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# Dimethylamine as a major alkyl amine species in particles and cloud water: Observations in semi-arid and coastal regions

J.-S. Youn [a], E. Crosbie [b], L.C. Maudlin [b], Z. Wang [c], A. Sorooshian [a, b, c, *]

[a] Mel and Enid Zuckerman College of Public Health, University of Arizona, Tucson, AZ, USA
[b] Department of Atmospheric Sciences, University of Arizona, Tucson, AZ, USA
[c] Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ, USA

## HIGHLIGHTS

- DMA exhibits peak mass concentrations between 0.18 and 0.56 μm.
- DMA:$NH_4^+$ molar ratios generally peak between 0.18 and 1.0 μm (up to 0.04).
- DMA correlates with BVOCs, sulfate, aerosol water, and marine emissions.
- Wildfires enhance DMA levels in cloud water via dissolution in drops.
- DMA correlates with vanadium in $PM_{1.0}$ in a populated semi-arid region.

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## ABSTRACT

Aerosol and cloud water measurements of dimethylamine (DMA), the most abundant amine in this study, were conducted in semi-arid (Tucson, Arizona) and marine (Nucleation in California Experiment, NiCE; central coast of California) areas. In both regions, DMA exhibits a unimodal aerosol mass size distribution with a dominant peak between 0.18 and 0.56 μm. Particulate DMA concentrations increase as a function of marine biogenic emissions, sulfate, BVOC emissions, and aerosol-phase water. Such data supports biogenic sources of DMA, aminium salt formation, and partitioning of DMA to condensed phases. DMA concentrations exhibit positive correlations with various trace elements and most especially vanadium, which warrants additional investigation. Cloud water DMA levels are enhanced significantly during wildfire periods unlike particulate DMA levels, including in droplet residual particles, due to effective dissolution of DMA into cloud water and probably DMA volatilization after drop evaporation. DMA:$NH_4^+$ molar ratios peak between 0.18 and 1.0 μm depending on the site and time of year, suggesting that DMA competes better with $NH_3$ in those sizes in terms of reactive uptake by particles.

## 1. Introduction

Alkyl amines ($NR_3$), one of many classes of species comprising the complex organic fraction of ambient aerosol, play a pivotal role in aerosol growth processes (Silva and Prather, 2000; Moffet et al., 2008; Barsanti et al., 2009), impact radiative and hygroscopic properties of particles (Lavi et al., 2013), and pose negative health effects (Greim et al., 1998). Reported amine sources in the gas phase include animal husbandry operations, the ocean, industrial operations, biomass burning, vehicular traffic, waste incineration and sewage treatment, carbon capture and storage, tobacco smoke, and the food industry (Ge et al., 2011).

Understanding the sources, transformations, and fate of particulate amines warrants research as these species are more likely to enhance new particle formation than ammonia ($NH_3$) (Kurten et al., 2008; Bzdek et al., 2010, 2011; Smith et al., 2010; Kirkby et al., 2011; Glasoe et al., 2015). For instance, dimethylamine (DMA) concentrations in the accumulation mode were 30 times higher during nucleation events in the boreal forest of Finland as compared to non-nucleation events (Makela et al., 2001). While $NH_3$ typically is responsible for the subsequent neutralization owing to higher ambient mixing ratios (Kurten et al., 2008; Bzdek et al., 2010, 2011), and thus higher accumulation mode concentrations (VandenBoer et al., 2011), fine particle measurements have shown that amines

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* Corresponding author. PO Box 210011, Tucson, AZ, 85721, USA.
*E-mail address:* armin@email.arizona.edu (A. Sorooshian).

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accounted for up to 20% of organic mass during the wintertime in Utah (Silva et al., 2008), and reached up to 23% of measured ammonium mass concentration levels downwind of a major bovine source (Sorooshian et al., 2008). Amines have been shown to play a role in production of secondary organic aerosol (SOA) via acid-base chemistry with inorganic and organic acids to form amine salts (Angelino et al., 2001; Murphy et al., 2007) and via reactions with ozone ($O_3$), the hydroxyl radical (OH), and the nitrate radical (Tang et al., 2013). Amines can partition from being gases in the atmosphere to condensed aqueous phases in the form of deliquesced particles (Chan and Chan, 2013) and cloud and fog drops (McGregor and Anastasio, 2001; Sellegri et al., 2005).

The most abundant amines in ambient aerosol tend to be low molecular weight aliphatic amines with carbon numbers less than six (Ge et al., 2011). Dimethylamine is of particular significance as it is one of, if not the most, abundant aliphatic amine in ambient particles (Muller et al., 2009; this study), in the gas phase (Hellen et al., 2014), in fog water (Wang et al., 2015), and in cloud water (this study). Dimethylamine is important for aerosol formation as it is less volatile than $NH_3$ (vapor pressures of 203 kPa and 1003 kPa at 298.15 K, respectively). The goal of this work is to use field data of DMA in ambient particles and cloud water in marine and semi-arid regions to address the following: (i) mass size distribution of DMA; (ii) factors related to DMA concentrations; and (iii) the size-dependent molar ratio of DMA to ammonium.

## 2. Experimental methods

### 2.1. Tucson aerosol characterization observatory (TACO)

Aerosol composition measurements were conducted at TACO, which is on top of a building (30 m AGL, 720 m ASL; 32.2299°N, 110.9538°W) in inner city Tucson (metro population ~1 million; U.S. Census Bureau, 2011) on the campus of the University of Arizona. $PM_{1.0}$ composition was measured between July 2012 and June 2013 using a single-stage filter sampler (24–72 h) with pre-baked 47 mm quartz fiber filters. Size-resolved aerosol composition was measured using two micro-orifice uniform deposit impactors (MOUDI, MSP Corporation; Marple et al., 1991) with aerodynamic cut-point diameters of 0.056, 0.1, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10.0, and 18.0 μm. Teflon filters were used for MOUDI sampling (PTFE membrane, 2 μm pore, 46.2 mm, Whatman). MOUDI sample sets were collected between August 2013 and February 2015 with sampling details shown in Table 1.

The chemical analysis procedure for the $PM_{1.0}$ and MOUDI samples was the same. Filters were cut in half to use one half for chemical speciation analysis and the other for storage. Filter halves and 10 mL of milli-Q water were put in glass vials that underwent sonication at 30 °C for 20 min. The aqueous extracts were then analyzed with inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700 Series) for elements and ion chromatography (IC; Thermo Scientific Dionex ICS − 2100 system) for anions and cations. The dual IC system includes AS11-HC (2 × 250 mm) and CS12A (2 × 250 mm) columns for anion and cation analysis, respectively, in addition to a 25-μL injection loop. Anion IC analysis was conducted with a 38-min multi-step gradient with potassium hydroxide eluent (2 mM–5 mM from 0 to 8 min, 5 mM to 10 mM from 8 to 20 min, 10 mM from 20 to 25 min, 10 mM–18.67 mM from 25 to 38 min). Cation IC analysis was conducted with a 38-min isocratic method with methanesulfonic acid eluent (10 mM), which was sufficient to resolve DMA without interferences from neighboring peaks. The limit of detection (LOD) DMA was equivalent to 1 ng $m^{-3}$. LODs for other species are reported by Wang et al. (2014). Other amines were not detected above detection limits, or if they were like diethylamine (DEA), they were in the minority of samples and thus not discussed here. Of the 72 $PM_{1.0}$ samples collected, 68 exhibited reportable DMA levels along with 142 of 253 MOUDI filters (combined between TACO and NiCE, which is introduced below).

To determine how meteorological and source factors are related to DMA, other datasets are used. Collocated data were obtained for temperature (T), relative humidity (RH), water vapor mixing ratio (WVMR), wind speed (WS), and wind direction (WD). As a representation of biogenic emissions, monthly values of the Normalized Difference Vegetation Index (NDVI) were obtained from the Moderate Resolution Imaging Spectroradiometer (MODIS) between July 2012 and June 2013 for the spatial area bounded by 32–33°N and 110–112°W. Modeled surface concentrations of isoprene and monoterpenes were adopted from Youn et al. (2013) for Tucson with spatial resolution of 1.9° latitude by 2.5° longitude.

### 2.2. Nucleation in California Experiment (NiCE)

The NiCE campaign, based out of Marina, California, included surface measurements and 23 research flights with the Center for Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS) Twin Otter between July and August 2013. The study region was influenced at times by biomass burning emissions originating from wildfires near the California–Oregon border by the coast (Big Windy, Whiskey Complex, and Douglas Complex forest fires; Coggon et al., 2014). From the aircraft portion of the experiment, we focus on the cloud water measurements made using a Mohnen slotted-rod collector (Hegg and Hobbs, 1986). A total of 119 samples were collected during flights in polyethylene bottles that were subsequently analyzed for chemical composition using the IC and ICP-MS techniques mentioned above. Eighty seven of these samples exhibited reportable DMA concentrations. Further details about the collection, storage, and chemical analyses can be found elsewhere (Prabhakar et al., 2014a). Airborne $PM_{1.0}$ composition measurements were obtained using a particle-into-liquid sampler (PILS; Sorooshian et al., 2006) coupled to ion chromatography, with measurements in cloud conducted downstream of a counterflow virtual impactor (CVI) to characterize droplet residual particle properties (Shingler et al., 2012). During NiCE, the CVI $D_{p,50}$ cutsize was approximately 11 μm.

Ten sets of MOUDI samples were collected at a surface site in Marina, ~5 km from the coastline (36.7° N, 121.8° W), between 4 July and 9 August 2013 (see Table 1 for details). The sampling and post-processing procedures were identical to those of the TACO MOUDI filters.

To complement the MOUDI measurements, meteorological data during NiCE were gathered from the Monterey Peninsula station (KMRY; 36.6° N, 121.8° W) from the Mesowest database (Horel et al., 2002). Averages of several meteorological variables were calculated for each MOUDI set (Table 1). Eight day averages of chlorophyll-*a* data derived from MODIS-Aqua (8-Day Global 4-km Product) are used as a proxy for ocean bio-productivity as a potential DMA source. The spatial area of the MODIS data (36–38° N/ 121–123° W) corresponds to the region encompassing the area over which three-day back-trajectories covered (Fig. S1).

## 3. Results and discussion

### 3.1. Meteorological conditions

Prior to discussing aerosol composition results, a summary of the average meteorological conditions coinciding with the TACO and NiCE measurements is provided. TACO data are divided into different groups based on the time of year to reflect different meteorological conditions. As the TACO $PM_{1.0}$ data cover more