Atmos. Chem. Phys. Discuss., 5, S3500–S3509, 2005
www.atmos-chem-phys.org/acpd/5/S3500/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Application of positive matrix factorization in estimating aerosol secondary organic carbon in Hong Kong and insights into the formation mechanisms" *by* Z. B. Yuan et al.

Z. B. Yuan et al.

Received and published: 28 October 2005

We thank both reviewers for their constructive comments. Our responses to the review comments are listed below.

Referee #1 (B. Bonn)

Reviewer: The present paper by Yuan *et al.* deals with the challenging job of source apportionment for atmospheric aerosols in Hong Kong using the positive matrix factorization method for a dataset of 4.5 years. The challenge therein arises from the

multitude of different sources in the city and the surrounding area as well as 'long range' sources, transported to Hong Kong by advection. Neither the latter nor the local sources are understood in detail yet, partly not even in the basics such as most of the secondary organic sources of anthropogenic volatile organic compound (VOC) oxidation products participating in the production of the aerosol mass. Additionally, the contribution of different VOCs to the total ambient VOC concentration will vary with measurement site and season, causing different aerosol constituents throughout the year with different characteristic properties.

Response: We share the view by the reviewer that it is a challenge to do source apportionment for atmospheric aerosols in Hong Kong. We believe that through a combination of statistic modeling analysis (i.e., PMF) of ambient monitoring data and application of established knowledge in atmospheric dynamics of the major aerosol constituents, we have advanced our understanding in aerosol secondary organic carbon in Hong Kong.

Reviewer: The structure of the paper is well done and written in an understandable way, but I would have liked more details concerning the exact method. Sometimes the referenced web pages were hard to reach, so the reader has to patient in some way. The presented results are fitting nicely into the scope of ACPD and are certainly of interest. However, the claim to have found indications for cloud-processes acting to form aerosol mass is not valid in this context. Although this might be the case, the conclusion cannot be drawn from the present dataset as outlined below in 'specific comments'. Therefore, the title might be changed somewhat at the end.

Response: The details on the PMF analysis of the same data set have been presented in a separate paper, entitled "Identification and Spatiotemporal Variations of Dominant PM10 sources over Hong Kong". This paper was submitted to Atmospheric Environment. It has received favorable reviews (see editor's decision letter attached at the end of this document) and a revision has been submitted to Atmospheric Environment. We apologize for the inconvenience in accessing the preprint version of this companion

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manuscript. With this paper pending for publication in Atmospheric Environment, we do not feel it is necessary to include more details on the PMF method.

We concede that on the basis of the synchronicity and the good correlation alone, it is difficult to persuade the reviewers to agree with our inference that in-cloud processing plays an important role in SOC formation. In recognition of this difficulty, we have removed from the abstract the sentence on the in-cloud formation, and changed the title to "Application of Positive Matrix Factorization in Estimating Aerosol Secondary Organic Carbon in Hong Kong and Its Relationship with Secondary Sulfate".

Reviewer: Several specific comments need to be made to this presentation. One specific point to be made concerns the annual averaging of the source apportionment in Table 1. Although quite useful for long-term aerosol effects, this will smooth out seasonal effects and impacts on human health. Especially the secondary sources vary significantly between the different sites and throughout the year, causing most probably different health effects. Because of this, the authors did monthly analysis for the elemental carbon (EC), organic carbon (OC), secondary carbon (SOC) and sulfates. Doing this, the authors indicated a stronger increase of SOC from summer to winter time than the sulfates, but showing a clear dependency of SOC on sulfates or vice versa. This is all reasonable and valid.

Response: The referee suggested that the annual averaging of source apportionment listed in Table 1 would smooth out the seasonal effects and impacts. We do not agree with this comment. Although the PMF model assumes that the source profiles remain unchanged for the entire year (i.e., an average source profile for each identified source is assumed), the PMF model calculates the impact of each source (i.e. source intensity) for each individual daily sample. The source intensity may vary significantly from sample to sample; therefore it was incorrect to say that seasonal effects and impacts on human health were smoothed out.

Reviewer: However, the conclusion to link this to cloud processes is much more dif-

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ficult and can not be done in that way because of the multitude of linkages in atmospheric processes and chemistry. For example aromatic compounds like benzene and toluene as well as further anthropogenic VOCs are oxidized nearly exclusively by OH with some small exceptions similar as SO2. Therefore in the presence of a strong OH source like intensive solar radiation photochemistry is impacting on both similarly, only with a higher velocity for the VOCs because of their faster reaction rate constants. Once the anthropogenic VOCs are released either by transport, industries or heating, they are oxidized rapidly because of their local high concentrations capable to start aerosol mass production quite fast but not hours or days later as stated by the authors. Some of these compounds are emitted in conjunction with SO2 (heavy fuels etc) even pronouncing this relationship.

Response: It is true that the lifetime of some typical abundant VOCs in urban areas is in the order of a few hours (e.g., toluene); however, the SOA formation continues even after the primary VOCs have been reacted because oxidation products of the first generation and beyond could undergo further oxidation and produce more SOA. Without a modeling exercise, it is difficult to state whether the majority of SOA formation takes place in the first few hours or go far beyond that.

Reviewer: Interesting further is the minimum of both secondary aerosol sources during summertime compared to a maximum in the winter.

As the authors stated, rainfall is substantial higher during summertime than during wintertime reducing at least the water-soluble compounds by washing-out significantly. Because of the tropical conditions the temperature differences between the two seasons is not that large and due to the mild climate rather small compared to e.g. the mega-cities in the Northern hemisphere. Nevertheless, local pollution sources like heating, changes in transport and changes in weather pattern including transport of pollutants might be the reason for the increase in e.g. VOC (total NMHC) concentrations. This is expressed by the variation in total NMHC during the year clearly marking the transition periods as well as summer and winter. By contrast, SO2 possesses quite

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a long lifetime with respect to gas-phase oxidation by OH (about 10 days), which is reduced by cloud-phase reactions to about 3 days, causing a rather well mixing in the troposphere as a source for aerosol sulfates. Therefore, Figure 7 of the present paper is quite understandable. But I would not claim to prove any cloud-phase aerosol production, which nevertheless might be acting.

The findings can be explained by local sources and photochemistry as well. For me as a reader it seems that the wash-out processes (rainy seasons) and the distribution and strength of the individual sources are determining both the obtained results. To proceed in this context an analysis with respect to the wind direction or back trajectories would be worth, checking about the results after passing clouds. But most probably the obtained data points are too scarce for this.

Response: In essence, the reviewer suggested that in-cloud processing does not have to be brought up to explain the observed synchronicity and correlation. Several studies (e.g., McHenry et al., 1994; Warneck et al., 1999) concluded from modeling results that in-cloud processes convert 50-80% of SO_2 to sulfate in the troposphere. The in-cloud production of sulfate is very efficient, reaching 100% h^{-1}, that is, the reaction is nearly instant (Meng and Seinfeld, 1994). This heterogeneous pathway requires the presence of clouds and clouds are discrete events. In comparison, formation of sulfate through gas phase oxidation of SO_2 by OH is a continuous process.

Hong Kong is located at the sub-tropical region, cloud events occur year around due to its humid climate. Hong Kong observatory reports an average cloud amount of 58% in the winter months and 70% in the summer months (source: Hong Kong Observatory, http://www.hko.gov.hk/wxinfo/climat/normals.htm). Size distribution measurements of sulfate in Hong Kong (Zhuang et al., 1999; Yao et al., 2002) showed a dominant droplet mode, suggesting in-cloud processing was a dominant sulfate forming mechanism in Hong Kong. If we can agree on that in-cloud processing is a dominant pathway for sulfate forming in Hong Kong, then it is more reasonable to expect that in-cloud process is also significant for SOC forming on the basis of the high synchronicity and

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correlation. Had SOC been predominately formed through gas-phase OH oxidation of VOC precursors AND sulfate been mainly formed through in-cloud processing, a high synchronicity between the two species in the daily samples would have been hard to achieve. The suggestion by the reviewer that local sources and photochemistry could explain the findings is not supported by our analysis of the data. As shown in Fig. 3, the SOC levels at different air quality monitoring stations (1.7$\pm$0.3 μgC/m^3 in the summer and 7.0$\pm$0.9 μgC/m^3 in the winter averaged across all ten stations) were similar despite the site characteristic varying from rural to roadside environment. Such a spatial variation characteristic did not support the suggestion of a dominant role by local photochemistry for SOA formation.

In summary, we believe that in-cloud processing played an important role in SOA formation in Hong Kong. Nevertheless, we recognize the difficulty in drawing conclusive marks without a modeling study that incorporates the representative emission characteristics of SO_2 and VOCs and the detailed formation chemistry for both sulfate and SOC, which we are not yet able to do at the moment. For this reason, we have removed the claim of importance of in-cloud production of SOC. Instead we just report the correlation relationships between the two, hoping that this provides preliminary impetus for further field and modeling studies to probe the role of clouds in SOA formation.

The referee suggested checking results after passing clouds. It is not feasible to carry out this exercise because all the samples were collected on a daily basis. It is also unlikely to differentiate the gas-phase and cloud-phase formation pathways by inspecting the wind data against the sulfate and SOC data.

References:

McHenry, J.N. and Dennis, R.L. The relative importance of oxidation pathways and clouds to atmospheric ambient sulfate production as predicted by the regional acid deposition model. J. Appl. Meteorol. 33, 890-895 (1994).

Meng, Z.; Seinfeld, J. H. On the source of the submicrometer droplet mode of urban

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and regional aerosols. Aerosol Sci. Technol. 1994, 20, 253-265.

Warneck, P. The relative importance of various pathways for the oxidation of sulphur dioxide and nitrogen dioxide in sunlit continental fair weather clouds. Phys. Chem. Chem. Phys. 1, 5471-5483 (1999).

Yao, X.; Fang, M.; Chan, C. K. Size distributions and formation of dicarboxylic acids in atmospheric particles. Atmos. Environ. 2002, 36, 2099-2107.

Zhuang, H.; Chan, C. K.; Fang, M.; Wexler, A. S. Size distributions of particulate sulfate, nitrate, and ammonium at a coastal site in Hong Kong. Atmos. Environ. 1999, 33, 843-853.

Reviewer: Further I would be interested in any intercomparison with a chemical transport model as described for the second approach for source apportionment. How much is understood at the moment and how does this fit to the results using the OC/EC technique and the positive matrix factorization. This would give a hint for the cloud issue too. Unfortunately this is not available here, but this would be a challenging and time consuming step too.

Response: We wish to further study the SOC contributions to ambient aerosol in Hong Kong using a chemical transport model; however, we have not yet developed such a modeling capability.

Reviewer: 3 Technical comments

Response: Suggestion taken. The two references are now added in the manuscript.

Referee #2

Reviewer:1 General Comments

The paper by Yuan et al. presents an extensive amount of PM10 measurements and analyses in Hong Kong - an area which is concerning climate relevant topics very important. Yuan et al. use a new interesting method, the positive matrix factorization

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to estimate the SOC contribution in aerosol mass. Although most of the VOCs reaction products involved in the condensation growth of particles are unknown the paper gives some interesting features especially in the quantity and seasonal behavior of SOC in this area. The paper is written in a good structured way and well inside the scope of ACD. For this I recommend to publish the paper with some additional aspects which are listed below.

2 Specific Comments

The PMF method and the source identification procedure which are only mentioned by the authors very shortly in chapter 3.2 should be described in a more approved way. For the reader it is not satisfying that these methods, where all the data analyses are based on can be found at some web-pages which are difficult to reach concerning the experience of referee #1. In the last paragraph of chapter 4.1 some explanation of the PMF method are made, however this should be replaced into chapter 3.2.

Response: (1) This issue has been addressed in our response to the first reviewer's general comment. (2) We take the reviewer's suggest to move the last two sentences in section 4.1 on PMF to section 3.2.

Reviewer: In chapter 4.2 the authors discuss the seasonal pattern of SOC in Hong Kong in comparison with other areas. The surprising result that SOC concentration is much higher in winter compared to summer in the Hong Kong area is explained by meteorological conditions without any further analyses. I recommend that the authors should at least at this point include some analyses of free available meteorological data (trajectories, humidity, rain fall, temperature, ą E) for some specific days. In my opinion such results are worth and scientific very interesting to explore and will give the whole scientific community further discussion reasons. During the summer month the washout could be one responsible process in the tropics for lower SOC concentrations beside the lower concentrations of NMHC mentioned by the authors. However, it is too speculative without any further analyses.

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Response: We have expanded this part to provide more details to explain the summer-low-winter-high seasonality. More specifically, the following sentences shaded in yellow are now added to the manuscript.

"The unusual seasonal pattern of SOC in Hong Kong can be explained by the meteorological conditions unique to Hong Kong. The summer-winter rainfall contrast was an average of 1400 mm in the summer versus 130 mm in the winter for the period of 1961-1990 (source: Hong Kong Observatory, www.hko.gov.hk). The frequent and more abundant rainfall in the summer effectively removed aged aerosols. Higher mixing heights in the summer also contributed to lower SOC concentrations. Estimates of mixing layer heights from dialy temperature soundings indicated that the average mixing height in the winter ($\sim$0.7 km) was only two-thirds of that in the summer ($\sim$1.1 km) (Tung et al., 2005). Located in the subtropical region, Hong Kong had abundant sunlight and mild ambient temperatures (15-21^{o}C) even during the winter; therefore local production of SOC by photooxidation in winter was still considerable. In addition, northerly and northeasterly winds were prevalent in the winter and brought in aged and more contaminated air masses from northern China. In comparison, southerly or southeasterly winds prevailed in the summer and brought in clean marine air masses from South China Sea or Northwest Pacific Ocean, therefore diluting particulate matter loadings, including SOC."

Reference:

Tung, J. W. T., Yu, J. Z., Lau, A. K. H., Louie, P. K. K.: Abundance and sources of ambient dioxins in Hong Kong: A review of dioxin measurements from 1997-2001, Chemosphere, 59, 1387-1398, 2005.

Reviewer: At the end I also agree with referee #1 that the selected title is somehow misleading. Application of positive matrix factorization in estimating aerosol organic carbon in Hong Kong is completely correct. However the phrase - insights into the formation mechanisms - is with the presented analyses overvalued. I would highly rec-

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ommend the authors to change the title or include more data analyses in this direction which would contribute new scientific results into the formation mechanisms.

Response: Referring to our response to the first reviewer, we have changed the title to "Application of Positive Matrix Factorization in Estimating Aerosol Secondary Organic Carbon in Hong Kong and Its Relationship with Secondary Sulfate".

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