Photochemical Production and Consumption Mechanisms of Nitric Oxide in Seawater

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Abstract

Nitric oxide (NO•) is an active odd-nitrogen species that plays a critical role in determining the levels of ozone (O3) and other nitrogen species in the troposphere. Here, we provide experimental evidence for photochemical formation of NO• in seawater. Photoproduction rates and overall scavenging rate constants were measured by irradiation of surface seawater samples collected from the Seto Inland Sea, Japan. Photoproduction rates of NO• ranged from 8.7 × 10−12 M s−1 to 38.8 × 10−12 M s−1 and scavenging rate constants were 0.05−0.33 s−1. The steady state concentrations of NO• in seawater, which were calculated from the photoproduction rates and scavenging rate constants were in the range 2.4−32 × 10−11 M. Estimation from the scavenging rate constant showed that the NO• lifetime in seawater was a few seconds. Our results indicate that nitrite photolysis plays a crucial role in the formation of NO•, even though we cannot exclude minor contributions from other sources. Analysis of filtered and unfiltered seawater samples showed no significant difference in NO• photoformation rates, which suggests a negligible contribution of NO• produced by photobiological processes. Using an estimated value of the Henry's law constant (kH ≈ 0.0019 M atm−1), a supersaturation of surface seawater of 2 to 3 orders of magnitude was estimated. On the basis of the average values of the surface seawater concentration and the atmospheric NO• concentration, a sea-to-air NO• flux was estimated.

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