

# Observations of alkylamines in the East Mediterranean atmosphere

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**Abstract:** Atmospheric amines have a variety of natural and anthropogenic sources. They are stronger bases than ammonia and have been shown as an important contributor to new particle formation in the atmosphere. Amines measurements are scarce and mostly covering short time-periods because they are highly reactive and therefore present in low concentrations. In order to determine the atmospheric levels of gaseous amines in the East Mediterranean, a methodology developed to sample and analyze alkylamines has been optimized, standardized and used.

Samples were collected at the Finokalia monitoring station of the University of Crete on the north east coast of Crete, using glass fiber filters impregnated with phosphoric acid in order to trap gas-phase amines in the form of salts. The filters were stored in refrigeration until analysis by a Liquid Chromatography Triple Quadrupole Mass Spectrometer. Ethylamine, dimethylamine, trimethylamine, propylamine, diethylamine and triethylamine are the here studied amines.

## 1 Introduction

About 150 amines and 30 amino acids have been identified in the atmosphere emitted by several natural and anthropogenic sources. Animal husbandry, various industrial processes, combustion, composting operation and automobiles are the main anthropogenic sources while ocean, biomass burning, vegetation, and geologic sources consist the main natural ones (Ge et al. 2011).

Amines are derivatives of ammonia and their acid-neutralizing capacity is very important even in the presence of ammonia (Sorooshian et al. 2008). Due to their higher basicity, amines are likely to bind to sulfuric acid molecules more efficiently than ammonia and they may play a key to new particle formation (Kurtén et al. 2008, Kürten et al. 2016). However, even at such low concentrations they can affect atmospheric composition. Almeida et al. (2013) showed that few pptv of dimethylamine can enhance the nucleation rate by more than three orders of magnitude compared to NH<sub>3</sub> (Almeida et al. 2013).

Amines' high reactivity in combination with their neutralizing capacity and their low concentrations incommode the detection of amine's concentrations in the atmosphere. So, their measurements are scarce and mostly covering short time-periods. Moreover, the majority of the studies took place in cities, urban and suburban areas.

In the present study, the methodology of sample collection and subsequent analysis for the detection of gas-phase alkylamines initially developed by (Kieloaho et al., 2013) has been optimized and standardized for samples in the Eastern Mediterranean. Specifically, dimethylamine (DMA, (CH<sub>3</sub>)<sub>2</sub>NH), ethylamine (EA, (C<sub>2</sub>H<sub>5</sub>)NH<sub>2</sub>), trimethylamine (TMA, (CH<sub>3</sub>)<sub>3</sub>N), propylamine (PA, (C<sub>3</sub>H<sub>7</sub>)NH<sub>2</sub>), diethylamine (DEA, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH) and triethylamine (TEA, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N) have been detected in the atmospheric gas-phase at the Finokalia station. This study is therefore limited to the detection of gaseous amines in the remote coastal atmosphere at Finokalia station. The potential association of their levels to the observed at the site new particle formation (Kalivitis et al., 2019) "ISSN": "16807324", "abstract": "© 2019. This work is distributed under the Creative Commons Attribution 4.0 License. Atmospheric new particle formation (NPF as suggested by (Almeida et al. 2013). is the topic of a separate ongoing study.

## 2 Data and Methodology

### 2.1 Measurements site

For this study atmospheric samples have been collected at the atmospheric monitoring station of the University of Crete at Finokalia (35°20'N, 25°40'E, 250m a.s.l), a remote site on the north east coast of the island of Crete 50km away from the nearest major urban center Heraklion (<http://finokalia.chemistry.uoc.gr/>, Figure 1). The site that operates since 1993 is well characterized (Mihalopoulos et al. 1997) nitrate (NO<sub>3</sub><sup>-</sup>) and representative for the marine background conditions of the Eastern Mediterranean (Lelieveld et al., 2002), with negligible influence by local anthropogenic sources.

## 2.2 Sample collection

The sampling and the analytical methods were based on the procedure introduced by (Kieloaho et al., 2013) with optimizations for the ambient samples at Finokalia and the analytical system used at the University of Crete for subsequent analysis. Overall 111 samples were collected in 2015. Every week three samples were collected, one weekly and two 3-days samples that were operated in parallel. Here we focus on the 3-days samples.

The samples were collected in filters that were appropriately treated prior sampling. For each sample three filters were collected using a triple filter holder (Figure 1). The upper filter in the holder was a polytetrafluoroethylene (PTFE) filter (Zefluor™ 2.0µm, 47mm, Pall Corporation, Michigan, USA) that was used in order to collect the particles. The second filter in the holder was a glass fiber filter (GFF, 1.5 µm, 47mm Whatman, Fisher Scientific) impregnated with a solution of sodium carbonate / glycerole, which was used for trapping sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The third filter was a GFF impregnated with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), which was used for trapping gas-phase amines as salts. The treatment of the latest GFF filters was in accordance with Rampfl et al. 2008 (Rampfl et al., 2008). Amines reacted with H<sub>3</sub>PO<sub>4</sub> and formed aminium phosphate (R<sub>3</sub>NH<sup>+</sup>H<sub>2</sub>PO<sub>4</sub><sup>-</sup>). H<sub>3</sub>PO<sub>4</sub> that was used was 5% in methanol. After impregnation, the methanol was removed from filters in a drying oven at 65°C with air. As acid-base indicator, bromocresol green was used for the visualization of the sorbent saturation. Sampling was performed 3m above ground level using a pump with a flow rate of 16L/min. Samples were subsequently transported to the laboratory where they were stored in freezing (-18°C).



**Figure 1.** from left to right: The location of Finokalia station on the northeast coast of Crete, view of the station, and sample collector with a triple filter holder used for gas-phase amines sampling.

## 2.2 Analytical method

Before extraction of amines from the filters, an internal standard, deuterated diethyl-d10-amine (C/D/N Isotopes INC., Quebec, Canada) was injected on each filter. Applying the extraction procedure presented by Kieloaho et al. (2013), who used ultrapure water to extract amines from the H<sub>3</sub>PO<sub>4</sub>-impregnated filters, resulted in deformed peaks of the detectable compounds in our chromatograms.

To improve the chromatograms many tests were performed in the laboratory; extraction was performed with different apparatuses (for example a rotor), different materials, different temperatures. Measuring the pH of the extracts, we concluded that the extraction with ultra-pure water produced too acidic extracts for our analytical column (which operates within a pH range of 2.0 to 7.5). Controlling the pH of the extracts by using a buffer solution improved the chromatograms. Sensitivity tests to determine the appropriate buffer solution and the appropriate pH were performed. Several buffer solutions were tried, such as Potassium Phosphate buffer of several concentrations (1M, 1.2M, 1.5M), Pyrolidine of several concentrations (2M, 1M, 0.5M, 0.1M 0.005M 0.001M). They were unsuccessful, as we could not achieve the desirable pH. Finally, using a buffer solution of NH<sub>4</sub>OH/NH<sub>4</sub>Cl of 8.58 pH in an ultrasonic bath for 1 hour was found to be the optimal condition for aminium ions extraction from the H<sub>3</sub>PO<sub>4</sub>-impregnated filters.

The extracts were analyzed at the Department of Chemistry of the University of Crete by a high-performance liquid chromatography (HPLC) triple quadrupole mass spectrometer (TSQ Quantum Mass Spectrometer System, Thermo Finnigan, CA, USA). The reverse phase HPLC was equipped with a LC pump, injector and autosampler (Surveyor Autosampler, CA, USA). A Discovery® HS F5 HPLC was used as analytical column (10 cm x 2.1 mm, 3 µm) and a Discovery® HS F5 Guard Column Kit was used as a pre-column (2 cm x 2.1 mm, 3 µm) (both Supelco Analytical, Bellefonte, PA, USA). As solvents acetonitrile and water, with 0.02% of formic acid as ion-exchange reagent, were

used. The analytical method used, has been modified when compared to the proposed by Kieloaho et al. (2013). A shorter analytical column (10 cm instead of 15 cm) has been used and the flow rate has been reduced accordingly (from 250  $\mu\text{l}/\text{min}$  to 200  $\mu\text{l}/\text{min}$  here). In addition, the time of the analysis has increased by 10 minutes to allow full elution of sample and thus resulting in a sufficiently clean column for the next analysis. The analysis ran for 40 minutes with flow rate 200  $\mu\text{l}/\text{min}$ . Gradient elution was performed with an increasing content of acetonitrile from 5% the first 5 minutes to 25% the following 7 minutes, 50% during the next 23 minutes and finally it was decreased to 5% during 5 minutes. The chromatograms were divided into segments for each amine and for each segment a target compound-specific mass range was followed by a mass spectrometric analysis, for achieving higher analytical precision. The analytical column was unable to separate all the alkylamines and hence DMA and EA, eluted together were handled as pair. The precision of the analysis was defined as the percentage coefficient of variation (CV%) of 6 parallel analyses of standard solutions. The detection limits were reported as three times the standard deviations of the field blanks.

### 3 Results

Six alkylamines in the gas phase were studied in the eastern Mediterranean atmosphere, dimethylamine (DMA), ethylamine (EA), trimethylamine (TMA), propylamine (PA), diethylamine (DEA) and triethylamine (TEA), with an offline system: sampling on filters and subsequent extraction and analysis with a high-performance liquid chromatography coupled to a triple quadrupole mass spectrometer. DMA and EA, which have the same molecular masses were eluted together and thus could not be quantified individually. The precision of the method was found at 4 -6%. The detection limits were low: 1.69, 0.84, 0.22 and 0.54 pptv for DMA+EA, TMA, DEA and TEA, respectively. DMA + EA, TMA, DEA and TEA were detected above detection limits, while PA wasn't found in our samples. DMA+EA, TMA, DEA were detected in the 83%, 86% and 41% of our samples, respectively. TEA, which concentrations were close to the detection limit, was detected in about the 17% of our samples.

DMA+EA and TMA were the most abundant alkylamines throughout the whole period, with average concentrations  $10.82 \pm 8.32$  and  $13.22 \pm 9.63$  pptv respectively. The average concentration of DEA was  $0.73 \pm 0.22$  pptv and the average concentration of TEA was  $0.61 \pm 0.54$  pptv.

### 4 Conclusions

In the present study, a method for the determination of the atmospheric levels of gaseous amines in the eastern Mediterranean, has been optimized and standardized. Alkylamines measurements at Finokalia covered the entire 2015; 111 samples have been analyzed with different sampling duration (7 or 3-days). The sampling and analytical procedures were based on Kieloaho et al. (2013) but a lot of adjustments were performed for our samples and system as explained in section 2. These concerned mainly the control of the pH of the extracts and ii) the use of a smaller analytical column and a lower flow rate. The extraction of  $\text{H}_3\text{PO}_4$ -impregnated filters using ultrapure water produced very acidic extracts that were not appropriate for the used analytical column and led to chromatograms' deformation. Controlling the pH of the extracts by using a buffer solution  $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$  of 8.58 pH improved chromatograms. In addition, a 33% shorter analytical column and 20% lower flow rate compared to those used by Kieloaho et al. (2013) have led to 25% longer analysis time.

DMA and EA, which have the same molecular masses were quantified as a pair. DMA + EA, TMA, DEA and TEA were detected above detection limits of 1.69, 0.84, 0.22 and 0.54 pptv, respectively, while PA was not found in our samples. DMA+EA and TMA were the most abundant alkylamines throughout the whole period with average concentrations of  $10.82 \pm 8.32$  and  $13.22 \pm 9.63$  pptv respectively.

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## References

- Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., ... Kirkby, J. (2013). Molecular understanding of sulphuric acid–amine particle nucleation in the atmosphere. *Nature*, *502*(7471), 359–363. <https://doi.org/10.1038/nature12663>
- Ge, X., Wexler, A. S., & Clegg, S. L. (2011). Atmospheric amines – Part I. A review. *Atmospheric Environment*, *45*(3), 524–546. <https://doi.org/https://doi.org/10.1016/j.atmosenv.2010.10.012>
- Kalivitis, N., Kerminen, V.-M., Kouvarakis, G., Stavroulas, I., Tzitzikalaki, E., Kalkavouras, P., ... Mihalopoulos, N. (2019). Formation and growth of atmospheric nanoparticles in the eastern Mediterranean: Results from long-term measurements and process simulations. *Atmospheric Chemistry and Physics*, *19*(4). <https://doi.org/10.5194/acp-19-2671-2019>
- Kieloaho, A.-J., Hellén, H., Hakola, H., Manninen, H. E., Nieminen, T., Kulmala, M., & Pihlatie, M. (2013). Gas-phase alkylamines in a boreal Scots pine forest air. *Atmospheric Environment*, *80*, 369–377. <https://doi.org/https://doi.org/10.1016/j.atmosenv.2013.08.019>
- Kürten, A., Bergen, A., Heinritzi, M., Leiminger, M., Lorenz, V., Piel, F., ... Curtius, J. (2016). Observation of new particle formation and measurement of sulfuric acid, ammonia, amines and highly oxidized organic molecules at a rural site in central Germany. *Atmos. Chem. Phys.*, *16*(19), 12793–12813. <https://doi.org/10.5194/acp-16-12793-2016>
- Kurtén, T., Loukonen, V., Vehkamäki, H., & Kulmala, M. (2008). Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia. *Atmospheric Chemistry and Physics*, *8*(14), 4095–4103. <https://doi.org/10.5194/acp-8-4095-2008>
- Lelieveld, J., Berresheim, H., Borrmann, S., Crutzen, P. J., Dentener, F. J., Fischer, H., ... Ziereis, H. (2002). Global Air Pollution Crossroads over the Mediterranean. *Science*, *298*(5594), 794 LP – 799. Retrieved from <http://science.sciencemag.org/content/298/5594/794.abstract>
- MIHALOPOULOS, N., STEPHANOU, E., KANAKIDOU, M., PILITSIDIS, S., & BOUSQUET, P. (1997). Tropospheric aerosol ionic composition in the Eastern Mediterranean region. *Tellus B*, *49*(3), 314–326. <https://doi.org/https://doi.org/10.1034/j.1600-0889.49.issue3.7.x>
- Rampfl, M., Mair, S., Mayer, F., Sedlbauer, K., Breuer, K., & Niessner, R. (2008). Determination of Primary, Secondary, and Tertiary Amines in Air by Direct or Diffusion Sampling Followed by Determination with Liquid Chromatography and Tandem Mass Spectrometry. *Environmental Science & Technology*, *42*(14), 5217–5222. <https://doi.org/10.1021/es071755+>
- Sorooshian, A., Murphy, S. M., Hersey, S., Gates, H., Padro, L. T., Nenes, A., ... Seinfeld, J. H. (2008). Comprehensive airborne characterization of aerosol from a major bovine source. *Atmos. Chem. Phys.*, *8*(17), 5489–5520. <https://doi.org/10.5194/acp-8-5489-2008>