

## ***Interactive comment on “Average molecular weight of surfactants in aerosols” by M. T. Latif and P. Brimblecombe***

**Anonymous Referee #3**

Received and published: 17 October 2007

General comments:

This paper presents new results on the determination of the average range of molecular weight of surfactants found on atmospheric aerosol particles. The methodology used in this work is based on the determination of surfactant concentrations in aerosol extracts before and after they have been processed by centrifugation. The concentrations of anionic surfactants in aerosols extracts are determined as MBAS (methylene blue active substances) and EVAS (ethyl violet active substances). MBAS and EVAS with molecular weight below 5K Da predominate in fine mode aerosol samples at University of East Anglia (UEA) and PM10 at Malaysia, though MBAS with molecular weight above 5k Da constitute a greater fraction for aerosols collected in Malaysia derived from an episode of biomass burning. The authors provide a correlation between surfactant

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

concentrations and surface tension determined by pendant drop analysis by showing that the effect of surface activity is more notable in the fine mode aerosol extracts. Additionally, MBAS and EVAS are correlated with the yellowish color of aerosol extracts by spectrophotometric measurements. These results are consistent with earlier studies showing that HULIS are present in atmospheric aerosols. In additional experiments with petrol soot, diesel soot and commercial humic acid, the authors have characterized MBAS and EVAS with molecular size below 5K Da, and have also observed that ozonolysis products of these compounds can increase the concentrations of MBAS and EVAS with molecular weights below 10K Da.

This paper provides a reliable estimate of the molecular weight of surfactants on atmospheric aerosols, which makes it of great interest to the readership of ACD. However, I have numerous comments that address the presentation of the results, the unclear wording and the organization of the paper. I find this paper acceptable once the authors have addressed the following specific comments and several technical comments, as outlined below:

#### Specific Comments:

1- It would be helpful to reword the abstract since it seems to present the determination of surfactant concentrations in atmospheric aerosols. It is not simple to establish a direct link between this abstract and the determination of the range of molecular weight of surfactants found in atmospheric aerosols, which is the central subject of this study.

2-P13807, Line 24: it is stated that surface-active material are present in atmospheric aerosol. But, how important are they quantitatively?

3-In P13807, Lines 3-21 and Lines 27-29, the chemical nature of the surface active materials found in atmospheric aerosols is presented in a disorganized and confusing manner. It would be helpful to reword this section by describing that HULIS is a fraction of the surface-active material of macromolecules compounds with high molecular weights; that their chemical properties (molecular weight) are mostly unknown and dif-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

difficult to determine; how concentrations can be estimated; and discuss previous reports on the estimation of molecular weight of these compounds.

4-P13807, Lines 22-27: In this part of the introduction, it seems unnecessary to include this paragraph (lines 22-27) describing humic substances when HULIS is the topic.

5-P13808, Surfactant concentrations: Could you comment about the uncertainty associated with the determination of concentration using MBAS and EVAS methods? By comparing all figures in the paper, EVAS can be seen at higher concentrations than MBAS. Could you comment this?

6-P13811: The title Soot exposure to ozone should be modified considering that you have analyzed several compounds. Related to these organic compounds, could you add more information about their chemical composition, the formation of soot, and preparation of solutions for ozonization?

7-P13811, Results and discussion: Because this study was based on the determination of surfactant concentrations in extracts from aerosol samples collected in different sites (UK, Malaysia), a summary of the measured concentrations (MBAS and EVAS) should be presented in this section. However, why the analysis presented throughout this paper is focused on apparently just two cases (UEA, Malaysia) and not considers other samples? Or, are these two cases representatives of all aerosol extracts?

8-P13811: It is stated that the decrease in the surface tension as a function of time is due to surfactant agglomeration on the surface. Since the equilibrium in surface tension measurements of solutions (containing surface-active materials) is a time dependent process, wouldn't be possible that this decrease is because the system hasn't reached equilibrium? -How many drops are measured? Do you have estimated the uncertainty associated with these measurements of surface tension? The authors show results for an aerosol extract. But, what does happen for other aerosol samples? -Concerning Fig. 1, it would be interesting to plot the measurements of surface tension as a function of the surfactant concentrations (MBAS and EVAS) determined in the aerosol extracts.

Interactive  
Comment

9-P13811: Could you introduce the abbreviations (n, r, p) of lineal regression? They should be used consistently throughout the paper and the values obtained should be given in the text and in figure legends. In the last paragraph of section 3.2, I don't understand the statement: This suggests that acidic pollutants that ... are related to the surfactants.

10-P18312: It would be useful to move section 3.3 just before section 3.1: Surface tension of aerosol extracts. This would allow the presentation of the relation between the concentrations of anionic surfactants with DOC and then how these concentrations are correlated with the different measured properties.

11-P18312: What does overall bar represent in Fig. 5a and 5b? Have you measured MBAS and EVAS concentrations for the aerosol coarse mode?

12-P13813: UV-Vis spectra are analyzed to provide evidence of the chemical structure in aerosol extracts. Considering that the wavelength of 254 nm is characteristic of the PI to PI\* electron transition for most aromatic hydrocarbons (like in HULIS), is there a particular reason to choose 400 nm? Have you tried to test the similarity between aerosol extracts by analyzing ratios of absorbance at two wavelengths [ $A(\sim 250\text{nm})/A(\sim 400\text{nm})$ ]?

13-P13814: Have you taken UV-Visible spectra of aerosol extracts from these sources before and after ozonolysis? If you have, how these data compare with atmospheric aerosols from UEA or Malaysia?

## Technical Corrections:

P13806, Line 18: affects should be may affect; and effect on health should be health effects

P13806, Line 23: Loglio et al. 1986, 1985 should be Loglio et al. 1985, 1986

P13807, Line 3: The exact chemical nature of ... is still did not clear should be deleted, since the information is repeated in P13806: line 24-25

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

P13807, Line 27: the citation Likens et al (1983) is not listed in the reference list

P13807, Line 28: for more than 50% should be for 35-43%

P13807, High MW carbon compounds are believed to be involved in cloud condensation (references) in Line 29 should be moved to line 2

P13808, Line 03: Facchini et al., 1999a should be added and a reference is missing in ind blown soil

P13808, Line 19 and P13818, Line 23: Mezaros should be Meszaros

P13809, Line 18: non-dispersived should be non-dispersive

P13811, Line 2: Dry diesel and petrol soot and humic acid (50mg) was should be Samples of dry diesel soot, petrol soot and commercial humic acid (50mg) were

P13811, Line 12 and P13813, Line 21: A reference indicating the source of these aerosol samples is missing

P13811, Line 19: surrogate should be surrogate

P13812, Line 5: aerosols should be aerosols extract from UEA (as fine and coarse modes) and Malaysia (as PM10)

P13812, Line 26: Fig. 5 should be Fig. 5a and Fig. 5b

P13812, Line 26: To help readers in Fig. 5a and 5b, could you comment which bars correspond to before and after ultrafiltration?

P13813, Line 3: reference Facchini et al., 2000 should be added

P13813, Line 11: Fig. 4 should be Fig. 5a

P13813, Line 13: concentrations should be concentrations of these samples (Fig. 5b)

P13813, Line 26: the reference Facchini et al. (1999), is 1999a or 1999b?

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

P13814, Line 7: Fig. 7 should be Fig. 7a and Fig. 7b

P13814, Line 9: (not shown) should be added after Malaysia

P13814, Line 17: Fig. 8 should be Fig. 8a and Fig. 8b

P13814, Line 23: Latif and Brimblecombe (2004) should be (Latif and Brimblecombe, 2004)

P13815, Line 8: range should be deleted

P13815, Line 19: soot should be petrol soot, diesel soot

P13815, Line 20: Fig. 11 should be Fig. 11a, 11b and 11c, respectively

P13815, Line 25: Da should be added after 5K

P13816, Line 13: molecu~~r~~ should be molecule

P13816, Line 16: produces should be products

Reference list:

The names abbreviations and the surnames of several authors are not correctly named in:

P13817, Line 6: the abbreviation letter B should be erased

P13817, Line 29: the abbreviation letter S should be erased

P13817, Line 1: the reference Balasubramanian et al, 2003 is missing in the paper

The journal title abbreviations are incorrectly presented for the following citations:

Tellus B at P13817, Line 6

Atmos. Environ. at P13817, Line 17 and Line 21

J. Coll. Interface Coll. at P13817, Line 32

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Mar. Pollut. Bull. at P13818, Line 1

Atmos. Chem. Phys., 6, 729-753, 2006 at P13818, Line 3

Environ. Monit. Assess at P13818, Line 30

Appl. Surf. Sci. at P13819, Line 6

Ann. For. Sci. at P13819, Line 13

Atmos. Chem. Phys., 5, 2163-2170, 2005 at P13819, Line 14

Atmos.o.Environ. should be Atmos. Environ. at P13819, Line 31

The following references should be included:

P13806, Line 21: Gill, P.S., Graedel, T.E., Weschler, C.J., Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops and snow flakes, Reviews of Geophysics and Space Physics 21 (4), 903, 1983

P13807, Line 2: Rudich, Y., Laboratory perspective on the chemical transformation of organic matter in atmospheric particles, Chem. Rev. 103, 5097, 2003

P13807, Line 2: Saxena, P., Hildemann, L.M., Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds, Journal of Atmospheric Chemistry 24, 57, 1996

P13807, Line 6: Russell, L.M., Maria, S.F., Myneni, S.C.B., Mapping organic coatings on atmospheric particles, Geophysical Research Letters 29 (16), doi:10.1029/2002GL014874, 2002

P13807, Line 20: Dinar E., Taraniuk I., Graber E.R., Katsman S., Moise T., Anttila T., Menatel T.F., Rudich Y., Cloud condensation nuclei properties of model and atmospheric HULIS, Atmos. Chem. Phys., 6, 2465, 2006

P13808, Line 8: Ellison, G.B., Tuck, A.F., Vaida, V., Atmospheric processing of organic aerosols, Journal of Geophysical Research 104 (D9), 11633, 1999

S6058

ACPD

7, S6052–S6059, 2007

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

Figures:

Fig. 1: Legend (b) Fine mode aerosol is missing. Fig. 1a and Fig. 1b should be presented together in a single figure and the surface tension of pure water (72mN/m) should be indicated on it. Where were collected these aerosol samples?

Fig. 2 and Fig. 3: It would be helpful if the MBAS and EVAS concentrations determined for aerosol collected at UEA (fine and coarse modes) and Malaysia sites could be compared as a function of free H<sup>+</sup> in the same graphs: Fig. 2a and Fig. 3a would be Fig.2; Fig. 2b and Fig. 3b would be Fig.3.

Fig. 4: Could you include lineal regression values in Fig. 4a and Fig. 4b?

Fig. 7a and 7B: Replace aerosol by aerosol samples collected at UEA

Fig. 10 and 11: The captions for petrol soot, diesel soot and laboratory humic acid are missing in both graphs.

Fig. 11: Replace MBAS by EVAS

---

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13805, 2007.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper