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Comment on "Aqueous Phase Chemical Processes in Deliquescent Sea-Salt Aerosols: A Mechanism That Couples the Atmospheric Cycles of S and Sea Salt" by W. L. Chameides and A. W. Stelson

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INTRODUCTION

Keene et al. [1990] measured substantial Cl^- deficits relative to sea salt in coarse aerosol sampled over the North Atlantic Ocean. These deficits were not balanced by NO_3^- or non-sea-salt (nss) SO_4^{2-} in the aerosol and thus could not be explained completely by acid-displacement reactions [*Brimblecombe and Clegg*, 1988] or by reactions involving nonacidic N gases [*Finlayson-Pitts*, 1983; *Finlayson-Pitts et al.*, 1989]. To account for the unexplained Cl^- deficits, *Keene et al.* [1990] adopted from *Behnke and Zetzsch* [1989a, b] a stoichiometric description of the action of O_3 on sea-salt aerosol to produce Cl_2 . They then developed and assessed a model for Cl cycling in the gas phase. The quality of the *Keene et al.* [1990] data and the validity of their interpretation have been questioned by *Chameides and Stelson* [1992] who report no significant Cl volatilization in photochemical model simulations of deliquescent sea-salt aerosol in the marine boundary layer (MBL). We wish to comment on some aspects of the *Chameides and Stelson* [1992] analysis in light of our previous work and that of others. Our comment focuses on the quality of the *Keene et al.* [1990] data and on mechanisms of Cl volatilization from sea-salt aerosol.

DATA QUALITY

Quality assurance procedures were reported in detail by *Keene et al.* [1990]. Cascade impactor substrates from aerosol samples were extracted quantitatively and analyzed without bias for the species of interest. Ancillary data indicate that wall losses and gas-to-particle reactions in the sampler did not bias the relative concentrations of species within different size classes of particles. The Cl^- deficits observed by *Keene et al.* [1990] are also consistent with previous measurements of size-segregated aerosol in the

North Atlantic region [e.g., *Martens et al.*, 1973; *Meinert and Winchester*, 1977; *Sievering et al.*, 1990; *Church et al.*, 1991]. To our knowledge, *Keene et al.* [1990] were the first to investigate mechanisms for Cl volatilization based on an ion balance analysis of relevant constituents (nss Cl^- , nss SO_4^{2-} , NO_3^- , and NH_4^+) in coarse aerosol sampled over the open ocean. *Talbot et al.* [1992] have since conducted a similar analysis for coarse marine aerosol sampled in the Arctic and found results consistent with those of *Keene et al.* [1990]. Although acid neutralization by NH_3 was not considered explicitly in their analysis, *Sievering et al.* [1990] also observed Cl^- deficits in coarse aerosol sampled over the western North Atlantic Ocean that could not be balanced by NO_3^- and nss SO_4^{2-} . Much of the case for acid displacement of HCl from sea-salt aerosol was built on ionic relationships in bulk aerosol [e.g., *Hitchcock et al.*, 1980], but these data are suspect due to mixing of fine H_2SO_4 aerosol with coarse sea-salt aerosol on sample filters.

Chameides and Stelson [1992] suggest that the mixing of particulate organic C (POC) with sea-salt aerosol on impactor substrates may have caused artifact loss of Cl^- in the *Keene et al.* [1990] samples. Specifically, they hypothesize that marine fulvic acids (MFA) acidified samples subsequent to collection resulting in volatilization of HCl. We think this unlikely for two reasons.

First, *Chameides and Stelson* [1992] assume implicitly that all potential H^+ sites are occupied by H^+ when MFA is incorporated into sea-salt aerosol, and thus MFA contributes free acidity to the aerosol. This assumption may not be valid. Carbon isotope data suggest that the fraction of POC associated with coarse sea-salt aerosol is marine-derived [*Chesselet et al.*, 1981] and most likely originates directly from seawater when the aerosol is formed [*MacIntyre*, 1974; *Hoffman and Duce*, 1976, 1977]. Potential H^+ sites on MFA dissolved in seawater are occupied by base cations not H^+ . As such, marine-derived MFA would not be expected to contribute free acidity to sea-salt aerosol. With an effective pK_a of 3.6 in 0.7 M NaClO_4 solution [*Huizenga and Kester*, 1979], it appears that MFA associated with sea-salt aerosol would simply buffer increases in free acidity resulting from subsequent incorporation of strong mineral acids and would thus retard rather than contribute to the displacement of HCl.

Second, even if the H^+ sites were occupied by H^+ when MFA was incorporated into sea-salt aerosol, it appears that atmospheric concentrations of MFA are too low to displace significant concentrations of HCl. Although POC was not measured in conjunction with the *Keene et al.* [1990] samples, typical concentrations in open ocean MBL air are 0.3–0.5 $\mu\text{g C/m}^3$ [*Duce et al.*, 1983], near the lower end of the range given by *Chameides and Stelson* [1992]. The data

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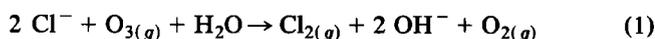
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of Barger and Garrett [1976], which define the higher end of their range, are considered suspicious [Peltzer and Gagosian, 1989]. In addition, Hoffman and Duce [1977] and Chesselet et al. [1981] found that less than 20% of POC in open ocean MBL aerosols resides in the sea-salt particle size range. To estimate the potential magnitude of HCl displacement by MFA, we assume that 20% of $0.4 \mu\text{g POC/m}^3$ is in the sea-salt size fraction, that there are $11 \mu\text{eq fulvic acid H}^+$ sites/mg organic C [Huizenga and Kester, 1979], and that all these sites are occupied by H^+ . The resulting $0.9 \text{ neq H}^+/\text{m}^3$ of total acidity from MFA in the sea-salt size fraction may be sufficient to titrate sea-salt alkalinity (0.7 neq/m^3 , Chameides and Stelson [1992]) but cannot account for the average 10 neq/m^3 of unexplained Cl deficit observed by Keene et al. [1990]. As noted above, MFA in coarse aerosol would be titrated by the subsequent addition of strong mineral acidity, so their net contribution to free acidity below pH 3, and thus to HCl volatilization, would be considerably less than their estimated $0.9 \text{ neq H}^+/\text{m}^3$ contribution to total acidity.

We agree with Chameides and Stelson [1992] that it would be possible for MFA to displace HCl from acidified sea-salt particles if (1) associated H^+ sites are occupied by H^+ rather than base cations when MFA is incorporated into sea-salt aerosol and (2) concentrations of MFA in coarse aerosol are substantially higher than those considered above based on current literature. We believe that both points are unlikely, however, and conclude that MFA probably does not contribute appreciably to displacement of HCl from sea-salt aerosol either in ambient air or after the aerosol has been sampled using a cascade impactor.

MECHANISMS FOR CL VOLATILIZATION FROM SEA-SALT AEROSOL

Keene et al. [1990] did not attempt to model details of aqueous phase chemical processes in deliquescent sea-salt aerosol. They simply hypothesized a stoichiometric description for oxidative dechlorination of the aerosol, that is,



based on smog chamber observations by Behnke and Zetzsch [1989a, b] which documented the formation of Cl_2 from irradiation of artificial NaCl aerosol and Cl^- -containing aqueous films in the presence of O_3 . As pointed out by Chameides and Stelson [1992], the discovery of artifact reactions in these chamber experiments led Behnke and Zetzsch [1990] to withdraw some of the results published previously by Behnke and Zetzsch [1989a, b]. Significant production of Cl atoms was, however, observed in more recent experiments using natural seawater as an aerosol source in the presence of O_3 and light but no NO_x (W. Behnke and C. Zetzsch, unpublished manuscript, 1993). About 4% of particulate Cl^- was converted to atomic Cl during 6-hour periods of irradiation. Similar rates of Cl atom production were not found when pure NaCl or artificial seawater was used as the aerosol source suggesting that trace species in natural sea-salt aerosol may be involved in the dechlorination reactions. Artifacts identified in earlier studies were not a source of bias for these experiments. These observations indicate that equation (1) remains a potentially viable stoichiometric description for dechlorination of atmospheric sea salt.

Chameides and Stelson [1992] use a detailed photochemical model of aqueous aerosol chemistry to argue that a mechanism such as described by (1) cannot account for significant Cl volatilization. Their model, however, fails to simulate the Cl^- losses documented by a large body of field data, which implies that the model is missing some important chemical process operating in deliquescent sea-salt aerosol. As such, we think that Chameides and Stelson [1992] present an inconclusive case for rejecting the mechanism.

Indeed, one conclusion to be drawn from the work of Chameides and Stelson [1992] is that the mechanisms responsible for observed dechlorination of sea-salt aerosol are not well understood. It is possible that current models underestimate radical production in deliquescent aerosol and hence the supply of Cl_2^- , precursor of Cl_2 . For instance, the photolysis of dissolved organic compounds is not considered in current models, yet it may provide a large source of radicals in hydrated aerosol [Faust and Allen, 1992]. Alternatively, it is possible that the dechlorination may proceed by a nonradical mechanism. Recent measurements near Miami [Keene et al., 1993; Pszenny et al., 1993] reveal significant concentrations of inorganic Cl gases other than HCl (probably HOCl or Cl_2) that accumulate during the night and decrease after sunrise. These observations suggest a nonphotochemical, presumably nonradical, pathway for dechlorination although nighttime generation of radicals by reaction of O_3 with MFA [Xiong et al., 1992] may need to be considered. We view the general state of uncertainty surrounding Cl cycling in the MBL as a crucial issue in global tropospheric chemistry considering the potential implications for the budgets of a number of species including O_3 , dimethylsulfide, and alkanes [Keene et al., 1990; Pszenny et al., 1993].

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