

Characterization of Atmospheric Organic Matter  
and its Processing by Fogs and Clouds

by

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## ABSTRACT

The atmosphere contains a substantial amount of water soluble organic material, yet despite years of efforts, little is known on the structure, composition and properties of this organic matter. Aqueous phase processing by fogs and clouds of the gas and particulate organic material is poorly understood despite the importance for air pollution and climate. On one hand, gas phase species can be processed by fog/cloud droplets to form lower volatility species, which upon droplet evaporation lead to new aerosol mass, while on the other hand larger nonvolatile material can be degraded by in cloud oxidation to smaller molecular weight compounds and eventually CO<sub>2</sub>.

In this work High Performance Size Exclusion Chromatography coupled with inline organic carbon detection (SEC-DOC), Diffusion-Ordered Nuclear Magnetic Resonance spectroscopy (DOSY-NMR) and Fluorescence Excitation-Emission Matrices (EEM) were used to characterize molecular weight distribution, functionality and optical properties of atmospheric organic matter. Fogs, aerosols and clouds were studied in a variety of environments including Central Valley of California (Fresno, Davis), Pennsylvania (Selinsgrove), British Columbia (Whistler) and three locations in Norway. The molecular weight distributions using SEC-DOC showed smaller molecular sizes for atmospheric organic matter compared to surface waters and a smaller material in fogs and clouds compared to aerosol particles, which is consistent with a substantial fraction of small volatile gases that partition into the aqueous phase. Both, cloud and aerosol samples presented a significant fraction (up to 21% of DOC) of biogenic nanoscale

material. The results obtained by SEC-DOC were consistent with DOSY-NMR observations.

Cloud processing of organic matter has also been investigated by combining field observations (sample time series) with laboratory experiments under controlled conditions. Observations revealed no significant effect of aqueous phase chemistry on molecular weight distributions overall although during cloud events, substantial differences were apparent between organic material activated into clouds compared to interstitial material. Optical properties on the other hand showed significant changes including photobleaching and an increased humidification of atmospheric material by photochemical aging. Overall any changes to atmospheric organic matter during cloud processing were small in terms of bulk carbon properties, consistent with recent reports suggesting fogs and clouds are too dilute to substantially impact composition.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Importance of fogs and clouds for Atmospheric Chemistry, Air Pollution and Climate

Clouds are a common occurrence on Earth, with more than 50% of the surface of the Earth usually covered with clouds and roughly 7% of the volume of the troposphere contains clouds (Wayne, 2000). This ubiquity and distribution leads to substantial interactions with atmospheric constituents, impacting atmospheric composition, and with solar radiation, impacting Earth climate.

Clouds, aerosols and cloud/aerosol interactions have significant impact on atmospheric solar radiation balance through optical and latent heat effects. Clouds in the troposphere interact with both solar and terrestrial radiation. Clouds can reflect incoming solar radiation back to space, which results in a cooling effect while simultaneously trapping terrestrial long wavelength thermal radiation leading to a warming effect (Ramaswamy and Ramanathan, 1989; Harrison et al., 1990; Hartmann, 1992). The net thermal effect of clouds is complex, depends on the lifetime of clouds and their altitude in the atmosphere among others. The magnitude of cloud effects and cloud/aerosol effects on Earth radiative balance remains one of the largest sources of uncertainty in our current understanding of the climate system (IPCC, 2013).

In terms of impact on atmospheric composition, clouds and in particular fogs (clouds touching the ground) have a substantial impact on local and regional air quality. Fogs and clouds can process atmospheric particles and gases through uptake into the droplet phase followed by chemical reaction and or heterogeneous reactions at the droplet interface. Some of the worst air pollution episodes in history have been associated with

fogs. The most notorious incident, the London smog (smoke and fog) episode in 1952, caused an estimated 4,000 deaths within 5 days, and the event left thousands with respiratory diseases, potentially shortening their lives (Wayne, 2000). More recently a lot of air pollution issues in California's Central Valley as well as in Chinese locations are associated with fogs and fog/gas, fog aerosol interactions, playing a substantial role. Therefore investigating the physical and chemical properties of fogs and clouds is crucial to improve our understanding of atmospheric processes and eventually air pollution and climate change.

## 1.2 Physical properties of fogs and clouds

Aerosols are defined as solid and liquid material that is suspended in the air. When relative humidity reaches 100% or more, the air is supersaturated. It is kinetically preferable for cloud droplets to form on nuclei from vapor phase through heterogeneous nucleation since normally there are sufficient hygroscopic aerosols in the air that can act as cloud condensation nuclei (CCN) (Rogers and Yau, 1989).

Cloud droplets typically have sizes ranging from several micrometers to tens of micrometers (Pruppacher and Klett, 1997). A fairly dense cloud could have 1000 droplets within  $1 \text{ cm}^3$  of air under the assumption of 10 micrometer diameter which possesses a total water surface area about  $3 \times 10^{-3} \text{ cm}^2$ , the total surface area and volume of water within clouds are enormous (Wayne, 2000). However, only 10% of clouds actually precipitate (Lelieveld and Crutzen, 1990) while 90% evaporate to become an aerosol particle again. Hence atmospheric particles, on which cloud drops form, might go through 3-7 cloud cycles before their eventual removal as precipitation (Lelieveld and Heintzenberg, 1992).

In the present study we focus on liquid clouds and fogs but ice fogs and clouds (e.g. cirrus clouds) also exist. An ice fog was found causing 10°C/day cooling (Gotaas and Benson, 1965), however nucleation processing of ice crystals is still unknown and ice fog is the major hazardous condition for transportations in the northern latitudes (Charlton and Park, 1984). In this work we also adopt the convention of the fog chemistry community that a cloud that touches the ground is referred to as a fog. At a droplet level and in terms of chemistry, there are no differences between fogs and clouds, although from a meteorological formation point of view, they form through different atmospheric processes. As a result, some microphysical parameters differ between fogs and clouds. The liquid water content (LWC) in fogs is typically less (0.02-0.8 g/m<sup>3</sup>) than in clouds where the LWC ranges from 0.05 to 2.0 g/m<sup>3</sup> (Herckes and Collett, 2015).

In this work fogs and clouds are being investigated, and most commonly radiation fog samples were collected in field studies. These fogs typically form at night time in winter, when radiative cooling close to the ground leads to moist air in which humidity increases until condensation and eventually coalescence of fog droplets is observed. Radiation fogs typically last only a few hours and dissipate in the morning hours when the sun heats the ground, resulting in an increase in temperature and decrease in humidity with droplets evaporating. In some instances the radiation fogs might have been enhanced with an advection component. In mountain studies, fogs were or stratus clouds, or orographic clouds that form through the cooling of air masses along an altitude gradient on the mountain during updrafts. In many cases however it is impossible to determine the exact nature of the fog/cloud in field studies, so was the case here except for the clear cases of radiation fogs in California's Central Valley.

Finally, from a chemical point of view, the initial composition of cloud droplets is determined by the composition of the condensation nuclei on which the clouds form but as soon as a liquid phase is present, gas/liquid exchanges, like the dissolution of soluble gases can occur as well as aqueous phase chemical reactions (IPCC, 2013; Herckes and Collett, 2015). Examples of multiphase interactions are shown in Figure 1.1.

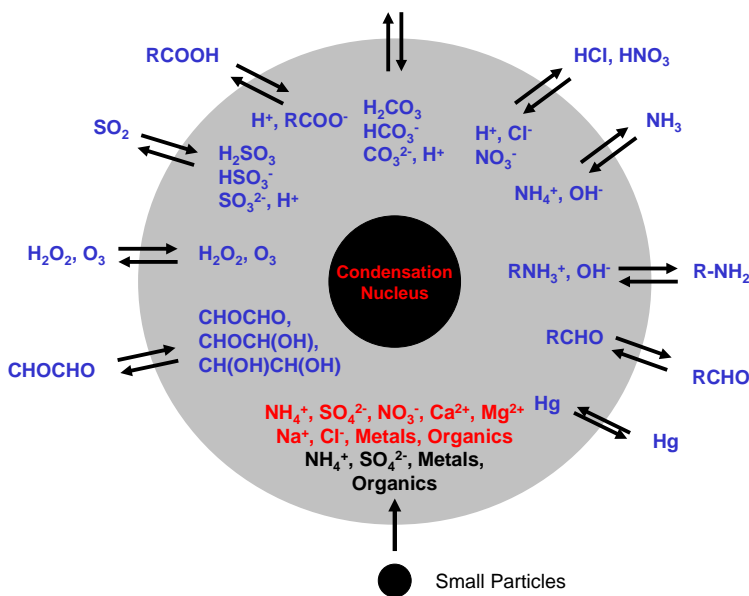


Fig 1.1 Schematic representation of the influence of particles and gases on cloud/fog drop composition. Adopted from Herckes and Collett, 2015.

### 1.3 Present knowledge of cloud and fog chemistry

#### 1.3.1 Inorganic chemistry

Acid precipitation, especially acid rain was a great concern back in the 1980s. At that time, research on cloud and fog chemistry intensified to uncover the mechanisms of acid precipitation generation. Observational studies uncovered highly acid fog, like observations ranged from 2.2 to 4.0 in Los Angeles and Bakersfield (Waldman et al.,



1982). Numerous field and laboratory investigations were performed, mainly in the U.S. and Europe, during the 1980s to understand cloud/fog acidification, especially the processing of sulfur dioxide (examples: Munger et al., 1983; Hoffman, 1986; Hering et al., 1987; Stumm et al., 1987; Gervat et al., 1988, 1989).

The observational cloud/fog composition studies during the 1980s were mainly focused on inorganic species involved in acidification like protons, nitrate, sulfate and ammonium. Some studies included oxidants like hydrogen peroxide, oxidation catalysts like manganese and iron or reduced sulfur and nitrogen species.

Weathers and coworkers (1988) summarized a large observational effort the Cloud Water Project (CWP) which studied cloudwater composition for 2 years at 10 different sites in North America. Results of these studies confirmed isolated earlier work that substantial differences between sites exist. At that time, sites in the Western US showed moderate acidity with pH values ranging from 4.4 to 4.6 compared to eastern sites ranging from 2.42 to 4.85, consistent with chemical patterns in wet deposition reported in the literatures (Likens and Butler, 1981). On average, ions at East Coast sites were dominated by sulfate, nitrate, hydrogen ion and ammonium ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{H}^+$ ,  $\text{NH}_4^+$ ), whereas in the western coast ions were dominated by chloride sulfate, hydrogen ion and sodium with overall lower concentrations lower than in the East. Sulfate in fog and cloud could result from aerosol sulfate scavenging or in situ oxidation of dissolved sulfur dioxide. Nitrate is derived from both anthropogenic and biogenic sources. Ammonia-the precursor of ammonium in fogs and clouds is emitted by agriculture, livestock and nitrogen-fixing bacteria. Sea salt made significant impact on all of the costal sites both on the west coast and the east coast. These observations were consistent with similar work in

Europe and illustrated that cloud and fog solute concentrations were typically at least one order of magnitude higher than precipitation concentrations.

In the 1990s interest in acid rain decreased and so did the number of observational studies in the US and Europe, however especially since the end of the 1990s work intensified in Asia, with a local increased concern for acid precipitation. Novel insights in the 1990s were gained from the observations on droplet size-resolved cloud composition, showing substantial differences in concentrations and chemistry with droplet size (Collett et al., 1993; Collett et al., 1994; Bator et al., 1997).

In recent years, post 2000, in terms of inorganic composition and reactivity in clouds, the main developments were an increase in studies globally, especially in Asia, increasing our understanding of fogs and clouds globally (Aikawa et al., 2007; Safai et al., 2009; Guo et al., 2012; Niu et al., 2010 and references therein). Some research has focused on trace metals and redox catalyzed processes (Deguillaume et al., 2004; Liu et al., 2012). Another aspect was the further improvement of models and observations for the quantification of depositional fluxes by direct cloud deposition, through gravitational or turbulent deposition onto surfaces and ecosystems. A number of studies evaluated deposition fluxes of nutrients like nitrates, acidity or trace metals and showed that at high altitude sites, direct cloud deposition can substantially enhance material fluxes (Weathers et al., 2000; Herckes et al., 2002a; Kalina et al., 2002; Beiderwieden et al., 2007). In many cases the hydrologic input by direct cloud deposition was small but given the high concentrations in fogs and cloud, occult (not detected by rain gauges) deposition can equate wet deposition fluxes by precipitation (rain and snow) (Herckes et al., 2002a; Jung et al., 2013).

Finally in recent years in Europe, Japan and the US studies emerged looking at temporal changes in inorganic cloud chemistry. Herckes and co-workers showed that following emission control measures, pH substantially increased in urban fogs in Strasbourg (France) over a 10 year period while lead concentrations decreased by more than one order of magnitude (Herckes et al., 2002b). Similar pH changes were observed in Japan (Aikawa et al., 2007). Finally in California's Central Valley, likely the region with the most extensive dataset, results also showed a decrease in acidity over time, following the implementation of sulfur emission reduction policies (Herckes et al., 2015).

### 1.3.2 Organic chemistry

In the 90s researchers' attention gradually shifted from inorganic components in fogs and clouds to investigating fog/cloud processing of atmospheric organic matter. First observations showed the presence of high concentrations of organic carbon in fog. In later years, more studies included carbon measurements (cf Herckes et al., 2013). Some studies showed that up to 77% of the total organic carbon (TOC) in cloud and fog water is dissolved organic carbon (DOC), operationally defined as passing through a filter (Herckes et al., 2002c). Insoluble substances present in fog droplets could be soot or insoluble organic or inorganic residues (Herckes et al., 2013). The concentrations of organic matter are substantial when compared to inorganic species. Organic matter concentrations are slightly lower than nitrate, similar to ammonium and higher than sulfate in relative polluted California radiation fog reported by Herckes and coworkers (2007a) while at Whistler, organic matter is observed being as important as the total of sulfate nitrate and ammonium in intercepted clouds (Lee et al., 2011).

Numerous studies have been conducted to identify and quantify individual organic species in fog and cloud water to elucidate its molecular composition. Among the species that have been identified, small chain carboxylic acids (formic and acetic), dicarboxylic acids (oxalic acid), carbonyls (formaldehyde), and dicarbonyls (glyoxal and methylglyoxal) (Millet et al., 1997; Van Pinxteren et al., 2005; Collett et al., 2008; Ervens et al., 2013 and references therein) are the most commonly reported and abundant. Meanwhile, organic nitrogen species (amino acids and amines) (Zhang and Anastasio, 2001, 2003), polycyclic aromatic hydrocarbons (PAH), oxygenated polycyclic aromatic compounds have been detected and investigated (Ehrenhauser et al., 2012). An organic speciation of fog samples from Fresno in early 2000s (Collett et al., 2008) showed the mass of DOC was comprised by organic acids such as acetic acid (21-31%), formic acid (6-7%), oxalic acid (3-4%), propionic acid (2-3%), carbonyls like formaldehyde (3-4%), methyl glyoxal (2-4%), glyoxal (2-3%). The rest of the organic acids (pyruvic, glutaric, succinic, malonic, lactic, butyric, and pinic acids) and carbonyls (acetaldehyde, acetone/acrolein, isovaleraldehyde, tolualdehyde and hexaldehyde) account for 5% and 3% of total DOC separately (Collett et al., 2008). It is often true that more than 50% of DOC remain uncharacterized not only because of the scope and techniques used by the different investigators but also because a portion of DOC defies characterization by traditional analytical methods. It is very challenging to reveal the identities and characteristics of the unknown portion of DOC because of the complexity of chemical precursors in particles and gas phase and reaction mechanisms that could happen in gas phase or on the surface of particles and in fog/cloud droplets which also vary by location, temperature and other meteorological parameters.

#### 1.4. Observational Fog studies

Observational cloud and fog studies go back all the way to the 1800s (Möller, 2008). The major challenge is the collection of fog and cloud droplets for chemical analysis in sufficient amounts because of the low liquid water contents in fogs and clouds (typically less than  $1 \text{ g/m}^3$  often less than  $0.1 \text{ g/m}^3$ ). Initial studies looked solely at fog deposition while in later studies passive fog and cloud samplers were used that relied on the wind to impact fog and cloud droplets onto collection surfaces. This collection can be strongly dependent on atmospheric conditions (wind speed) and easily leads to biases in sampling by missing or larger or smaller droplets. Observational fog studies really took off with the use of active collectors that actively draw droplet laden air into a device where the droplets are collected. Fog/cloud samples in were collected by different types of Caltech Active Strand Cloud water Collector (CASCC) and a stainless steel version collector with similar configuration (Demoz et al., 1996; Herckes et al., 2002d). The most commonly used in this study, a CASCC type collector is shown in Figure 1.2.

During a fog/cloud event, air with aqueous droplets is drawn by a fan located at the end of the duct under a flow rate of  $24.5 \text{ m}^3/\text{min}$  through six rows of  $508 \text{ }\mu\text{m}$  diameter Teflon strands placed at the front of the duct. The strands are installed at a  $35^\circ$  angle. Roughly 86% of droplets hit the strands, coalesce, and then flow into a HDPE bottle driven by gravity and aerodynamic drag.



Fig. 1.2 A single stage Caltech Active Strand Cloud water Collector being used on top of Whistler mountain, Canada.

The size cut (droplet diameter collected with 50% efficiency) is predicted to be 3.5  $\mu\text{m}$ . Various CASCC versions have been designed to fulfill different research goals, a size fractionating CASCC also exists which is a two stage collector that allows droplets be separated by their size. The CASCC 2 is a smaller collector for bulk sample collection while its modified version Caltech Heated Rod Cloud water Collector is equipped with heatable collecting surfaces to remove rime formed during collecting super cooled cloud droplets. A stainless steel version CASCC with larger flow rate was first deployed by Herckes et al. (2002d) aimed for collecting samples that were more suitable for analysis of organic compounds, later results of organic carbon content showed that different building materials did not have any substantial effect.

The liquid water content (LWC) is a physical parameter that corresponds to the mass of liquid water per volume of air LWC is essentially a measure of fog or cloud density or abundance. It is a crucial value to transform aqueous phase concentrations observed in

cloud water into air concentrations and hence compare fog/cloud concentrations to gas and particle concentrations. Frequently what is known is the concentration in the aqueous phase (per volume of cloud water)  $C_{aq}$  but what is wanted for data analysis is the concentration of the species per volume of air in droplets or  $C_{air}$ . The link between both of these concentrations is the liquid water content (LWC) or the amount of liquid water contained per volume of air.

$$C_{air} = LWC \times C_{aq} \quad (1)$$

There is also an indirect approach with a cloud sampler to estimate the LWC. This is typically done by using the run time of the collector, the flow of the collector, the amount of water collected and the collection efficiency of the collector (Demoz et al., 1996).

$$LWC \text{ (mg/m}^3\text{)} = \frac{\text{amount of water collected (mg)}}{\text{collection time (min)} \times \text{flow rate (m}^3\text{/min)} \times \text{collection efficiency}} \quad (2)$$

In this study a Gerber Particle Volume Monitor (Gerber et al., 1994) and/or an optical fog detector (Carillo et al., 2008) were connected to a Campbell CR1000 datalogger to provide quantitative or semi-quantitative LWC values, also to achieve automated sampling by setting up a LWC trigger threshold. Such automated sampling approaches have been used in earlier studies (Hutchings et al., 2009). Alternatively people used visibility as a tool to automatically trigger collection (e.g. Straub et al., 2012).

## 1.5 Goals and objectives

The overall goal of this work is to improve our understanding of cloud and fog processing of atmospheric constituents. A special focus is on the processing of organic matter and its impact on bulk properties like functionality, fluorescence and molecular weight distributions. To that effect several field studies were performed, analytical approaches novel to cloud chemistry developed and complementary laboratory studies on authentic and model solutions performed.

In the second chapter, I will present field observations on the chemical composition of fogs and clouds collected in the Central Valley of California, in Whistler and in Norway. These studies allowed for an increase in the observational database on cloud chemistry and the compositional differences will be discussed. These studies also provided the samples and data for the organic matter work detailed in the next chapters.

In the third chapter, different bulk analytical approaches for the characterization of organic matter in fogs and clouds, some novel to atmospheric science, were applied to fogs and clouds collected in different environments. These investigations allowed us to increase our understanding of organic matter characteristics in fogs and clouds, explore site and event related differences and compare atmospheric organic matter to surface water organic matter.

In the fourth chapter the analytical tools from chapter 3 are used to investigate the changes of organic matter during a fog/cloud event. A major hypothesis was that fog processing of organic matter will lead to higher molecular weight compounds as well as to higher degrees of oxidation. Laboratory studies replicating atmospheric aqueous phase



processing under controlled conditions are performed. The same bulk characterization techniques are used to relate detailed mechanisms to field studies

The fifth chapter summarizes the observations and provides suggestions for future research.

## CHAPTER 2

### CHEMICAL COMPOSITION OF FOGS AND CLOUDS

#### 2.1 Introduction

While fog and cloud composition has been studied for decades, observational studies remain rather rare and many are confined to a few areas like Italy's Po Valley (e.g. Decesari et al., 2000) or the Central Valley of California (e.g. Collett et al., 2002), hence observations are strongly geographically limited. Recent work showed that even in the same location fog and cloud chemistry might have changed substantially over the years due to changes in emission patterns (Herckes et al., 2015), as a result older studies might not be reflective of today's conditions. While overall fog studies became more geographically diverse 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).

In the present work, five fog/cloud and aerosol field studies were conducted between 2010 and 2012 in Fresno, CA; Whistler, BC; Davis, CA; three locations in Norway and Bakersfield, CA and allowed the collection of the samples used for chemical characterization methods (Chapter 3) and in situ processing studies (Chapter 4). Norway,

fog samples were obtained in autumn 2011 at Hakadal (suburban Oslo) then in the fall of 2012 at Bakka and Sundsbø (coastal) and these were the first observations in the area.

In this chapter we will present the general chemistry and composition of fogs in these various locations as well as discuss the differences in chemistry and composition between these very diverse sites.

## 2.2. Sampling locations and experimental set-up

### 2.2.1. Central Valley of California

Fog studies have been conducted since the 1980s in the Central California Valley making it the most studied area in the US. The area gained its reputation for winter fog mainly due to the topography of the basin and strong temperature inversions. Clouds are rare during winter stagnant air condition, allowing nighttime radiative surface cooling to cause radiation fog formation (Holets and Swanson., 1981). Observations show that fogs in this area normally last from sunset to the next midday for 12-18 hours but in some cases persist for days due to surface heating lifting fog into a low stratus cloud. A detailed history of past studies in Central Valley of California has been reviewed by Herckes et al., (2015). Two field campaigns were conducted in Fresno and Davis (Figure 2.1) to collect both fog and ambient aerosols.



Fig. 2.1 Locations of fog and aerosol collection sites in Central California Valley. Map source: Google maps.

In Fresno, the sampling site was located on the experimental farm of California State University, Fresno. The sampling site was situated in a large agricultural plot but relatively close (hundreds of meters) to major highways and residential areas.

The Davis sampling location was located on a small-scale agricultural field near the UC Davis campus, close to a small airport and adjacent to highways. Moderate air pollution was observed at both sites (Ehrenhauser et al., 2012). The sampling period in Fresno lasted from January 9<sup>th</sup> to 16<sup>th</sup> 2010 while in Davis it lasted from January 6<sup>th</sup> to 25<sup>th</sup> 2011

At both sites an array of samplers was used, including plastic and stainless steel versions of the Caltech Active Stand Cloudwater Collector CASCC (Demoz et al., 1996). In addition Hi-Volume aerosol samples were collected on quartz fiber and cellulose substrates. Additional information is available in Ehrenhauser et al., 2012.

#### 2.2.2. The Whistler Aerosol and Cloud Study (WACS)

The ‘Whistler Aerosol and Cloud Study’ (WACS2010) was conducted between June 15<sup>th</sup> and July 28<sup>th</sup> 2010 on Whistler Mountain, Whistler, British Columbia, Canada. Two sampling sites were established during WACS field campaign as shown in Figure 2.2. A first site was located at Whistler mountain mid-station known as Raven’s nest (WRN) with an altitude of 1320m-asl, fog sampling operated from June 18<sup>th</sup> to July 26<sup>th</sup>. A second site was located at the peak of Whistler mountain (2182m-asl), operated from July 3<sup>rd</sup> to July 26<sup>th</sup> 2010.

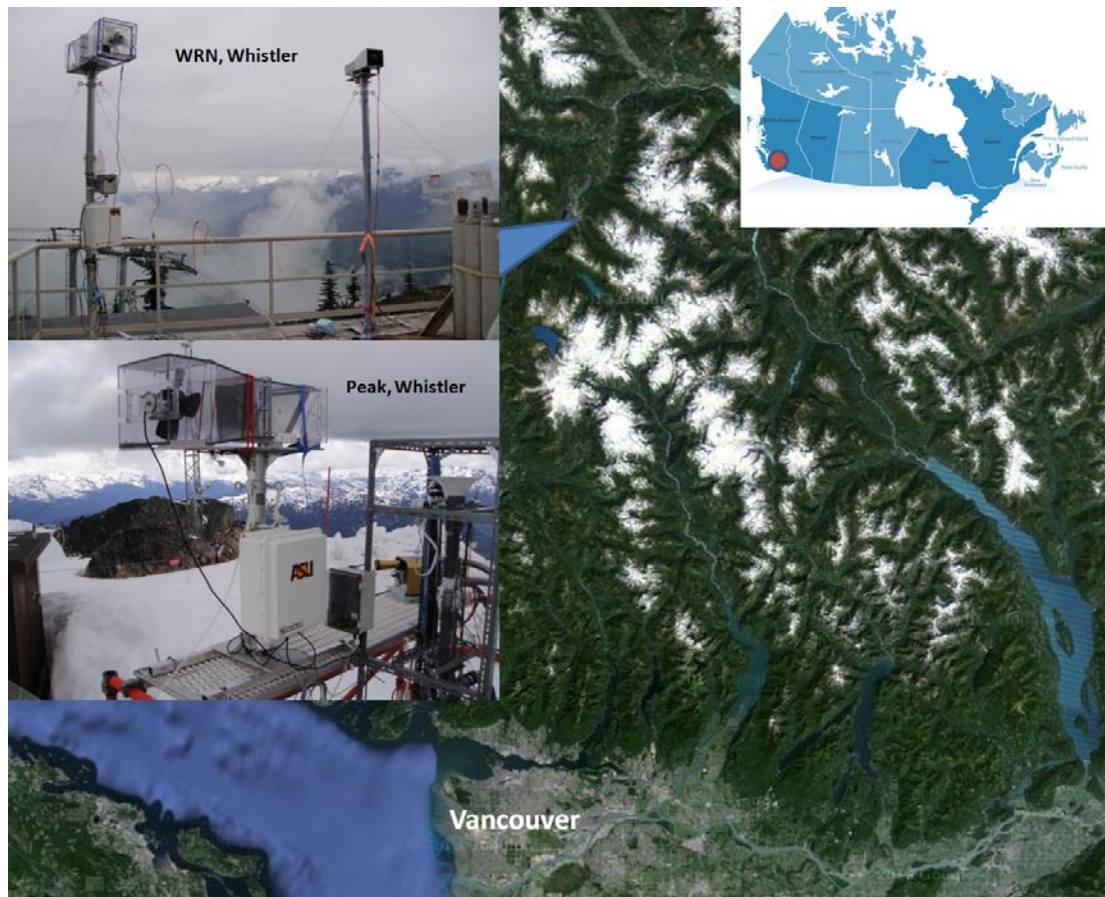


Fig. 2.2 Locations of cloud collection sites in Whistler.  
Map source: Google maps.

Fogwater collection at both sites was performed using automated systems which consisted of a CASCC, a Gerber particle volume monitor (Gerber et al. 1994) and a datalogger/controller unit. The PVM allows for the detection of fogs and a measurement of cloud liquid water content (LWC). The data from the PVMs were collected on Campbell Scientific dataloggers. The PVMs were calibrated regularly against a calibration disk. When the PVMs reached a threshold value (LWC of  $60 \text{ mg/m}^3$  for 3min) fog collection was initiated. The collection ceased when the PVMs dropped below the threshold value of  $60 \text{ mg/m}^3$  for one minute.

The CASCCs were cleaned with Milli-Q water (>18 M $\Omega$ -cm) after each sample retrieval to ensure the integrity of the collected samples. In addition, in the absence of cloud, 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 cloudwater samples.

Fogwater samples and datalogger information were typically retrieved within 2-24 h of the event. All samples and blanks were treated identically. Samples were kept in cold storage (4°C) in WRN then mailed to ASU by overnight shipping at the end of WASC. Ambient air samples were collected along with the fog samples in daily resolution.

### 2.2.3. Norway

Fog water was collected at three locations in Norway (Figure 2.3). In autumn 2011, fog samples were collected at the meteorological station of Hakadal (170 m a.s.l.; 60.117 N; 10.833 E), ca. 17 km north of Oslo. In the fall of 2012, fog samples were collected in Sundsbø (28 m a.s.l., 60.769336 N; 5.15262 E) and in Bakka (27 m a.s.l., 60.767389 N, 5.006311 E). 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 as a background site with respect to Mongstad refinery (Tønnesen, et al., 2011). PM<sub>2.5</sub> measured at Bakka in October 2012 was on average 2.4  $\mu\text{g}/\text{m}^3$ , with a maximum hourly average concentration of 13  $\mu\text{g}/\text{m}^3$ , confirming that Bakka is less influenced by pollution from the refinery.





Fig. 2.3 Locations of fog collection sites in Norway.

Map source: Google maps.

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) (Carillo 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) (Carillo 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  $60 \text{ mg/m}^3$  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  $60 \text{ mg/m}^3$  for one minute.

The CASCCs were cleaned with Milli-Q water ( $>18 \text{ M}\Omega\text{-cm}$ ) 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.

### 2.3. Chemical analysis

Chemical analyses for each study follows well established protocols (e.g. Hutchings et al., 2009) and were also detailed in the peer reviewed manuscripts from the present studies (Ehrenhauser et al., 2012; Ervens et al., 2013)

#### 2.3.1. pH measurements

Fog sample pH on site in each study using a Denver Instruments IB-5 pH meter equipped with a Fisher Scientific Accumet gelfilled pH electrode, calibrated against pH 4



and 7 buffers.

### 2.3.2. Major ions

Major ions were determined using ion chromatography. Inorganic anion concentrations ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) were determined using a Dionex IC20 ion chromatography system equipped with an IonPac®AG12A guard column, IonPac®AS12A analytical column, a Dionex Anion Self-Regenerating Suppressor (ASRS), and a conductivity detector. Separation was achieved using a 2.7 mM  $\text{Na}_2\text{CO}_3$ /0.3 mM  $\text{NaHCO}_3$  eluent at a flow rate of 1.2 mL/min.

Inorganic cation ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) concentrations were determined using a IC20 ion chromatography system equipped with an IonPac® CG12A guard column and an IonPac® CS12A analytical column, a Dionex Cation Self Regenerating Suppressor (CSRS), and a conductivity detector. Separation was achieved using a 20 mM methanesulfonic acid eluent at a flow rate of 1.0 mL/min. Both IC systems were calibrated daily using a series of laboratory-prepared ion standards.

### 2.3.3. Dissolved Organic Carbon (DOC) concentrations

Sample aliquots for dissolved organic carbon (DOC) analysis were filtered through glass fiber filters (VWR North America 691) in the field and stored in pre-baked amber glassware with a Teflon lined septa caps. DOC concentrations were determined using a Shimadzu total organic carbon (TOC) analyzer (TOC-5050A) which was calibrated against potassium hydrogen phthalate standards.

## 2.4. Results and discussion

### 2.4.1 Fog/Cloud occurrence and Liquid Water Content (LWC)

In the 2010 Fresno study, 4 significant fog events were sampled that typically started in the evening hours and dissipated in the morning hours, lasting between 7 and 8 hours. The average liquid water content as measured by a Gerber PVM 100 was on the order of  $70 \text{ mg/m}^3$ . In Davis, in 2011, five fog events were observed, one of them lasting two consecutive days. While PVM data were not available during this sampling campaign, average LWC values were estimated using collected fog water volumes and correcting for collection efficiency (Demoz et al., 1996). The OFD was used as a semi-quantitative LWC indicator to trigger fog samplers. The average values in Davis range from 6 to  $111 \text{ mg/m}^3$ . This is similar than the observations in Fresno, which is typical for urban fogs in the region (Herckes et al., 2015) although slightly on the lower end. Actually a comparison of the LWC with prior studies suggests a decrease in LWC over time although the reasons were unknown (Herckes et al., 2015). An additional field study in Fresno and Bakersfield conducted simultaneously to NASA's Discover-AQ Fresno project in 2012 (Jan 15<sup>th</sup> to Feb 13<sup>th</sup>) did not yield a single fog sample because no fog events occurred during the sampling period at these locations.

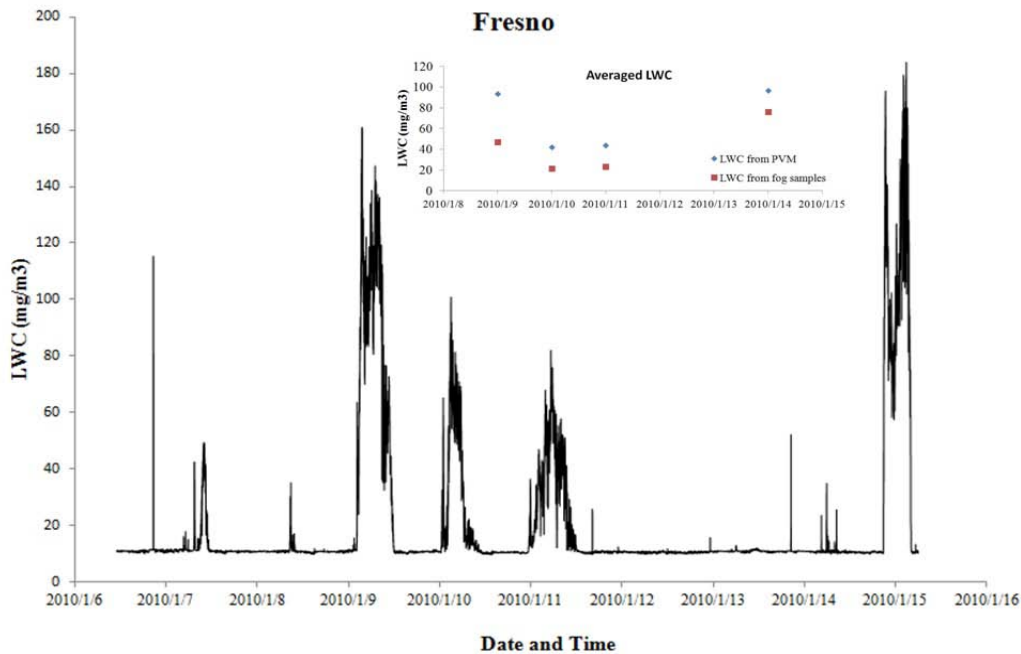


Fig. 2.4 LWC of 2010 Fresno field campaign and comparison of PVM reading with calculated values from sample volume.

During the Whistler study most clouds collected were orographic in character while some might have had a stratus component to it. Nine cloud events were recorded at the Raven’s Nest (WRN) site from June 18<sup>th</sup> to July 26<sup>th</sup> and 3 at the Peak site from July 3<sup>rd</sup> to July 26<sup>th</sup> as shown in Figure 2.5. Harsh winter conditions persisting into July allowed an installation of the Peak site only at a later date. Both sites had 1 fog record on July 4<sup>th</sup> with a three hour time overlap. Most of the fog events occurred at the beginning of the WACS study then followed a large and unique biogenic aerosol event. Figure 2.5 shows raw LWC reading from each PVM, since the PVM at the peak site was provided by EC and hasn’t been parallel tested with the one at WRN; “actual” LWC was calculated based on collected sample volume with 86% collecting efficiency. LWC at WRN ranged from 82-310 mg/m<sup>3</sup> and 13-50 mg/m<sup>3</sup> at peak. Table 2.1 summarized calculated LWC of

Fresno, Davis and Whistler fog/cloud events along with typical LWC ranges of polluted cloud/fog and remote cloud documented in Herckes et al., (2015).

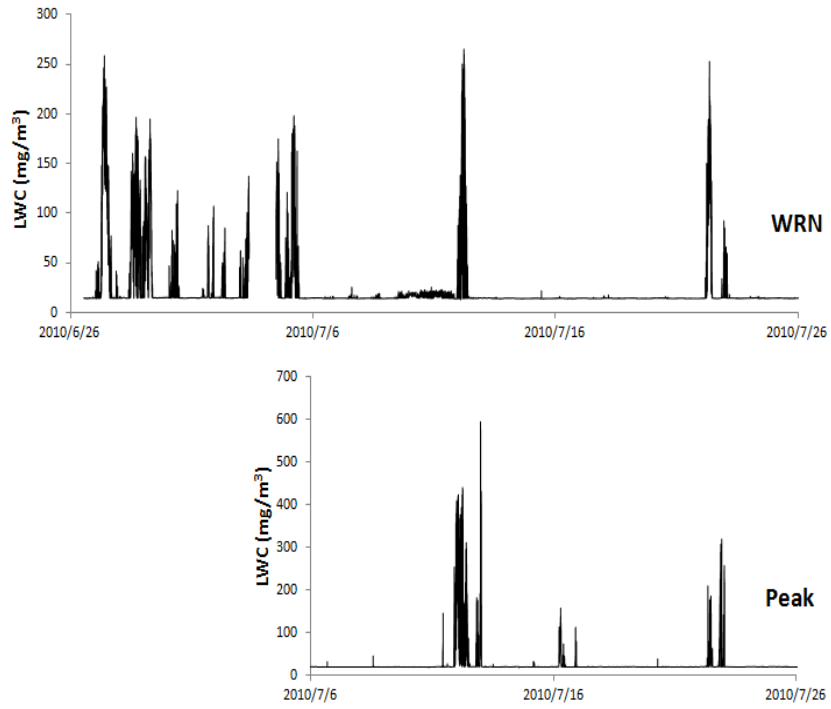


Fig. 2.5 LWC of WRN site and Peak site during Whistler aerosol and cloud study.

Table 2.1 Calculated LWC ( $\text{mg}/\text{m}^3$ ) of fog/cloud samples collected in Fresno, Davis, Whistler and typical LWC ranges of polluted cloud/fog and remote cloud (Herckes et al., 2015)

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Sampling location	Median (Min-Max)
Fresno	63 (4-95)
Davis	30 (5-86)
Whistler WRN	171 (82-310)
Whistler Peak	50 (31-55)
Polluted cloud	(50-1000)
Polluted fog	(20-800)
Remote cloud	(50-2000)

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In Norway, fogs were likely partly radiation fogs, especially in the Hakadal area which is in the outskirts of Oslo. In the measurement period September 28<sup>th</sup> and November 14<sup>th</sup> 2011, Hakadal experienced a series of radiation fog events that yielded 6 samples. The fog events typically started after sunset and dissipated in the night or lasted until the morning hours. The LWC, while mainly below  $100 \text{ mg}/\text{m}^3$ , could reach up to  $180 \text{ mg}/\text{m}^3$  (based on the OFD). Several of the fog events were accompanied with drizzle and rain.

In the fall of 2012, only very few fog events occurred at the sampling sites on the West Coast of Norway. It is unclear if these were advection fogs or advection/radiation fogs. Only one single fog sample was collected at each site during the sampling period; for Bakka Oct 23<sup>rd</sup> to Nov 21<sup>st</sup> and Sundsbø Sep 17<sup>th</sup> to Nov 21<sup>st</sup>. The LWC reached

values of up to 200 mg/m<sup>3</sup> based on the OFD. A higher LWC in the more remote location is not unexpected as likely less condensation nuclei are available, resulting in larger droplets carrying more liquid water rather than many small condensation nuclei taking up water without growing into full fog droplets.

#### 2.4.2 Fog and cloud acidity

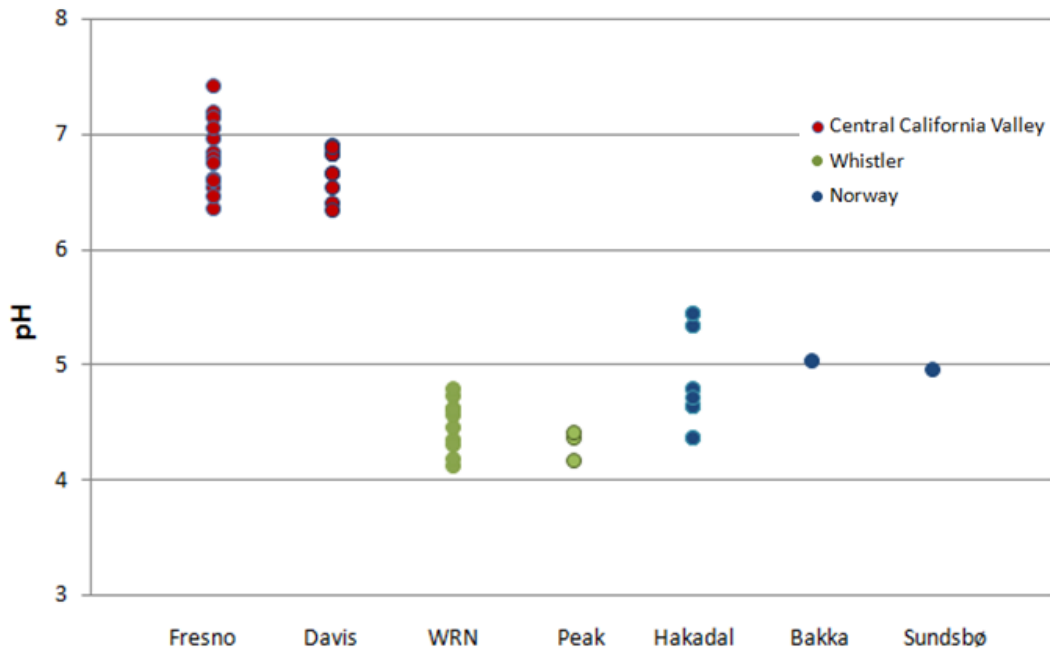


Fig. 2.6 pH values observed at each of the study sites.

Figure 2.6 presents an overview of all pH measurements of all sampling sites. The acidity of fogs and clouds sampled was substantially different from site to site. Clouds in Whistler were acidic with a pH ranging from 4.1 to 4.8 at WRN (median 4.4) and close to 4.4 on average for the Peak. These observations were less acidic compared to fog pH data (mean value 3.7-4.2) from multiple sites in southern Quebec (Schemenauer et al., 1995) the closest comparable data from studies long ago. While there are little local emission sources for Whistler, air masses from Asia with long range transport of pollutants will

impact these sites resulting in a certain acidity observed both at the Peak and the Raven's nest site.

The Norwegian sites had slightly higher pH. The pH in the coastal fog water samples (Bakka and Sundsbø) was slightly above 5, which 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> (pH~5.6). The pH in Hakadal was 4.7 (4.4-5.5) so slightly acidic but less than in Whistler. This is consistent with the proximity to local sources that in fog conditions are typically important.

Finally the Central California sites showed high pH, more basic than water in equilibrium with CO<sub>2</sub>. This is consistent with prior observations throughout the Central and Northern part of the Central Valley where low sulfur but high ammonia emissions more than neutralize fogwater acidity resulting in slightly basic atmospheric droplets.

#### 2.4.3 Major ionic species

Figure 2.7 summarizes the major ionic species in the present studies. Again for different sites distinct patterns both in terms of concentrations and relative make up emerge. Fresno and Davis fog water has substantially higher ion concentrations than remote cloud (Whistler) and remote fog (Norway) water and dominated by ammonium, nitrate and sulfate, which is consistent with previous studies (Collett et al., 2002; Herckes et al., 2007a). Whistler cloud water has the lowest pH, therefore, highest proton concentration. Relative abundant nitrate and sulfate concentrations reflect clear anthropogenic influences. Interestingly, all Whistler Peak site cloud samples have relatively high calcium concentrations. Particles rich with water soluble calcium, most often CaSO<sub>4</sub> have both marine sources and land-based sources (Hoornaert et al., 1996).

The marine sources are less likely here as the fog samples look substantially different from the samples collected in Norway, close to the ocean (and hence similar to sea spray with high  $\text{Na}^+$  and  $\text{Cl}^-$ ). High calcium concentrations in Peak cloud water are hence more likely the result of a combination of eolian transport of calcium rich particles with in cloud processing of acid sulfate with minerals (Andreae et al., 1986).

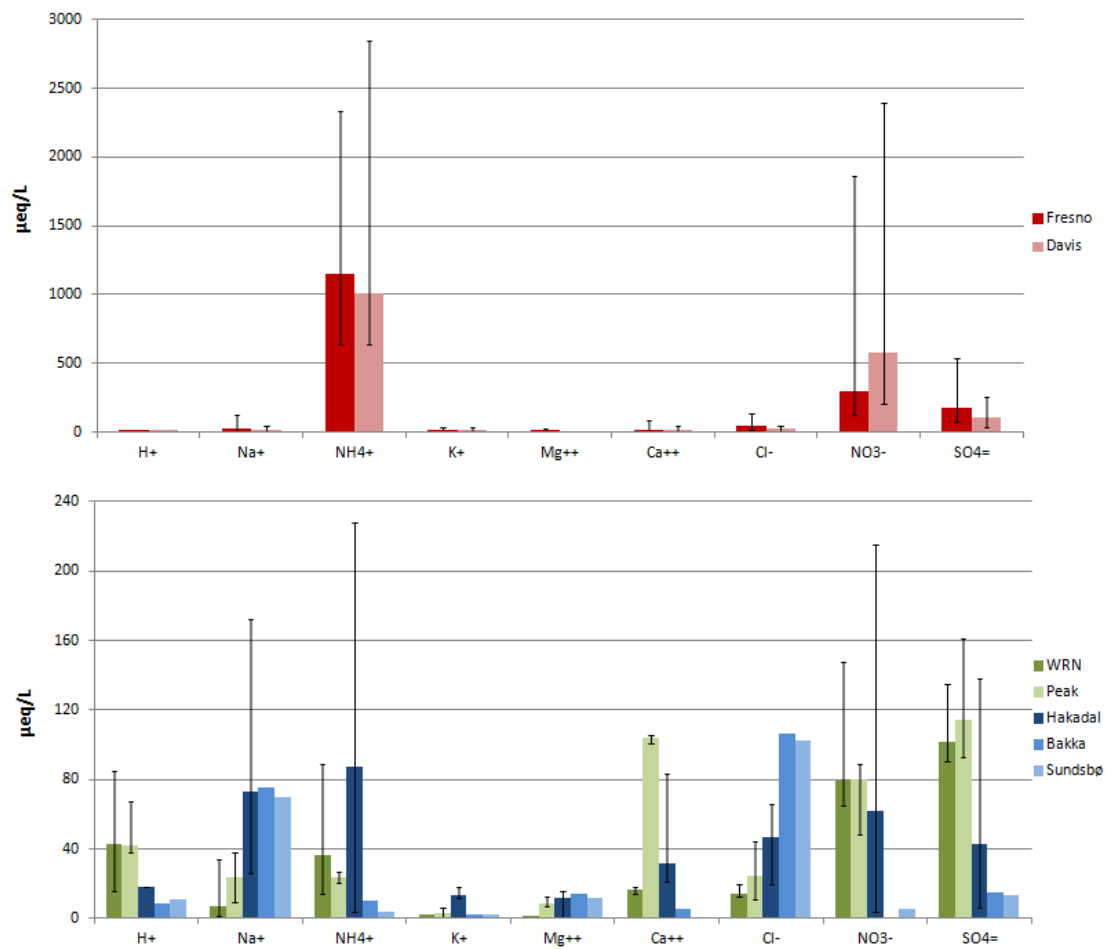


Fig. 2.7 Major ion concentrations of fog/cloud water, bars represent median values and error bars represent min-max data.



For Bakka and Sundsbø, as expected for a marine environment, the major solutes are sodium and chloride. Surprisingly, the ratio  $\text{Cl}^-/\text{Na}^+$  is 1.4 in both cases which is a little higher than the typical sea salt ratio of 1.16 (e.g. Möller. 1990). A higher  $\text{Cl}^-/\text{Na}^+$  ratio in fog samples in the past might be due to HCl partitioning into the droplets (Millet et al., 1996). While this explanation could be possible, no direct HCl sources are known and the pH is not indicative of additional acidity. Other ion concentrations (nitrate, ammonium and sulfate) were very low at these coastal sites compared to typical fog and cloud studies. Nitrate concentrations in fog samples collected in Norway were approximately 100 times lower and sulfate 3 times lower than in polluted California radiation fogs (e.g. Zhang and Anastasio, 2001; Herckes et al., 2007a). All concentrations were also substantially lower compared to marine cloud studies (Straub et al., 2007). Nitrite was not detected ( $<1 \mu\text{eq/L}$ ). In Hakadal, in suburban Oslo, major ion concentrations were substantially higher (sulfate, nitrate and ammonia), which is consistent with a more anthropogenically impacted location. Sodium concentrations in Hakadal were similar than at the coastal sites while chloride concentrations were lower. This could be the result of a different sodium source (possibly soil) or depletion of chloride from sea salt by exchange with nitrate as commonly reported in fog chemistry studies (e.g. Clegg and Brimblecombe, 1985; Millet et al., 1996). The latter appears most likely as sulfate and nitrate substantially exceed ammonia on an equivalent basis, but the pH is still rather high suggesting that part of the nitrate would be derived from  $\text{NaNO}_3$  rather than  $\text{HNO}_3$ . The ratio of quantified cations to anions is close to unity for Bakka (0.82) and Sundsbø (0.97) suggesting all major ions have been analyzed. For Hakadal an average ratio of 1.56 is observed, likely the result of a significant presence of small carboxylic acids (like formic

or acetic acid). These species were not included in the present study but are typically the dominant organic species in fogs (e.g. Herckes et al., 2013).

#### 2.4.4 Dissolved organic carbon

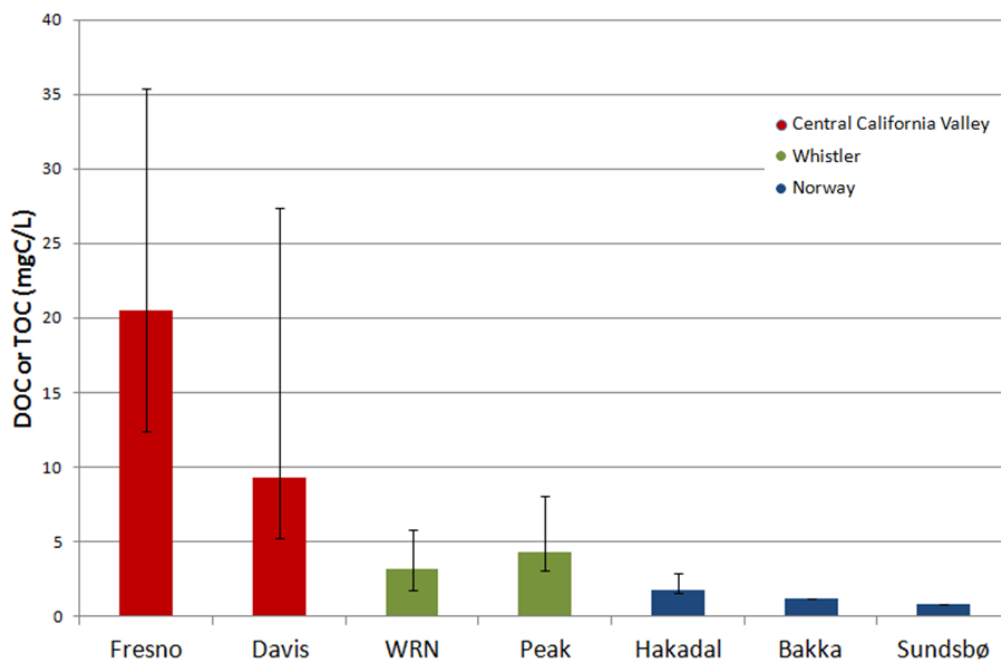


Fig. 2.8 DOC observed (TOC when no DOC values were available) in this study. Boxes represent median values, lines represent the range of values (min-max).

Dissolved organic carbon concentrations were determined in the collected fog/cloud samples. Fresno and Davis show the highest DOC concentrations consistent with the urban character of these sites. The results fall within the range typically observed for moderately polluted fogs (several tens of mg/L). The origin of the organic matter is likely anthropogenic from scavenging of gas and particulate matter from sources like vehicle emissions or wood combustion, a substantial source of wintertime particulate matter in the area (Gorin et al., 2006). The concentrations in Whistler are significantly lower,

although higher than at the Norwegian sites. The Whistler study occurred in the summer months and was specifically designed to study the impact of biogenic emissions on local aerosols and clouds. The DOC concentrations result largely from biogenic aerosol and particulate material with only a small fraction of anthropogenic contribution. The Norwegian coastal sites, Sundsbø and Bakka, were very low in organic matter concentrations and only slightly higher than field and transport blanks. The concentrations are lower than what is typically reported for fogs (e.g. Herckes et al., 2015). In Hakadal, DOC concentrations were higher than at the coastal sites but still very low compared to typical urban and suburban fogs like Fresno or Davis. The concentrations are also low compared to pristine clouds in which a substantial part of DOC is from biological sources (e.g. Whistler). Hakadal while suburban is a much smaller community than any of the California sites, also while there is an impact of Oslo (larger city), the impact is overall small because of the local topography. Finally the Norwegian studies were performed in the winter time, at low temperatures which results in little biological emissions (on land and in the ocean) and hence explain lower DOC values.

## 2.4.5 Overall fog composition

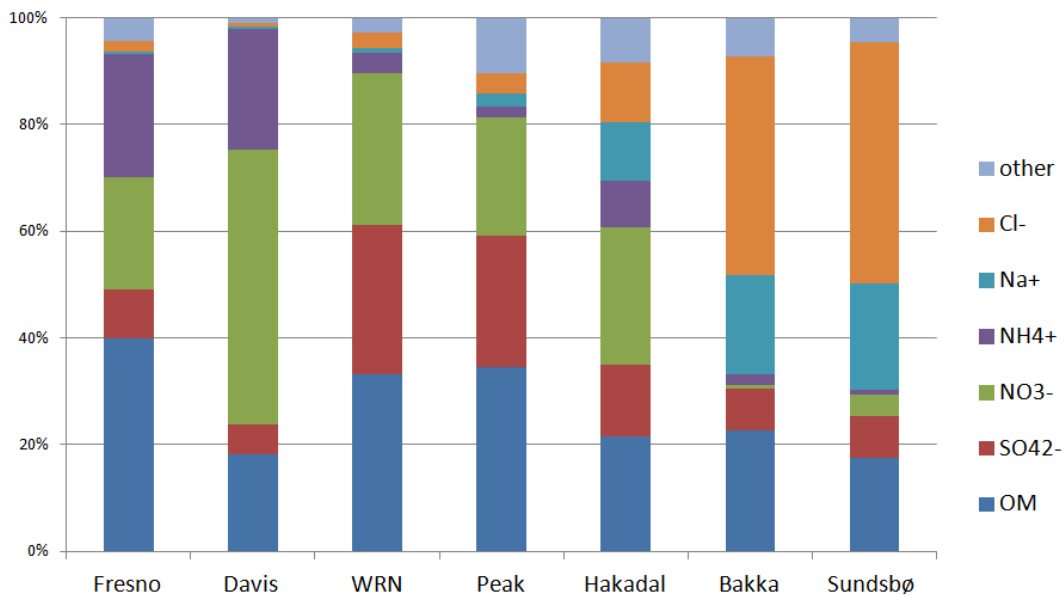


Fig. 2.9 Average mass composition of bulk fog and cloud water samples. Organic Matter (OM) is assumed equal to 1.8 times the DOC concentrations. Other ions include  $H^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $K^+$ .

Figure 2.9 shows the relative importance of major ions and organic matter in fog/cloud samples. Major ionic species are  $NH_4^+$ ,  $NO_3^-$  and  $SO_4^{2-}$  except at the remote coastal site Bakka and Sundsbø where sodium and chloride dominate, common for marine impacted environments. The results are typical for what is known for areas such as the Central Valley of California with high agricultural activity, ammonia and nitrate being dominant while in more typical continental areas, a substantial part of fog and cloud water solute remains sulfate. The real interesting result is the substantial contribution of organic matter to fog and cloud solutes, ranging from 20-40% in many cases of similar importance as sulfate or nitrate.

## 2.5 Summary and conclusions

Fog and cloud water samples were collected during field studies in California's Central Valley (Fresno and Davis), in Canada (Whistler Mountain) and in Norway (suburban Oslo and coastal sites). Sampling was challenging with sometimes only one sample collected during several weeks of field studies but this is not uncommon for such studies. Average LWC of Whistler clouds is three fold higher than fogs in Central California Valley. Observations in this study further confirmed a decreasing trend of LWC in the valley of the past three decades while the reason is still unclear.

The chemical composition results showed substantial differences between locations. The California sites presented high pH (6.4-7.4) and overall substantially higher ion concentrations than any other sites, consistent with prior work in the intensely studied Central Valley. The Norwegian sites were the first observational fog studies in Norway. The suburban site of Hakadal showed neutral pH (4.4-5.5, CO<sub>2</sub> equilibrium with water is 5.6) while ion and organic matter concentrations were low, showed a little impact of anthropogenic sources, consistent with the close proximity to urban emission sources. The coastal sites in Norway showed very low concentrations. The compositional data suggests these sites are quite pristine and the fog chemistry is consistent with a marine environment with sodium and chloride dominating. Major ions and organic matter concentrations do not indicate a substantial impact of a close-by refinery.

Cloud samples collected during the Whistler Aerosol and Cloud Study (WACS) showed low ionic concentrations consistent with the remote character of the sites, however a small anthropogenic component and slight acidity (4.1-4.7), likely the result of long range transport of anthropogenic emissions are apparent. Organic matter concentrations

at these sites are higher than at the Norwegian sites and high for a remote area. However the WACS study aimed a period of high biogenic activity (emissions from trees) and the organic matter concentrations are likely the result from substantial scavenging of gases and particulate matter from biogenic sources.

Overall all sites present a significant contribution organic matter to the total solute concentrations ranging from 20 to 40% and of the same order than sulfate or nitrate. This stresses the importance of organic matter in cloud and the need for an improved characterization of this material and the impact of fog and cloud processing. This will be performed in the following chapters based on samples and observations during the field studies detailed here.

## CHAPTER 3

### CHARACTERIZATION OF ATMOSPHERIC ORGANIC MATTER USING BULK APPROACHES

#### 3.1 Introduction

##### 3.1. 1. State of the knowledge on atmospheric organic matter characterization

Clouds and fogs play an important role in the processing of atmospheric trace gases and particles. They integrate gas and particulate species and might transform them into novel materials or deposit them through precipitation processes. Clouds and fogs can contain substantial concentrations (1-200 mgC/L) of organic carbon and up to 77% of the total organic carbon (TOC) in cloud and fog water is dissolved organic carbon(DOC), operationally defined as passing through a filter (Herckes et al., 2002c).

Several studies have characterized DOC in fog and cloud water to elucidate its chemical composition. A variety of analytical approaches have been used to improve our understanding of cloud and fog DOC material as well as the WSOC present in atmospheric particulate matter (e.g. Kiss et al., 2001; Fuzzi et al., 2002; Herckes et al., 2002d; Collett et al., 2008; Raja et al., 2009; Mazzoleni et al., 2010). As introduced in section 1.3.2, small chain carboxylic acids (formic and acetic), dicarboxylic acids (oxalic acid), carbonyls (formaldehyde), and dicarbonyls (glyoxal and methylglyoxal) are the most abundance individual species, while organic nitrogen species (amino acids and mines) and PAH compounds among others have also been reported. However in many cases more than 50% of DOC eludes speciation not only because of the scope and techniques used by the different investigators but also because a portion of DOC defies characterization by traditional analytical methods. Therefore in this study we focused on applying bulk property characterization techniques and aimed to show structural and compositional information in the perspective of molecular weight distribution, functionality and optical properties. Techniques used in the present work are briefly discussed next.

### 3.1.2. Chromatographic approaches

Different chromatographic approaches with offline or inline carbon quantification and/or further characterizations have been applied to atmospheric organic matter, mainly the water soluble component of aerosols (WSOC).

Ion-exchange chromatography has been proposed by Decesari and coworkers (Decesari et al., 2000) as a means to characterize DOC and WSOC by separating it into different categories based on the molecular charge of the species present. While the method has

been widely applied (e.g. Fuzzi et al., 2001; Mayol-Bracero et al., 2002) and it provided interesting insights into the variability of atmospheric organic matter, the interpretation of the results had been a matter of discussion (Chang et al., 2005; Decesari et al., 2005). The separated fractions were quantified or analyzed using nuclear magnetic resonance (NMR) spectroscopy and useful insights were gained. Size-exclusion chromatography (SEC) combined with a XAD-8 resin column was applied by Sullivan and coworkers to separate the WSOC component of ambient aerosols into acid, neutral and basic functional groups and quantified by TOC detection (Sullivan and Weber, 2006). A different set of isolation/characterization techniques aimed at separating and hence classifying the organic matter using molecular weight rather than chemical properties. These works included ultrafiltration (Herckes et al., 2002c) or electrospray mass spectrometry (Kiss et al., 2003). Each technique having its own challenges, all studies suggest that a part of the organic matter has substantial molecular weight (>500 Da).

Similar challenges to characterize atmospheric organic matter exist for surface waters where the analytical approach of SEC is used (Pelekani et al., 1999; Lepane et al., 2004; Allpike et al., 2005; Her et al., 2008; Haberkamp et al., 2011). For atmospheric materials, Krivácsy et al., (2000) applied SEC coupled with ultraviolet (UV) and fluorescence detection and concluded that atmospheric humic-like substances (HULIS) has similar retention and migration behavior with reference humic materials. Samburova et al. (2005) used SEC and laser desorption/ionization mass spectrometry (LDI-MS) to confirm that the upper mass limit of HULIS reached 700 Da. Despite all these efforts the organic matter remains unknown and the interpretation challenging and confusing.



The present work aims to contribute to the characterization of atmospheric organic matter by using a well established size-exclusion chromatography method coupled to inline organic carbon characterization (SEC-DOC). SEC is a separation method based on the ability of an organic compound to enter the pores of the stationary phase via molecular diffusion (Her et al., 2002a). In theory larger molecules have a shorter retention time because they enter fewer pores than smaller molecules. However, in practice nonideal hydrophobic and electrostatic interactions exists between the solutes and gel matrix which makes the separation not entirely dependent on the molecular size but also influenced by eluent compositions and columns (Sullivan and Weber, 2006). Even though interactions can be minimized by optimizing factors like pH, ionic strength of the eluent, packing materials of columns, they still can't be totally excluded (Pelekani et al., 1999). Cautious calibrations have been conducted to test SEC's ability of separating functional groups (Sullivan and Weber, 2006). The results showed SEC is not an ideal method to resolve individual species due to peak overlapping but still can serve as a powerful tool in terms of providing overview sample compositions. In this chapter the method has been applied to aerosol, cloud and fog samples and new insights on composition variability will be discussed.

### 3.1.3. Fluorescence spectroscopy approaches

Fluorescence spectroscopy techniques have been widely applied to chromophoric dissolved organic matter (CDOM) in various environmental water matrices such as surface water, waste water effluent or landfill leachates to exploit chemical composition information and so forth due to advantages like high sensitivity (ppb level) towards compounds with fluorophores, short experiment time required (down to few minutes

based on scanning resolutions), little sample pretreatment, non-destructive and small quantity of sample needed (around 1ml) (Edzwald, 1993; He et al., 2011; Laurentiis et al., 2013). These approaches are attractive to characterize DOM in fogs/clouds because fluorescence can detect subtle differences in distribution and properties among similar samples with low DOC concentrations (Birdwell et al., 2010). With improvements of the techniques, Excitation-Emission Matrix (EEM) fluorescence spectroscopy is able to scan over a range of excitation wavelengths while collect emission wavelengths simultaneously instead of scanning emission wavelengths at fixed excitation wavelengths, therefore, to rapidly provide a complete picture of the composition and characteristics of the fluorophores in DOM.

#### 3.1.4. Nuclear Magnetic Resonance spectroscopy approaches

Various Nuclear Magnetic Resonance (NMR) spectroscopy techniques have been applied to environmental matrices including soil, ocean sediments and surface water to address questions such as chemical composition characterization, interactions with pollutants, and source appointment and modeling (Decesari et al., 2007). NMR is known for its ability to unravel complex structures/interactions, highly repeatable result, little or no pretreatment requirement and robustness and can be applied to diverse physical phases (solids, liquids, gels and gases). Limited NMR experiments were conducted on atmospheric samples. These studies were mostly focused on atmospheric particulate matter (Graham et al., 2002; Duarte et al., 2005; Cavalli et al., 2006; Tagliavini et al., 2006; Cleveland et al., 2012; Shakya et al., 2012), fewer were targeted fog water (Suzuki et al., 1998; Herckes et al., 2007b;) and rainwater (Seaton et al., 2013). While hundreds of NMR experiments are possible, there are only a select few that are commonly used by

environmental chemists. One dimensional (1D) methods include: solution state  $^1\text{H}$  NMR; High-Resolution Magic-Angle Spinning NMR (HR-MAS); solid state Cross Polarization Magic-Angle Spinning  $^{13}\text{C}$  NMR (CPMAS) (Herckes et al., 2007b). 2D or 3D methods include: Correlation Spectroscopy NMR (COSY); Total Correlation Spectroscopy NMR (TCOSY); Heteronuclear Single/Multiple Quantum Coherence NMR (HSQC/HMQC) and Heteronuclear Multiple Bond Correlation NMR (HMBC). Generally multidimensional methods can provide more detailed structural information since one dimensional experiments suffer from severe peak overlapping due to structural similarity of organic molecules. COSY can provide connectivity information of protons on adjacent carbon, while TCOSY can map long-rang protons that interact with 2 or 3 bonds (Simpson and Simpson, 2014). While HSQC/HMQC can show 1 bond  $^1\text{H}$ - $^{13}\text{C}$  correlation, HMBC is able to reveal 2 to 4 bond  $^1\text{H}$ - $^{13}\text{C}$  correlation. Due to the low natural abundance of  $^{13}\text{C}$  (<1.13%), achieving an acceptable signal to noise ratio, often requires 10-50mg carbon which can be a challenge for environmental samples including aerosols or clouds. Frequently samples collected during different timeframes need to be combined to achieve sufficient carbon levels which prevents the investigation of temporal differences. In order to obtain more detailed information such as partial  $^1\text{H}$ - $^{13}\text{C}$  backbone configuration, more scan numbers (longer time) are required, up to several days, including more sophisticated experiment setups, higher expertise to conduct experiments and to interpret data while also facing various limitations, like instrumental miscalibrations and knowledge of sample composition required for experimental parameter setup (Simpson et al., 2011). Therefore it is important to know what level of information is needed for the specific research topic then decide which method to be used.

In addition to providing molecular structural information, NMR could also offer experiments that could measure diffusion rate of molecules which is proportional to their molecular sizes. Diffusion-ordered Nuclear Magnetic Resonance Spectroscopy (DOSY-NMR) is a 2D NMR method widely used to differentiate chemical compounds in a relatively simple mixture with 4 or 5 species max (Huo et al., 2003) according to their diffusion coefficient. By applying Pulsed magnetic Field Gradient sequences (PFG), a series of spin echo spectra can be acquired. Then the signal decays can be calculated to obtain diffusion coefficients of all the compounds that show signal in the 1D chemical shift dimensions. The diffusion coefficient of a molecule in solution can be used to estimate its hydrodynamic radius (its molecular size) based on the Stokes-Einstein equation under the assumption that the molecule exists as a compact sphere:

$$r_H = \frac{kT}{6\pi\eta D} \quad (1)$$

Where  $r_H$  is the hydrodynamic radius of a molecule,  $T$  is temperature,  $k$  is Boltzmann constant ( $1.3806 \times 10^{-23} \text{ kgm}^2\text{s}^{-2}\text{K}^{-1}$ ),  $\eta$  is viscosity of the solution at temperature  $T$ ,  $D$  is diffusion coefficient. The intensity of a resonance in NMR spectrum ( $I$ ) is related to the diffusion rate of the molecule ( $D$ ) by equation 2

$$I = I_0 \exp \left[ -D \left( \Delta - \frac{\delta}{3} - \frac{\tau}{2} \right) (g\gamma\delta)^2 \right] \quad (2)$$

Where  $I_0$  is the intensity in absence of a gradient pulse;  $\Delta$  is time through which diffusion occurs ;  $g$  is the amplitude of the gradient pulses;  $\delta$  is the duration of the gradient pulses;  $\tau$  is the delay after each gradient pulse and  $\gamma$  is the gyromagnetic ratio (For  $^1\text{H}$ ,  $\gamma = 2.675 \times 10^8 \text{ T}^{-1}\text{S}^{-1}$ ). Then as Figure 3.1 shows a number of attenuated spectra will be collected with increasing amplitudes of gradient pulse. The stack of 1D spectrum

will be processed into 2D spectra with chemical shift on one axis and diffusion coefficients on the second axis (Simpson et al., 2001).

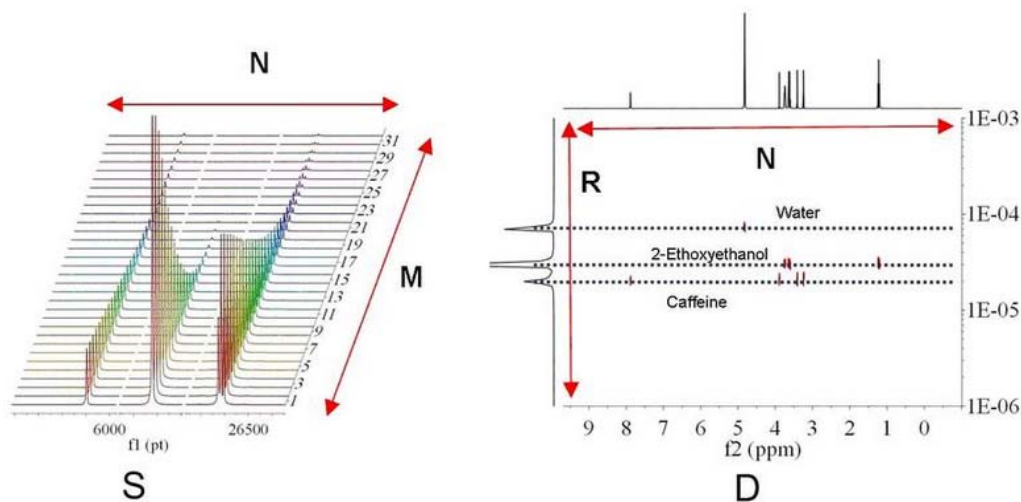


Fig. 3.1 A demonstration of raw PFG-NMR spectra data processing of Caffeine, 2-Ethoxyethanol mixture in D<sub>2</sub>O solution using MNOVA software. S is stacked 1D data matrix and D is processed 2D spectrum with chemical shift as X axis and diffusion coefficient as Y axis. Figure cited from MNOVA DOSY instruction section: <http://mestrelab.com/resources/dosy/>

DOSY-NMR has been considered to a special chromatographic method that has a great advantage over many other analytical separation techniques which is it allows a pseudo-separation of different components without invasive physical separation and sample pretreatment which might disrupt the chemical environment of the components such as aggregation and partitioning (Lucas et al., 2002). After acquiring the stacked attenuated spectra, data processing is the most important step to interpret the result. The major drawback of DOSY is that an accurate diffusion coefficient can only be calculated based on well-resolved resonance signals. Mixtures with minor signal overlapping can usually be well handled by DOSY. However when the mixture becomes more complex and leads to severe signal overlapping or components have small differences in diffusion

coefficient, data processing becomes far from straightforward. In order to extract meaningful diffusion coefficients, several computational data processing methods have been introduced. Huo and coworkers (2003) evaluated a number of existing DOSY data processing methods, which can be attributed into two categories: univariate methods and multivariate methods. Common univariate methods include SPLine MODel (SPLMOD) and continuous diffusion coefficient (CONTIN) and multivariate methods include Direct Exponential Curve Resolution Algorithm (DECRA) and Multivariate Curve Resolution (MCR) (Huo et al., 2003). Univariate methods process each signal individually while multivariate methods process the whole spectra simultaneously. These data processing methods all have their pros and cons. In short, SPLMOD is applicable to discrete diffusion components which by definition should contain monodisperse species and each component should have one value of its corresponding diffusion coefficient. The method only allows two components and their decay rates are preferable larger than a factor of two. CONTIN is able to process overlapping signal of polydisperse samples and provide overall diffusivities, however it will “over smooth” the data and with the cost of serious compromise the resolution. Multivariate methods are designed to unravel signal overlapping to achieve ideal components separation, however these methods relies on assumptions on the decay shapes and constraints like number of components must be known which is the information that can't be possessed when dealing with nature organic matter. Moreover multivariate methods are only capable to resolve a limited number of components (4-5) (Huo et al., 2003). Therefore mono-exponential, one of the single channel methods was applied to process DOSY spectra of atmospheric organic matter. Instead of focusing on component attribution based on their diffusion coefficient, mono-

exponential counts all the components that contributed to the overlapped signal and provides the continuous apparent diffusion coefficients. Each peak in the diffusion dimension is a Gaussian centered on the fitted diffusion coefficient with a width determined by the statistics of the fit (Nilsson, 2009). Besides acquiring diffusion coefficients of simple mixture, DOSY has been applied to humic/fulvic acids (Morris et al., 1999), Suwannee River dissolved organic matter (Lam et al., 2009) and soil organic matter (Simpson et al., 2001) to investigate their aggregation behavior and to what extent the separation can be achieved by DOSY. To our knowledge this is the first attempt to explore NMR protocols and to acquire diffusion coefficient information of fog/cloud and soluble aerosol organic matter while cross compared their apparent molecular size with SRNOM using DOSY.

In this chapter, SEC-DOC, NMR and EEMs are applied to fog and cloud samples from different environments. The observations will be discussed based on our understanding of the structure and functional of atmospheric organic matter. A special focus is on the investigation of differences between sample types (fog vs cloud vs WSOC), between locations (same sample type, different sampling site) and between atmospheric organic matter and a surface water organic matter reference material (Suwannee River Natural Organic Matter - SRNOM).

## 3.2. Experimental

### 3.2.1. Fog and aerosol sampling

Fog and aerosol sampling has been extensively described in Chapter 2. In addition to those field studies, a few fog samples were collected near Selinsgrove, PA and provided by Prof. Derek Straub from Susquehanna University. Field site and chemistry data has

been published on earlier seasons (Straub et al., 2012). In brief, the Susquehanna University sampling site is located in the ridge and valley region of Pennsylvania near the confluence of the north and west branches of the Susquehanna River and characterized as open grassy fields surrounded by active farms. An automated Caltech Heated Rod Cloudwater Collector (CHRCC) was used to collect fog water with an OFD to measure LWC.

### 3.2.2. SEC-DOC (Wang et al., 2013)

Fog and cloud water samples for SEC-DOC characterization were filtered using 0.22 $\mu$ m glass fiber filters (Whatman, UK). The conductivity of the samples was adjusted to 4.57 mS/cm with a phosphate buffer eluent (Sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) and 0.0016 M disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ), pH= 6.8). A section of each aerosol sample (PM<sub>2.5</sub> and PM<sub>>2.5</sub>, section area of 9.81 cm<sup>2</sup>) was extracted with 15mL deionized (DI) water (>18 M $\Omega$ -cm) then filtered using a 0.22  $\mu$ m glass fiber filter to obtain the WSOC aliquot.

All samples were analyzed on a SEC-DOC system composed of a High-Performance Liquid Chromatography system (Waters 2695 Separation Module, Milford, MA) followed by an online TOC detector (Sievers Total Organic Carbon Analyzer 800 Turbo) adapted to inline detection using an inorganic carbon remover (900 ICR, GE). The column used for separation was a TSK 50S column (250 mm x 20 mm Tosho Toyopearl HW-50S resin, Japan). Isocratic elution was with a phosphate buffer eluent ( $\text{NaH}_2\text{PO}_4$  and 0.0016 M  $\text{Na}_2\text{HPO}_4$ , pH= 6.8) containing 0.025 M  $\text{Na}_2\text{SO}_4$  which has ionic strength of 0.1 M (conductivity of 4.57 mS/cm.). The set-up and its performance are discussed in more detail in earlier work (Her et al., 2002b; Her et al., 2003; Allpike et al.,



2005). The eluent reservoir was purged by nitrogen gas to reduce the inference on the stationary phase from dissolved inorganic carbon and oxygen. The void volume of the SEC column was determined to be 27 ml (approximate corresponding MW = 240,000 Da) by using dextran blue. The permeation volume was determined to be 67 ml (approximately corresponding to a MW = 120 Da) by using a deionized water injection and electrical conductivity monitoring. The sample injection volume was 1mL and the flow rate was set to 1 mL/min. 10 mg/L-C polyethylene glycol (PEG) standards (Sigma Aldrich) with the MW of 600, 1000, 1450, 3350, 4600, 8000 and 10000 Dalton were used to generate a MWD calibration. Suwannee River natural organic matter (SRNOM) stock solution (8 mg/L-C) and nanopure water samples were run for each sample set as quality control.

### 3.2.3. Spectroscopic measurements

Fog and cloud water samples for spectroscopic characterization were filtered using 0.22  $\mu\text{m}$  glass fiber filters (Whatman, UK). Spectroscopic characterization experiments were conducted on the filtered samples using a HORIBA Aqualog system (Jobin Yvon, Edison, NJ, USA) equipped with a 150 W ozone free vertically mounted xenon arc lamp. Samples were placed in a 1-cm quartz cuvette. A SRNOM standard was run with each batch of samples and values varied less than 2%, illustrating a high reproducibility of measurements.

EEM fluorescence spectra were obtained by collecting emission scans from 240-600 nm at 3 nm intervals and excitation scans from 240-450 nm at 2 nm intervals. During data processing with Aqualog V3.6, the inner-filter effect was corrected, while elastic Rayleigh scattering and non-elastic Raman scattering was mitigated by subtracting a DI

water blank. Different data analysis approaches were used.

First, we used a Fluorescence Regional Integration (FRI) technique, first proposed by Chen et al. (2003) to capture the heterogeneity of CDOM. This approach operationally divides an EEM spectrum into 5 regions based on literature reports and illustrated with model species in Figure 3.2. The signal intensities for each are integrated and supposed to reflect organic material with similar properties as suggested in Chen et al., 2003:

$$\phi_i = \sum_{ex} \sum_{em} I(\lambda_{ex}, \lambda_{em}) \Delta\lambda_{ex} \Delta\lambda_{em} \quad (3)$$

In which  $\phi_i$  is the volume beneath region “i” of the EEM,  $I(\lambda_{ex}, \lambda_{em})$  is the fluorescence intensity at each excitation-emission wavelength pair,  $\Delta\lambda_{ex}$  is the interval of excitation wavelength and  $\Delta\lambda_{em}$  is the interval of emission wavelength.

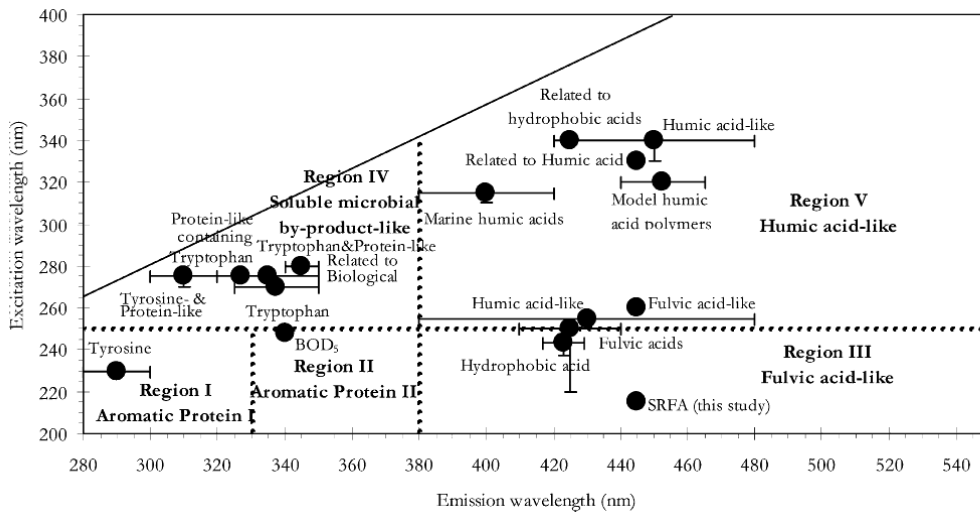


Fig. 3.2 Five EEM regions based on literature reports. Figure adopted from Chen et al., 2003.

Regions I and II (Determann et al., 1994; Ahmad and Reynolds, 1999) represent simple aromatic proteins like tyrosine, whereas regions III and V are fulvic and humic-like substances (Miano et al., 1990; Mounier et al., 1999; Artinger et al., 2000). Region IV is related to soluble microbial byproduct-like material (Coble, 1996; Reynolds and Ahmad, 1997; Ismaili et al., 1998).

Second, Fluorescence Index (FIX), Biological Index (BIX) and Humification Index (HIX) were calculated from the EEM data to evaluate relative contributions of organic substances derived from terrestrial and microbial sources and the degree of humification as summarized in Table 3.1 (Birdwell et al., 2010). FIX was calculated as the ratio of emission intensity at 450nm to that of 500nm for a fixed excitation wavelength of 370nm. FIX values smaller than 1.4 are indicative of a terrestrial origin with higher aromaticity, while values larger than 1.9 indicate microbial sources with lower aromaticity (McKnight et al., 2001). BIX was proposed by Huguet et al (2009) using the ratio of emission intensity of 380 nm to that of 430 nm at fixed excitation wavelength of 310 nm. BIX values larger than 1.0 exhibit freshly produced biologically or microbial derived organic material and values smaller than 0.6 indicate little material of microbial origin. Finally the HIX was applied to evaluate organic matter's degree of humification. Humification process is considered to be associated with a decrease in H/C ratio caused by more condensed fluorescing molecules and lead to shifting to longer emission wavelengths. (Tam and Sposito, 1993; Zsolnay et al., 1999). HIX is the ratio of sum of emission intensities from 435 to 480 nm divided by sum of emission intensities from 300 to 345 nm at excitation wavelength of 254 nm. HIX <10 suggests little humification of biological materials.

Table 3.1 Summary of fluorescence indices.  $I_{(\lambda_{em}, \lambda_{ex})}$ , I as fluorescence intensity. The unit of wavelength  $\lambda$  is nm

Index	Calculation	Comments
Fluorescence index (FIX)	$\frac{I_{(450,370)}}{I_{(500,370)}}$	< 1.4 indicative of terrestrial origin, >1.9 indicate microbial sources (McKnight et al., 2001)
Biological Index (BIX)	$\frac{I_{(380,310)}}{I_{(430,310)}}$	<0.6 contain little biological material, >1 correspond to freshly produced biological or microbial material (Huguet et al., 2009)
Humification Index (HIX)	$\frac{\sum_{i=435}^{480} I_{(i,254)}}{\sum_{i=300}^{345} I_{(i,254)}}$	< 10 correspond to relatively non-humified DOM derived from biomass (Zsolnay et al., 1999)

#### 3.2.4. 1D-<sup>1</sup>HNMR characterization

Aqueous (fog and cloud) samples were filtered through 0.22  $\mu\text{m}$  glass fiber filters (Whatman, UK) then freeze-dried using a Labconco FreeZone system before re-dissolving them into 1ml of deuterium oxide  $\text{D}_2\text{O}$  with 99.9% atom D containing 0.05 wt% Trimethylsilyl propanoic acid (TSP) (Sigma-Aldrich, St. Louis, MO). Water soluble

organic carbon WSOC samples were prepared by extracting an aliquot of a quartz fiber three times using 20 mL DI water ( $>18 \text{ M}\Omega\text{-cm}$ ) under sonication. The combined 60ml WSOC solution was treated the same as fog water samples. The International Humic Substances Society (IHSS) Suwannee River Natural Organic Matter (SRNOM) was used as a reference complex sample, similar to other organic matter characterization studies (e.g. Wang et al., 2013). The SRNOM was directly dissolved into  $\text{D}_2\text{O}$  then underwent 5 minutes centrifuging at a speed of 12k rpm before being moved to a Norell 5 mm 500MHZ NMR tube.

Solution-state  $^1\text{H}$  NMR was carried out on an Agilent Inova 500MHz spectrometer equipped with a 5 mm Inverse Direct Broadband PFG Probe at 298K. The  $^1\text{H}$  spectra were acquired using 256 scans and a relaxation delay of 10s. 1 mgC dissolved in 1 ml of  $\text{D}_2\text{O}$  was expected to provide a decent signal to noise ratio. To ensure sufficient material, sample volumes were optimized to have 1-5 mg C/ml of  $\text{D}_2\text{O}$ , based on carbon measurements in the parent samples and material available for analysis. Typically acquisition times ranges from 10 to 14 hours because of still low concentrations.

NMR spectra were processed and integrated using the software MestReNova version 8.1 (Mestrelab Research, Santiago de Compostela, Spain).

Four major functional groups were assigned to  $^1\text{H}$  NMR spectra: aliphatic protons (0.5-1.9 ppm, H-C), protons bound to aliphatic carbon atoms adjacent to unsaturated groups (1.9-3.2 ppm, H-C-C=), protons on carbon atoms singly bound to oxygen atom (3.3-4.1ppm, H-C-O) and aromatic protons (6.5-8.3 ppm, H-Ar). Even though the ranges of the four functional group regions slightly vary (Decesari et al., 2000; Graham et al., 2002; Simpson et al., 2011), the differences of integrated areas are less than 0.5% of the total

integrated areas based on comparing integrated area using different ranges of functional group regions.

### 3.2.5. 2D-<sup>1</sup>H NMR characterization

A concentration of 1 mg/ml was enforced to all of the DOSY experiments including SRNOM standards for cross comparison purpose, since the viscosity of the solution is proportional to solute concentration. A concentration effect on aggregation of SRNOM was investigated by Lam (2009), and the result shows little to no aggregation occurred at the level of 1 mgC/ml which supports the idea of minimizing artificial effect to observe organic matter in its natural state. DOC was measured using a Shimadzu TOC-VCSH analyzer (high temperature combustion at 720°C non-dispersive infrared detection with TNM-1 unit chemiluminescence detection) (Shimadzu Corp., Tokyo, Japan). The recovery rate of DOC after freeze drying was tested by re-dissolving solid organic matter extracted from a Whistler cloud water sample collected on June 20<sup>th</sup> into DI water followed by DOC measurement. 8% DOC was lost due to evaporation of volatile species and transportation. No pH adjustment was performed since Simpson (2002) demonstrated that the aggregation behavior of NOM will be disrupted by acidifying the sample. Solution-state <sup>1</sup>H NMR was carried out on an Agilent Inova 500MHz spectrometer equipped with a 5mm Inverse Direct Broadband PFG Probe at 298K. The <sup>1</sup>H spectrum was acquired using 256 scans and a relaxation delay of 10 s. PFG NMR data were collected using the Dbppste (DOSY Bipolar Pulse Pair STimulated Echo) PFG sequence (Wu et al., 1995) to achieve 90% signal attenuation at the maximum gradient. Gradient pulses ranged from 0.21 to 6.83 T/m in 15 increments with a diffusion delay of 20 ms and

a diffusion gradient length of 3 ms. All 2D DOSY spectra were processed by Varian Vnmrj 3.2 with mono-exponential fitted to each data point.

### 3.3. Results and discussion

#### 3.3.1. SEC-DOC observations

##### 3.3.1.1. Molecular weight distributions in radiation fogs

Figure 3.3 shows SEC-DOC chromatograms recorded for fog samples collected in Fresno. Each sample was from a different fog event and contained different DOC concentrations, therefore chromatograms have been normalized by DOC response signal (mV). A SEC-DOC chromatogram of a SRNOM is shown for comparison purposes. Integrated areas below the entire chromatogram correspond to the DOC (mg C/L) of the sample. To quantitatively compare the data, the inset shows integrated areas corresponding to “small, medium and large MW material”. Areas are subjectively defined by three discrete peaks (S=MW<170 Da, M=MW between 170 and 600 Da, L=MW between 600 and 100 kDa). The fog organic matter appeared significantly different from SRNOM. In particular compared to SRNOM or other surface waters (Song et al., 2010), the fog organic matter eluted substantially later in what corresponds to smaller molecular weight regions. The small size (<500 Da) of atmospheric organic matter has been documented in other studies using liquid chromatography coupled to electrospray mass spectrometry (Kiss et al., 2003) or ultrafiltration (Herckes et al., 2002c). It was also consistent with observations that small molecular weight compounds like small carboxylic acids (formic, acetic) and carbonyls (formaldehyde, glyoxal) account for a substantial fraction of the organic matter in radiation fogs (Collett et al., 2008).

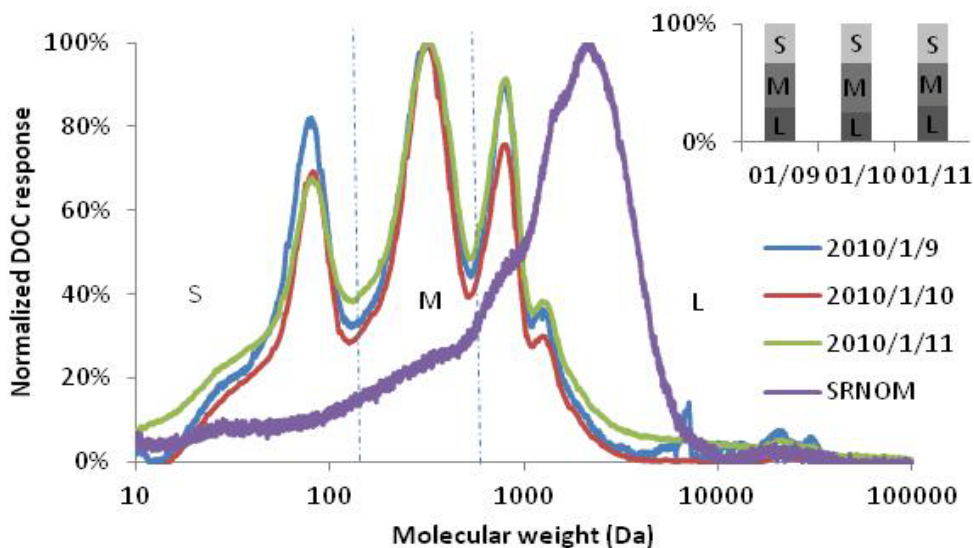


Fig. 3.3 SEC-DOC chromatogram of Fresno fog samples as well as SRNOM. Inset presents integrated peak areas. S=MW<170 Da, M=MW between 170 and 600 Da, L=MW between 600 and 100 kDa.

Chromatograms from different events all showed a similar pattern and there is little variability in shape and distribution of the organic matter as observed by the SEC-DOC method. Most samples exhibited 2 or 3 distinct fractions in the resulting DOC response peaks, which differed significantly from SRNOM which exhibited a major response peak in the high MW area and a relatively small peak in the low MW area. A similar pattern was also observed for fog samples from other locations as shown in Figure 3.4 except that the Selinsgrove sample has a peak in the area of MW>10 kDa. We attributed it to biogenic nanoscale material and will discuss it extensively later in the text.



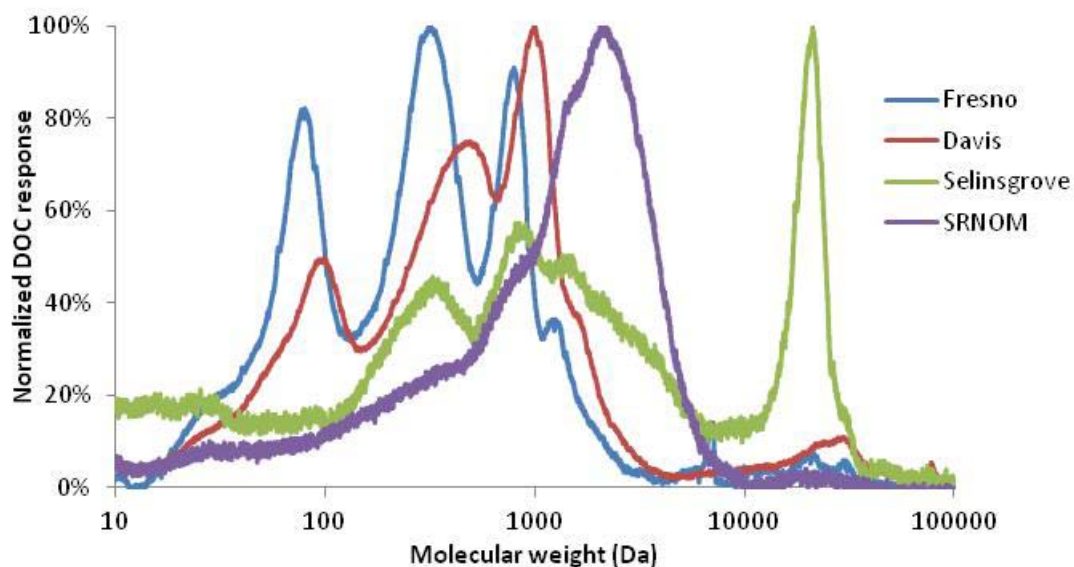


Fig. 3.4 SEC-DOC chromatograms of fog samples collected at 3 locations and the SRNOM standard.

Discrete distributions have been observed by Decesari and co-workers using an anion-exchange chromatography technique and attributed to three fractions: neutral/basic compounds, mono- and dicarboxylic acids and polyacidic compounds (Decesari et al., 2000). This interpretation has been debated (Chang et al., 2005; Decesari et al., 2005). In the present case, checking individual organic species elution times against the calibrated molecular weight was inconclusive. It was obvious that the calibration based on PEG did not account for properties like the electrostatic effect, eluent chemical composition which affect size exclusion separations beyond pure size. Therefore the scale of the x-axis in molecular weight should be considered an indication of molecular size and not as an absolute standard. This was consistent with species eluting after the permeation volume (corresponding to <120 Da) which is an indication that the separation was not based solely on size but additional interactions with the stationary phase increased compound retention.

### 3.3.1.2. Molecular weight distributions in clouds

Figure 3.5 shows cloud organic matter molecular weight distributions from samples collected in Whistler during different cloud events. SRNOM was plotted for comparison purposes. TOC contents were substantially lower in Whistler (2-11 ppmC) compared to Fresno (12-35 ppmC).

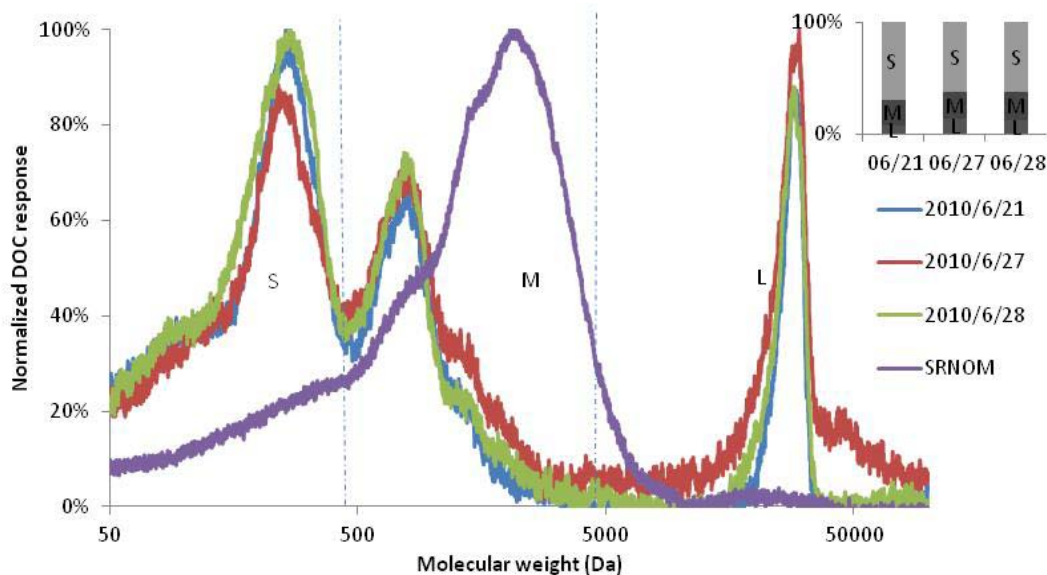


Fig. 3.5 SEC-DOC chromatograms of Whistler cloud samples as well as SRNOM. Inset presents integrated peak areas. S=MW<500 Da, M=MW between 500 and 3 kDa, L=MW between 3 kDa and 100 kDa.

The molecular weight distribution for cloud organic matter is similar to fog samples (Figure 3.5), with a predominance of late eluting material, indicative of “small molecular weight” species. The classification scale was not uniform from site to site, therefore areas subjectively defined by discrete peaks cannot be directly compared. The organic matter was resolved in distinct peaks although less peaks are apparent compared to Fresno fog samples. The higher molecular weight material (MW between 500 and 3 kDa) appeared

partly in what was seen for SRNOM, an indication consistent with a number of studies that attributed similar molecular properties to atmospheric organic matter and humic substances (Krivácsy et al., 2000; Kiss et al., 2003; Samburova et al., 2005) although, here it was only a fraction of the total organic matter present. For these cloud samples, there was again little variability in the molecular weight distribution between different cloud events.

It can be seen from Figure 3.5 that there is a relative peak around >10 kDa in all samples. This peak was barely visible in Fresno fog samples (Figure 3.3; 1-3% of Fresno DOC) but its proportion became larger in Whistler cloud samples (12-17% DOC) and Selinsgrove fog samples (5-21% DOC). The observation of such high molecular weight material (several 10ks Da) was surprising but not an artifact of the analytical method as studies using the same analytical approach to surface waters observed peaks in the same region. In fact, Song et al.(2010) showed that organic matter can have such MW and size, which can be classified as biogenic nanoscale material (BONM) or macromolecules. BONM is likely composed of organic nitrogen, proteinaceous compounds and polysaccharides, which is consistent with previous research conducted by Zhang and Anastasio (2001). Their results showed that proteins and peptides account for approximately 13% and 16% of the organic carbon and nitrogen in fog water. Birdwell and Valsaraj (2010) used excitation-emission matrix fluorescence spectroscopy to characterize organic compounds that cannot be speciated in fog water, and further confirmed that a protein-like substance is present. Also a significant amount of biological materials, such as yeast and bacteria, was observed in fog water (Fuzzi et al., 1997). Some of the biological materials are referred to as transparent exopolymer particles (TEP)

and they are gel-like polysaccharide materials released from algae and bacteria that are ubiquitous in marine and fresh waters (Grossart et al., 1997; Verdugo et al., 2004). In addition, Orellana and coworkers (2011) showed that marine microgels can serve as an important source of cloud condensation nuclei in high arctic summer. These studies indicate that biological materials are an important contribution to organic matter in fog/cloud water.

#### 3.3.1.3. Molecular weight distributions of aerosol WSOC

Besides clouds and fog droplets, a substantial part of the atmospheric carbonaceous particulate matter is water-soluble. The latter can be analyzed after aqueous extraction of aerosols collected on filters and is commonly referred to as WSOC. Figure 3.6 shows WSOC molecular weight distributions for samples collected in Fresno compared to one local fog sample. The aerosol samples were 24 h samples collected on different days. The WSOC samples showed little variability from one day to the next.

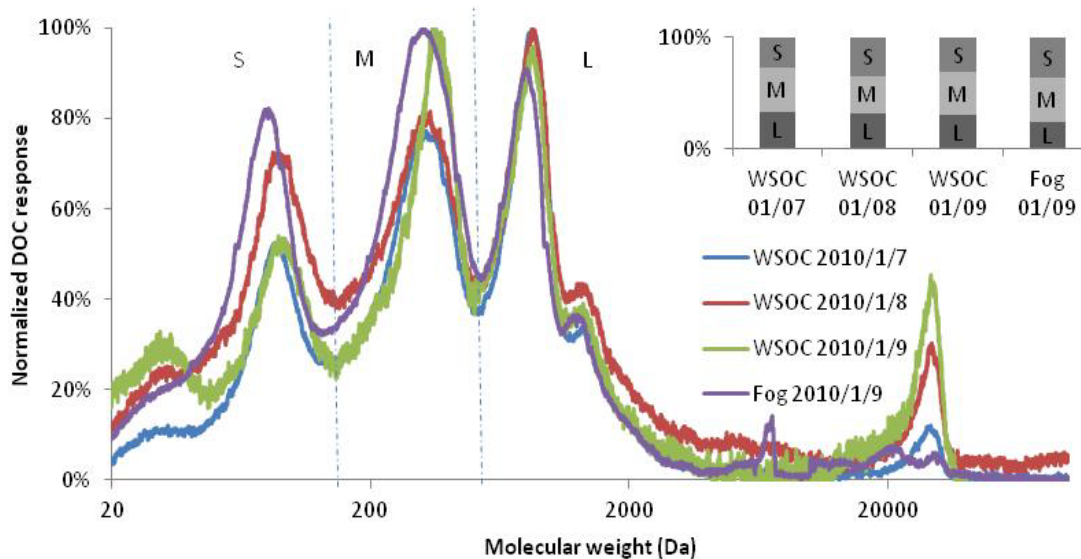


Fig. 3.6 Comparison of WSOC in ambient aerosol and DOC in fog water. Inset presents integrated peak areas. S=MW<170 Da, M=MW between 170 and 650 Da, L=MW between 650 and 100 kDa.

The WSOC similar to fog and cloud organic matter showed discrete peaks and material shifted towards smaller molecular weight material. This is not surprising as the fog droplets grow on existing aerosol particles and hence the water-soluble material is passed from the aerosol to the aqueous droplets. Still the fog droplet distribution was shifted a little towards smaller molecular weight material which would be consistent with the presence of low molecular weight volatile species that partitioned into the aqueous phase and were absent from aerosol particles.

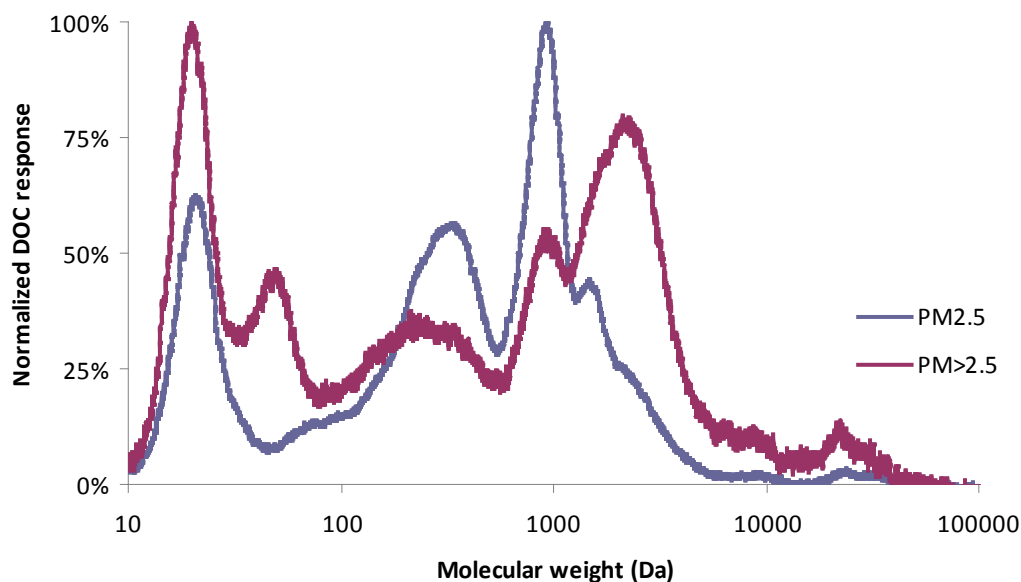


Fig. 3.7 Comparison of WSOC in PM<sub>2.5</sub> (particulate matter with aerodynamic diameter <2.5 μm) and large (PM>2.5 or larger than >2.5 μm aerodynamic diameter) aerosol collected simultaneously in Whistler.

While there was little variability at a single sampling site between different daily samples (Figure 3.6), there is a substantial difference with aerosol particle size. Figure 3.7 presents SEC-DOC chromatograms for two WSOC samples collected in Whistler, one of fine (PM<2.5) and one for large (PM>2.5) particulate matter. The results showed that the organic matter in the larger particulates was shifted towards larger sizes. This could be the result of a stronger contribution of soil organic matter and biological materials which tend to have higher molecular weight organics.

### 3.3.2. Chromophoric properties of dissolved organic matter in fogs/clouds

#### 3.3.2.1. EEM matrix results for fog organic matter and WSOC from Central California Valley

EEM contour maps of Davis fog samples and WSOC of Bakersfield aerosol samples are shown in Figure 3.8. No significant variations can be found from fog collected on

January 15<sup>th</sup> and January 14<sup>th</sup> in Davis 2011 while Bakersfield WSOCs collected on January 19<sup>th</sup> and January 20<sup>th</sup> in 2013 also showed very similar contour profile. Even though compared to Davis fog, no visually identifiable humic acid-like peak can be found in Bakersfield WSOC, the integrated volume of humic acid-like region of Bakersfield WSOC actually accounts for 66% of the total integrated volume which is higher than Davis fog (64%). The evidence of contour shapes of Davis fogs are very alike to Bakersfield WSOCs suggests the properties of CDOM in fogs and aerosols from Central California Valley have highly degree of similarity.

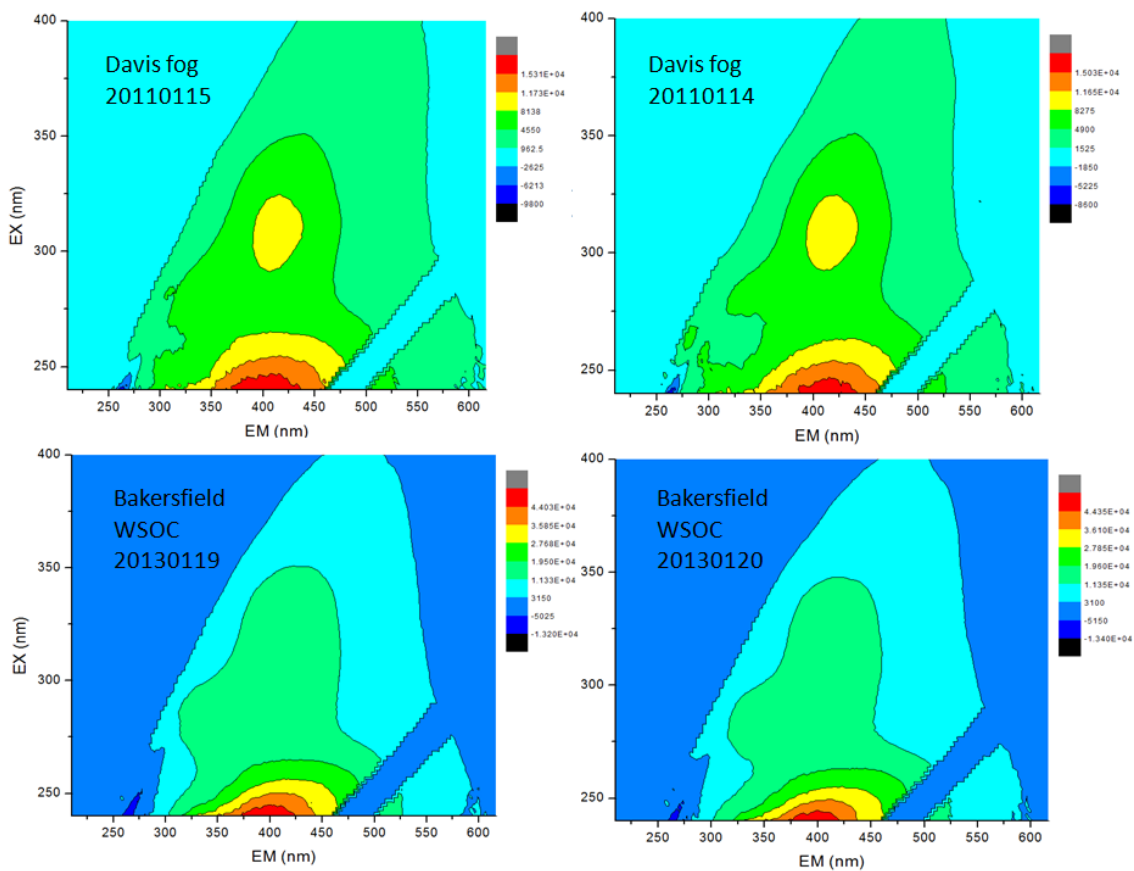


Fig. 3.8 EEM spectra of Davis fog samples and Bakersfield aerosols collected from consecutive days. Spectrum intensities decrease from red to blue and show in arbitrary units.

### 3.3.2.2. Fluorescence Regional Integration Analysis

Figure 3.9 present EEM plots of Whistler cloud, Selinsgrove fog and Davis fog samples as well as SRNOM as a reference material. As a first data analysis approach, the fluorescence regional integration (FRI) approach was applied with 5 predefined regions (cf experimental section 3.2.3). Visually clear differences can be observed between the different sample types and locations. The Whistler cloud has two distinct peaks located in soluble microbial byproduct-like region IV, while the Selinsgrove fog has one. The peak at lower excitation-emission pair suggests the presence of tyrosine & protein-like substances while the peak at longer wavelengths indicates tryptophan & protein-like substances (cf Figure 3.2). Davis fog has moderate fluorescence signals at region IV, however no obvious peaks were found. All fog/cloud samples have abundant humic acid-like signals show in region V. Instead of discrete peaks, the Selinsgrove fog spectrum exhibits as more continuous distribution which might suggest more complex fluorophore compositions. Besides ubiquitous existence of strong fulvic acid-like signals, SRNOM shows little protein related materials in region I II and III.



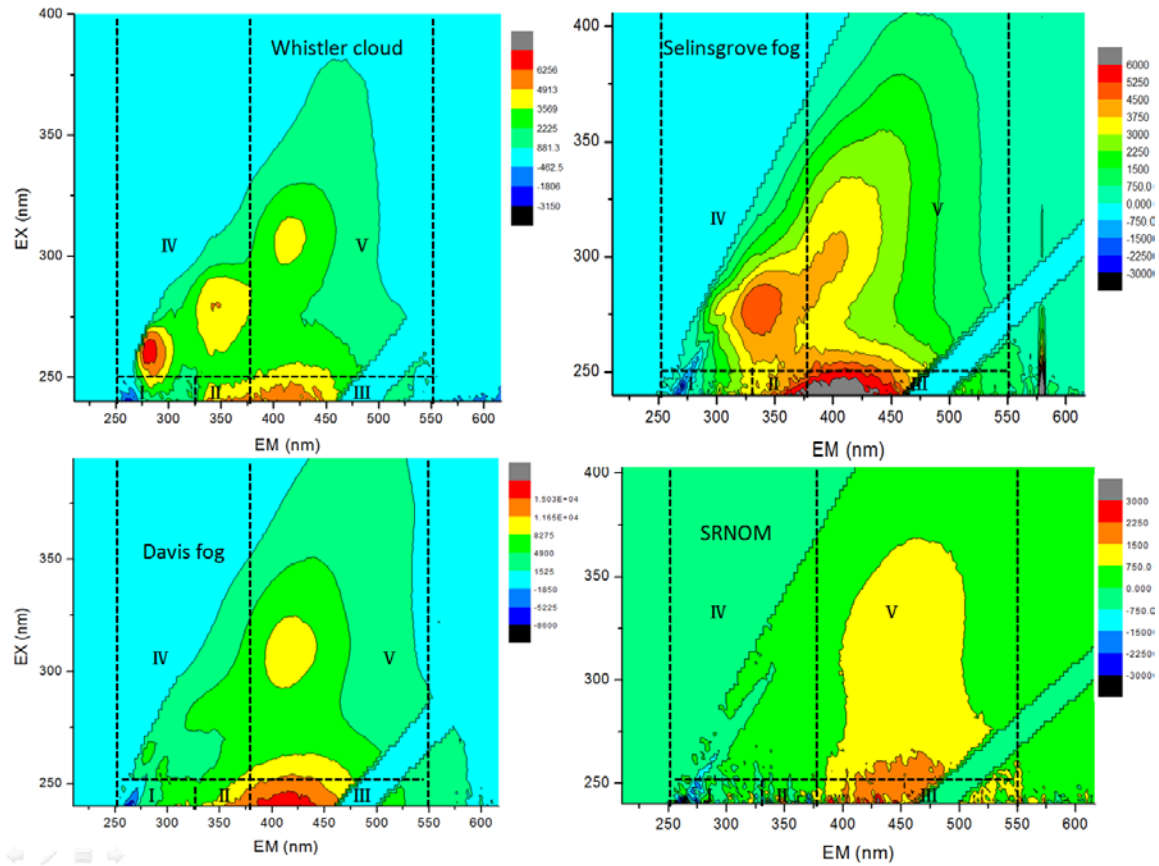


Fig. 3.9 EEM matrices of Whistler cloud, Selingsgrove fog, Davis fog and SRNOM with 5 defined regions Spectrum intensities decrease from red to blue and show in arbitrary units.

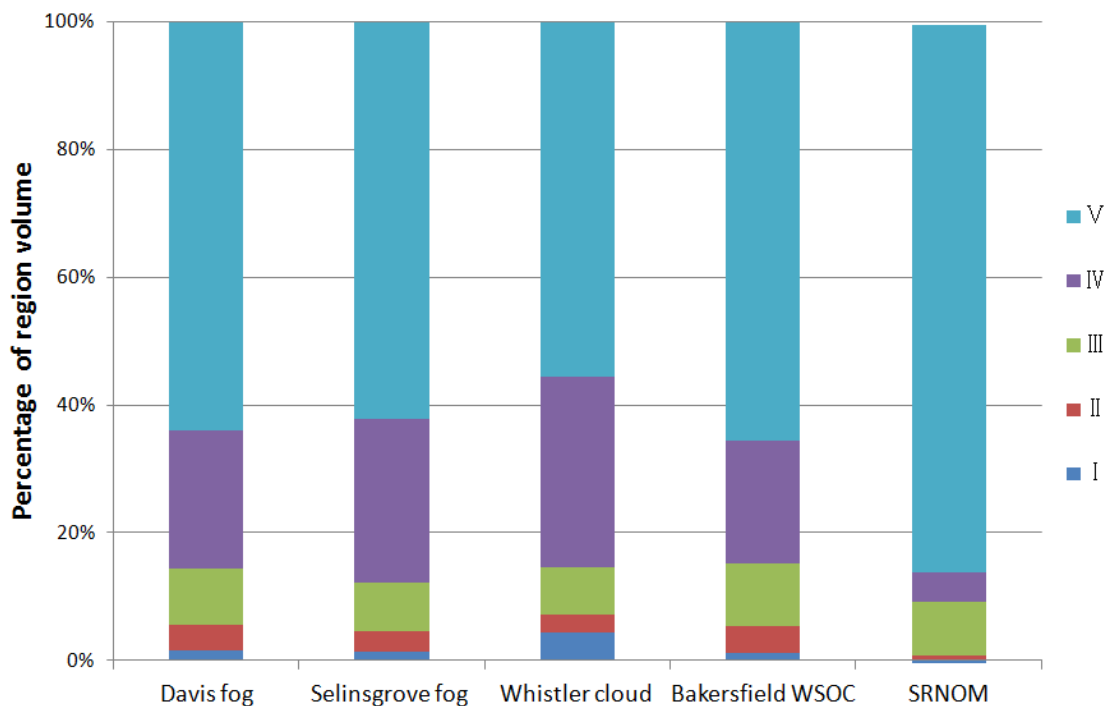


Fig. 3.10 FRI distribution of Davis fog, Selinsgrove fog, Whistler cloud, Bakersfield WSOC and SRNOM.

Figure 3.10 presents the quantitative results of applying FRI integrations to EEM spectra. The fog samples from Davis, Selinsgrove and Bakersfield WSOC share similar FRI distributions. The Whistler cloud sample has the highest volume of region I (4.4%) compare to Davis fog (1.6%), Selinsgrove fog (1.3%) and highest volume of region IV (30%) while Davis, Selinsgrove fog and Bakersfield WSOC have 22%, 26% and 19% respectively which supports the fact that Whistler is the location most influenced by biological activities. SRNOM aromatic content is dominated by humic acid-like substances and has little trace of protein related substances. The quantitative results need to be interpreted with caution since the quantum yield of different molecules varies and can't be accurately predicted because the composition and molecular structures are unknown. Therefore the results are more qualitative and while differences between

samples can be discussed, no concentration information on different compound classes can be derived from the EEM spectra.

### 3.3.2.3. Fluorescence Indices Analysis

Table 3.2 Summary of fog/cloud water fluorescence indices (min-max)

Location	FIX	BIX	HIX
Davis	1.4-1.5	0.7-1.0	1.5-2.6
Whistler	1.4-1.6	0.9-1.2	0.4-2.2
Selinsgrove	1.4-1.7	0.9-1.1	1.1-1.7
Davis PM <sub>2.5</sub>	1.4	1.0	2.0-2.5
Davis PM <sub>&gt;2.5</sub>	1.2	0.8	1.8-3.9
SRNOM	1.1	0.5	12

In the second analysis approach, the fluorescence indices FIX, BIX and HIX were calculated and summarized in Table 3.2. FIX of fog/cloud samples ranged from 1.4 to 1.7 which is similar to fog samples collected from Prairieville, Louisiana and from Tai Mountain in central-eastern China (1.42-1.8)(Birdwell and Valsaraj, 2010) while higher than 1.1 of SRNOM, the numbers indicate contributions from both terrestrial and microbial sources. BIX of fogs/clouds ranged from 0.7 to 1.2, Whistler clouds and Selinsgrove fogs are generally 0.2 higher than Davis which indicate relatively more contribution from fresh microbial origin substances. BIX of Prairieville and Tai Mountain ranged from 0.64 to 1 which is similar to Davis but lower than Whistler and Selinsgrove. SRNOM has a BIX value of 0.5 and lower than all atmospheric fog/cloud samples which

suggest low biological content involved. HIX of SRNOM is around 12 whose humification degree is significantly higher than fog/cloud samples in this study (0.4-2.6), while also higher than Prairieville fog water (1.76-3.74) and Tai Mountain (3.23-6.78) (Birdwell and Valsaraj, 2010). HIX of Tai Mountain is noticeable higher than the rest of the fog/cloud samples but still much lower than SRNOM (12) and humic substances extracted from soils (10-30) (Birdwell and Engel, 2009).

#### 3.3.2.4. Parallel Factor (PARAFAC) Analysis

Parallel Factor (PARAFAC) analysis has also become a common technique to process EEM data. It can decompose an EEM data matrix by mathematically fitting into a specific number of components with common spectral characteristics to reveal specific fluorescence information (Sanchez et al., 2013). PARAFAC was applied to the EEM results of this study, however during model development many challenges were encountered that jeopardized the validity of the model. The major challenge was from component number determination and validation process. In order to ensure the right number of components being fitted, core consistency check and split half analysis are the normal procedure to validate the model (Stedmon and Bro, 2008), however it requires larger number of samples with very similar EEM landscape to pass the validation, unusual sample (outliers) with spectra different than major samples will be revealed by leverage checking and removed manually. The number of samples required and outliers-removal involves some extent of subjectivity but normally more than 50 of samples, even hundreds (Ortiz et al., 2009; Murphy et al., 2013) are used to develop a valid model which is difficult to acquire considering the nature of fog/cloud sampling. Besides significant site dependent variations, interstitial differences could also makes model

validation more difficult, therefore PARAFAC is more suitable for surface water, sea water or other subjects that could provide large data set with modest variations.

### 3.3.3. 1D-<sup>1</sup>H NMR observations of fogs, cloud and water soluble aerosol organic matter

To explore appropriate acquisition time and exam reproducibility of the technique, two aliquots of SRNOM with 1mgC dissolved in 1ml D<sub>2</sub>O were ran for 2 hours and 14 hours respectively. It can be seen from Figure 3.11 that the major difference between 2 and 14 hours scan duration is the revealing of four extra sharp peaks but this only accounts for a small portion of the entire integrated area. The rest of the signals remain unresolved and possess very similar shapes which suggests overnight experiment time (typically around 10 hours) is adequate to obtain sufficient spectrum resolutions while the system has high degree of reproducibility.

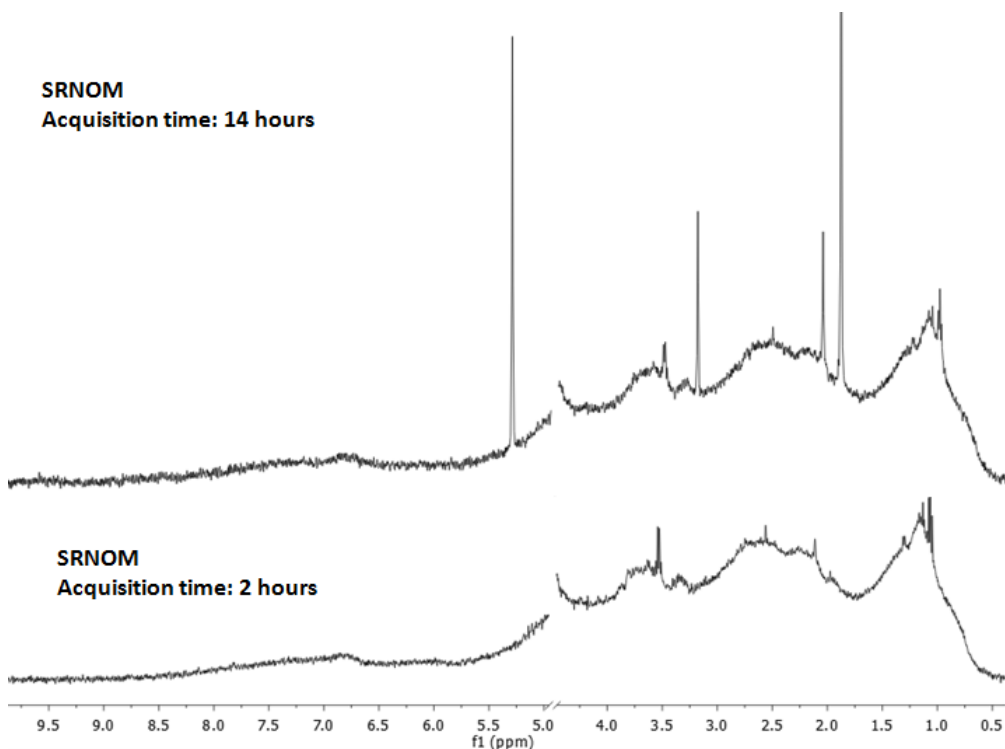


Fig. 3.11 <sup>1</sup>H NMR spectra of 1mgC/ml SRNOM with 14 and 2 hours acquisition time.

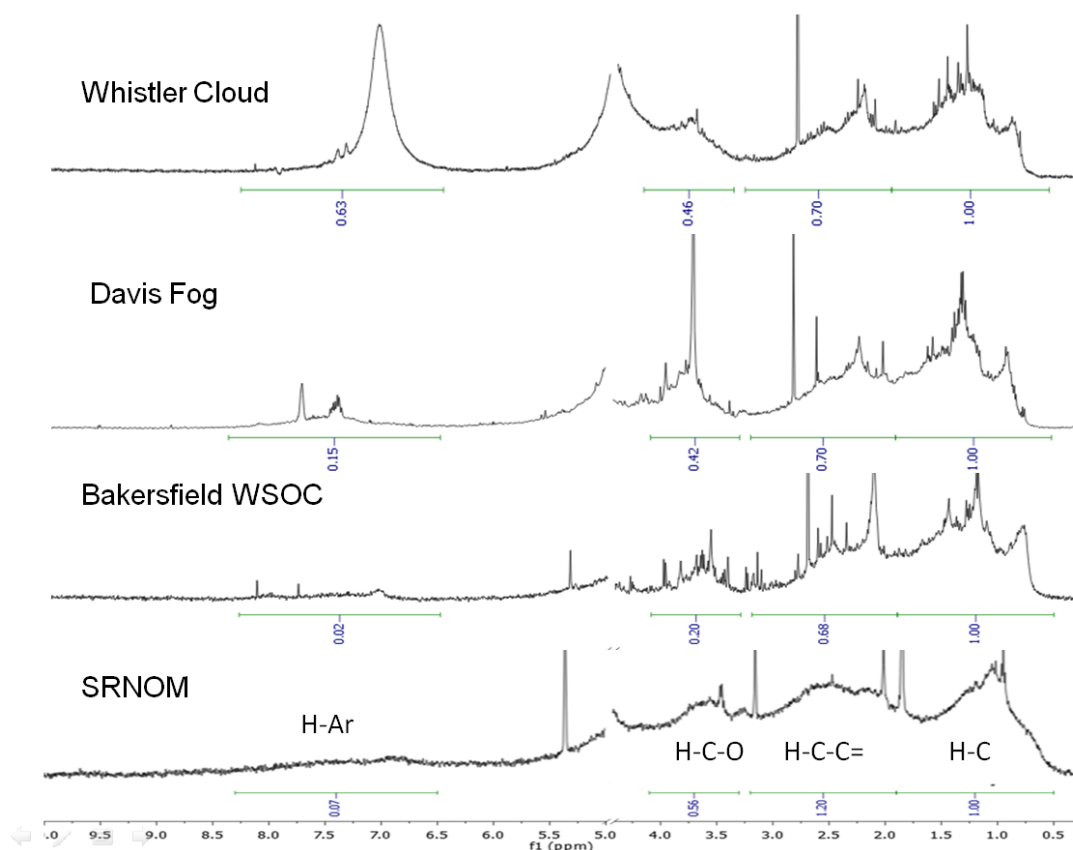


Fig. 3.12  $^1\text{H}$ NMR spectrum of Whistler cloud ,Davis fog, Bakersfield WSOC and SRNOM. Four spectral regions are defined as: 0.5-1.9ppm alkyl proton (H-C); 1.9-3.2ppm protons bound to aliphatic carbon atoms adjacent to unsaturated groups (H-C-C=); 3.3-4.1ppm protons bound to oxygenated aliphatic carbon (H-C-O); 6.5-8.3ppm aromatic protons (H-Ar).

Figure 3.12 presents the  $^1\text{H}$ NMR spectrum of a cloud sample from Whistler, a fog sample from Davis, WSOC in Bakersfield aerosol sample and SRNOM as a reference. A couple of sharp peaks can be observed in all three atmospheric samples but fewer in SRNOM which suggests the presence of relative high concentration of individual small molecules or highly mobile segments of the structural assemblies. The major portion of the signals remained unresolved and distributed continuously, which reflects the

complexity of the organic matter present. The four predefined functional group regions represent a majority of the spectral signals, indicating that organic matter in fog/cloud is comprised mainly of oxygenated functional groups, partially aliphatic and aromatic groups. However, due to the inherent limitation of  $^1\text{H}$  NMR, it is impossible to detect molecular structures that do not carry protons (e.g., substituted aromatic compounds) or acidic protons (hydroxyl and carboxyl) that rapidly exchange with a deuterium from the solvent  $\text{D}_2\text{O}$ . Studies showed that 14-25% of carbon content eluded detection by  $^1\text{H}$  NMR (Decesari et al., 2000; Tagliavini et al., 2006). HDO solvent peaks were cut from 4.5 to 5.0 ppm and potentially block the signals of hydrated aldehydes.

All atmospheric samples show abundant methyl groups from 0.7 to 1.1 ppm which is consistent with other aerosol, fog even rain studies (Decesari et al., 2000; Graham et al., 2002; Tagliavini et al., 2006; Seaton et al., 2013). However, surface water organic matter SRNOM shows scarce signals in the same range. In the aromatic protons region (6.5-8.3 ppm), Bakersfield WSOC and SRNOM show weak signals while the Davis fog and especially the Whistler cloud sample show higher aromatic structure content which might be caused to a certain extent by biogenic influences with various vegetation coverage of sampling sites. Aromatic protons in Whistler cloud were detected at around 7.0 ppm which suggests the existence of electron-donor substituent (e.g. phenolic groups). Lignin was then confirmed by DOSY-NMR and will be elaborated in the next section. Davis fog has aromatic protons detected at around 7.6 ppm revealing an electron-acceptor substituent like carbonyls and/or carboxyls. The major signal distributions of fog, cloud and aerosols collected from various locations show strong similarity indicating a certain

degree of composition similarities in atmospheric organic matter within North America and a close connection between fogs/clouds and aerosols.

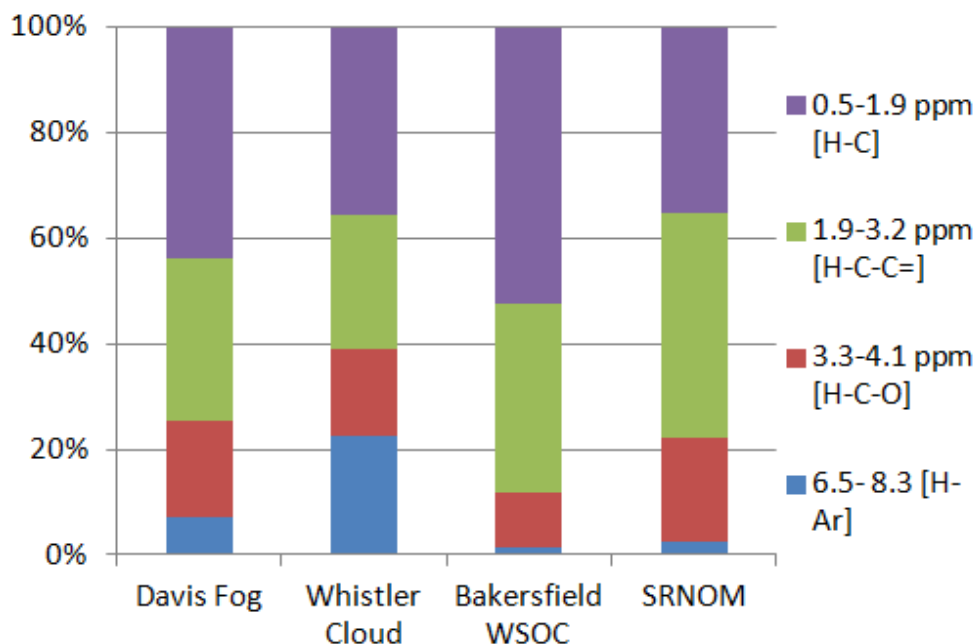


Fig. 3.13 Normalized abundance of nonexchangeable protons in Davis fog, Whistler cloud, Bakersfield PM2.5 WSOC and SRNOM.

To evaluate relative abundance, four major regions were integrated and shown in Figure 3.13. Atmospheric water samples both have lower aliphatic proton portion but higher percentage of oxygenated aliphatic protons than WSOC in Bakersfield aerosols which is consistent with result from Po Valley (Decesari et al., 2000). WSOC of aerosols collected from Huston (Cleveland et al., 2012) have similar functional group abundance as in Davis fog, Bakersfield WSOC and Po Valley WSOC. Whistler cloud samples show the highest relative importance of aromatic protons which will require further investigations to clarify if this is the result of the important biogenic influence on the organic matter structure. Only the SRNOM sample shows H-C=C higher than aliphatic



protons which indicates a higher degree of unsaturation in surface water organic matter as compared to atmospheric organic matter.

Overall atmospheric organic matter functional group compositions show a certain degree of similarity. The abundances are normally in the order of H-C > H-C-C= > H-C-O > H-Ar. However evidence shows this order might be altered by anthropogenic (e.g., biomass burning) or biogenic activities (e.g., the emission of plant materials) which makes the technique potentially useful for source appointment (Graham et al., 2002; Decesari et al., 2007).

#### 3.3.4 2D-<sup>1</sup>HNMR DOSY observations

Figure 3.14 shows the two-dimensional diffusion-ordered spectroscopy of a 1 mgC/ml sample of SRNOM. The vertical axis shows the value of the diffusion coefficient with the units of  $10^{-10} \text{ m}^2/\text{s}$  while the horizontal axis is the chemical shift dimension. A continuous diffusion coefficient distribution can be observed which ranged from 2 to  $6 \times 10^{-10} \text{ m}^2/\text{s}$  except a “gap” between 4.6 and 5 ppm. This is due to the fact that peak shapes of NMR follow Gaussian distribution: when peak overlapping occurs, adjacent peak signals interact with each other and signal strength accumulates. After getting processed by a mono-exponential method, diffusion coefficients will be presented as an apparent value for which all the components that contribute to the signal are counted. As a consequence of low sample concentrations, the water signal is dominant in the “gap” area. The diffusion coefficient of free water is  $18 \times 10^{-10} \text{ m}^2/\text{s}$  which is significantly faster than the major organic species in the sample. The broad water peak is averaged with the rest of the peaks and “pulling” diffusion value into lower molecular size area as pointed by arrowheads.

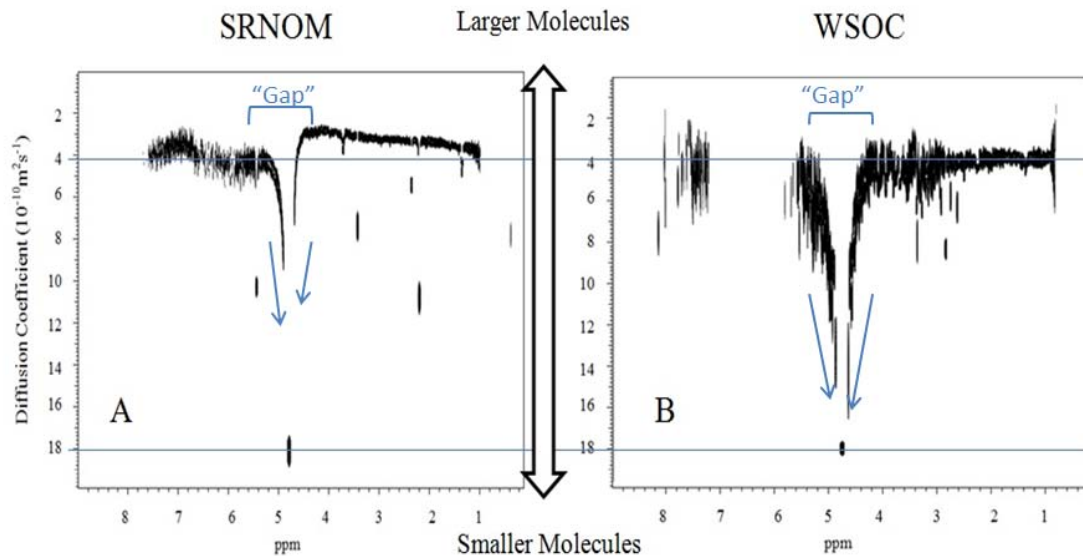


Fig. 3.14 2D-DOSY projection of (A) 1 mgC/ml SRNOM in D<sub>2</sub>O; (B) 1 mgC/ml Bakersfield WSOC in D<sub>2</sub>O.

Only limited scattered components with diffusion values lower than the major signals can be spotted due to their relative high peak height and sharp peak shape while weaker signals of many other low molecular weight species that were detected in the 1D spectrum were averaged with major components and shown as apparent diffusion coefficients. Diffusion coefficient distribution shows a decreasing trend from 1 to 4.5 ppm indicating that polysaccharides and lignin-like components (3-4.5 ppm) have larger molecular sizes than aliphatic components. This observation is similar to Simpson's (2002) results on a fulvic acid extract. In Simpson (2001), aromatics with similar diffusion rate as aliphatics were observed in a fulvic acid sample and were confirmed as lignin-derived species while aromatics with higher molecular sizes were found in a whole-soil extract. In this study the aromatic region (6.5-8 ppm) of SRNOM contains a continuous distribution of diffusion coefficients ( $2-4.5 \times 10^{-10} \text{ m}^2/\text{s}$ ) that covers both

aromatic areas in fulvic acid and whole-soil extract supports the existence of fulvic acid and contribution from terrestrial substances as depicted in Figure 3.14A.

Considering that previous SEC-TOC results show WSOC of aerosols share similar molecular weight distribution pattern with fog water DOC at the same sampling site, WSOC samples were used for optimization and testing purposes rather than fog samples due to the scarcity of the latter ones. Since there was no Whistler aerosol sample available, PM<sub>2.5</sub> samples from the latest 2013 Bakersfield study were prepared for DOSY experiment and shown in Figure 3.14B. The 2D diffusion spectrum is comprised by two distinctive bands with similar diffusion coefficients at around  $4 \times 10^{-10} \text{ m}^2/\text{s}$ . A line was drawn at free water's diffusion rates ( $18 \times 10^{-10} \text{ m}^2/\text{s}$ ) suggesting experiment parameters were well maintained for cross comparison. Broader water peaks were found in all atmospheric samples which were possibly caused by microbial metabolism activities. Another line was drawn to demonstrate the average diffusion rate of Bakersfield WSOC and shows overall smaller molecular size than SRNOM which is consistent with SEC-TOC results.

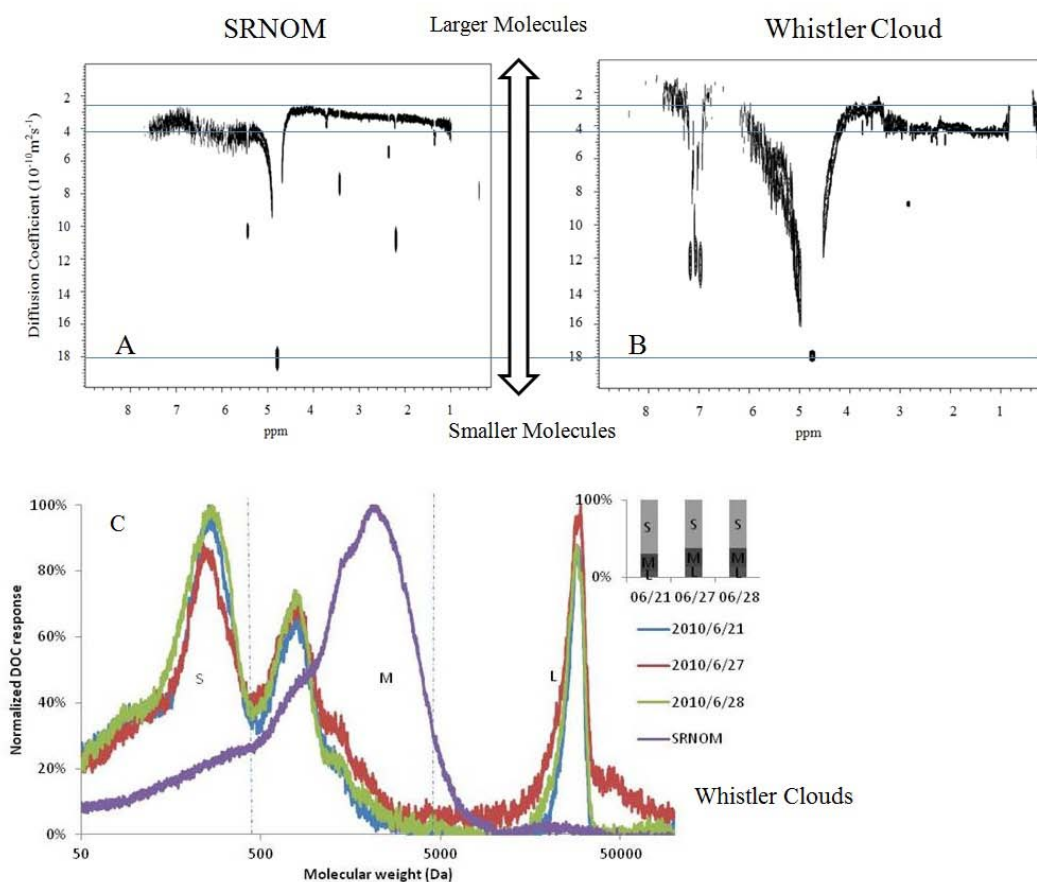


Fig. 3.15 2D-DOSY projection of (A) 1mgC/ml SRNOM in  $\text{D}_2\text{O}$ ; (B) 1 mgC/ml Whistler cloud water in  $\text{D}_2\text{O}$ ; (C) SEC-TOC chromatogram of three Whistler cloud samples as well as SRNOM.

Up to 17% of DOC with molecular size larger than 10 kDa was detected by SEC-TOC and attributed to BONM as shown in Figure 3.5. A Whistler Cloud sample collected on June 21<sup>st</sup> was tested and the 2D-DOSY result is shown as Figure 3.15. No major signal was detected between 6 to 6.8 ppm like Bakersfield WSOC however Whistler cloud samples show more abundant signals in the aromatic region. Considerable amount of small aromatic species with diffusion coefficient at  $12 \times 10^{-10} \text{ m}^2/\text{s}$  were identified while the existence of aromatic species larger than SRNOM with diffusion coefficient lower

than  $2 \times 10^{-10} \text{ m}^2/\text{s}$  was also confirmed. The larger aromatic structures could belong to tyrosine and tryptophan in protein molecules whose presence were confirmed by EEM and discussed in section 3.3.2.2. The average apparent diffusion coefficient of Whistler cloud DOC is  $4 \times 10^{-10} \text{ m}^2/\text{s}$  which is the same as Bakersfield WSOC and smaller than SRNOM, again, consistent with SEC-TOC results. High molecular weight lignin-like content with diffusion rate of  $2.5 \times 10^{-10} \text{ m}^2/\text{s}$  were found in Whistler cloud sample but not in Bakersfield WSOC which could be explained by: lignin are more expected to be seen in a dense vegetation area than in an industrial oil mining field with limited plants.

As shown in the previous section, DOC of Selinsgrove fog water contains the highest percentage of BONM (up to 21%). Due to limited sample volume of a single fog event, four fog water samples collected through 2013 from Selinsgrove were mixed to represent the general composition of the area.

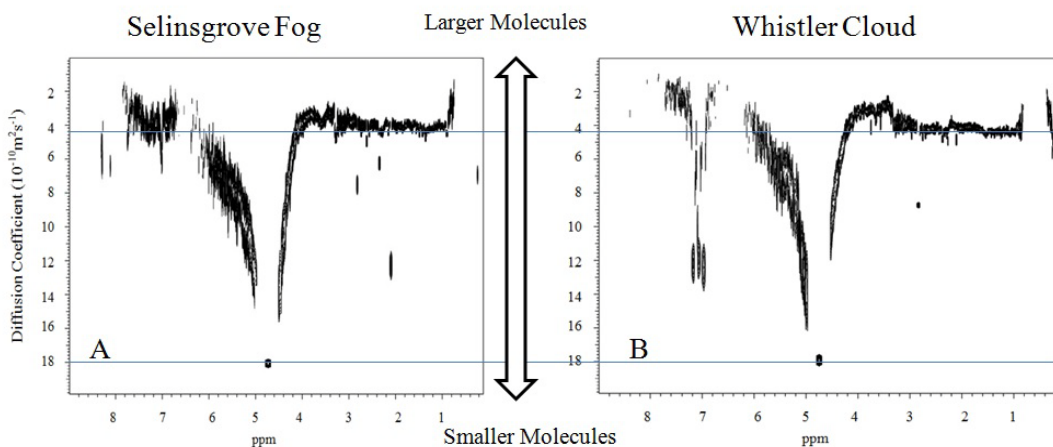


Fig. 3.16 2D-DOSY projection of (A) 1 mgC/ml mixed Selinsgrove fog water in  $\text{D}_2\text{O}$ ; (B) 1 mgC/ml Whistler cloud water in  $\text{D}_2\text{O}$ .

A comparison between Selinsgrove fog and Whistler cloud is shown in Figure 3.16. Fog and cloud samples share a very similar diffusion pattern in general, whereas more intense aromatic signals in Selinsgrove fog indicates that a larger portion of BONM exists in the pooled Selinsgrove fog aliquot than in Whistler cloud collected on June 21<sup>st</sup> 2010. Even though unlike Whistler cloud, no small aromatic molecule peak was spotted in Selinsgrove fog, the diffusion rates are pulled to the smaller molecule area at the same chemical shift which might indicate a contribution from the same small species.

#### 3.4. Summary and conclusions

Different bulk characterizations were used to characterize atmospheric organic matter, including size exclusion chromatography coupled to inline organic carbon detection (SEC-DOC), nuclear magnetic resonance spectroscopy (NMR) and fluorescence spectroscopy (acquisition of excitation emission matrices EEM).

For SEC-DOC the results showed little variability in molecular size distributions between samples collected at a specific site and limited variability between sites and types of atmospheric samples. The atmospheric organic matter is distributed across a wide range of nominal molecular weight (120-10 KDa) consistent with work performed using different analytical techniques. The results on the atmospheric samples differ substantially from aquatic organic matter (e.g. Suwannee river natural organic matter) in terms of molecular weight (smaller) and distribution (several clearly defined peaks). A major difference between types of samples is a larger fraction of small molecular weight organic species in fog and cloud samples compared to the water soluble fraction of aerosols, consistent with the partitioning of small molecular weight volatile species into the atmospheric aqueous phase. With aerosol samples, there is a noticeable difference

between the molecular weight distribution organic carbon in fine (PM<sub><2.5</sub>) and larger (PM<sub>>2.5</sub>) aerosol samples. Samples from select environments presented a substantial fraction of organic matter in a very high molecular weight region (>10000 Da) corresponding to biogenic nanoscale or macromolecular materials.

Analysis of Excitation Emission Matrices (EEMs) by fluorescence regional integration for cloud and fog samples showed that the organic matter is very similar in these types of samples, no matter the location. The atmospheric organic matter is however substantially different from surface water which is mainly represented by humic acid-like components and with little biological features. Analyzing the EEMs in terms of fluorescence index showed that all fog/cloud and aerosol organic matter have both terrestrial and microbial origins and little degree of humification. Whistler and Selinsgrove atmospheric water have higher BIX than Davis but all show biological influences to a different extent. The ranges of indices are close to published observations especially samples from the US and very different from SRNOM which has features of terrestrial origin, little biological substances and higher degree of humification.

Finally NMR spectroscopy was applied to the atmospheric samples. The results show that in terms of functionality, organic matter in fog/cloud and aerosols share certain similarity with major difference of aromatic content. A set of DOSY protocols were developed on a Varian NMR system and were the first attempt to our knowledge to characterize diffusion coefficient of atmospheric organic matter. Diffusion coefficients of major atmospheric organic matter components are alike and smaller than SRNOM which is consistent with SEC-TOC results, while Selinsgrove fog and Whistler cloud have high molecular weight aromatic constituents, further confirmed by the SEC-TOC finding of

BONM. DOSY experiments were shown to be a powerful complimentary tool to qualitatively characterize complex natural organic matter.

Overall the bulk characterization results suggest that atmospheric organic matter is rather similar in regards to structure and functionality. Distinct differences, mostly on smaller scale exist with aromatic components and biological influences reflected by fluorescence spectroscopy. Atmospheric organic matter is however substantially different from surface water organic matter with smaller molecular sizes, higher aromaticity and more biological derived substances.

The methods presented here, while previously applied to other types of samples are novel for atmospheric organic matter. While NMR methods have low sensitivity and require rather large sample amounts to have sufficient organic matter mass, SEC-TOC and EEM allow for the use of small sample volumes. The latter makes these techniques amenable to investigate temporal changes of organic matter with short time scales especially for fogs and cloud where even high volume sampling techniques provide only small sample volumes. In the next chapter the ability of these methods to work on small samples and hence study dynamic changes will be explored.



## CHAPTER 4

### FOG/CLOUD PROCESSING OF ATMOSPHERIC ORGANIC MATTER

#### 4.1 Introduction

Inorganic fog chemistry has been studied for decades especially relative to sulfur oxidation. This research showed that aqueous phase reactions, in fog and cloud droplets, could lead not only to the formation of high droplet acidity (acid rain) by oxidation of gas phase  $\text{SO}_2$  and  $\text{NO}_x$  into sulfuric and nitric acid in the droplets but also to the formation of additional particulate mass. In fact, when the generated acid species were neutralized in the aqueous phase by  $\text{NH}_4$  from gas phase  $\text{NH}_3$  incorporation, then upon droplet evaporation ammonium sulfate or ammonium nitrate remained in the particulate phase. Hence aqueous phase processing transformed gas phase species into particulate material, resulting in secondary inorganic aerosol material creation.

In recent years, more research has focused on organic matter in fogs and clouds and with an improved understanding of the organic matter present, processing of organic materials by clouds became the center of attention. First studies showed the presence of a substantial amount of organic material in fogs and clouds and a number of speciation studies even detailed the material at molecular level. Processing studies looked then at the incorporation of aerosol and gas phase organics into fogs and clouds (Collett et al., 2001; Acker et al., 2002; Herckes et al., 2007a). The major challenges to an improved understanding were however the limited number of observations, and partly related, the poor temporal resolution of the observations.

Simultaneously in the air pollution and climate community, a substantial discrepancy between aerosol observations and model results emerged. Observational

studies on particulate mass concentrations and modeling efforts on regional scale disagreed significantly with the observed presence of much higher organic aerosol concentrations than predicted by models, up to two orders of magnitude (Tsigaridis and Kanakidou, 2003; Heald et al., 2005). Traditional partitioning theory that only involves organic matter in gas phase and in preexisting particles failed to explain field data (Lim et al., 2010) such as: organic matter in atmospheric SOA is more oxidized (higher O/C ratio) than SOA formed by gas phase chemistry (e.g. dry smog chamber (Aiken et al., 2008)); aerosol concentration and distribution are inaccurately predicted by models who only consider gas and particle phases (Tsigaridis and Kanakido, 2003; Heald et al., 2005) and in some cases SOA surrogates were stronger correlated to liquid water than to organic matter in ambient aerosol (Hennigan et al., 2008, 2009). This lead to the hypothesis that aqueous phase chemistry in fogs, clouds and wet aerosol particles could be of substantial importance in the generation of secondary organic aerosol and account for the “missing” SOA source in the model calculations.

Many lab and modeling studies have investigated this hypothesis over the last years. A typical approach was studying model species. The most prominent model species for both modeling and lab work were dicarbonyls, especially glyoxal and methylglyoxal since they derive from both biogenic (isoprene) and anthropogenic (aromatics, acetylene) precursors, are commonly found in urban, rural and remote areas (Kawamura and Yasui, 2005) and are within the most abundant individual species in fogs and clouds (Herckes et al., 2013). The evidence of irreversible uptake of dicarbonyls by fog/cloud droplets also suggests they are important sources of SOA formation (Fu et al., 2008).

Atmospheric aqueous reactions can be divided into two categories: radical reactions and non-radical reactions. The OH radical represents the major oxidant in fog/cloud droplets (Ervens et al., 2003). One third of OH radicals are formed in the aqueous phase through the photolysis of H<sub>2</sub>O<sub>2</sub> and photo-Fenton reactions ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2 + h\nu \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}$ ) where redox pair Fe<sup>2+</sup>/Fe<sup>3+</sup> serve as catalyst in the degradation reactions of organic ligands such as oxalate (Lim et al., 2005; Herckes et al., 2015). Extensive experiments have been conducted with glyoxal and methylglyoxal (DeHaan et al., 2009; Yasmeen et al., 2010; Lee et al., 2012) and various reaction mechanisms were proposed (Lim et al., 2010; Ervens et al., 2011). Particularly, solute concentrations play as a key factor to determine reaction pathways. In cloud relevant concentrations (Glyoxal < 1 mM) which is considered dilute, the oxidation of glyoxal by OH radical leads to formation of glyoxylic acid then oxalic acid; with increasing concentration towards wet aerosol relevant concentrations (>1 M) substantial formation of larger organic acids and oligomers is observed (Tan et al., 2009). For methylglyoxal, the same pattern of smaller oxidation products at dilute concentrations and oligomeric series at high concentrations was reported (Tan et al., 2010). Other SOA precursors were also been studied such as methacrolein (MACR) and methylvinyl ketone (MVK) (El Haddad et al., 2009; Zhang et al., 2010). All species mentioned above had time-based aqueous SOA product with initial increasing yields then oxidation to CO<sub>2</sub> which is also the final product of photochemical reactions of oxalic, glyoxylic and pyruvic acid in fog water (Zuo and Hoigne, 1994). However, these experiments were performed in pure water and/or limited species, which cannot reflect the chemical nature of atmospheric water matrices (fog and clouds) which involve complex and abundant inorganic and organic compounds.

In this part of the work, we investigated aqueous phase processing of atmospheric organic matter in field and laboratory experiments. Instead of focusing on individual species, which only account for a small fraction of organic content, we investigated if any changes in bulk properties of organic matter occur during fog processing. Therefore time series samples were taken to evaluate fog/cloud impact on molecular weight distribution and optical properties throughout a fog/cloud event using some of the methods developed in Chapter 3. These experiments were complemented by laboratory studies looking at the impact of photochemistry on organic matter properties, under conditions commonly occurring in the field. In fact although most fog events take place during night time many persist till early morning, when they can experience solar irradiation and hence photochemistry. Clouds, of course occurring also in the daytime can be photolytically processed. Therefore a solar simulation system was also applied to authentic fog samples to investigate the effects of photochemistry on atmospheric aqueous organic matter.

## 4.2 Experimental

### 4.2.1 Field observations and analysis of field samples

Time series samples were taken during the field studies in Fresno, Whistler and Davis (cf section 2.2) by removing aliquots from the CASCC sampler at defined time intervals, to investigate temporal changes in chemical composition. Sample volumes and consequently temporal resolution is affected by LWC, collector availability, event duration. Six time series aliquots were taken from a Fresno fog event on January 14<sup>th</sup> 2010, which lasted from 8:00 pm to the next day 3:00 am. Samples were taken at 70 minutes sampling intervals. Whistler time series samples were collected on June 21<sup>st</sup> 2010 with three aliquots taken from 8:30 am to 10:30 am, 10:30 am to 4:00 pm and 4:00

pm to the next day 8:30 am respectively. Four Davis time series fog samples were collected on January 15<sup>th</sup> from 5:30pm to the next day 2:00 am with two hour sampling interval. LWC of Whistler cloud was higher than values of Central California fog, however there was only one CASCC available for cloud collecting therefore the sampling resolution was lower than the other two sites.

Time series samples were analyzed for molecular weight distribution using the method size exclusion chromatography method detailed in Chapter 3 (section 3.2.2). Excitation Emission Matrices were obtained following the same procedure as described in Chapter 3.2.3.

#### 4.2.2 Laboratory studies

Laboratory studies were conducted on authentic fog samples and select model solution to investigate the effect of photolysis on fog organic matter under controlled conditions. In order to achieve sufficient volume, several fog samples collected in Selinsgrove in 2013 were pooled (150 ml) then placed into a solar simulation set-up as described below for a two hour irradiation experiment. Time series aliquots were taken and analyzed using SEC-DOC, EEM and TOC analyzer as elaborated in Chapters 2 and 3. As shown in Figure 4.1, the solar simulator used in this study, consists of a 300 W ozone-free Xe lamp, a water filter, an air mass 1.5 global (AM 1.5 G) filter, a Spectra-Physics (Stratford, CT) 300 W power supply, a manual shutter, a 200 ml jacketed flask and a recirculating water chiller. The flask can be sealed by a Teflon lid with a Suprasil quartz window ( $\Phi$ 3.2 cm).

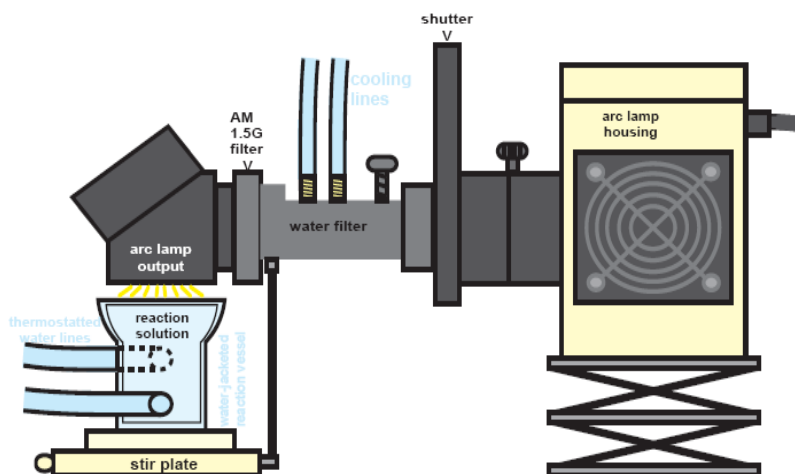


Fig. 4.1 Irradiation set-up with the water chiller, irradiation flask, lamp, filters and power source.

With the AM1.5 G filter, the system could simulate solar irradiation at a  $48.2^\circ$  solar zenith angle which corresponds to the solar irradiation in the 48 contiguous states of the United States. The actinic flux was determined using 2-nitrobenzaldehyde as a chemical actinometer following the method described in Allen et al (2000). The output actinic flux of the system for the experiments described here was measured to be  $1.07 \times 10^{16}$  photon $\cdot$ cm $^{-2}$  $\cdot$ s $^{-1}$  which is lower than measurements in Davis, California at noon during summer 2000 ( $3.6 \times 10^{17}$  photon $\cdot$ cm $^{-2}$  $\cdot$ s $^{-1}$ ) (Stockwell and Goliff, 2004) but comparable to the actinic flux at noon during winter in Pheonix, Arizona ( $1.31 \times 10^{16}$  photon $\cdot$ cm $^{-2}$  $\cdot$ s $^{-1}$ ) (Finlayson-Pitts and Pitts, 2000).

#### 4.3 Results and discussion

##### 4.3.1 Molecular weight distributions of Fresno time series fog samples

Six time series samples were taken on January 14<sup>th</sup> 2010, during the Fresno field campaign. Two high-volume aerosol samples were collected during fog event (interstitial

aerosol) and compared with pre and post fog ambient aerosol samples. SEC-DOC chromatograms are shown in Figure 4.2. The nomenclature “pi” (i=1, 2, 3..., I) stands for period number (time series sampling order) of the fog/cloud event. First, there are no dramatic changes in the molecular weight distribution during fog events. There is no large scale shift towards larger molecular weight or smaller molecular weight that is observed. This does not mean that chemistry is not occurring during fog events but only that if the organic matter as a whole is concerned, the changes are minor and do not impact overall bulk properties.

Two noticeable changes in relative peak intensity were observed. In the low molecular weight area (indicated by 100 Da, as based on PEG calibration) carbon signals decreased during the event with higher concentrations at the beginning and end of the event as shown by the left arrow. After the initial phase p1 (deep blue) it decreased but went back to similar intensities by the end of the event at p6 (brown). A similar evolution is seen at the peak around 1000 Da pointed by the right arrow. With the development of the fog event, the intensity of the peak started to decrease after p2 (red) until p4 (purple) then went back gradually (light blue then brown) to the level as initial phases of the event (p1 and p2).

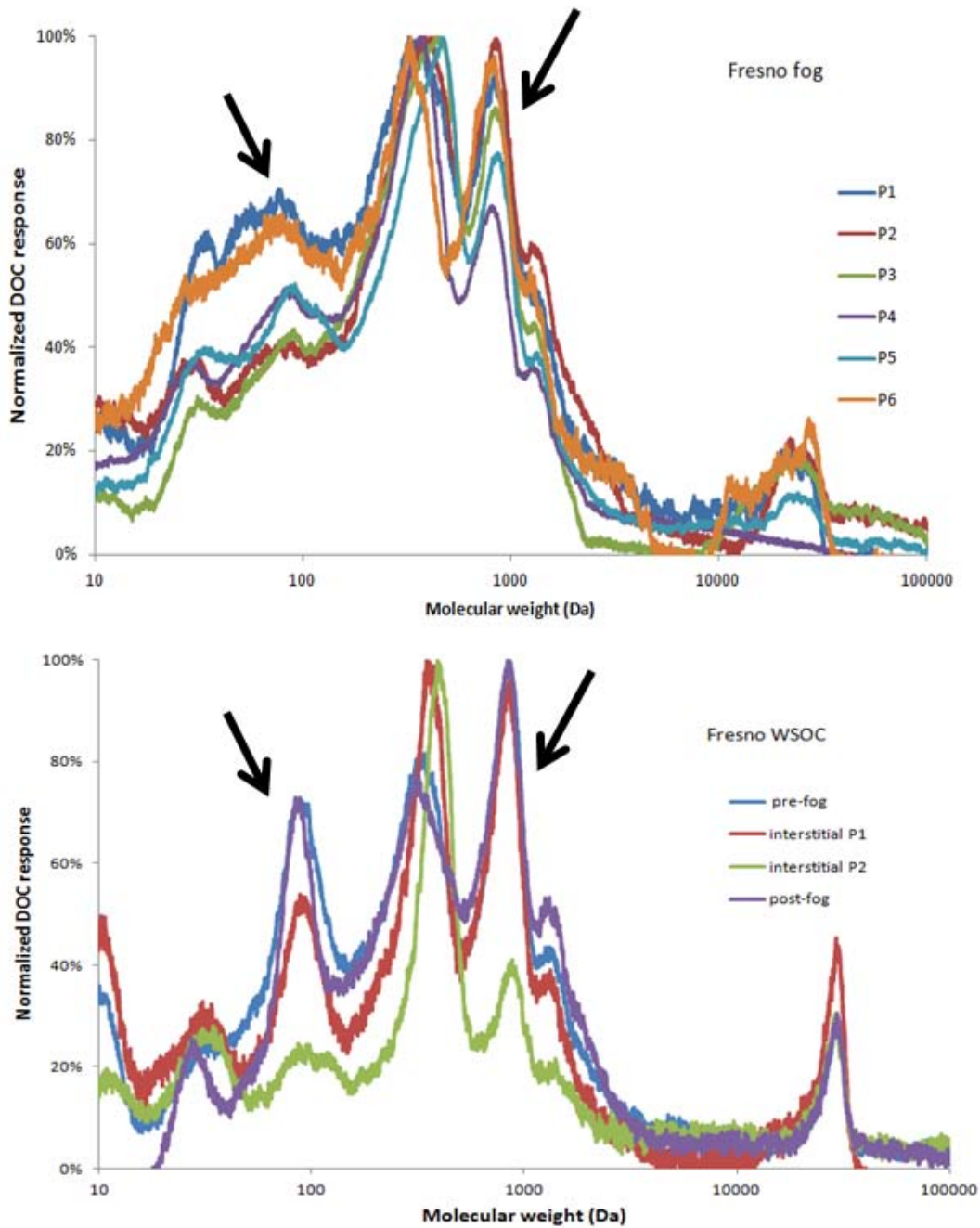


Fig. 4.2 Molecular weight distributions of Fresno time series fog samples and WSOC of pre, interstitial and post fog event aerosols.

The observed pattern is difficult to interpret. In absolute concentrations one often sees higher concentrations during the initial and final stages of the fog events as the



droplets are more concentrated during formation and dissipation (condensation or evaporation with lower LWC) than during the middle (maintenance) stages (Fuzzi et al., 1984; Huang et al., 1992). However this would not really explain these changes in molecular weight distribution.

For the water soluble organic aerosol samples from the same event, we observe a clearer pattern. Pre and post fog aerosol show a very similar distribution suggesting that fog processing does not alter substantially the molecular weight distribution in the ambient aerosol. However, we are observing that during the fog event, the interstitial (not activated into fog droplets) aerosol material shows substantially different molecular weight distributions with far less material around 100 and 1000 Da (Figure 4.2). This observation would suggest that material rich in organic matter of these sizes is scavenged preferentially into the fog samples leaving the interstitial aerosol relatively depleted in this material. This is consistent with these peaks being more prominent in the initial stages of the fog as they are being scavenged preferentially into the aqueous phase. While we still do not understand how this changes over time in the fog, an increase in these peaks at the end of the fog is consistent with the difference upon fog evaporation between the last interstitial and the first post-fog samples, where the material returns to the particle phase. Unfortunately no EEM data was available for the Fresno samples.

### 4.3.2 SEC-DOC and EEM results of Davis and Whistler time series fog/cloud samples

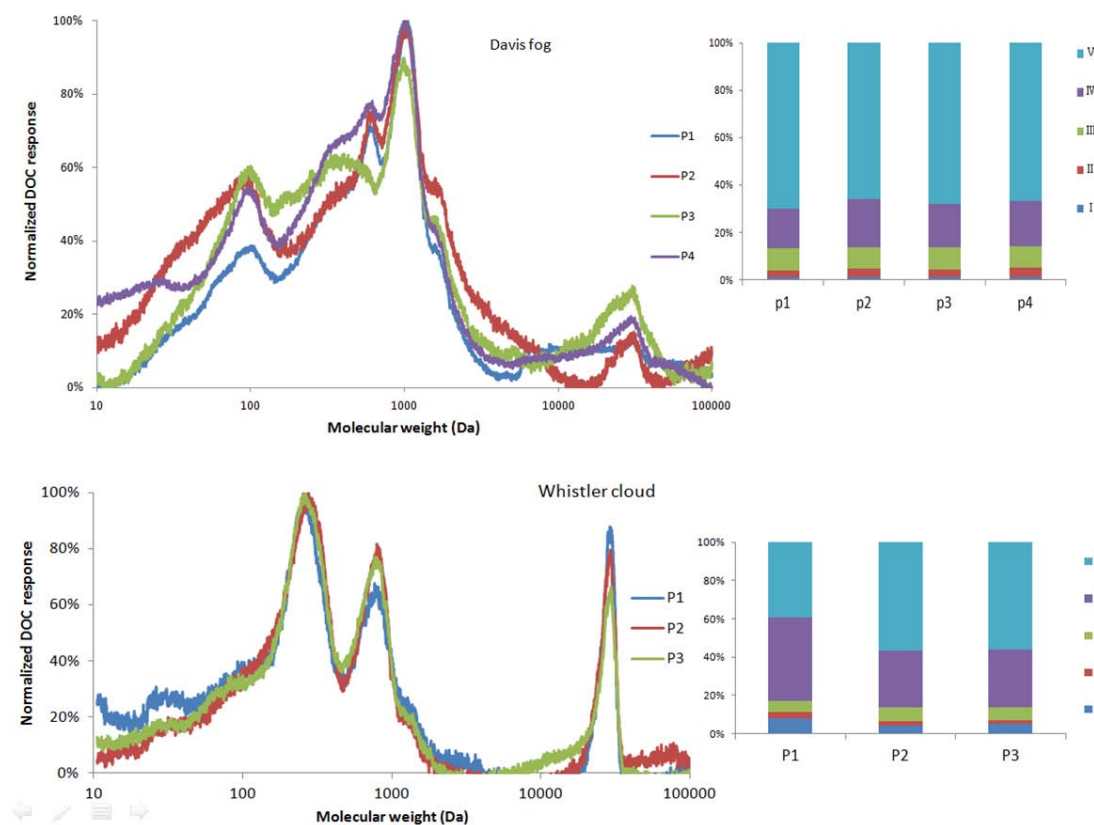


Fig. 4.3 Molecular weight distributions and FRI of Davis and Whistler time series fog/cloud samples.

Only Whistler and Davis samples were available for EEM analysis and FRI results along with SEC-DOC spectra. The results for one event at each location are shown in Figure 4.3. No significant changes of molecular mass distribution were found in Davis fog and even less changes for the Whistler cloud event, considering the variability of the baseline (in the case of Davis). This is consistent with the observations in the Fresno samples as detailed earlier.

Investigating the optical properties and using the FRI approach (see also section 3.2.3) only small and no systematic differences can be seen over the course of a fog/cloud event both in Davis and in Whistler. Now it could be possible that due to lower sampling resolution compared to Fresno, temporal changes remain undetected. However, it is not surprising to see different temporal evolutions since chemical composition of gas phase and particulate species varies dramatically from site to site while also considering average DOC concentration of Fresno fog is 2 times higher than Davis and 5 times higher than Whistler.

Our original hypothesis, based on laboratory and modeling studies with model species, glyoxal and methylglyoxal, was that an important part of the organic matter will take part in various aqueous phase reactions enhanced by irradiation and OH radical reactions that will either lead to oxidation or oligomerization processes and affect molecular weight distributions (De Haan et al., 2009; Yasmeen et al., 2010). However, no significant peak shifts can be observed in our experiments which indicate aforementioned species behavior is not representative of all organic matter and they only account for a small portion of total organic content. Hence the work on model species cannot adequately represent the fates of major organic components within fog/cloud droplets. In addition, increasing evidence suggests that other than fog/cloud water, aerosol water is the important media for aqueous SOA formation. SOA formation rates in laboratory aerosol waters are 2-3 orders faster than in dilute (cloud) solutions (Ervens and Volkamer, 2010). In addition, aerosol water can experience cycles of elevated relative humidity through repeated diurnal temperature cycle or altitude changing to have hours or days of processing time compare to typical fog/cloud droplets activation-evaporation cycle with

lifetime of several minutes. Long time scale SOA formation experiments also reported highest yield of oligomers after 22h of reaction (El Haddad et al., 2009).

#### 4.3.3 Laboratory time series on irradiated samples

Fresno and Davis time series samples were obtained during night time while Whistler samples had limited solar irradiation due to heavy cloud coverage and relatively short lifetimes. Hence none of the observational time series had a substantial photochemical radical formation which would be more likely to alter organic matter molecular weight distribution according to the model species work (Lim et al., 2010).

Figure 4.4 exhibits SEC-DOC chromatograms of time series aliquots from a 120min irradiation experiment using a Selinsgrove pooled fog water sample along with SRNOM and DI water blank. The irradiation by sunlight does not appear to impact the molecular weight distributions. DOC concentrations were also monitored and are presented with in the inset of Figure 4.4. There is no significant change in DOC which would indicate any substantial oxidation of organic matter to CO<sub>2</sub> illustrating too that no extensive photodegradation occurred.

The lack of any substantial changes even in controlled laboratory experiments was unexpected. While we hoped to see a shift towards larger (oligomerization) or smaller (oxidation) molecular sizes, we do not see any change. OH radical is considered the main oxidant of organic species in cloud droplets (Ervens et al., 2003). Photolysis of H<sub>2</sub>O<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, dissolved humic substances and ion ligands all can generate OH radicals in atmospheric liquid phases (Zuo, 2003). While we did not measure OH radical concentrations, the fact that we used authentic fog water should assure substantial

hydroxyl radical concentrations. In fact, solar irradiation of fog and cloudwater is known to generate substantial concentrations (e.g. Zuo, 2003).

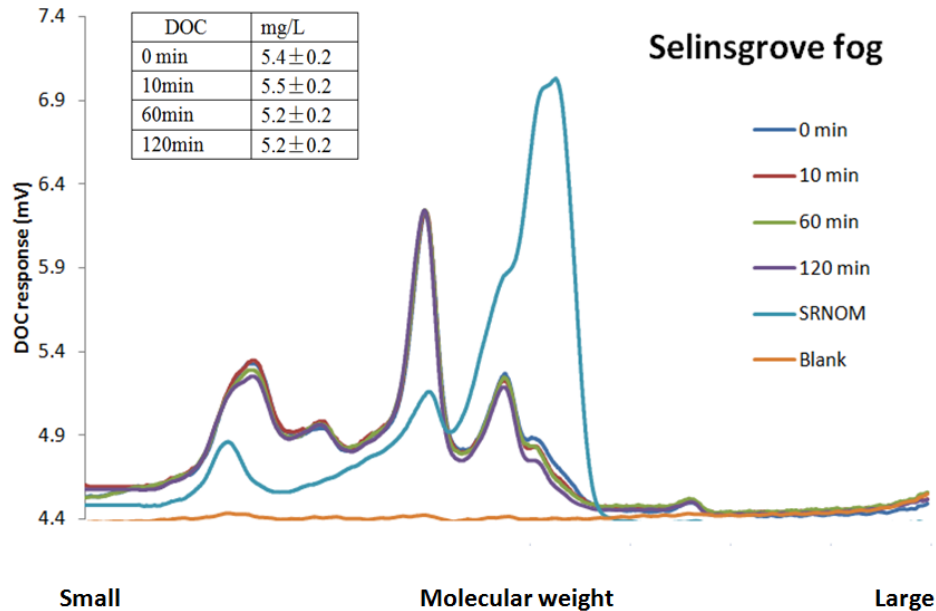


Fig. 4.4 Molecular weight distributions of SRNOM and time series aliquot from two hours irradiation experiment using fog mixture from Selinsgrove.

Fluorescence indices and FRI results from the same irradiation study are presented in Figure 4.5. To the opposite of the molecular weight distributions, clear changes are apparent in these optical properties. The FIX and BIX indices, which are indicative of relative terrestrial and biological source origin, were decreasing over time, while HIX was increasing. The trend shows that dissolved organic carbon in the Selinsgrove composite fog sample shows more resemblance to surface water (here SRNOM as example) with longer irradiation times.

The development of FRI exhibits less portion of region IV (soluble microbial byproduct-like) and more of region V (humic acid-like) which also makes FRI band more similar to SRNOM. The results might indicate the optical properties of relative stable surface water organic matter are related to solar irradiation aging.

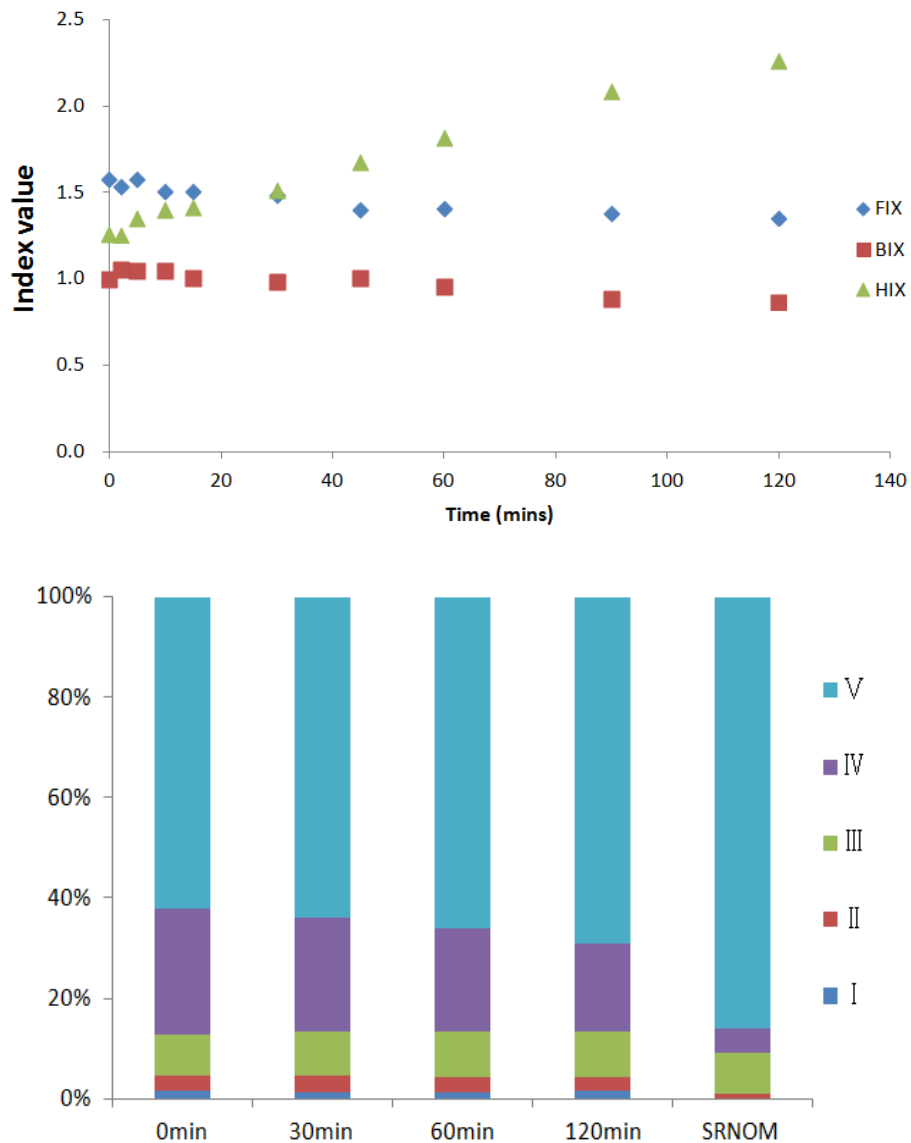


Fig. 4.5 Temporal evolution of fluorescence indices and FRI of two hours irradiation experiment using Selinsgrove fog mixture. The FIX, BIX and HIX values of SRNOM are 1.1, 0.5, and 11 respectively.

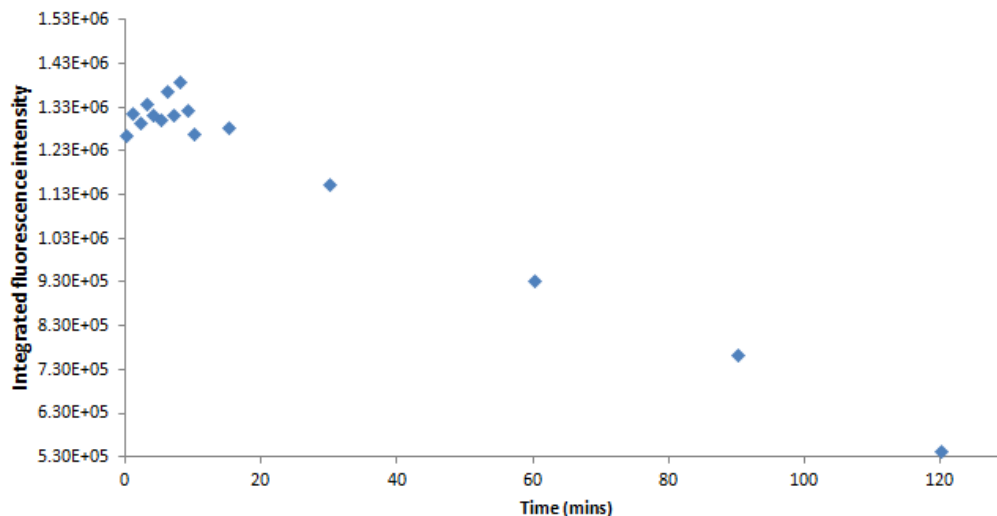


Fig.4.6 Total integrated intensity of EEM landscape.

Figure 4.6 shows the evolution of the total fluorescence measured in an EEM (total integration over the EEM matrix). We observed that over time fluorescence decreases. This is commonly observed for natural organic matter and referred to as photobleaching. The latter is the result of fluorophores which can only be excited a limited number of times and will be eventually destroyed by light exposure (e.g. Vecchio and Blough, 2002). However within the first 10 minutes of irradiation, fluorescence intensity gradually increased up to 10% of the original value then decreased following what appears to be zero order kinetics. The increase phenomenon might be attributed to introducing extra electron-donating functional groups like hydroxyl which can increase fluorescence intensity. For example an aromatic ring like benzene could react with OH radicals and form phenol (Laurentiis et al., 2013) and would explain such an increase.

Overall time series experiments on fog/cloud processing and solar irradiation didn't show significant changes in terms of molecular sizes. This shows that unlike for

individual species like glyoxal or methylglyoxal, neither oxidation nor oligomerization through photochemical processes or dark processes, were observed to impact overall molecular weight distributions. This is consistent with the field observations where no clear shifts were observed (section 3.3.1). This result might be explained by a lower aqueous phase reactivity in dilute solutions as cloud and fog droplets in our field and laboratory experiments are more dilute than some of the model experiments suggested in literature and the reactions instead of taking place in fog/cloud droplet occur in wet aerosols upon fog/cloud droplet evaporation where solute concentrations could reach millimolar or even molar levels (Munger et al., 1990; Volkamer et al., 2009). Similar conclusions were reached in several recent studies (Ervens et al., 2011 and references therein). Hence our results would confirm those experiments. However from an optical property perspective, there is clearly reactivity and transformations occurring, only on a change in functionality level rather than a difference in molecular weight.

#### 4.4 Summary and conclusions

Fog and cloud processing of atmospheric organic matter was studied through field study time series and laboratory observations on irradiated authentic fog samples. Size exclusion chromatography (SEC-DOC) and fluorescence spectroscopy (EEM) were applied to these samples as these methods require small sample volumes.

SEC-DOC results show no significant shifts in the molecular weight distributions in the field or laboratory studies. However, in the field studies the relative importance of several size ranges changes, between ambient aerosol and interstitial aerosol, clearly showing a differential scavenging of the organic matter with different molecular weight ranges being scavenged preferentially. The reason for this differential scavenging is not



clear and requires further investigation. In addition the initial and final stages of the fog molecular weight distributions are consistent with the scavenging hypothesis while in the intermediate stages the distribution changes, but again the reasons remain unclear. Finally optical properties of organic matter during the laboratory experiments show clear changes over time, under controlled irradiation condition. However, no conclusive variations were found from field time series samples. Fluorescence indices and FRI all suggested photochemical “aging” makes atmospheric organic matter more resembling to surface water organic matter. Total integrated fluorescence intensity increased up to 10% within first 10mins of irradiation experiments which might be attributes to radical reactions, then started decreasing due to photodestruction of fluorophores. Optical property alterations in laboratory experiments were not reflected by substantial changes in carbon concentration or molecular size distribution. A possible explanation is that organic matter concentrations in fog water are too low to initiate substantial oligomerization or oxidation reactions, to alter the bulk of the organic matter present.

## CHAPTER 5

### SUMMARY AND OUTLOOK

#### 5.1 Summary

The present work was aimed at increasing our understanding of fog and cloud chemistry in general and the processing of atmospheric organic matter in particular. The first objective was increasing our observational database on fog and cloud composition in various environments. A second objective was improving the characterization of organic matter in fog/cloud water by investigating its bulk properties rather than extending

molecular speciation which eludes even present-day's analytical techniques. Finally we aimed at investigating the processing of atmospheric organic matter by clouds and fogs and were especially interested in testing the hypothesis that cloud processing substantially alters bulk properties of ambient organic matter. The present work is based on five fog/cloud and aerosol collecting field campaigns that were conducted in the Central California Valley, Canada and Norway. The second chapter of this thesis details the observations during these studies including fog and cloud occurrence and Liquid Water Content (LWC). Extensive chemical characterization for ions, pH and dissolved organic carbon (DOC) was performed for all these studies and results showed a substantial variation between different locations. Fresno and Davis fogs showed slightly basic pH, due to the abundance of ammonia released by agricultural activities. These samples also showed substantial amounts of organic carbon consistent with strong local emissions in the wintertime (e.g. combustion). The Central Valley is a well studied area and observations were consistent with prior work. On the opposite, no prior work existed in Norway and our observations were the first on clouds and fogs locally. Overall fogs had a much lower ionic content than the California fogs and the pH was substantially lower, slightly acidic. Even within Norway there was a clear difference between the suburban site, which showed some anthropogenic impact resulting in ammonium, nitrate and sulfate as main species but a low dissolved organic carbon content. This was substantially different from the coastal sites, for which the collected samples were quite pristine, with DOC values close to blank levels, sodium and chloride the dominant species (common in a sea salt rich environment) and low concentrations of sulfate nitrate and ammonia. Finally detailed cloud characterization as performed as part of the Whistler

Aerosol and Cloud Study (WACS). Our observations showed very similar composition at the Peak and Raven's Nest (half mountain) sites. Locally clouds were slightly acidic pH and some anthropogenic impact by long range transport was apparent and consistent with other measurements during the study. In this rather remote location, DOC values were higher than in Norway although lower than in California fogs. The substantial DOC for a remote site was due to biogenic emissions locally, quite different from the other sites as the WACS Study occurred in a heavily forested area in summer time as opposed to all other studies in the wintertime.

The samples collected during the field studies served as basis for an extended development of novel approaches to characterize atmospheric organic matter including size exclusion chromatography (SEC-DOC), fluorescence spectroscopy (EEMs) and nuclear magnetic resonance spectroscopy (NMR). While the techniques were not completely novel, their application to fog and cloud samples was original and novel. The results are detailed in Chapter 3. SEC-DOC and EEM results indicated that molecular weight distribution and chromophoric properties varied significantly from site to site. However, they showed limited variability at a same location. Fog/cloud water organic matter in this study typically possess lower molecular sizes compared to a surface water organic matter reference material SRNOM (Suwanee River Natural Organic Matter), but still high molecular weight materials were detected and attributed to biogenic nanoscale material (BONM). NMR functionality analysis illustrated that a major difference between heavy forested areas and urban location was the degree of aromaticity. DOSY NMR was to our knowledge for the first time applied to fog/cloud organic matter and the results well supported SEC-DOC data by showing an important fraction of larger

molecular weight material in atmospheric organic matter. Water soluble organic carbon (WSOC) in aerosol particles was also investigated and compared to fog/cloud DOC. DOC and WSOC from a same location were very alike in terms of molecular weight distribution, functional group composition and optical properties. Fog and cloud DOC typically showed a larger fraction of low molecular weight material consistent with the partitioning of small soluble gas phase species into the droplets. These were all novel insights on the bulk properties of atmospheric organic matter.

In the fourth chapter, the temporal evolution of select bulk properties was investigated. In fact SEC-DOC and EEM analysis are amenable to small (few ml) sample volumes. This property allows us to apply these analytical techniques to time series samples where a whole fog event is being sampled in small consecutive aliquots to investigate changes over time. The principal goal was to test the hypothesis that atmospheric aqueous phase processing (by cloud and fogs) significantly alters the molecular weight distribution and optical properties of atmospheric organic matter. In terms of molecular weight distributions, Fresno time series samples showed some changes over the course of a fog event that were hard to interpret. Overall however we only observed some degree of selective scavenging in terms of what molecular size organic material ended up in the aqueous phase. There was however no net effect in terms of processing on molecular size distributions as pre- and post-fog aerosol were not significantly different. No significant changes were observed for Whistler and Davis samples either. While for Fresno unfortunately only SEC-DOC data was available, EEM matrices were acquired for Whistler and Davis time series samples. Only Davis samples showed slight differences and no general trend was found. The results prompted us to

perform laboratory studies under controlled conditions using authentic fog samples and solar irradiation to evaluate if there would be any effect under these conditions as previous studies had established such effects for model species (e.g. glyoxal and methylglyoxal). Unlike those studies on specific SOA precursors, in this work aiming total carbon characterization, neither clearly oxidation nor oligomerization reactions with a substantial change in bulk properties, like molecular weight distribution shifts, were identified. These results are consistent with other emerging results in the aerosol community that suggest that fogs and clouds are too dilute as reaction media to allow for substantial oxidation or oligomerization reactions to occur, instead the new hypothesis is that these reactions would occur in aerosol water, not in actual aqueous droplets. However the laboratory experiments did show clear evidence of chemical reactivity in the cloud phase as the optical properties of cloud organic matter clearly changed. After an initial increase in fluorescence of the organic matter, a photobleaching effect was observed over time. Hence cloud organic matter is reactive and does undergo transformations in the aqueous phase, however the transformations do not substantially alter some bulk properties like molecular weight distributions of the total organic matter present.

## 5.2 Outlook

Even though no significant effect of fog/cloud processing was observed in the field and lab in terms of molecular weight distributions, lab studies show that organic matter does react based on chromophoric property observations. Maybe a better time resolution and in situ analysis in the field could reveal the same optical property changes as seen in the laboratory. The small changes in optical properties could occur during sampling and storage if caused by high reactivity species and remain undetected in delayed offline

measurements. Hence as future work it could be important to perform high temporal resolution measurements by analyzing the samples directly in the field.

Future experimental set-ups in the laboratory and in the field will have to tackle the issue of analyzing processes ongoing in aerosol water. Currently observational facilities are limited for direct observations, nonetheless important advances in understanding the role of so called haze processing of atmospheric compounds will only come observationally, when we can study the transition regime between a dry aerosol and an atmospheric droplet. Here lies a clear challenge for future research.

Finally, more observational studies are always needed. The work in Norway detailed here, emerged from the need to have observational data which did not exist for this part of the world. Even in areas of the world where some data exists, an issue is that fog and cloud chemistry, like atmospheric chemistry in general, is constantly evolving, hence observational studies need to be maintained and reflect temporary data. These studies should not include only basic (inorganic) cloud chemistry, but also attempt to do some form of bulk organic matter characterization. Hopefully the present thesis, with the method development and application of fluorescence and NMR spectroscopy as well as size exclusion chromatography, has laid the basis for future more widespread use of comprehensive approaches to the characterization of atmospheric organic matter and its processing.

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