

The authors would like to thank the reviewers for their careful review.

I. Author Response to Reviewer #1

This paper describes an experimental study of near-highway (~15-20 m away) air pollution concentrations in a diesel dominated environment. They measured ambient concentrations using a suite of high resolution instruments (HR-AMS, SMPS, and PTR-MS). They also collected filter samples for offline analysis (OC/EC, sulfate, organic molecular markers). They performed what is now relatively routine PMF analysis of the AMS data, presenting a 6 factor solution. They performed some analysis of the PTR-MS data, focusing on nitrogen containing fragments. They analyzed aerosol nitrate using approach of Farmer. They compared the results to other previous field studies (they largely agree). They present results from fossil/modern carbon analysis– as expected for this sort of site two-thirds or more of the carbon is fossil.

The paper is well written and very comprehensive (16 figures and 2 tables!). The experiments seem to be well executed. There is nothing fundamentally wrong with the paper, but I found it relatively uninteresting. It breaks little new ground, rather it presents results that are basically consistent with the current AMS world view. The points made are largely those that have been made by previous studies. The most potentially interesting result was that almost none of the oxidized organic aerosol appears to be fossil. The paper could be improved by streamlining (cut the number of figure in half) and focus on the more novel aspects of the results relegating the rest to online supplement.

Due to comments by both reviewers, we have removed a number of graphs and discussions and moved these to the supplementary information. Specifically, we have moved detailed discussion of the NO and NO₂ (gas) and NO_x factor, discussion of the spectral differences between LO-OA and MO-OA, and particle-size to the supplementary information section. We also have expanded the section on the fossil vs. modern carbon. The paper now includes only 9 graphs.

Specific comments:

The paper frequently references BC concentrations. It was not clear how they were measured. The paper does discuss thermal-optical analysis of quartz filters to determine EC concentrations. Did they just switch terminology? EC and BC are different quantities. If they were using the thermal-optical analysis then I would recommend that they refer to it as EC. Figure 3 suggests they were running an Aethalometer or PAX.

In fact, both BC (via MAAP) and EC (using a Sunset Laboratories OC/EC measurement system) were measured. The MAAP instrument had a greater time resolution than the EC instrument and thus was used for the time series graphs and the comparison of BC to AMS factors. EC values from the thermo-optical analyzer were used to perform this calculation, and have now been

correctly labeled as such (we thank the reviewers for pointing out this error!), and a comparison between the measurements has been included in section 3.3.1. We also now include a figure in the supplementary information showing the comparison between BC and EC concentrations. The two instruments agree fairly well, and as the reviewer suggested, the slope of the MAAP BC and thermo-optical EC data was 1.5 (higher BC than EC). This answers the reviewers concerns below (that perhaps the optical measurement from the MAAP was overestimating the EC/BC concentrations).

I found the discussion of the fossil/modern carbon data (Figure 16) to be the most interesting part of the paper. The figure suggests that very little of the oxidized organic aerosol (i.e. SOA) is fossil (I assume fossil SOA would be the bright green part of bar, but was not entirely clear to me when I read the text). This seems surprising (e.g. see Zotter et al. JGR 2014). A key detail here may be how they determined BC concentrations.

Is this a true carbon measurement (i.e. thermal optical) or was it inferred from an optical measurement? If it was inferred from the optical measurement what mass absorption cross section was used to convert the absorption data to carbon? This is a critical detail because as an optical measurement often overestimate the true elemental carbon concentration (many intercomparison studies have been published that show this) – potentially by as much as a factor of 2. This detail could change the interpretation of this figure substantially.

A new section with significantly more detail about this calculation has been added to the paper and a range of potential fossil-OOA has been calculated taking into account various potential errors in our calculation assumption. Additionally, the figure has been redone and relabeled to hopefully make the meanings of the values presented more clear.

We used EC data for the fossil/modern carbon calculation, and have now correctly labeled the value EC (versus the BC we used for its higher time resolution in other parts of the paper). We also include a range of possible 'fossil-ooa' assuming some modern carbon contribution to HOA/EC from biofuels and biomass burning. Here is the expanded section 3.3.1:

A source of uncertainty in the global particulate emissions of vehicles is the formation of SOA from gas-phase emissions and the aging of POA. To discriminate between the relative concentration of modern and fossil carbon, and thus potentially discriminate between OOA from vehicular sources and from modern sources, daily filter samples were collected at the sampling site and ¹⁴C radiocarbon measurements were performed. From these measurements, the percentage of modern carbon from TC (OC+EC) was calculated. Modern carbon varied from 15-36% of the total aerosol carbon, a significant portion of the measured carbon considering the close proximity of the measurements to fossil carbon sources. In France, the contribution of biofuel was about 7% and 5% for diesel and gasoline fuel, respectively, in 2011 (UFIP, Union Française des Industries Pétrolières, 2011) and cannot explain this relative high proportion of modern carbon observed in the particulate matter. This is similar to findings shown in Hodzic et al. (2010), Minguillon et al. (2011), and El Haddad et al. (2013), which indicate that modern carbon is

often more significant than fossil carbon in the carbonaceous fraction of PM, even in cities with high vehicular emissions (e.g., Mexico City, Barcelona or Marseille).

As radiocarbon measurements have been performed through a thermal approach (combustion of the samples at 850°C), we consider in the following section EC measured by the thermo-optical method. As shown in figure S12, EC and BC do not differ significantly at low mass loadings, but have a wider scatter in the data at higher mass loadings. The calculation of BC (measured by the MAAP) using an absorption cross-section is imprecise and, at high loadings of BC, may under or overestimates this mass loading. Figure S12 shows a comparison between the MAAP (BC) and thermal measurement (EC) data, with a 1:1 line. As the thermal-optical analysis of EC is a more direct analysis, EC was chosen to be used in this calculation.

Assuming that the majority of EC was traffic-related, and thus from fossil origin, the concentration of modern organic carbon and fossil organic carbon was then calculated. While evidence for the presence of biomass burning aerosol was measured at the field site, the main source of EC was likely diesel exhaust. Figure 8 shows the fraction of EC and OC, HOA, and a partitioning between fossil and modern carbon. In Figure 8A, a rough calculation was performed to determine the concentration of non-primary fossil organic carbon. For a first estimate, all EC was assumed to be fossil in origin. Additionally, the HOA aerosol was also assumed to be vehicular, and thus fossil, in origin. The HOA factor concentration has been divided by its OM: OC ratio to remove any non-carbon mass (HOA C, calculated from the elemental formulas of the PMF factor mass spectra, Aiken et al. (2008)). Both EC and HOA C had high ($R^2=0.89$ and 0.85 respectively, $n=10$) correlations with the fossil C mass, which supported a largely fossil source for these two species. The remaining fossil organic carbon mass after subtraction was then assumed to be from non-primary sources (in blue).

This calculation provided a lower estimate of the amount of fossil carbon contributing to SOA mass, and involves several assumptions and potential sources of error. Sources of error in this calculation include error in the PMF resolution of primary (HOA) organic aerosol spectra and error in the calculated OM:OC ratio of this factor species, biodiesel vehicular emissions contributing modern carbon to measured HOA, and biomass burning aerosol contributing modern carbon to measured EC.

As the measured HOA:EC ratio was in-line with previous measurements in high diesel environments, HOA concentrations did not appear to be significantly over or under estimated. Up to 7% of fuel use in France was biodiesel, thus, part of the HOA concentration could be from modern sources. While research has shown that the use of biodiesel fuels reduces the overall primary particulate matter emissions (Cheung et al, 2010), biodiesel could still be a modern carbon contributor to OC and EC mass. Additionally, although the concentration of BBOA was generally low (a campaign average of $0.34 \pm 0.23 \mu\text{g m}^{-3}$) and the ratio of BBOA:EC has been found to be on the order of 3-4 in

other areas of France (Crippa et al., 2013), some contribution to EC from biomass burning may have been present at the measurement site. In Figure 8B, a range of fossil non-primary organic carbon, normalized to total measured organic carbon, is presented. For the upper limit of this range, HOA C and EC were considered to be 95% fossil and 5% modern (7% biodiesel fuel use and an estimated 25% reduction in particulate emissions from biodiesel fuel). Also for this upper limit, the calculated concentration of BBOA was divided by 3 and used to calculate possible modern EC from biomass burning (Crippa et al., 2013).

Figure 15 – I assume that the light/bright green is the defined as the difference between the other quantities? This needs to be clarified. *The reviewer is correct; we have now clarified this point. Line 437 (769 in merged revised document): The remaining fossil organic carbon mass after subtraction was then assumed to be from non-primary sources (in light green originally, now in light blue in the redone graph).*

Figure S1 compares filter and AMS data. The AMS data in this figure are uncorrected? If so that should be noted in the caption. What does the comparison of organic carbon look like? They mention using a TEOM but never discuss the data. How was the mass closure between the speciated and the mass based measurement? If there is poor mass closure then what does that mean for the results?

Yes, this is uncorrected data, included in the caption as per the reviewer's suggestion. Figure S3 shows a comparison of AMS data and TEOM data. The general time trends are good but the quantitative comparison of AMS+BC and TEOM data is not perfect, as the TEOM and AMS have different size cut-offs (1 micron and 2.5 microns, respectively) and measure different species (the AMS cannot measure refractory species, and road dust, particularly in supermicrometer sizes, may play a large role in the differences in mass between the TEOM and AMS+BC measurements during high traffic periods). On line 255 (line 392 in the marked merged document), to include TEOM data within the main paper body, we now include the statement "PM2.5 had a somewhat higher mass variation than the AMS + BC measured mass (Figure S3), likely due to the smaller measurement size cutoff for AMS (1 μm) and the presence of road dust in the local environment, a large portion of which may be non-refractory and those unable to be measured by the AMS."

The two papers from Hellebust seemed interesting, but neither is published. Not clear it is appropriate to reference.

The paper will be submitted to ACPD within the next few days, or we can remove this reference.

Response to Reviewer #2

This paper presents analysis of the data from an approximately 2 weeklong measurement campaign at a site adjacent to a large freeway outside Grenoble, France. An extensive set of real-time instrumentation for measurement of particle- and gas-phase species was used including an SMPS for particle size/count, an HR-TOF-AMS for particle composition/size, a MAAP for BC light absorption, a TEOM for PM mass (though I did not see mention of these data), ***(PM data is included in the supplementary information and mentioned in the text)*** a PTR-TOF-MS for VOC measurement and a NO_x analyzer. Integrated samples were collected for multiple analyses, including carbon isotope analysis to determine the modern/fossil fraction of total particulate carbon (TC). Supporting measurements included detailed traffic flow, speed and composition measurements and a meteorological station to measure wind parameters, temperature and RH. The analysis presented in the paper is similarly comprehensive and includes: examination of diurnal trends, linkages with traffic conditions, PMF decomposition of AMS data and factors' relations with other measurements (e.g. VOCs, NO_x, BC), and analysis of the fossil/modern carbon fraction of the total carbon.

This is a large and comprehensive dataset, and it appears that the data collection and analysis were well planned and executed. These data have the potential to provide valuable insights into the characteristics of emissions from a large and diverse vehicle fleet and to their contribution to urban/regional air pollution. Further, the title of the manuscript indicates that this is the goal of analysis. My major issue with this analysis is that it does not proceed in a way that can truly address this objective. Rather, as presented, the analysis treats the data set as a 'standard' ambient monitoring study, that pays little attention to the relationship between the source in question (the roadway) and transport of these emissions to the point of measurement (e.g. wind direction). If this work were presented as a routine monitoring effort at a site that happens to be near a large road, I might not take issue with this presentation. However, given that 'emission' is in the title, I expect to see more of a focus on trying to find the 'emission' signature, rather than just expecting it to be there and constant during all measurements. Therefore if the title were something like 'Comprehensive gas- and aerosol-measurements collected near a roadway in a high-diesel peri-urban environment', I would expect this kind of analysis. However, characterization of emissions should make efforts to separate or characterized the background vs roadway contributions.

So, one approach could be to change the title of the paper and apply some of the changes suggested here and by the other reviewer. However, to actually address the objective implied by the title, more work needs to be done to extract the roadway 'emission' signature from the data. My sense is that not doing this additional analysis would be a missed opportunity.

We understand the reviewer's point and agree that we have not provided enough emission calculations to have 'emission' in the title. We have both

changed the title of the paper to reflect the reviewer's concerns and also included more information on traffic-heavy periods within the paper (particularly in Figure 2 and Figure 7, discussed further below).

There is a rather extensive literature of near-road air pollution measurements ((Karner et al. 2010) is a good place to start), which seems to be largely ignored in this analysis aside from the few studies in which an AMS was used. The important message from

these previous studies are that concentration gradients are: a) steep near roadways, b) a strong function of wind direction/speed and mixing conditions. However, the spatial and meteorological aspects of this data set are entirely absent from the analysis as presented.

Unfortunately, the measurement station was fixed in location, so gradient changes were impossible to determine, but we have now added more details in Figure 1 and discussed in more detail the wind direction, wind speeds, and location of the highway relative to the measurement site. Supplementary information included polar plots showing mass loadings of different AMS factors as a function of wind direction. As noted at the beginning of section 3.1, wind speed was low and the station location was noted both in words and in Figure 1.

Now, following the reviewer's suggestion, Figure 1 has been updated to include more details on the measurement location and now includes polar plots of BC and NO_x as well as a wind rose to make the meteorological conditions more clear. Section 3.1 includes this description of the meteorological conditions at the sampling site: Wind speeds were generally low throughout the campaign (<1-2 m/s) with higher wind speeds peaking in the afternoons and tapering off in the evenings. The wind direction was primarily from the northwest, from the direction of the nearby highway. A diagram of the two measurement stations, the wind rose plot for the Massalya location, and polar plots showing the concentration of NO and BC as a function of wind direction are shown in Figure 1, along with a map of the local area and the position of Grenoble within France. " There is also already a discussion of boundary layer conditions, which has a large effect on aerosol concentrations.

We have now cited the suggested paper and included this sentence about gradients "The fixed location of the measurement stations made determination of concentration drop-off as a function of distance from the roadway impossible to determine with the dataset, although that has been shown to be important in other studies (such as Karner et al., 2010). However, the measurements were all taken closer to the roadway (~15 m) than the calculated distance where roadway emission drop off to background levels (115-570 m, Karner et al., 2010)."

The air sampled at this site will be a combination of the background/regional mixture (heavily influenced by other roadways with similar diurnal various to traffic and fleet among the multitude of other sources) and emissions from vehicles on the adjacent roadway. Strength of having all of these highly sensitive, high-time-resolution instruments is that the authors should be able to pick the 'emission' signal out from the background, by sorting data based on wind speed/direction. It

could be that due to the low wind speeds observed in this study (I cannot comment on wind direction, as no data were shown, nor was the relationship of the measurement site to the roadway) that is a small portion of the overall data set, but it would still get at the 'emissions' question.

We thank the reviewer for pointing out the need for more detail and clarification regarding the meteorology of the sampling site. This was discussed in the section 3.2 General Atmospheric Conditions: "Wind speeds were generally low throughout the campaign (<1-2 m/s) with higher wind speeds peaking in the afternoons and tapering off in the evenings. The wind direction was primarily from the northwest, from the direction of the nearby highway." As per the reviewer's suggestion, we have added a wind rose, polar plots as a function of wind direction of BC and NO in addition to the polar plots of AMS factors previously included in the supplementary information, and a more detailed diagram of the measurement site to hopefully make the meteorological conditions more clear.

Starting on Line 313 in the merged/revised document with tracked changes, we now include this paragraph (some repeated from the past version): Wind speeds were generally low throughout the campaign (<1-2 m/s) with higher wind speeds peaking in the afternoons and tapering off in the evenings. The wind direction was primarily from the northwest, from the direction of the nearby highway. A diagram of the two measurement stations, the wind rose plot for the Massalya location, and polar plots showing the concentration of NO and BC as a function of wind direction are shown in Figure 1. BC and NO were associated with all wind directions, though slightly higher from the highway direction, which suggested that the measurement site was directly and strongly influenced by the traffic emissions. However, in order to better describe the traffic influence, we defined high traffic periods (HT). These HT periods were selected as follows : wind direction >40 or <320, NO in the 75th percentile, and from 6:30-9:30 or 17:00-20:00 (rush hour periods). The fixed location of the measurement stations made determination of concentration drop-off as a function of distance from the roadway impossible to determine with the dataset, although that has been shown to be important in other studies (such as Karner et al., 2010). However, the measurements were all taken closer to the roadway (~15 m) than the calculated distance where roadway emission drops off to background levels (115-570 m, Karner et al., 2010).

Based on the factor-based wind roses in Figure S8, I would hazard a guess that the roadway was to the North/Northwest of the sampling location give the asymmetry in the HOA contribution on the wind rose (correction – just found the mention of this in Sec. 3.2). I would expect that the authors could extract portions of the data set that allow them to more directly evaluate traffic emissions, ideally by contrasting with other periods where the measurements were upwind from the roadway. Other measurements

from regional air quality monitoring stations might be of use in assessing changes in regional levels to extract the roadway signal. The existing analysis can be

presented along a more directional approach; there are likely valuable insights gained from each approach.

We have now defined a period of time as high traffic, based on wind direction, NO concentrations, and times correlating to morning and evening rush hour. These HT periods were selected as follows : wind direction >40 or <320, NO in the 75th percentile, and from 6:30-9:30 or 17:00-20:00 (rush hour periods). More detail is provided both in Figure 2 and Figure 7 (comparison of the relative contribution of AMS organic/inorganic species and BC, and PMF factors, respectively, for all and high-traffic time periods. PM_{2.5} and PM₁₀ increased slightly during HT periods (a 1.25 and 1.3x increase, respectively). BC and m/z 57 increased 1.5x, benzene by 20%, CH₄NO₂ by 8%, and 1.9x increase for HOA and 1.3x increase for NOA PMF factors.

Apart from this framing/objectives concern, the main other concern I have is concerning the analysis of the fossil/modern carbon fractions. This analysis needs more attention, and I find it somewhat difficult to follow the process described, the results shown in Fig. 15 and the conclusions of this analysis. For one, a number of assumptions appear to be made in the process of apportioning the modern/fossil contribution to OA, but these are not at all clear. It appears that the modern C contribution to EC/BC is ignored, as is the potential modern C contribution to HOA, but I may not be clear on this. Given the statement that as much as 7% of diesel may be biodiesel and that BBOA made a reasonably large contribution (Fig. 10b) to the OA loading at times, these assumptions seems to be potentially biasing and also unnecessary (given all of the other supporting data/analysis that is presented). I would like to see this process better spelled out and the uncertainties in the various assumptions required apportion the modern/fossil C better constrained and the impact of measurement uncertainties and uncertainties due to assumptions propagated through to this overall apportionment exercise. In particular, the measurement of EC/BC is a potentially large source of uncertainty that would introduce an enormous bias into this analysis. That the light-absorbing carbon is discussed as BC suggests that these quantities are based on an optical measurement, and there is huge variability/uncertainty in the absorption cross-section and thus the BC concentration measurement generated by something like a MAAP. There is mention of a thermo-optical analysis of filters, I think mainly from the other site, but no data are ever shown. Ideally, all of these comparisons would be on a mass basis (i.e. EC, not BC) and the uncertainties incorporated into the analysis. If these various uncertainties are addressed, a more quantitative apportionment of C mass will be possible, giving the discussion of SOA sources/etc. a more solid footing. In addition, Fig. 15 is not clearly labeled – preferably segments would be labeled as either OC or EC to avoid any ambiguity.

We thank the reviewer for their corrections. We used EC data for the calculation of this figure and have now correctly labeled it as such, and thank the reviewer for pointing out this error. Additionally, we compare EC (Sunset Laboratories thermal analyzer) and data from the MAAP instrument (optical) in the

supplementary information. These instruments were not located at the same station (EC at the Air Rhone Alps station, MAAP within the Massalya platform) but agree fairly well and show no large higher bias in the MAAP data until higher loadings. Additionally, a range of fossil-OOA has been calculated. We have also re-labeled the graph, hopefully making the values presented on the graph clearer.

We have added significantly more detail about the calculation in section 3.4.1, including sources of error and discussion of possible biases in data. As the reviewer suggested, we include a range for possible modern-C from the EC and HOA factors to account for the potential contribution of biomass burning and biofuel use to these species. While biofuel is thought to emit less particles/car than traditional diesel vehicles, we agree it is important to include the possibility of biofuel contribution to EC and HOA in this calculation.

Following is the revised section, beginning on line 731 in the merged document:

A source of uncertainty in the global particulate emissions of vehicles is the formation of SOA from gas-phase emissions and the aging of POA. To discriminate between the relative concentration of modern and fossil carbon, and thus potentially discriminate between OOA from vehicular sources and from modern sources, daily filter samples were collected at the sampling site and ^{14}C radiocarbon measurements were performed. From these measurements, the percentage of modern carbon from TC (OC+EC) was calculated. Modern carbon varied from 15-36% of the total aerosol carbon, a significant portion of the measured carbon considering the close proximity of the measurements to fossil carbon sources. In France, the contribution of biofuel was about 7% and 5% for diesel and gasoline fuel, respectively, in 2011 (UFIP, Union Française des Industries Pétrolières, 2011) and cannot explain this relative high proportion of modern carbon observed in the particulate matter. This is similar to findings shown in Hodzic et al. (2010), Minguillon et al. (2011), and El Haddad et al. (2013), which indicate that modern carbon is often more significant than fossil carbon in the carbonaceous fraction of PM, even in cities with high vehicular emissions (e.g., Mexico City, Barcelona or Marseille).

As radiocarbon measurements have been performed through a thermal approach (combustion of the samples at 850°C), we consider in the following section EC measured by the thermo-optical method. As shown in figure S12, EC and BC do not differ significantly at low mass loadings, but have a wider scatter in the data at higher mass loadings. The calculation of BC (measured by the MAAP) using an absorption cross-section is imprecise and, at high loadings of BC, may under or overestimate this mass loading. Figure S12 shows a comparison between the MAAP (BC) and thermal measurement (EC) data, with a 1:1 line. As the thermal-optical analysis of EC is a more direct analysis, EC was chosen to be used in this calculation.

Assuming that the majority of EC was traffic-related, and thus from fossil origin, the concentration of modern organic carbon and fossil organic

carbon was then calculated. While evidence for the presence of biomass burning aerosol was measured at the field site, the main source of EC was likely diesel exhaust. Figure 8 shows the fraction of EC and OC, HOA, and a partitioning between fossil and modern carbon. In Figure 8A, a rough calculation was performed to determine the concentration of non-primary fossil organic carbon. For a first estimate, all EC was assumed to be fossil in origin. Additionally, the HOA aerosol was also assumed to be vehicular, and thus fossil, in origin. The HOA factor concentration has been divided by its OM: OC ratio to remove any non-carbon mass (HOA C, calculated from the elemental formulas of the PMF factor mass spectra, Aiken et al. (2008)). Both EC and HOA C had high ($R^2=0.89$ and 0.85 respectively, $n=10$) correlations with the fossil C mass, which supported a largely fossil source for these two species. The remaining fossil organic carbon mass was then assumed to be from non-primary sources. This calculation provided a lower estimate of the amount of fossil carbon contributing to SOA mass, and involves several assumptions and potential sources of error. Sources of error in this calculation include error in the PMF resolution of primary (HOA) organic aerosol spectra and error in the calculated OM:OC ratio of this factor species, biodiesel vehicular emissions contributing modern carbon to measured HOA, and biomass burning aerosol contributing modern carbon to measured EC. As the measured HOA:EC ratio was in-line with previous measurements in high diesel environments, HOA concentrations did not appear to be significantly over or under estimated. Up to 7% of fuel use in France was biodiesel, thus, part of the HOA concentration could be from modern sources. While research has shown that the use of biodiesel fuels reduces the overall primary particulate matter emissions (Cheung et al, 2010), biodiesel could still be a modern carbon contributor to OC and EC mass. Additionally, although the concentration of BBOA was generally low (a campaign average of $0.34 \pm 0.23 \mu\text{g m}^{-3}$) and the ratio of BBOA:EC has been found to be on the order of 3-4 in other areas of France (Crippa et al., 2013), some contribution to EC from biomass burning may have been present at the measurement site. In Figure 8B, a range of fossil non-primary organic carbon, normalized to total measured organic carbon, is presented. For the upper limit of this range, HOA C and EC were considered to be 95% fossil and 5% modern (7% biodiesel fuel use and an estimated 25% reduction in particulate emissions from biodiesel fuel). Also for this upper limit, the calculated concentration of BBOA was divided by 3 and used to calculate possible modern EC from biomass burning (Crippa et al., 2013). Total organic carbon concentration appeared to be more driven by processed/aged OOA concentrations than by primary emissions. During the period with the highest organic concentrations (September 15th-17th), most of the non-HOA carbon measured was modern carbon. Also during this time period, the winds were also slightly more southerly and SO_4 and OOA concentrations increased, which could indicate a more regional

contribution to the measured air mass during this time. After a period of heavy rain on the 19th, almost none of the non-HOA, organic carbon was fossil; however, this also coincided with a period of increased BBOA, which may have contributed to modern-EC emissions and thus an underestimate of fossil-OC emissions (Figure 7). At other times during the campaign, HOA concentrations alone could not adequately explain all of the measured fossil organic carbon and additional sources of fossil organic carbon (such as photochemical reactions forming aerosol from vehicular VOC emissions) would be needed. Additionally, the origin of the NOA factor remains unclear, and if fossil in origin, could explain part of the non-HOA organic fossil carbon measured at the site, further reducing the OOA fossil-C (at times to almost zero).. Overall, throughout the campaign the majority of OOA observed was most probably modern in origin. The high levels of modern carbon OOA suggested that biogenic compounds had the greatest effect on the overall aerosol population in this location, even directly adjacent to a large anthropogenic emission source (i.e., traffic). Interaction between anthropogenic oxidants and biogenic VOCs (or BVOCs) has been found to increase the formation of SOA (Chameides et al., 1988; Goldstein et al., 2009; Shilling et al., 2013), isoprene oxidation reactions leading towards SOA have been shown to vary depending on the level of NO_x (Chen et al., 2014; Kroll et al., 2005; Ng et al., 2007; Xu et al., 2014), and likely BVOC concentrations were greater and the aromatic VOC concentrations were lower in the wider Grenoble Valley.

Finally, while I am suggesting additional analysis, I agree with the other reviewer that the number of figures is excessive. Figures 2, 6, 11, 12 and 14 could easily be moved to SI without diminishing the readability of the manuscript.

These figures and the discussion of these figures were moved to SI as suggested, there are now 9 figures in the manuscript.

Other specific points: P27376, L15-18 – Somewhat nitpicky, but the use of ‘rate’ here is not really appropriate, as this really depends on engine size. You could say ‘emission factor’ or ‘ratios’...

Changed to factor, as suggested.

P27376, L25-30 - Suggest reorganizing this paragraph as there is a transition to discussion of engine-type-specific emissions to results of several specific field measurements.

We have removed some of this paragraph, which hopefully will make the transition smoother.

L6 – There has been no previous mention of smog chamber studies, so this way of starting the paragraph is a bit confusing.

We have removed this line.

P27377, L16-30 – Not so clear how this particular paragraph pertains to the study objectives. Seems like it could be replaced with a sentence stating that there is controversy concerning the relative contributions of gasoline and diesel engine emissions to primary and secondary OA in the US.

This relates somewhat to the fossil v modern carbon OOA calculations later in the paper, but this paragraph has been shortened as per the reviewer's suggestion.

P27378, L17-20 – This seems like a major objective of the study, but then there is very little comparison (apart from e.g. HOA/BC ratios. This could be highlighted more and then more fully addressed.

The reviewer is right, this was one of the goals of the study. Also compared are NO_x measurements, HOA chemical composition (unfortunately the same for diesel and gasoline), and partially relates to the fossil or modern-carbon OOA (as previous studies have suggested that VOC emissions from gasoline vehicles can lead to more SOA formation than those from diesel).

To help draw this point more clearly, the authors have moved the discussion of these three things into a new section “3.4.3. Differences between diesel-heavy and gasoline-heavy near-roadway measurements” where we discuss in more detail the comparison of gasoline-rich and diesel-rich near-highway measurement campaigns.

P27379, L19 – This seems like a natural place to discuss the meteorology of the site, location of measurements relative to roadway, prevailing wind directions, etc.

We now include a more detailed figure (Figure 1) including a wind rose.

P27382, L13 – It is not clear where this site is relative to the mobile lab, how these are impacted differentially by wind, and where data from the two sources are used in concert in this analysis. Were there any duplicate instruments on the two platforms on which this comparison can be made? In general, the contribution of data from the different sites could be better delineated.

The aerosol and VOC measurements were from the MASSALYA mobile lab, while the gas-phase NO_x measurements and filter samples were taken at the Air Rhone Alps station, as detailed in their sections. No exact overlapping measurements were collected; however, the EC measurements from the Air Rhone Alps station are now compared with the BC MAAP measurements from the Massalya platform in the supplementary information as an answer to another question, and agree fairly well. Both measurement sites were close and on the same side of the highway, as is now more clearly shown in Figure 1. They were 20 m apart (Air Rhone Alps station 20 m to the east).

P27383, L5-18 – This discussion of the fleet composition on this roadway is only really directly relevant if you are measuring emissions from these vehicles (see discussion above). Otherwise, you are better served by talking about the regional fleet composition (and other potential sources). This is a very detailed description of the source term, but is not relevant if you're not sampling from this source.

We have now moved the fleet composition graph into the supplementary information and have removed more of the detailed discussion of the fleet as per the reviewer's suggestion.

P27384, L5 – The only mention of meteorology. There should be data accompanying this, including a more detailed diagram of the placement of the road, mobile lab and the regulatory monitoring site.

There is now more detail regarding meteorology (a wind rose) and mobile lab placement in Figure 1, as well as a statement on the wind speeds. The proximity of the highway and the low wind speeds, as well as close proximity of other highways, made the meteorology less important than it would have been in perhaps other measurement locations with higher wind speeds and/or more variable wind speeds and directions.

P27384, L21 – BC measurements need to be defined (e.g. comparison with EC, etc.)

Now there is a comparison between BC and EC in the SI.

P27385, L6-7 – The Org/BC ratio is much lower during this period as well. There seems to be an opportunity to analyze specific periods/episodes to try to better extract the vehicle signature from other things. The BC variation is relatively consistent, but the 15th-18th has a much larger OA fraction and more of these other factors, and also much lower NO, this seems to be a different type of period than the rest of the study. Can you use differences between periods to infer the difference between roadway/regional contributors to measured levels?

The reviewer is correct that, during this time period, more regional aerosol was measured at the station site. That was one way we were able to separate out regional OOA (in the middle period, with high Org, lower BC/Org ratio) and discuss regional contributions. We now have added the statement "The slow rise of organic concentration during these periods, the lower BC/Org ratio, the enhancement of organic concentration outside of normal traffic periods, and the low level of NO during these accumulation periods all suggest that this increase in organic aerosol concentration was driven by regional influences, not by nearby vehicular emissions." (line 426 in merged revised document).

P27386, L6 – this is not really 'BLH-corrected', as it's not clear that's something you can correct for. In any case, the rationale and approach could be better described. What is the motivation for this approach versus just plotting the diurnal variation in ratios (e.g. benzene: BC or some other primary vehicle emission tracer).

Yes, we agree with the reviewer that this terminology should be changed. We have now changed the wording to BLH-scaled. The motivation behind scaling for boundary layer height was to more directly compare vehicle concentrations with aerosol/VOC concentrations on an hourly

basis. We chose not to scale to benzene or BC as VOC and aerosol emissions change both with vehicular concentration and with vehicle running conditions (idling, start/stop, typical highway driving). By performing this rough scaling calculation using an estimated BLH, differences in the concentrations of vehicular-related species as a function of both vehicle numbers and vehicle speeds was more apparent (and thus VOC and aerosol response to traffic speed and concentration could be more readily compared).

P27387, L27-28 – The evidence for this is not really shown, also need to show the mass in each size bin and the contribution of HOA/OOA to each size bin. Also, I'm not clear of showing the average values for the entire campaign. This represents a snapshot of the climatology of the local aerosol, but this analysis might be more useful if it compares times with different roadway vs. non-roadway contributions. ***Right now it would be very time consuming and potentially fraught with error for the authors to separate HOA and OOA in each size bin using their PMF model. M/Z 44 and 57 are commonly used as markers for OOA and HOA, respectively, in AMS data. The authors have moved this graph and the accompanying discussion to the supplementary information, as it largely agrees with previous findings that primary organic vehicular aerosol (apart from resuspended road dust) is smaller than aged/secondary aerosol (e.g., Sun et al., 2010).***

P27998, L26 – 'was SOA' is a very definite statement. . .

Changed to was OOA.

Figure S2 – It is hard to see in this presentation, but it appears that the PM data (presumably from TEOM?) has substantially more variation than the AMS data. Was the mass estimate from the MAAP benchmarked against the EC data? A scatter plot would be helpful. What about comparisons with SMPS volume data.

A scatter plot of MAAP and EC data is now shown in figure S13. The PM data is from the TEOM, yes. Likely the different size cutoffs (1 micron for the AMS versus 2.5 microns for the TEOM) is a large cause of the variability, as well as the difference in what each instrument can measure (the AMS cannot measure refractory species). A few larger road dust particles, for example, could drive much of the mass-variability in the TEOM data that would not be seen in the AMS data.

The SMPS in turn both has a different size cut-off than the TEOM instrument and measures both refractory and non-refractory compounds, a difference between SMPS measurements and AMS measurements. Road salt, dust, etc. would be measured by both the TEOM instrument and the SMPS instrument, but not by the AMS or the MAAP. As the general time trends are the same for both the TEOM instrument and the AMS instrument, we believe they were capturing similar events but their absolute concentrations are not directly comparable.

We now explain this in the text:

Line 392 "PM_{2.5} has a somewhat higher mass variation than the AMS + BC measured mass (Figure S3), likely due to the smaller measurement size cutoff for AMS (1 μm) and the presence of road dust in the local environment, a large portion of which may be non-refractory and those unable to be measured by the AMS. "

References: Karner, A. A., Eisinger, D. S., and Niemeier, D. A. (2010). "Near-Roadway

Air Quality: Synthesizing the Findings from Real-World Data." *Environmental Science & Technology*, 44, 5334–5344.
Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 27373, 2014.
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Near-Highway Aerosol and Gas-phase Measurements in a High Diesel Environment

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Abstract

Diesel-powered passenger cars currently outnumber gasoline-powered cars in many countries, particularly in Europe. In France, diesel cars represented 61% of [light duty vehicles](#) in 2011 and this percentage is still increasing (French Environment and Energy Management Agency, ADEME).

As part of the September 2011 joint PM-DRIVE (Particulate Matter- DiRect and Indirect on-road Vehicular Emissions) and MOCOPO (Measuring and mOdeling traffic COngestion and POLLution) field campaign, the concentration and high-resolution chemical composition of aerosols and volatile organic carbon (VOC) species were measured adjacent to a major urban highway south of Grenoble, France.

Alongside these atmospheric measurements, detailed traffic data were collected from nearby traffic cameras and loop detectors, which allowed the [vehicle type](#), traffic concentration, and traffic speed to be quantified. Six aerosol age and source profiles were resolved using the positive matrix factorization (PMF) model on real-time high-resolution aerosol mass spectra. These six aerosol source/age

categories included a hydrocarbon-like organic aerosol (HOA) commonly associated with primary vehicular emissions, a nitrogen containing aerosol (NOA) with a diurnal pattern similar to that of HOA, oxidized organic aerosol (OOA), and biomass burning aerosol (BBOA). While quantitatively

separating influence of diesel versus gasoline proved impossible, a low HOA: Black Carbon ratio, similar to that measured in other high-diesel environments, and high levels of NOx, also indicative of diesel emissions, were observed. Although the measurement site was located next to a large source of

primary emissions, which are typically found to have low oxygen incorporation, OOA was found to comprise the majority of the measured organic aerosol, and [isotopic analysis showed that](#) the measured OOA contained mainly modern carbon, not fossil-derived carbon. Thus, even in this heavily vehicular-emission impacted environment, photochemical processes, biogenic emissions, and aerosol oxidation

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72 dominated the overall organic aerosol mass measured during most of the campaign.

73 1. Introduction

74 Aerosols are known to have adverse effects on human health and [on](#) the global climate. The
75 World Health Organization (WHO) recently added anthropogenic aerosol and air pollution to their list
76 of known carcinogens (WHO, 2013), and high mass concentrations of particles less than 2.5
77 micrometers in diameter (PM2.5), such as those emitted by vehicular combustion processes, are
78 particularly harmful (Lighty et al., 2000). Vehicular traffic is a large source of submicrometer
79 anthropogenic aerosol and proximity to large sources of vehicular emissions has been shown to
80 increase lung and heart disease, especially in children (Brugge et al., 2007). [A recent WHO report](#)
81 examined the toxicological effects of black carbon (BC) aerosol, a known emission of diesel vehicles.
82 Although no difference in toxicology between PM2.5 and BC aerosol inhalation was found, BC was
83 cited as a marker for more general vehicular emissions, which have been shown to have negative health
84 effects; diesel exhaust was added as a known carcinogen the year before general air pollution and
85 PM2.5 (Janssen, World Health Organization, 2012). Aside from the potential detrimental health
86 effects of BC, BC also has significant implications for climate change. Unlike the majority of aerosol
87 (e.g., most organic aerosol, ammonium sulfate, ammonium nitrate), BC aerosol is associated with
88 global warming due to its high absorption of solar radiation (Bond et al., 2013). Diesel vehicles have
89 been singled out as important sources of BC to regulate as, unlike most other BC sources, diesel
90 vehicles tend not to co-elute high concentrations of other, less absorbing (thus more cooling) aerosol
91 and therefore have a higher net heating effect than mixed-emission black carbon sources (Bond et al.,
92 2013).

93 In France, the lower cost of diesel fuel (due to a lower taxation rate of diesel fuel versus
94 gasoline fuel) and the generally higher fuel efficiency of diesel engines have [increased the popularity of](#)
95 [diesel passenger cars](#). [In 2011, 82% of the fuel consumed in France was diesel \(World Bank, 2011\).](#) For
96 comparison, this percentage in 2011 was 28% in the US, 57% in China, 70% in the European Union,

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Deleted: For vehicular aerosol emissions, factors such as the fuel used (diesel versus gasoline), age of the car engine, and highway speed (stop and go traffic versus constant speed) can affect the concentration and physical and chemical composition of the aerosol emitted.

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Deleted: to outnumber gasoline passenger cars: in 2011 diesel cars represented 60% of the total vehicular fleet (Light Duty Vehicles, LDV) (61% in 2013) according to the French Environment and Energy Management Agency (ADEME). The influence of diesel vehicles increases if we consider the total fuel consumption per capita, which better captures the use of diesel and gasoline vehicles on the road (road sector only, World Bank, 2011).

115 49% in Latin America and the Middle East, and 83% in low-income countries.

116 The emission characteristics and emission limits of these two types of engines (diesel and
117 gasoline) are quite different: diesel vehicles have higher emission [factors](#) for primary organic aerosol
118 (POA) and BC, while gasoline-powered vehicles have higher emission [factors](#) for carbon monoxide
119 (CO), carbon dioxide (CO₂), and volatile organic carbon (VOCs) (e.g., [trimethylbenzene](#), benzene)
120 (Platt et al., 2013). Black carbon, in particular, is closely associated with diesel: in Europe, North
121 America, and Latin America, an estimated 70% of BC emissions are from diesel-powered vehicles
122 (Bond et al., 2013). [These differences in emissions were observed in studies performed in Mexico City,
123 where particulate and VOC emissions were measured both at stationary measurement sites and during
124 vehicular chases with the Aerodyne Mobile Laboratory \(Thornhill et al., 2010\). During this study,
125 diesel and gasoline vehicles on the road were manually counted and specific vehicles were followed
126 and their emissions captured. From these data, diesel was found to contribute almost all of the BC
127 mass and particle number concentration, along with the majority of PM2.5, while gasoline emissions
128 were found to have elevated levels of toluene and benzene \(Thornhill et al., 2010\).](#) In Marseille,
129 France, a traffic tunnel experiment measured an organic carbon/elemental carbon ratio (OC/EC) in
130 PM2.5 of 0.3-0.4, which indicates that significant amounts of black carbon is emitted from local traffic
131 in Marseille (El Haddad et al., 2009). Recent measures have been taken in Europe to reduce the
132 particulate emission from diesel vehicles: from Euro 4 to Euro 5, a diesel particle filter (DPF) was
133 introduced in diesel vehicles and the regulated emission limit for PM2.5 was halved for diesel cars and
134 trucks.

135 [Aerosol](#) and VOC emissions from both vehicle types, as well as biogenic emissions, industrial
136 emissions, and emissions from other sources, will react together in the atmosphere and potentially form
137 secondary organic aerosol (SOA). Thus, primary aerosol emissions may not be the most important
138 emission factor to take into account for global reduction in anthropogenic aerosol. After emission,
139 VOCs can react in the atmosphere and form SOA. From these reactions, gasoline VOC emissions could

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both aerosol

145 ultimately lead to the formation of higher concentrations of organic aerosol than organic aerosol
146 released directly from diesel vehicles, as reported in a recent study comparing the SOA formation from
147 a Euro 3 diesel LDV and a Euro 5 gasoline LDV (Platt et al., 2013).

148 | [A recent study by Bahreini et al. \(2012\)](#) measured similar levels of SOA in the heavily traffic-
149 influenced LA Basin during both weekend and weekday afternoons. While diesel-powered vehicle
150 numbers on the road decrease significantly on the weekends in the LA area, the measured SOA does
151 not, which leads to the conclusion that gasoline emissions are more responsible for SOA than diesel
152 emissions (Bahreini et al., 2012). Nordin et al. (2013) performed smog-chamber studies on SOA
153 formation from gasoline-vehicle VOC emissions during simulated cold start and idling driving
154 | conditions, and confirmed the high potential of SOA formation from gasoline car exhaust. [Another](#)
155 recent paper calculates the reactivity potential of diesel and gasoline fuel and comes to the opposite
156 conclusion: that due to the reactivity potential of diesel fuel, diesel-powered vehicles should contribute
157 greater amounts of SOA than gasoline-powered vehicles to the atmosphere (Gentner et al., 2012). [Thus,](#)
158 [controversy still exists regarding the eventual aerosol emission factors of diesel and gasoline engines](#)
159 [when considering both primary emissions and potential SOA formation.](#)

160 | Finally, gas-phase NO and NO₂ (NO_x) ambient concentrations are also [mostly](#) associated with
161 diesel fuel use (Vestreng et al., 2009). Throughout Europe, while NO_x emission standards for diesel
162 vehicles have increased in stringency in recent years, ambient NO₂ levels have not shown a
163 corresponding decrease (Vestreng et al., 2009). The reduction of atmospheric NO_x is important for
164 health-related reasons as an increase in NO_x leads to an increase in tropospheric ozone, which is a
165 known lung irritant. NO_x levels have also been shown to affect the formation rate, formation
166 pathways, and chemical composition of secondary organic aerosol from the reaction of primary species
167 in numerous chamber studies (Carlton et al., 2009; Kroll et al., 2005; Ng et al., 2007, 2008; Presto et
168 al., 2010).

169 | European vehicular emissions, near-highway pollution levels, and the chemical composition of

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Deleted: They show that after a cumulative OH exposure of $\sim 5 \times 10^6 \text{ cm}^{-3} \text{ h}^{-1}$, the formed SOA was 1–2 orders of magnitude higher than the primary OA emissions.

180 highway pollution may be quite different than those measured in North America due to many factors,
181 including: 1) different emission standards and fuel regulations [in the two regions](#) 2) different after-
182 treatment devices to reduce the emission of certain pollutants and 3) a much larger percentage of
183 diesel-powered passenger cars on the road. A comparison between European and North American
184 near-highway measurements could lead to further understanding of the effects of diesel versus gasoline
185 on near-highway atmospheric chemistry.

186 To fully categorize the aerosol, VOC, and NO_x emissions of traffic in France, the joint PM-
187 DRIVE (Particulate Matter- DiRect and Indirect on-road Vehicular Emissions) and MOCOPO
188 (Measuring and mOdeling traffic COngestion and POLLution) field mission took place in the Grenoble
189 basin, France during the fall of 2011 at a near-highway location south of the city center. During the
190 field measurements discussed in this paper, traffic cameras allowed vehicle type determination through
191 license plate automatic identification. Traffic densities, speed and total flow were quantified through
192 loop detectors, while measurements of the chemical composition, concentration, and size of aerosol
193 were collected using both real-time and offline analysis, and parallel data on the gas-phase chemical
194 composition of the roadway-adjacent environment were also collected. A source apportionment model
195 was applied to real-time aerosol chemical composition data. Particular attention was paid to the
196 chemical composition of particles and VOCs emitted during morning and evening rush hours in an
197 attempt to elucidate the primary vehicular influence on near-highway air pollution.

198 2. Experimental Methods

199 2.1. Description of the Measurement Site

200 The sampling site was located at 45.150641 N, 5.726028 E (Figure 1), just south of Grenoble,
201 France adjacent to a major highway (south of E712, with A480 2 km to the [east](#)). During the week, the
202 total traffic on the highway was about 95,000 vehicles day⁻¹ (65,000 during the weekend). Grenoble, a
203 large city with over half a million people, is located in the southeast of France at the foothills of the
204 Alps. The surrounding mountain ranges both buffer the Grenoble area from the effects of transported

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212 aerosol and can also trap pollution within the valley, particularly during the winter months and periods
213 of temperature inversions. The isolating effect of the mountains thus simplifies the potential sources
214 for aerosol, making it an interesting location for the study of specific aerosol emission sources.

215 *2.2. Traffic Cameras and Loop Detectors*

216 Traffic cameras mounted to a roadway sign were used to capture the license plate numbers of
217 vehicles driven on the highway close to the field measurement site. These numbers were later used to
218 classify vehicular traffic into different categories: vehicle type (LDV, Heavy duty vehicles (HDV),
219 buses) and age, vehicle size and engine capacity, fuel type (diesel or gasoline), and Euro number (i.e.
220 the pollutant emission regulation that the vehicle complies with), The speed of the passing vehicles
221 was also monitored with the classical traffic detector (double electromagnetic loops, able to identify the
222 passing of all vehicles and their speeds), which allowed the identification of periods of stop-and-go,
223 dense, or free-flow traffic.

224 *2.3. Massalya Platform*

225 The MASSALYA platform is a mobile laboratory equipped for air quality measurements with a
226 hub located at the Aix Marseille Université. For the field campaign, PM_{2.5} and PM₁ sampling heads
227 situated above the roof of the stationary truck were connected to a variety of online instrumentation
228 located within the truck body. Complementary off-line analysis was performed on filter samples
229 collected by HiVol samplers located adjacent to the MASSALYA platform. All sampling occurred
230 approximately 15 m from one of the traffic lines, [as shown in Figure 1](#). Further details can be found in
231 Polo-Rehn, (2013).

232 A High-Resolution Time-of-Flight Aerosol Mass Spectrometer (Aerodyne, HR-ToF-AMS) was
233 used to analyze the chemical composition, size, and concentration of non-refractory submicrometer
234 particles in the ambient atmosphere (DeCarlo et al., 2006). Instrument specifications have been
235 discussed in detail elsewhere (DeCarlo et al., 2006). Briefly, both high resolution and size-speciated
236 chemical information for ambient aerosol were obtained from this instrument. Aerosols were

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238 vaporized at 600 °C, ionized using electron ionization (EI) at an energy of 70 eV, and the chemical
239 composition of bulk aerosol was measured using a ToF mass spectrometer (TOFWERK). Aerosol
240 spectra were continuously collected and a two-minute average spectrum was obtained. Aerosol
241 vacuum aerodynamic diameter was calculated by setting a particle start time using a chopper wheel
242 and measuring the particle flight time along the particle ToF (pToF) sizing region (DeCarlo et al.,
243 2006). Typical resolution during the campaign was around 2800 $m/\Delta m$ (where $m=m/z$ and Δm =full-
244 width at half max of the mass peak).

245 In addition to the HR-ToF-AMS, a Size-Mobility Particle Scanner (TSI, SMPS) was used to
246 measure the size distribution and concentration of ambient aerosol and a Multiangle Absorption
247 Photometer (ThermoFischer, MAAP 5012) was used to measure the concentration of black carbon.

248 High resolution mass spectra of VOCs were obtained using an Ionicon Proton-Transfer
249 Reaction Time of Flight Mass Spectrometer 8000 (PTR-ToF-MS, hereafter referred to as PTR-MS)
250 (Gaus et al., 2010). The PTR-MS analyzes trace (parts per trillion by volume) VOCs with high mass
251 resolution, which allows the separation of different species with the same nominal mass and the
252 identification of each peak's elemental formula. The PTR-MS was run with a 25 second time
253 resolution and a flow of 100 $\text{cm}^3 \text{min}^{-1}$. Drift tube parameters of the PTR-MS were as follows:
254 Voltage: 560 V, Drift tube pressure: 2.11 mbar, Drift tube temperature: 333 K, resulting in an E/N
255 (electric field/number concentration of neutral particles) of 133 Td.

256 The SMPS, PTR-ToF-MS, and HR-ToF-AMS were connected to the same sample inlet with a
257 PM2.5 sampling head and a sample flow of 1 $\text{m}^3 \text{hr}^{-1}$. Particles were dried ($\text{RH}<30\%$) using a Nafion
258 dryer prior to measurement with the HR-ToF-AMS and SMPS. The MAAP was connected to a
259 separate PM1 sampling head. PM1 filter HiVol (30 $\text{m}^3 \text{h}^{-1}$) samples were collected on quartz filters
260 (Tissuquartz) on a daily basis and analyzed for radiocarbon isotope data. Radiocarbon measurements
261 were conducted using ARTEMIS Accelerator Mass Spectrometry, at Saclay (CNRS-CEA-IRD-IRSN,
262 France) on the total carbon (TC) fraction [after a combustion of the samples at 850°C](#). The method is

264 fully described in El Haddad et al. (2011).

265 A Young meteorological station was also installed to capture wind speed, wind direction,
266 relative humidity, and temperature data at the measurement location.

267

268 2.4. Air Rhône Alpes station

269 Twenty [meters east of the Massalya platform, still adjacent to](#) the highway, the Air Rhône Alps
270 station collected PM_{2.5} HiVol (30 m³ h⁻¹) samples on quartz fiber filters (Tissuquartz) with a time
271 resolution of 4 hours. PM_{2.5} samples were analyzed for EC/OC, inorganic ions, and targeted organic
272 tracers (Polo-Rehn, 2013).

273 Organic compounds in these PM samples were also quantified by gas chromatography coupled
274 with mass spectrometry (GC-MS), following the method detailed in El Haddad et al. (2009) and Favez
275 et al. (2010). EC and OC measurements were performed using the Thermo-Optical Transmission
276 (TOT) method on a Sunset Lab analyzer (Birch and Cary, 1996; Jaffrezo et al., 2005) following the
277 EUSAAR2 temperature program (Cavalli et al., 2010). Ionic species were analyzed with Ionic
278 Chromatography (IC) following the method described in Jaffrezo et al. (1998).

279 All filters used in this study were preheated at 500 °C during 3 h. Samples were stored at -18 °C
280 in aluminum foil and sealed in polyethylene bags until analysis.

281 In addition, NO_x (NO and NO₂), PM₁₀ and PM_{2.5} mass concentrations were measured and a
282 Tapered Element Oscillating Microbalance equipped with a Filter Dynamic Measurement System
283 (TEOM-FDMS, Thermo Scientific) for real-time measurements of PM₁₀ and PM_{2.5}.

284 3. Results and Discussion

285 3.1 Traffic Conditions at the Measurement Site

286 [A detailed view of the measured traffic is presented in the supplementary information \(Figure](#)
287 [S1\). Briefly, the overall makeup of the traffic remained fairly steady throughout the campaign. The](#)

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Deleted: LDVs accounted for the majority of traffic (94%) and only experienced a small drop-off in flow over the weekends (87% of the weekday flow). HDVs and buses, however, were present in much higher concentrations during the week versus the weekend (2.7 times less buses and HDVs on the weekends), and also were in lower numbers on the road during the early morning and late evening hours. The ratio of LDVs to HDVs increased by a factor of 4 from the morning rush hour peak to the evening rush hour peak.

308 bulk of the vehicles directly affecting the measurement site were Euro 4 (released in 2005) or older;
309 thus, the most recent emission regulations had only a small effect on the air quality around the field
310 site. [The ratio between diesel and gasoline cars was found to be 2.6, or 72% diesel, with a high](#)
311 correlation ($R^2=0.96$) between diesel and gasoline vehicles.

312 [3.2. General atmospheric conditions and aerosol and VOC concentrations and evolution](#)

313 Wind speeds were generally low throughout the campaign (<1-2 m/s) with higher wind speeds
314 peaking in the afternoons and tapering off in the evenings. The wind direction was primarily from the
315 northwest, [from the direction of the nearby highway. A diagram of the two measurement stations, the](#)
316 [wind rose plot for the Massalya location, and polar plots showing the concentration of NO and BC as a](#)
317 [function of wind direction are shown in Figure 1. BC and NO were associated with all wind directions,](#)
318 [though slightly higher from the highway direction, which suggested that the measurement site was](#)
319 [directly and strongly influenced by the traffic emissions. However, in order to bett](#)
320 [er describe the traffic influence, we defined high traffic periods \(HT\) within the dataset. These](#)
321 [HT periods were selected as follows : wind direction >40 or <320, NO in the 75th percentile, and from](#)
322 [6:30-9:30 or 17:00-20:00 \(rush hour periods\). The fixed location of the measurement stations made](#)
323 [determination of concentration drop-off as a function of distance from the roadway impossible to](#)
324 [determine with the dataset, although that has been shown to be important in other studies \(such as](#)
325 [Karner et al., 2010\). However, the measurements were all taken closer to the roadway \(~15 m\) than the](#)
326 [calculated distance where roadway emission drop off to background levels \(115-570 m, Karner et al.,](#)
327 [2010\).](#)

328 The campaign time series concentration of submicrometer non-refractory aerosol sulfate (SO_4),
329 ammonium (NH_4), nitrate (NO_3), and organic species from the HR-ToF-AMS is shown in Figure [2A](#).
330 The limit of detection for each species was calculated using the method described by DeCarlo et al.
331 (2006) and found to be 0.30, 0.21, 0.06, and 0.33 $\mu g m^{-3}$ for SO_4 , NH_4 , NO_3 , and organic aerosol,
332 respectively, for our measurements with a time resolution of 2.5 min. A collection efficiency (CE) of

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Deleted: From the 15 minute time-resolution traffic data (not shown), approximately five times as many Euro 4 as Euro 5 cars were counted on the road during the measurement period, while similar numbers of Euro 3 and Euro 4 cars were observed. A relatively high correlation

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Deleted: the different Euro classifications of vehicles was observed (R^2 values of 0.7 for Euro 5 and Euro 4, 0.9 for Euro 3 and Euro 4, using 15 minute time resolution traffic data). For diesel cars, from Euro 4 (released in 2005) to Euro 5 (released in 2009), NOx emission limits decreased from 0.25 to 0.18 $g km^{-1}$ and particulate emission limits decreased from 0.025 to 0.005 $g km^{-1}$. From Euro 3 (released in 2000) to Euro 4 another two-fold decrease in NOx and PM emission limits was implemented for diesel vehicles. Gasoline NOx emission limits were reduced from 0.15 to 0.08 to 0.06 $g km^{-1}$ from Euro 3 to Euro 5, and total hydrocarbon emission limits were reduced from 0.20 to 0.10 $g km^{-1}$ from Euro 3 to Euro 4. No PM limits were implemented for gasoline-powered vehicles until Euro 5, where a limit of 0.005 $g km^{-1}$ for direct-injection vehicles was introduced, and no total hydrocarbon emission limits have been introduced for diesel-powered vehicles.

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Deleted: on the highway was found (Figure 2B). The ratio between diesel and gasoline (the slope of the line) was found to be 2.6, or 72% diesel. This value is slightly higher than that reported by ADEME for French vehicle fleet (61%). However ADEME data represent the registered vehicles and not the on-road vehicles. This difference highlights most probably the combined effects of fuel costs and of vehicles consumption. Additionally, no weekly variation (weekend versus weekday) in the ratio of diesel: gasoline powered vehicles on the road was observed, unlike that commonly observed on North American highways (Bahreini et al., 2012).

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383 0.75 was applied to HR-ToF-AMS aerosol concentration measurements taken during this campaign.

384 The CE factor compensates for incomplete vaporization of non-refractory species due to particle
385 bounce, the likelihood of which changes with particle phase and chemical speciation (Huffman et al.,
386 2005; Matthew et al., 2008). This CE was calculated by comparing the HR-ToF-AMS SO₄
387 concentrations to 4 hour filter concentrations (Figure S2). This comparison gave a value of 0.75±0.03
388 for the slope between the two types of measurements.

389 PM2.5 averaged 17 µg m⁻³ for the campaign (Figure S3) while PM10 averaged 22 µg m⁻³.

390 These values increased slightly during HT periods (a 1.3 and 1.25x increase, respectively). Black
391 carbon and organic aerosol species dominated the measured aerosol composition throughout the
392 campaign, and comprised 39 and 40% of the total speciated submicrometer aerosol, respectively.

393 PM2.5 had a somewhat higher mass variation than the AMS + BC measured mass (Figure S3), likely
394 due to the smaller measurement size cutoff for AMS (1 µm) and the presence of road dust in the local
395 environment, a large portion of which may be non-refractory and those unable to be measured by the
396 AMS. Increases in BC and the aerosol marker *m/z* 57 (C₄H₉⁺), a marker for primary organic carbon in

397 the HR-ToF-AMS (Zhang et al., 2005), correlated in time to the observed morning and evening traffic
398 peaks (Figure 2B), with BC levels reaching 10-16 µg m⁻³ during the mornings (Figure 2A) for 2.5 min
399 averaged measurements. As expected, an increase of BC and *m/z* 57 (1.5x) was observed during HT
400 periods. Note that BC concentrations during high filter loadings (BC accumulation rate > 0.14 µg

401 min⁻¹) have been removed to compensate for the underestimation of BC by the MAAP during periods
402 of high concentrations (Hyvärinen et al., 2013). Along with increased concentrations of *m/z* 57 and
403 BC, elevated number concentrations of small particles (up to 1-2x10⁵ cm⁻³ during peaks from daily
404 base levels of 2-4x10⁴ cm⁻³) were observed during periods of HT (Figure 2D), for 5 min measurements.

405 BC and *m/z* 57 had similar daily averages throughout the campaign; however, overall organic

406 concentration rose significantly during the period from 9/12-9/14, when particle growth events were

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Deleted: 3A), and comprised 39 and 40% of the total speciated submicrometer aerosol, respectively.

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417 | observed (Figure 2D). The geometric number mode diameter rose over the course of each day to a
418 | maximum diameter each afternoon, when photochemical processing was the most intense. A marker
419 | for oxidized, aged organic aerosol (Figure 2C, m/z 44, COO^+) also rose in concentration during this
420 | time period, further confirming that the larger aerosol and higher organic mass concentrations were due
421 | to aging and secondary organic aerosol formation processes. A period of heavy rain on the 18th and
422 | 19th of September removed much of the organic aerosol from the local atmosphere. Black carbon
423 | concentrations and small particle concentrations quickly returned to their previous levels. A new
424 | accumulation period was observed after rainfall (Figure 2D), with the mode diameter of particles
425 | increasing as secondary aerosol was formed again. [The slow rise of organic concentration during these](#)
426 | [periods, the lower BC:Org ratio, the enhancement of organic concentration outside of normal traffic](#)
427 | [periods, and the low level of NO during these accumulation periods all suggest that this increase in](#)
428 | [organic aerosol concentration was driven by regional influences, not by nearby vehicular emissions,](#)
429 | [and a more southerly wind direction during this time confirmed the transport of non-highway air](#)
430 | [masses to the measurement site.](#)

431 | These findings are similar to those presented recently by Sun et al., (2012), who measured
432 | aerosol size and chemical composition adjacent to the Long Island Expressway in New York and
433 | observed that traffic-influenced aerosol emissions were primarily small particles which varied in
434 | concentration with changes in traffic throughout the day. During periods with less traffic influence,
435 | more oxygenated organic aerosol (OOA) and inorganic ions with larger mode diameters and lower
436 | temporal variations were observed (Sun et al., 2012).

437 | The time series concentrations of selected VOC peaks are shown in Figure 3. Primary traffic
438 | related VOC species, such as aromatics (benzene and [trimethylbenzene](#)), were found to have high
439 | temporal variations similar to those of traffic-related aerosol species and NO_x (Figure 4C and D). NO_x
440 | levels were often over 400 ppbv during the morning rush hours, while the PTRMS peak corresponding
441 | (in part) to toluene and benzene peaked around 2 to 1 ppbv (respectively). During a recent chamber

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447 study in Ispra, Italy, fresh diesel emissions PTR-MS VOC spectra were found to contain peaks with the
448 same mass as CH_4NO_2^+ and $\text{C}_2\text{H}_5\text{O}^+$ (Hellebust et al., 2013, 2014), not present in fresh gasoline
449 emissions. These same peaks were also observed during this work and found to vary with traffic
450 during this measurement period, but had a smoother variation than the observed aromatics (Figure 3B).
451 While this species is unique for fresh diesel emissions versus gasoline emissions, aging processes occur
452 rapidly and other sources may contribute to this mass peak. Thus, these species, while increasing with
453 traffic, cannot be assumed to be tracers for primary diesel emissions in particular; no high-
454 concentration unique tracer peak for diesel VOC emissions was resolved from the fresh diesel emission
455 spectra in these chamber experiments (Hellebust et al., 2015). [A slight increase of the traffic related
456 VOCs \(1.2x for benzene and trimethylbenzene\) was observed during HT periods compared to the
457 campaign average. For \$\text{CH}_4\text{NO}_2^+\$ this relative increase during HT periods is lower \(8%\), which could
458 confirm multiple sources of this compound.](#)

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459 In addition to traffic-related VOC emissions, mass peaks corresponding in exact mass to
460 biogenic emissions, such as isoprene, were measured in ppbv levels. These peaks were found to rise in
461 concentration with the ambient temperature (Figure 3A), typical of isoprene peaks. The presence of
462 isoprene and its oxidation product, methyl vinyl ketone (MVK) or its isomer methacrolein (MACR), in
463 similar concentrations as that of the major traffic-related VOC peaks (ppbv levels) suggested that
464 biogenic emissions also significantly influenced the local atmosphere despite close proximity to
465 anthropogenic emission sources (i.e., road traffic).

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466 The high morning concentrations of traffic-related pollutants, compared to evening
467 concentrations, were caused in part by a low early morning boundary layer that rose during the day and
468 fell during the night. Boundary layer heights (BLH) were estimated using the Hybrid Single Particle
469 Lagrangian Integrated Trajectory (HYSPLIT) backtrajectory model. The HYSPLIT model either
470 extracts the BLH from meteorological file input into the model or, if no BLH exists in the
471 meteorological file, BLH is estimated using the vertical temperature profile. A selection of the BLH-

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475 [scaled](#) diurnal profiles of traffic and biogenic emission related VOC concentrations are shown in Figure
476 [4A](#) along with traffic (speed, vehicular flux) diurnal profiles and the calculated boundary layer heights
477 and measured temperatures (Figure [4B and C](#)). [This calculation was performed to more directly](#)
478 [compare vehicle concentration and speed to vehicular emissions and temperature with biogenic](#)
479 [emissions \(by removing the dilution of emissions by the changing boundary layer height\)](#). Biogenic
480 species, such as isoprene, peaked in concentration during the afternoon, when temperatures were the
481 warmest. Aromatic species peaked in concentration, even after the rough boundary layer correction
482 was applied, during periods of low speeds. This is consistent with other findings that show cold starts
483 and idling speeds cause an increase in aromatic VOC emissions from gasoline-powered vehicles (e.g.,
484 Broderick and Marnane, 2002).

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486 [3.3 PMF Analysis](#)

487 The positive matrix factorization (PMF) model was applied to the HR-ToF-AMS aerosol data
488 using the process described in detail by Ulbrich et al. (2009). Six aerosol factors were resolved by their
489 source and relative aging using the PMF model: a hydrocarbon-like organic aerosol (HOA) factor, a
490 regional oxidized organic aerosol (OOA) factor associated with sulfate aerosol, two oxidized organic
491 aerosol factors with opposing diurnal patterns, one more oxidized than the other (Less Oxidized
492 Organic Aerosol, or LO-OA, with peak concentration during the mornings/nights, and More Oxidized
493 Organic Aerosol, or MO-OA, with peak concentrations during the afternoons), a biomass-burning
494 organic aerosol factor (BBOA), and a nitrogen-containing organic aerosol factor (NOA). The mass
495 spectra for the six resolved factors is shown in Figure [5](#), labeled with their identifications. Evaluation
496 graphs for the six-factor PMF solution are shown in the Supplementary Information (Figures [S5-S8](#)).
497 Polar plots of the factor concentrations and wind direction are shown in Figure [S9](#). A six factor
498 solution was the lowest number of factors where a BBOA factor was resolved; BBOA was suspected to
499 be present in the air mass measured during the campaign due to periods of increased levoglucosan

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511 measured on filter samples. However, its concentrations were very low ($15 \text{ ng}\cdot\text{m}^{-3}$ on average, Polo-
 512 Rehn, (2013)) compared to concentrations measured in Grenoble in winter (around $800 \text{ ng}\cdot\text{m}^{-3}$ (Herich
 513 et al., 2014)). Solutions with more than six factors appeared to split the OOA factor further until
 514 differences between each OOA factor were difficult to justify. [The calculated elemental ratios of O:C,](#)
 515 [H:C, and Organic Mass: Organic Carbon \(OM:OC\), \(Aiken et al., 2008\) are shown in Table 1.](#)
 516 The diurnal pattern and the relative concentrations of each resolved factor, averaged over the
 517 campaign period, are shown in Figure 6, along with the standard deviation of their concentrations.
 518 Morning and evening peaks, correlating in time to rush hour traffic, were clearly observable for the
 519 HOA factor. Also clearly visible in Figure 6A is the opposing diurnal trends of LO-OA (peaking at
 520 night and early morning) and MO-OA (peaking around 3pm each afternoon). Regional OOA had no
 521 discernable diurnal trend. An interesting finding in these data is that the HOA and NOA factor
 522 concentrations both peaked during morning and evening high traffic periods (Figure 6A). This is not
 523 the general behavior demonstrated in most studies for the NOA factor, although a similar NOA factor
 524 has been previously measured in the Po Valley, Italy (Saarikoski et al., 2012). [This behavior was](#)
 525 [confirmed by examining HT periods, with an increase of 1.3x and 1.9x for NOA and HOA](#)
 526 [concentrations, respectively, during HT periods. While many of larger hydrocarbons or of other](#)
 527 [organics, only N-containing peaks whose fitting significantly reduced the residual mass at each unit](#)
 528 [mass were fit \(Figure S8\). Additionally, and when possible, the w-ToF mode data was examined to](#)
 529 [determine if the N-containing peak was resolved enough from neighboring peaks for certain](#)
 530 [identification.](#)
 531 [In Figure 7, the time series of each factor are shown with oxalate \(\$\text{C}_2\text{O}_4^{2-}\$, a marker for aged and](#)
 532 [oxidized organic aerosol\), sulfates, and levoglucosan \(a marker for biomass burning\) measurements](#)
 533 [from filter samples. Table 2 summarizes the \$R^2\$ values between key tracer species and the resolved](#)
 534 [aerosol factors. The two main factors resolved, in terms of mass concentration, were the OOA factors](#)
 535 [with opposite diurnal trends, MO-OA and LO-OA. The concentration of MO-OA rose as the aerosol](#)

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Deleted: As suggested by the relative mass contribution of m/z 57 and m/z 44 (see previous section), HOA was not the largest average contributor to the bulk measured aerosol mass over the campaign period, despite the fact that these measurements were conducted 15 m from a major highway (Figure 9B). The relative size of each type of particle (primary, or HOA, and OOA) likely plays a major role in the relative mass concentrations of each factor. The variability of each factor over the campaign was high as, unlike measurements in more rural areas, the proximity to a primary aerosol source (highway) and to an urban center (Grenoble), as well as large green spaces (the Alps) allowed the full range of aged and locally transported aerosol to be observed at this station. The calculated elemental ratios of O:C, H:C, and N:C, along with the
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587 [number-weighted geometric mode diameter rose, also indicative of increasing aerosol age/coagulation.](#)
588 [The LO-OA factor resembled the SV-OOA factor reported by Docherty et al. \(2008\) measured during](#)
589 [the Study of Organic Aerosols \(SOAR\) project at Riverside, CA, which was also found to decrease](#)
590 [during the afternoon as temperature and photochemical processing increased. The chemical differences](#)
591 [between these two spectra are show in Figure S10 and described in the Supplementary Information.](#)
592 [The increase in MO-OA concentration occurred as both PTR-ToF-MS isoprene signal was increasing](#)
593 [\(also a temperature-related process\) and as the 9-carbon aromatic: benzene \(\$C_9H_{13}^+ : C_6H_7^+\$ \) VOC ratio](#)
594 [was at its minimum \(related to photochemical age of air mass, \(Parrish et al., 2007\)\). Thus, the](#)
595 [increase MO-OA could be linked to photochemical aging of vehicular emissions during the day and/or](#)
596 [to increasing biogenic VOC emissions and their subsequent photochemical aging and condensation into](#)
597 [aerosol form.](#)

598 The BBOA factor was found to correlate with levoglucosan ($R^2=0.65$, $n=38$), while significant
599 levels of biomass burning from wood-burning stoves and other combustion-related heating are known
600 to affect the Grenoble Valley in winter, such a large contribution during this season is surprising. Likely
601 the PMF-resolved BBOA factor was somewhat mixed with emissions with close spectral signature
602 (vehicular emissions or potentially cooking aerosol emissions), Episodic local yard-waste burning
603 could also have contributed to the bulk aerosol spectrum, as spikes in the BBOA concentration do not
604 appear to correlate with a particular wind direction (Figure S9). The ratio of levoglucosan: BBOA is
605 quite low (0.03); however, it is within the order of magnitude of previously reported measurements
606 (e.g., 0.06, (Aiken et al., 2009)). Additionally, the higher levels of oxidants found in the atmosphere in
607 the summer could cause a faster degradation of levoglucosan in the atmosphere after emission
608 (Hennigan et al., 2010). Thus, the BBOA concentrations reported here shall be considered as an upper
609 limit of the biomass burning contribution.

610 Of the factors resolved, the HOA factor had the lowest O: C ratio (0.07) and a good ($R^2=0.58$,
611 $n=3928$) correlation with BC concentration. The mass spectrum of the resolved HOA factor highly

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646 resembled ($R^2 > 0.95$, $n = 100$) previously resolved HOA factors and direct AMS measurements of diesel
647 and gasoline emissions (Mohr et al., 2009; Zhang et al., 2005). HOA was not the largest average
648 contributor to the bulk measured aerosol mass over the campaign period, despite the fact that these
649 measurements were conducted 15 m from a major highway. The relative size of each type of particle
650 (primary, or HOA, and OOA) likely played a major role in the relative mass concentrations of each
651 factor (Figure S11 and discussion), and the higher increase above background of particle number
652 versus particle mass found in this study agrees with previous studies (Karner et al., 2010, Sun et al.,
653 2010). The variability of each factor over the campaign was high as, unlike measurements in more
654 rural areas, the proximity to a primary aerosol source (highway) and to an urban center (Grenoble), as
655 well as large green spaces (the Alps) allowed the full range of aged and locally transported aerosol to
656 be observed at this station.

657 3.3.1 Fossil and Modern Carbon

658 A source of uncertainty in the global particulate emissions of vehicles is the formation of SOA
659 from gas-phase emissions and the aging of POA. To discriminate between the relative concentration of
660 modern and fossil carbon, and thus potentially discriminate between OOA from vehicular sources and
661 from modern sources, daily filter samples were collected at the sampling site and ^{14}C radiocarbon
662 measurements were performed. From these measurements, the percentage of modern carbon from TC
663 (OC+EC) was calculated. Modern carbon varied from 15-36% of the total aerosol carbon, a significant
664 portion of the measured carbon considering the close proximity of the measurements to fossil carbon
665 sources. In France, the contribution of biofuel was about 7% and 5% for diesel and gasoline fuel,
666 respectively, in 2011 (UFIP, Union Française des Industries Pétrolières, 2011) and cannot explain this
667 relative high proportion of modern carbon observed in the particulate matter. This is similar to findings
668 shown in Hodzic et al. (2010), Minguillon et al. (2011), and El Haddad et al. (2013), which indicate
669 that modern carbon is often more significant than fossil carbon in the carbonaceous fraction of PM,
670 even in cities with high vehicular emissions (e.g., Mexico City, Barcelona or Marseille).

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Deleted: Thus, the increase MO-OA could be linked to photochemical aging of vehicular emissions during the day and also to increasing biogenic VOC emissions and their subsequent photochemical aging and condensation into aerosol form.

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714 As radiocarbon measurements have been performed through a thermal approach (combustion of
715 the samples at 850°C), we consider in the following section EC measured by the thermo-optical
716 method. As shown in figure S12, EC and BC do not agree well at low mass loadings, but have a wider
717 scatter in the data at higher mass loadings. The calculation of BC (measured by the MAAP) using an
718 absorption cross-section is imprecise and, at high loadings of BC, may under or overestimate this mass
719 loading. Figure S12 shows a comparison between the MAAP (BC) and thermal measurement (EC)
720 data, with a 1:1 line. As the thermal-optical analysis of EC is a more direct analysis, EC was chosen to
721 be used in this calculation.

722
723 Assuming that the majority of EC was traffic-related, and thus from fossil origin, the
724 concentration of modern organic carbon and fossil organic carbon was then calculated. While evidence
725 for the presence of biomass burning aerosol was measured at the field site, the main source of EC was
726 likely diesel exhaust. Figure 8 shows the fraction of EC and OC, HOA, and a partitioning between
727 fossil and modern carbon. In Figure 8A, a rough calculation was performed to determine the
728 concentration of non-primary fossil organic carbon. For a first estimate, all EC was assumed to be
729 fossil in origin. Additionally, the HOA aerosol was also assumed to be vehicular, and thus fossil, in
730 origin. The HOA factor concentration has been divided by its OM: OC ratio to remove any non-carbon
731 mass (HOA C, calculated from the elemental formulas of the PMF factor mass spectra, Aiken et al.
732 (2008)). Both EC and HOA C had high ($R^2=0.89$ and 0.85 respectively, $n=10$) correlations with the
733 fossil C mass, which supported a largely fossil source for these two species. The remaining fossil
734 organic carbon mass after subtraction was then assumed to be from non-primary sources (in light blue).

735 This calculation provided a lower estimate of the amount of fossil carbon contributing to SOA
736 mass, and involves several assumptions and potential sources of error. Sources of error in this
737 calculation include error in the PMF resolution of primary (HOA) organic aerosol spectra and error in
738 the calculated OM:OC ratio of this factor species, biodiesel vehicular emissions contributing modern

739 carbon to measured HOA, and biomass burning aerosol contributing modern carbon to measured EC.
740 As the measured HOA:EC ratio was in-line with previous measurements in high diesel environments,
741 HOA concentrations did not appear to be significantly over or under estimated. Up to 7% of fuel use in
742 France was biodiesel, thus, part of the HOA concentration could be from modern sources. While
743 research has shown that the use of biodiesel fuels reduces the overall primary particulate matter
744 emissions (Cheung et al, 2010), biodiesel could still be a modern carbon contributor to OC and EC
745 mass. Additionally, although the concentration of BBOA was generally low (a campaign average of
746 $0.34 \pm 0.23 \mu\text{g m}^{-3}$) and the ratio of BBOA:EC, has been found to be on the order of 3-4 in other areas
747 of France (Crippa et al., 2013), some contribution to EC from biomass burning may have been present
748 at the measurement site. In Figure 8B, a range of fossil non-primary organic carbon, normalized to
749 total measured organic carbon, is presented. For the upper limit of this range, HOA C and EC were
750 considered to be 95% fossil and 5% modern (7% biodiesel fuel use and an estimated 25% reduction in
751 particulate emissions from biodiesel fuel). Also for this upper limit, the calculated concentration of
752 BBOA was divided by 3 and used to calculate possible modern EC from biomass burning (Crippa et
753 al., 2013).

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754 Total organic carbon concentration appeared to be more driven by processed/aged OOA
755 concentrations than by primary emissions. During the period with the highest organic concentrations
756 (September 15th-17th), most of the non-HOA carbon measured was modern carbon. Also during this
757 time period, the winds were also slightly more southerly and SO₄ and OOA concentrations increased,
758 which could indicate a more regional contribution to the measured air mass during this time. After a
759 period of heavy rain on the 19th, almost none of the non-HOA, organic carbon was fossil; however, this
760 also coincided with a period of increased BBOA, which may have contributed to modern-EC emissions
761 and thus an underestimate of fossil-OC emissions (Figure 7). At other times during the campaign,
762 HOA concentrations alone could not adequately explain all of the measured fossil organic carbon and
763 additional sources of fossil organic carbon (such as photochemical reactions forming aerosol from

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764 vehicular VOC emissions) would be needed. Additionally, the origin of the NOA factor remains
765 unclear, and if fossil in origin, could explain part of the non-HOA organic fossil carbon measured at the
766 site, further reducing the OOA fossil-C (at times to almost zero). Overall, throughout the campaign the
767 majority of OOA observed was most probably modern in origin.

768 The high levels of modern carbon OOA suggested that biogenic compounds had a large effect
769 on the overall aerosol population in this location, even directly adjacent to a large anthropogenic
770 emission source (i.e., traffic). Interaction between anthropogenic oxidants and biogenic VOCs (or
771 BVOCs) has been found to increase the formation of SOA (Chameides et al., 1988; Goldstein et al.,
772 2009; Shilling et al., 2013), isoprene oxidation reactions leading towards SOA have been shown to vary
773 depending on the level of NOx (Chen et al., 2014; Kroll et al., 2005; Ng et al., 2007; Xu et al., 2014),
774 and likely BVOC concentrations were greater and the aromatic VOC concentrations were lower in the
775 wider Grenoble Valley.

776 3.4.3. Differences between diesel-heavy and gasoline-heavy near-roadway measurements.

777 Older diesel vehicles have been shown to emit both higher levels of PM, particularly BC, and
778 higher levels of NOx. Indeed, high concentrations of NOx were measured at the field site, up to 450
779 ppbv (NO+NO₂), for 15 min averaged measurements. NO₂ levels exceeded the 100 ppbv European
780 hourly limit almost every morning. The campaign average for NO₂ was 94 +/- 64 ppbv. For
781 comparison, at a measurement site adjacent to a major highway in New York, Sun et al. (2012)
782 measured an average of 48 +/- 30 ppbv NO₂, about half that of this campaign's average, with 15 min
783 average peaks ranging from 100-300 ppbv. The hourly traffic concentrations at each site were close
784 (approximately 10,000 vehicles/hour reported during the Sun et al. (2012) measurement periods
785 compared to approximately 8,000 vehicles/hour observed during daylight driving hours on Grenoble's
786 highway); thus, increased NOx cannot be explained by increased traffic. Rather, increased diesel fuel
787 use is a very likely hypothesis.

788 High levels of BC were also measured in this work. A comparison of the HOA: BC ratio from

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807 | this study and from previously reported field studies is shown in Figure 9A. As expected, since the
808 | French fleet includes a much higher percentage of diesel car with increased BC emissions, this ratio
809 | was significantly lower than that reported for an urban-downwind site in Pittsburgh (1.41, Zhang et al.
810 | (2005)), a highway adjacent site in New York (1.02, Sun et al. (2012)), an urban/highway site in
811 | Ontario (0.7-1.1, Stroud et al. (2012)), a rural site in NW England (1.61-1.91, Liu et al. (2006)), and an
812 | urban site in [Zürich](#), Switzerland (1.1, Lanz et al. (2007)). As for measurements in France, a study in an
813 | urban site in Paris observed a HOA:BC ratio of 0.61 (Crippa et al., 2013); this site was most probably
814 | influenced by a vehicle fleet similar to Grenoble's, but measurements were collected during winter
815 | (lower temperatures) and within Paris (increased urban emissions). Tailpipe measurements of Euro 4
816 | diesel and gasoline-powered vehicles (a Renault Kangoo and a Ford Ka, respectively) at IFSTTAR
817 | (Institut Français des Sciences et Technologies des Transports, de l'Aménagement et des Réseaux)
818 | performed during this PM Drive research program also show a much higher HOA: BC ratio for
819 | gasoline vehicles versus diesel vehicles (unpublished data). This was due to much higher BC
820 | emissions from the diesel vehicle, as opposed to higher HOA emissions from the gasoline vehicle. [Similarly, the](#)
821 | [HOA factor measured near Grenoble was similar to that measured by Sun et al. \(2012\), in](#)
822 | [a high gasoline environment next to a highway in New York, both in absolute concentration and](#)
823 | [chemical composition,](#) thus, an increase in BC emissions (from diesel) rather than a reduction in HOA:
824 | vehicle number was likely the cause of our low HOA: BC ratio.

825 | [The change in HOA: BC ratio as a function of the diesel: gasoline fuel use \(Road sector, World](#)
826 | [Bank, 2011\) is shown in Figure 9B. A decrease in HOA: BC with an increase in percent diesel is](#)
827 | [clearly observable with a strong correlation \(\$R^2=0.85\$, \$n=10\$ \), despite the many different factors](#)
828 | [possibly influencing BC and HOA concentrations at each location \(e.g., local aerosol sources,](#)
829 | [meteorology\). Such a linear relationship between HOA: BC and diesel percentage is very interesting,](#)
830 | [but was not necessarily expected, since the emission factors of HOA+BC differ significantly between](#)
831 | [diesel and gasoline cars, especially for pre EURO5 vehicles.](#)

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Deleted: This low HOA:BC ratio in the campaign in Grenoble is in-line with reported measurements from diesel exhaust; for example, Chirico et al. (2010) found a OA:BC ratio of 0.28 in smog chamber emission (where most of the OA is likely to be 'HOA-type' aerosol).

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Moved up [11]: The hourly traffic concentrations at each site were close (approximately 10,000 vehicles/hour reported during the Sun et al.

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Deleted: (2012) measurement periods compared to approximately 8,000 vehicles/hour observed during daylight driving hours in the Grenoble's highway);

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Deleted: Although HDV have higher PM emission limits than LDVs for the same Euro classification, the HOA: BC ratio remained fairly steady throughout the day even as the LDV: bus/HDV ratio increased by a factor of four from morning to evening. This suggested that LDVs, rather than HDVs or buses, were more responsible for the low HOA: BC ratio and the high BC concentrations. This differs from the Sun et al. (2012) measurements. Sun et al. (2012) attribute a period of strong correlation between BC and HOA, along with a low HOA: BC ratio (of 1.02) to the influence of diesel trucks (12%) and a day of high HOA with little to no BC due to the influence of local bus emissions powered by compressed natural gas.

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Deleted: Of the measurements presented in Figure 12, the French measurement sites had by far the highest proportion of diesel vehicles and diesel fuel use.

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874 [Additionally, an AMS factor with a diurnal pattern peaking during rush hour and with N-](#)
875 [containing peaks was observed](#), Saarikoski et al., (2012) found a similar amine-containing NOA factor
876 in measurements taken in the Po Valley (Italy) that also had a strong diurnal pattern. However, their
877 NOA factor was attributed to marine influence due to a correlation with MSA (Saarikoski et al., 2012),
878 although it is possible that MSA was from the local industrial use of DMSO as a solvent, and had a
879 higher H:C ratio (1.91) than the factor resolved from this data set (1.38). [Like France, Italy has a large](#)
880 [percentage of diesel fuel consumption \(71%, World Bank 2011\)](#). Aiken et al., (2009) and Sun et al.,
881 (2011) also resolved N-containing OA factors from data measured in Mexico City and New York,
882 respectively, but did not observe a similar diurnal pattern. In the PTR-ToF-MS mass spectra results
883 obtained from Euro 5 vehicle emission smog chamber studies, Hellebust et al., (2015, and 2013) found
884 higher nitrogen-containing emissions from fresh and aged diesel mass than from fresh and aged
885 gasoline mass spectra (e.g., peaks such as CH_4NO_2^+). Similar nitrogen-containing VOC peaks were
886 found by Inomata et al. (2013) in diesel exhaust. [Thus, diesel-related emissions could possibly be the](#)
887 [source for the observed NOA factor, although no significant correlation between this factor and other](#)
888 [vehicular emissions, such as BC, was found. More detail on the NOA factor can be found in the](#)
889 [Supplementary Information and Figure S13](#).

890 [And finally, only small amounts OOA measured at the field site were calculated to contain](#)
891 [fossil-OC](#). Work by Bahreini et al., (2010) found that much of the measured SOA in the Los Angeles
892 [Valley was from gasoline passenger cars, not from diesel trucks, and perhaps the relatively low](#)
893 [concentration of gasoline vehicles on the road in France is related to the low concentration of fossil-](#)
894 [OOA](#).

897 4. Conclusions

898 During this campaign, highly time resolved particle and gas-phase chemical composition and

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Moved up [9]: NO₂ levels exceeded the 100 ppbv European hourly limit almost every morning. The campaign average for NO₂ was 94 +/- 64 ppbv. ... [4]

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Moved up [10]: (2012) measured an average of 48 +/- 30 ppbv NO₂, about half that of this campaign's average, with 15 min average peaks ranging from 100-300 ppbv. ... [5]

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Moved up [12]: . Rather, increased diesel fuel use is a very likely hypothesis. ... [6]

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Deleted: One possible effect of increased NOx on aerosol formation is the formation of organic nitrate aerosols from the photochemical reactions of various VOC precursors in the presence of high levels of NOx (Ng et al., 2007). During the field campaign, little evidence of typical organic nitrate peaks (e.g., CH₄NO, C₂H₅NO, C₃H₄NO, CH₂NO₃, CH₂NO₂ (Farmer et al., 2010) was found in the high resolution mass spectra. In low concentrations, organic ... [6]

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Moved up [4]: Modern carbon varied from 15-36% of the total aerosol carbon, a ... [7]

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Moved up [6]: has been found to be on the order of 3-4 in other areas of France (C ... [11]

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1189 concentration measurements were obtained alongside parallel traffic data of the speed, fluxes, vehicle
1190 type, and fuel type of passing cars on a highway in the Grenoble Valley. [An](#) analysis of the local
1191 primary (traffic) aerosol and the more regional, aged secondary organic aerosol was performed for the
1192 PM1 fraction observed by the HR-ToF-AMS. The PMF model was run on the high-resolution HR-
1193 ToF-AMS aerosol data and six factors were resolved from the bulk aerosol data: 1) an HOA factor,
1194 related to traffic 2) a BBOA factor 3) a regional OOA factor, which covaried with sulfate 4) a MO-OA
1195 factor, increasing in concentration during sunny afternoons 5) a LO-OA factor, with the opposite
1196 diurnal pattern as MO-OA, likely due to gas-particle phase partitioning and photochemical processing
1197 and 6) an NOA factor with a diurnal pattern similar to that of HOA and to traffic peaks.

1198 The resolved mass spectrum for the HOA factor was chemically similar to mass spectra from
1199 both gasoline and diesel-emitted organic carbon and previously resolved HOA factors in high-gasoline
1200 environments; however, the HOA: BC ratio measured was low (<0.3) throughout the campaign. This
1201 ratio agrees with previously reported HOA: BC ratios in high diesel environments and from direct
1202 measurements of diesel emissions in smog chamber and tailpipe measurement studies. The fraction of
1203 diesel-powered vehicles on the road appeared to control, to some extent, this ratio. [Diesel also](#)
1204 [influenced local NOx concentrations, as the measured NOx was two times higher than concentrations](#)
1205 [near a similarly-trafficked highway in New York, USA.](#)

1206 [While high levels of both black carbon \(5 +/- 3 µg m⁻³\) and organic aerosol \(8 +/- 4 µg m⁻³\)](#)
1207 were measured, when examined, only 20% of the total organic mass signal could be attributed to
1208 primary vehicular emissions (i.e., [HOA](#)). [Significant amounts of modern organic carbon were also](#)
1209 [measured, and fossil carbon appeared to contribute only a small amount to the measured OOA.](#)

1210 [Although NOx and VOCs emitted by diesel and gasoline engines, respectively, may have influenced](#)
1211 SOA formation in the Grenoble Valley, the majority of [OOA](#) measured was modern in origin, even
1212 adjacent to a major source of fossil carbon. Whether this is due to a lower overall gas+particle
1213 emission of diesel vehicles, the lack of aromatic compounds in diesel VOC emissions, high NOx

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Deleted: Periods of heavy traffic were associated with both increased HOA and BC along with increased particle number concentration and lower particle size.

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Deleted: HOA). Traffic emissions dominated the aerosol particle number concentration, but the majority of the organic aerosol mass concentration measured was SOA. NOx concentrations in these measurements were two times higher than concentrations near a similarly-trafficked highway in New York, USA.

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1228 reducing the efficiency of vehicular VOC to SOA formation mechanisms, an acceleration of BVOC to
1229 biogenic aerosol formation in the presence of vehicular emissions, or simply the more global source
1230 and higher efficiency of BVOC to SOA reactions is unclear, but in a high diesel environment, SOA
1231 OOA from fossil-fuel carbon was only a small source of the measured OOA , while modern C-
1232 containing OOA dominated the organic aerosol mass in the fine fraction of PM1.

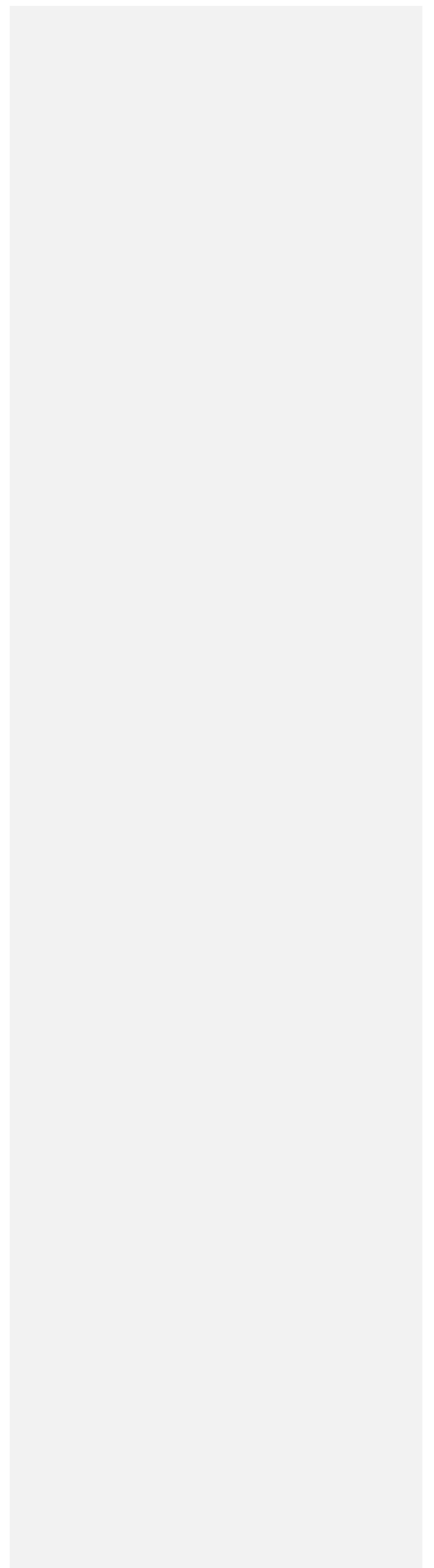
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1238 **Acknowledgments:**

1239 *This work was supported by the French Environment and Energy Management Agency (ADEME,*
1240 *Grant number 1162C0002), The authors gratefully acknowledge the NOAA Air Resources Laboratory*
1241 *(ARL) for the provision of the HYSPLIT transport and dispersion model (<http://www.ready.noaa.gov>)*
1242 *used in this publication. We also gratefully acknowledge Air Rhone Alpes staff (particularly Yann*
1243 *Pellan) for their support during the campaign as well as Y. Sun and Q. Zhang for providing near-*
1244 *highway aerosol data from their paper Sun et al., (2012) for comparison with these measurement, and*
1245 *the MASSALYA instrumental platform (Aix Marseille Université, ice.univ-amu.fr) for the analysis and*
1246 *measurements used in this publication. Finally, the authors would like to acknowledge and thank the*
1247 *two anonymous reviewers who provided constructive advice on the formation of the final paper.*

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Table 1

PMF FACTOR	OM:OC	H:C	O:C
HOA	1.25	1.89	0.07
NOA	1.69	1.38	0.4
LO-OA	1.74	1.34	0.47
MO-OA	2.15	1.16	0.78
BBOA	1.56	1.47	0.32
OOA-REG	1.85	1.54	0.52

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PMF FACTOR	Oxalate (N=53) R ²	BC ^a (N=3928) R ²	Levoglucosan (N=38) R ²	Sulfate (N=3328) ^b R ²
HOA	0.01	0.58	0.12	0.004
BBOA	0.04	0.05	0.65	0.005
MO-OA	0.50	0.01	0.02	0.54
LO-OA	0.32	0.01	0.08	0.07
NOA	0.01	0.09	0.12	0.06
OOA-REG	0.62	0.02	0.01	0.65

1289 ^a BC data smoothed to remove underestimated BC concentrations during periods of high filter loading
1290 (Hyvärinen et al., 2013)

1291 ^b R² value calculated after initial high SO₄ period.

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1324 [Figure Captions](#)

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1327 [Figure 1:](#) The measurement site [location](#) is marked by a [red square on the map](#), and the adjacent

1328 [highway has been colored in red](#). A detailed view of the measurement site and the two measurement

1329 [stations is shown in the lower right-hand corner in the upper right-hand corner is the wind rose and](#)

1330 [polar plots for black carbon and NO_x](#), with the red lines denoting the direction of the highway. Grenoble

1331 is to the north.

1332

1333

1334 [Figure 2:](#) The non-refractory submicrometer aerosol concentration in $\mu\text{g m}^{-3}$ of SO_4 , NH_4 , NO_3 , and

1335 Organic species is plotted along with black carbon [both for the campaign time series and the average](#)

1336 [concentration of each species for the whole campaign and during high traffic periods](#) (A), 15 minute

1337 traffic concentration (missing data due to malfunction in the traffic cameras on those days) (B) COO^+

1338 (m/z 44) and C_4H_9^+ (m/z 57) (C), and the number-weighted geometric size distribution (D) with the

1339 total number concentration of particles as a function of time (D, right axis).

1340

1341 [Figure 3:](#) The concentration in ppbv of PTR-ToF-MS VOC species identified isoprene and

1342 MVK/Methacrolin (left axis, A), VOC species associated with diesel exhaust (CH_4NO_2^+ , $\text{C}_2\text{H}_5\text{O}^+$,

1343 B), VOC species associated with gasoline exhaust (C_6H_7^+ , $\text{C}_9\text{H}_{13}^+$, C). NO and NO_2 (gas-phase) ppbv

1344 concentrations (D) and ambient temperature (right axis, A) during the measurement period are also

1345 shown.

1346

1347 [Figure 4:](#) Diurnal profiles of boundary-layer scaled VOC peaks from PTR-ToF-MS measurements and

1348 BC peaks from MAAP measurements (A), temperature (right axis, B), boundary layer height (left axis,

1349 B), vehicular speed (left axis, C) and vehicle concentration (right axis, C).

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1351 [Figure 5:](#) The mass spectra of the six resolved factors, more oxidized organic aerosol (MO-OA), less

1352 oxidized organic aerosol (LO-OA), regional oxidized organic aerosol (reg-OOA), biomass burning

1353 organic aerosol (BBOA), hydrocarbon-like organic aerosol (HOA), and nitrogen-containing organic

1354 aerosol (NOA). Fraction of total signal is plotted against m/z and the peaks are color-coded to show

1355 their high-resolution identifications.

1356

1357 [Figure 6:](#) The diurnal profiles (A) and concentration and standard deviation of the six resolved aerosol

1358 factors (B).

1359

1360 [Figure 7:](#) The time series of the six-factor PMF solution (A), the resolved BBOA factor time series

1361 concentration (right axis, B) and off-line levoglucosan measurements (left axis, B), the resolved HOA

1362 factor time series concentration and BC (right axis, C), HR-TOF-AMS-measured SO_4 and the resolved

1363 regional OOA factor (left axis, D) and off-line oxalate measurements (right axis, right). [The inset](#)

1364 [shows the calculated mass contribution during all \(left\) and high traffic \(right\) periods of each resolved](#)

1365 [PMF factor](#).

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1368 [Figure 8:](#)

1369 [Calculated HOA and measured BC concentrations from the campaign and HOA: BC ratios from](#)

1370 [previous field campaigns. Grey area is shaded to include a diesel-only environment and two French](#)

1371 [HOA: BC ratios: one from Crippa et al., \(2013\) and from this study \(A\). The HOA: BC ratio from](#)

1372 [various literature sources versus percent diesel fuel use out of total fuel use for the country of study](#)

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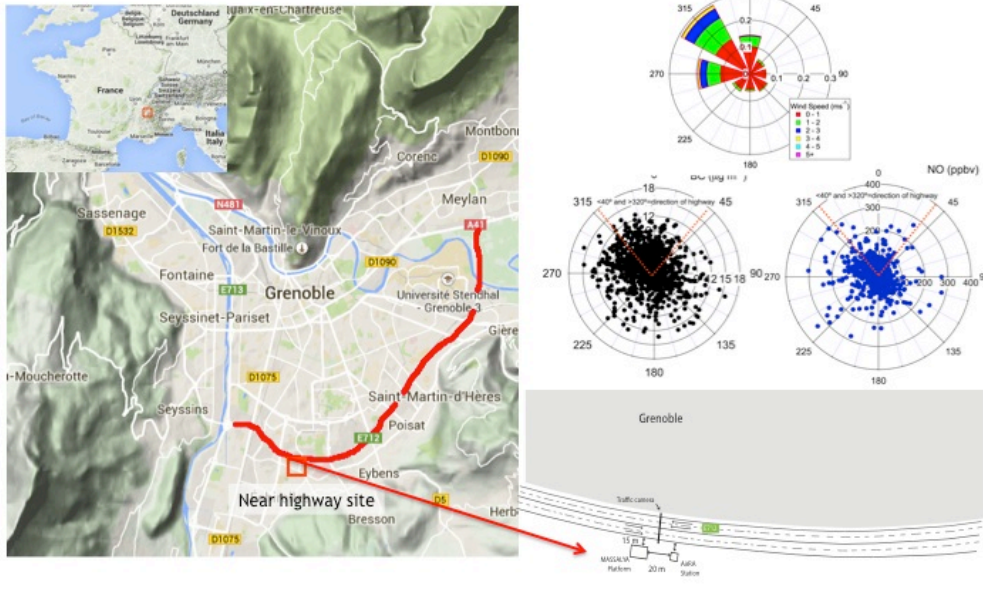
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(B).

Figure 9: Measured EC and OC, with calculated contribution of non-primary fossil organic carbon (assuming 100% fossil EC and HOA, A) and assuming partial modern organic carbon EC and HOA contribution (B). The possible fossil OOA (light blue) was calculated by the subtraction of HOA from the fossil-OC fraction (assuming HOA either all fossil, A, or 95% fossil, B, and EC either all fossil (a) or 5%+BBOA/3 modern (b).

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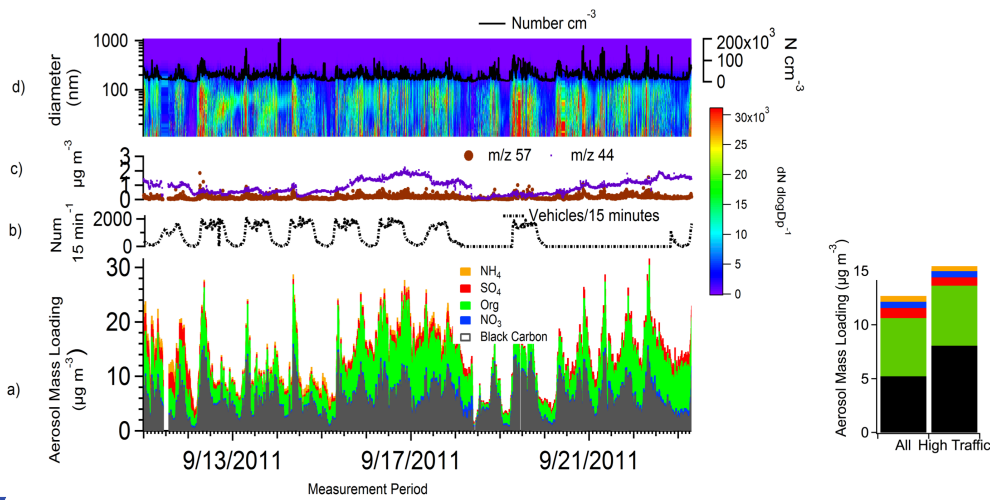


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Figure 1

The measurement site location is marked by a red square on the map, and the adjacent highway has been colored in red. A detailed view of the measurement site and the two measurement stations is shown in the lower right-hand corner in the upper right-hand corner is the wind rose and polar plots for black carbon and NO, with the red lines denoting the direction of the highway. Grenoble is to the north.

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Figure 2: The non-refractory submicrometer aerosol concentration in $\mu\text{g m}^{-3}$ of SO_4 , NH_4 , NO_3 , and Organic species is plotted along with black carbon both for the campaign time series and the average concentration of each species for the whole campaign and during high traffic periods (A), 15 minute traffic concentration (missing data due to malfunction in the traffic cameras on those days) (B) COO^+ (m/z 44) and C_4H_9^+ (m/z 57) (C), and the number-weighted geometric size distribution (D) with the total number concentration of particles as a function of time (D, right axis).

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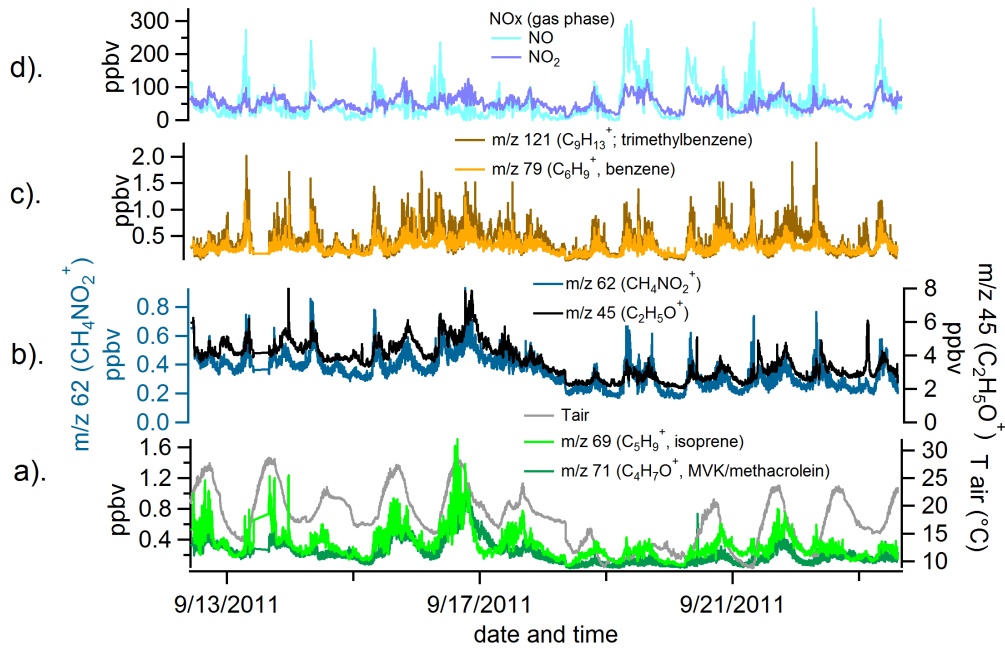
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Figure 3

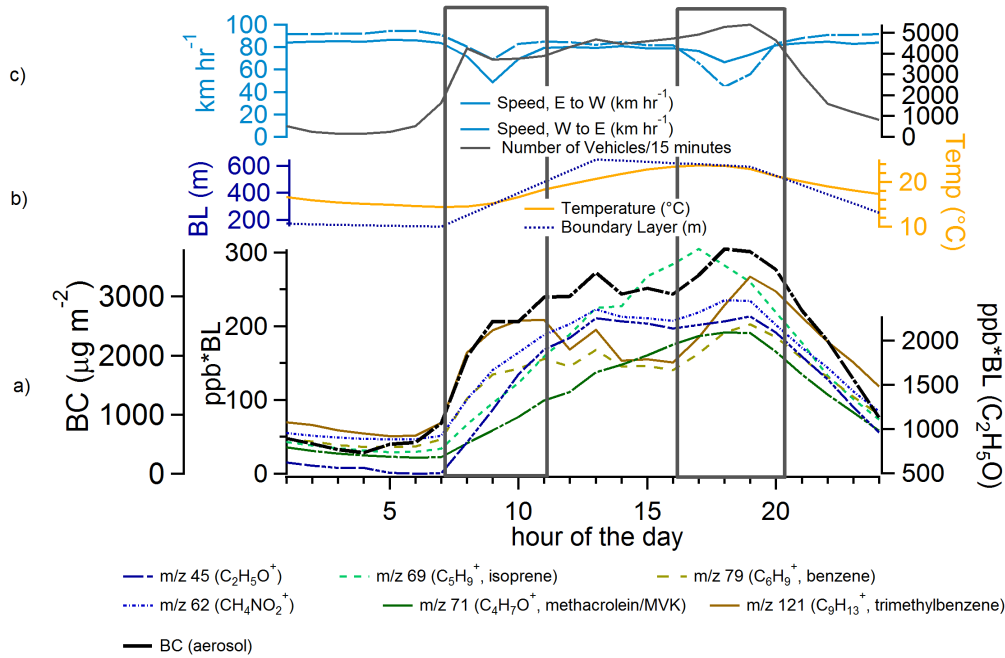
The concentration in ppbv of PTR-ToF-MS VOC species identified isoprene and MVK/Methacrolin (left axis, A), VOC species associated with diesel exhaust (CH_4NO_2^+ , $\text{C}_2\text{H}_5\text{O}^+$, B), VOC species associated with gasoline exhaust (C_6H_7^+ , $\text{C}_9\text{H}_{13}^+$, C), NO and NO₂ (gas-phase) ppbv concentrations (D) and ambient temperature (right axis, A) during the measurement period are also shown.

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 1567 Figure 4 Diurnal profiles of boundary-layer scaled VOC peaks from PTR-MS measurements and BC
 1568 peaks from MAAP measurements (A), temperature (right axis, B), boundary layer height (left axis, B),
 1569 vehicular speed (left axis, C) and vehicle concentration (right axis, C).

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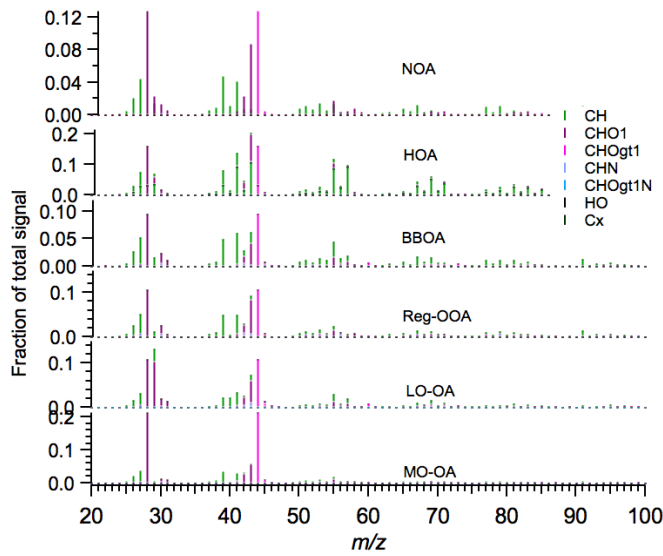
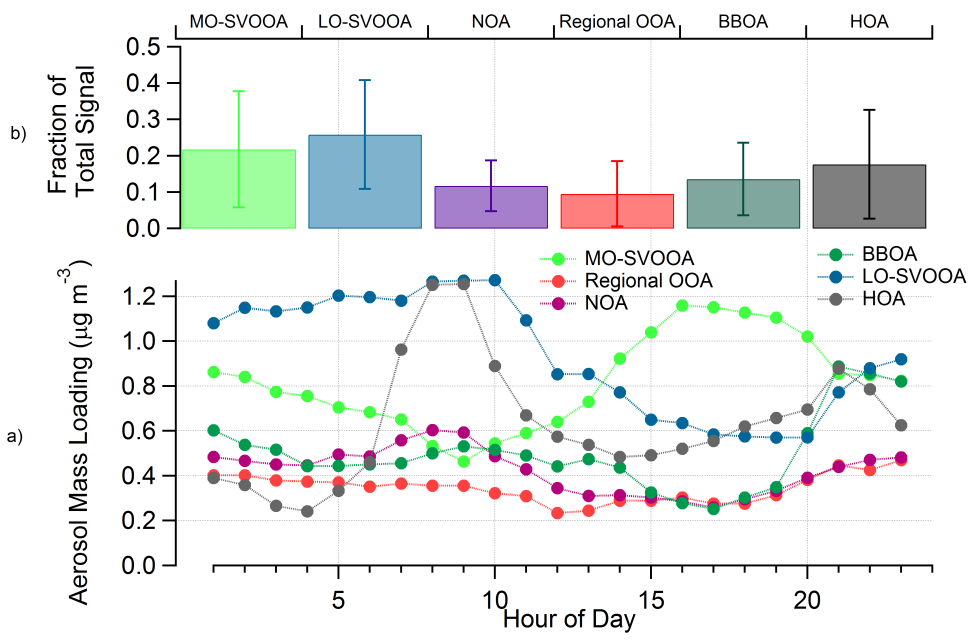
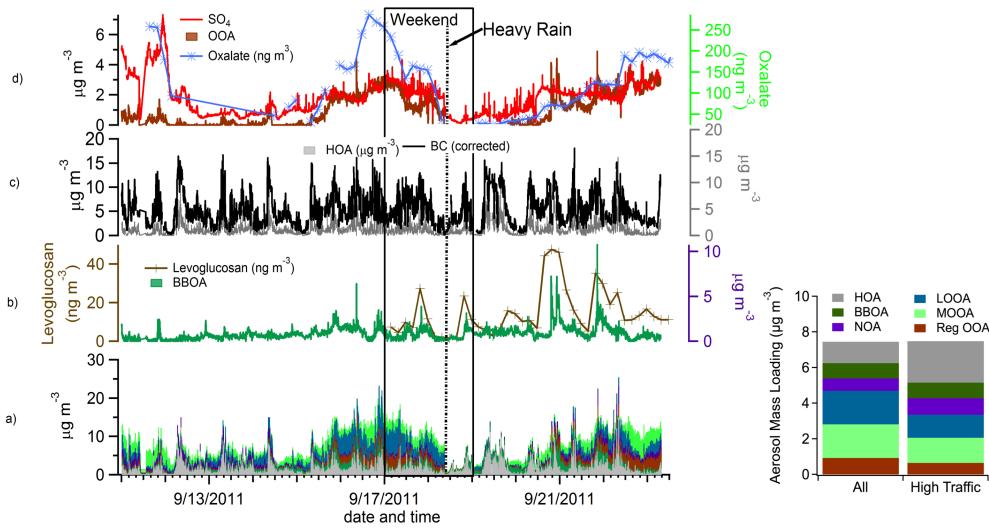


Figure 5: The mass spectra of the six resolved factors, more oxidized organic aerosol (MO-OA), less oxidized organic aerosol (LO-OA), regional oxidized organic aerosol (reg-OOA), biomass burning organic aerosol (BBOA), hydrocarbon-like organic aerosol (HOA), and nitrogen-containing organic aerosol (NOA). Fraction of total signal is plotted against m/z and the peaks are color-coded to show their high-resolution identifications.

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 1616 [Figure 6: The diurnal profiles \(A\) and concentration and standard deviation of the six resolved aerosol](#)
 1617 [factors \(B\).](#)
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Figure 7:

The time series of the six-factor PMF solution (A), the resolved BBOA factor time series concentration (right axis, B) and off-line levoglucosan measurements (left axis, B), the resolved HOA factor time series concentration and BC (right axis, C), HR-TOF-AMS-measured SO₄ and the resolved regional OOA factor (left axis, D) and off-line oxalate measurements (right axis, right). The inset shows the calculated mass contribution during all (left) and high traffic (right) periods of each resolved PMF factor.

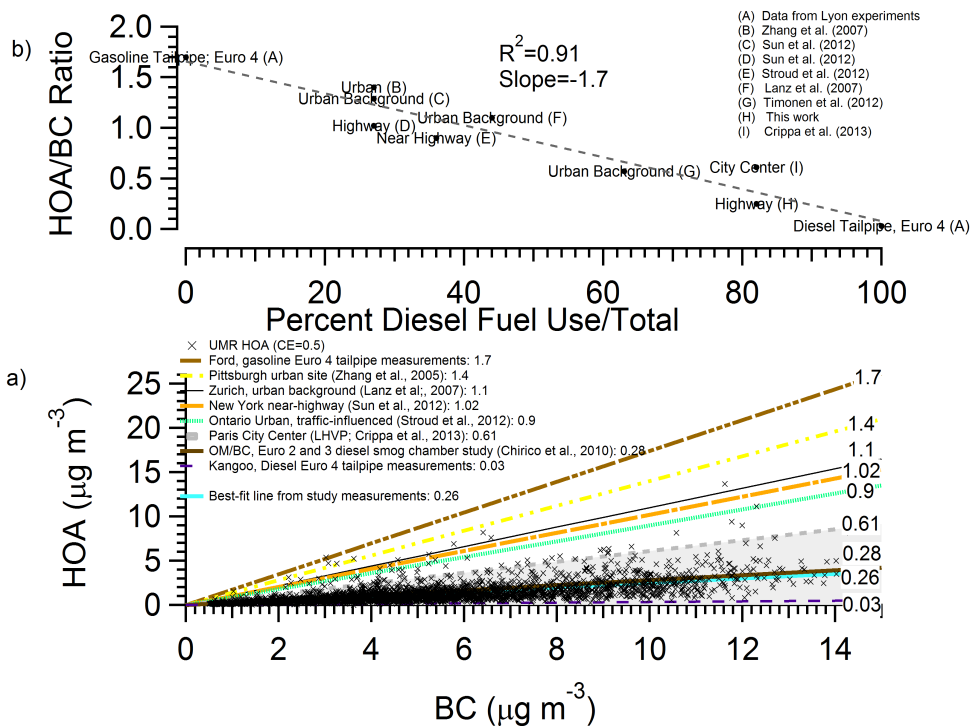
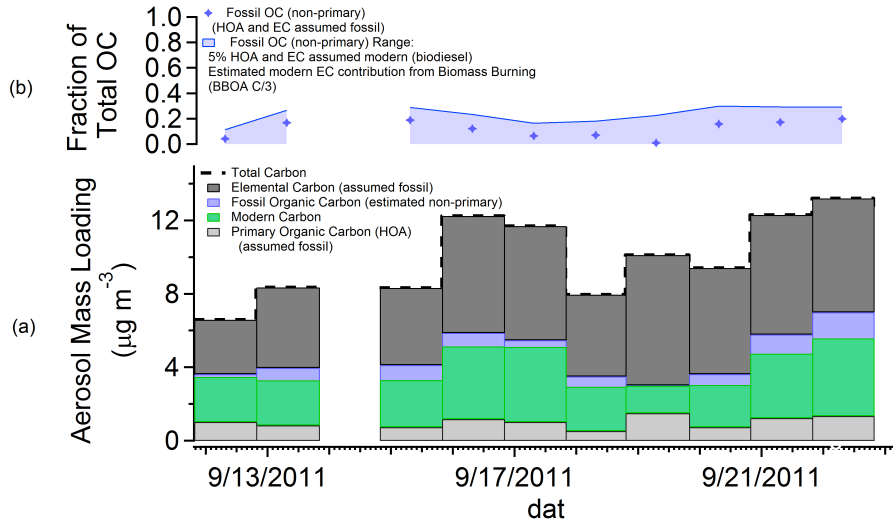


Figure 8

Calculated UMR HOA and measured BC concentrations from the campaign and HOA: BC ratios from previous field campaigns. Grey area is shaded to include a diesel-only environment and two French HOA: BC ratios: one from Crippa et al., (2013) and from this study (A). The HOA: BC ratio from various literature sources versus percent diesel fuel use out of total fuel use for the country of study, (B).

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Figure 9: Measured EC and OC, with calculated contribution of non-primary fossil organic carbon (assuming 100% fossil EC and HOA, a) and assuming partial modern organic carbon EC and HOA contribution (b). The possible fossil OOA (light blue) was calculated by the subtraction of HOA from the fossil-OC fraction (assuming HOA either all fossil, A, or 95% fossil, B, and EC either all fossil (a) or 5%+BBOA/3 modern (b)).

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