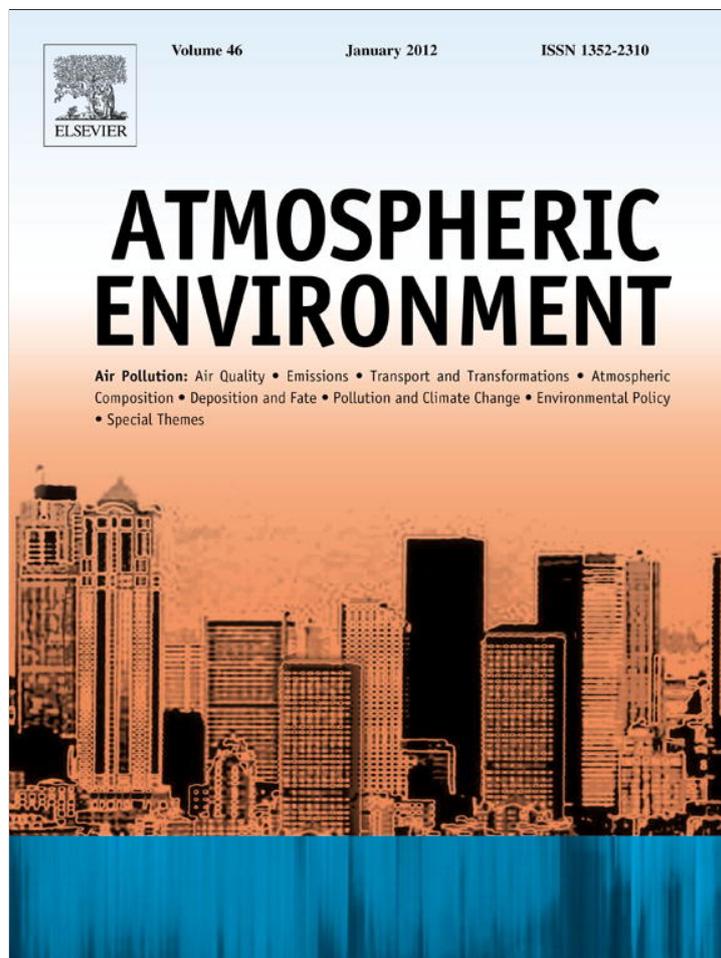


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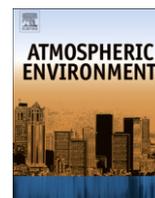
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Cloud water composition over the southeastern Pacific Ocean during the VOCALS regional experiment

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

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

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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.

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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

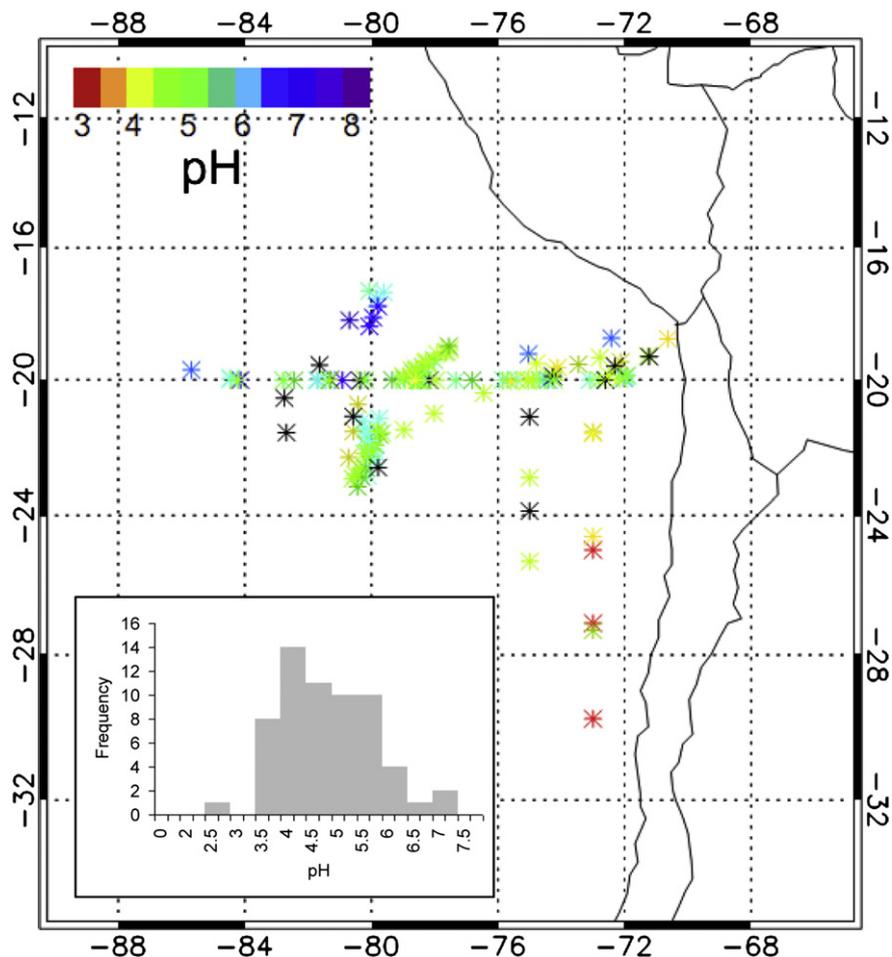


Fig. 1. Sampling region for all research flights. Stars indicate the middle of each sampling leg where cloud water was collected. Cloud water pH values are denoted by the color scale; black stars indicate samples where pH was not measured but cloud water was collected and analyzed for other constituents.

p-hydroxyphenylacetic acid (POPHA). POPHA forms a stable dimer with hydrogen peroxide; the dimer product is quantified by fluorescence (Lazrus et al., 1985). Analysis was performed with a Shimadzu RF-1501 spectrofluorophotometer with an excitation wavelength of 320 nm and emission wavelength of 400 nm.

Samples for S(IV) analysis were preserved by addition of a solution of formaldehyde, CDTA, and sodium hydroxide to form the stable adduct hydroxymethanesulfonate (HMS). Catalase was added to destroy peroxides in the sample which could oxidize free S(IV). At the time of analysis HMS was decomposed to free S(IV) and formaldehyde. S(IV) was quantified by the pararosaniline method (Dasgupta et al., 1980) using a Hitachi U-2000 UV/VIS spectrophotometer absorbance measurement at 580 nm. Reported S(IV) concentrations represent the sum of dissolved sulfur dioxide, bisulfite, sulfite, and HMS in sampled cloud water.

Samples for total formaldehyde analysis were preserved by addition of a NaOH, CDTA, and NaHSO₃ solution to form HMS and refrigerated. The HMS was decomposed to free S(IV) and formaldehyde immediately prior to analysis. Reaction of formaldehyde with excess 2,4-pentanedione and ammonia produced diacetyldihydropyridine (Dong and Dasgupta, 1987) which was analyzed with a Shimadzu RF-1501 spectrofluorophotometer at an excitation wavelength of 412 nm and emission wavelength of 510 nm. Reported formaldehyde concentrations include the sum of formaldehyde and HMS in collected cloud water.

Sample aliquots for total iron and manganese analysis were preserved by acidification with trace metal grade nitric acid.

Samples were analyzed using a Varian AA-G40Z Graphite Furnace Atomic Absorption Spectrometer with Zeeman correction. If sufficient sample was left it was stored, refrigerated, in a clean glass vial with Teflon-lined cap for TOC analysis. TOC analysis was performed using a Sievers 800 Total Organic Carbon analyzer that was calibrated at the factory and periodically checked using an oxalic acid standard.

The collector was cleaned before every flight. Deionized (DI) water was sprayed into the collector to rinse all interior surfaces. All seven sample valves were opened and the collector was rotated to flush all sample lines. After rinsing the collector several times, blanks were taken. Blanks were aliquotted and analyzed using the sample procedures described above. Detection limits at the 95% confidence level for all species are provided in Table 1. Replicate measurements were performed for most analyses and the resulting sample analyte precision values are listed in Table 2.

3. Results and discussion

A total of 72 cloud water samples were collected during 14 VOCALS-REx flights. The samples were collected over a region extending from approximately 71–85° west and from approximately 18–30° south. The number of samples analyzed for different analytes ranged from a maximum of 72 for inorganic ions to a minimum of 19 for TOC. These samples, to our knowledge, represent the first offshore measurements of cloud composition in this region of the world.

Table 1
Detection limits at the 95% confidence limit for VOCALS-REX cloud water analyses.

Cl ⁻	1.8	μN	Lactate	0.7	μM
NO ₃ ⁻	0.4	μN	Acetate	0.6	μM
SO ₄ ²⁻	6.5	μN	Formate	0.4	μM
Na ⁺	1.4	μN	Butyrate	0.4	μM
NH ₄ ⁺	0.5	μN	Malonate	8.1	μM
K ⁺	0.8	μN	Oxalate	0.6	μM
Mg ²⁺	1.1	μN	Valerate	0.6	μM
Ca ²⁺	3.3	μN	Pyruvate	0.2	μM
TOC	83	μmol C/L	Propionate	0.1	μM
H ₂ O ₂	3.0	μM	Pinonate	11.0	μM
HCHO	1.5	μM	MSA	1.7	μM
S(IV)	0.2	μM	Pinate	6.8	μM
Fe	4.5	μM	Maleate	13.4	μM
Mn	0.4	μM			

3.1. Average cloud water composition

The concentration ranges and volume-weighted average concentrations for collected samples are listed in Table 3. The average pH (determined from the volume-weighted average H⁺ concentration) for all samples was 4.3. The cloud water pH ranged from 2.9 to 7.2, with the majority of pH values between 3.5 and 6. The spatial pattern of observed cloud pH is illustrated in Fig. 1. More acidic pH values tended to be observed closer to shore, although not all samples collected near shore were acidic. The wide range of observed pH values and the substantial number of samples with pH values above 5 is somewhat surprising given the narrower range of cloud water pH (3.3–5.2) typically measured in other studies of maritime clouds (Hegg et al., 1984; Lenschow et al., 1988; Borys et al., 1998; Vong et al., 1997; Collett et al., 2002; Watanabe et al., 2001; Straub et al., 2007).

The mass average composition of measured inorganic and organic species is shown in Fig. 2. For many samples there was insufficient cloud water collected to analyze for all species of interest, particularly TOC. When discussing the organic component of the cloud water we only consider the 19 samples with TOC data. Average concentrations for all species using data from all samples can be found in Table 3 (the full data set can be ordered from: <http://data.eol.ucar.edu/codiac/dss/id=89.134>). Inorganic species

Table 2
Precision of analyte concentration measurements calculated from replicate analyses.

Analyte ^b	# of replicate sets	Conc. unit	RSD (%)
Cl ⁻	9	μN	4.8
NO ₃ ⁻	9	μN	8.1
SO ₄ ²⁻	9	μN	9.2
Na ⁺	6	μN	2.9
NH ₄ ⁺	6	μN	0.7
K ⁺	6	μN	9.7
Mg ²⁺	6	μN	2.8
Ca ²⁺	6	μN	7.8
TOC	6	ppb	15
H ₂ O ₂	23	μM	5.7
HCHO	7	μM	9.7
Fluoride	6	μM	7.6
Lactate	6	μM	3.9
Acetate	6	μM	3.3
Formate	6	μM	3.2
Butyrate	6	μM	5.3
Malonate	6	μM	8.8
Oxalate	6	μM	5.7
Fe	—	μg L ⁻¹	2.4 ^a
Mn	—	μg L ⁻¹	1.5 ^a
S(IV)	—	μM	8.5 ^a

^a Repeat sample analysis was not conducted for Fe, Mn or S(IV). Representative values are included from Straub et al. (2007).

^b Valerate, Pyruvate, Propionate, Pinonate, MSA, Pinate, and Maleate were not detected in any of the replicate sample pairs.

Table 3
Volume weighted average, minimum, and maximum analyte concentrations in VOCALS-REX cloud water samples.

	# Samples	Aqueous Concentration			Air Equivalent Concentration		
		Average	Min	Max	Average		
pH	—	61	4.4	2.9	7.2	—	—
H ₂ O ₂	μM	56	120	1.9	610	18	nmol m ⁻³
S(IV)	μM	54	0.9	0.1	3.3	0.08	nmol m ⁻³
HCHO	μM	28	6.3	3.5	13	0.46	nmol C m ⁻³
TOC	μmol C L ⁻¹	19	160	110	290	26	nmol m ⁻³
Cl ⁻	μN	72	460	18	6700	130	nmol m ⁻³
NO ₃ ⁻	μN	72	38	1.4	650	11	nmol m ⁻³
Total SO ₄ ²⁻	μN	72	140	6.7	2300	22	nmol m ⁻³
nss-SO ₄ ²⁻	μN	72	79	1.3	1500	177	nmol m ⁻³
Na ⁺	μN	72	530	19	10,000	24	nmol m ⁻³
NH ₄ ⁺	μN	72	44	0.4	890	11	nmol m ⁻³
K ⁺	μN	72	12	0.4	200	3.8	nmol m ⁻³
Mg ²⁺	μN	72	120	4.8	1500	18	nmol m ⁻³
Ca ²⁺	μN	72	57	4.0	970	8.9	nmol m ⁻³
Fe	μM	43	84	25	250	17	μmol m ⁻³
Mn	μM	43	7.6	1.1	43	2.0	μmol m ⁻³
Acetate	μmol C L ⁻¹	36	5.0	1.2	42	1.0	nmol C m ⁻³
Formate	μmol C L ⁻¹	36	4.7	1.0	21	0.92	nmol C m ⁻³
Oxalate	μmol C L ⁻¹	36	3.9	0.1	74	0.53	nmol C m ⁻³
Other OA ^a	μmol C L ⁻¹	36	8.0	0.06	18	0.86	nmol C m ⁻³

Pyruvate, pinonate, maleate, valerate, and pinate were not detected in any samples.

^a Other Organic Acids (OA) – these include lactate, propionate, butyrate, MSA, glutarate, succinate, and malonate.

dominate the measured solute load, contributing 88% of the measured solute mass. On average organic matter (OM) was found to contribute only 12% of the measured solute load, assuming an OM to organic carbon (OC) multiplier of 1.8 to account for other elements (e.g., H, O, N) associated with organic molecules (Turpin and Lim, 2001; El-Zanan et al., 2009; Simon et al., 2010). High OM to OC ratios are often found in clouds and fog as shown in Mazzoleni et al. (2010) where the majority of the compounds identified had ratios between 1.5 and 2.25. Although the appropriate value of the multiplier (1.8) is uncertain, it is clear that any reasonable choice of value will not change the conclusion that organic matter represents a small contribution to total cloud solute content in the region.

Analysis of water soluble carbon in marine aerosols from other studies indicates a similar fraction of water soluble organic mass as found in these VOCALS-REX cloud water samples. O'Dowd et al. (2004) measured total organic carbon in marine aerosols during biologically active periods and found that 63% of the submicron mass was organic; however, only 18% was water soluble. During the winter, a less biologically active period, the water soluble fraction decreased to 15%. Miyazaki et al. (2010) measured water soluble organic carbon to be 15–21% of the submicron aerosol mass in the western North Pacific.

Na⁺ and Cl⁻, not surprisingly, dominate the inorganic composition, contributing 37% and 32%, respectively, to the average inorganic ion content (based on ion charge equivalents). Similarly, Straub et al. (2007) found that Na⁺ and Cl⁻ together comprised approximately two-thirds of total ions in solution for clouds sampled in the eastern Pacific off the coast of southern California. Sulfate is the third largest contributor to the inorganic ion content (9%) while magnesium is the next largest contributor at 8%. Approximately 45% of the sulfate is non-sea salt sulfate (nss-SO₄²⁻) on average. Vong et al. (1997) found that nss-SO₄²⁻ comprised a similar fraction (44%) of total sulfate in coastal cloud water from the northeastern Pacific. Borys et al. (1998), meanwhile, found nss-SO₄²⁻ to constitute approximately 75% of total sulfate in the more polluted eastern Atlantic. The fraction of nss-SO₄²⁻ has been found to vary widely during individual studies. For example, Straub et al. (2007) and Watanabe et al. (2001) measured 27%–90%

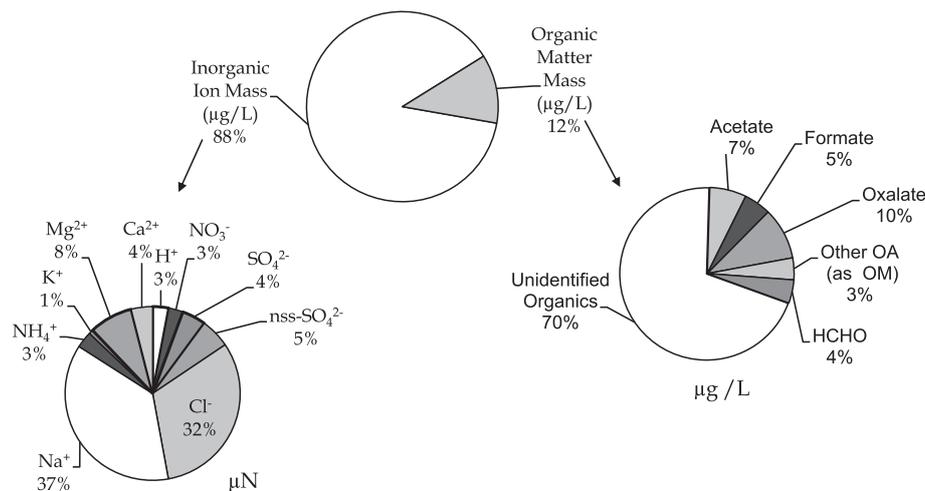


Fig. 2. Volume-weighted average composition of VOCALS-REx cloud water samples. The two pie diagrams including organic matter content represent the 19 samples with TOC observations. The inorganic composition diagram represents the 61 samples with inorganic ion and pH observations. Organic matter was calculated as $1.8 \cdot \text{organic carbon}$ (see text) to account for non-carbon elements contained in organic molecules (e.g., O, H, N).

and 15%–60% of sulfate as nss-SO_4^{2-} . The nss-SO_4^{2-} fraction of the VOCALS samples presented here ranged from 8 to 95%, indicating a wide range of influence from biogenic (e.g., DMS), nss-geogenic (e.g., volcanoes), and/or anthropogenic sulfur sources. In general, lower fractions of nss-SO_4^{2-} were observed farthest from shore suggesting relatively less influence of non-sea salt sources. Measurements of submicron aerosols during VOCALS also suggest a cleaner environment farther from shore as concentrations of sulfate decreased from a mean of $2 \mu\text{g m}^{-3}$ at 71°W to less than $0.5 \mu\text{g m}^{-3}$ at 84°W (Allen et al., 2011).

Individual organic compounds identified in VOCALS cloud water samples typically constituted only a small fraction of the measured TOC. Of the identified species formaldehyde, oxalate, formate, and acetate contributed the most, together accounting for an average of approximately 27% of the total organic matter mass. The majority of organic matter (70% on average) was not identified. It is interesting that MSA, included in 'other organic acids' in Fig. 2 and Table 3, doesn't contribute much to the observed TOC. This is somewhat surprising since emissions of DMS from the ocean and subsequent oxidation can produce MSA and contribute to aerosol formation. However, the VOCALS-REx study occurred prior to the expected maximum in atmospheric DMS concentrations associated with high biological productivity, which generally occurs in mid-summer (Belviso et al., 2004; Ayers et al., 1991).

3.2. Contributions of solutes from seawater

Over the remote ocean, sea spray is expected to be an important source of CCN, which in turn exerts an important influence on cloud properties and cloud water composition. Fig. 3 compares the ratios of several key species measured in collected cloud water to standard seawater concentration ratios of these compounds. Sodium is used as a seawater reference species because it is non-volatile, unlike chloride which can be displaced to the gas phase as hydrochloric acid due to sea salt reaction with strong acids, such as nitric or sulfuric acids or their precursors (e.g. Robbins et al., 1959; Keene et al., 1990; McInnes et al., 1994; Watanabe et al., 2001). Depletion of chloride is commonly seen in the cloud samples collected during VOCALS-REx (Fig. 3a) indicating the influence of other acidic species on sea salt aerosol composition. Chloride depletion in the cloud water samples occurred most commonly near the coast and in the western part of the study region (Fig. 4) and shows a modest

correlation with the sum of cloud water nitrate and nss-sulfate concentrations. Near-shore chloride depletion is not surprising since this area is most likely to be influenced by anthropogenic NO_x and SO_2 emission sources onshore and in the coastal region. Chloride depletion in samples collected from approximately $82\text{--}86^\circ\text{W}$ is interesting since fewer continental NO_x and SO_2 emission sources are expected to influence this offshore region, although increased ship emissions from shipping lanes located in this region (Kareiva et al., 2007) may be important.

Cloud water concentration ratios of K^+ to Na^+ closely match the expected seawater ratio (Fig. 3b), suggesting little biomass burning influence on cloud composition (Andreae (1983) and others indicate the value of K^+ as a biomass burning tracer). Allen et al. (2011) reported that along the South American west coast there were few active fire sources during the study period; however, fires were burning in northern and western Australia. The presence of NO_3^- indicates a non-sea salt source as it is not expected to be present in seawater. Nitrate in cloud water can come from uptake of gaseous nitric acid and/or aerosol nitrate. Nitrate concentrations are highest close to shore likely indicating a coastal source. Results from other VOCALS measurements indicate polluted air masses reside in a number of different isolated, vertically stacked layers (Allen et al., 2011) indicating sources from the coastal region and long transport, possibly in the upper levels.

The sulfate to Na^+ ratio exceeded that in standard seawater, indicating a non-sea salt source of sulfate (Fig. 3e). Sources of excess sulfate may include scavenging of aerosol sulfate (e.g., ammonium sulfate, ammonium bisulfate, or sulfuric acid acting as CCN) or uptake of gaseous sulfur dioxide followed by aqueous oxidation in the cloud drops. Regional sources of gaseous sulfur dioxide can include DMS emitted by oceanic phytoplankton which is partly oxidized in the atmosphere to sulfur dioxide, as well as direct SO_2 emissions by ships and volcanoes, power plants, and smelters in the nearby Andes Mountains (Huneeus et al., 2006; Chand et al., 2010). As mentioned previously, DMS concentrations were not expected to be at their maximum during the study and measurements of DMS on-board the C-130 indicated fairly low concentrations; 85 ppt was the maximum concentration measured for all flights. Additionally, Yang et al. (2011) report that DMS was only enhanced in isolated pockets near shore during the VOCALS study period (refer to Yang et al. (2011) for further discussion of DMS fluxes and spatial distribution).

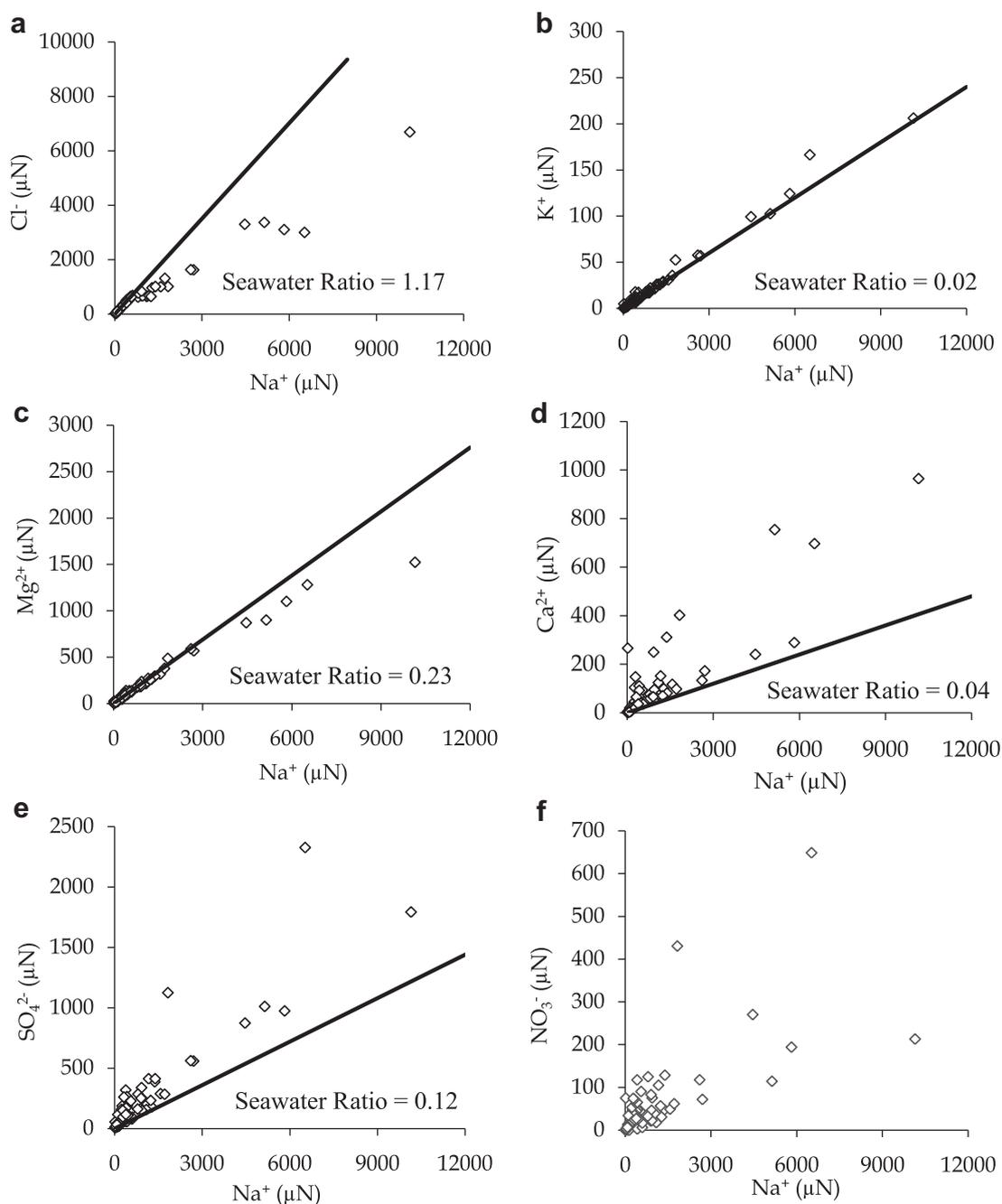


Fig. 3. Ratios of several cloud water species concentrations to cloud water Na⁺ concentrations. Standard seawater concentration ratios are indicated.

The cloud water samples were enriched relative, to seawater, in Ca²⁺ (Fig. 3d) while Mg²⁺ (Fig. 3c) matched the expected ratio fairly well except for one high concentration sample. Previous studies have also observed enrichment of Ca²⁺ in sea salt aerosols or cloud water (e.g. Junge, 1972; Gurciullo et al., 1999; Straub et al., 2007). Excess Ca²⁺ may come from continental transport of soil dust (e.g., as CaCO₃) and from bubble bursting which emits biogenic CaCO₃ skeletal fragments that are concentrated in the surface microlayer (Sievering et al., 1999). While introduction of CaCO₃ can cause an increase in cloud water pH and influence nss-SO₄²⁻ production (Gurciullo et al., 1999), our results do not indicate a strong correlation between pH and Ca²⁺, perhaps because many other factors also influence cloud water pH simultaneously.

3.3. S(IV) oxidation

Partitioning of gas phase SO₂ into a cloud drop followed by aqueous phase oxidation to sulfate is important for increasing both aerosol mass and the acidity of cloud drops. According to Faloona (2009) the third largest source of uncertainty in the sulfur cycle is the heterogeneous oxidation of SO₂. Increasing our knowledge of atmospheric conditions that affect the rate of sulfur processing is important to closing this gap in understanding.

In the aqueous phase S(IV) oxidation can occur by several pathways, including oxidation by ozone or hydrogen peroxide and trace metal-catalyzed autooxidation. In order to examine the importance of these oxidation pathways for regional clouds, oxidation rates were

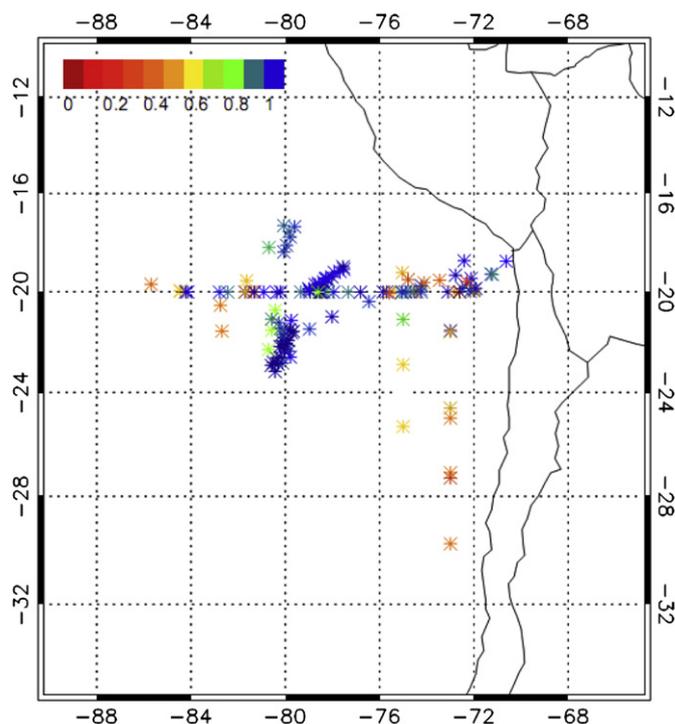


Fig. 4. The ratio of chloride to sodium in cloud water to the expected ratio (1.17) of chloride to sodium in seawater. A ratio of one indicates no depletion of chloride. Chloride depletion in the cloud water samples occurred near the coast and at the westernmost sampling sites.

computed based on measured cloud water pH, measured cloud water concentrations of hydrogen peroxide, iron, and manganese, and calculated equilibrium concentrations of dissolved O_3 and $SO_2 \cdot H_2O$, HSO_3^- , and SO_3^{2-} . Equilibrium concentrations of O_3 , $SO_2 \cdot H_2O$, HSO_3^- , and SO_3^{2-} were calculated based on measured gas phase O_3 and SO_2 concentrations, measured cloud pH, and published equilibrium constants. Oxidation rates were calculated using published rates laws for oxidation by H_2O_2 (Hoffmann and Calvert, 1985), O_3 (Hoffmann, 1986), and by O_2 in the presence of Fe(III) and Mn(II) (Ibusuki and Takeuchi, 1987). Fe(III) was assumed to comprise 25% of the total measured Fe while all Mn was assumed to be present as Mn(II) (Rao and Collett, 1998; Xu et al., 1999). All rate and equilibrium constants were adjusted to reflect the average temperature during each cloud water sampling leg. Calculations are made assuming that the average cloud water composition is suitable for predicting the overall rates of S(IV) oxidation in the studied clouds. They do not reflect possible effects due to differences in chemical composition between individual droplets in the cloud (e.g., Collett et al., 1994; Bator and Collett, 1997). These differences tend to be most important in cases where the ozone or metal-catalyzed autooxidation pathways are fastest, since they both include non-linear dependence of oxidation rates on cloud acidity (and catalyst concentrations in the latter case). Differences between the pH of individual droplets do not influence the average aqueous sulfate production rate when H_2O_2 is the dominant oxidant (Rattigan et al., 2001; Reilly et al., 2001).

In order to understand which oxidation pathways were most important for aqueous sulfate production in the region, oxidation rates for each of the three pathways were calculated (Fig. 5). Oxidation rates were not calculated for all samples since the required analytical analyses were not performed when low sample volumes were collected. Trace metal-catalyzed autooxidation rates were calculated for 25 samples, hydrogen peroxide oxidation rates were calculated for 49 samples, and ozone oxidation rates were

calculated for 63 samples. When comparing oxidation rates only those samples where all three oxidations rates were calculated are used. S(IV) oxidation by hydrogen peroxide was fastest 76% of the time while oxidation by O_3 was fastest 24% of the time. Oxidation

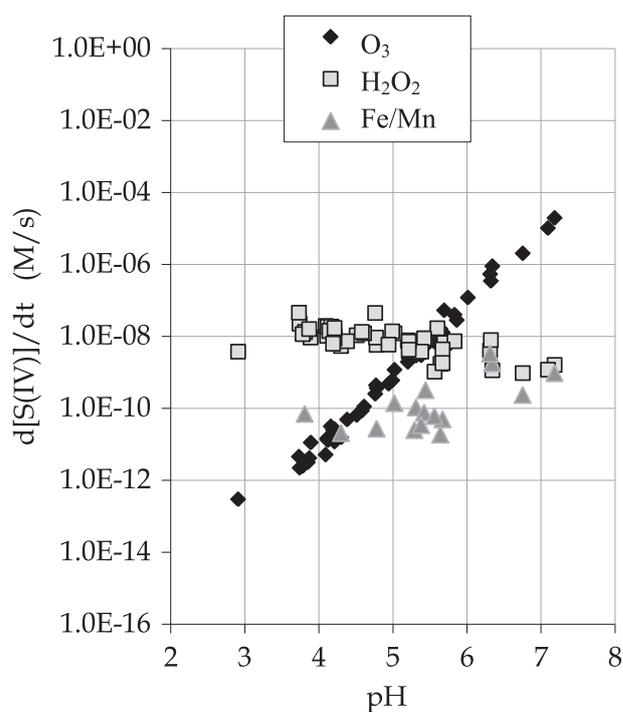


Fig. 5. Rates of aqueous phase S(IV) oxidation by different pathways for cloud water samples collected during VOCALS-Rex.

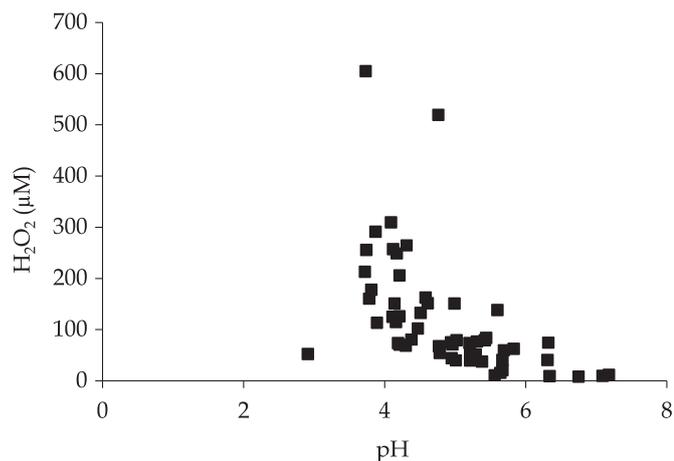


Fig. 6. The relationship between VOCALS-REx cloud water hydrogen peroxide concentrations and pH.

by ozone is highly pH dependent (at higher pH SO_2 solubility increases and speciation of the dissolved S(IV) shifts to more reactive forms) and becomes important as cloud water pH climbs above 5.5 to 6, depending on oxidant concentrations. Hydrogen peroxide oxidation was most important for samples that had a pH less than approximately 5.5. The metal-catalyzed pathway was

never the fastest pathway but was the slowest pathway only 37% of the time. The relative importance of the trace metal-catalyzed pathway would increase little even if all measured Fe was assumed to be present as catalytically active Fe(III).

Measurements of aqueous phase S(IV) and hydrogen peroxide provide information about which reactant is present in excess, since the timescale for the S(IV)– H_2O_2 reaction in the aqueous phase is fast relative to the timescale (hours) between sample collection and sample preservation immediately after landing back at Arica. Concentrations of S(IV) were always low while concentrations of hydrogen peroxide were relatively high indicating the potential for additional oxidation if more sulfur dioxide was present. Summer measurements in the eastern Pacific during DYCOMS II also indicated a similar potential for additional SO_2 oxidation by H_2O_2 (Straub et al., 2007).

H_2O_2 concentrations in cloud water varied significantly across the study region (1.6–610 μM). In order to better understand the relationship between hydrogen peroxide abundance and general pollution levels, we examined the correlation between H_2O_2 and the sum of nss-SO_4^{2-} and NO_3^- (a proxy for pollution) in the cloud water. A modest positive correlation was found ($R^2 = 0.36$). We also note an interesting relationship between hydrogen peroxide concentrations and pH: as the acidity of the cloud water increased, the hydrogen peroxide concentration also increased (Fig. 6). Both of these relationships are consistent with greater photochemical peroxide production in more polluted environments. The limited number of cloud water TOC measurements on the flights prevented

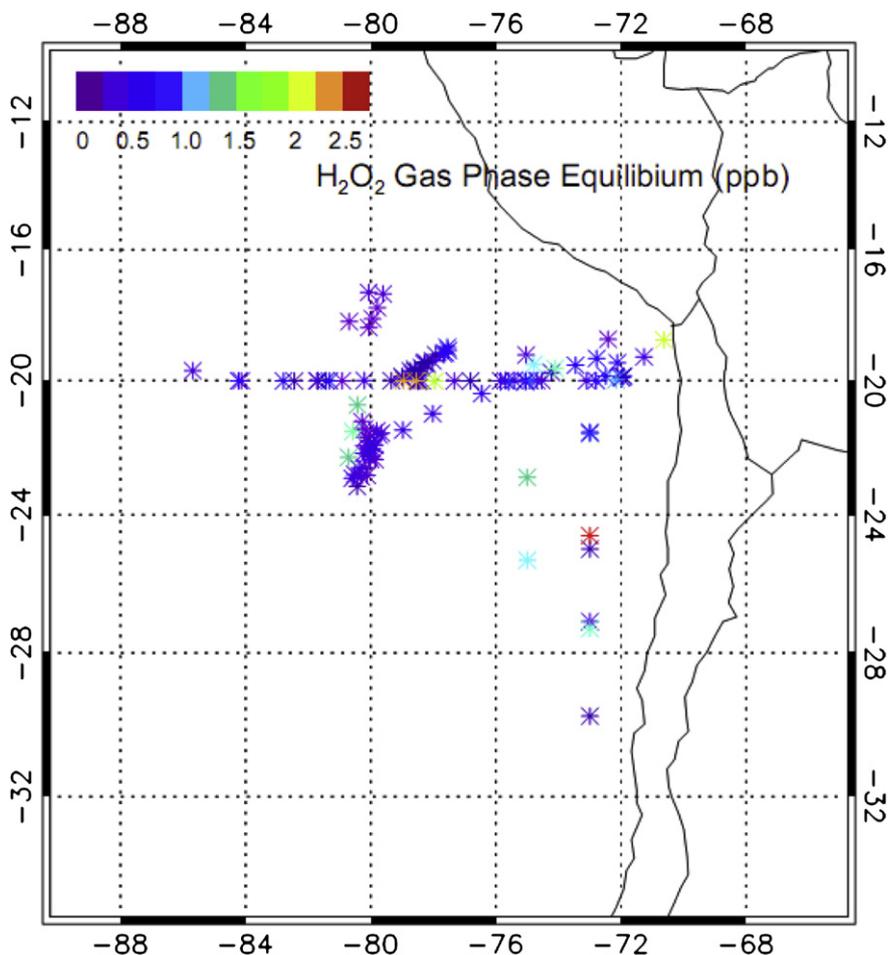


Fig. 7. Calculated H_2O_2 gas phase equilibrium concentrations for all samples where H_2O_2 (aq) was measured.

a meaningful analysis of the correlation between hydrogen peroxide concentrations and TOC, which could serve as a useful proxy for the gas phase volatile organic compound (VOC) concentration. Efficient gas phase production of H_2O_2 is expected at high VOC/ NO_x ratios due to increased probability of peroxy radical-peroxy radical termination reactions.

Equilibrium gaseous H_2O_2 concentrations were calculated based on measured cloud water H_2O_2 concentrations and the average temperature during each sample leg. Calculated gas phase concentrations of H_2O_2 ranged from 0.05 to 2.6 ppb with an average of 0.5 ppb. There was no clear hydrogen peroxide concentration spatial pattern evident from the samples collected (Fig. 7). Previous studies have shown high concentrations (1.8–2.5 ppb) of $\text{H}_2\text{O}_2(\text{g})$ over the ocean in September and October in the southern hemisphere between 0 and 20°S (Jacob and Klockow, 1992), while measurements in Santiago, Chile from April to June 2004 found lower concentrations between 0.03 and 0.87 ppb (Rubio et al., 2006). The range of H_2O_2 concentrations calculated from the data presented here likely represent a mix of air masses from both remote and more polluted regions.

4. Summary and conclusions

72 stratocumulus cloud water samples were collected off the coast of northern Chile during 14 research flights as part of VOCALS-REx. Collected samples were analyzed for pH and concentrations of major ions, peroxides, sulfur (IV), total Fe/Mn, organic acids, formaldehyde, and total organic carbon. These observations increase our understanding of cloud water composition in a marine environment and provide a set of unique offshore cloud chemistry observations for this region of the world. Integrating the cloud water measurements with analysis of other VOCALS data sets, specifically those with aerosol and gas chemistry, provides a clearer picture of the atmospheric chemistry in the region.

The spatial coverage of the flights provided the opportunity to collect samples close to shore where anthropogenic sources were more likely to influence the sampled air masses as well as far off the coast in a more pristine environment. Analysis of the VOCALS data sets including the cloud water chemistry measurements indicated that the coastal area was polluted while cleaner air masses were sampled further from shore. We observed changes in the chemistry of the clouds with longitude which agree well with changes seen in cloud droplet number and aerosol and trace gas concentrations (Bretherton et al., 2010; Allen et al., 2011). Yang et al. (2011) report that both sulfur dioxide and sulfate were elevated near shore in the marine boundary layer (80–800 pptv) and decreased rapidly offshore to an average of 25 pptv. Additionally, cloud droplet number was highest closest to shore, greater than 200 cm^{-3} east of 75W and rarely larger than 300 cm^{-3} west of 75W (Bretherton et al., 2010) supporting the various levels of pollution recorded. Hawkins et al. (2010) identified three types of air masses (continental, marine, and mixed), using back trajectories and filter-based radon measurements, that influenced the study area during VOCALS-REx. The variability of conditions encountered is reflected in the cloud chemistry data set by the wide range of pH values and concentrations of all measured species.

The average pH for all samples was 4.3 with a range from 2.9 to 7.2. Sodium and chloride dominated the inorganic solute mass followed by sulfate. On average approximately 45% of sulfate measured in regional cloud water was non-sea salt sulfate. Sulfate comprised 8% of the solute mass in the cloud water samples and measurements of aerosol chemistry by the Aerodyne Aerosol Mass Spectrometer (AMS) on board the BAe-146 during VOCALS-REx indicate, on average, 20% of the aerosol mass was sulfate and a similar fraction was organics (Allen et al., 2011). In the cloud water samples organic

matter comprised approximately 12% of measured cloud solute mass, on average. Formaldehyde, oxalate, formate, and acetate contributed a combined 27%, on average, of measured cloud water organic matter. The majority of organic matter was not identified. The difference in species mass fractions between the aerosol and cloud water is not surprising. Cloud composition typically includes a strong influence from soluble gas uptake and the AMS is not designed to characterize the supermicron sea salt particles that clearly contributed substantially to cloud solute loadings.

Using sodium as a sea salt tracer, potassium and magnesium were found to be present in cloud water in proportions similar to seawater. Sulfate, nitrate, and calcium were enriched in cloud water while chloride was depleted. The properties of sea salt aerosols have been more widely measured and are better understood than the chemical properties of clouds in marine environments. The average composition of cloud water samples collected during VOCALS-REx share several properties that have been widely found in sea salt aerosol and clearly indicate that cloud composition in remote environments is strongly influenced by sea salt aerosol. It is important to note that the results reported here reflect mass contributions of individual species to cloud composition. They do not necessarily indicate the relative numbers of CCN of different types that are involved in droplet nucleation and exert a strong influence on cloud microphysical and radiative properties. Modeling results from Kazil et al. (2011) do indicate that wind driven sea salt emissions are an important source of boundary layer CCN in the VOCALS region, relative to other sources, including oxidation of DMS to produce sulfuric acid which can nucleate to form new particles and entrainment of aerosol from the free troposphere.

Measurements of cloud pH and key oxidants and catalysts, indicate that aqueous phase sulfur oxidation in regional clouds is dominated by the H_2O_2 pathway, which was fastest 76% of the time. O_3 was determined to be the dominant oxidant in 24% of the samples and was most important at cloud pH values above 5.5. The low concentrations of residual S(IV) in collected cloud water and high concentrations of H_2O_2 indicate aqueous phase sulfate production was limited primarily by the availability of SO_2 .

Observations of cloud chemistry during VOCALS-REx provide new insights into cloud composition and sulfur oxidation pathways in marine environments. A range of conditions were encountered, including more polluted environments (typically near shore) and more pristine conditions (typically farther west). The wide range of compositions observed here clearly indicates a need for more cloud composition measurements, in the SE Pacific and elsewhere, if we are to fully appreciate the role that clouds play as processors of trace species in marine environments.

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