Reports

Nitric Oxide in Seawater

Abstract. *Nitrite photolysis at natural light intensities and normal nitrite concentrations in seawater produced detectable concentrations of nitric oxide, which was consumed rapidly by a dark chemical reaction in the laboratory. Nitric oxide was also detected in situ in nitrite-rich surface waters of the central equatorial Pacific, where it formed in daylight and disappeared rapidly at sunset. The formation and rapid cycling of nitric oxide implies the presence of other free radicals in seawater, perhaps as intermediates in ongoing autoxidation processes. The central equatorial Pacific is a nitric oxide source to the atmosphere.*

The surface layer of the world ocean contains many reduced inorganic and organic compounds primarily produced and cycled biologically. These thermodynamically unstable constituents may also react chemically in this relatively warm, oxygenated, sunlight-irradiated environment, undergoing thermal and photochemical free-radical processes analogous to those that occur in other autoxidations (*1*) and tropospheric trace-gas chain reactions (*2*). However, the direct observation of radical intermediates in seawater is, in general, beyond the current detection capabilities. We summarize evidence here (*3*) concerning the presence, behavior, and possible significance of nitric oxide (NO) in seawater. To our knowledge, this is the first detection of any free radical in natural waters.

Sunlight (hν) photolyzes NO_2^- in surface seawater (*4*) by the well-known reaction (*5*)

$$NO_2^- + HOH + h\nu\ (295 \leq \lambda \leq 410\ \text{nm}) \rightarrow NO + OH + OH^-$$

Daytime NO production rates are estimated from NO_2^- disappearance rates (*4*) to be $> 10^{-12}M$ sec^{-1} for large oceanic areas (10^6 to 10^7 km^2) with surface NO_2^- concentrations $> 0.1\ \mu M$. These rates correspond to radical production rates in the surface water of $> 30\ \mu M$ year^{-1}. A daytime steady-state NO concentration of $> 10^{-11}M$ results from a balancing of this production against consumption by radical recombination, if we assume second-order diffusion-controlled reaction of NO with small daughter radicals derived from OH (*6*). The corresponding NO lifetime is ~ 10 to 100 seconds. The vapor pressure, pNO, over $10^{-11}M$ NO_{aq} is about 5×10^{-9} atm (*3, 4, 7*). Since tropospheric background concentrations of NO or oxides of nitrogen (NO_x) have vapor pressures of $< 10^{-9}$ atm (*8*), this simple scheme implies that NO_2^- photolysis renders regions of the sea a source, not a sink (*9*), of atmospheric NO. The pNO over such seawater should reach easily measurable levels.

We measured NO in seawater samples and in situ at the sea surface by partitioning ("stripping") NO into an air or N_2 stream and measuring NO in the gas stream by passing it through the same chemiluminescence-type detector used for marine air (*10*). We exposed water samples to ultraviolet (UV) light in a UV-transmitting cylindrical borosilicate vessel underlain by a porous glass frit (*11*); we measured the light with a broadband UV radiometer with peak sensitivity at 340 nm (*11, 12*). Nitrite absorbs maximally at 356 nm. We either pulsed quiescent solutions with light and stripped after variable delays in the dark (pulse mode) or continuously illuminated and stripped (steady-state mode).

To detect NO in situ, we forced 5 liter min^{-1} [at standard temperature and pressure (STP)] of high-purity compressed air or N_2 through a frit 8 cm in diameter ~ 20 cm below the sea surface. The gas bubbles rose, broke, and about 4 liter min^{-1} (STP) collected in a translucent polyethylene bell jar 30 cm in diameter with its lip submerged about 15 cm. The frit and jar were attached to a float-supported frame tethered to the bow of R.V. *Knorr*. The detector inspired gas from the bell jar at 4 liter min^{-1} (STP). The annulus between the frit and the bell jar allowed surface water to circulate freely, but the device probably does not provide an air sample in equilibrium with pNO (sea); that would require processing more than 200 liter min^{-1} of seawater. Although the recovery factor is unknown, the device appears to operate consistently; if its efficiency remains constant, the measured values are proportional to pNO (sea). The in situ measurements provide a lower limit on pNO (sea), since losses occur through incomplete equilibration, partial shadowing, and occasional inspiration of ambient air.

In laboratory experiments, several samples of aged coastal and Sargasso Sea surface water with $[NO_2^-] \leq 0.01$ μM, stored in darkness, showed no NO signal before, during, or after UV irradiation. Samples spiked with 0.02 to 0.5 μM NO_2^- generated NO signals in seconds on photolysis with 0.1 to 5 mW cm^{-2} of UV light (*12*). Short light pulses yielded NO signals proportional to light intensity at constant $[NO_2^-]$ and proportional to $[NO_2^-]$ at constant light dose. These signals decayed in the dark with approximately first-order kinetics and half-lives, $\tau_{1/2}$, in the range 60 to 400 seconds. Authentic trace-level NO prepared by dynamic dilution and dissolved in seawater yielded a signal that decayed at the same rate as the light-generated signal. Both decays were severalfold slower in water preequilibrated with N_2 rather than air; therefore, oxygen is probably a factor in the dark reaction.

Similar measurements were made in the equatorial Pacific along a transect encompassing a large ($> 10^6$ km^2) productive region (*13*) with high NO_2^- photolysis rates flanked by NO_2^--free water (Fig. 1). North of the equator, we sampled sunlit surface water with a polyethylene bucket on a nylon line. At ~ 7.3°N, water with $[NO_2^-] \leq 0.015\ \mu M$ yielded a steady-state mode signal equivalent to a pNO of ~ 10^{-10} atm at a UV insolation of 4.4 mW cm^{-2} (*12*). Spiking this water with increasing amounts of NO_2^- yielded increasing steady-state mode signals of up to $p\text{NO} = 3 \times 10^{-8}$ atm at $[NO_2^-] = 0.8\ \mu M$ and a UV insolation of 2.5 mW cm^{-2}. Samples with $[NO_2^-] = 0.05\ \mu M$ from ~4.7°N yielded signals equivalent to $p\text{NO} = 2.5 \times 10^{-9}$ to 4.4×10^{-9} atm at 4.7 mW cm^{-2}, whereas at the equator samples yielded steady-state signals of $p\text{NO} = \sim 1.5 \times 10^{-8}$ atm at $[NO_2^-] = 0.40\ \mu M$ and a UV insolation of 4.0 mW cm^{-2}. Pulse-mode experiments showed very fast NO decays in these samples, $\tau_{1/2} = 20$ to 100 seconds.

Several experiments clarified the source of these signals. We collected water from a small boat in a clean glass carboy, sealed it in glass, and autoclaved the water, a stripper body, and some glass tubing. The steady-state mode signal from the sterile sample-stripper system was equivalent to $p\text{NO} = 5 \times 10^{-9}$ to 14×10^{-9} atm at $[NO_2^-] = 0.46\ \mu M$

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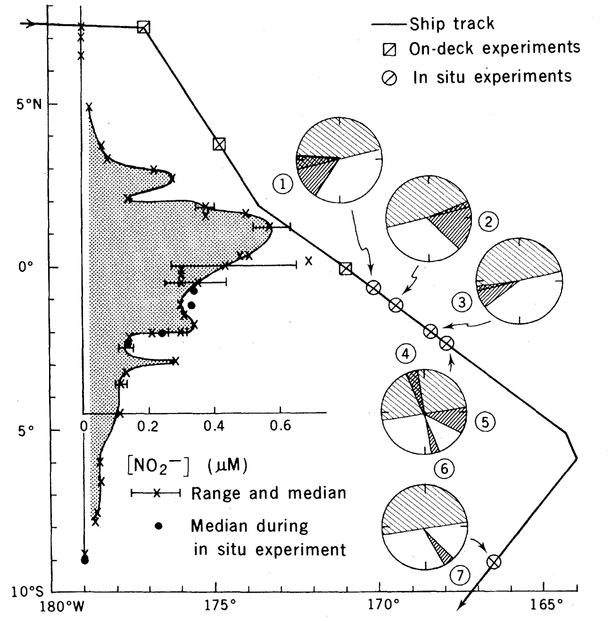

Fig. 1. Study locations and surface water NO_2^- section (left inset) from R.V. *Knorr* cruise 73, leg 7 (Kwajalein to Samoa), 14 July to 16 August 1978. Light hatching on the 24-hour clocks indicates local night; heavy hatching indicates the duration of the observation periods (circled numbers).

and 4.3 mW cm^{-2}, roughly comparable to the bucket sample. Doubling the stripper surface area by adding sterile glass tubing decreased the signal 30 percent; stripping with only a thin sample film on the walls and frit greatly decreased the signal. Thus, contamination with hypothetical NO precursors or mimics during sample recovery, biological production, or wall reactions are unlikely signal sources.

South of the equator, in situ stripping on seven occasions (Fig. 1) yielded signals equivalent to pNO = 0 to 6 × 10^{-9} atm (*14*), roughly comparable to the results of on-deck experiments. High values invariably occurred in sunlit NO_2^--rich water (Fig. 1); the lowest values, indistinguishable from values below the detection limit (*14*), occurred at night (period 4) or in low-NO_2^- water (period 7). During sunrises and sunsets, pNO rose and fell concurrently with UV insolation. For example, data from a sunrise and a midday period at the same location are shown in Fig. 2. The signal is clearly roughly proportional to UV insolation over a large range. Similar trends dominated other sunrise and sunset data. Since the signal does not persist beyond sunset (*14*), the in situ NO half-life is < 500 seconds. The floating device is isolated from the ship's influence on air and water and flushes continually. Since the on-deck and in situ signals are roughly comparable, it is very unlikely that both are experimental artifacts.

Thus, both on-deck and in situ experiments establish that NO is formed in illuminated, NO_2^--rich central equatorial Pacific waters and decays rapidly in the dark by a chemical process. Since the highly sensitive detector is not absolutely specific for NO, some signal might be due to an unknown interference. Also, in situ biological NO sources are conceivable (*15*). However, on-deck experiments show that the signal can be generated nonbiologically and that its decay rate and sensitivity to pO_2 are very similar to that of authentic NO. Furthermore, samples spiked with NO_2^- yielded signals similar in size to those from waters initially containing the same NO_2^- concentrations. Taken together, these data constitute a compelling case for the presence of NO in these waters, probably derived from the solar photolysis of NO_2^-. The pNO values that were found approach those predicted by the simple calculation given in the second paragraph, despite the first-order, rather than second-order, NO loss observed.

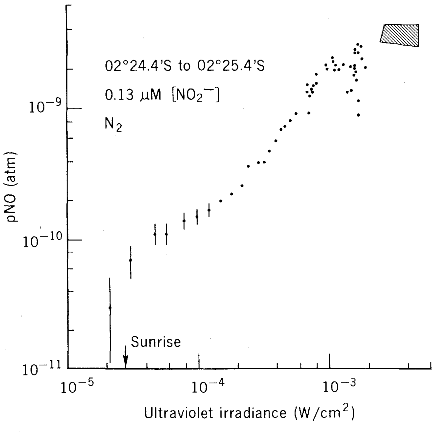

Fig. 2. Plot of the pNO in gas from the in situ stripper as a function of the UV insolation: log-log plot of background-corrected (*14*) signals from observation periods 5 (points) and 6 (hatched area) of Fig. 1 (7 August 1978). Data are 3-minute running averages of continuous records (*3*). The low-pNO points are shown with estimated error bars of ± 0.02 × 10^{-9} atm. The corrected signal (*14*) was 0 ± 0.02 × 10^{-9} atm during period 4 (Fig. 1).

The direct observation of a rapidly cycling free radical in seawater suggests that other radical processes occur concurrently. The oxygen-dependent first-order dark consumption may arise from the reaction of NO with other thermally or biochemically generated radicals; NO is an excellent trap for the alkylperoxy radicals expected in oxygenated aqueous solution (*16*). The direct NO-O_2 reaction is too slow in water to account for the observed loss rate (*4*).

The lower limits on pNO (sea) range up to 1000 times the atmospheric pNO, ≤ 10^{-11} atm, found on this cruise (*10*). If diurnal effects are taken into account, the equatorial Pacific and similar oceanic regions must be a net source of NO to the atmosphere. If we assume linear pNO (sea) versus [NO_2^-] behavior, NO_2^- below the usual detection limit, 0.02 μM (*17*), we find pNO (sea) ≥ pNO (air), for either the pNO (air) we measured (*10*) or for estimates of pNO in background air (*8*). However, the strength and extent of source regions are unclear and the sea surface might elsewhere be a NO sink (*9*). Therefore, the direction and magnitude of the global NO flux from sea to air is unknown.

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11. In the laboratory a xenon-arc lamp with Pyrex filter provided UV light approximating the sea-level sunlight spectrum; at sea, solar UV was used. The UV sensor signal was proportional to that from another UV sensor immersed several meters.
12. The maximum UV insolation we measured in the equatorial Pacific was 5.83 mW cm^{-2}.
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14. The signal from 4 liter min^{-1} (STP) of the N_2 used, equivalent to pNO = 0.13 × 10^{-9} atm, has been subtracted from reported in situ stripping data. If this signal is a water-soluble NO mimic rather than NO (no evidence suggests this), the subtraction is unwarranted. The correction is < 3 percent of the maximum p NO reported.
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18. Woods Hole Oceanographic Institution Contribution 4328. This work was supported in part by National Science Foundation grants OCE 76-08696 and ATM 78-00997. We thank Capt. H. Babbit and the crew, especially J. Cotter, of R.V. *Knorr* for making in situ measurements possible.

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Radioactive Plume from the Three Mile Island Accident: Xenon-133 in Air at a Distance of 375 Kilometers

Abstract. *The transit of an air mass containing radioactive gas released from the Three Mile Island reactor was recorded in Albany, New York, by measuring xenon-133. These measurements provide an evaluation of Three Mile Island effluents to distances greater than 100 kilometers. Two independent techniques identified xenon-133 in ambient air at concentrations as high as 3900 picocuries per cubic meter. The local γ-ray whole-body dose from the passing radioactivity amounted to 0.004 millirem, or 0.004 percent of the annual dose from natural sources.*

We observed the passage of radioactive ^{133}Xe, released from the Three Mile Island reactor, through the Albany, New York, area from 29 March through 2 April 1979. After the announcement of the reactor accident and possible releases of fission products into the atmosphere, air samples were collected in Albany and were analyzed for ^{133}Xe, which has a half-life of 5.3 days. We also monitored ^{133}Xe directly in ambient air throughout the entire transit period by observing the 81-keV γ-ray line with a planar intrinsic Ge detector located in a low-background steel chamber. To our knowledge, these measurements provided the only evaluation of Three Mile Island effluents at distances greater than 100 km.

Gas analyses of 1- to 3-m^3 samples of air were performed in two stages: cryogenic and chromatographic separation of Xe, followed by analysis of the β-decay spectrum (maximum energy, 346 keV) by internal gas-proportional counting in low-background systems (*1*). Aged compressed-air samples were processed through the gas separation system as blanks between Albany air samples. A low residual activity found after the processing of the higher-activity samples did not substantially reduce the sensitivity.

Ambient laboratory air was monitored by an intrinsic Ge diode with an area of 500 mm^2 and a resolution of 630 eV (full width at half-maximum at 81 keV). This instrument was in a low-background steel chamber (3.3 m square; 2.4 m high; wall thickness, 14.5 cm) in which outside air was exchanged about ten times an hour. During the entire period when ^{133}Xe was recorded, the thin window was covered by a pressed pellet of lake sediments with a thickness of 0.76 g cm^{-2}, which reduced the counting efficiency for ^{133}Xe by about 15 percent. After the transit the detector was calibrated under the same conditions with a virtual point source of ^{133}Xe. The net count rate in the 81-keV photopeak was measured as a function of the angular and radial position of the source over the entire field of view. Integration yielded an overall efficiency of 1.03 × 10^{-4} cpm pCi^{-1} m^3. The air volume effectively seen by the detector was 10.2 m^3.

Errors reported are ± 2 standard deviations from the root-mean-square counting statistics of sample measurements and background determinations. An additional uncertainty of ± 5 percent is introduced by the calibration. Detection limits are three times the background standard deviation.

Air samples collected on 30 March showed high ^{133}Xe concentrations: 3120 ± 160 pCi m^{-3} at 1500 Eastern standard time (EST), 3530 ± 180 at 1900, and 3900 ± 200 in a 10-hour sample (from 1545 to 0145 the next morning). By 31 March at 0900 the concentration had fallen to 39 ± 4 pCi m^{-3}. Samples collected on 3 April at 1600 and on 4 April at 1500 contained 11 ± 4 and 5 ± 2 pCi m^{-3}, respectively.

Ambient air analyses showed the same pattern of ^{133}Xe concentrations: no counts above background (< 360 pCi m^{-3}) before 29 March, but 1390 ± 290 pCi m^{-3} in a sample spanning 29 March (1230 EST) to 30 March (1500) and 1060 ± 180 pCi m^{-3} in a sample spanning 30 March (1530) to 2 April (0830). No excess counts were recorded after 2 April. The peak concentrations were more than three orders of magnitude higher than those normally present in ambient air. In 1974 the concentration of ^{133}Xe from all sources including routine releases from nuclear reactors was 2.6 pCi m^{-3} for the Albany area (*1*).

The results (plotted in Fig. 1) indicate that the air mass containing ^{133}Xe arrived in the Albany area after 1230 on 29 March and before 1500 on 30 March. A more precise arrival time could not be determined, since the diode measurements were integrated over a 24-hour pe-

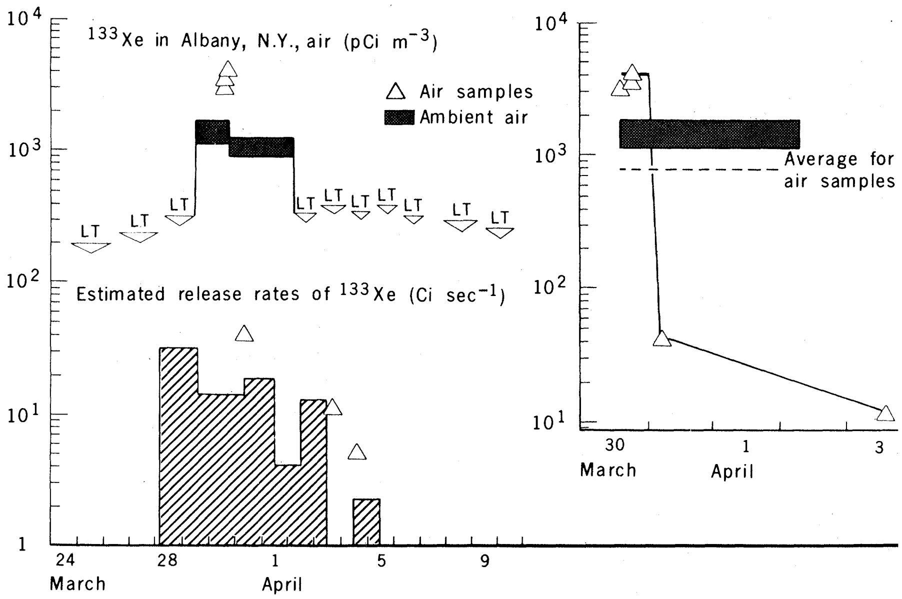

Fig. 1. Xenon-133 activity (picocuries per cubic meter of air) in Albany, New York, for the end of March and early April 1979. The lower trace shows the time-averaged estimates of releases (curies per second) from the Three Mile Island reactor (*2*). The inset shows detailed values for air samples (gas counting) and concurrent average values for ambient air (Ge diode). Abbreviation: *LT*, less than.

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