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# Fog chemistry at three sites in Norway

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ABSTRACT

Fog composition was investigated at three sites in Norway, one in suburban Oslo and two coastal sites in the area of the Mongstad refinery. Overall fog frequency during the study periods was low. Fog pH was around 5 with slightly lower values at Hakadal, the suburban site, compared to the coastal sites, which were slightly above 5. Major ions at the coastal sites were sodium and chloride consistent with the marine environment. The ion chemistry at the suburban site was dominated by ammonium, sulfate and nitrate, consistent with fogs in anthropogenically impacted environments. Overall concentrations of major ions were very low, orders of magnitude lower than those in polluted urban fogs. Organic matter concentrations were also low (<3 mgC/L) consistent with limited anthropogenic impact and little biogenic activity in the winter months. Selected amine concentrations were determined and ranged from nanomolar concentrations for ethylamines to several hundred nanomolar concentrations for dimethylamine, the most abundant amine investigated. While N-nitrosodimehylamine was detected in fog, the concentrations were very low in the fogs.

## 1. Introduction

Fogs and clouds are known to impact atmospheric composition and chemistry. They can incorporate gas and particulate species and can transform them through aqueous phase or heterogeneous reactions into other species. Fog chemistry has been studied for more than 30 years with most observational work performed in a limited number of locations, mainly the Central Valley of California (e.g. Zhang and Anastasio, 2001, 2003; Herckes et al., 2007a,b; Collett et al., 2008; Mazzoleni et al., 2010; Ehrenhauser et al., 2012) and the Po Valley in Italy (Decesari et al., 2000; Fuzzi et al., 2002), with some work performed in other locations including Japan (Watanabe et al, 2006; Aikawa et al., 2007), the Texas–Louisiana Gulf Coast (Raja et al., 2005, 2008, 2009), rural Pennsylvania (Staub et al., 2012) and Strasbourg (France) (Millet et al., 1995, 1996). In recent years, the observational database increased, with fog composition and chemistry investigated in more diverse environments (e.g. Li et al., 2011; Guo et al., 2012; Herckes et al., 2013 and references therein). However in some geographical areas, data on local fog chemistry are still rare; in particular, observations in Northern Europe and Scandinavia are scarce (Freud et al., 2008; Lihavainen et al., 2008; Błaś et al., 2010).

Most of the original fog chemistry research focused on inorganic species, acidity and sulfur oxidation processes. In recent years, organic species (e.g. Fuzzi et al., 2002; Herckes et al., 2013) as well as the potential for clouds and fogs to contribute to secondary organic aerosol formation (Dall'Osto et al., 2009; Ervens et al., 2011) or process environmental pollutants like polycyclic aromatic hydrocarbons (Ehrenhauser et al., 2012) came more in the focus of attention. Several studies also quantified dissolved organic nitrogen (DON). One study showed that DON comprised an average of 66% (range 19–97%) of the total nitrogen in cloud waters from Costa Rica (Weathers et al., 2000) while a different study found similar, although

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slightly lower (11–78%), DON values for clouds in Puerto Rico (Reyes-Rodríguez et al., 2009). Zhang and Anastasio (2001) found a lower contribution 16% (4–28%) of total dissolved nitrogen in Davis, CA fogs. Zhang and Anastasio (2001) also showed substantial absolute concentrations ranging from 120 to 1630 μM N with a median concentration of 303 μM N. Collett et al. (2008) reported that DON in Fresno, CA fog water samples contributed 10–17% to total nitrogen with concentrations ranging from 121 to 321 μM N.

Atmospheric DON comprises a wide range of compounds that are chemically reactive (e.g. amines) (Zhang and Anastasio, 2001; Herckes et al., 2007b) and compounds that show dynamically changing morphology (e.g. polysaccharides and proteins); ranging from simple molecules to complex biological polymers (Altieri et al., 2009). Still, overall little is known about the speciation and processing of reduced organic nitrogen compounds in fog. Some studies identified and quantified amino acids and alkyl amines in atmospheric fog and cloud samples (McGregor and Anastasio, 2001; Zhang and Anastasio, 2003; Gioda et al., 2011). Relatively high concentrations of primary amines (up to 23.8 μM in total), especially of methylamine (MA) and 2-aminoethanol (MEA), have been reported for fog water (Zhang and Anastasio, 2003). These species might play an important role in secondary organic aerosol (SOA) formation when they react with oxidants such as ozone and nitrogen oxides (Murphy et al., 2007). Also, secondary amines such as dimethylamine and diethanolamine can be oxidized by nitrogen oxides to yield nitrosamines (Hanst et al., 1977; Pitts et al., 1978; Hutchings et al., 2010). The latter have been shown to result in tumor formation for approximately 90% of 300 nitrosamines tested in laboratory animals and bioassays (Låg et al, 2011). This has recently become a matter of concern as alkyl amines such as mono-, di- and tri-ethanolamines are widely used in $CO_2$ capture processes (Nielsen et al., 2012).

In the present study, we report on the fog composition at three locations in Norway, one suburban and two coastal sites. Fog composition data is reported and discussed relative to other studies. A special focus of this work was on organic nitrogen species, therefore concentrations of several primary, secondary and tertiary amines as well as of nitrosamines have been determined.

## 2. Experimental

### 2.1. Sampling

Fog water was collected at three locations in Norway (Fig. 1). In autumn 2011, fog samples were collected at the meteorological station of Hakadal (170 m a.s.l.; 60.117N; 10.833E), ca. 17 km north of Oslo. In the fall of 2012, fog samples were collected in Sundsbø (28 m a.s.l., 60.769336N; 5.15262E) and in Bakka (27 m a.s.l., 60.767389N; 5.006311E). Sundsbø is situated 8 km southeast and Bakka 5 km southwest of the Mongstad refinery. Sundsbø is at the shoreline of the Fensfjorden and occasionally downwind of the refinery (about 17% of the time in the fall of 2012). Bakka is considered a background site with respect to Mongstad refinery (Tønnesen et al., 2011). $PM_{2.5}$ measured at Bakka in October 2012 was on average 2.4 μg/m$^3$, with a maximum hourly average concentration of 13 μg/m$^3$, confirming that Bakka is less influenced by pollution from the refinery.

At all locations, fog water collection was performed using automated systems (Hutchings et al., 2009) which consisted of a Caltech Active Strand Cloudwater Collector (CASCC) (Demoz et al., 1996), a Colorado State University optical fog detector (OFD) (Carrillo et al., 2008) and a datalogger/controller unit. The OFD allows for the detection of clouds and the measurement of cloud liquid water content (LWC) (Carrillo et al., 2008). The data from the OFDs were collected on Campbell Scientific dataloggers. The OFDs were calibrated regularly against a custom calibration disk. When the OFDs reached a threshold value (LWC of 60 mg/m$^3$ for 5 min, corresponding approximately to a visibility of less than 500 m) cloud collection was initiated. The collection ceased when the OFD measurement dropped below the threshold value of 60 mg/m$^3$ for one minute.

The CASCCs were cleaned with Milli-Q water (>18 MΩ) after each sample retrieval to ensure the integrity of the collected samples. In addition, in the absence of fog, collectors were regularly cleaned. Field blanks were collected by spraying Milli-Q water on the strands and collecting the impacted water after cleaning. Field blanks and field deionized water aliquots were processed by the same analytical procedures as the cloud water samples.

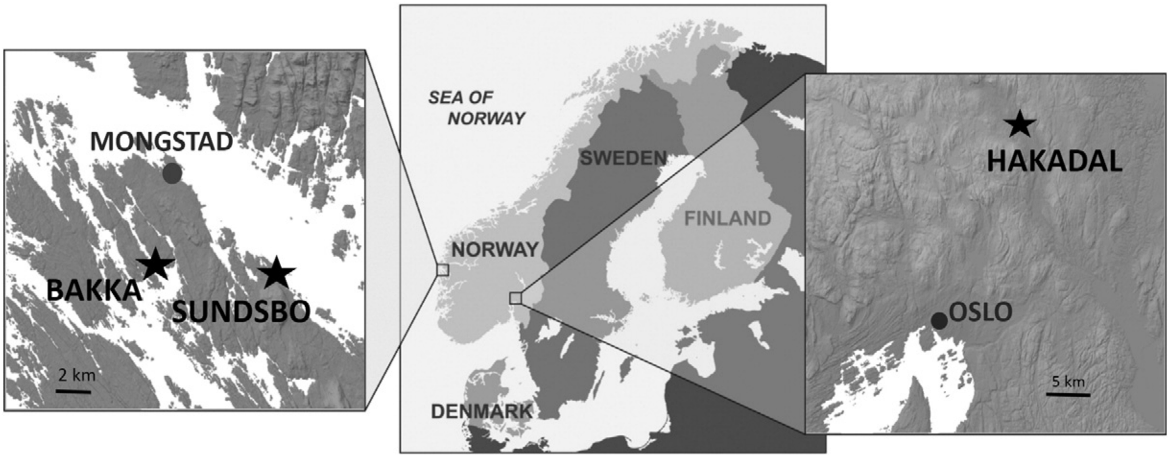

**Fig. 1.** Location of fog collection sites.