Responses to Referee 2 Comments

This paper gives an interesting account of a sampling campaign that took place in the Himalayas foothill, with sampling and analyses of EC/OC and organic acids. This paper merits publication, since such data are not so common in the literature, and the location is pretty interesting for the understanfind of the Brown Cloud processes and characteristics. However, this version needs improvements on several points, including some level of corrections for the english. Below are other more specific comments for precise issues.

We appreciate the referee's valuable comments on our work. Our responses to the specific comments are given below.

Page 937 : Line 6 : Â´n . . ..of great interest. . .. Â¨z Lines 10-15 : reference should be made to some papers from the recent ACP - Special Issue "Atmospheric brown cloud in the Himalayas" Line 23 : ". . .due to their. . .."

Response: In the revised manuscript, the above-mentioned sentences are included and the suggested references are added (please see page 3, lines 42-43, 46 and 51-54).

Page 938 : Lines 10-11 : English

Response: The sentence is modified in the revised manuscript (page 4, lines 76-77) as follows;

Himalaya Mountain range exists over northern part of these highly populated and the industrialized areas.

Page 940, section 2.2 : you should indicate how many samples were collected and analyzed in each category

Response: The total numbers of samples (N = 39) collected for winter and summer seasons as well as day and night are described in revised manuscript (page 7, lines 140-142).

Page 944 ; Line 3 : "Therefore" is not correct since the following part of the sentence is not a consequence of the sentence in lines 1-3. Lines 24 and 27 : English

Response: Yes, we agree. "Therefore" is removed from the sentence.

In the revised manuscript (page 11, lines 248-253) the suggested English correction is made as follows;

Hopkins et al. (2007) studied the particles emitted during combustion of several plant fuels at different temperatures and suggested that flaming conditions produce more EC and less OC while smoldering fires result in higher OC content. Regional air quality over the northwestern part of India during winter season will considerably be influenced by the regular practice of crop harvesting. But, wood fuel/coal burning for domestic use will continue throughout the year.

Sentence on page 944-945 : check English

Response: This part of the text has been revised (page 11, lines 254-259), as follows;

A campaign mode measurement by Engling et al. (2011), from the top of a mountain site (1960 m asl) over a remote part of the Tibetan Plateau (Yunnan Province) during spring (April and May), reported higher OC/EC ratios (4.3 ± 2.1). This experiment also unveiled a substantial regional build-up of carbonaceous particles accompanied by fire activities and transport of pollutants from the nearby regions of Southeast Asia and the northern part of the Indian Peninsula.

Page 945 : Lines 5-8 : no relation between the two parts of the sentence.

Response: In the revised manuscript (page 11, lines 260-261), the sentences have been modified, as follows:

The major part of aerosol carbon is derived from smoldering process in the form of water-soluble organics and it can also act as cloud condensation nuclei (CCN) (Andreae et al., 1996).

Lines 18-19: I do not get why this is an explanation

Response: In the revised manuscript (page 12, lines 270-272) the sentence is modified as follows; A good correlation between WIOC and EC was also apparent (except for winter night samples), indicating the influence of fossil fuel primary emissions over the study region.

Line 19 : why is it "Consequently . . ." ?

Response: (page 12, line 272) The word "Consequently" is replaced by "Further".

Page 946 Lines 13-21 : all of this section is highly speculative, since the calculation of SOC with this method is subjected to many uncertainties. Further, it is known that a large fraction of WSOC is of primary origin (particularly in biomass burning). To conclude that there is a similarity in the chemistry of SOC and WSOC based on these information is plain speculation.

Response: We thank the Referee's suggestion for this important point. Yes, we do agree that SOC calculation has some degree of uncertainty depending on the choice of primary OC/EC ratio. To estimate the primary OC/EC ratio people use tracers of combustion-related primary emissions such as CO through a linear fit using selected OC and EC observations (e.g., Miyazaki et al., 2006). For our observation site Nainital, we do not have any tracer data for present study period (2006-07). Therefore, we used minimum value among the observed OC/EC ratios in each season. For SOC calculation we have chosen the observed minimum OC/EC ratio in each season ($[OC/EC]_{min}$ values of 2.15 μg m^{-3} and 1.91 μg m^{-3} for winter and summer seasons, respectively) and they are reasonable as the concentrations of EC and OC vary depending on the type of biofuel and burn rate (Stone et al., 2010). Following the reviewer's suggestion, we have changed this part of the text in the revised manuscript (page 12-13, lines 282-312) by including the estimation of uncertainties as follows;

Primary OC (POC) is directly emitted in particulate form by emission sources like vehicular exhaust, fuel combustion and cooking. Whereas, secondary OC (SOC) is formed through gas/particle partitioning of semi and nonvolatile products of chemical reactions

involving reactive organic gases (Blando and Turpin, 2000). Due to lack of a direct chemical analysis method separating primary and secondary organic aerosol and the enormous complexity of organic aerosol have restricted researchers to estimate POC and SOC using EC tracer methods (Lim and Turpin, 2002). EC is one of the good tracers of primary combustion generated carbonaceous aerosols (Yu et al., 2009). The limitation of the EC tracer method is to assume a representative ratio of primary OC/EC for a given area because EC and POC typically have the same source (Miyazaki et al., 2006). By this method, POC and SOC were estimated using the following equations,

$$[POC] = [OC/EC]_{min} \times [EC] + c \quad \text{.....(1)}$$

$$[SOC] = [OC]_{meas} - [POC] \quad \text{.....(2)}$$

where $[OC/EC]_{min}$ is the minimum ratio of OC/EC for all the samples in every season, c is the parameter to account for non-combustion sources contributing to POC, and $[OC]_{meas}$ is the measured OC concentration. In the equation (1) we have used the $[OC/EC]_{min}$ values of 2.15 μg m^{-3} and 1.91 μg m^{-3} for winter and summer seasons, respectively. If we consider the POC contribution from non-combustion sources (e.g., primary biogenic sources) are negligible $[OC/EC]_{min}$ values used here seems to be reasonable because OC/EC ratio depends upon the type of biomass as well as burn rate (Stone et al., 2010).

In order to calculate the possible uncertainties associated with the assumption of $[OC/EC]_{min}$ values representative for primary combustion generated carbonaceous aerosols the following exercise has been done. For the estimation of SOC, instead of minimum value of OC/EC ratio, we considered the lowest 10% of OC/EC values from both the seasons. Lim et al. (2002) have shown that the lowest 10% of OC/EC ratios are likely contributed by primary carbonaceous aerosols. The SOC values calculated using lowest 10% of OC/EC ratios were found to be always lower than that estimated using minimum OC/EC ratio. The uncertainty for the average SOC was 28 % and 39 % for winter and summer seasons, respectively. The observed uncertainties in the present study are comparable to the reported values in the literature for Tokyo (28%) (Miyazaki et al., 2006) and Chennai (22 %) (Pavuluri et al., 2010).

Page 948 Lines 7-9 : a discussion should take place at this point about the fact that the contribution of C-diacids to OC is higher in winter than in summer.

Response: Thanks for suggesting the sequence. The text is reorganized starting with diacid-C/OC ratios followed by diacid-C/TC discussion (please see page 16, lines 371-379).

Page 950 : Lines 3-7 : how come that there is such a large difference in concentrations for oxalic acid between Winter and Summer, that is not found for the other acids ? Invoking change is the air masses should impact all of these species coming mainly from secondary processes . . . ? Is this the meaning of the section 12 -27 in the same page? In this case, it should be stated clearly.

Response: Yes. It is true that a higher concentration of oxalic acid is observed only during winter season and it is comparable with other studies (e.g., Ho et al., 2007). However, such large differences in concentrations between the two seasons have not been reported so far in the literature (except for Antarctic aerosols; Kawamura et al., 1996 reported higher succinic acid comprised approximately 70% of the total diacids during summer season). In one of the south Indian cities Chennai, Pavuluri et al. (2010) reported higher concentrations of oxalic acid during winter season (~ 2 times) due to lower temperature, higher relative humidity and lower vertical mixing of pollutants that favors the production. In contrast, during summer period opposite situation was noticed. Similar observation is also found in another metro city along south west coast of India, Trivandrum (8º29'N, 76º59E) (Hegde et al., manuscript under preparation). Over Nainital, local productions of pollutants are bare minimum for entire observation period. The observed concentration of most of the compounds depends on the source region (back trajectories path). Therefore, we consider that higher concentrations of oxalic acid in Nainital samples during winter period are due to the enhanced production over Indo Gangetic plain areas. Another possible path way for the higher concentration during winter is the contribution of isoprene for C_2 formation. Lim et al. (2005) proposed the C_2 production through isoprene oxidation. Here, glyoxal, methyl glyoxal, pyruvic and glyoxylic are the intermediate compounds. It is important to note that in this reaction scheme from the oxidation of isoprene oxalic acid is the ultimate product (without involving longer chain diacids). Isoprene is ubiquitous in the troposphere at a mixing ratio of about 0.1-7.0 ppb by season and location (von Kuhlmann et al., 2004). Measurements conducted by Padhy and Varshney (2005) over New Delhi and surrounding areas revealed annual average isoprene emission of 6.2 ± 3.2 μg g^{-1} leaf dry weight h^{-1} (average of six commonly grown tree species) with higher Isoprene emission during September and October months.

But during summer period, the back trajectory path change and wind comes from NW of the Indian subcontinent (air mass rich in mineral aerosols). Higher wind speed and temperatures will help to bring this air mass more quickly to the receptor site. The photolysis of the iron-oxalate complexes are an efficient pathway for the destruction of oxalic acid during transport (Kawamura et al., 2010; Pavuluri and Kawamura, 2012) seems to be the only possible reason for the observed lower concentrations during summer period.

The above points are described in the revised manuscript (please see page 18-19, lines 422-467).

Page 951 Lines 1-3 : this can hold as long as the removal processes (including the process explained in the previous section) is taken into account. Lines 18-20: I do not understand this sentence: what do you mean by “relate” ? These formation processes should indeed increase the ratio C2 / total diacids . . .

Response: Yes, we agree with the reviewers comment that it is the continuation of previous section (removal processes). Now, in the modified text we have deleted this subtitle.

As this process (aqueous production) is not observed during summer, the sentence is removed from the text.

Page 952 Lines 10-19 : what is the purpose of the last two sentences of this paragraph?

Response: Thanks for the suggestion. Last two sentences are removed from this paragraph as they are not relevant here. This part of the text is rewritten to explain the formation path way of oxalic acid in our samples (page 21, lines 499-505).

Page 953 Line 21 : english Lines 27-28 : it is the production, not the oxydation, of benzene / toluene that occurs mainly in the urbain atmosphere ..

Response: English correction is made in the revised manuscript (page 22, lines 532-533) as follows;

Unsaturated fatty acids can originate from phytoplankton in the marine region and domestic cooking as well as higher plants in the continental region.

The word "oxidation" is replaced by "production" in the revised manuscript (page 22, line 539).

The entire paragraph (page 22, lines 529-545) is rewritten to explain the formation pathways more clearly.

Page 956 Line 16 : what are the hypotheses for explaining this observation, that is conterintuitive with current believe of increased oxidation of OC in summer ?

Response: A strong positive correlation between $\sum(C_2+C_3+C_4)$ and WSOC for winter period (Figure 12a), indicates that they might both be produced by secondary processes of same type of precursors (preferably volatile organic compounds from biomass burning). On the contrary, a relatively poor correlation observed in summer period (Figure 12b) is also likely because the contributions from anthropogenic sources are significant. Anthropogenic VOCs extensively contribute to WSOC whereas the rate of production of short chain ($C_2 - C_4$) diacids may not be similar to that of WSOC. Miyazaki et al. (2009) reported higher concentrations of WSOC in daytime than nighttime but opposite (higher in night time than daytime) in the case of short chain ($C_2 - C_4$) diacids in New Delhi aerosols, although they correlated well in both day and night, and attributed to enhanced production of WSOC in daytime. Further, the observed high concentrations of several anthropogenic molecular markers (e.g., phthalic acid) in Nainital aerosols particularly during summer season indicate the influence of anthropogenic sources on the increase in WSOC (but not for short chain diacids). It is also of interest to note that the concentrations of WSOC and even C_3 and C_4 are higher in summer, indicating the higher production of secondary aerosols in summer than in winter. However, due to differences in source types, the OC concentration was also found to be higher in summer than in winter.

The above points are included in the revised manuscript (page 25, lines 605-616).

Page 958 Lines 14-15 : does this sentence mean that other sources are more important than biomass burning in general, or just for these species ? Lines 15-17: this is not discussed previously in the paper

Response: We are sorry for confusing sentence. The text is corrected in the revised manuscript (page 27-28, lines 672-674) as follows;

Higher C_6/C_9 ratios were observed for winter season whereas Ph/C_9 ratios were higher during summer season, indicating that other anthropogenic sources were more important than biomass burning in the latter season.

Phthalic/adipic acid ratios are given in Table 2, together with the values reported from other areas for comparison. The comparison results (Ph/C_9 ratios) are explained in the revised text (page 23, lines 565-568). Now, the summary section text (page 28, lines 674-676) is modified as follows;

Higher phthalic/adipic acid (Ph/C_6) ratios were observed during summer as compared to winter season indicating the potential sources from diesel fuel vehicles than gasoline vehicles.

Figure 2 There should be a reference in the caption, or a thorough description on how this figure is obtained

Response: Daily mean diurnal and seasonal variation of temperature and relative humidity are obtained from an automated weather station (located at aerosol sampling station). Factory calibrated standard meteorological sensors provided continuous data (every 5 min interval). The method of data retrieval and accuracy of the sensors are explained in detail in our previous publications (Hegde et al., 2007 and references there in). For Figure 2, five-minute interval data (temperature and relative humidity) during September 2006 to June 2007 daily mean data are considered and plotted in 3D color contour by using graphic interface (Sigma plot version 8).

Now, in the modified manuscript (page 6-7, lines 119 to 134), we have included more description of the figure with minimum and maximum values during the observation period.

Figures 7, 8, 10, and 11 Not readable

Response: Figure 7 is redrawn with lines and symbols. Figure 8, 10 and 11 are combined and shown with legends.

Figure 7;

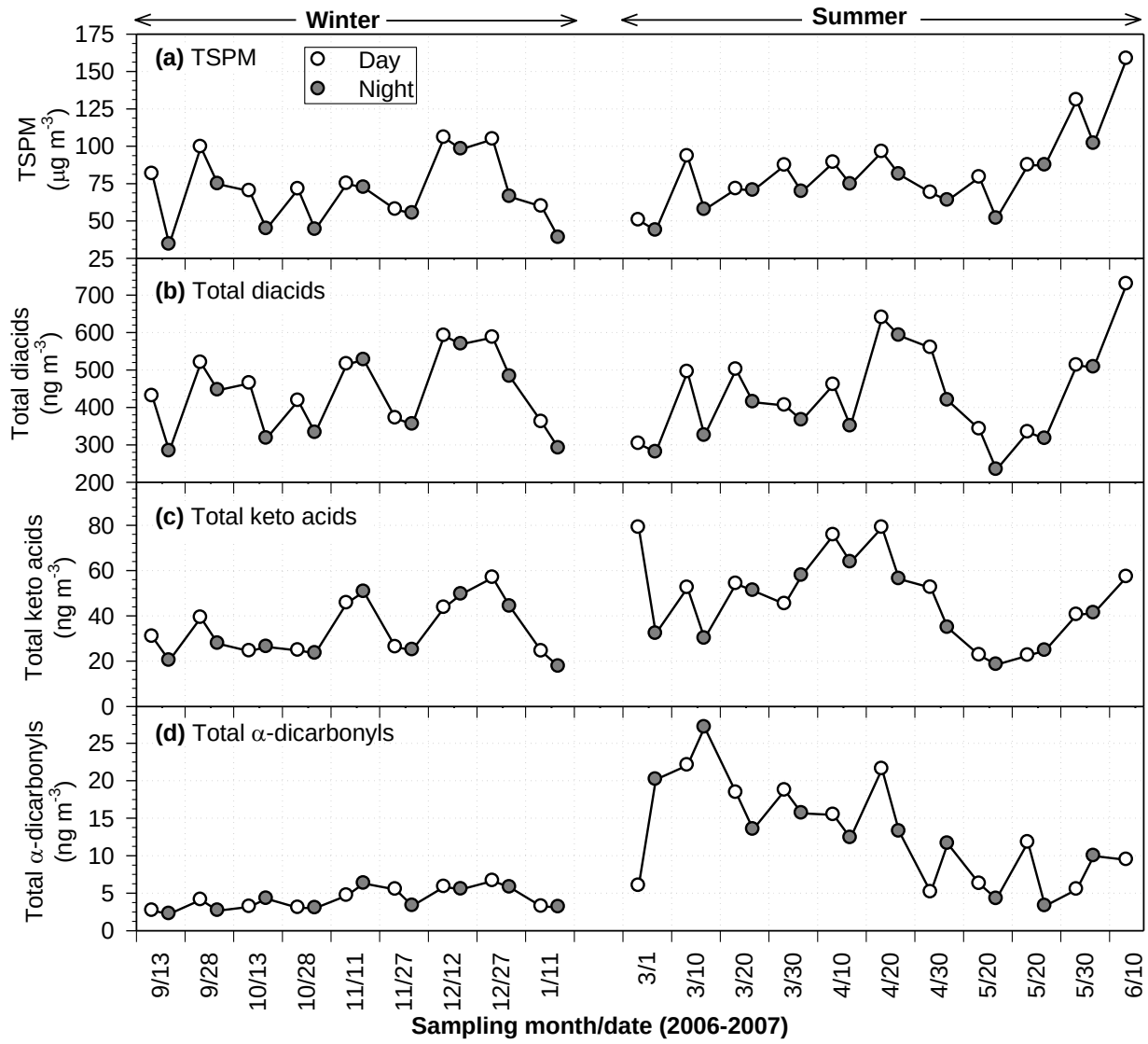

Winter
Summer
(a) TSPM
Day
Night
TSPM (μg m-3)
(b) Total diacids
Total diacids (ng m-3)
(c) Total keto acids
Total keto acids (ng m-3)
(d) Total α-dicarbonyls
Total α-dicarbonyls (ng m-3)
9/13
9/28
10/13
10/28
11/11
11/27
12/12
12/27
1/11
3/1
3/10
3/20
3/30
4/10
4/20
4/30
5/20
5/20
5/30
6/10
Sampling month/date (2006-2007)

Figure 8;

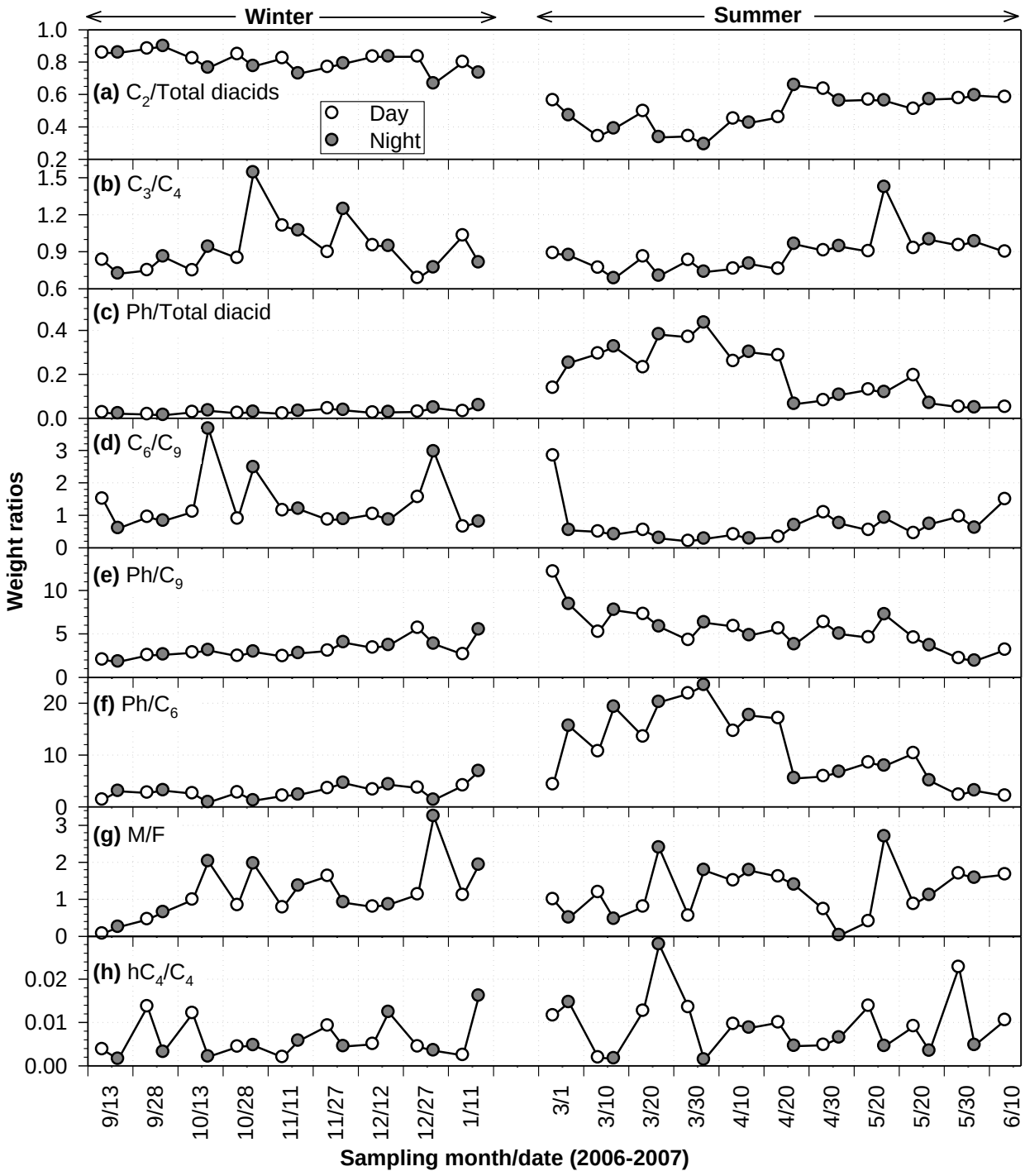
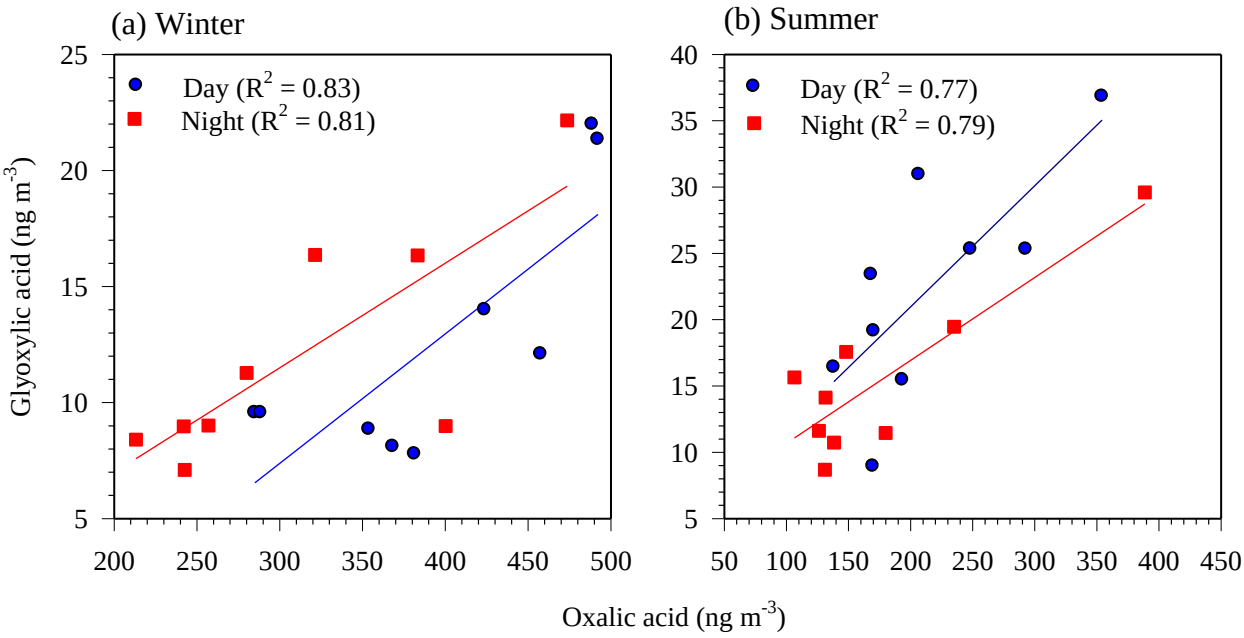

Winter
Summer
(a) C2/Total diacids
Day
Night
(b) C3/C4
(c) Ph/Total diacid
(d) C6/C9
(e) Ph/C9
(f) Ph/C6
(g) M/F
(h) hC4/C4
Weight ratios
9/13
9/28
10/13
10/28
11/11
11/27
12/12
12/27
1/11
3/1
3/10
3/20
3/30
4/10
4/20
4/30
5/20
5/20
5/30
6/10
Sampling month/date (2006-2007)

Figure 9 Why don't you put r2 on the figures, like in figure 4?

Response: R^2 values are now included in Figure 9.

Figure 9;



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