

Interactive comment on “Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides” by C. Degrendele et al.

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melymuk@recetox.muni.cz

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Below please find the reviewer comments, followed by author responses to each comment.

Reviewer #2:

General comments Data on size distribution of CUPs are scarce. Results of size distribution of CUPs in this paper improve our understanding of the impact of CUPs on human health and also on the environmental fate of CUPs. Data of this work is in good

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quality. However, some data description or discussion parts are not attractive enough and purpose of few parts of the discussion is not clear, so I suggest to rephrase them (see details in the specific comments).

Specific comments P2: The words 'certain compounds', 'other compounds', 'nine pesticides', 'four pesticides' make the abstract sounds like this paper only report data or phenomenon while there is a lack of an explanation of the data. I suggest to rephrase the sentence in a more attractive way. P2 L16: I suggest to clearly state how is the “anomalous partitioning...suggesting the influence of current pesticide application on gas- particle distributions”. P2 L19: Generally, 'find particles' means PM_{2.5} (<2.5 μm). Fine particles can reach lung via breathing. Here, if health effect of the size distribution of pesticides is emphasized, it is better to choose 2.5 μm as the cut point.

Author response: Thank you for the suggestions. Given the considerable improvement on the gas-particle partitioning section, we have considerably modified the abstract and improve the clarity. The modified part of the abstract now reads: “Major differences were found in the atmospheric distribution of OCPs and CUPs. The atmospheric concentrations of CUPs were driven by agricultural practices while secondary sources such as volatilization from surfaces governed the atmospheric concentrations of OCPs. Moreover, clear differences were observed in gas-particle partitioning with an influence of adsorption onto mineral surfaces for CUPs while OCPs were mainly partitioning to aerosol through absorption. A predictive method for estimating the gas-particle partitioning has been derived for polar and non-polar pesticides. Finally, while OCPs and the majority of CUPs were largely found on fine particles, four CUPs (carbendazim, isoproturon, prochloraz and terbuthylazine) had higher concentrations on coarse particles (>3.0 μm), which may be caused by the application technique. This finding is particularly important and should be further investigated given that large particles results in lower risks from inhalation (regardless the toxicity of the pesticide) and lower potential for long range atmospheric transport. “ Regarding the suggestion of 2.5 μm as the cut point, unfortunately in this case we are limited by the instrument chosen. For

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the size specific determination, we used a Tisch Environmental cascade impactor, and cut points were 0.49 μm , 0.95 μm , 1.5 μm , 3.0 μm , 7.2 μm and 10 μm . This provides us with a lot of information on the particle size distribution of the pesticides, but does not allow us to distinguish exactly at the 2.5 μm cut point.

P3 L14: "Finally, pesticides can volatilize from soils, plants and from old industrial sites." Volatilization from water bodies (e.g. ocean, lake) should be included. Actually, that means volatilization of pesticides happen during all kinds of air-surface exchange of pesticides.

Author response: We have corrected this. The text now reads: "Finally, pesticides are affected by air-surface exchange such as the volatilization from plants and soils, surface waters, and from old industrial sites (Cabrerizo et al; 2011)."

P5 L1: For study of gas/particle partitioning, why collect PM10 but not total suspended particles (TSP)?

Author response: To study gas-particle partitioning, we were limited by the high-volume air sampler from the on-going air monitoring programme, which had a cut off of 10 μm . However, at typical Central European rural sites, the majority of TSP by mass is captured within the PM10 category (e.g., 90-91%, from Gomišček et al., 2004, Atmospheric Environment), and so we believe this does not significantly bias the results.

P7 L20: what does "timing" mean? The seasonality of detection frequency?

Author response: We have clarified this. The sentence now reads "In general, the detection frequency of CUPs [...] (Table 1)."

P7 L21: "their persistence in the environment". But this section "3.1 Detection frequency at the background site" don't discussed the relation between detection frequency and the persistence of pesticides.

Author response: This section does not discuss the persistence of individual compounds but the detection frequency brings information relevant to environmental per-

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sistence. For example, CUPs which were not in use (e.g. fenitrothion, simazine and terbufos) were not detected or infrequently detected (<6%), suggesting less environmental persistence, in contrast to all OCPs, which were detected in more than half of the samples although they have been banned for decades, demonstrating their high persistence.

P9 L8-23: I am not clear this part of discussion is for explanation of which part of the data.

Author response: We agree with the reviewer that the logical flow of the discussion was not clear, and have adjusted accordingly. These sentences have been replaced with the following text: "The lack of correlation may be caused by the use of a national pesticide usage database obscuring regional differences, which are of importance given the relatively low atmospheric residence time of CUPs (Coscollà et al., 2013b). Moreover, the pesticide physicochemical properties, their environmental persistence and the pesticide application technique used (e.g., seed treatment vs. spray application) may also influence the atmospheric concentrations of CUPs. Indeed, spray application parameters such as the volatility and viscosity of the pesticide formulation, equipment, weather conditions at the time of application (wind speed and direction, temperature, relative humidity and stability of air at the application site) and operator care, attitude and skill have been identified as factors that influence the emission of pesticide droplets to the air (Gil and Sinfort, 2005), thereby affecting local air concentrations."

P10: "3.3 Seasonal variations at the background site". Do the seasonal variations of pesticide concentration relating with air masses from different regions in different seasons? How about evaluating the air mass back trajectories (e.g. with the open software HYSPLIT).

Author response: We appreciate the suggestion. We investigated whether HYSPLIT would provide us with greater insight into the seasonal variations, but unfortunately the wind directions/back-trajectories do not provide additional information. On a local

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scale, the land-use surrounding the background site is agricultural in all directions in ~50 km radius of the site. Therefore, a back-trajectory in any direction would pass over many km² of agricultural fields, and no direction would clearly dominate as a source of emissions over any other. Similarly, on a larger scale, no clear source region is apparent; Central Europe is dominated by agricultural land use (Czech Republic is 55% agricultural land, and other countries in the region are also highly agricultural (Germany – 48%, Poland – 48%, Slovakia – 40%, Austria – 38%, Hungary – 60%; data from World Bank database - <http://data.worldbank.org/>). So, for this particular area, back trajectories do not help significantly in interpretation of seasonal variations.

Reviewer #3:

Review of “Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides” This manuscript reports a novel data set on the occurrence, gas-particle partitioning and size distribution of a number of pesticides. This is already a nice contribution. On the other hand, there is some discussion on the processes driving this occurrence and partitioning, but my impression is that this side of the manuscript lacks of novelty, and does not make a great contribution. In any case, as the data set seems to be of good quality (and it is novel) I suggest that this manuscript can be published after some modifications in the discussion.

Specific comments: - Gas-particle partitioning is thought to be a fast process (fast response times to equilibration). I doubt that concurrent emissions lead to lack of equilibrium between gas and particle.

Author response: We agree with the reviewer that equilibrium between gaseous and particulate phases is generally a fast process (although for compounds with logK_{oa}>10 such as PBDEs, previous research have pointed out that G/P equilibrium may not have been reached months after emissions, see Cetin and Odabasi, 2008, Chemosphere and Li et al., 2015, ACP). We have now considerably modified the section on gas-

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particle partitioning.

- Page 23653, line 13-15. These two statements need a citation or two.

Author response: We have now included two citations related with those statements (Glotfelty et al., 1989 and Cabrerizo et al., 2011).

- Page 23653-line 21. In addition to Pankow 1987, other papers have contributed to substantiate this statement.

Author response: We have now added the references to two reviews about gas-particle partitioning by Cousins and Mackay, 2001 and by Lohmann and Lammel, 2004.

- Page 23655, line2. The average sample volume was above 4000 m³, which it looks too much for a temperate region. I wonder about the breakthrough of some of the compounds. This potential artifact should be evaluated before the assessment of gas-particle partitioning. Looking at tables S6 and S7, it seems that potential breakthrough is observed for HCHs, metribuzin, isoproturon, and few others. The nice fact, is that the breakthrough has been evaluated for each sample, and therefore, when it is detected, my impression is that those particular samples should not be used for assessment of gas-particle partitioning.

Author response: The breakthrough experiments took place only in 2012 for 26 samples for both OCPs and CUPs. In 2013, the two PUFs were analyzed together. So unfortunately we cannot use this information to exclude particular samples from the overall dataset. Based on this breakthrough experiment, several CUPs were previously removed from the results. We appreciate the suggestion regarding HCHs and metribuzin, and agree that since breakthrough happened in some cases and that these compounds were infrequently detected (in the particulate phase or in general), we removed them from the section on gas-particle partitioning. In case of isoproturon, this compound was detected in 13 samples in the upper PUF and only once in the lower PUF. Thus, the breakthrough of isoproturon seems to be minor and the sampling proce-

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ture with 2 PUFs and such high volume is considered appropriate for trapping this compound in the gaseous phase. The manuscript now includes: "It has been well known that several sampling artifacts such as blow-on, blow-off, breakthrough and degradation may occur and affect the results about gas-particle partitioning (Melymuk et al., 2014). The reported gas-particle partitioning of pesticides are therefore operationally defined, given the sampling configuration, where gas-phase is defined as the mass of the sample captured on the PUF and particulate-phase is the mass captured on the QFF. Given the large volumes used in this study, breakthrough tests were performed (Table S7) and HCHs were excluded from the discussion of gas-particle partitioning to avoid any bias due to gas-phase breakthrough sampling. Breakthrough is typically the most significant sampling artifact; bias due to filter blow-on/blow-off is not expected to be significant (Melymuk et al., in press)."

- Page 23661. I guess that recent application and surface-air exchange are important processes for explaining the atmospheric occurrence of OCP (Cabrerizo et al. ACP 2011) and CUPs. For CUPs, it is possible that a relevant fraction of them is degraded after weeks/months of application, which would explain a lack of maximum values for the time periods with higher temperatures.

Author response: We have now added the reference to the study from Cabrerizo et al. We also added a statement about the rapid atmospheric degradation of some CUPs. The manuscript now includes "This is in agreement with a previous study showing that atmospheric levels of OCPs at different European background sites were controlled by air-soil exchange (Cabrerizo et al., 2011)." and "For some CUPs, their atmospheric lifetime in relation with OH reaction is relatively small (e.g. about 2 hours for chlorpyrifos, (Muñoz et al., 2014)), which may explain the lack of maximum concentrations observed during the warmest periods."

- For many CUPs there is no previous literature on volatilization and gas-particle partitioning, but for some CUPs and especially HCHs and DDTs the literature is abundant and should be cited and discussed. Alternatively, there are studies on soil-air parti-

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tioning of pesticides (for example the recent Davie-Martin EST 2015) that could be tentatively used for assessing gas-particle partitioning.

Author response: Thank you for the interesting suggestion. As a consequence, we have now significantly modified the section on gas-particle partitioning. These changes are highlighted in the proposed revised manuscript which is currently included as a supplement. Indeed, we plotted $\log K_p$ vs. $\log K_{oa}$ and $\log K_{sa}$ and found significant correlations for both OCPs and CUPs. However, major differences were observed for CUPs, with a higher K_p for similar K_{oa} , revealing the influence of adsorptive contributions to K_p . The predicted soil-air partitioning coefficient derived by Davie-Martin et al; (2015) was found to be a really good predictor of gas-particle partitioning of pesticides.

- Figure 2 and 3. The aerosol type may be different for different seasons, thus different OC type, leading to different partitioning. In addition there is an important uncertainty on the KOA temperature dependence. I doubt that these plots can be used to say anything about lack of equilibrium.

Author response: We have now moved these figures into the SI.

- I would appreciate to see a K_p versus K_{oa} plot for the different compounds and sampling events.

Author response: We have now included different figures of K_p vs K_{oa} and K_{sa} for all samples, and also for spring and autumn.

- The manuscript makes a contribution with a novel dataset. The size distribution work is also a nice contribution. However, I think that the gas-particle partitioning assessment should be significantly improved in order to make a clear contribution to the field.

Author response: We appreciate the suggestion and believe the addition of the comparison with K_{sa} , and more thorough discussion of the important factors in CUP partitioning has helped to significantly improve the discussion of gas-particle partitioning (section 3.4).

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Reviewer #4: This manuscript reported measurements for selected OCP and CUPs in air at two atmospheric monitoring stations in Czech Republic. The novelty of this work is several current used pesticides have been detected in certain atmospheric samples. As for the part of gas-particle partitioning of OCPs and CUPs, I am doubt if the air sampling method used in this work is applicable to fulfill this proposal. As it is described in the manuscript, a high-volume air sampler was used to collect weekly air sample, with an average of 4310 m³. It is well known that there are several weaknesses to use highvolume air sampler for the determination of gas/particle partitioning for semi-volatile organic compounds. First, fine particles less than the pore size of the QFF may penetrate the filter and part of them can be caught by the PUF. Second, with 7 days sampling time, particle-bound OCPs or CUPs may happen with desorption and enter into gaseous phase. These aspects may lead overestimated gaseous concentrations for both OCPs and CUPs. Especially for the polar CUPs, their occurrence in the gaseous phase might be just caused by the fine particles caught by PUF slice. Therefore, such samples can only provide a sum concentration of OCPs and CUPs in the atmosphere, and are not efficient for evaluation of gas/particle partitioning process at all. Moreover, as the authors intended to compare the gas-particle partitioning of and size distributions of both OCPs and CUPs, the factors, e.g. the fraction of total organic carbon in the particles and humidity of air which could affect the partitioning process of OCPs and CUPs should be included in the study as well. However, there are no such data available to support the dada analysis. Furthermore, there are many studies have been published for OCPs in rural atmosphere, and some CUPs have been included as well. As the CUPs have relatively high polarity, their gas/particle partitioning behaviors may differ to the legacy OCPs, and should be highlighted in the discussion of the manuscript However, this issue is not presented in the manuscript. Overall, it seems that the entire work such as sampling method and sample analysis have not been systematical organized that the measurements of this work could not support a reliable evaluation for seasonal gas/particle partitioning and size distribution of CUPs. I guess this manuscript is hard to be accepted for publication in ACP.

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Author response: We appreciate the reviewers concerns regarding the sampling method, but we disagree that high volume air sampling is inappropriate to characterize gas-particle partitioning. Any air sampling method is susceptible to sampling artifacts based on the design of the sampler and choice of sampling media, and it is true that to some extent, the discussion of gas-particle partitioning is operationally defined based on where the cut-off between gaseous and particulate phase is chosen. However, these inherent challenges in air sampling should not preclude us from attempting to infer information from air sampling, assuming appropriate actions are taken to reduce sampling artifacts as much as possible. High volume air samplers are an extremely commonly used method to determine gas- and particle-phase concentrations (for example, Sauret et al. 2008, Atmos. Env.; Yang et al. 2013, ES&T; Lohmann et al. 2000, ES&T; sites in the EMEP monitoring network; sites in the North American Integrated Atmospheric Deposition Network (IADN) - e.g., Venier and Hites, 2008) While several sampling artefacts (blow on, blow off, breakthrough, degradation) may occur during sampling, the influence of blow on and blow offs is small relative to the influence of environmental factors such as temperature (Melymuk et al; in press, Environmental Pollution). Breakthrough is considered as the major sampling artifact that could severely affects the results about gas-particle partitioning. The extent of breakthrough has been assessed in this study (Tables S6-7) and several CUPs were removed from the list of compounds. Based on the suggestions of Reviewer #3, we now also decided to exclude also all HCHs from the discussion on gas-particle partitioning due to concerns about breakthrough. Therefore, given these considerations and the fact that high volume sampling techniques are widely used, we consider the gas and particulate concentrations reported in this study as valid. Regarding the section on gas-particle partitioning, based on the reviewer suggestions (reviewers 3&4) major modifications have been made to section 3.4. These changes are highlighted in the revised manuscript which is currently included as a supplement. We now more concisely investigated the relationship between logK_p and logK_{oa} and logK_{sa} (the soil-air partitioning coefficient) and major differences were found for OCPs and CUPs, suggesting the influence of

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adsorptive contributions to Kp for CUPs.

Specific comments Title "Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides" There are only limited OCPs and CUPs studied in this work, it is not appropriate to use such title.

Author response: The title is informative as required by ACP. Indeed, there are only limited OCPs and CUPs investigated in this study but the key goal of a title is to be wide enough such that it will attract many readers from different disciplines while remaining informative about the nature of the work. We believe that this title fulfill both purposes.

Abstract: It is hard to understand the important findings of this work when I read the abstract. For example "In general, gas-particle partitioning of pesticides was governed by physicochemical properties, with higher vapor pressure leading to higher gas phase fractions, and associated seasonality in gas-particle partitioning was observed in nine pesticides", this statement is suitable for most organic chemicals including organic pesticides, should be not a major finding of this study.

Author response: We agree with the reviewer that this part of the abstract could apply to many organics, including polar pesticides. Given the new findings, we have now considerably changed the abstract: "Major differences were found in the atmospheric distribution of OCPs and CUPs. The atmospheric concentrations of CUPs were driven by agricultural practices while secondary sources such as volatilization from surfaces governed the atmospheric concentrations of OCPs. Moreover, clear differences were observed in gas-particle partitioning with an influence of adsorption onto mineral surfaces for CUPs while OCPs were mainly partitioning to aerosol through absorption. A predictive method for estimating the gas-particle partitioning has been derived for polar and non-polar pesticides. Finally, while OCPs and the majority of CUPs were largely found on fine particles, four CUPs (carbendazim, isoproturon, prochloraz and terbuthylazine) had higher concentrations on coarse particles ($>3.0 \mu\text{m}$), which may be

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caused by the application technique. This finding is particularly important and should be further investigated given that large particles results in lower risks from inhalation (regardless the toxicity of the pesticide) and lower potential for long range atmospheric transport. "

P23653, L5, "and the relative lack of information regarding their toxic effects" Are you sure there are lack information for toxic effects of CUPs? Which CUP do you mean?

Author response: For many CUPs, there are available information about the acute effects related with pesticides but this is limited concerning the chronic effects linked with a lifetime exposure (e.g agricultural workers). Moreover, in case of chlorpyrifos which has been widely studied, the European Food Safety Authority listed several points which were not available in order to assess the human health risk of this compound (e.g. dermal absorption data for different formulations, standard hydrolysis study; http://www.efsa.europa.eu/sites/default/files/scientific_output/files/main_documents/3640.pdf). Additional discussion about these gaps can be found in Bányiová et al; 2015 (Environmental Science and Pollution Research) and 2016 (Chemosphere).

P23654, L5, "with a focus on the gas-particle partitioning and the particle size distribution. For many of these CUPs, this is the first time that their seasonal gas-particle partitioning and size distributions have been examined" if gas-particle partitioning and particle size distribution are the major objectives of this study, the characters of the particle itself should be examined as well, e.g. TOC and organic matter fraction on PM10 and grain size of particles, and origin of the particles.

Author response: We agree with the reviewer that it would have been ideal to know the characters of the particles. Unfortunately, at the time of sampling and analysis, it was not possible to measure those parameters. Regarding the importance of knowing fOM for the analysis of pesticide size distribution, we would like to argue that we observed distinct differences for different pesticides for the same samples, so with the same fOM. However, we acknowledge this as an uncertainty in the discussion, and mention this in

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the manuscript.

Air sampling P23655, L3, what is the pore size of QM-A?

Author response: We apologize for omitting this information from the manuscript. The pore size of QM-A is 2.2 μm and it is now included in the manuscript.

I am wondering, if it is necessary to collect 7-days, 4310 m³ for each air sample. I do not think it is so hard to determine the OCPs and CUPs selected in this study with 500 or 1000 m³ air. When the authors intend to estimate gas/particle partitioning, you do need consider about breakthrough of both particle-bound and gases chemicals, and degradation as well.

Author response: It may not be necessary to collect 7 days or 4310m³ for every compound, but in some cases, these large volumes were enough to detect some CUPs but insufficient for quantification (<LOQ; Tables S12-S13), indicating in this study the large sample volumes were useful, particularly for the CUPs. It is true that larger volume or sampling time are associated with potential higher sampling artefacts. However, as mentioned earlier, blow on and blow off were considered to have minor effects and gas-phase breakthrough was considered (Tables S6 and S7) and several CUPs were removed from the analysis as they were experiencing breakthrough. We now include these sources of uncertainties at the beginning of the section on gas-particle partitioning. The manuscript now includes: "It has been well known that several sampling artifacts such as blow-on, blow-off, breakthrough and degradation may occur and affect the results about gas-particle partitioning (Melymuk et al., 2014). The reported gas-particle partitioning of pesticides are therefore operationally defined, given the sampling configuration, where gas-phase is defined as the mass of the sample captured on the PUF and particulate-phase is the mass captured on the QFF. Given the large volumes used in this study, breakthrough tests were performed (Table S7) and HCHs were excluded from the discussion of gas-particle partitioning to avoid any bias due to gas-phase breakthrough sampling. Breakthrough is typically the most significant

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sampling artifact; bias due to filter blow-on/blow-off is not expected to be significant (Melymuk et al., in press)."

P23657, In the section "results and discussion", it is not necessary to emphases "Detection frequency at the background site".

Author response: We believe that this section is needed as it provides information about the persistence of OCPs in the environment (i.e. all OCPs were detected in >50% of the samples) while highlighting the different CUPs that were highly detected and will be further discussed in the next sections.

P23660, L8-13, there are many other studies for CUPs in rural air, you may compare with literature data if you like.

Author response: Thank you for the suggestion. We have now added a Table in the SI reporting comparisons with concentrations of individual OCPs and CUPs at different sites, and a reference to these studies in the manuscript text.

P23660, "Seasonal variations at the background site", you may use air mass back trajectories to figure out possible origin for high concentrations of OCPs and CUPs determined in this work. At least, the authors should not always simply address the high concentrations to certain application of pesticides around the sampling site. A statistics analysis may be helpful as well.

Author response: As we have described in the response to reviewer #1, examination of the wind directions/back-trajectories does not provide additional information, as the land-use surrounding the background site is agricultural in all directions in ~50 km radius of the site. Therefore, a back-trajectory in any direction would pass over many km² of agricultural fields, and no direction would clearly dominate as a source of emissions over any other. Similarly, on a larger scale, no clear source region is apparent; Central Europe is dominated by agricultural land use (Czech Republic is 55% agricultural land, and other countries in the region are also highly agricultural (Germany – 48%, Poland –

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48%, Slovakia – 40%, Austria – 38%, Hungary – 60%; data from World Bank database - <http://data.worldbank.org/>) The reason of attributing the higher CUP concentrations to direct application around the sampling site is that many of these CUPs have a short atmospheric lifetime and thus are unlikely to be associated with long-range transport. For example, the lifetime of chlorpyrifos in relation with OH reaction is about 2 h (Muñoz et al., 2014).

P23663, L17-26, this paragraph should be move to introduction.

Author response: Thank you for the recommendation. We have now moved this paragraph to the introduction.

For the section “Gas-particle partitioning at the background site”, there are many studies for Gas-particle partitioning of OCPs, which can be refered and compared with this work.

Author response: Thank you for the recommendation. We have now compared our results for OCPs with previous studies.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/15/C11908/2016/acpd-15-C11908-2016-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 23651, 2015.

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