

## Introduction

Fogwater has the ability to concentrate gas and particle phase species from the atmosphere. While numerous field observations on fog chemistry exist, most studies are geographically limited to a few select environments like Italy's Po Valley or the Central Valley of California. Traditionally fog chemistry research focused on acidity and inorganic composition. More recently organic carbon became a focus of attention and some studies showed a significant contribution of organic nitrogen to fog organic matter. However, little is known on the processing of organic nitrogen species by fogs.

In this study we present results on fogwater chemistry at 3 sites in Norway. Beyond acidity, inorganic species and bulk carbon measurements, several nitrogen species were included in the present study.

## Sampling sites

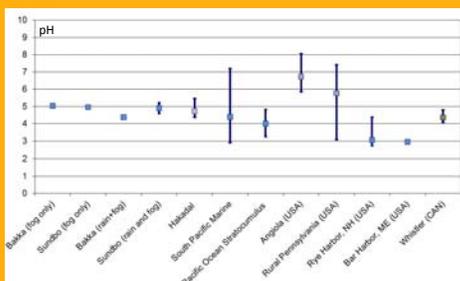


Bulk water samples were collected at the meteorological station of Hakadal, ca. 17 km north of Oslo in autumn 2011. Fog water samples were also collected at two NILU monitoring stations at the west coast of Norway: Sundsbø and Bakka in autumn of 2012 in the framework of the ongoing measurement campaign of meteorological data by CCM related to the Environmental Impact Assessment for a fullscale CO<sub>2</sub> capture plant at Mongstad (Karl et al., 2011). A custom build fog collection system comprised of a CSU optical fog detector (OFD) and a Caltech Active Strand Cloud Collector (CASC) unit (Carrillo et al., 2008) was employed.



## Fogwater Acidity

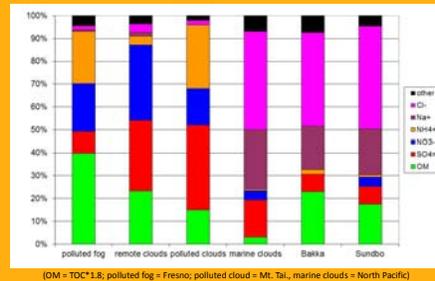
The pH of fog samples in Bakka and Sundsbø was ≈5.0. The suburban fogs in Hakadal showed a similar pH of 4.7 (4.2-5.5). A pH around 5 is an indication of low acid contamination as it is close to the pH expected for natural waters in equilibrium with atmospheric CO<sub>2</sub> (≈5.6). The value is lower than pH in continental polluted fogs like the Po Valley in Italy of the central Valley of California. The values are in the range of pristine clouds and marine clouds. Comparison to other coastal fog studies is a little biased as since the 1980s hardly any studies occurred, hence there is a substantial time delay during which SO<sub>2</sub> emissions in both Europe and North American have strongly decreased.



## Major ions

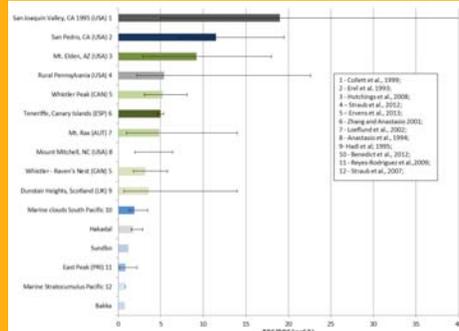
The relative composition for Bakka and Sundsbø fog samples shows a composition similar to marine clouds (figure below) with the dominant components chloride and sodium. Interestingly the molar ratio Cl<sup>-</sup>/Na<sup>+</sup> is 1.4 in both cases which is a little higher as the typical sea salt ratio of 1.16. Nitrate, ammonium and sulfate concentrations are very low compared to other fog and cloud studies. The sum of all ions was only around 200 µeq/L compared to 2000s µeq/L for polluted Fresno fogs. The contribution of organic matter seems a little higher than for typical marine environments, however this is likely biased and a result of the very low ionic concentrations.

For the suburban location Hakadal, there is some contribution of sea salt but then noticeable contributions of sulfate, ammonium and nitrate, more similar to radiation fogs in urban environments. Overall concentrations are higher than for the marine sites (~400 µeq/L) but substantially lower than polluted urban fogs (Fresno).



(OM = TOC\*1.8, polluted fog = Fresno; polluted cloud = Mt. Tai; marine clouds = North Pacific)

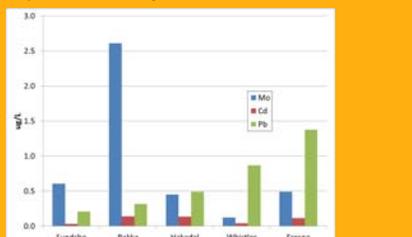
## Dissolved Organic Carbon (DOC)



Dissolved organic carbon (DOC) concentrations were very low at all locations with concentrations lower than 1.5 mg C/L for both coastal sites, which is close to field blanks and lower than 3 mg C/L for the suburban site. These concentrations correspond to observations in very pristine marine environments and in the case of suburban Oslo are within the lowest values ever reported for fog events in a populated area. All collection occurred in the fall and winter time so there were very limited biogenic emissions, which explains the lower concentrations compared to a rather remote environment like Whistler.

## Metals

Metal concentrations were very low except Mo at the marine sites, however this is based on single samples. In Hakadal, concentrations were low compared to urban fog environments.



## Amines

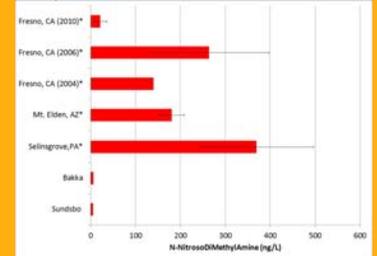
Little is known about the processing of reduced organic nitrogen compounds in fog and only few studies on concentration levels of reduced organic nitrogen species in rain, cloud, and fog water are available. In this study the concentrations of several primary and secondary amines have been determined in fog water samples. Amine concentrations in fog water at the three Norwegian sites were rather low. DMA showed highest level (5-20000 ng L<sup>-1</sup>) among the identified amines (Table lists select amines; concentrations in ng L<sup>-1</sup>).

| Compound            | Hakadal | Sundsbø | Bakka |
|---------------------|---------|---------|-------|
| Ethanolamine (MEA)  | 948     | 434     | n.d.  |
| Methylamine (MA)    | 5000    | 277     | 13    |
| Dimethylamine (DMA) | 19637   | 11484   | 5865  |
| Ethylamine (EA)     | 64      | n.d.    | n.d.  |
| Diethylamine (DEYA) | 438     | 127     | 422   |

## Nitrosamines

Nitrosamines, a family of highly toxic and carcinogenic organic nitrogen species, can form in the atmosphere through reactions of amines with NO<sub>x</sub>. In carbon capture processes, this could occur within a scrubber unit using amines or downstream of a unit in an emission plume.

Nitrosamine presence and concentrations were investigated at Bakka and Sundsbø. N-Nitrosodimethylamine (NDMA) was detected but at very low concentrations, close to detection limits. This is substantially lower than any other fog or cloud study we investigated NDMA. In addition another nitrosamine was detected N-Nitrosopyrrolidine, but its presence remains to be confirmed. No traces of pyrrolidine were found in the fog water.



## Summary

Fog chemistry was investigated at 3 sites in Norway: Bakka (marine), Sundsbø (marine) and Hakadal (suburban location).

Fog events were rather rare and only a few events occurred at the sites during the study periods.

Fog liquid water content (LWC), as measured by the OFD, ranged from 150 to 250 mg m<sup>-3</sup> during the fog events.

Fog water samples were slightly acidic (pH around 5) with overall very low solute concentrations. Metal and organic matter concentrations were overall low (<3 mg/L), even at the suburban location.

Amines were detected but their concentrations were very low, in the nanomolar range.

Most nitrosamines investigated were not detected in the Mongstad area fogs. N-Nitrosodimethylamine, while detected, was at very low concentrations.

## Acknowledgements

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## References

Karl, M., R. F. Wright, T. F. Bergling, and B. Denby. Worst case scenario study to assess the environmental impact of amine emissions from a CO<sub>2</sub> capture plant. Int. J. Greenhouse Gas Control, 5, 430-447, 2011.  
 Carrillo, J.H., Emert, S.E., Sherman, D.E., Herckes, P., Collett, J.L., 2008. An economical optical cloud/fog detector. Atmos. Res. 87, 259-267.