THE SOURCE OF Pb, Cu, AND Zn IN FOGWATER

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Abstract. The variation in the concentrations of Zn, Pb, and Cu in water and acid extracts of airborne particulates and in fogwater collected in the rural northern San Joaquin Valley of California during the fall and winter of 1983–1984 was determined by anodic stripping voltammetry. There is a good correlation between water extracts of airborne particulates and fogwater for the concentrations of Cu and Pb and the concentration ratio (Cu/Pb), suggesting that the concentrations of these metals in fogwater is controlled by the concentration of extractable metal in the particulates on which the fog droplet forms. The major ion composition of the fogwater samples was measured by ion chromatography and compared with literature values for urban fogwater.

1. Introduction

Transition metals such as Mn, Fe, Pb, Cu, and others have been detected in fogwater at the micromolar level by several workers (Munger et al., 1983; Jacob et al., 1984, 1985; Fuzzi et al., 1984). These metals are potential catalysts for droplet phase reactions. For example, the oxidation of SO$_2$ to H$_2$SO$_4$, an important source of acid fog, is catalyzed by Fe(III) and Mn(II) (Munger et al., 1983). In addition, some of these metals are themselves toxic, and their presence in fog may present a threat to public health.

A mechanism by which these metals are incorporated into the fogwater droplets has not been identified. A plausible mechanism is nucleation scavenging, the dissolution by fogwater of metals contained in the condensation nuclei. Nucleation scavenging is an important source of H$^+$, NH$_4^+$, SO$_4^{2-}$, and NO$_3^-$ in fogwater collected in the Los Angeles Basin (Munger et al., 1983). Nucleation scavenging is also a significant source of SO$_4^{2-}$ and NO$_3^-$ in fogwater collected in Bakersfield, California (Jacob et al., 1984), and in cloudwater collected over the Northwestern United States (Hegg et al., 1984).

The purpose of the work described here is to investigate the contribution of the nucleation scavenging mechanism as a source of Pb, Zn, and Cu in fogwater. Our approach was to measure the temporal variations of these metals in fogwater and in water and acid extracts of aerosol particles. In order to permit the comparison of our results with those of other fogwater studies, the fogwater was also analyzed for several major ions.

2. Methods

2.1. STUDY AREA

Fogwater and airborne particulate samples were collected in Turlock which is located in the middle of California’s Central Valley. The valley is about 70 km in width and
650 km in length, running in a northwest—southeast direction between the Coast Range on the west and the Sierra Nevada mountains on the east. The meteorology of the Valley in late fall and winter is characterized by light southerly winds, low temperatures, high humidity, a stagnant air mass, and frequent periods of night radiation fog which typically forms in the early morning and persists until midday.

2.2. REAGENTS

Molar HNO₃ was prepared from G. F. Smith redistilled HNO₃. Molar NH₄OH was prepared by isothermal distillation. Milli-Q water was used throughout and standard solutions were prepared from ACS Reagent Grade chemicals. The supporting electrolyte for determination of metals was 0.10 M sodium citrate adjusted to pH 3.0 ± 0.1 with NH₄OH.

2.3. EQUIPMENT

Pb(II), Cd(II), Zn(II), and Cu(II) from their aquo and other labile complexes (Copeland et al., 1974) were measured by Differential Pulse Anodic Stripping Voltammetry (DPASV) using a PAR Model 364 Polarographic Analyzer in conjunction with a PAR Model 303 Static Mercury Drop Electrode and a Ag–AgCl reference electrode. Henceforth, we will refer to these analyte metals as Pb, Cu, and Zn.

Na⁺, NH₄⁺, Cl⁻, NO₃⁻, NO₂⁻, and SO₄²⁻ were determined by Ion Chromatography (IC) using a Waters model 6000A Solvent Delivery System equipped with a Waters model U6K Injector, Wescan Standard Anion Column, Wescan High Speed Cation Column, and Wescan model 213A conductivity detector.

Nitrate ion was also measured by UV absorption after correction for interference by organic matter (APHA, 1980) using a Varian model DMS 90 spectrophotometer.

Ambient Air Samples. Airborne particulate samples were collected on Millipore 47 mm Teflon filters using a Radeco model HD28/B Air Sampler. Pore size of the filters was 0.5 μm.

Samples were collected on the roof of the two-story Science Building on the Turlock campus of California State University, Stanislaus (CSUS). Flow rate was 2.0 ± 0.1 CFM and collection time was approximately 6 hr.

Water extracts were obtained by floating the filter on the surface of 50 mL of Millipore water in a covered 100 mL beaker and stirring for 3 hr. The pH of the water used for the extractions was in the range which is close to that found for the fogwater. One sample with relatively high metal levels was tested for completeness of extraction by doubling the volume of water and extracting an additional 3 hr. Within experimental error no additional metal was extracted, indicating not only that extraction was complete after 3 hr, but also that the trace metal levels in the water extract were not limited by the solubility of the trace metal species.

After a 25 mL aliquot of the water extract was removed for trace metal and major ion analysis 3 mL of 1 M HNO₃ was added to the remaining solution and the filter was extracted an additional 3 hr. This extract was adjusted to pH 4.5 with 1 M NH₄OH and diluted to 50 mL. On one occasion, after the normal acid extraction the filter was rinsed