

VOCALS/Southeast Pacific science: Cloud water composition over the southeastern Pacific

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Cloud water was collected over the remote southeastern Pacific off the coast of northern Chile in October and November 2008. Samples were collected with an axial-flow cloud water collector aboard the NSF/NCAR C-130 aircraft. Multiple samples were collected during each flight in a wing pod canister. Sample pH was measured on-site after each flight while samples for peroxide, formaldehyde, a suite of organic acids, total organic carbon, sulfur (IV), trace metals and major ions (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺) were preserved on-site and analyzed after the field campaign. Over the 5 week study period there were 14 flights and 72 samples collected over a region extending from approximately 71 to 85 degrees west and from approximately 18 to 30 degrees south. This work provides a set of key cloud chemistry measurements for this remote region of the world. The results presented here will address the chemical composition of marine clouds present in the study region, examine spatial variability in cloud composition, and address the relative importance and rates of aqueous S(IV) oxidation by hydrogen peroxide, by ozone, and by oxygen (catalyzed by iron and manganese). Sample pH varied somewhat significantly over the course of the campaign, the highest pH measured was 7.2 while the lowest was 2.9. Concentrations of major anions and cations also varied significantly from flight to flight and on some flights from sample to sample. Unsurprisingly, an average of all samples indicates that Na⁺ and Cl⁻ comprised the largest fraction of measured anions and cations followed by SO₄²⁻, Mg²⁺, NH₄⁺, Ca²⁺, NO₃⁻, and K⁺. In addition, total mass was dominated by inorganic species with organic matter contributing only 12% of the mass. The majority of organic species have not been identified. Of the identified organic species formaldehyde, oxalate, formate, and acetate contributed the most to the mass and combined account for 27% mass of organics. Cloud processing is an important pathway for oxidation of SO₂ to sulfate. Aqueous S(IV) oxidation by hydrogen peroxide, by ozone, and by trace metal-catalyzed auto-oxidation are all potentially important pathways. Oxidation by hydrogen peroxide was found to be fastest for 73% of sample. Observed cloud water S(IV) concentrations ranged from 0.09-3.3 μM while concentrations of peroxide were much higher, ranging from 1.8-611 μM. These observations suggest that in-cloud sulfate production was typically unlikely to be oxidant-limited in the region during the spring study season. Additionally, the range of concentrations suggests air masses from both remote and polluted regions were sampled.