Atmospheric
Chemistry
and Physics
Discussions

Open Access

Interactive comment on "Source apportionment and the role of meteorological conditions in the assessment of air pollution exposure due to urban emissions" *by* K. Schäfer et al.

K. Schäfer et al.

klaus.schaefer@kit.edu

<The topic of meteorological influences upon nearly all air pollutants is studied in a comprehensive view for the first one. The meteorological influences upon each measured PM component (4), gaseous pollutant and VOC (7), size fraction mass (2 modes) and number concentration (5 modes) as well as positive matrix factorization (PMF) source factor (8) are presented here. These data are measured in one-hourly temporal resolution at the same time in the same urban atmosphere during a high air pollution event in winter. It is shown by correlation analyses that these influences can explain major parts of certain PM compound and gaseous air pollutant exposure. These influ-

ences were investigated already by Tai et al. (2010) for PM2.5 concentrations but not for PM compounds and gaseous air pollutants, Wen et al. (2010) for air pollutants but not for PM compounds, Wu et al. (2013) for daily mean values only and Tandon et al. (2010) for eight-hourly mean data only. Finally, the comparison of our results with those from Paris during the MEGAPOLI campaign (Crippa et al., 2013) shows: same temporal resolution, study in comparison with meteorological parameters, but no detailed correlation analyses as done there, i.e. no comparable analyses results. We like to comment generally that we did not describe all results of our complex statistical analyses of measured data. We selected those results, which are necessary to describe the main outcomes of the paper and to justify those. Naturally, we discussed those results which were important from our point of view. But we understand the reviewer comments and added additional results as the heatmaps of all measurement periods into the supplements.>

Review 1: The paper presents the results of a comprehensive measurement campaign that took place in Augsburg in winter. An impressive array of instrumentation was used, monitoring meteorological parameters as well as gaseous and particulate species with ultrahigh time resolution. The results were mostly interpreted in an overly simplistic way, i.e. by various complex statistical methods. This type of approach is certainly not the most elegant one, since it totally ignores well-known casual relationships that exist between various gaseous pollutants and aerosol sub-modes. <We did not ignore these relationships. All measured data are from an urban background site only and not from sites inside and outside the city. So we could study the statistical relations between these compounds at one site only. There we investigated the relationships between different compounds and between these compounds and meteorological parameters. Not only PM compounds but also different aerosol sub-modes (particle number concentrations (PNC) in 5 different size modes ranging from 3 to 500 nm) and PMF derived factors from the analysis of particle size distributions (PSD) have been investigated. In Figure 4 these correlations are shown for the total measurement period. As there are differences between the different phases we added the heatmaps with the Pearson

intercorrelations of compounds, particle size sub-modes and source factors for all 10 phases in the supplements (Figure S2). The meteorological influences, which are different from temporal phase to temporal phase, are shown for three groups of phases of similar behavior and the special phase (Figure 6). The discussed gaseous pollutants and aerosol sub-modes are e.g. NOx, NH4+, OOA. The concentrations of these compounds vary with the age of the particles and could not be studied. Freshly emitted carbonaceous aerosols for instance mainly exist as an external mixture (PMF factor based on PSD: fresh traffic aerosol). In contrast, chemical and physical (coagulation and condensation) processes and coating or secondary aerosol formation (mainly water-soluble organic compounds, SO42- and NO3-) do not only change the mixing state but also morphological features and size of PM. The aerosol sub-modes related to secondary aerosol are summarized in one PMF factor from PSD (secondary aerosol) only.> However, it might be quite useful to find relations between certain meteorological parameters (e.g. wind direction) and pollution profiles. In spite of the deployment of extensive monitoring instrumentation, most of the conclusions are rather trivial and have been established previously in many studies. The fact that low mixing layer height and low wind speed lead to elevated pollution levels and cause the exceedance of PM limits is an example of such trivial statements. Another trivial message is that variations in the level of pollution are mainly due to changes in meteorological conditions and not in emissions. <We summarize here the main contents of the paper which justify their publication: - First, it is hypothesised that the MLH and other meteorological parameters influence not only gaseous air pollutants but also PM compound concentration and PSD. The data material is sorted by means of definition of temporal phases with relatively constant levels of PM concentration and composition, PMF factors, which are determined from chemical composition and particle size distribution, temperature as well as wind speed and wind directions. 10 phases are found and used for correlations: âĂć The relatively high mass concentrations of PM1, PM2.5 and PM10 (6 of the 8 limit value exceedances) were accompanied by higher organic and SO42- content as well as high NO3- content in PM1 and the highest detected CO, NO and NOx concen-

trations. This was correlated with the lowest wind speeds (below 7 m/s), south-easterly wind directions (influence of road traffic) and temperatures which are mostly below 0°C. âĂć The relatively very low mass concentrations (PM1, PM2.5, PM10) occurred during high organic content in PM1 and some peak CO, NO and NOx concentrations. The correlations provided the highest wind speeds (up to 14 m/s) with wind directions from west-southwest to south-southeast (influence of university and residential areas, edge of the city) and the highest temperatures (up to +13°C). This shows the well-known influences of emissions, advection and mixing upon PM compound and gaseous pollutant concentrations. Further, emissions and temperature influence the chemical composition of ambient air including PM with some specifics in the case of the sampling site in Augsburg. So, the first hypothesis is correct. - Second, it is hypothesized that a basis of one-hourly mean data provides the possibility to differentiate the relevant processes as emissions, transport and mixing as well as photochemistry which are of different temporal variation during the day. These data enable the study of the local as well as the regional scale and thus to find out the reasons for PM10 limit value exceedances as well as variations of particle size distribution, chemical PM characteristics and air pollutant concentrations. The hierarchical clustering analysis with the Ward method was applied to provide a deeper understanding in comparison to other studies of high temporal resolved data of urban air pollution: âĂć Wind speed (negative), wind direction, mixing layer height (negative) and relative humidity (positive) influence primary pollutant (including CO and benzene) and accumulation mode particle concentrations. âĂć Temperature (negative), absolute humidity (negative) and also relative humidity (positive) influence secondary PM compound and fine particle concentrations. It is a new result that secondary aerosol forming processes are dependent from meteorological parameters including absolute humidity. âĂć Ultrafine particle and fresh traffic aerosol concentrations are mostly driven by emissions. This is supported by the circumstance that the specific particle size distribution during relatively "clean" air mass does not provide enough particle surface for coagulation of ultrafine particles. In this sense the second hypothesis is approved. - Third, the new results, presented

here on the basis of hourly-mean data and thus daily variations, provide more detailed information about the processes to be simulated in circulation and chemistry transport models. These models are applied to calculate influences of climate change upon air quality. The statistical investigations of meteorological influences upon PM compounds and gaseous air pollutants as shown here for nearly all air pollutants present more implications for the sensitivity of PM compounds and gaseous air pollutants to meteorological parameters and as a consequence to a change of climate.> A critical issue of source apportionment measurement is whether secondary organic aerosol component could indeed be predominant in winter or it is just an artifact resulting from biased source profile assignment (e.g. due to improper consideration of temperature-dependent partitioning of organic compounds). This is a promising question that is not exploited in the paper despite the wealth of available data. Since semivolatile VOCs are generally more abundant in emission plumes than their aerosol-phase counterparts, and condense readily at low temperatures followed by chemical transformations, they may add to the identified SOA components in the particles. This process may not show up well in a statistical study using real-time correlations, since an undefined time-lag exists for their formation depending, for example, on irradiation which was not monitored during the study. <We agree with the reviewer that the origin of the OOA factor derived from PMF analysis of aerosol mass spectrometry (AMS) data to be predominant of secondary origin can be questioned. From AMS measurements it is not possible to unmix the complex multiphase processes leading to the formation and transformation of SOA in ambient aerosols. For instance it is not possible to differentiate products from homogenous gas-phase oxidation followed by condensation of lower volatile products onto particles (SOA) from products formed from (heterogeneous) oxidation of condensed or adsorbed compounds in the particle phase (aging). The interpretation of the OOA factor to be strongly associated with SOA has been discussed by Elsasser et al (2012) and we refer to this. From PMF analysis and similarities with profiles observed from wood combustion aerosols it was discussed that some parts of the OOA could be originated from primary particles from wood combustion, too. On

C4489

the other hand, the observed diurnal profile of the OOA with maximum concentration during daytime, when with higher photo-oxidative activity and higher temperatures, was discussed as indication for secondary aerosol formation. The high correlation of both secondary aerosol factors, which is discussed in our study (OOA from AMS data and secondary aerosols from PSD data, r = 0.89, see Table S2), is another indication for OOA being predominantly of secondary origin.> It can be stated that a good tropospheric chemical model backed up with the measured high-resolution chemical and meteorological data may have improved our understanding to a much larger extent than the current statistical exercise did. <We agree totally with this statement. But this would be another study and paper. Our statistical study provides information from experimental data. This is an advantage because a tropospheric chemical model requires an emission inventory, which is not available for real time conditions normally. Further, a scaling problem exists. Appropriate to the point measurements a small-scale or box model is required with a corresponding emission inventory which must be determined also. Finally, general circulation and chemistry-transport models, which are applied to calculate the influences of climate change upon air quality, need detailed information about the processes to be simulated. The statistical investigations of meteorological influences upon PM compounds and gaseous air pollutants, as shown here for nearly all air pollutants, provide such information in the present atmosphere (see also Tai et al., 2010).> However, there is some potential in the statistical evaluation of the data which is not exploited in the paper. For example, variations in the nitrate-to-OOA ratio may reveal some interesting features. In general, correlations between various derived parameters could have been more useful than between absolute values. There is a lot more potential in chemical data that would corroborate the somewhat arbitrary and fixed source categories set up by the authors for their statistical analyses. These source categories are in fact far from being confined, they do evolve into one another under certain conditions (e.g. fresh traffic emission ages into aged one with corresponding shifts in size distribution and chemical properties, etc.). It could have been interesting to see focused case studies on specific nucleation episodes, etc. <We fully

C4490

agree with the reviewer with regard to the potential of additional data analysis being carried out. One example is of course the mentioned ratio of NO3- to OOA and its dependencies from (or correlations with) the various parameters investigated. This is one example that was investigated to some extent by us. To summarize our observations it could be stated that the ratio is similar in most phases (see these data in the improved supplements also) except phase 4, which is discussed separately. The ratio of SO42- to OOA was even more stable. No clear dependency of the ratios with any of the meteorological parameters was observed. We also agree that there's much more data that would corroborate our results. The source categories we investigated are result of a separate investigation (Gu et al., 2011). It was one aim of our data analysis to investigate dependencies or correlations of these source factors to other aerosol properties and meteorological parameters. The result from the statistical data analysis we've chosen for these investigations (hierarchical clustering) allowed a deeper understanding of mechanisms involved in urban air quality. Regarding the proposal to focus on nucleation episodes we only can say we very much would have liked to include such events in our study. Unfortunately, we did not observe a nucleation event during our measurement period. On the other hand, we observed one special phase with high PM concentrations. This phase 4 is separately discussed as a special event.> Overall, the paper is not very innovative in using the very valuable measurement database and its standard certainly needs major improvement before consideration for publication in ACP. <Major improvements are performed as described above.>

Review 2: The paper presents correlation between sets of data with concentrations of gaseous air pollutants, PM composition (organic & inorganic), PM size distribution and meteorological parameters. This is a topic relevant to ACP. The PM composition data and the source apportionment have been already published by Elsasser et al. (2012). In this paper the data are presented together with concentrations of gaseous air pollutants and the meteorological data which adds a dimension to the data presented by Elsasser et al. (2012). Cross correlations between this extensive set of parameters are presented. Drivers behind the observed concentrations (emissions/meteorology) are

identified with help of these correlations. Not much is said about the statistical methods used in the paper. <The statistical analyses performed in this paper are described in Section 3.4. Pearson correlation is a standard tool to examine the relationship between two variables. Since the variables are measured in different units, we utilized standardized data for all analyses. Hierarchical cluster analysis is a standard tool to examine groups of "similar" variables that can be grouped in clusters. The similarity of the variables can be examined by different methods or algorithms. One of the most known and utilized methods is given by Ward (Ward, 1963), also known as "Ward's minimum variance method". This method aims at finding compact, spherical clusters by examining the variance between cluster members. The heatmaps presented in all figures are just a color-matrix representation of the Pearson correlation coefficients with the dendrogram obtained after the clustering printed on the margins of the heatmap.> There is no reference given to the hierarchical clustering analysis with the Ward method. It is therefore difficult to assess if the method is the most suitable. <The Ward method for hierarchical cluster analysis is a very well-known and popular method. We assumed that no reference was necessary, but this is now included in the paper.> For such a complex dataset with many dependent variables one would expect use of the Multivariate Analysis of Variance to investigate the effects of independent variables on dependent ones as well as the interactions between the dependent variables. <Multivariate analysis of variance (MANOVA) is indeed an appropriate tool to examine the interactions between a set of dependent versus independent variables. However, there are two inconveniences of applying MANOVA in our study: 1) To make the best use of MANOVA, an a-priori knowledge of the possible nature of each variable (i.e., dependent or independent) is required. In some cases, the heatmaps can provide hints to discover such dependencies. However, without more input information to differentiate independent from dependent variables and given the large number of variables available, the MANOVA analysis could be of considerable dimension and complexity (which is beyond the scope of this paper). 2) MANOVA works best when there are only moderate correlations between variables. However, several of our variables are very

highly correlated (e.g., Figure 4: two orange/red squares at the top-right and bottom-left corners are clearly visible). This suggests that there is not a lot of variance left to be explained for linear models between these variables. The Pearson correlation cluster analysis provides similar conclusions as a MANOVA analysis (albeit with a more descriptive than inferential approach): dependency relationships between variables are examined. The goal of our study is limited to explore such relationships in different time phases and between different components.> Taking the lack of methodology description into account the conclusions of the paper are not strong and only qualitative. <This is discussed for the first review already. We concentrated and re-formulated the main parts of the paper.> The presentation is well structured, however, the text is in places rather difficult to follow as there are very long sentences and a large number of abbreviations. <This is improved.>

Please also note the supplements to these comments: - The revisions in the manuscript with the revised supplements of the manuscript.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C4485/2014/acpd-14-C4485-2014-supplement.pdf

---

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 2235, 2014.