source apportionment; fine aerosol

1. Introduction

Fine and ultrafine particulate matter (PM) significantly contributes to air pollution in many regions and cities. Exposure to high aerosol concentrations has been found to increase adverse effects on human health, in particular related to respiratory, cardiovascular, and even neurological diseases [1–7]. A comprehensive set of mechanisms able to explain this link has not been determined yet, but various experimental studies have attributed PM health effects to the oxidative properties of ambient particles [2,8,9]. It has been hypothesized that the exposure of cells to aerosol particles could lead to a cascade of reactions which ends in the overproduction of reactive oxygen species (ROS) in vivo. ROS are molecules, ions, or radicals containing oxygen with high oxidizing capacity, such as the hydroxyl radical ($^{\bullet}$OH), superoxide radical ($O_2^{\bullet-}$), and hydrogen peroxide (H_2O_2). These species can exist in PM (exogenous or particle-bound ROS) or be produced inside the cell as the by-product of oxygen metabolic activity (endogenous) [10]. When overproduced, ROS can deplete the natural antioxidant defenses in biological systems and induce the

oxidative stress state [11–15]. The ability of PM to induce the formation of ROS is defined as aerosol oxidative potential (OP); this property is currently widely investigated as a potentially important metric to describe the capability of aerosol particles to generate health impacts [16]. Indeed, PM mass concentration, the traditionally used air quality parameter for epidemiological studies, is a poor metric for explaining the mechanisms by which PM exposure can induce a deterioration in human health [17]. It may underestimate the overall impact of PM, since it does not consider the different sizes, compositions, and toxicological effects of its components and their interactions with other pollutants [16]. OP, instead, integrates various biologically relevant properties of particles, such as size, surface, and chemical composition and can be measured following several kinds of procedures, including both cellular and acellular methods [18].

Acellular assays are currently faster and less resource-demanding than cellular assays, allowing for the more rapid development of reasonably large datasets in different locations for use in PM source apportionment and health analyses [18]. Comparative studies have shown that each assay is associated with different aerosol components since each one is sensitive to specific ROS-generating compounds. The DTT (dithiothreitol) assay, introduced by Cho et al. [19], is one of the most commonly used acellular methods for OP measurements. DTT is considered to be a chemical surrogate of natural antioxidants like NADH/NADPH. When a sample of PM extract is incubated at 37 °C in the presence of excess DTT, the DTT consumption rate (OP_DTT) [20] is proportional to the concentration of redox-active compounds associated with the ROS-generating PM. Other commonly used acellular OP assays are the Ascorbic Acid (AA) and Dichlorofluorescin (DCFH) ones [18]. The latter is the most common probe used for quantifying particle-bound ROS [21,22], while the former is based on a similar principle as the DDT assay but makes use of a different antioxidant molecule.

The redox activity of fine and ultrafine particles is typically higher than the coarse fraction [23–27], suggesting that fine particles have a greater impact on human health. Several organic particulate components are responsive to the DTT assay, including water-soluble organic carbon (WSOC) [19,28–30], humic-like substances (HULISs) [31–33], quinones, and PAHs [20,34,35]. Secondary organic aerosols (SOAs) have also shown a non-negligible OP_DTT, depending on their formation conditions and processes [33,36–40]. Other studies have emphasized the role of transition metals, such as Fe, Cu, and Mn, in enhancing OP_DTT [18,25,41]. However, the DTT assay has been reported as the least sensitive assay to metals among the most common OP methods [24,42]. Secondary inorganic aerosols (SIAs, including SO_4^{2-}, NO_3^-, and NH_4^+) can contribute to a large amount of aerosol mass, but despite this they do not contribute directly to OP_DTT [43–45]. Nevertheless, it is worth highlighting that the SIAs' composition may produce acidic conditions [25,41], which could induce inflammation through synergistic action with other PM components (e.g., transition metals whose solubility is affected by pH) [27], contributing to cellular oxidative stress. Conversely, the AA assay has shown significant sensitivity with both soluble and total metals, including copper, manganese, lead, zinc, and iron [28,46,47], while its sensitivity to organic molecules is not considered relevant [18].

The identification of specific ROS-emitting sources and of ROS-generating processes in the atmosphere may constitute a useful tool to better estimate the PM exposure-associated risk [24,28,30,48–52]. The present work investigates aerosol oxidative potential properties in Birr (central Ireland), a site characterized by elevated organic aerosol loadings, mainly attributable to the residential burning of solid fuels for home heating [53–55]. Aerosol chemical composition and source apportionment data were combined with the OP_DTT assay to assess the ROS-generating potential of organic aerosols and, in particular, of biomass burning emissions [53,54].

2. Experimental Methods

2.1. Sampling Site

The measurements were performed in Birr, a small town which lies in the midlands area of Ireland with a population of ~5000 located ~150 km to the west of Dublin. The sampling site in Birr was located at the council yard in St. John's Place (53°05'47.1'' N, 7°54'29.9'' W) ~100 m from the central square in the town.

2.2. OP Determination

Aerosol samples ($PM_{2.5}$) were collected on 150 mm diameter quartz fiber filters using a DHA-80 high-volume sampler (Digitel, Switzerland) operating at 500 L min^{-1} [50]. Samples were collected every 6 h for two weeks (2–15 December 2015), resulting in a total of 56 filter samples. Half of each filter was dedicated to the analysis of the water-soluble aerosol oxidative potential by the dithiothreitol (DTT) assay, following the procedure introduced by Cho et al. [19] and Verma et al. [29]. The filter portions were extracted in deionized water, and the extracts were filtered using PTFE 0.45 μm pore syringe filters to remove insoluble materials and any filter debris. The extracts were stored at 4 °C if they could not be analyzed immediately. For the DTT analysis, 2.5 mL of extract was added to 0.5 mL of potassium phosphate buffer (0.5 M, pH = 7.4) in an amber vial (primary vial), which was subsequently placed in a water bath. When the temperature of the buffered extract reached 37 °C, 30 mL of the DTT solution, with a concentration of 10 mM, was added to the vial, thus initiating the reaction (time zero). After 5, 10, 15, 20, and 25 min, an aliquot of 0.5 mL was removed from the vial and added to a second amber vial (secondary vial) containing 0.5 mL of 10% trichloroacetic acid to stop the reaction. After all solutions were collected, 50 mL of 10 mM DTNB solution in phosphate buffer at pH 7.4 was added to all secondary vials, mixed, and allowed to react for 5 min in the dark. Then, 2 mL of a solution of 0.4 M Tris-HCl buffer at a pH of 8.9 and EDTA 20 mM was added. The reaction between the residual DTT and DTNB forms 2-nitro-5-thiobenzoic acid (TNB), which was quantified at its maximum absorption at a 412 nm wavelength by a TIDAS E (J&M) UV-VIS spectrophotometer. The decrease in DTT was measured over the course of the reaction. The DTT depletion rate (nmol DTT min^{-1}), which is proportional to the ROS concentration, was determined from the slope of the best line of fit through the five measurements of the DTT concentration as a function of the reaction time (5, 10, 15, 20, and 25 min). Slopes obtained by the field blank filters, following the same approach, were subtracted from the slopes of the samples to compensate for signals coming from the filter matrix. By replicating measurements of standards (9,10-PQN) at different concentrations and two representative samples, the reproducibility of the method was evaluated to be within 12%, in line with the estimation of DTT uncertainty by Molina et al. [56] but higher than the estimate by Borlaza et al. [57] (3%).

### 2.3. Characterization of the Aerosol Components and Organic Aerosol Source Apportionment

The composition and mass of non-refractory submicron aerosol ($NR\text{-}PM_1$), with a time resolution of 30 min, was measured in Birr using an ACSM (Aerosol Chemical Speciation Monitor, Aerodyne Research Inc., Billerica, MA, USA) [58]; for the determination of the amount of equivalent black carbon (eBC), an Aethalometer (AE-33, Magee Scientific, Berkeley, CA, USA) was deployed. A detailed description of the measurement approach and source apportionment strategy was provided by Lin et al. [55]. In this work, we focus on a subset of the data presented in the above paper, covering the filter sampling period 2–15 December 2015. The mass concentrations of the chemical species measured by the ACSM and of eBC were summed to provide an estimate of the fine aerosol mass concentration.

3. Results

3.1. Aerosol Chemical Composition and Sources

The atmospheric concentrations and trends of the main submicron aerosol chemical components measured online in Birr have been discussed in detail by Lin et al. [55]. Here,

we report only the aerosol composition data averaged over the filter sampling times (6 h) (Figure 1), which will be compared with the OP data. The average sub-micrometer aerosol concentration during the study period was 7.1 ± 8.5 µg m^{-3}, varying over the range < 0.5 to 47.5 µg m^{-3}. As a consequence of the 6 h averaging, the peak concentrations shown in the present work are necessarily lower than those previously reported by Lin et al. [55]. The aerosol chemical composition was dominated by organic aerosol (OA), accounting for $67 \pm 12\%$ of the total mass (average concentration of 5.2 ± 6.8 µg m^{-3}), followed by eBC, with a contribution of $15 \pm 9\%$ (or 0.8 ± 0.7 µg m^{-3}). Inorganic ions (sulfate, SO4, nitrate, NO3, and ammonium, NH4) accounted for the rest of the mass (Figure 1a). The six-hour-averaged PM mass showed a clear diurnal cycle with peak concentrations in the late afternoon and night samples, indicating a source of aerosol from nearby home heating, as previously reported by Lin et al. [55,59]. Over the course of the night-time pollution episodes, the relative contribution of the main aerosol components did not vary significantly, with the exception of eBC, which decreased from 19 ± 11 to $11 \pm 3\%$ ($p < 0.05$). Lin et al. [55] showed that Birr, a midland town with a population of less than 1% of that of Dublin and located about 150 km away from the capitol city, for relatively short periods of time, had sub-micron particle concentrations comparable with those of the most polluted cities in Europe.
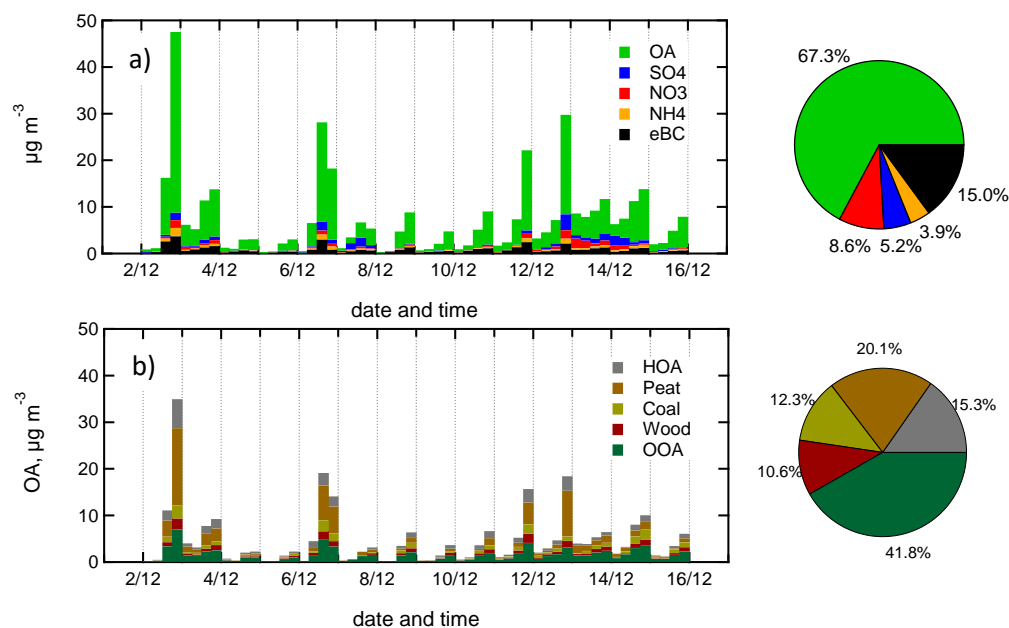
Figure 1. (**a**) PM$_1$ chemical composition during the study period, averaged over the filter sampling time and campaign average (pie chart); (**b**) OA components during the study period determined by PMF source apportionment, averaged over the filter sampling times and campaign average (pie chart).

Positive matrix factorization (PMF) analysis applied to the ACSM data distinguished five factors [55]. Four factors were attributed to primary emissions from combustion processes (Figure 1b). Hydrocarbon-like OA (HOA) was shown by Lin et al. [55] to represent the emissions from oil combustion for domestic heating rather than traffic. The remaining three primary factors were attributed to the combustion of different kinds of solid fuels for domestic heating: peat, coal, and wood. Finally, the oxygenated organic aerosol (OOA) was associated with secondary organic aerosols (SOAs) and/or aged organic aerosols. For a full detailed description of the PMF analysis, the reader is referred to Lin et al. [55].

On average, the major part of the OA mass was attributed to OOA ($42 \pm 11\%$), followed by peat ($20 \pm 11\%$), HOA ($15 \pm 6\%$), coal ($12 \pm 5\%$), and wood ($11 \pm 3\%$) (Figure 1b),

making the contribution from solid fuel combustion (the sum of peat, coal, and wood) the largest source of OA at the Birr site ($43 \pm 9\%$).

During the night (samples collected between 18:00 and 24:00 and 0:00 and 6:00), the contribution from solid fuel combustion increased with respect to the day-time samples (from 6:00 to 12:00 and 12:00 to 18:00) ($46 \pm 9\%$ vs. $40 \pm 9\%$). This difference is statistically significant with a confidence interval of 95% ($p < 0.05$) according to a standard *t* test. Focusing on the single fuel types, the contribution from peat increased from $17 \pm 10\%$ to $23 \pm 11\%$ ($p < 0.05$), while coal and wood contributions showed only minor variations ($11 \pm 5\%$ vs. $13 \pm 5\%$ and $12 \pm 3\%$ vs. $10 \pm 3\%$, respectively). Accordingly, the contribution from OOA during the night decreased ($39 \pm 10\%$ vs. $45 \pm 10\%$, $p < 0.05$). This highlights that the high aerosol concentration events observed during the night-time were mainly driven by primary OA sources, with the residential burning of solid fuels, especially peat, being the major contributor. The occurrence of these pollution events was often favored by night-time meteorological conditions, such as atmospheric stability and a shallow mixing layer, which do not facilitate the dilution of locally emitted particles [55,59].

3.2. Temporal Variability of OP

The temporal variation in OP_DTT across the sampling period is shown in Figure 2. The results are expressed as the rate of DTT consumption normalized by both the volume of sampled air (OP_DTT$_v$, or extrinsic OP_DTT, expressed in units of nmol min^{-1} m^{-3}) and the particulate mass (OP_DTT$_m$, or intrinsic OP_DTT, expressed in units of nmol min^{-1} mg^{-1}).
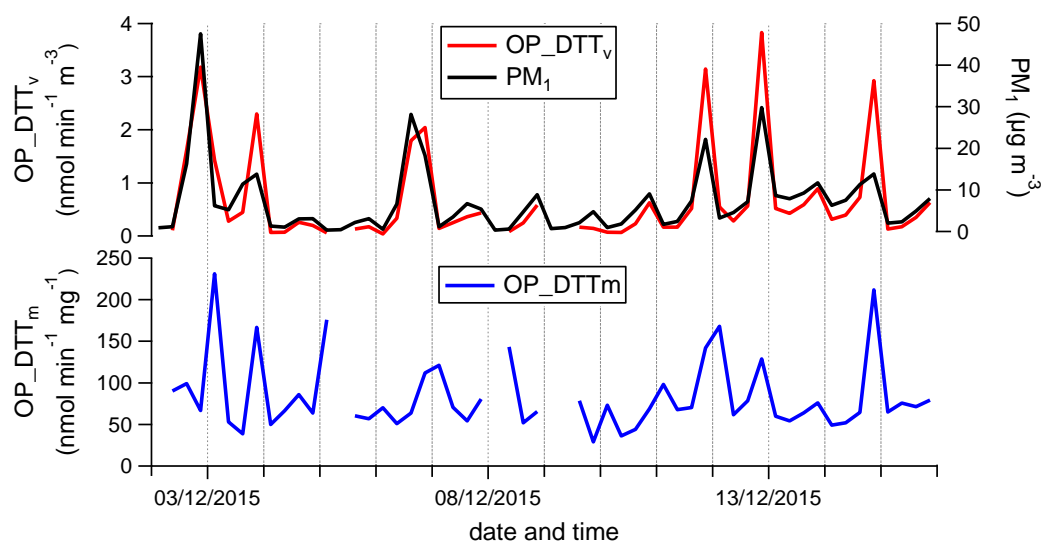
Figure 2. Time trends of OP_DTTv (**a**) and OP_DTTm (**b**). For comparison, the PM$_1$ mass concentration derived from online measurements and averaged over the filter sampling times is reported as well.

The average OP_DTT$_v$ value was 0.6 ± 0.9 nmol min^{-1} m^{-3}, with high variability both within and between different days (relative standard deviation, RSD, = 143%), ranging up to 3.83 nmol min^{-1} m^{-3}. The time trend of OP_DTT$_v$ shows a strong and significant correlation ($p < 0.05$) with the concentration of PM (Figure 2a), as well as maximum and minimum values during night-time and day-time, respectively (correlation coefficient, R = 0.87, Table 1). A correlation between OP_DTT$_v$ and PM mass is sometimes reported in the literature [2,24,60,61], but cases in which this correlation was not observed have also been reported, particularly for the summer season [62,63]. The lack of correlation between the OP and PM mass can be interpreted as evidence that the main factors responsible for OP are aerosol components that do not contribute strongly to the mass. Conversely, in the case of Birr, it can be hypothesized that OP is related to major aerosol components (such as OA) or to some species with a similar time trend as the mass.

Table 1. Pearson's correlation coefficients (R) of volume-normalized and mass-normalized species concentrations with OP_DTTv and OP_DTTm, respectively. Statistically significant correlations ($p < 0.05$) are reported in bold.

	OP_DTT_v		OP_DTT_m
OA	**0.87**	OA/PM	**0.28**
SO4	**0.59**	SO4/PM	−0.25
NO3	**0.63**	NO3/PM	0.07
NH4	**0.87**	NH4/PM	0.12
eBC	**0.79**	eBC/PM	−0.17
PM	**0.87**		
HOA	**0.84**	HOA/PM	0.15
Peat	**0.81**	Peat/PM	**0.29**
Coal	**0.79**	Coal/PM	0.2
Wood	**0.88**	Wood/PM	0.16
solid fuels **	**0.86**	solid fuels **/PM	**0.36**
OOA	**0.83**	OOA/PM	−0.08

** sum of peat, coal, and wood.

The average OP_DTT_m was 76 ± 48 nmol min^{-1} mg^{-1}, with lower variability than OP_DTT_v (RSD = 63%) and ranging up to 231 nmol min^{-1} mg^{-1} (Figure 2, bottom). As expected, its trend shows no correlation with the particulate mass concentration (R = 0.21, $p > 0.05$).

Both OP_DTT_v and OP_DTT_m showed higher values during the night-time (average 0.9 ± 1.2 nmol min^{-1} m^{-3} and 89 ± 60 nmol min^{-1} mg^{-1} for OP_DTT_v and OP_DTT_m, respectively) compared to day-time periods (average 0.4 ± 0.4 nmol min^{-1} m^{-3} and 62 ± 27 nmol min^{-1} mg^{-1}, respectively, $p < 0.05$; Figure 3). In the case of OP_DTT_v, the nocturnal increment is clearly related to the increasing concentrations of all the aerosol components, as observed also in other studies [32]. On the other hand, the higher OP_DTT_m values during night-time may suggest a larger relative abundance of redox DTT-active species during the pollution events than in the day-time.
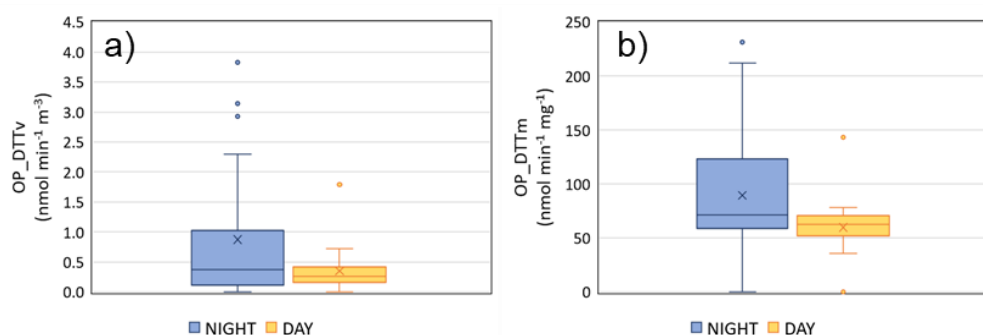
Figure 3. Data distribution of OP_DTTv (**a**) and OP_DTTm (**b**) in night and day samples. The boxes represent the interquartile range, while the whiskers indicate the 5th and 95th percentile; the horizontal bars and the crosses represent the median and mean value, respectively.

Overall, the DTT-based oxidative potential measurements obtained in the present study fall within the range of the values reported in the literature. In order to compare the present results with the literature data, often obtained on daily aerosol samples, we calculated the daily mean of the OP_DTT observed in Birr. The OP_DTT_v values observed in Birr (from 0.08 to 1.3 nmol min^{-1} m^{-3}) tend to be higher than those typically reported for rural locations in similar winter conditions [26,64,65]. This is not unexpected, as typically rural background sites are located far from direct aerosol sources, while in the present study, measurements were performed downtown in a town of 6000 inhabitants. Noteworthy exceptions are represented by the studies by Vörösmarty et al. [66] and Costabile et al. [67], reporting OP_DTT_v levels ranging between 0.3 and 3.1 nmol min^{-1} m^{-3} (median 1.2) and

between 0.01 and 2.0 nmol min^{-1} m^{-3} (median 0.86) for the rural background sites of K-Puszta (Hungary) and San Pietro Capofiume (Po Valley, Italy), respectively. Studies in the literature taking place at sites with similar characteristics to Birr are not very common: Pietrogrande et al. [68] measured wintertime OP_DTT$_v$ at the village of Novaledo (1000 inhabitants) in the alpine region of Northern Italy. The site was heavily impacted by biomass burning from domestic heating, similarly to Birr, but it presented lower OP_DTT$_v$ levels (0.33 $\pm$ 0.007 nmol min^{-1} m^{-3}). Similar OP_DTT$_v$ levels as those detected in Birr, or higher, were instead observed during the winter time in Thessaloniki, Greece (3.10 $\pm$ 0.49, [50]); Rotterdam, the Netherlands (1.4, [24]); Lecce, Italy (~0.1--~1.2, [69]); Grenoble, France (up to 2.5); Bologna, Italy (0.3–1.7, [47]); and Milan, Italy (3.38 $\pm$ 0.46, [70]). All these studies were located in cities much larger than Birr, evidencing the peculiarity of the air quality conditions at the study site.

The OP_DTT$_m$ values (27–122 nmol min^{-1} mg^{-1}) resulting from the Birr observations are generally on the upper side of the range of values reported in the literature (see the above cited studies); nevertheless, OP_DTT$_m$ values higher than those observed in the present study have been reported, for instance in Thessaloniki, both in summer and winter [71], at Rotterdam [24], and in Milan [72]. The generally high OP_DTT$_m$ may indicate that the aerosol collected in Birr during the study period was particularly redox-active. It should be noted that OP_DTT$_m$ was derived from the reconstructed PM$_1$ mass (see above), assuming that this is representative of the PM$_{2.5}$ mass collected on the filters. Although this assumption is reasonable, a discrepancy between the two aerosol mass metrics may have contributed to the resulting high OP_DTT$_m$ values.

OP has been linked with various negative health outcomes by several epidemiological studies, even though this association has still to be fully elucidated and contrasting outcomes have been presented in the literature [18]. According to the review by Bates et al. [18], OP_DTT$_v$ was positively associated with airway inflammation, acute cardiorespiratory endpoints, asthma, rhinitis, and cardiovascular diseases (microvascular function, congestive heart failure, ischemic heart disease), often with a stronger association than the PM mass concentration (e.g., [73–76]). Although there is no direct evidence of such negative health outcomes at the study location, the episodic occurrence of high OP_DTT$_v$ levels during the night evidences a potential risk for the exposed population that needs to be further investigated.

3.3. OP Source Apportionment

To identify specific components contributing to OP_DTT, simple linear and multi-linear regression approaches were employed. Pearson's correlation coefficients were calculated by comparing OP_DTT$_v$ with the absolute mass concentrations of the aerosol components and OP_DTT$_m$ with the relative contributions of the aerosol components. The correlation results are shown in Table 1; statistically significant correlations ($p < 0.05$) are highlighted in bold.

High correlation coefficients were obtained for OP_DTT$_v$ with all the aerosol chemical species and PMF factors, except SO4 and NO3, which nevertheless show a moderate correlation coefficient. This is probably due to the strong covariance among PM components during the study period. High correlations between all the components suggest that common processes and conditions (meteorology and planetary boundary layer dynamics) govern the aerosol atmospheric concentrations at the sampling site [59].

The highest correlation coefficients are observed for PM, NH4, and OA (R = 0.87 for each of these). Significant correlation between OP_DTT$_v$ and the organic aerosol concentration is commonly reported in the literature [2,19,23–25,30,32,47,60,61]. Furthermore, organic aerosols have been reported to contain many important DTT-active compounds able to interact with antioxidants (emulated by DTT), causing cascade reactions and then oxidative stress, so OA generally correlates well with the oxidative potential [19,20,25,28,30]. On the contrary, the high correlation coefficient observed for NH4 is very likely an indirect relation, as ammonium nitrate and ammonium sulfate have been demonstrated to be

DTT-inactive in laboratory studies [19,43,73]. For the same reason, the moderate correlation observed for the other inorganic species (NO3 and SO4) is also considered indirect and a consequence of the general correlation of all the components in the sampling period. Finally, the high correlation coefficient for eBC was somewhat unexpected. Although this aerosol fraction has previously been associated with OP_DTT, eBC should not contribute to water-soluble OP_DTT, as measured in this study, considering its largely water-insoluble nature [19,43]. As a result, the correlation is likely due to the co-emission of black carbon with the other aerosol components, as also observed in other studies [23,28].

A highly significant ($p < 0.05$) correlation with OP_DTT_v was also observed for all the OA factors, with wood showing the highest correlation (R = 0.88), followed by HOA (0.84), OOA (0.83), peat (0.81), and coal (0.79). When the contributions of peat, coal, and wood are summed ("solid fuels" in Table 1), another very high correlation coefficient is obtained (R = 0.86). These results strongly link the ROS-generating potential of aerosol in Birr to the organic fraction of PM.

From Table 1, it is evident that almost no significant correlation is obtained between OP_DTT_m and both the mass contribution of aerosol species and the OA factors. The only exceptions are OA, peat, and, particularly, the sum of the solid-fuel-related factors which show weak, but still significant ($p < 0.05$), correlations (R = 0.28, 0.29, and 0.36, respectively). This result hints at the importance of the organic fraction in determining the oxidative stress of PM and suggests that solid fuels' combustion may play a role in determining the oxidative potential of aerosol in Birr.

In order to investigate the OA contribution to OP in more detail, PMF factors were used as independent variables to run a multiple linear regression model for OP_DTT_v, following the approach presented by Verma et al. [33]. The coefficients of the regression equation (the multiplication factors associated with each independent variable, shown in Table 2) represent an intrinsic property of the aerosol species to generate ROS, as measured by the DTT assay (i.e., OP_DTT_m). To ensure physically meaning values of the source-specific OP_DTT_m from the analysis, multi-linear regression was run, imposing a non-negativity constrain to the coefficients. It is important to note that the OP measured in this study is only from the water-soluble fraction of PM, while the online measurements included total mass concentrations of the organic aerosols. Thus, the values reported in Table 2 should be considered as intrinsic "water-soluble" DTT OP and not as "total" OP. Another important caveat to consider is that, in the present study, no information on aerosol metal components was available; therefore, we are implicitly attributing the whole aerosol ROS-generating potential to the organic fraction, which surely leads to an overestimation. In this sense, this approach is valid if we consider the organic factors as tracers of aerosol sources whose emissions may also contain metals. Furthermore, considering the site characteristics (e.g., away from heavy traffic, industry, railroads) and that the DTT assay is less sensitive to metals [23,37] than any other assay, the assumption of a minor contribution of metals to OP is reasonable.

Table 2. Results of the multi-linear regression model analysis performed using OP_DTT_v (dependent variable) and PMF OA factors (independent variable).

PMF OA Factor	Multi-Linear Regression Coefficient * (nmol min^{-1} mg^{-1})
HOA	$1.94 \times 10^{-6} \pm 0.51$
Peat	85.5 ± 132
Coal	$-6.97 \times 10^{-2} \pm 697$
Wood	1108 ± 964
OOA	$-9.61 \times 10^{-2} \pm 420$

* The intercept was not constrained to zero, but it also resulted in being negligible (~10^{-6}).

OP_DTT_v variability was explained reasonably well by the multi-linear regression model, with a coefficient of determination between the model and measurements (R^2) being

equal to 0.82. According to the model, only two OA factors contributed significantly to the observed OP_DTT, namely wood and peat (F-test, $p < 0.05$; Table 2). The wood factor yielded the highest regression coefficient (OP_DTT$_m$) of 1108 ± 960 nmol min^{-1} mg^{-1}. It is noteworthy that this value is significantly higher than OP_DTT$_m$ obtained for wood burning in the majority of publications that use a similar approach, which is of the order of 100 nmol min^{-1} mg^{-1} and ranging between <1 and ca. 250 nmol min^{-1} mg^{-1} [33,51,54,57,64,70,77–80]. The higher intrinsic OP_DTT of wood burning aerosol in Birr may be due to different burning conditions at the site or be a result of different atmospheric aging of the wood-burning-generated OA [10]. It may also arise from the assumption that PM$_{2.5}$ mass could be approximated by the ACSM non-refractory mass, or the fact that no explicit metal contribution was considered in the regression. In any case, these results indicate that biomass burning emissions pose a potentially serious health hazard. A significant contribution of wood burning to the aerosol oxidative potential has been previously reported in the literature. Indeed, the combustion of biomass represents one of the major sources of water-soluble organic compounds found in continental aerosols, and it contains chemical species (i.e., PAH, hydrocarbons, and quinones) able to catalytic oxidize the DTT and contribute to OP_DTT [10,28,30,33,50,73,81–83].

The peat factor was associated with a regression coefficient of 85 nmol min^{-1} mg^{-1}. This suggests that peat burning also produces DTT-active aerosols, but with an intrinsic OP_DTT which is about one order of magnitude lower than wood burning. In contrast, the contribution from the HOA, coal, and OOA factors to OP_DTT was negligible. A similar result regarding HOA was also reported by Farahani et al. [72]. It is worth highlighting that HOA and coal burning aerosols are mainly water-insoluble, and this may explain the negligible contribution obtained in the present study [33]. On the other hand, other studies [73,79,84] reported that fine particles resulting from traffic contributed significantly to water-soluble or total OP_DTT.

Some previous studies have reported that OOA contributed to the aerosol oxidative potential [33,37,84]. The insignificant contribution of OOA to OP_DTTv observed in this work is probably due to the fact that OOA is treated as a whole in this study, without distinguishing between different SOA types. A higher resolving power for OOA would probably be necessary to investigate in more detail the OP-relevant properties of SOAs, which are composed of thousands of different compounds with different properties and origins.

The average intrinsic water-soluble OP_DTT of the different PMF factors was multiplied by their respective ambient concentrations for each sample to reconstruct the total OP_DTT$_v$ associated with the OA components (Figure 4). Overall, the major contribution to the water-soluble OP_DTT was from the wood factor (average $87 \pm 9\%$). This finding is consistent with several previous studies in which biomass burning was identified as the top contributor or the main driving factor to water-soluble OP_DTT$_v$ of fine PM in various environments [30,73]. Despite a lower intrinsic water-soluble activity than wood, the high concentrations of the peat factor result in a substantial contribution to OP_DTT$_v$ of $13 \pm 9\%$. The peat contribution was particularly high during the night-time pollution episodes, reaching up to $21 \pm 9\%$. The contributions from other OA components were negligible as a result of their very low OP_DTT$_m$ coefficients.
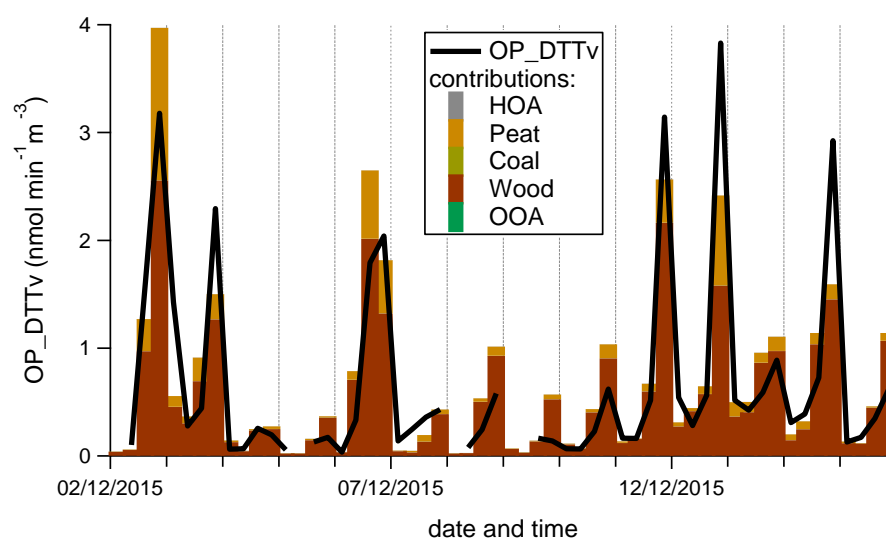
Figure 4. Reconstructed and measured water-soluble OP_DTTv. The reconstructed OP_DTTv is fractionated into the contributions of the main OA components.

4. Conclusions

The DTT assay for determining the ROS-generating potential of atmospheric aerosols was applied to samples collected in Birr (Ireland) during December 2015. Oxidative potential data, both volume-normalized extrinsic (OP_DTT$_v$) and mass-normalized intrinsic (OP_DTT$_m$), were integrated with online-measured aerosol chemical composition data with the aim of identifying the main sources of OP.

The results show that OP_DTT$_v$, an indicator of personal exposure to reactive oxygen species at a specific site, correlated strongly with PM mass and with all the main aerosol components analyzed. OP_DTT$_v$ showed higher values for night-time peak samples corresponding to pollution events driven by solid fuel combustion for residential heating. On the contrary, the intrinsic oxidative potential (OP_DTT$_m$) was poorly correlated with the aerosol mass concentration and presented lower variability compared to OP_DTT$_v$, reflecting the lower variability in the aerosol chemical composition. Nevertheless, OP_DTT$_m$ also showed a significant night-time increase, which suggests that residential solid fuel burning emissions enhance aerosol OP with respect to other sources.

OP_DTT source apportionment, performed by using both linear and multi-linear regression models, confirms the association of the observed aerosol OP to solid fuel burning. In particular, wood and peat combustion were found to be the main drivers of OP during the study period in Birr.

OP_DTT$_v$ and OP_DTT$_m$ observed during the study are comparable or higher than values measured in big cities in Europe, the USA, and Asia. This result is highly significant considering that the sampling occurred in a small town, where continuous air quality monitoring was not being carried out. The results of the present study show how residential solid fuel burning, coupled with unfavorable meteorological conditions, can have a severe impact on air quality, even in small towns, with potential negative health effects on the exposed population.

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