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Urban case studies: general discussion

William Brune, William Bloss, Zongbo Shi, Francis Pope, Gary Fuller, Paul S. Monks, Alison Tomlin, Thomas Karl, Matthew Hort, Claudia Mohr, Rob MacKenzie, Athanasia Vlachou, Zhe Tian, Louisa J. Kramer, Dwayne Heard, Ruth Purvis, Xavier Querol, Urs Baltensperger, Rachel Dunmore, Roy Harrison, Tim Murrells, Jose L. Jimenez, Eben Cross, Gordon McFiggans, Astrid Kiendler-Scharr, Tzer-Ren Ho, Aurélie Charron, Timothy Wallington, Nivedita Krishna Kumar, Simone Pieber, Franz Geiger, Andreas Wahner, Edward Mitchell, André Prévôt, Andreas Skouloudis, Markus Kalberer, Brian McDonald, C. N. Hewitt, Costas Sioutas, Neil. M. Donahue, James Lee, Dominik van Pinxteren, Sarah Moller, María Cruz Minguillón, Martin Shafer, David Carslaw, Christian Ehlers and Spyros Pandis

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Simone Pieber opened a general discussion of the paper by Spyros Pandis: from your presentation together with recent source apportionment studies such as *e.g.* Crippa *et al.* for Europe,[1] the relative importance of other emissions from the residential heating and cooking sector, especially wood combustion, becomes more and more evident. Despite this, big efforts are still being made to clean up emissions from the transport sector. Do you think this is still relevant, or should we focus our attention differently, and what do you think is currently hindering us from tackling the heating sector?

1 M. Crippa *et al.*, *Atmos. Chem. Phys.*, 2014, **14**, 6159–6176.

Spyros Pandis answered: This is an excellent observation and it is one of the main points that our paper tries to make in the "Age of Foolishness" section. While transportation remains a significant source sector in urban areas, its importance has been decreasing. Despite this change, the required rebalancing of our control efforts is not happening in most cities. This is partially due to inertia: we have all been taught that transportation is the main cause of air quality problems in big cities and we have a hard time realizing that all our efforts to control it are actually having an impact and what was true in the 1980s and 90s may not be true any more in the 2010s. The second problem is the challenge of dealing with a lot of small individual sources and a lot of people responsible for these heating and cooking emissions. These two obstacles together have made progress in controlling these "non-traditional" urban air pollution sources difficult.

Athanasia Vlachou asked: In your paper you suggest that primary OA can be categorized as fresh and aged POA by performing tests on cooking and biomass burning. What about traffic? Could one make such a separation for this primary source as well?

Spyros Pandis responded: In the present paper we discuss evidence of the conversion of cooking and biomass burning OA to more oxidized forms that then appear in the PMF analysis as the corresponding AMS source-specific factors. When the chemical conversion is fast, as is the case for the COA, we could find only one of the factors: the fresh one in the winter and the more oxidized one in the summer. For wood burning, two factors could be found in the same period, at least in some cases.[1] This suggests a more gradual conversion of the fresh biomass burning OA, to its more aged form, and finally to the oxidized OA (OOA). To the best of our knowledge, there has not been a report of an aged form of HOA in a field study. One could speculate that HOA, as it ages chemically, is converted to one of the reported forms of OOA (SV-OOA and/or LV-OOA) without maintaining its source identity, at least from the point of view of the AMS.

1 A. Bougiatioti, I. Stavroulas, E. Kostenidou, P. Zarmpas, C. Theodosi, G. Kouvarakis, F. Canonaco, A. S. H. Prévôt, A. Nenes, S. N. Pandis, and N. Mihalopoulos, *Atmos. Chem. Phys.*, 2014, **14**, 4793–4807.

Astrid Kiendler-Scharr said: You point out the strong contribution of SOA to fine PM. How would SOA be regulated? Does this call for stronger VOC emission controls? What would your take-home message be?

As a brief comment, I would also like to point out that cooking organic aerosol (COA) is not observed in sites like Cabauw,[1] which is categorized as a rural site. If the reason for the lack of COA is atmospheric aging during transport, which patterns should we look for in AMS or ACSM data sets to assign this source?

1 P. Schlag, A. Kiendler-Scharr, M. J. Blom, F. Canonaco, J. S. Henzing, M. M. Moerman, A. S. H. Prévôt, and R. Holzinger, *Atmos. Chem. Phys. Discuss.* 2015, **15**, 35117–35155.

Spyros Pandis replied: The regulation of SOA clearly requires regulation of its precursor vapors (volatile, intermediate volatility and semi-volatile organic compounds). Reductions of sulphur dioxide, oxides of nitrogen, and primary OA could also help, but there is a lot of debate and uncertainty regarding the effectiveness of these measures in reducing OA in specific urban areas. Dilution and chemical aging are expected to reduce the contribution of fresh COA to total OA in rural sites to a few percent. At the same time the COA temporal signal will be smeared out to a large extent, so it will be difficult to separate from sources like the HOA. So I am not surprised that PMF does not find a COA factor in Cabauw. Unfortunately, the features of the COA spectrum do depend on the cooking habits in each area. Therefore one would probably need to obtain a representative Dutch COA spectrum in Amsterdam or another big city in the area, and then use it in ME-2 as a way to get a rough estimate of the probably small COA contribution to the total OA.

Neil Donahue opened a general discussion of the papers by Dominik van Pinxteren and Spyros Pandis: I have a question for both speakers and for Astrid

Kiendler-Scharr as well. The cooking factor COA is associated with distinct maxima at mealtimes, especially lunch. This feature will be in the data for local sources but may well be smeared out for upwind sources by the time they arrive at the receptor site. Does this mean that the PMF methods will be biased toward finding the COA factor in urban settings but will fail to find it in the background?

Spyros Pandis replied: Indeed the ability of PMF to identify and separate sources relies heavily on the temporal evolution of the contribution of each source. As one moves away from the source, this temporal information gets weaker and weaker and eventually the regular PMF algorithm cannot separate the specific source from the rest. However, the contribution of the fresh OA from the source to the total will also be getting lower and for COA it will probably be just a few percent. Techniques like the ME-2 algorithm may help in this case as long as there is reliable information about the COA AMS spectrum for the specific area. In general, all these source apportionment techniques have a hard time with the identification and accurate quantification of sources that contribute only a few percent to the total and do not have unique features in their fingerprint.

Dominik van Pinxteren said: I cannot really add to the AMS COA factor interpretation, but generally I would agree that if there is not enough variance in contributions from a given source (e.g. because concentration peaks are smeared out) PMF will not be able to resolve it. In our study, I think the (tentatively identified) cooking source was only resolved because we pooled different sites into one dataset which included the residential site, where factor concentrations were significant, and other sites, where its concentrations were negligible.

Astrid Kiendler-Scharr added: A fundamental assumption that is made in factor analysis is that factors feature invariant mass spectral profiles and show variable concentration over time. Therefore an additional level of complexity in source identification is added when the primary aerosol changes composition - and thereby mass spectral fingerprint - during transport. As we heard before, COA changes mass spectral fingerprint after exposure to oxidation. This and the diversity of mass spectral signatures from different COA will make the source identification difficult away from direct sources.

Roy Harrison asked: On the specific issue of AMS/PMF analysis of cooking aerosols, I was a collaborator in a study at a rural site in Northern Italy. This was well away from any source of cooking emissions, but picked up signals with mass spectral characteristics and temporal variation that matched previously published cooking emissions. We came to the conclusion that this factor was largely unrelated to cooking, and some other studies refer to cooking-like organic aerosol. I think we need to be extremely careful with this.

Spyros Pandis answered: I agree that one needs to be careful with the attribution of any AMS/PMF factor to cooking emissions and that the temporal profile of the factor may not be sufficient. In the case of Athens as discussed in our paper, we performed similar measurements in another Greek city (Patras), analyzed the data separately and came up with practically the same AMS COA spectra in the two cities in each season. We then performed laboratory experiments by cooking meat (greek souvlakia) and confirmed that the AMS spectrum of the fresh emissions was the same as the one that the PMF analysis determined during the winter, in both Athens and Patras. Finally we exposed the fresh COA to ambient levels of ozone (around 60 ppb) or sunlight and showed that the AMS spectrum changed rapidly, so it now matched the one determined by the PMF in the two cities during the summertime. Additional evidence like this can help improve our confidence regarding the assignment of the corresponding PMF factor to cooking activities in urban areas.

Roy Harrison addressed Dominik van Pinxteren and Spyros Pandis: As part of the ClearfLo programme in London, we measured a range of organic molecular markers. It was during the winter campaign so hopefully there was not much photochemistry at the time. We carried out source apportionment with a chemical mass balance model using organic molecular markers and compared our results to simultaneous estimates of aerosol sources, including cooking aerosol, measured by James Allan at Manchester University using an AMS. For the cooking organic aerosol (COA), the AMS results were about double those from the mass balance model. There was a later report in the literature that showed that the collection efficiency of the AMS for cooking aerosol is close to 100%, whereas James had used 50%, which reconciles the difference in the two measurements. Do you think there are often over-estimations in measurements due to this? Regarding the Leipzig measurements, I do not believe that the PMF chemical profile can be very convincingly associated with cooking emissions. It could be due to a number of things, including vegetative detritus.

Spyros Pandis answered: The AMS collection efficiency issue does introduce additional uncertainty in the AMS/PMF results. In our ambient measurements we did not dry the ambient particles, something that in general leads to higher collection efficiencies and lower uncertainties. We then estimated the AMS CE, combining the corresponding AMS size/composition distributions with the SMPS ones using the volume distribution matching algorithm of Kostenidou *et al.*[1] Our laboratory measurements of COA are consistent with a CE of unity. I do agree with your assessment that the AMS CE (especially if it is different for different OA particles) introduces additional uncertainty in the corresponding source apportionment results. The authors of the Leipzig study are clearly better qualified to address your comment regarding the results of their study, so I will defer to them.

1 E. Kostenidou, R. K. Pathak and S. N. Pandis, *Aerosol Sci. Technol.*, 2007, **41**, 1002–1010.

Dominik van Pinxteren added: Regarding our Leipzig measurements, I agree that the identification of the cooking factor is only tentative, and we also state this in the paper. Beyond the (indeed ambiguous) chemical profile, the association was mainly done based on the pattern of factor concentrations for the different sites and seasons (no seasonal trend, highest concentrations at a residential site with a number of restaurants) which we thought fit better to cooking emissions rather than *e.g.* plant detritus. It is clear, however, that the inclusion of cooking-specific molecular tracers, such as cholesterol or others, would be needed to increase confidence in this factor, and we are planning to do this in future studies.

André Prévôt commented: In an urban area, what you show and what we have also shown, is that where you have lots of restaurants, cooking is a factor. But if you have externally mixed oil droplets then we might overestimate by a factor two. Any unmixed organics and secondaries might also be overestimated. An additional problem is that PMF is tough. Primary organic aerosol contributions are very low – 10 to 15% - and cooking etc. and often the emissions happen at the same time and thus correlate. One issue concerning cooking is probably that organics from cooking change their mass spectra a bit faster, as their mass spectra are less stable, so you have partially oxidised organic aerosols.

Gordon McFiggans addressed Spyros Pandis: In the source apportionment of the various contributions of the short-, medium- and long-range sources to PM, there will inevitably be dependencies on the prescribed volatility distributions of the organic components, their ageing rates and the assumptions used in matching the VBS boundary condition and emissions to the reported "OC" emissions from, for example, the TNO database. Could you comment on the magnitude of these uncertainties and robustness of the attributions? I would recommend inclusion of error bars to represent these uncertainties in the paper.

Spyros Pandis answered: The uncertainty of the contributions of different source areas, shown for example in Figure 3, is different for different PM components and depends on the uncertainty of their emissions (or the emissions of their precursors), production mechanisms, atmospheric processing, and removal mechanisms. These uncertainties are lower for the elemental carbon and sulfate shown in the first two graphs of this figure. For SOA the uncertainties are higher, but much lower than the uncertainty of the overall VBS scheme used in this study. The source area attribution for SOA is determined to a large extent by the corresponding timescales for the oxidation of its precursors to SOA. These timescales (*e.g.*, reaction rates of VOCs and IVOCs with oxidants) are relatively well known and this makes the attribution of the SOA to source areas (with the coarse resolution of short-, medium- and long-range used here) quite robust. For example, the conclusion that most of the SOA in Paris during the summer MEGAPOLI campaign was due to medium-range sources does not change for reasonable choices of the volatility distributions, aging ranges, emissions, *etc.* A detailed calculation of the error bars of these estimates in a 3D chemical transport model is clearly challenging.

Nivedita Krishna Kumar asked: Did you not identify a cooking organic aerosol factor in your PMF results from Athens, like Crippa *et al.* did in Paris?[1]

[1] M. Crippa *et al.*, *Atmos. Chem. Phys.*, 2014, **14**, 6159–6176.

Spyros Pandis answered: In our measurements in both Athens and Patras during both winter and summer fresh cooking organic aerosol was as important as hydrocarbon-like organic aerosol which is attributed mostly to transportation emissions. These finding were similar to the results of Crippa *et al.* in the MEGAPOLI campaigns in Paris despite the differences in size and practices among the three cities.

Zhe Tian continued the discussion of the paper by Dominik van Pinxteren: I have noticed that the traffic contributions are much higher than traffic exhaust in your paper. Could you give us more details about how you define "traffic" and "traffic exhaust" and your choice of tracers? And have you tried any organic markers in your PMF model?

Dominik van Pinxteren answered: Traffic exhaust was mainly identified from high mass contributions of water-insoluble carbon (*i.e.* EC and hydrophobic organics), high species contributions of hopanes, and a homohopane index close to mineral oil derived emissions (rather than coal combustion, which can be another source of hopanes). This source was, however, only resolved in the ultrafine and the coarse particle size ranges. In accumulation mode particles it was mixed into a "general traffic" factor, which in addition to exhaust emissions also includes other traffic-related sources such as brake wear, tire wear, dust resuspension *etc.* and was characterised by large contributions of several metals (see our paper for details). With our PMF results we can thus not fully differentiate exhaust and non-exhaust across all particle size ranges and "traffic exhaust" contributions in total PM_{10} are therefore missing the accumulation mode fraction, which is at least part of the reason why they are smaller than "general traffic". With regards to organic markers – yes, we included many of them, and you can find all the details in the paper.

Spyros Pandis added: Our paper focuses on traffic emissions including both exhaust and non-exhaust emissions. In the analysis presented here only AMS spectra have been used. There have been a number of efforts in the literature (for Mexico City, Los Angeles, and Pittsburgh) in which separate source apportionment analysis has been performed using AMS data and organic tracer measurements; however, the comparison of the corresponding results were outside the scope of the current work.

Edward Mitchell said: Both studies have identified residential solid fuel combustion as an increasingly important source of ambient pollution. In comparison to other sources such as traffic, it can be argued that regulations and abatement technologies for heating stoves are decades behind. In Europe we now have the Ecodesign regulations limiting efficiency, PM, CO, NO_x and OGC emissions, but these will not apply until 2022. Do the speakers believe that policies such as this will be sufficient to reduce emissions from this source, or do we need additional abatement technologies such as filters and catalysts as already used in the traffic sector?

Spyros Pandis responded: I think that the Ecodesign regulations will help, but I am afraid that it will be too little too late. I personally believe that it does not make any sense to allow wood burning in fireplaces or wood stoves in large urban areas that already have air pollution problems. The same applies also to agricultural and open burning in areas around big urban centers.

Dominik van Pinxteren said: In Germany, emissions from small wood stoves have been regulated already to some extent, leading to the replacement of very old stoves within a transition period. Given that these old and very inefficient stoves have much higher pollutant emissions than more modern ones, I would expect a decrease of emissions. Additional technological developments would certainly help to reduce emissions even more. Whether this will be enough, however, to observe substantial reductions of emissions at a given site is another question. In our study in Leipzig we have seen that during the most intense pollution episodes, more than 80% of solid fuel combustion aerosol was transported into the city, likely due to long-range transport from Eastern European areas. A modernisation of house heating infrastructure in these countries might thus have a large positive influence on the air quality in Leipzig, and many other cities as well.

Tim Wallington returned to the discussion of the paper by Spyros Pandis: Figure 1 in your paper reminded me of the Kuznets curve. Is there scope for an economic analysis looking at level of urban air pollutant emissions in the 5 cities as a function of economic activity to compare with the Kuznets curve?

Spyros Pandis answered: This is a very interesting observation. The curve in Figure 1 does indeed look like the Kuznets curve after replacement of the economic inequality axis of the former with the pollution level here. There is clearly room for interesting economic analysis here, trying first to add actual data points in the graph. One of our observations for Athens is that the path along this curve may not be reversible, but may actually include a hysteresis if a city moves from right to left. A modest (but rapid) decline in development due to a financial crisis may result in significant increase in air pollution levels if practices like wood burning are widely adopted.

Zongbo Shi remarked: We often see that when people describe different PMF factors they give a percentage of, for example, COA, HOA, or SOA. What are the uncertainties in these estimates? Should all papers be clear that these are estimates which have relatively large uncertainties?

Spyros Pandis replied: There are a number of formal methods for the estimation of the uncertainty of PMF solutions. These include classical bootstrap, displacement of factor elements, and bootstrap enhanced by displacement.[1] These approaches capture the uncertainty of the PMF results due to random errors and rotational ambiguity. These approaches have been used in a number of AMS/PMF studies. For example, Lanz *et al.* estimated moderate uncertainties for the OA components in Zurich during summertime: OOA-I 39.8–50%, OOA-II 18.9–22.3%, HOA 5.6–8.6%, COA 10.1–14.7%, wood burning 7.4–10.3%, and other minor sources 5.2–7.4%.[2] Even lower uncertainties have been reported by Ulbrich *et al.* for Pittsburgh.[3] These ranges could be optimistic, because they probably capture only some of the sources of uncertainty. Another approach is to view these source apportionment results as revealing the relative magnitude of the corresponding sources: small, medium and large. For example, if PMF suggests that a component represents 20% of the total OA in a polluted area, it is probably quite significant and its sources should be controlled. I refer you also to my response to the previous comment by Roy Harrison.

1 S. G. Brown, S. Eberly, P. Paatero and G. A. Norris, *Sci. Total Environ.*, 2015, **518–519**, 625-635.

2 V. A. Lanz, M. R. Alfarra, U. Baltensperger, B. Buchmann, C. Hueglin and A. S. H. Prévôt, *Atmos. Chem. Phys.*, 2007, **7**, 1503–1522.

3 I. M. Ulbrich, M. R. Canagaratna, Q. Zhang, D. R. Worsnop and J. L. Jimenez, *Atmos. Chem. Phys.*, 2009, **9**, 2891–2918.

Xavier Querol returned to the discussion of Spyros Pandis' and Dominik van Pinxteren's papers: Thanks a lot for your excellent presentations and papers. Two comments; firstly, I missed in "A tale of five cities" the inclusion of the non-exhaust vehicle emissions and their contributions to ambient PM. I think these are relevant for air quality science in the urban atmosphere, and yet there hasn't been much discussion about them in the meeting either. There are very interesting points, such as phase transformations and toxicity of brake and tyre wear (Mo, Cu, Zn and Mn compounds) – also how to apportion the brake, tire, pavement and resuspension contributions – that should be taken into account when dealing with urban PM. Secondly, Dominik's paper attributed the reduction in elemental carbon (EC) to the efficiency of the Low Emission Zone (LEZ) in Leipzig. There is a lot of scientific debate on that. Can you identify effects due exclusively to the LEZ implementation rather than effects due to other actions, such as the progressive renewal of the fleet by Euro 5 diesel (with filter traps for PM) since 2009, or other simultaneous actions? Other cities such as Barcelona, without LEZ being implemented, did reduce EC levels in a similar proportion. This does not contradict at all the potential efficiency of the LEZ on EC levels, it is meant only as a consideration to take into account.

Dominik van Pinxteren responded: In our study we compare the urban EC increment in the years 1999–2000 (way before the implementation of the LEZ) with the ones observed in 2013–2015 (a few years after its implementation) and we therefore cannot exactly distinguish between the impacts of the LEZ and other actions. However, we know from another study we have done at the same traffic site in Leipzig[1] that BC concentrations sharply decreased immediately after the implementation of the LEZ in 2011 due to a reduction of heavy-duty traffic. It has also been shown that the Leipzig LEZ accelerated the modernisation of the car fleet as compared to other Saxonian cities.[2] This is why we believe that the LEZ did indeed have a strong impact on the observed EC reduction in Leipzig.

1 F. Rasch, W. Birmili, K. Weinhold, S. Nordmann, A. Sonntag, G. Spindler, H. Herrmann, A. Wiedensohler and G. Löschau, *Gefahrstoffe - Reinhalt. Luft*, 2013, **73**, 483–489.

2 G. Löschau *et al.*, *Umweltzone Leipzig, Teil 3 Immissionssituation 2010-2013,* Dresden, Germany, 1st edn, 2015, https://publikationen.sachsen.de/bdb/artikel/23885 (German only).

Spyros Pandis replied: The non-exhaust vehicle emissions are clearly important for the urban atmosphere - refer also to my response to Zhe Tian's earlier question. However, a significant fraction of these particulate emissions are in the coarse size range, so they are a lot more important for the regulation of PM_{10} compared to the fine PM ($PM_{2.5}$ or PM_1) that is the focus of our work. These components (metal oxides, crustal material, *etc.*) are included in the primary fine PM in Figures 2 and 4 of our paper. I do agree with your statement though, that these emissions do not receive the attention that they deserve. The examples that you mention do underline the challenge of attributing a reduction in the concentration of a pollutant (EC in this case) to a specific measure when multiple changes are taking place at the same time.

Claudia Mohr addressed Spyros Pandis: In your presentation and paper you make the statement that SOA is becoming relatively more important. In absolute numbers, does it show a decreasing trend as well? Do we know how it is evolving globally? Does better POA control also lead to SOA reduction? Are there studies on this?

Spyros Pandis responded: The available data in specific areas like Los Angeles with long fine particulate matter data sets suggest that SOA is decreasing too in areas where significant reductions of pollutant emissions have taken place. Unfortunately, generalizing to other urban areas or even globally is a lot more challenging because older PM chemical composition data sets have little information about the chemical composition of OA. AMS data sets go only back to the early 2000s. The effect of POA control on SOA levels depends a lot on the ability of these compounds to form a common solution (see also Neil Donahue's paper (DOI: 10.1039/C5FD00214A). This ability appears to be limited initially but it increases as the POA ages chemically and is converted to SOA. Based on this, one would expect a small effect near the sources when POA is still fresh and a modest effect further away when the POA has been oxidized but has also been diluted. However, the reduction of SOA precursors (volatile, intermediate volatility, and semivolatile organic compounds) that often accompanies the reduction of POA will cause a reduction in SOA. There have been a number of modeling efforts to quantify these effects (for example Megaritis *et al.*[1]) but their results do depend a lot on the assumptions about the mixing state of the OA components.

[1] A. G. Megaritis, C. Fountoukis, P. E. Charalampidis, C. Pilinis, and S. N. Pandis, *Atmos. Phys. Chem.*, 2013, **13**, 3423-3443.

Jose-Luis Jimenez said to Spyros Pandis: Following up on Gordon McFiggans' comment that there is a lot of uncertainty about SOA results with the VBS due to different yield and aging parameters available: when one fits urban SOA results to fast OA mass observations, you can only extract 2 pieces of information, an amount and a timescale of SOA formation (see, for example, Hodzic and Jimenez[1] and Hayes *et al.*[2]). Then one can simulate regional SOA with many VBS versions, which have from dozens to over 100 parameters. Many of those parameters may give similar results for the urban SOA over short timescales, although sometimes those results are still inconsistent with observations when analyzed trying to isolate the urban component (*e.g.* Woody *et al.*[3]) - especially, the different versions can give very different answers over longer timescales (see *e.g.* Hayes *et al.*[2]), and also for biogenic SOA (*e.g.* your own work, and several other papers). So I would argue that the VBS versions in use are very under-constrained, and we don't really know whether often we are getting agreement for a combination of wrong reasons.

[1] A. Hodzic and J. L. Jimenez, *Geosci. Model Dev.*, 2011, **4**, 901–917.
[2] P. L. Hayes *et al. Atmos. Chem. Phys.*, 2015, **15**, 5773–5801.
[3] M. C. Woody, K. R. Baker, P. L. Hayes, J. L. Jimenez, B. Koo and H. O. T. Pye, *Atmos. Chem. Phys.*, 2016, **16**, 4081–4100.

Spyros Pandis answered: I agree that while the VBS is a robust modeling framework, it requires a number of parameters that are not well constrained right now. There is a lot of ongoing work around the world providing constraints with measurements of volatility distributions, emissions of IVOCs, chemical aging rates, *etc.*, but there are still a lot of knowledge gaps. If a set of such VBS parameters captures the SOA formation, it probably means that it is capturing the two important SOA formation characteristics: the SOA formed and the formation rate. This can still result in the right answer for the wrong reasons. However, returning to the comment by Gordon McFiggans, a model that can capture these two characteristics is probably providing a decent answer to the source attribution question, at least for the coarse resolution used here.

Simone Pieber continued the discussion of the paper by Dominik van Pinxteren: Contribution of coal burning emissions were observed dominantly during the winter period and when air masses arrived from the east. Does this imply that the role of emissions from industrial coal burning and coal burning in power plants for electricity generation, which should also contribute during summer, is negligible? Could you please comment on the relative importance of the residential *vs.* the industry sector for those fuels?

Dominik van Pinxteren answered: Yes, it would be also my interpretation that coal burning emissions are dominated by house heating, and I think it is consistent with industrial coal burning emissions being much more regulated than emissions from house heating. Also, a recent review on PM_{10} apportionment in cities[1] shows that domestic fuel burning explains a much larger share of PM_{10} in Central and Eastern Europe than industrial emission as a whole (including oil and coal combustion, but also other emissions).

1 F. Karagulian, C. A. Belis, C. F. C. Dora, A. M. Prüss-Ustün, S. Bonjour, H. Adair-Rohani and M. Amann, *Atmos. Environ.*, 2015, **120**, 475–483.

Gary Fuller addressed Spyros Pandis: There was no mention in your paper about the progressive dieselisation in your five cities. There are contrasting trajectories between the European and non-European cities, and within Europe, Athens is following a different trajectory to other countries. Where would you put dieselisation into your matrix of foolishness, wisdom, hope or despair? Secondly, we should be careful how we present the concept of medium range contributors. Policy makers often think they can't do anything about this, but it really depends on where you are standing; someone's medium range is someone else's local source. Uniform policies across multiple cities could be a helpful approach.

Spyros Pandis responded: This is indeed an interesting potential additional chapter in the “Tale of Five Cities”, with diesel cars dominating the new additions to the corresponding fleet in Paris (as well as in a lot of the EU countries), while gasoline-powered ones can be mainly found in the other four cities. Paris is currently rethinking its strategy and considering a move away from diesel, while Athens has recently allowed the use of diesel cars, but appears to have had second thoughts and may change its mind again and ban them once more. As a first approximation, the modern cars (either gasoline or diesel) emit a lot less than the corresponding cars in the late 20th century. As a result, all five cities have managed to reduce their fine particulate matter concentrations, even if they have followed different trajectories. I think that the ultimate answer to your question depends on the city, and varies from hope for some European cities to foolishness. I would use foolishness for Athens, due to the low quality of the diesel fuel often found in the Greek market that can create major problems for the control systems of modern diesel cars. I do agree with your comment about the need for uniform policies across multiple cities and even better large areas. I think that the US approach, with the definition of Transport Regions and then the development of policies for all sources in the states in the Transport Region together (including emissions trading), has proven to be quite effective. It could be a good policy model for groups of European countries (or even all of Europe) that face more or less the same fine particulate problem, exchanging particles and their precursors with each other.

William Bloss opened a general discussion of the paper by Kebin He:† Does the change in the NOR and SOR ratios imply a change in the oxidation capacity of the atmosphere over the period of the emissions reductions – *i.e.* a reduction in OH. Is there any evidence for this in terms of changes in *e.g.* O_3?

Zongbo Shi responded: As shown in Fig. 7, the SOR and NOR decreased substantially during both day and night, implying that the secondary oxidation processes of SO_2 and NO_2 were suppressed due to emission reductions. This was consistent with the changes of O_3, which reduced from 0.065 ppm before the parade to 0.040 ppm during the parade.

Gary Fuller said: You said in the summary presentation and in the paper that COA also went down during the parade period. I assume that there wouldn't have been any cooking restrictions. Was this reduction because there were fewer people in the city, or was this because what we think of as cooking emissions is actually something else – an industrial emission for example?

Zongbo Shi replied: As described in line 34 of page 9, open charcoal grills were strictly banned during the emission control period, which may have led to the reduction of COA. Our result was consistent with that observed during the 2014 APEC control period, which also showed a reduction of COA from 7.8 to 5.2 $\mu g\ m^{-3}$. No further evidence showed that cooking emissions may be actually an industrial emission.

Roy Harrison addressed Zongbo Shi : I am very concerned with the interpretation of sulphur oxidation and nitrogen oxidation ratios. Taking sulphur as an example, sulphate is likely to be generated from SO_2 emissions originating at a considerable distance from the point of measurement, whereas SO_2 will probably be emitted rather locally. As a consequence, I am not convinced that we can infer anything about the efficiency of reduction of sulphate concentrations in response to reduced emissions of SO_2 using the ratio, as it is comparing two measurements which are responding to emissions into different locations. Do you think that this is a fair interpretation?

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† Kebin He's paper was presented by Zongbo Shi, *University of Birmingham, UK*

Zongbo Shi answered: I agree that sulphate could be generated from both locally and regionally emitted SO_2. But the lifetime of SO_2 could also be from several hours to several days, leading to the regional transport of SO_2. In addition, the emission controls during the parade were not only implemented in Beijing but also the surrounding areas, as described in the introduction of our paper. Thus I think it is reasonable to use sulphur oxidation and nitrogen oxidation ratios here.

Claudia Mohr opened a general discussion of the paper by María Cruz Minguillón: What were the numbers of vehicles on the road at the "low" and "high traffic" periods, respectively? What was the difference in the numbers of diesel and non-diesel vehicles? Were diesel and non-diesel car numbers affected equally by holiday and non-holiday season?

María Cruz Minguillón replied: The traffic intensity increased 37% from the low to the high traffic periods (from about 40 000 vehicles per day to about 55 000 vehicles per day on average, including weekends). The % of diesel light duty vehicles of the fleet is up to 50%, according to statistics from the DGT (the traffic authority in Spain). Nevertheless, there is no information available about the % of diesel and non-diesel vehicles for specific periods such as the ones in our study. We can assume that the % of diesel vehicles was similar between both low and high traffic periods. The average daily patterns of the traffic intensity for the low and high traffic periods are shown in Fig. S5.

Athanasia Vlachou queried: Barcelona is characterized by high dust concentrations. Did you account for carbonates, especially in the radiocarbon analysis, to avoid any overestimation of the organic carbon?

María Cruz Minguillón responded: The ^{14}C analyses were performed for $PM_{2.5}$ samples. The content of carbonates in these samples can be estimated based on the Ca concentrations, which were experimentally determined. The estimated average carbonate concentrations for the five days with radiocarbon analyses ranged between 0.3 and 0.5 $\mu g\ m^{-3}$. These concentrations are considered negligible compared to the OA concentrations (ranging between 7 and 14 $\mu g\ m^{-3}$).

Andreas Wahner remarked: you showed in your Barcelona study that you had a higher biogenic component to SOA formed in high traffic conditions. Is your conclusion based on the assumption that the photochemical state of the atmosphere was the same under both conditions? Or could this be the reason, and not the different emissions?

María Cruz Minguillón answered: The conclusion is based on the assumption that the photochemical state of the atmosphere was similar, since the toluene/benzene ratio is not significantly different between the low traffic and the high traffic periods (average daily ratios ranged from 3.1 to 4.3 for the days when ^{14}C measurements were carried out), although the toluene/benzene ratios were quite noisy on an hourly basis. If no changes occurred in terms of the nature of sources between the two periods (additional sources with a higher toluene/benzene ratio during the HT period, for example), OH concentrations in the atmosphere of

Barcelona cannot be considered as significantly different from one period to another. Nevertheless, some other sources of toluene may exist, as indicated by the PMF analysis applied to the PTR-MS dataset (results not shown in the paper).

Astrid Kiendler-Scharr asked: Is the strong increase in particulate nitrate during the second part of your measurements significant? Is the higher non-fossil SOA contribution a consequence of higher NO_x concentrations and gas phase precursor chemistry or do you have indications for other sources of the non-fossil SOA?

María Cruz Minguillón responded: The nitrate concentrations increased from 0.5 μm^{-3} on average during the low traffic period to 1.0 $\mu g\ m^{-3}$ during the high traffic period. These concentrations are quite low and close to the detection limit of the instrument, and hence the reported increase in percentage (+99%) should be considered with caution, and should not be strictly compared to the increase in OA concentrations, for instance, which were well above the detection limit. Nitrate only represents 5% of the PM_1 mass concentration on average.

Our hypothesis is that the increase in the % of non-fossil SOA during the high traffic period is related to the increase in NO_x concentrations, by favoring the formation of SOA from the available biogenic precursors. Nevertheless, the presence of other non-fossil sources, such as SOA from cooking, should not be discarded, as this contribution has been found to be significant at other places; for example, Hayes *et al.* found that SOA from cooking was 19–35% of total SOA in Los Angeles.[1] Hence, considering that the COA contribution increased by about 60% from the low to the high traffic period (due to the higher activity as people is back from holidays), the associated SOA-cooking could well have increased as well.

[1] P. L. Hayes *et al.*, *Atmos. Chem. Phys.*, 2015, **15**, 5773–5801.

Jose-Luis Jimenez said: My question concerns the possible interpretations for the higher non-fossil carbon during the period with the higher vehicle and NO_x emissions, which appears surprising. I think you propose that the increase of NO_x leads to higher regional levels of NO_3 radicals at night, which then oxidize more biogenic VOCs at night regionally. That is certainly a plausible explanation, and it would be very useful to try to evaluate it with a 3D model with the relevant chemistry. However, I wonder about an alternative or complementary explanation. At high NO_x levels such as those in Barcelona, it is expected that OH radical levels are substantially reduced as NO_x increases. This was clearly shown, for example, in the recent CalNex 2010 study for the Los Angeles area.[1] Thus it is plausible that the lower OH during the high NO_x period reduces SOA formation from anthropogenic precursors, thus reducing the fossil SOA. One would need to normalize the fossil SOA per excess CO in order to properly account for this possibility. Could you comment on this hypothesis?

[1] I. B. Pollack *et al.*, *J. Geophys. Res.*, 2012, **117**, D00V05.

María Cruz Minguillón replied: The suggested explanation is well received; it may well be that during the high traffic period, when higher NO_x concentrations are recorded and hence there are lower OH radical levels, the SOA formation from anthropogenic precursors is reduced.

Two different calculations have been made to further investigate this possibility: normalized fossil SOA per excess CO, and percentage of fossil SOA with respect to total fossil OA (in terms of OC : OOCf/OCf). It should be noted that the precision of the available CO measurements is 0.1 mg m^{-3} (equivalent to about 85 ppb) and the hourly concentrations ranged from 0.2–1.2 mg m^{-3}, and hence the interpretation of the CO and excess CO (CO concentrations after subtracting 100 ppb as the CO background) should be made with caution. The results obtained support the suggested hypothesis, since the fossilSOA/excessCO ratios were found to be higher for the samples during the low traffic period and the first sample for the high traffic period (17-21 μg m^{-3} of fossilSOA per ppm CO), whereas they were lower for the second and third samples of the high traffic period (13 and 10 μg m^{-3} of fossilSOA per ppm CO, respectively), pointing to lower fossil SOA formation under high NO_x conditions (the NO_x average concentrations were 23, 21, 33, 40, and 59 μg m^{-3} for the five samples analyzed, in chronological order). The difference between the low traffic and the high traffic period, on average, is 17%. Regarding the percentage of fossil SOA with respect to total fossil OA, it remains relatively constant for all the samples (OOCf/OCf is between 0.72–0.76) except for the last one, with a ratio of only 0.51. This last sample corresponds to the day with a higher impact of road traffic based on the BC, NO_x and HOA concentrations. The difference between the OOCf/OCf ratios in the low traffic and the high traffic period, on average, is 10%, which agrees reasonably well with the 17% difference found for the fossilSOA/excessCO considering all the uncertainties associated with these calculations. However the toluene/benzene ratio is not significantly different between the low traffic and the high traffic period (average daily ratios ranging from 3.1 to 4.3). If no changes occurred in terms of the nature of sources between the two periods (additional sources with a higher toluene/benzene ratio during the HT period, for example) OH concentrations in the atmosphere of Barcelona cannot be considered as significantly different from one period to another.

Considering all of the above, we acknowledge the comment and certainly accept the hypothesis as a possible complementary explanation of the observed measurements.

Andreas Wahner remarked: The conclusion that enhanced BSOA formation during the HT period compared to the LT period could be due to enhanced NO_x concentration during HT depends on the correlation of NO_x to OH radical, which is not linear but has a maximum at a specific NO_x concentration. Did you analyze the consequences of this dependence?

María Cruz Minguillón responded: As you say, the NO_x influence on SOA formation is not linear. We may not have enough information to completely attribute the enhanced BSOA formation to the NO_x difference, but it is a plausible explanation for the observations/measurements made.

Dwayne Heard said: Normally if you plot the concentration of OH *versus* the concentration of NO_x, there is initially an increase in OH (owing to the HO_2 + NO reaction increasing in importance as an OH source), but once a certain level of

NO_x is reached, the OH concentration peaks and then starts to decrease again (owing to the importance of the OH + NO_2 reaction in forming nitric acid removing OH). What concentration of NO and NO_2 do you have here?

María Cruz Minguillón responded: Concentrations of NO and NO_2 were 2.5 and 15.8 $\mu g\ m^{-3}$ on average, respectively, during the low traffic period and 4.6 and 28.8 $\mu g\ m^{-3}$ during the high traffic period. This means an increase of about 80% in both NO and NO_2 concentrations from the low to the high traffic period. Maximum hourly concentrations reached 120 and 130 $\mu g\ m^{-3}$ of NO and NO_2, respectively. Unfortunately we do not have OH information available.

André Prévôt said: I was wondering if you could use the relative VOC composition to say something about the OH levels, or even NO_3 levels. Toluene/benzene ratios will change during the day. How much oxidation of OH is there and in the evening, how prominent is the decrease in alkanes due to VOC chemistry? The ratios of VOCs may indicate how much oxidation is going on.

María Cruz Minguillón answered: The toluene to benzene ratio (on an hourly basis) was relatively noisy during the first period (from 1 to >10), and more stable (from 2 to 6) during the second period. There was not a clear daily pattern that repeated every day, so the average daily pattern does not give very valuable information.

It is possible that there is an additional source of toluene, as indicated by the PMF analysis carried out on the PTR-MS dataset (results not shown in the paper). Anyway, considering an OH concentration of 5.106 molecule cm^{-3} and following the equation described by El Haddad *et al.*,[1] we obtain 0–0.5 days of aging during the campaign, but it is quite noisy, maybe due to the low concentration measured.

For the alkanes point, the PTR-MS data does not allow dissociation of the alkanes from the alkenes, as they give the same fragments (43, 57, 71…).

1 I. El Haddad, *Atmos. Chem. Phys.*, 2013, **13**, 7875–7894.

Simone Pieber commented: On the question of a changed fleet composition during the high traffic and low traffic period in the data-set, as raised by Dr Claudia Mohr: if those data are available, it might be useful to look, in addition to BC/NO_x traces, into changing mass spectra for the VOCs as identified with the PTR-MS, in order to obtain more information on relative compositions of diesel and gasoline fuelled vehicles; these should have different VOC compositions based on the differences in the raw fuel and after-treatment systems.

María Cruz Minguillón replied: The BC/NO_x ratios varied between 39 and 61 (ng m^{-3} of BC per $\mu g\ m^{-3}$ of NO_x) during the low traffic period and between 38 and 60 (ng m^{-3} of BC per $\mu g\ m^{-3}$ of NO_x) during the high traffic period, calculated on an hourly basis for the average daily pattern for each of the periods. Regarding the differences in VOCs, Fig. 2 shows the average daily pattern for some selected VOCs. The toluene and benzene concentrations in that plot show a similar variation. To better check this, the same data treatment (average daily pattern values) for the toluene/benzene ratio has been applied. The toluene/benzene ratio is higher during the night for both the low and high traffic periods (around 4), and lower during the middle hours of the day (12–16 UTC) (toluene/benzene ratio around 3). More intra-day variation is observed for the low traffic than for the high traffic period.

Sarah Moller asked: In your paper you state that similar meteorological patterns were observed during both the high and low traffic periods. You then go on to say that during the high traffic period, lower wind speed and higher pressure were recorded as a consequence of an anticyclonic episode, leading to atmospheric stagnation. You also say that there were differences in air mass origin between the two periods. Do you believe that the observed changes in atmospheric concentrations and composition are due predominantly to the change in traffic flow rather than meteorological variation? Did you attempt to quantify the impact, or relative importance, of the meteorological changes?

María Cruz Minguillón responded: The changes are mainly attributed to the increase in traffic intensity, although an effect of other factors is also present, of course. The traffic intensity increased by 37% from the low to the high traffic period on average, whereas the BC concentrations increased by 60%, and the NO and NO_2 concentrations increased by 80%. Hence, there are two things here: a) the variations in traffic intensity do not have a linear relationship with the BC, NO and NO_2 concentrations, and/or b) there are other factors favoring the accumulation or low dispersion of pollutants during the high traffic period with respect to the low traffic period. We did not attempt to quantify the impact of these meteorological changes. Maybe to do so we'd need a longer sampling period, so that we can really identify similar patterns in a significant number of days so that the differences are meaningful. Alternatively, and most likely a better option, modelling the formation of SOA could help in the interpretation.

Jose-Luis Jimenez commented: Our results from Los Angeles, as well as results from several other groups, show that biogenic VOCs emitted within the urban area make too little SOA to affect the urban concentrations (see *e.g.* Hayes *et al.*[1] or Heo *et al.*[2]). It is the biogenic VOCs emitted over much larger regional scales that produce the large majority of the biogenic SOA observed at the urban sites. Do you agree with this result for Barcelona?

1 P. L. Hayes *et al.*, *Atmos. Chem. Phys.*, 2015, **15**, 5773–5801.
2 J. Heo, B. de Foy, M. R. Olson, P. Pakbin, C. Sioutas and J. J. Schauer, *Atmos. Environ.*, 2015, **103**, 171–179.

María Cruz Minguillón answered: We do not have evidence that the precursors for the biogenic SOA present in Barcelona are emitted within the Barcelona metropolitan area, as we do not have evidence to the contrary. Considering the VOC emissions information, it makes sense to conclude that the biogenic SOA precursors are coming from outside the city. This would make a lot of sense considering the wind regime, dominated by NW flow during the night and SE-S flow during the day. This wind regime facilitates both the transport of pollutants from the city inland during the day and the transport of emissions from outside the city (such as biogenic precursors) towards the city during the night. It also agrees with the relatively higher monoterpene concentrations during the night (as shown in Fig. 2), and the relatively higher SV-OOA concentrations during the night (Fig. 8).

Jose-Luis Jimenez returned to the discussion of Kebin He's paper: From previous work on which I collaborated, on air quality during the Beijing Olympic Games, I understand that the emission area that affects Beijing is very large – at least a radius of 500km/1000km, – since fine aerosols are dominated by secondary species that are formed over such length scales. Thus a very large radius for the emission controls would have needed to obtain the reported results. What was the radius of the area where emissions control was applied around Beijing? Was it big enough to have an effect?

Zongbo Shi answered: As the question described, the emission area that affects Beijing is very large. During the 2008 Beijing Olympic Games, Beijing and its five neighboring administrative regions (*i.e.*, Tianjin, Hebei, Shanxi, Shandong and Inner Mongolia) enacted strict emission control measures to improve the air quality. And many previous studies have indicated significant reduction of air pollutants during the Beijing Olympic Games. For this study, as we elucidated in the paper, Henan province was also involved in the emission control action during the V-day Parade, besides the six regions we mentioned above. The radius of the area for emission controls is almost 500km–800km. We thought it was big enough to have an effect.

Urs Baltensperger inquired: I would expect that primary OA would react more rapidly to a change in emissions than the secondary OA, but your study shows the opposite – what are your thoughts on this?

Zongbo Shi answered: Thanks for the question. In this study, our monitoring site was located in the urban area of Beijing. While primary OA was mainly influenced by local emission sources, secondary OA could react to emission changes on a large regional scale. In the paper, we have taken the cluster 1 case as an example to explain this. Consistent with the significantly reduced VOC emissions of 58%–66% of southern Hebei, the concentration of secondary OA under cluster 1 decreased by 48% as a response to the regional emission control. For primary OA, it was also reduced by 48% in the cluster 1 case, mainly influenced by local emissions.

Andreas Skouloudis said: In the emission control period for the Parade Blue, this work focused on the effects before and during this parade. However, it would be interesting to generalise this. Did you observe similar effects afterwards, and if this happened several years running, will draw the same conclusions?

Zongbo Shi answered: Thanks for the question. The periods after this parade were much influenced by high precipitation. Thus it may be not reasonable to explore the effects of emission control by comparing aerosol characteristics during and after the parade. As the same emission control would not be continuously implemented for several years at this stage, I am not sure if we would draw the same conclusions. But the results concluded from this study are consistent with those from other two similar emission control periods, during the

2008 Beijing Olympic Games and the 2014 Asia-Pacific Economic Cooperation summit in Beijing.

Aurélie Charron addressed María Cruz Minguillón: Have you considered the contribution of biofuels included in fuels to the amount of non-fossil carbon? As an example, I give you the average percentage of biofuels in French fuels – that is, 7% – although I do not know the figures for Spain.

María Cruz Minguillón replied: The biofuel use in Spain is very low (below 2%, according to the statistics of the DGT, the traffic authority in Spain), and this is true also for the study region. Hence we did not consider biofuels when doing the calculations and interpretations in our study. In case the use of biofuel increases, future studies should consider it. Some studies highlight the formation of SOA from biofuel vehicles.[1] To better understand how the use of biofuel affects the mixture of ambient OA in terms of fossil and nonfossil fractions, specific studies on the biofuel combustion emissions and aging are required. The primary emissions from biofuel vehicles are expected to be still partially fossil, given that the biofuel engines use lubricating oils, responsible for primary OA emissions. On the other hand, the SOA produced from the precursors emitted from biofuel vehicles would be non-fossil (or mainly non-fossil), considering that the precursors are compounds from the biofuel that have been released to the atmosphere by evaporation. On the other hand, the % of biofuel use, even if it is very low as stated, is not expected to change between the first and the second periods of our study.

1 R. Suarez-Bertoa *et al.*, *Atmos. Environ.*, 2015, **117**, 200–211.

Matthew Hort returned to the discussion of Kebin He's paper: In the paper, you talk about the fact that the analysis was grouped by similar meteorological conditions. This is a very good thing to do and I am pleased to see it. However, it was not clear to me what time period had been used in defining the similar meteorology.

I also wondered what meteorological data had been used to draw the comparison. It seemed that a single point had been used. Depending on the relevant transport and possibly reaction times, it might mean that meteorology of the wider synoptic picture would be a better method for characterisation (*i.e.* as a single point can be the same under different wider conditions that may affect the trajectory of the air mass). Though this might be harder to define, one possibly useful technique is the use of Lagrangian back trajectories.

Zongbo Shi replied: The procedure that we followed to select data populations with similar meteorological conditions has been described in detail in the second part of our results. Not only a single point was used for comparison. Briefly speaking, local temperature, RH, wind speed and PBL height were very similar before and during the emission control period, as presented on page 10 of the paper. However, local wind direction was very different. Then we further used the back trajectory cluster analysis to select comparable conditions of wind direction and regional air mass transport. Finally, the cases of cluster 1 and cluster 3 following back trajectory analysis were selected. As shown in Fig. 4, data populations under these two cases had similar weather conditions.

Neil Donahue asked Costas Sioutas and Martin Shafer: Can you comment on the DTT assay and biogenic SOA?

Costas Sioutas responded: in LA we don't have much SOA derived from biogenic photo-oxidation; however, the DTT studies in Atlanta by Weber and Verma (and others) do indicate a relationship between biogenic SOA and DTT activity.[1]

1 T. Fang *et al.*, *Atmos. Chem. Phys.*, 2016, **16**, 3865–3879.

Martin Shafer added: I don't believe our study can contribute substantially to furthering our understanding of the role of biogenic SOA versus anthropogenic SOA on the oxidative potential of the SOA as estimated with the DTT assay. Studies have clearly shown the role of anthropogenic SOA precursors (SO_2, NO_x) on biogenic SOA formation, and thus the oxidative potential of these PM/SOA components are intimately linked. That said, it is reasonable to expect that the oxidation products of biogenic precursors (isoprene, terpenes, etc.) may be more active in the DTT assay than the SOA from major anthropogenic sources. I would refer readers to Kramer *et al.*[1] and Chen *et al.*,[2] and references cited within.

1 A. J. Kramer, W. Rattanavaraha, Z. Zhang, A. Gold, J. D. Surratt, and Y. H. Lin, *Atmos. Environ.*, 2016, **130**, 211–218.
2 X. Chen, P. K. Hopke and W. P. L. Carter, *Environ Sci Technol.*, 2011, **45**, 276–282.

Gary Fuller addressed Costas Sioutas: I'm really intrigued about the sub-story in the paper; the increase in abrasion products. These are traced by copper, barium, manganese in your study, so by abrasion do you mean brake wear? Can you account for it? We have found in some London roads that there is an increase in PM_{10} despite a decrease in $PM_{2.5}$ (as shown in Fig. 1) – largely these are locations where we have an increase in heavy duty vehicles.

1 A. Font and G. Fuller, Roadside air quality in London – identifying the outliers: Part 1, King's College London, 2015.

Costas Sioutas answered: We do mean mostly tire wear – please read the related discussion in our paper.

Urs Baltensperger asked: I presented in my talk yesterday that the brake wear size distribution is such that most of its mass is found in the coarse or medium mode, and only a small fraction is found in the fine mode (see Visser *et al.*[1]). So, could the brake wear effects that you see in the fine mode be due to a cross correlation with the traffic exhaust from exhaust pipes?

1 S. Visser *et al.*, *Atmos. Chem. Phys.*, 2015, **15**, 11291–11309.

Costas Sioutas responded: We don't necessarily agree with the statement that brake wear is in the coarse PM mode only – Ba as a tracer for brake wear almost exclusively comes from brake wear abrasion.[1]. Brake wear abrasion contributes to both fine and coarse PM. Several studies have shown that particles generated from brake wear abrasion in fact maximize at around 4 μm – for instance, the study of Ijima *et al.*[2] on particle size and composition distribution of automotive

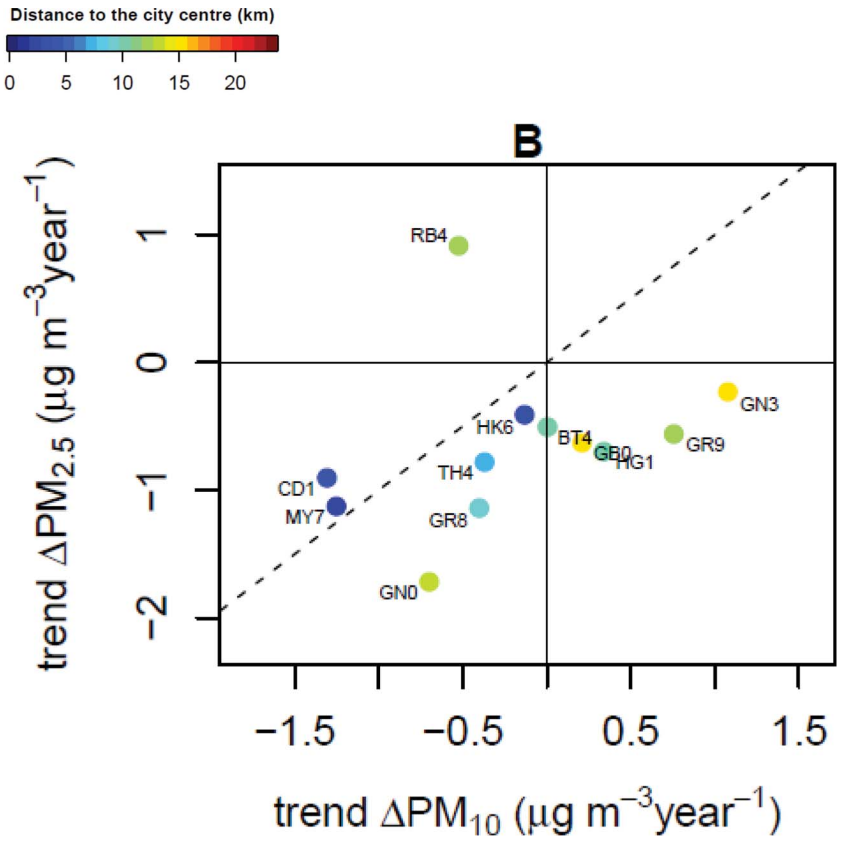

Fig. 1 Trends in roadside increment of $PM_{2.5}$ and PM_{10} from London 2010–2014. Reproduced with permission from Font and Fuller[1]

brake abrasion, where the shapes of the distributions of five metallic elements (Fe, Cu, Zn, Sb and Ba) were very similar to the total mass distribution of the brake abrasion dusts and had a mode of around 3–4 μm. This is also in line with the study of Harrison *et al.*[3] in which they took Ba as a tracer of brake dust - their scaled Ba representative of brake abrasion also showed a peak at around 4 μm and a smaller peak in the $PM_{2.5}$ range. A study by Ntziachristos *et al.* also showed that "Most elements fall into two distinct concentration profiles with particle size. First, several elements present a monotonic increase in their profile with size, such as Na, S, Ti, V, Mn, Fe, Sn, and Ba. The highest concentrations appear in the $PM_{0.18-2.5}$ mode."[4] In their study of urban air, Birmili *et al.* found similar profiles for Na, Fe, and Ba in the size range 0.5–7.2 μm,[5] while Lough *et al.* also presented similar monotonic profiles up to 2.5 μm for Ba in a road-tunnel.[6]

One should also take into account the effect of brake pad materials itself in contributing to size-fractionated PM emission. The brake dust profiles which Schauer *et al.* reported[7] were for semimetallic and low-metallic brake pads. The semimetallic and low-metallic designations are types of brake pads discussed in the literature, but the range of actual brake pad formulations on the market is vast. They reported their profiles for PM_{10} and $PM_{2.5}$. Interestingly, the contribution of low metallic brake pads to $PM_{2.5}$ (13.2 mg g^{-1} brake dust PM) was about 2.3 times higher than for PM_{10} (5.8 13.2 mg g^{-1} brake dust PM). However, for semimetallic ones they were more or less comparable (13.4 and 14.2 for $PM_{2.5}$ and PM_{10}, respectively).

In our own work on source apportionment of metals in the ultrafine size range in LA,[8] we state that, "While road dust has been identified as a major source of coarse particle emissions (Amato *et al.*;[9] Pakbin *et al.*[10]), other studies have consistently been reporting road dust emissions originating from tire–pavement interactions to be present in the smaller size fractions as well, with mass mean particle diameters between 15 and 50 nm (Dahl *et al.*;[11] Gustafsson *et al.*[12,13])."

1 P. Sanderson, J. Maria Delgado-Saborit and R. M. Harrison, *Atmos. Environ.*, 2014, **94**, 353–365.
2 A. Iijima, K.I Sato, K. Yano, H. Tago, M. Kato, H. Kimura and N. Furuta, *Atmos. Environ.*, 2007, **41**, 4908–4919.
3 R. M. Harrison, A. M. Jones, J. Gietl, J. Yin and D. C. Green, *Environ. Sci. Technol.*, 2012, **46**, 6523–6529.
4 L. Ntziachristos, Z. Ning, M. D. Geller, R. J. Sheesley, J. J. Schauer and C. Sioutas, *Atmos. Environ.*, 2007, **41**, 5684–5696.
5 W. Birmili, A. G. Allen, F. Bary and R. M. Harrison, *Environ. Sci. Technol.*, 2006, **40**, 1144–1153.
6 G. C. Lough, J. J. Schauer, J.-S. Park, M. M. Shafer, J. T. DeMinter and J. P. Weinstein, *Environ. Sci. Technol.*, 2005, **39**, 826–836.
7 J. J. Schauer, G. C. Lough, M. M. Shafer, W. F. Christensen, M. F. Arndt, J. T. DeMinter and J.-S. Park, *Res. Rep. Health Eff. Inst.*, 2006, **133**, 1–76, discussion 77–88.
8 A. Saffari, N. Daher, M. M. Shafer, J. J. Schauer and C. Sioutas, *Environ. Pollut.*, 2013, **181**, 14–23.
9 F. Amato, M. Pandolfi, A. Escrig, X. Querol, A. Alastuey, J. Pey, N. Perez, and P. K. Hopke, *Atmos. Environ.*, 2009. **43**, 2770–2780.
10 P. Pakbin, Z. Ning, M. M. Shafer, J. J. Schauer and C. Sioutas, *Aerosol Sci. Technol.*, 2011, **45**, 949–963.
11 A. Dahl, A. Gharibi, E. Swietlicki, A. Gudmundsson, M. Bohgard, A. Ljungman, G. R. Blomqvist and M. Gustafsson, *Atmos. Environ.*, 2006, **40**, 1314–1323.
12 M. Gustafsson, G. R. Blomqvist, A. Gudmundsson, A. Dahl, E. Swietlicki, M. Bohgard, J. Lindbom and A. Ljungman, *Sci. Total Environ.*, 2008, **393**, 226–240.
13 M. Gustafsson, G. R. Blomqvist, A. Gudmundsson, A. Dahl, P. Jonsson and E. Swietlicki, *Atmos. Environ.*, 2009, **43**, 4699–4702.

Eben Cross asked: The composition of fuel and lubricant additives include metal species that overlap with the non-tailpipe chemical emission profile characterized here. Can the authors comment on how potential exhaust-derived metal contributions are separated from non-tailpipe sources?

Costas Sioutas responded: That's a good point when it comes to species such as Zn, CU *etc,*; however, Ba is a very reliable tracer of brake wear.

Markus Kalberer inquired of Costas Sioutas and Martin Shafer: I have a general question to both of you – you have DCFH measurements on one hand, and DTT assays on the other, while some groups use biological measurements instead. So there are many different methods to use in trying to come up with a metric for oxidative potential. What's your opinion on which is best?

Costas Sioutas answered: I am in no position to offer an informed response, since I have not evaluated carefully each of these methods individually and using evaluation metrics that are yet to be defined; I can at least speak for DTT, for which we have evidence of correlations with health effects observed in human panel studies.

Martin Shafer added: Our ROS measurements are biologically based (using alveolar macrophages) and in our opinion incorporating "biology" in increasingly relevant models is key to advancing oxidative potential metrics. The issue really is less the specific ROS probe, and more the complexity of the biological model and how close a surrogate it is for the functioning of human systems. Multi-cellular *in-vitro* models likely provide a more robust predictive capability. That said, in going after the integrated oxidative potential (in whatever model), a general probe like DCFH is most useful. If pathway analysis is needed, then less effort should be placed on characterizing specific ROS species, but instead focus should be on expression/production of pathway characteristic signaling molecules (cytokines, chemokines, *etc.*).

Urs Baltensperger commented: I do not believe that we will be able to describe biological effects on human beings with just a single assay. This means we need to run a variety of tests in order to see which combination provides us with the best possible answer. Here I would love to see closer collaboration between chemists and biologists to come up with a combined and more complete picture of what is going on, and then in the future possibly try to reduce the number of assays.

Xavier Querol addressed Costas Sioutas and Martin Shafer: Thanks a lot for your excellent presentations and papers. Two questions; firstly, did you evaluate if the higher ROS of the fine *versus* coarse fraction is softened if you normalise the ROS by the surface area of these fractions? Or do you think that the higher ROS is due to the differences in chemical composition and oxidation state, of the two fractions? Secondly, I observed in tables of the paper relating to European cities that ROS was highly correlated for the coarser fraction with a group of elements of typically crustal origin (Ca, Ti, Mg, Al, and specially K, the latter in the coarser fraction being usually associated with minerals more than biomass burning). The correlation is better for these than for other typically ROS-associated trace metals. However, as we move to finer fractions the correlation decreases. What do you interpret as being the causes for this?

Costas Sioutas replied: We did not reach conclusive results by normalising ROS *vs.* surface area, but this can be done with specific surface area measurements.

Martin Shafer responded: Thank you for your insightful comments. We did not examine the potential influence of surface area normalization on the specific activity of the PM size classes – primarily because, as noted in your comments, a large fraction of the PM mass (and an even larger fraction of the ROS activity) in the PM_3 size class (and a somewhat smaller fraction in the larger size classes) was water soluble. This is fundamentally driven by a contrast in chemical composition of the size-classes. Additionally, particle phagocytosis is a primary initiating step in ROS generation in our macrophage model, and this process is relatively insensitive to particle size (within some limits).

The contrast in ROS activity across PM size classes reflects the net effect of several factors, including major differences in chemical composition, water solubility and mechanisms of uptake/interaction with the macrophages. The specific activity (*i.e.* mass normalized) of the PM_3 fraction is actually significantly greater (more than 2-fold) than PM_{7-3} and over 4-fold greater than the super-coarse fraction. This likely reflects a greater contribution from soluble higher activity organic species such as SOA, some contribution from soluble transition metals, and "dilution" of the specific activity of larger PM by relatively inactive components. The chemical species correlations in the larger size fractions likely reflect only secondarily the chemical composition but more importantly the greater insoluble fraction (which effectively means crustal material –thus the enhanced correlation with Ca, Ti, Mg, Al, K). Macrophages are particularly sensitive to particulates "themselves", which are strong initiators of the respiratory burst upon phagocytosis. The chemical components with which Ca, Mg and K are associated in the fine PM are different to those in the coarser fractions and are significantly more soluble. These elements are inherently non-reactive, thus the ROS correlation with these elements in the fine fraction "dissolves".

With regards to the finding of a higher specific activity of PM at the background sites, we hypothesize a greater contribution of higher activity organic SOA components at these sites.

Xavier Querol replied to Martin Shafer: I agree with this, but this does not answer my question, because what you have found is a correlation between ROS and Ca in the coarse fraction, and no correlation or even negative correlation of these two parameters in the fine fraction. And why is ROS more correlated in the coarse fraction with K than with classical ROS-related metals?

Roy Harrison remarked: I have been interested in these *in vitro* tests of particle toxicity for many years. I convened a meeting in London almost 10 years ago which was attended by leading international workers, including Professor Sioutas. This left me deeply sceptical over the value of the tests and I have not had reason to change my view since. Martin's paper raises a number of important issues. Firstly, the tests using a measure of exposure (*e.g.* the DTT assay) do not correlate with those giving a measure of effect (*e.g.* the TNF alpha measurement), hence I wonder if the exposure tests are telling us anything useful. Work that I have done in this field collaborating with Professor Frank Kelly of Kings College London uses a simulated lung fluid and looks at depletion of anti-oxidant in the lung fluid. This shows the greatest activity in the coarse particle fraction at roadside which is in complete contrast to Martin's results. Clearly, the Kings College test is being driven by very different factors from the DTT assay. These kinds of inconsistencies come up quite widely. Also, the spatial distribution of activity in Martin's results is most unexpected. Since the urban background aerosol is typically a mixture of the regional background with urban emissions, one would expect its activity to lie between the rural and street samples, but in Martin's data it shows the highest oxidative potential per unit mass, which is highly counter-intuitive. My other concern beyond the lack of correlation of the results of different tests of oxidative potential is that there is a scarcity of evidence of clinically significant effects in human populations. This is critical to establishing the value of such tests.

Costas Sioutas replied: I will send you one of our papers[1] in which we clearly demonstrate the strong association between these assays and biomarkers of systemic inflammation in human subjects in LA.

[1] R. J. Delfino, N. Staimer, T. Tjoa, M. Arhami, A. Polidori, D. L. Gillen, S. C. George, M. M. Shafer, J. J. Schauer and C. Sioutas, *Epidemiology*, 2010, **21**, 892–902.

Xavier Querol added: I remember a paper by the Sioutas team where they found more ROS in the LA pollution plume than in the city, and they attributed this to ROS of SOA.

Urs Baltensperger remarked: We know that a large fraction of the atmospheric aerosol is water soluble, so for anything water soluble the surface area is not relevant. The same is true for the number concentration. This needs to be taken into account when searching for additional metrics that could describe the health effects of aerosols.

Xavier Querol responded: I agree, but I am still convinced that surface area might have a role here, because when we applied a DNA array assay to fine and coarse fractions and we normalised these by surface area, differences were reduced. Many PM components having a high ROS effect, such as metallic species and PAH for example, are not water-soluble.

Neil Donahue commented: I agree with Urs that surface area may be irrelevant when most of the material on fine particles is water soluble. However, I can easily hypothesize a situation where the urban background could show the highest toxicity. The organic fraction evolves dynamically, and if relatively short-lived first- or second-generation oxidation products are the most toxic, we would see the greatest toxicity some time after emission. That could be the urban background.

Tzer-Ren Ho asked Martin Shafer: did you measure the cellular viability of the macrophage when exposed to the aerosols? Exposure time is only two hours, so cells may have undergone apoptosis but not be dead - this might explain why the TNF alpha results don't correlate to the ROS results. In my results, when I exposed cells to diesel exhaust particles some of the cells did die, which might have affected your results in this case.

Martin Shafer responded: We have measured plasma membrane integrity with either PI or Sytox green fluorescent probes. These probes of cell viability (not necessarily apoptosis) show no indication of NR8383 cell death at a 2 h exposure time in most of the samples that we have examined. In addition, our detailed dose-response exposure protocol is designed to detect sub-lethal toxicity, and if such non-linearities are observed data at those concentrations are not included in the slope analysis. If necessary, exposures are repeated at more dilute concentrations to ensure that the dose-response line is adequately predicted. The generally poor correlation between the TNF alpha data and ROS in this data set is likely the result of several factors, including (a) a contrast in the kinetic profiles of ROS and cytokine induction, (b) a much stronger preference of particulate phases over soluble phases for TNF alpha expression in comparison with ROS generation, and (c) a smaller cytokine dataset in comparison with the ROS dataset in this study.

Tzer-Ren Ho remarked: One of the ways to be sure is to use annexin V staining during flow cytometry, to ensure cells are not undergoing apoptosis

Martin Shafer answered: Yes, that is a good suggestion. We have considered this protocol, but it would require some modification to our exposure media (and added uncertainty) as a result of the sensitivity of this stain to calcium concentrations. While we believe apoptosis is probably not a significant issue in our cell model and exposure protocols (as mentioned in my response to your previous question), it is something we will consider evaluating in on-going studies.

Markus Kalberer said: I have a comment regarding Roy Harrison's remark on the seeming inconsistencies of the different assays. We have tried the DCFH assays as well as determining ascorbic acid consumption of aerosol extracts. There will be different reactivity for different assays depending on what you throw at them – for example, ascorbic acid is easily oxidised by transition metals, but you can add milligrams of OAs to it and it won't react. Secondly, I have a comment to Neil Donahue regarding short lived components – this relates to the poster which we have presented at this Discussion, where we try to convert the DCFH methodology to an online method so we can measure within a couple of seconds. This could be a strategy to follow up, to get a more consistent picture.

Andreas Wahner returned to the discussion of Costas Sioutas' paper: you showed in your studies that you identified certain fractions of aerosols to be reactive in your test on oxidative potential. Did you also confirm with artificial aerosols that they give the same results and in similar quantities? For example, could you use just aerosols from brakes?

Costas Sioutas replied: We haven't done tests with artificial brake aerosols – for more information I refer you to Shuster-Meiseles *et al.*[1] and Zhao *et al.*[2]

1 T. Shuster-Meiseles, M. M. Shafer, J. Heo, M. Pardo, D. S. Antkiewicz, J. J. Schauer, A. Rudich and Y. Rudich, *Environ. Res.*, 2016, **146**, 252–262.
2 J. Zhao, N. Lewinski and M.l Riediker, *Aerosol Sci. Technol.*, 2015, **49**, 65–74.

Urs Baltensperger addressed Martin Shafer: You showed in your talk that you found spatially quite a uniform oxidative activity across Europe, while other people see substantially higher activity in street canyons than at urban background sites. I guess you must have come up with some kind of hypothesis to explain this?

Martin Shafer answered: It was uniform within a general factor of 5 when expressed in terms of air concentrations (activity per volume of air), and a bit more uniform when normalized to PM mass. And yes, in general the "background" sites exhibited comparable activity (or higher when normalized to PM mass) to the urban canyon sites. Our working hypothesis is that the PM at the background sites are reflecting a significantly higher fraction of intrinsically higher activity PM components. SOA from urban emissions formed on time-scales of multiple hours and SOA transported into the urban air-shed from more rural regions is a likely candidate. This hypothesis is supported by our observation of the generally poor correlation of the PM_3 elemental species typically considered as vehicle emission tracers with ROS and DTT activities.

Urs Baltensperger remarked: We have shown at PSI in our smog chamber that with the formation of secondary organic aerosol the ROS concentration increases substantially, regardless of the precursor type. So secondary aerosol will definitely contribute to the toxicity.

Roy Harrison addressed Costas Sioutas: One big unsolved question in this field is the fact that assays of this kind, and human challenge studies, attribute low toxicity to sulphate. But many epidemiological studies show sulphate as showing the strongest correlation with mortality and adverse outcomes. Could it be that actually sulphate is a surrogate for low volatility SOA, and it's actually SOA that's driving this toxicity?

Costas Sioutas replied: Indeed, sulfate could be a surrogate of SOA.

Martin Shafer added: I agree with Prof. Harrison's observation/analysis that assays of this type generally indicate that sulfate has little or no ROS activity, and that is not unexpected from a biochemistry perspective. In fact, in the large number of field studies in which we have performed these ROS assays, sulfate at best shows no positive correlation with ROS, and in several studies is anti-correlated. So while the interpretation of epidemiological data in terms of chemical drivers is complex, I do not disagree with the hypothesis that sulfate may indeed be acting as a surrogate for SOA in these models, particularly for large spatial scale studies with a mix of rural and urban samples.

William Brune commented: There are a few studies of air pollution effects on humans that are being done using human subjects, including studies of inhalation of diesel exhaust. These studies are much more expensive than studies with cells and it can be hard to find volunteers, but these studies are being done.

Tzer-Ren Ho said to Martin Shafer: If you look at the sputum obtained from sputum challenge, you can find macrophages and dendritic cells in the upper airways as well, so you can definitely find them there. Henceforth, particles that deposit in the upper airways cannot be disregarded.

Martin Shafer replied: I don't believe there is much disagreement on this fact, though mucus can be escalated up the respiratory tract from quite deep in the lungs. The toxicity of coarse PM may also speak to the fact that upper airway processes cannot be ignored.

William Brune asked: Following up on Neil Donahue's comment about oxygenated hydrocarbons in particles being important for air pollution impacts on human health, do you think that the way that you collect the particles for analysis can affect their chemical composition and thus their impact on human health? If the particle chemical composition is degraded, how do you deal with this?

Martin Shafer replied: Most likely – that is the case with nearly all commonly implemented field techniques for aerosol sampling. Quantifying that potential bias is very challenging and requires both new approaches for PM collection and new tools that are sensitive to the speciation relevant to human health. On the inorganic side, chemical speciation (*e.g.* oxidation state), not chemical composition, is the biggest concern and we (and others) are developing and implementing techniques that will address this for the primary elements of concern. On the organic compound side, our analytical tools have advanced to the point where relevant species quantification is likely not the limiting factor in addressing collection biases – one must build these tools into studies comparing field collection methods and proxies for human health impacts. Obviously we take great care to minimize post-collection biases by freezing and in many recent studies (including the European Aerosol Study) sealing the filter in air-impermeable, nitrogen purged bags. Significant efforts are being dedicated to developing more sensitive assays that can be used with much shorter time-integrated samples (1–2 hours, where potential speciation biases are likely to be much smaller). Novel tools for collection of aerosol PM for health studies are being developed that collect and concentrate PM directly into aqueous media (or even culture media) on time scales of an hour, and couple this with near-real time chemical characterization. Our group has several publications where these novel approaches are detailed. On an encouraging note, the limited toxicological data from these novel methods appears to confirm the integrity and validity of 24-hour integrated filter samples. But clearly more directed study is essential.

Costas Sioutas added: This is an important issue and obviously we thought about it – we have conducted a detailed characterization of our PM in all of our publications and have shown that the chemical composition is very similar to that measured by reference samplers (USEPA frm) sampling in parallel.

Neil Donahue said: My mental model is that there are many toxicants in fine particles, with different dose responses, and that the overall toxicity is some sort of combination of these effects. There is no magic bullet. However, I have always been puzzled why particles seem to be especially toxic. Is there any evidence that particles deposited on cells more or less overwhelm individual cells or groups in ways that the same amount of vapor, distributed across the lung, could not?

Costas Sioutas responded: Neil, as you know we have discussed this and indeed it could be the foundation of an interesting series of inhalation experiments whereby we provide an atmosphere containing SVOC in their particle phase and the same amount/concentration of SVOC in the gas/vapor phase to see how different the results might be. We developed/modified our VACES concentrators to do just this experiment, but never got a chance to carry it out – see our paper discussing VACES modification.[1]

[1] P. Pakbina, Z. Ning, A. Eiguren-Fernandez and C. Sioutas, *J. Aerosol Sci.*, 2011, **42**, 555–566.

Martin Shafer said: I totally agree that ambient PM toxicology is very complex, both in the chemical/physical drivers of responses and the biochemical modes of action, and clearly no single assay can reproduce that complexity – a battery of assays will be required. Direct comparisons between particles, water soluble components of those particles, and vapor forms of the particulate species are difficult to construct, let alone interpret. Such experiments would be extremely interesting and valuable and new tools may allow us to do this with environmentally relevant PM/SVOC species. But, yes there is literature indicating that alveolar response is especially sensitive to particulates. This may reflect the mode in which invading particulates are dealt with in the airways – usually by recruitment of macrophages to the PM. Phagocytosis of the particles is a powerful initiator of the oxidative stress cascade, a pathway that would not be expressed with a similar mass of vapor.

André Prévôt inquired: It's intriguing that the ROS activity per mass is so much lower at the urban canyon than the urban background. Could you look at the mass balance, especially for the small particle size, to see whether the road emissions contribute anything? Can you work this out from the data?

Martin Shafer responded: It would be conceptually possible to source apportion the ROS (*e.g.* using the approach we used in our previous work[1]). And we may attempt to do so in a planned follow-up manuscript; however, we cannot at this stage define explicitly the road emissions contribution. There is little doubt though that primary road emissions do contribute to the ROS burden as evidenced in numerous roadside studies and in studies of tailpipe, brake, tire, and roadway dust source samples.

[1] Y. Zhang, J. J. Schauer, M. M. Shafer, M. P. Hannigan and S. J. Dutton, *Environ. Sci. Technol.*, 2008, **42**, 6502–7509.

William Brune addressed Martin Shafer and Urs Baltensperger :I may have missed this in the published literature, but are there scatter plots of ROS *versus* an indicator of aerosol particle oxidation, such as perhaps O:C ratio?

Martin Shafer responded: I'm not aware of published correlations between metrics of the bulk oxidation status/state of the aerosol particle and macrophage-based ROS or DTT. Oxygen is rarely if ever quantified in the PM and though theoretically derivable from detailed organics analysis, I suspect the uncertainty would be large. Several papers have examined correlations of ROS with specific organic components or fractions of OC that could potentially serve as surrogates of the oxidation status of the PM and depending upon the ROS indicator, correlations of reasonable significance are observed. However most of these studies were not specifically designed to address this issue and confounding with other variables contributes to high uncertainty. Even less work has been published examining the relationships between oxidation status of redox active metals in the PM and ROS and this is an area that we are exploring in on-going research.

Urs Baltensperger responded: We did not publish a scatter plot, but we showed the temporal evolution of the normalized ROS concentration (ROS concentration measured in moles of hydrogen peroxide equivalents normalized to the molar organic carbon concentration per m^3) and the O:C ratio.[1] There we indeed saw a correlation in the first one to two hours, but after this the relative ROS concentration stopped increasing, while the O:C ratio continued to increase.

[1] S. M. Platt *et al.*, *Nat. Commun.*, 2014, **5**, 3749.

Markus Kalberer said: You discussed a possible link between O:C ratios in organic aerosols and the response of biological assays. One should be very careful in interpreting such correlations. One of these assays, DCFH, is very sensitive to hydrogen peroxide but not at all to carboxylic acids, even though these functional groups have the same number of oxygens. I would call to go back to more basic laboratory experiments to characterise these assays with different aerosols, rather than doing more field experiments where everything is extremely complex.

Martin Shafer answered: I concur (nearly) completely with your comments. Clearly the utility of bulk O:C ratios in the context of ROS/DCFH sensitivity must be interpreted with appropriate circumspection. And much can/should be done in the lab with well-defined aerosols (and controlled “aged” aerosols) to understand the response (and utility) of a broad range of *in vitro* assays. Field studies do have a place, if only to provide context and limits to lab studies. Also deconstructing (in the lab) actual field aerosol to provide information on the activity of specific PM components (using targeted physical/chemical “separation” tools) can actually be quite powerful and relevant.

Rachel Dunmore opened a general discussion of the paper by Christian Ehlers: You state that a GC instrument was specifically designed to be able to measure C8–C16 VOCs; could you provide a justification for this statement? Specifically, details of the sampling and analysis method for the larger carbon number VOCs. Also, what was the sensitivity of this instrument for C11 VOCs (*i.e.* n-undecane) in your calibration standard *versus* that of a smaller carbon number VOC (such as pentane)? Fig. 2, which is taken from our own work, shows a reconstituted 1D GC chromatogram from a winter ClearfLo GCxGC chromatogram (using Zoex GC Image software) with three major aromatics and the C8–C12 n-alkanes identified. The majority of the material in between these is made up of other aliphatic compounds, with a few aromatics and oxygenated compounds. Without the addition of GCXGC the additional aliphatic material, made up of many low concentration isomers, is hard to quantify and after 45 min appears as an increasing baseline with a small number of peaks. With the GCxGC chromatogram, it was possible to quantify this other VOC loading and separate the contribution from grouped aliphatic, aromatic and oxygenated compounds. For example, in winter in London, the average mixing ratio for n-undecane was 397 pptv (*cf.* toluene 635 ppt) while the average for the grouped C11 aliphatics was 459 pptv.[1] This additional aliphatic material would be impossible to quantify using the 1D chromatogram alone. Did you make any estimation of the other aliphatic VOCs in addition to the n-alkane?

[1] R. E. Dunmore, J. R. Hopkins, R. T. Lidster, J. D. Lee, M. J. Evans, A. R. Rickard, A. C. Lewis and J. F. Hamilton, *Atmos. Chem. Phys.*, 2015, **15**, 9983–9996.

Christian Ehlers replied: The GC instrument was originally developed to analyze sesquiterpenes and monoterpene compounds. It consists of a thermodesorption system combined with a cold injection system where the components are refocused (TDS, Gerstel, Mülheim). The compounds are separated on a 60 DB1-column before they are detected by FID and MS (Agilent, MSD 5975c). The adsorption tubes were desorbed at 320°C. The transfer lines were held at 300°C and the column was ramped to its maximum temperature of 320°C to prevent losses of high boiling compounds. Compounds lighter than octane are not completely retained in the focusing unit. When sampling diesel exhaust a large number of peaks between decane and tetradecane were observed which appear as a baseline increase in the FID signal. By using the single ion traces in the mass spectrometer it was possible to deconvolute the compound mix which consists of straight chained alkanes, and single and double methyl substituted alkanes as well as substituted cyclohexanes. Also, substituted benzenes, naphthalenes and decalins were found. Still, the total FID signal of compounds larger than dodecane was low compared to the lighter compounds.

Alison Tomlin opened a general discussion of the paper by James Lee: Even in the interpretation of the measurements it seems that you are using a model: *e.g.* to calculate the relevant footprint. Can you be sure that the remaining discrepancy (following the update of the emissions inventory) is due to an inventory problem and is not due to sensitivities to other model parameters? One parameter which may be important is the assumed roughness length for each city neighbourhood. The method of Drew *et al.* that you cited in your paper does not account for heterogeneous building heights and therefore is likely to underestimate

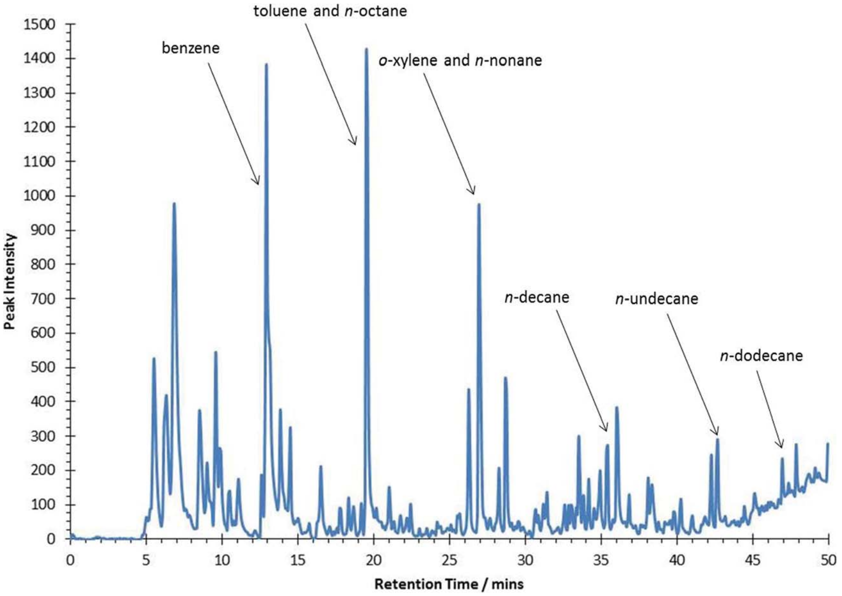

Fig. 2 1D GC chromatogram from a winter ClearfLo GCxGC chromatogram (using Zoex GC Image software) with three major aromatics and the C8–C12 n-alkanes identified. Reproduced with permission from Dunmore *et al.*[1]

roughness lengths and displacement heights for London's central region, based on the work of Millward Hopkins *et al.*[1] Can you comment on the sensitivity to these surface aerodynamic parameters?

[1] J. T. Millward-Hopkins, A. S. Tomlin, L. Ma, D. Ingham and M. Pourkashanian, *Boundary-Layer Meteorology*, 2011, **141** 443–465.

James Lee responded: This is a good point. Our footprint model is dependent on a variety of factors, including the roughness length, which as is pointed out we have taken from the Drew *et al.* 2011 paper.[1] We appreciate the comment that there are other measures of roughness length for urban areas and that the measurement we use may be an underestimate. We have now carried out a sensitivity study of our footprint model to roughness length by doubling the value we use. This does indeed cause a reduction in our footprint area and thus an increase in the NO_x emission from the inventory for central London. This data is shown in Fig. 3. In central London the ratio is reduced from about 1.5 to 1.35, although in the outer London zones the ratio is actually increased from around 1.05 to 1.15. This shows the importance of having the correct roughness length for the interpretation of our results, and we will work on using the best possible data in our future work.

[1] D. R. Drew, J. F. Barlow and S. E. Lane, *J. Wind Eng. Ind. Aerod.*, 2013, **121** ,98–105.

Thomas Karl addressed Christian Ehlers: In your paper (page 12, line 30) you state that the total decrease of NO_x emissions in your Fig 13 is quite comparable to the observed trend of NO_x concentrations (Fig 11), based on the updated HBEFA3.2 database that now also includes RDE. Yet, a closer look at these figures suggests that the NO_x emission inventory drops about 60% faster than NO_x concentrations during the discussed time period. Your statement therefore implies (1) either significant emissions of NO_x from other sectors in German cities, that have not declined or increased, (2) a significant increase of advected NO_x over German cities (*e.g.* due to agricultural activities) or (3) a significant change of other processes leading to lower atmospheric loss rates of NO_x in German cities (*e.g.* atmospheric oxidation, deposition, conversion to HNO3, alkylnitrates, PANs *etc.*). I would think that (1) is the most realistic; but in this case I was wondering whether you can really assume that a major fraction of NO_x in German cities really originates from sources other than traffic. Another possibility would be that even updated bottom-up emission inventories still largely underpredict urban NO_x from traffic related emission sources, questioning the reliability of these bottom-up models due to inherent uncertainties of the upscaling approach.

Christian Ehlers answered: For urban areas we would not expect other important sources of NO_x apart from traffic emissions. We would rather expect that even the updated emission inventories are still underestimating the emission factors.

Tim Wallington asked James Lee: Wouldn't the simplest explanation for the discrepancy in downtown London be that you're underestimating “other” emissions aside from traffic?

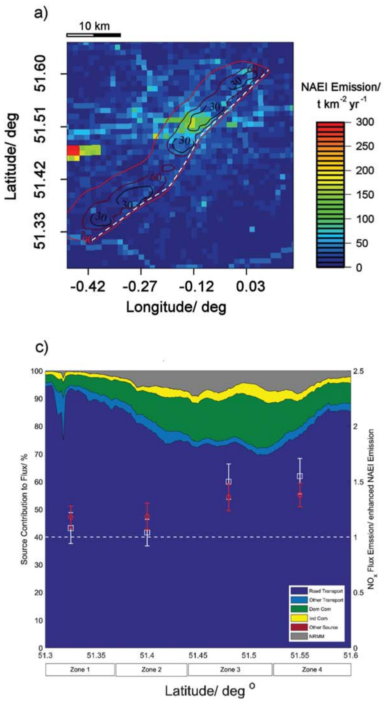

Fig. 3 a) The original footprint calculated using the Drew *et al.* roughness length as in our paper, b) the footprint calculated when we double the roughness length and c) the effect of this on the measured/NAEI emission ratio (white points are the original data, red points are the new data)

James Lee replied: This is a possible explanation. However, as even in central London traffic is estimated to account for around 80% of the NO_x source, it would need the other sources to be severely underestimated (by a factor of several) to bring the inventory in agreement with the measurement. We believe this is unlikely to be the case and therefore think traffic emissions are likely to be the main source of error in the inventory.

Marliyyah Mahmood asked Christian Ehlers: Did you measure and if so what are, the minimum and maximum concentrations of the local ozone production?

Christian Ehlers replied: The comparison to field observations was not done explicitly for the data shown in our paper. In principle, the local ozone production rate can be determined by measurements of RO_x and NO concentrations. Such observations were done from our institute in urban and sub-urban regimes in China and in the vicinity of Berlin and Freiburg. We know from past campaigns using the RO_x LIF technique that in environments with large R_VOC (above 10 s^{-1}) and small NO_x (in the NO_x limited regime) OH is underestimated by our models.[1] In these environments the concentration of HO_2 seems to be correctly calculated by our models (see Hofzumahaus *et al*[2]). In the R_VOC regime below 5 s^{-1}, the ozone production rate was calculated from direct measurements of peroxy radical and NO concentrations using the MIESR technique.[3] The observed

O3 production rate showed a strong increase with a NO mixing ratio between 0.1 and 0.3 ppb, where $P(O_3)$ reached a maximum value of 8 ppb h^{-1}. The dependence of $P(O_3)$ on NO at mixing ratios below 0.3 ppb had a positive slope of 53 ppb h^{-1} per ppb NO. Above 0.5 ppb NO the rate of ozone production decreased linearly with a slope of 3.3 ppb h^{-1} per ppb NO. These experimental data were explicitly compared to model calculations (MCM 3.1) showing good agreement. That gives us reason to believe that our current models can calculate the local ozone production rate from RO_x + NO, but not the degradation rate of VOCs by OH in the NO_x limited regime.

1 F. Rohrer *et al.*, *Nature Geoscience*, 2014, **7**, 559–563.
2 A. Hofzumahaus *et al.*, *Science*, 2009, **324**, 1702–1704.
3 D. Mihelcic *et al.*, *J. Geophys. Res.*, 2003, **108**, 8254.

Franz Geiger opened a general discussion of the paper by David Carslaw: The comment about diesel traffic being unique in central London made me think about the ongoing efforts to increase the share of biodiesel in transportation fuels. How do you think transitioning into biodiesel might affect air quality in London?

David Carslaw answered: For the issues covered in our paper, *i.e.* NO_x and NO2 emissions and concentrations, I do not think that a move to using more biodiesel would make much difference. There could, however, be greater effects on the concentrations of other species such as acetaldehyde.

Francis Pope remarked: Are the vehicle age dependent changes in the NO2:NO_x ratio accompanied by changes in the total NO_x emissions? Also, are the changing NO2:NO_x ratios accompanied by changes in the CO and particulate matter emissions?

David Carslaw responded: We find there has been essentially no change in total NO_x emissions for Euro 4/5 diesel passenger cars with vehicle age, as shown in Fig. 4 below. The CO data for diesel vehicles do not show obvious variation with vehicle age, although the data are noisier. We do not have data for particle emissions.

Paul Monks said to Christian Ehlers: Given that the VOC to NO_x reactivity has changed so markedly over the last 10 years, from about 70% reacting with VOC and 30% with NO_2 to about the opposite situation, would you imagine there would be more HNO_3 formed?

Christian Ehlers responded: The changes in the reactivity contributions of VOC and NO_x which were observed over the past years would lead to the assumption that more HNO_3 can be formed. Up to now we have not measured HNO_3 with our mobile laboratory, but we are considering investigating this topic in the future.

Astrid Kiendler-Scharr added: It has to be pointed out in the first place, that while the relative contribution of NO_x to OH reactivity in urban environments has increased, both the VOC- and NO_x-reactivity have decreased. It seems unlikely that this would result in an increase in HNO_3 formation.

Andreas Skouloudis addressed James Lee: It's interesting that you have this measuring campaign using an aircraft. These campaigns are very expensive but I wish we could have this. My question is: what made you select July as the date for this campaign and not winter? What would your conclusions mean for the annual emissions?

James Lee responded: We chose July as it was a month where we were most likely to get good weather. Conducting low flights over land requires no low cloud and so we decided that this was the best time of year to go for. We would also have found it difficult to fly within the boundary layer in winter, making flux measurements impossible. Funding restrictions did not allow us to conduct two separate campaigns at different times of year. We agree that ideally sampling should take place at different times of year in order to compare measurements with the annual estimate of inventories, however as we were not able to do this we used scaling factors to scale the inventory output to the time of year, day of week and time of day that the measurements were taken (as referenced in our paper).

Tim Murrells said: I value these discussions on the emissions inventory. One thing that is quite clear is that it's crucial to indicate what version of the national inventory you're comparing against. There clearly is an inconsistency with the national inventory's estimates for London, which should be addressed. Some of the differences are due to the fact that the NAEI is an inventory based on national data and trends, which is spatially distributed using some local data. The fleet in London is quite unique. We have been treating London in some more detail in

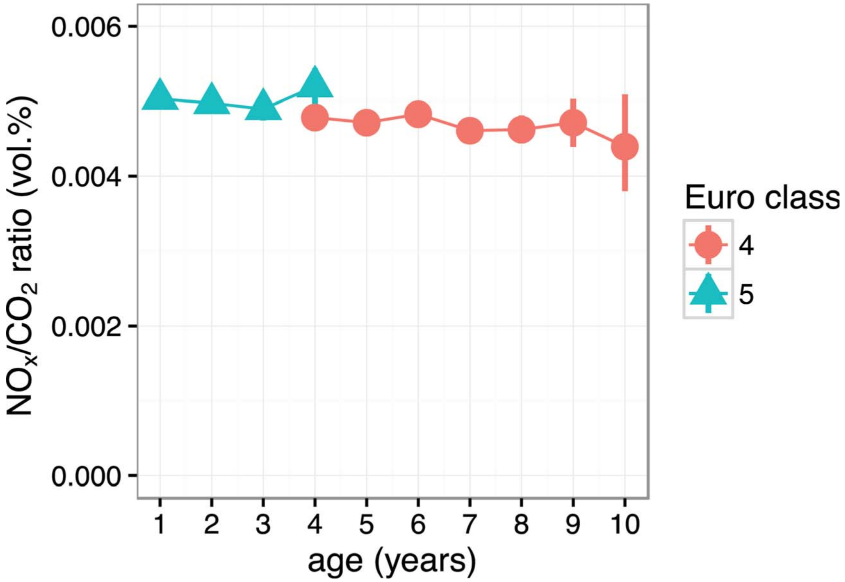

Fig. 4 NO_x/CO_2 ratio for Euro 4 and Euro 5 diesel passenger cars as a function of vehicle age more recent inventory versions using fleet data from TfL, although probably still not as much detail as used in the London Atmospheric Emissions Inventory. Most national inventories use the same source of emission factors, although databases of emission factors can be parameterised in different ways. I believe that the German inventory uses factors from HBEFA which are of the same origin as the COPERT factors used in the UK inventory, namely from the European ERMES source. These are published sources of factors specifically designed for national inventories. Both sources represent real-world emission factors, but factors for Euro 5 and later vehicles are based on tests done on a relatively small number of vehicles and none of the factors take into account recent remote sensing data. I note that the enhanced LAEI uses factors derived from remote sensing as well as more detailed traffic data which would explain the better agreement with your observations. Variability in NO_x and primary NO_2 emissions between vehicles with different technologies, but made to the same Euro standard, can be large and this makes it difficult to represent in an inventory without detailed knowledge of the local vehicle fleet. Another key point when making comparisons between measurements and inventories is how emission factors were parameterised. The NAEI uses simple relationships between average vehicle speed and emission factor which works alright on a national scale, but is not an ideal approach for modelling emissions on a more local scale and on specific roads. Here, a more dynamic vehicle emission simulation model to estimate emissions at a greater time and spatial resolution along lengths of a road would be better, but requires more detailed traffic data.

Gary Fuller addressed David Carslaw: Thanks, David, for the excellent paper. You present your findings as a change in primary NO_2 emissions leading to a repartitioning of NO and NO_2. Looking at London roadside measurements (2010–2014 inclusive) we have seen that about 2/3 of roads have decreasing NO_2, in agreement with your findings (see Fig. 5). However, in these places there's an approximate 1 : 1 correspondence with decreasing NO_x suggesting that NO_2 is being preferentially abated rather than simply emitted as NO. Can you offer insights on this from your review of the technologies? Additionally, in about 1/4 of roads we see increases in both NO_x and NO_2 which suggests that NO_2 might not have peaked everywhere.

1 A. Font and G. Fuller, Roadside air quality trends in London – identifying the outliers: Part 1, King's College London, 2015.

David Carslaw answered: Thank you for your interesting question. Overall I think there is considerable site-to-site variation in both the trends and the NO_2/NO_x ratios from vehicles, as your work nicely shows. One of the key influences for London I believe is the bus fleet, which is both large and highly variable with respect to NO_x – and particularly NO_2 emissions. Our earlier paper[1] shows that there is a considerable variation in NO_2 emissions from the London bus fleet; from almost zero direct NO_2 up to about 40% of the total NO_x. Because bus technologies tend to be associated with specific bus routes, this has the effect of adding additional variation to the estimated NO_2/NO_x ratios for ambient measurements close to London roads. It is challenging, however, to robustly link vehicle flow and type information on individual road links with observed changes and variations in NO_x and NO_2 concentrations. The approach in our paper has therefore focused on determining the overall effects, while acknowledging there is site-to-site variation that is captured well in your work. Finally, it has become increasingly challenging to make these linkages due to the much wider range of engine and aftertreatment technologies used on vehicles.

1 D. C. Carslaw and G. Rhys-Tyler, *Atmos. Environ.*, **81**, 339–347.

Francis Pope inquired of James Lee: Have you compared your NO_x observations with leaf area index or other proxies of plant density? Is there any evidence that plants increase the dry deposition of NO_x?

James Lee replied: We have not specifically looked at leaf area index. It is possible that there could be net deposition of NO_x in areas of London such as the parks, where there is little anthropogenic emission. However, our flux footprint is significantly larger than the area of a single park and thus we believe that any deposition of NO_x to plant surfaces within this will be insignificant compared to the emissions.

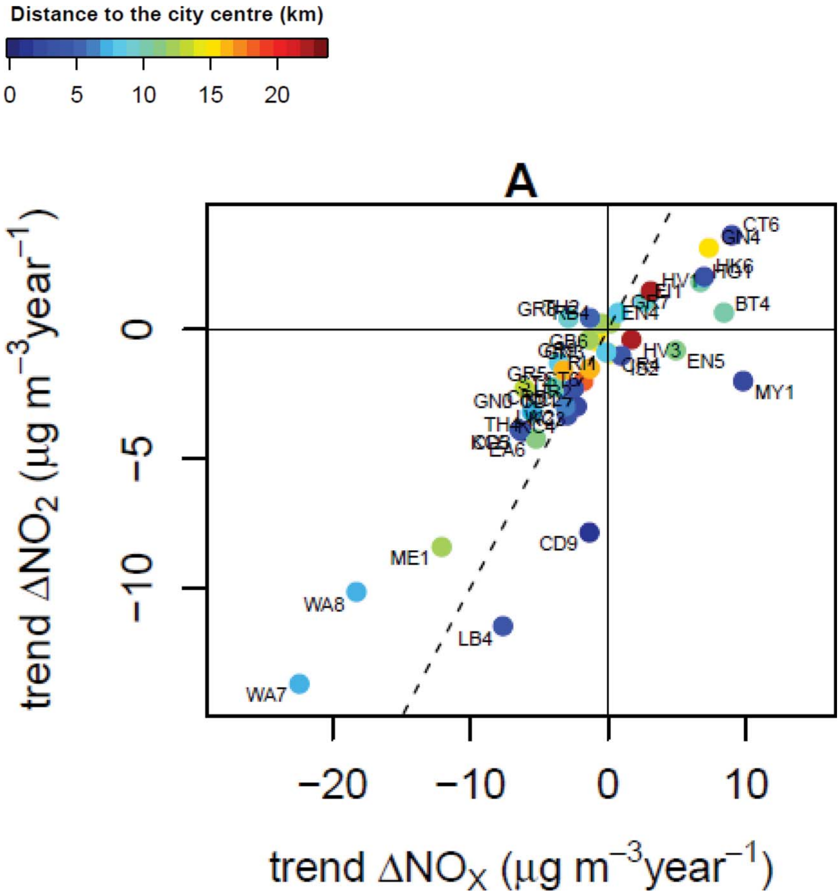

Fig. 5 Trends in roadside increment of NO_2 and NO_x from London 2010–2014. Reproduced with permission from Font and Fuller[1]

William Brune addressed Christian Ehlers: You showed the ozone isopleth diagram with NO_x and VOCs axes and the paths that a pollution plume might take through it. Can you think of a way to do an experiment to test if these paths are really what happens in the atmosphere?

Christian Ehlers responded: The path shown in the paper is a hypothetical pathway for an air-parcel originating from a pollution hotspot in an urban area and ending up in a forest. The starting point as well as the end-point in the forest can be related to measurements in the corresponding regions. The path in-between is based on two assumptions: starting from a pollution hotspot, a plume will be diluted while passing over an urban background region. Dilution here means mixing-in of air containing very much lower concentrations from the background (we have chosen $RVOC = 3\ s^{-1}$ and $RNO_2 = 0.2\ s^{-1}$). This will influence both the VOC and the NO_2 concentrations in an equal manner. So for the first part the trajectory is following a dilution path almost approaching background conditions. Entering a region with biogenic influence, the VOC reactivity will rise due to the biogenic emissions. A further clarification of the assumed path could be done by either installing a network of measuring stations or using a mobile laboratory. In both cases the effort would be high, as not only NO_x measurements but also specified VOC measurements from a mobile-system would be needed to obtain the required time resolution. In the future our mobile laboratory could be used for such a study, following the wind from a pollution source to the endpoint in the forest, because we are working towards such a mobile GC system. It is proposed to complement this type of investigation by releasing an appropriate tracer to track the specific air parcels on their way.

Dwayne Heard commented: When you calculated the ozone production you allowed the model to run for 10 min to allow NO, NO_2 and OH radicals to reach a *quasi*-steady state. Did you vary this at all to investigate any influence of the value on the results? Also did you compare the calculated OH concentrations for the various combinations of VOC and NO_x OH reactivities with any previous field measurements of OH at suitable locations?

Christian Ehlers answered: We tried two different pathways: a) we used a traffic-VOC-mix and a biogenic-VOC-mix dominated by isoprene with 10 min time scale, and b) we used time scales between 5 and 15 min to test the attainability of the *quasi*-steady state. When all important boundary conditions (HCHO/R_VOC ratio, CO/R_VOC ratio, O_3, H_2O, temperature, H_2O_2, HONO, J values, k(NO_2+OH), k(O_3+NO)) were matched, the results were very similar. Regarding your second question on comparison to field observations – please refer to my response to the question from Marliyyah Mahmood.

Louisa Kramer commented: You mention in the paper that ambient NO_2 was detected after conversion to NO using either a molybdenum converter or a photolytic converter. Were the photolytic converters used to replace the molybdenum converters in the ambient monitors? Or were they used in different monitors? Given that molybdenum converters are known to convert other nitrogen oxide species, resulting in an overestimation of NO_2, would this have a large impact on your results?

Christian Ehlers responded: For all the measurements, photolytic converters were used. For the measurements located close to the emission sources, one would not expect the molybdenum converters to cause a substantial artifact. Substances causing such artifacts are not emitted from traffic in large amounts but produced photochemically. As a consequence the artifact will be largest in rural regions and not in urban areas.

Ruth Purvis asked: Please could you explain your techniques for measuring the heavier weight hydrocarbons more fully, especially the sampling systems? Have the losses due to sampling systems (WAS *vs.* tubes *vs.* online) been investigated? As there is discussion as to whether these heavier weight hydrocarbons are actually seen in diesel emissions, are there any plans for a comparison with other measurement systems to rule out instrument error?

Christian Ehlers replied: The exhaust was sampled onto carbotrap cartridges to analyse heavier compounds. The cartridges were heated up to 320°C for desorption in a thermodesorber (Gerstel, Mülheim, Germany). Before separation the compounds where refocussed on cooled empty glass liners which were heated to 350°C for desorption. Transfer lines were held at a temperature of 300°C to avoid compound losses. Liners and transfer lines were passivated with SilcoNert 2000 (SilTek, Bad Homburg, Germany). The separation was performed on a 60 m x 0.25 mm DB1 capillary column which was heated to 320°C. One sample was analysed by both GCs and compared to direct OH loss measurement using laser induced fluorescence (LIF). Here the observed OH loss rate could be explained by the total contribution of the individual compounds measured.

Tim Wallington said: You showed a large reduction of VOCs from traffic over the past 20 years. Do you have an opinion on what the next 20 years will bring regarding NO_x and VOC emission trends from vehicles?

Christian Ehlers responded: Regarding petrol vehicles, the VOC emissions can be attributed to cold start conditions and conditions where the catalytic converter is not working at full efficiency. Here a heating system for the catalyst could increase the efficiency and reduce the VOC emissions. The VOC emissions from new diesel vehicles are quite low and possible further means of reduction will have less effect on atmospheric VOC concentration. For the NO_x emissions, selective catalytic reduction systems as they are used for EURO6 diesel vehicles could be further improved to reduce emissions. For petrol cars these systems could reduce the NO_x emissions in the same way. One point which should be regarded for all the possible emission-reduction systems is the energy consumption of these systems which will in consequence increase the CO_2emissions of such a vehicle.

Roy Harrison asked: Does this work inform us as to what the best strategy would be for the EU to adopt to control tropospheric ozone?

Christian Ehlers responded: In this study we calculated ozone production rates for air-masses close to the pollution sources and the pathway of the dilution to a biogenically dominated environment. The results of our calculation show that the decrease in the VOC/NO_x ratio resulted in decreasing ozone production rates for the regions close to the source and, as a consequence, a decrease of the highest peak concentrations of ozone. The results of this study showed a decreasing ozone production rate related to lower VOC/NO_x ratios for the urban areas. In rural regions where VOC emissions are biogenically dominated the effect could be opposite.

William Bloss said: Is there any significant influence from trends in background ozone levels on the modelled NO_2 abundance (NO_x speciation) for a given emission over the 1–2 decade timescale being explored?

Christian Ehlers replied: The background ozone trend seems to be small (see Fig. 1 in our paper) even on an 20-year time scale. But the NO_x speciation near traffic emissions is strongly influenced by the NO/NO_2 ratio from the car fleet and by the total concentration of NO_x reached at the hot-spots. Close to those hot-spots ozone is typically small and NO very large, sometimes larger than NO_2. As we explained in the paper, Fig. 26 was calculated without taking these effects into consideration. The ozone production rate at these locations would be altered *via* less OH production by ozone photolysis but at the same time affected positively by larger RO_2–HO_2 recycling by NO. We would expect the second effect to be larger, so we would expect larger ozone production rates than anticipated in these hot-spots. Since this effect depends on the concentrations of NO_x relative to background ozone, this problem would be restricted to NO_2 reactivities above 10 s^{-1} (equal to 44 ppb). Below that threshold, NO_x speciation and ozone concentration would approach normal conditions.

William Bloss addressed David Carslaw: The changing (reducing) urban decrement or titration of O_3 in urban environments also provides information on NO_x emissions and speciation - does this offer any additional constraint on trends in NO_x emissions over, for example, the past decade, or is this too spatially broad and imprecise to be useful?

David Carslaw answered: The more general role of O_3 on urban NO_2 trends is an important aspect of understanding the trends over the past decade. Any analysis needs to understand the competing influences of ozone and primary NO_2 emissions. The analysis in our paper using a simple constrained chemistry model accounts for the changes in ozone concentrations over time and the influence on concentrations of NO_2.

William Brune remarked: An experiment has been done on the East Coast of the US where coal-fired power plants have been replaced by natural gas power plants and the levels of NO_x have dropped dramatically. So has the ozone, even in the cities. So I think that the correct strategy to reduce ozone would be to get rid of NO_x.

Paul Monks responded: To add to the European context, it is clear that there is a distinction between the urban and “regional” contexts. In the urban context, reduction in NO_x raises ozone (due to a reduction in NO–O_3 titration) levels, while in the regional context, ozone is clearly mainly under NO_x control. Much of the current situation was summarised in our recent ozone review.[1]

[1] P. S. Monks *et al.*, *Atmos. Chem. Phys.*, 2015, **15**, 8889–8973.

Brian McDonald said: In the U.S., emissions of nitrogen oxides (NO_x) have been coming down from motor vehicles along with volatile organic compounds (VOCs). In general, ozone has decreased in different regions of the country. More stringent VOC control relative to NO_x appears to have been particularly effective in reducing ozone in California. However, we're now starting to see faster NO_x control over VOCs, due to emission controls implemented on power plants, and fuel-switching from coal to natural gas, and new regulations requiring selective catalytic reduction (SCR) systems on heavy-duty trucks. Consequently, the Eastern U.S. appears to be having greater sensitivity to these NO_x reductions. Overall, for all regions to benefit, it is important to just control both NO_x and VOCs.

Tim Murrells commented: Going back to Tim Wallington's question about future vehicle emissions: we have made some emission projections for the UK and it's hard to see how we can do much more for reducing VOCs from road traffic sources, at least for the lighter ones that are regulated. Our projections show that there will be much greater VOC emissions from other sources that need to be targeted. The big issue for road transport is NO_x and whether the new Euro 6 regulations based on Real Driving Emission test procedures (RDE), to be introduced from 2018, will deliver the anticipated reductions from diesel cars and vans. Our NO_x emission projections are critically dependent on this.

André Prévôt commented: I disagree with the statement that we have done everything we could regarding VOCs in the transport sector. There is more room to improve VOCs from gasoline cars, especially during cold starts.

Ruth Doherty said: I would suggest caution with the usage of “region” in seeing ozone reductions with precursor emissions controls. For the Task Force on Hemispheric Transport of Air Pollution[1] we have performed experiments to assess the ozone response to substantial (20%) emission reductions. In many mid-latitude regions, notably considerable parts of China and the Middle East as well as areas in Europe, we find ozone increases in response to emissions reductions all year round (due to reduced NO_x titration). Only when we move to the sub-tropics do we see year round regional ozone decreases due to 20% emission reductions, possibly due to less limitation on photochemistry that would reproduce ozone from NO_2.

[1] Hemispheric Transport of Air Pollution, www.htap.org

Rob MacKenzie asked Christian Ehlers: How will you communicate Fig. 26 of your paper to the transport sector and to policy-makers? The trajectories depicted on the figure seem to imply that the partial adherence to policy between 1994 and 2014 has had the “happy accidental consequence” of moving urban air to part of the “response space” in which ozone production is lower than it would have been if policy had been rigorously adhered to.

Christian Ehlers responded: In the 1990s, policy makers in Germany and elsewhere tried to decrease the concentration of ozone near the surface. At that time, ozone was known to be an important risk to human health and for the production of crops. For that reason, the catalytic reduction technique for VOC and NO_x emissions of petrol cars was introduced to meet the more and more stringent legislation for car emissions in Europe. Diesel cars were rare at that time and were believed to be environmentally preferable because they had fewer engine-emissions and lower fuel consumption compared to petrol cars. The subsequent shift in the passenger car fleet from petrol to diesel cars which took place in the last 20 years was therefore politically supported. The principle technical difficulty for diesel cars in reducing NO_x emissions was somehow overlooked. Although the photochemical principles shown in our Fig. 26 were known 20 years ago, we do not think that the strong reduction of VOC, and the very small reduction of NO_x, traffic emissions occurring in Germany were intended. Nevertheless, the original political intention to reduce the ozone problem was achieved. You may call that accidental. A good deal later than the first efforts for the reduction of ozone, there was a certain change in the line of action. Besides the regulation of car emissions, ambient concentrations of pollutants like NO_2 were recognized to be health risks on their own account and were therefore limited by the European legislation. And that is the situation nowadays.

Nick Hewitt remarked: There is a question as to whether or not street trees are beneficial to urban air quality – it is a highly topical and important question, but is difficult to answer. Trees in cities have at least four effects on air quality: 1) trees can enhance deposition of pollutants by increasing surface area and enhancing deposition velocities: modelling shows that enhanced deposition to trees can only have an appreciable effect on air quality when acting on a relatively small volume of air within a street canyon. 2) Trees are an important source of VOCs and can then contribute to SOA and ozone formation: whether this is significant for air quality depends on the local chemistry, but in any case any effects will probably occur downwind of the source region. 3) Trees planted in an urban street canyon can reduce ventilation and so reduce mixing of background air from above into the canyon, which can potentially dramatically increase street level concentrations of pollutants. This decrease in mixing is possibly the most important effect. 4) CFD modelling has shown that street trees can increase dispersion, hence reducing street level concentrations in some places and increasing them in others. It is therefore highly likely that planting significant numbers of trees in city centres may be beneficial to air quality in some circumstances, but detrimental to air quality in others. There is more information on this in work by Pugh *et al.*,[1] McDonald *et al.*[2] and Donovan *et al.*[3]

1 T. A. M. Pugh, A. Robert MacKenzie, J. Duncan Whyatt and C. Nicholas Hewitt, *Environ. Sci. Technol.*, 2012**46**, 7692–7699.
2 A. G. McDonald, W. J. Bealey, D. Fowler, U. Dragosits, U. Skiba, R. I. Smith, R. G. Donovan, H. E. Brett, C. N. Hewitt and E. Nemitz, *Atmos. Environ.*, 2007, **41**, 8455–8467.
3 R. G. Donovan , H. E. Stewart , S. M. Owen, A. R. MacKenzie and C. N. Hewitt, *Environ. Sci. Technol.*, 2005, **39**, 6730–6738.

María Cruz Minguillón responded: This is clearly an interesting point. To properly quantify the different effects caused by the presence of trees on the air quality, which may be opposite in terms of increasing or decreasing ambient PM concentrations, further research is needed. I would be interested in Neil Donahue's opinion on this.

Paul Monks commented: To add to the comments on the role that trees play in the urban atmosphere – a further role is illustrated in our recent paper[1] in that trees across an urban landscape can act to disperse pollution. In this modelling study it was shown that trees caused a net dispersion of 7% for a pollutant across urban Leicester.

1 A. P. R. Jeanjean, G. Hinchliffe, W. A. McMullan, P. S. Monks and R. J. Leigh, *Atmos. Environ.*, 2015, **120**, 1–14.

Nick Hewitt replied: It is important to recognise that placing trees in an urban street canyon can inhibit downward mixing of background air into the canyon, thus elevating street level pollutant concentrations, but can also cause greater turbulence within the canyon, aiding dispersion, as shown in the paper you mentioned. This latter effect will cause street level concentrations to fall in some places but to rise in others as the pollutant emissions become more effectively mixed at street level. Whether trees are good for urban air quality is obviously a difficult, and site specific, question to answer.

Andreas Skouloudis remarked: I would like to reassure you that we have used Ehlers' graphs, both during the first and second AutoOil programmes, and the industrial partners were fully aware of their importance for the emission reductions of ozone precursors. What is interesting is that this paper is the realisation of actual emission reductions over the years, and what these reductions meant for regional ozone.