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Atmospheric
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Discussions

Interactive comment on “Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands” *by* C. Müller et al.

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We would like to thank the reviewers for the careful consideration of the manuscript and for constructive comments and suggestions made to improve the manuscript. Those are addressed below. In the case we do not concur with the reviewers' comments, proper reasons have been given.

Responses to reviewer 1

1) Title and inside the text: the amines is not correct for condensed species detected in aerosol particles the author should use the term amine salts or alkyl ammonium.

This is a good point though the authors believe that both amine salts and alkyl ammonium are also not necessarily correct for this study. We did not see correlations between nss $SO_4{}^{2-}$ and MSA (or for that matter any inorganic anions) unlike the work of Facchini (2008a), leaving a possibility that a fraction of amines detected in this study may have existed in a free form in the aerosol. Furthermore, the analytical technique we used for the amine quantification does not differentiate between amines in its salt or free form. Therefore, we decided use a term ‘amine’ which is commonly used in earlier publications.

2) Abstract and Summary are somehow in contradiction: abstract is mainly cantered on impactor data while summary discusses Hi Vol data. I suggest to change the summary in the direction of abstract for the reason explained in the next point.

Based on the reviewer’s comment, we have included the impactor data in the summary.

3) There is a main problem in the data set: the impactor samples were analyzed only for stages 2, 3 and 4 excluding the coarse size range based on a previous observation in North Atlantic reporting amines salts distributed in the accumulation range and not detectable concentrations in the coarse fraction. The concentration obtained by summing the impactor stages 2, 3 and 4 (corresponding to 0.143.5 μm) is not superimposed with PM_{10} but a relevant fraction of coarse particle is missing. For this the author cannot compare impactor data to Hi Vol data which also show higher concentrations concluding that these are due or to positive artifacts or to negative artifacts on the impoctor foil. The author first have to show that the impactor coarse fraction not analyzed does not contain amine salts I suggest to analyzed a few impactor samples in the interval 3.510 μm and to show the comparison with Hi Vol on the same sampling period. From these data the author can conclude that Hi Vol overestimates the concentrations and discuss the reasons. Moreover the author can show with independent measurements the secondary origin of amine salts. Then I suggest to discuss the single component concentration only for impactros as done in the abstract and use Hi Vol data only for discussing the seasonal trend. For this reasons I think that it is very important to change the summary and making this coherent with the abstract.

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Indeed, the sum of stage two, three and four amines is not equal to the PM_{10} amines and the direct comparison of HV samples and impactor samples is rather difficult. Furthermore, unfortunately, samples from stage 1 and 5 were only partially available for amine analysis as they were needed for other analysis (i.e. inorganic ions and OC/EC). To make sure that the amines in stage 1 and 5 were not significant fractions of the detected PM_{10} amine concentrations, we have analyzed two sets of available impactor samples (five stages) from an intensive campaign performed in December 2008 – January 2009. Figures in Supplementary Information (Figure 3S, see attached file to this response) show the average of two 24 h samples (01 January02 January and 02 January03 January 2009) with air masses originating from the open North Atlantic Ocean. The highest amine salt concentrations were found in stage 2 samples except for DMA which showed similar concentrations for both the stage 2 and 5 samples. However, this does not explain the discrepancy between HV and Berner samples as the difference in amine concentrations between the two samplers was about a factor of ten. One possibility for this discrepancy is amine adsorption on dust particles during the winter months. Figures 4S in supplementary information show the average contributions of amines found at each impactor stage (24 h samples) with air masses originating from the African continent (29 December30 December 2008 and 03 January-04 January 2009). As can be seen, there is no significant contribution of amines from both the stage 1 and 5 sample, indicating no adsorption of amines on dust particles. On the basis of these results, it is reasonable to assume that the amine concentrations were higher in the sub-micrometer size range and the discrepancy between HV and Berner samples were mainly the result of gas phase amine absorption on quartz filter substrates.

4) The analytical technique in not published anywhere else? The text do not contain citation of previous papers. If not published before a more details description of the analytical methodology is needed including detection limits, errors and details on the calibration procedure based on a microscale derivatization.

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Although the exact method is not published in details, it is based on well established derivatization method and described elsewhere (Cohen and Michaud, 1993; van Wandelen and Cohen, 1997). The NHS (Nhydroxysuccinimide) activated carbamates are known as fast derivatization reagents for amino functional groups. The method used in this study utilizes a commercially available amino acid deivatization kit using 6-aminoquinolylNhydroxysuccinimidyl carbamate (Waters, AccQ Tag^{TM}). The method is widely used in the fields of biochemistry and food industry to determine amines and amino acids in different sample matrices (Bosch et al., 2006; PappaLouisi et al., 2007; Shindo et al, 1997; Ullmer et al., 2006; van Wandelen and Cohen, 1997). Derivatized amines and amino acids can be detected by UV and florescence detectors after HPLC separation.

This method was modified to be compatible with mass spectrometry by replacing phosphoric acid required in the derivatization procedure with acetic acid as phosphate can disturb electrospray ionization. A detailed description of the method is given in Supporting Information of the revised manuscript.

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Pappa-Louisi, A., Nikitas, P., Agrafiotou, P. & Papageorgiou, A.: Optimization of separation and detection of 6-aminoquinolyl derivatives of amino acids by using reversed-phase liquid chromatography with on line UV, fluorescence and electrochemical detection, Analytica Chimica Acta, 593, 92-97, 2007
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18 6-aminoquinolyl-carbamyl-amino acids by ion-pair chromatography, Analytical Biochemistry, 249, 79-82, 1997

Ullmer, R., Plematl, A. & Rizzi, A.: Derivatization by 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate for enhancing the ionization yield of small peptides and glycopeptides in matrix-assisted laser desorption/ionization and electrospray ionization mass spectrometry, Rapid Communications in Mass Spectrometry, 20, 1469-1479, 2006

vanWandelen, C. & Cohen, S.A.: Using quaternary high-performance liquid chromatography eluent systems for separating 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate-derivatized amino acid mixtures, Journal of Chromatography A, 763, 11-22, 1997

5) The author discuss N budget they did not measure total N and thus organic nitrogen. The relative contribution of amine salts to what is called “total N” (which is in reality the sum of inorganic plus aminic N) in misleading. I suggest to remove this session and in particular the discussion following the citation of Gibb et al. (1999) and Fig. 8. In alternative the author could measure organic N to discuss the topic properly.

In section 3.1.4, we discussed the importance of small volatile aliphatic amines on the carbon and nitrogen cycles in the marine environment. In this context we used the sum of ammonium, nitrate and the determined aliphatic amines as total nitrogen. Indeed, this is not the same as total water soluble nitrogen (WSN). This is explicitly noted in the text. We believe that this section is essential to demonstrate the importance of amines in the marine-atmosphere carbon and nitrogen cycles, especially during the winter months as the elevated level of amine contribution to the OC and detected nitrogen species was observed. Nevertheless, we agree with the reviewer that “total nitrogen” is misleading. Therefore, we have changed the term “total nitrogen” to "detected nitrogen species".

We would prefer to keep Gibb et al. (1999) as it emphasizes once more the role of the aliphatic amines in marine environment. Therefore, we believe the reference to Gibbs

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fit well with the context.

6) Introduction is quite poor: the author should discuss the possible primary origin (from sea spray origin) of amine salts suggested in many papers in literature in the case of organic N of marine aerosol as well as amine and amino acids. Moreover I also suggest to include in the introduction a brief review of the current knowledge of primary and secondary marine OA before starting the specific discussion on amines. Moreover literature references are needed in general in the text.

We have modified the introduction so that it includes more information regarding the comments made by the reviewer.

Minor Points

7) It is not true that Facchini et al. (2008a) found "not negligible" concentrations of DMA and DEA: these were relevant representing 11% of the sub micron SOA during high biological active period.

We have used a term "not negligible" as the amine contributions reported in Facchini et al. (2008a) is neither dominant nor minor fraction of the sub-micrometer SOA. Nevertheless, we have changed it to "considerable".

Changed to: Furthermore, Facchini et al. (2008a) have recently found considerable concentrations of dimethylamine and diethylamine in sub-micrometer marine aerosol collected in the North Atlantic region, demonstrating a potential importance of amines of biological origin for secondary organic aerosol (SOA) formation.

8) I suggest to eliminate the discussion on Morpholine from "Results and discussion" since this is clear an artifact product.

Indeed, morpholine was not detected in the impactor samples and this led us to assume that morpholine detected in the Hi-Vol samples was an artifact from the gas-phase absorption. This is clearly stated in the manuscript (line 1718 part 14833). We would like to include morpholine in the discussion even it may be an artifact as it provides information about other potentially important amines present in the atmosphere.

9) Chapter 3.1.4 (contribution of the detected amines to the OC and nitrogen content in submicron particles); first break (line 118): This discussion is too much detailed and fig 6 is very complicated and not necessary. Fig 7 or a table is sufficient to describe the contribution of amines salts to total OC.

Following the reviewer's comment, detailed statistical information is summarized in Table 2 and Figure 6 is moved to Supplementary Information.