

acpd-10-8415-2010 (He et al.)

We thank the reviewer for the constructive comments. We are giving below our point-by-point response to each of the comments in the same order as raised by the reviewer. All the points mentioned here will be added into the revised manuscript later on.

Overview:

Response:

- 1) Clearer definitions of some of the metrics and terms are provided in response to specific comments and will be incorporated into the revised manuscript.
- 2) In general, the Southwest monsoon season and pre-Northeast monsoon season in Southeast Asia are usually accompanied by atmospheric visibility reduction (i.e. hazy conditions) on a regional scale because of recurring, uncontrolled forest and peat land fires due to land-clearing activities in Sumatra and Borneo, and to a lesser extent Malaysia. These regional smoke haze episodes have occurred almost every dry season since the late 1990s in Southeast Asia (1-7). Moderate and dense smoke from these fires could be transported from South Sumatra and Kalimantan during the Southwest monsoon season such that the atmosphere over Singapore could be polluted by smoke haze to some extent. These smoke haze episodes are different from localized transient smog conditions occurring in urban areas from trapping of anthropogenic emissions in a nearly stagnant atmosphere. The spread of smoke haze resulting from biomass burning could lead to some local and regional air pollution problems over this area.

The satellite image (Figure 1(d)) has been provided in the manuscript, which was issued regularly by Singapore National Environment Agency (<http://www.weather.gov.sg/wip/web/ASMC/home>). This haze map provided the hotspot distribution and haze coverage (thick, mild and slight) in the surrounding area of Singapore. It clearly showed that in October 2006, Singapore was affected by the smoke haze due to biomass burning that occurred in Sumatra and Kalimantan (numerous hotspots were identified).

- 3) The analytical methodology and how it was applied to determine concentrations of organic compounds will be described in more detail in response to one of the specific comments.

Introduction:

Response:

We will provide more information in the introduction as suggested.

Experimental procedures:

1) p 8419, lines 12: “4 inches” will be replaced by “10.2 cm”; p 8419, line 13: “one-inch” will be replaced by “2.5 cm”.

2) As the referee pointed out, PUF plugs could be dirty. Pre-cleaning of PUF plugs was carried out using 33 mL stainless steel vessels of a Dionex ASE 200 with the pure hexane, mixture of hexane and acetone (3:1) and pure acetone for two cycles, respectively, to remove the possible interference from organic compounds of non-polarity, semi-polarity and high polarity. To check whether the PUF plugs were sufficiently clean after the pre-cleaning procedure, one more cycle (hexane, mixture, and acetone) extraction was applied and their extracts were analyzed by the same GC-MS protocols as used for the target compounds in this study. It was found that their concentrations were at the same level detected in pure solvents used for pre-cleaning.

3) p 8420, line 3-4: the pressure and temperature were 1500 psi, and 70 °C, respectively while the solvent volume was approximately 150 ml.

4) p 8420, line 10: The deuterated internal standards representing polar compounds were added prior to sample extractions. So, the phrase "25µl of additional internal standards" has been removed in the revised manuscript.

5) Quality control: The analytical quality of the data obtained was determined using the limit of detection (LOD), recovery, linearity of calibration, and by checking and eliminating sampling artifacts. During each set of extractions, the field blanks (filter and PUF plugs) were included and the mean blank value was subtracted from the measured levels. The reliability of the entire procedure for each sample was evaluated by using surrogate standards. Breakthrough was evaluated under field conditions by connecting three 2.5 cm plugs in series and analyzing them separately. For 24 hr samples, measured semi-volatile organic compounds (SVOCs) at the third plug were in the range of those found in blanks. Calibration standards spiked with internal standards were measured regularly to ensure the consistency of analytical instrument performance during chemical analysis.

Results and Discussion:

Response:

1) p 8422, line 14: Total suspended particulates (TSP) are solid matter or liquid droplets from smoke, dust, fuel ash, or condensing vapor that can be suspended in the air. They either come from natural sources such as the sea (wind-blown sea-salt) and soil (wind-blown soil particles) or from man-made sources such as diesel exhausts, construction activities and factories. TSPs include a range of different sized airborne particles. The coarser particles are 50-100 µm and finer particles are smaller than 10 µm in aerodynamic diameter. The quartz filters we used were with a pore size of 0.7 µm.

2) p 8423, line 8: n-alkanes are chemical compounds that consist only of the elements carbon (C) and hydrogen (H), wherein these atoms are linked together exclusively by

single bonds (saturated compounds) without any cyclic structure (loops). The number of carbon in alkanes can range from 1 up to 60 and even more. The sources of alkanes include earth soils/rocks, natural gas and oil, metabolism of bacteria (including archaea), fungi, animals as well as plants. In plants, the solid long-chain alkanes are found in the plant cuticle and epicuticular wax of many species. Through abrasion and volatilization under high temperature conditions (such as biomass burning occurring in agricultural/forest areas), these compounds can be emitted and incorporated into aerosols. The alkanes from different sources might have various characteristics in the distribution of carbons contained and preference of odd/even numbered carbon atoms in their molecules.

In this study, the number of carbon contained in n-alkanes detected mainly ranged from C12 to C35.

3) p8423, line 17: Based on the dataset of aliphatic hydrocarbons, C_{max} (carbon number maximum) and CPI (carbon preference index) can be used to differentiate biogenic (e.g. vascular plant wax) from petrogenic or anthropogenic (e.g. combustion of fossil fuels) sources in aerosols (8-13) sources.

Plant wax evaporates from vegetation under normal conditions. Biomass burning creates a high temperature environment in the forest area, which can expedite the volatilization and emission of wax from plants. We still consider that it is more appropriate to term this additional wax contribution by fires as biogenic source as it is primarily of vegetation origin, and this term is more commonly used in relevant literatures.

4) p8424, line 7: As stated on page 8423, line 27, the CPI is the ratio of odd-carbon numbered to even-carbon-numbered n-alkanes in a given sample. The CPI values can be used to identify the dominant sources of organic species, since the distribution of homologues is strongly associated with the formation mechanism of carbonaceous aerosols. The CPI for n-alkanes was calculated as follows (14,15):

(i) whole range for n-alkanes: $CPI_1 = \sum (C_{13}-C_{35}) / \sum (C_{12}-C_{34})$

(ii) petrogenic n-alkanes: $CPI_2 = \sum (C_{13}-C_{25}) / \sum (C_{12}-C_{24})$

(iii) biogenic n-alkanes: $CPI_3 = \sum (C_{25}-C_{35}) / \sum (C_{24}-C_{34})$

5) p8424, line 19: in the original manuscript, the plant wax alkane has been expressed by equation (1).

$$\begin{aligned} \text{Wax } C_n &= [C_n] - [(C_{n+1} + C_{n-1}) / 2] \\ \% \text{ WNA} &= \text{Wax } C_n / \sum (C_{12}-C_{35}) \times 100\% \end{aligned}$$

(6) p8424, line 19-27: It is known that n-alkanes originate from epicuticular waxes of terrestrial plants and exhibit high values of CPI (>1); on the other hand, CPI values for vehicular emission and other anthropogenic activities are close to unit (≈ 1). Therefore, the residual plant wax n-alkanes could be separated from fossil components by subtracting the corresponding n-alkane concentrations of CPI close to 1. Both of these two values are based on the entire carbon range of n-alkanes ($C_{12}-C_{35}$) in this study and can be considered as molecular ratios for the source apportionment of plant wax alkanes.

Their linear relationship was explored to determine the consistency of the source identification capabilities of these two diagnostic ratios.

7) p8425, line 14: As recommended, “such as biomass combustion, vehicular and industrial emissions” will be removed.

8) p8425, line 15-16: As suggested, “such as peat and forest fires” will be removed.

9) p8425, line 23-25: the “~” stands for the concentration range. For example, “2~7 pg m⁻³” means the concentration ranges from 2 pg m⁻³ to 7 pg m⁻³. We will use the latter style for the sake of clarity.

10) p8425, line 23-25: It is for sure that there is huge areas of tropical pine forests in Sumatra, Indonesia (http://en.wikipedia.org/wiki/Tropical_and_subtropical_coniferous_forests). In addition, dense hotspots were identified by satellite images during October 2006, which covered those coniferous forest areas. Consequently, it would be reasonable to assume that the conifer combustion occurred in October 2006.

11) p8425, line 24: As suggested, “of organic compounds” will be removed and “long-distant” will be replaced by “long-distance”.

As introduced in our response under “Overview” and the one above (#10) in “Results and Discussion”, both peat and forest fires took place in Indonesia in October 2006. Conifer combustion occurred in Sumatra during the hazy period, from which the biomass burning-impacted air masses were transported to Singapore (see cluster analysis of air mass backward trajectories in Fig 1(b)), most likely affecting the air quality of this state-city).

12) p8426, lines 1-30: p 8426, lines 1-30: Yunker et al. (2002) have quantified parent and alkyl PAHs (51 compounds and alkyl homologues) in both suspended particulates and sediments from the Fraser River system, British Columbia, Canada. By using ratios of the principal mass 178, 202, 228 and 276 parent PAHs and some alkyl PAH series, the researchers inferred sources of PAH to the Fraser basin and evaluated the consistency of these source assignments and the suitability of various commonly applied PAH ratios as indicators. More importantly, Yunker et al. put a lot of efforts on reviewing literature and summarized PAH diagnostic ratios for petroleum, single-source combustion and environmental samples. The sources have been categorized into three groups: vaporation from petroleum, combustion of natural gas, oil and coal, environmental samples including biomass burning, road dust, traffic emissions (Table 3 in Yunker et al. (2002) paper).

PAH ratios, especially parent PAH ratios, have been widely used to detect combustion-derived PAH. To minimize confounding factors such as differences in volatility, water solubility, adsorption, etc., ratio calculations usually are restricted to PAHs within a given molecular mass (18-20). Therefore, the parent PAH relative stability can be inferred and

recognized from different combustion and/or anthropogenic input. More details can be found in Yunker et al's work (18) and our discussion on p8427, lines 1-19.

Consequently, the PAH ratios for source apportionment summarized by Yunker et al. (18) are applicable to atmospheric samples and have been widely used in air quality studies under various conditions (till 05 May 2010, total citation of Yunker et al (2002) has been up to 348, out of which 89 papers have cited this work on air quality studies).

13) p8427, lines 8-10: We refer to the Section 3.1. "parent PAH relative stability" in Yunker et al. (2002) work (18) and our discussion on p8427, lines 1-19.

14) p8427, lines 10-20: On the contrary to what the referee pointed out, our observation is exactly consistent with what those references (provided by the reviewer) reported. P8427, line 10-14: "organic compounds with more volatility tend to be redistributed onto larger particles while the less volatile compounds remain onto the fine particles with which they were directly emitted from their corresponding sources". "High molecular weight PAHs" are found less volatile, so they prefer to remain onto the fine particles but are not redistributed into coarse particles.

15) p8427, lines 20-30: The concentrations of all target compounds (n-alkanes, PAHs and polar organic compounds) include both particulate and gaseous phases throughout the manuscript.

16) p8428, line 13: In this study, in the group of n-alkanedioic acid, the concentration of succinic acid (C4) was dominant in most of the samples and the analytical GC-MS chromatogram showed single peak. To avoid the confusion, "unimodal GC chromatograph" has been removed.

17) p8428, line 24: In Figure 7, the concentrations of both levoglucosan and TSP were presented on a daily sampling event basis from August to October 2006. Here the "temporal trend" refers to the trend of these two parameters with time.

18) p8428, line 25: It has been clearly stated in the text that the concentration of levoglucosan showed strong correlation (0.64) with that of TSP at the 0.01 significance level (2-tailed).

19) p8429, line 3: Emission factor is a measure of the average amount of a specific pollutant emitted into the atmosphere by a specific process such as combustion of fuel/material. It is expressed as the number of milligrams of this pollutant per kilogram of the fuel/material.

Kalimantan (Borneo) of Indonesia is covered by various types of vegetations in different regions (WWF's "Borneo: Treasure Island at Risk" Report (2005): <http://www.mongabay.com/borneo.html>). Mangroves are found in estuaries and coastal regions; peat swamp forests are the dominant form of remaining lowland forest in Borneo today; montane forests are generally found at an elevation from 900 meters to 3300

meters in Borneo; Heath or kerangas forest are found on well-drained, sandy soils; lowland dipterocarp forests are also available but they are most threatened forests in Borneo as timber resource.

In this area, swamp forests appear in places where dead vegetation becomes waterlogged and, too wet to decompose, accumulates as peat. These tropical peat lands, formed over hundreds of years, are giant stores of carbon. Draining and/or burning these lands, releases tremendous amounts of carbon dioxide into the atmosphere. These drained areas also become highly susceptible to combustion. Under the dry El Niño conditions of 1997-98 and 2006, thousands of fires raged in the peat swamps of Indonesia. Fires in peat swamps are extraordinarily difficult to extinguish because they can burn for months virtually undetected in the deeper layers of peat. In 2002 peat forests covered about ten million hectares in Borneo according to Langner and Siegert's report (16).

Another part of Indonesia is Sumatra, where most of endemic plant species are found in lowland forests below 500 meters and the rate of deforestation currently averages 2.5% per year (17). In Sumatra, especially in Jambi province, the regional government is promoting expansion of oil palm plantations. The situation in Jambi mirrors the magnitude of proposed oil palm expansion under development in at least Riau Province and in north Sumatra. At the same time, forest fires are rampant throughout Sumatra, especially in the central and southern regions. As the price of palm oil has increased, land-hungry plantation developers in Sumatra have deliberately burned large areas of forest, especially those lowland forests and plantations and land-clearing contractors used fire as the primary mechanism to clear land.

To sum up, two types of biomass burning can be expected in Indonesia: lowland forest fire and swamp peat land fire.

20) p8429, line 8: We thank the reviewer for the advice. Sheesley et al. have studied the characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia, but the exact emission factors of levoglucosan from Indonesian peat has not been reported yet.

21) p8429, line 9-12: We would condense these sentences and provide the most relevant details in the revised manuscript.

22) Figure 2: The reference line for PSI will be added and the line on two axes figure will be changed in the revised manuscript.

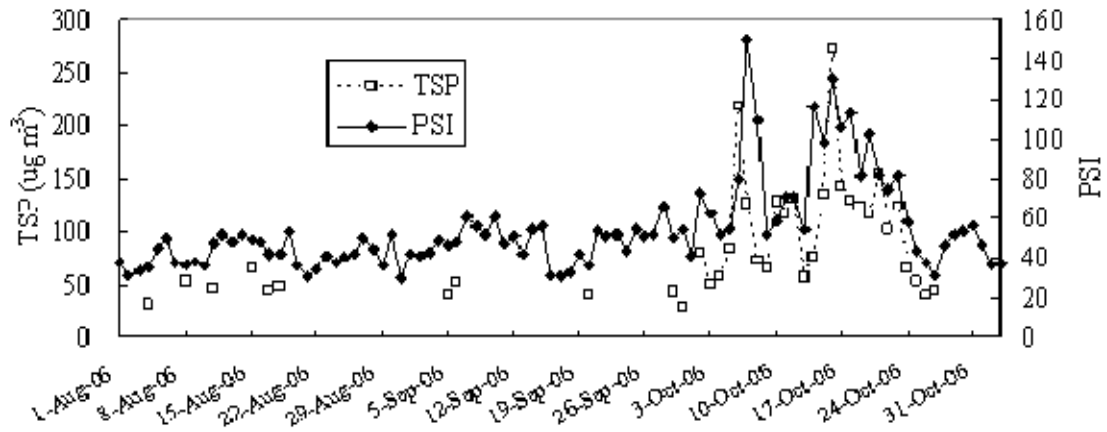


Fig.2. Temporal Changes in Total Suspended Particulate matter (TSP) concentrations and Pollutants Standard Index (PSI) from August to October 2006 (PSI from National Environment Agency of Singapore)

23) Figure 3: Y-axis will be kept as it is because it clearly shows the concentration levels of n-alkanes. X-axis will be changed to make it more clear and show the number of carbon contained in n-alkanes in the revised manuscript.

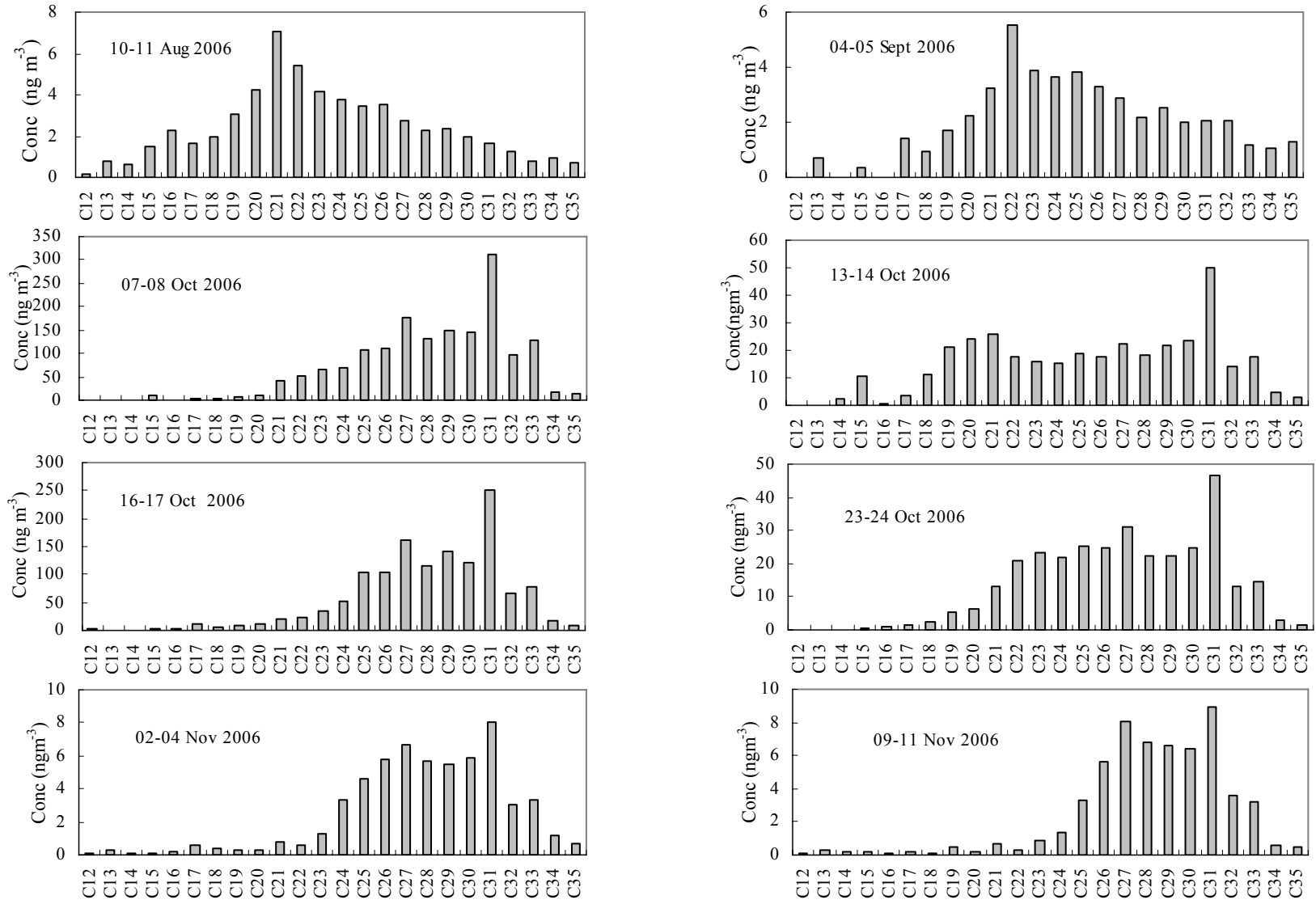


Fig. 3. Distributions of n-alkanes from August to November 2006

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