



Cloud water composition over the southeastern Pacific Ocean during the VOCALS regional experiment

Katherine B. Benedict, Taehyoung Lee, Jeffrey L. Collett Jr. *

Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA

ARTICLE INFO

Article history:

Received 27 April 2011
Received in revised form
30 September 2011
Accepted 6 October 2011

Keywords:

Sulfur oxidation
Cloud chemistry
Southeast Pacific
Chile

ABSTRACT

Relatively few measurements exist of cloud water composition over the open ocean, despite the importance of clouds as processors of atmospheric aerosols and trace gases in such regions. In order to improve understanding of cloud water composition in the southeast Pacific, and to determine the capacity of regional clouds for aqueous sulfate production, cloud water was collected aboard the NCAR C-130 during VOCALS-REx (VAMOS Ocean-Cloud-Atmosphere-Land Study Regional Experiment) in October and November, 2008. A total of 72 cloud water samples were collected on 14 flights using the NCAR/CSU airborne cloud water collector. Cloud water samples were collected over a region extending from approximately 71–85° west and from approximately 18–30° south. Cloud water pH ranged from 2.9 to 7.2 with an average of 4.3. Samples were also analyzed for major inorganic ions, hydrogen peroxide, sulfur(IV), carboxylic and dicarboxylic acids, formaldehyde, total Fe and Mn, and total organic carbon. Sodium and chloride were the most abundant solutes, while organic matter was found to contribute only 12%, on average, of the total measured solute load. Cloud water and trace gas measurements aboard the aircraft were used to examine the importance of various oxidation pathways for in-cloud sulfate production. S(IV) oxidation by H₂O₂ was found to be the most important pathway and excess cloud water H₂O₂ concentrations revealed considerable potential for additional, rapid in-cloud sulfate production by this mechanism. S(IV) oxidation by ozone was important when cloud water pH climbed above 5.5 and was the fastest oxidation pathway 24% of the time.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The stratiform cloud deck off the west coast of South America represents one of the largest and most persistent cloud features on the planet. Clouds in the region exert an important influence on the Earth's radiative balance and other phenomena including tropical precipitation and westward propagating Rossby waves (Wang et al., 2005). Satellite observations of this cloud deck typically show a strong spatial gradient in droplet effective radius with smaller droplets closer to the continent (George and Wood, 2010). This gradient may be driven by changes in sulfate-containing cloud condensation nuclei (CCN), with various emissions of reduced sulfur gases (smelters, volcanoes, oceanic phytoplankton) contributing to spatial variability in CCN concentrations. Our knowledge of the offshore gradient in aerosol and CCN has been limited by a lack of *in situ* measurements of aerosols and clouds in the region prior to

the 2008 VAMOS Ocean-Cloud-Atmosphere-Land Study Regional Experiment (VOCALS-REx).

One goal VOCALS-REx was to increase scientific understanding of factors controlling cloud properties in the region in order to improve atmospheric model simulations and predictions of the climate system in the southeast Pacific. Increased understanding of cloud–aerosol interactions, in particular, is needed to accurately quantify the effects of aerosols upon cloud properties. VOCALS-REx was designed to make *in situ* observations of regional aerosol and cloud properties (Wood et al., 2011) in order to better define such relationships.

Measurements of cloud composition provide direct information about the types of particles and gases scavenged by cloud drops and provide insight into processing of scavenged solutes by aqueous phase chemistry. The effects of interactions between aerosols and cloud drops on cloud properties have been a popular research topic in both the measurement and modeling communities (e.g., Feingold et al., 1998; Deutsch et al., 2001; Daum et al., 1984a, 1984b; Bower and Choulaton, 1993; Bower et al., 1999). Of particular interest are chemical changes inside cloud drops that can lead to physical changes as a species transitions from volatile to non-volatile forms.

* Corresponding author.

E-mail address: collett@atmos.colostate.edu (J.L. Collett).

Such a change is illustrated by the oxidation of SO_2 to SO_4^{2-} . Gas phase SO_2 taken up by cloud droplets can undergo rapid aqueous phase oxidation to form non-volatile SO_4^{2-} that contributes to an increase in fine particle mass when clouds evaporate. The importance of this reaction in the marine boundary layer remains uncertain (Faloona, 2009).

Direct measurements of marine cloud chemistry away from land (e.g., Lenschow et al., 1988; Straub et al., 2007) are limited, yet several studies have taken place in coastal regions in an attempt to measure the properties of clouds formed under marine conditions (e.g., Borys et al., 1998; Collett et al., 2002; Gioda et al., 2008, 2009; Hegg et al., 1984; Vong et al., 1997; Watanabe et al., 2001; Weathers et al., 1988). Ground-based measurements by Borys et al. (1998) and Vong et al. (1997) at coastal locations in the northern hemisphere identified conditions representative of a remote marine environment; however, there were strong continental sources at both locations. Work by Weathers et al. (1988) and Collett et al. (2002) found cloud pH values typically in the range of approximately 4.5–5.5 in relatively pristine coastal environments with more acidic clouds typical of more polluted coastal environments. Cloud samples collected in Puerto Rico from air masses identified as clean maritime had an average pH of 6.14 (Gioda et al., 2009), higher than the pH of cloud water typically measured at other coastal locations. Cloud samples collected in the eastern Pacific off the coast of California (Lenschow et al., 1988; Straub et al., 2007) exhibited variability between background marine conditions and periods of stronger continental influence. The pH range for both studies was 3.26–5.06 with a median of 4.01. Considering the expanse of Earth's oceans, these studies represent only a very small fraction of marine clouds.

While marine cloud chemistry measurements are limited globally, we know especially little about cloud composition in the Southern Hemisphere, including the composition of clouds comprising the important stratiform cloud deck in the SE Pacific off the west coast of South America. Measurements of cloud water composition have been made on the coast of Chile (29°27'S, 70°15'W) to determine the suitability of intercepted clouds as a domestic water source (Schemenauer and Cereceda, 1992). The pH of these samples range from 3.46 to 5.84. Additionally, recent measurements of fog advected over Chile (20°49'S, 70°09'W) from the Eastern Pacific stratus cloud deck found the pH to vary between 2.9 and 3.5 in contrast to locally formed fog which had a pH of 2.5 (Strater et al., 2010).

As part of VOCALS-REx, Colorado State University (CSU) collected samples of cloud water in the region during a series of flights in October and November 2008. Our focus during VOCALS-REx was to improve understanding of marine cloud composition and the capacity of regional clouds for aqueous sulfate production. This work provides a set of unique cloud chemistry measurements for this region of the world and insight into the importance of different chemical pathways for in-cloud oxidation of sulfur dioxide to sulfate.

2. Methods

2.1. Sample collection

Cloud water samples were collected during VOCALS-REx with the NCAR/CSU airborne cloud water collector (Straub and Collett, 2004). The collector is described thoroughly in Straub and Collett (2004) and Straub et al. (2007) so only a brief description will be given here. The collector separates cloud drops from the air stream with an axial flow cyclone. A fixed vane creates rotational flow and the drops move to the interior duct wall via centrifugal force. Droplets then move along the wall to an extraction slot for removal

to one of seven, operator-selectable sample bottles. The 50% size cut diameter for the collector is 8 μm (the collection efficiency at 5 μm is 30% and at 15 μm is 70%), in order to collect most of the cloud liquid water but exclude smaller, unactivated aerosol particles. The collector features a cover, which is opened only during cloud penetration, to prevent contamination of collection surfaces. The collector was mounted below the left wing on the NSF/NCAR C-130 in a modified Particle Measurement Systems (PMS) canister and was controlled from the cabin of the aircraft. An operator controlled the collector cover and selected which of the sample bottles would collect the cloud water during each cloud penetration.

The NSF/NCAR C-130 payload included instrumentation for *in situ* and remote sensing measurements of aerosol and cloud microphysics, trace gases (CO , O_3 , SO_2 , dimethylsulfide (DMS)), meteorology and aircraft parameters. In the analysis here we used trace gas observations and liquid water content data (PVM-100A, Gerber Scientific, Inc.). An overview of all the instrumentation is given by Wood et al. (2011). In addition to the NSF/NCAR C-130 other aircraft platforms collected data during the study, including the DOE Gulf Stream 1, CIRPAS Twin Otter, NERC Dornier 228, and UK BAE-146 Facility for Airborne Atmospheric Measurements.

Several different flight patterns were flown to fulfill mission objectives (see Wood et al., 2011). C-130 flights were based out of Arica, Chile located at 18°29'S, 70°20'W. The majority of flights were flown along the 20°S latitude line toward 80°W. Several additional flights were flown to target pockets of open cells (POCs) and their development over time. Regardless of the type of flight, every sampling leg included below-cloud, in cloud, and above-cloud sections. The sampling region and midpoints of all in-cloud sampling legs are shown in Fig. 1. Two adjacent in-cloud legs were often combined to get sufficient sample for planned analyses of collected cloud water and to maximize areal coverage with the 7-bottle capacity of the collector.

2.2. Sample analysis

Immediately after each flight, the cloud water sample mass and pH were measured and a variety of aliquots were prepared for subsequent chemical analyses, adding preservatives as appropriate. A combination pH electrode, calibrated with pH 7 and 4 buffers, was used to measure pH. Samples were further aliquotted for analysis (see details below) in the following priority order: major inorganic ions, hydrogen peroxide, sulfur (IV), total Fe and Mn, carboxylic and dicarboxylic acids, formaldehyde, and total organic carbon (TOC). Not all samples contained sufficient volume to permit all analyses to be conducted. Chemical analysis of aliquotted and preserved samples was completed after the field campaign in our laboratories at Colorado State University. All samples were refrigerated until analysis.

Samples for major ion analysis were aliquotted directly into polyethylene autosampler vials. Major ions were measured by ion chromatography (IC) with two Dionex DX-500 systems with self regenerating suppressors and conductivity detection. Cations were separated using a Dionex CS12 column and anions were separated with a Dionex AS14A column. Measured inorganic cations and anions included Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-} . In the field, chloroform was added as a biocide to samples aliquotted for organic acid analysis. Organic acids were also analyzed by IC with a Dionex AS11 separation column using a NaOH gradient elution, a self regenerating suppressor and conductivity detection. The organic acid method allows detection of acetate, formate, oxalate, lactate, propionate, butyrate, methylsulfonate, glutarate, succinate, valerate, malonate, pyruvate, pinonate, maleate, and pinate.

Aliquots of cloud water for hydrogen peroxide analysis were preserved by addition of potassium hydrogen phthalate, EDTA, and

Download English Version:

<https://daneshyari.com/en/article/4439243>

Download Persian Version:

<https://daneshyari.com/article/4439243>

[Daneshyari.com](https://daneshyari.com)