Laskin et al. (1) investigated the reaction OH + Cl− → OH + Cl at surfaces of deliquesced NaCl particles in the laboratory. They estimate that this source of alkalinity, which has not been described previously, is roughly comparable to that of aerosol acidity during daytime and thereby sustains significant S(IV) oxidation by O3 in ambient sea-salt aerosols with implications for the global S cycle and climate. Although the laboratory results are compelling, field observations do not support the inferred importance of this pathway in ambient marine air.

The assessment by Laskin et al. (1) is based on similarities between calculated rates of alkalinity production via this pathway and corresponding rates of aerosol acidification by H2SO4 originating from both S(IV) oxidation by O3 in both polluted (15) and remote (6) regions. S(IV) oxidation by O3 over this pH range is negligible (8). If, as suggested by Laskin et al. (1), substantial alkalinity were produced in sea salt during daytime by a chemical mechanism not considered in the models, simulated daytime pHs would systematically diverge from measurement-based estimates, particularly under very clean conditions [e.g., (6)]. Such divergence is not evident.

Finally, the phase partitionings of HCOOH and CH3COOH provide useful diagnostics of aerosol pH. Although these acids are infinitely soluble in alkaline solution, thermodynamic properties (16) indicate that they partition almost exclusively in the gas phase in the presence of acidic aerosols. Measurements over the North Atlantic Ocean indicate that virtually all HCOOH and CH3COOH partitions in the gas phase (11); with the exception of one sample collected during a large Saharan dust event, concentrations of dissociated + undissociated HCOO− and CH3COO− in size-resolved aerosols were undetectable (< ~20 pmol m−3). In addition, we have measured these carboxylic species in several hundred sea-salt size fractions sampled over discrete day and night intervals during onshore flow at Bermuda and Hawaii and in coastal air along the eastern United States (17). The frequency of detectable concentrations was indistinguishable from 0%; no diel variability was observed. These results also indicate no evidence for significant alkalinity production in sea-salt aerosols.

In conclusion, the weight of the available evidence based on measurements, thermodynamic relationships, and model calculations suggests that acids and precursors are present in most marine regions at levels sufficient to rapidly titrate alkalinity and acidify sea-salt aerosols. This evidence is inconsistent with the hypothesis that the proposed OH pathway slows aerosol acidification during daytime and thereby sustains S(IV) oxidation by O3 enough to affect S cycling significantly, except perhaps in very remote marine regions.

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References and Notes
17. W. C. Keene, unpublished data.
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