

Anomalous HNO₃/NO_x ratio of remote tropospheric air: Conversion of nitric acid to formic acid and NO_x?

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Abstract. The N oxidation ratio, [HNO₃]/[NO_x], in the free troposphere is measured at ~ 1 to 9 (averaging ~5), consistently lower than the values of 15-100 which known theory suggests to be reached rapidly. This discrepancy casts doubt on current models' abilities to predict effects of NO sources on remote [NO], and so also [O₃] and [OH]. HNO₃-to-NO_x recycling processes involving HCHO in solution are appealing explanations for the ratio. Known chemical theory are illustrated using a Lagrangian box model of the mid-troposphere which simulates characteristic episodes from NO_x input to HNO₃ washout. Ratio and budget constraint equations for NO_y can usefully restrict conceivable explanations of missing chemistry of fast nitrogen cycling; most explanations could be called "fast-cycles" or "re-NO_x-ification." These equations also show how current global models may suggest spuriously good N oxidation ratios and errors in OH. Aerosol or cloud droplets reactions with HCHO may produce (a) formic acid (which needs an appropriate source) and NO_x, or alternatively, (b) hydroxymethyl nitrate (or methyl dinitrate), which might supply a large, variable amount of "missing NO_y" not currently measurable except by NO_y instruments.

Current Theory

This note concerns the ratio [HNO₃]/[NO_x], as observed and as correctly and incorrectly simulated. (NO_x = NO + NO₂, compounds which interchange rapidly, given daylight.) Figure 1 (discussed below) depicts the activity of tropospheric nitrogen. NO is the N compound whose activity is most important, as it determines tropospheric oxidizing capacity, directly, in its effect on instantaneous local OH, and also cumulatively, in its control on ozone [Chameides and Walker, 1973, Liu et al., 1987]. Hence it has a key role with respect to future greenhouse gas and reactive chlorocarbon concentrations.

Gas-Phase Theory. A summary of the basic chemistry of the nitrogen oxides (NO_y) with an emphasis on the role of HNO₃ as a reservoir is shown in Figure 1. Active nitrogen enters the atmosphere as NO. The NO typically reacts with ozone or peroxy radicals in a few minutes to make NO₂, and the rapid daytime photolysis of NO₂ then establishes the NO_x "photochemical steady state" during the day (see Ridley et al., [1992], Liu et al., [1992], and references for reactions and details). The figure reminds us that oxidation by OH radical of the NO₂ form of NO_x is quite rapid, giving NO_x a lifetime by this process of ~1 day in the lowest kilometers of the free troposphere, and increasing to 3 days at 6.5 km, longer in the uppermost free troposphere, depending on conditions. We will analyze an archetypal situation for detailed chemical analysis, in which there are fresh, initially concentrated emissions, emissions which may be due to lightning, aircraft, or lofted near-surface NO_x. Only the stratospheric NO_y source should contribute primarily more HNO₃, not NO, and be very intermittent. Sinks of tropospheric NO_y are rainout and transport to the surface. In most likely situations, either the existing nitric acid vapor is removed when fresh emissions occur, or it may be considered overwhelmed by the new emissions. [Dickerson et al., 1987]. We analyze these situations using a Lagrangian

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box model, assuming that turbulent motions and removal of solubles from a parcel are very restricted in the mid troposphere for many-day periods between disturbance by deep, raining clouds that accompany storms. This intermittency of mixing is indicated by the laminated structure of many tropospheric species observed by aircraft. Consequently, the model should get local photochemical relationships as well as 3-d models highly resolved in time and height. Results of the model shown in the lower part of Figure 2 extend to ten days from an initial state of all NO_x and no HNO₃. The situation shown simulates subtropical East Pacific conditions appropriate to some observations described below.

The upper panel of Figure 2 shows the time course of the [HNO₃]/[NO_x] ratio. This low-ratio state starts what we may call a "NO_x clock:" the ratio increases monotonically over a period of several days, and so can be used to assign an age to the air parcel since the last disturbance. Starting the N oxidation ratio at zero allows the maximum opportunity for the simulated ratio to assume low values. The model displayed uses current chemistry, with C₂-C₃ hydrocarbons oxidized as described in Chatfield and Delany [1990]; where possible, we have updated to the recent recommendations of JPL [1992] or more comprehensive ones of Atkinson et al. [1992]. The photochemical conditions (fully diurnal, cloud-free) are appropriate for air away from the surface and upwind of the MLOPEX site in Hawaii [Ridley and Robinson, 1992, Ridley et al., 1992], and generally similar to regions sampled in the CITE-2 aircraft study [Huebert et al., 1990], especially in the marine samples. The figure and the analysis are generally relevant to the troposphere of the non-winter mid-latitudes and the tropics, and the region between 1.5 and 7 km altitude, regions significant for methane and HCFC destruction and also

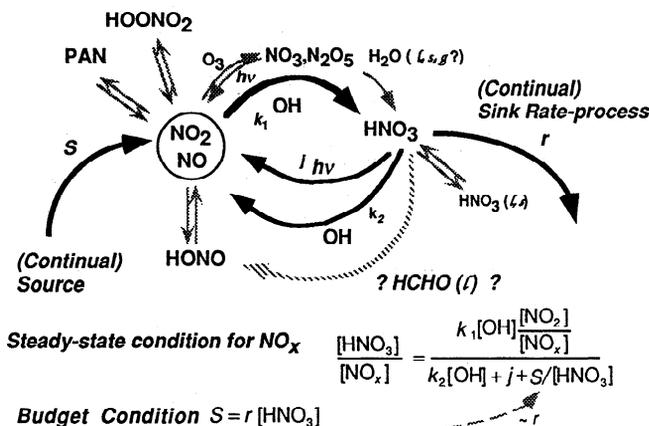


Fig. 1. An analysis of the basic chemistry of the operation of the NO_x clock. Reaction with hydroxyl radical converts NO₂ to HNO₃ within a day or so. Nighttime aerosol and cloud processes (written l and s for liquid and solid phase; g signifies gas-phase) can add to this conversion. The known NO_x recycling process involve the reaction of nitric acid with hydroxyl, and photolysis. Theory suggests that these are very slow, having time scales of nearly forty and sixty days. Theory suggests the time-scales of return to steady state from any conditions of NO_x and HNO₃ are set by the rapid forward conversion timescale: essentially, high-HNO₃ states need to convert very little material back to NO_x.

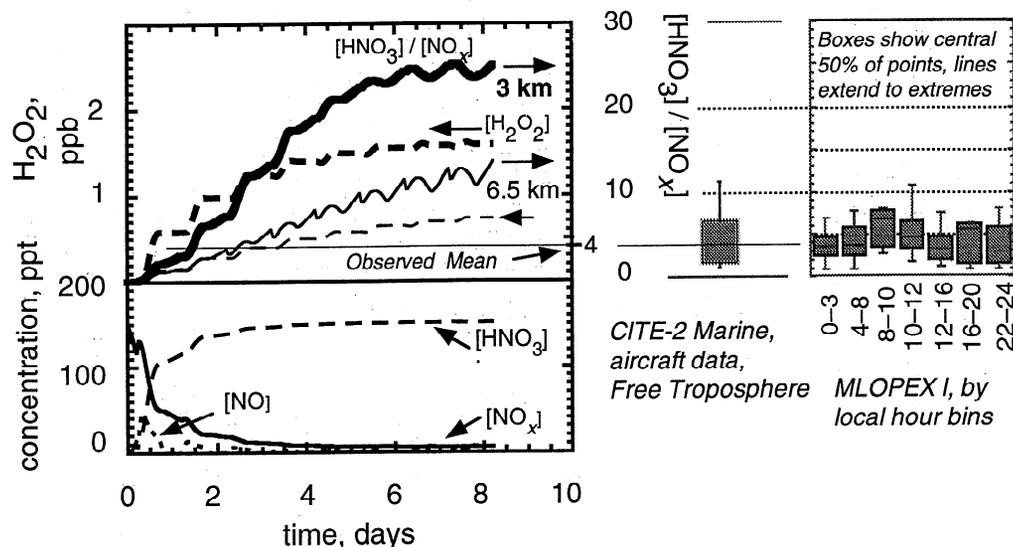


Fig. 2. (left) The NO_x clock (see text). Labeled plots show the increase of hydrogen peroxide and nitric acid as fresh emissions of nitric oxide are transformed through the nitrogen cycle. (Right) Nitric acid-to-NO_x ratio as measured in the CITE-2 observations (abstracted from Huebert et al., [1990]); and as observed in the MLOPEX experiments: for Mauna Loa downslope winds — a sample of the free troposphere: both show mean values near 4.

for O₃ production. Air below 1.5 km is excluded: it can mix to the surface, and pass often through shallow clouds. There, rapid deposition of HNO₃ may easily explain lower [HNO₃]/[NO_x] ratios; over land, new NO_x may appear.

The final models' asymptotic ratios (24 here, ~19 in Ridley et al., [1992], Liu et al., [1992]) and even the speed of quasi-exponential approach to these steady states tend to be relatively independent of the starting concentration of NO_x. The approach to the final steady state should be similarly fast, 2–3 days, in all mid-tropospheric cases, since OH depends little on NO_x when the latter is below ~300 pptv [Liu et al., 1992]. An additional pathway from NO_x to nitric acid is via the nighttime formation of NO₃ radical via the ozone reaction, and this can oxidize further to N₂O₅, which then becomes nitric acid upon contact with water in liquid, solid, and perhaps gas phase [JPL, 1992]. In attempting to minimize discrepancy, a minimal conversion rate 0.66 × the upper-limit gas-phase recommendation is included here. These conversion timescales accelerate with higher starting NO_x and species associated with early-stage photochemistry like ozone and aldehydes, and this compensates for lower OH frequently found above 1 ppb NO_x. Very similar behavior of the clock occurs for many different initial concentrations. Inclusion of reasonable values for surface reactions leads to theoretical ratios of 30–100 in our calculations, time-scales for transformation are correspondingly shortened.

A Ratio Condition. An algebraic relationship quantifies some ideas implicit in our discussion so far. A steady-state analysis of NO_x is reasonable when the time derivative of NO_x is small compared to the production and loss terms (after 1–2 e-folding times, 1–2 days). This analysis suggests a relationship for NO₂, and consequently for NO_x. Referring to Figure 1, the asymptotic N oxidation ratio should be, to a close approximation,

$$(1) \quad \frac{[\text{HNO}_3]}{[\text{NO}_x]} = \frac{k_1[\text{OH}] \times [\text{NO}_2]}{k_2[\text{OH}] + j + S[\text{HNO}_3]} \frac{[\text{NO}_2]}{[\text{NO}_x]}$$

where *S* is an indicator for any conjectured (or simulated), essentially continuous, sources of nitrogen oxides. Including N₂O₅ reaction with water raises the numerators. Since *k*₁[OH], the major determinant of the timescale for NO₂ destruction, is a day or so in the tropics or midlatitudes, and NO₂ is the dominant component of NO_x below 8 km, we may expect that this ratio will hold for situations that have not been disturbed for two or three days (see Figure 2). The chemical components of

the ratio are basic, simple photochemical terms which are thought to be well known. What the equation says is this: if a parcel is isolated from sources and (physical) sinks for times longer than the NO_x oxidation timescale, then the ratio of the species concentrations is the inverse of the ratio of their inter-conversion timescales, appropriately combined. If emissions *S* are continuous, they may be included to define the ratio appropriate for the situation: the timescale at which the ratio applies is the one numerically dominating the numerator and denominator of the right-hand side. The relationship also suggests why the ratio should be relatively insensitive to photolysis conditions and local OH radical concentrations, since short-wavelength photolysis and OH are thought to be closely interconnected (see Liu et al., [1992], who examine a low-OH hypothesis).

Observations

There is a small body of published data about the [HNO₃]/[NO_x] ratio. Figure 2 compares observations to some very basic theory described below. The figure summarizes observations from the CITE-2 aircraft sampling program (see above). The ratio of [HNO₃]/[NO_x] for the free troposphere varies widely from ~0 or up to about 10 or so, with a central tendency near 4. These measurements over the Eastern North Pacific and the Continental US (which differed little) may all be taken to be random samples of the free troposphere. The measurements of CITE-2 probably tended somewhat to avoid very convective regions of rainout and recent emissions, so they were typically at least several hours reaction-time downwind of sources.

Figure 2 also shows a summary of complementary observations made over a month's period at the Mauna Loa, Hawaii, observatory, at 3 km (a more stable operating environment). Details may be found in Carroll et al. [1992], Norton et al. [1992], and associated papers. The measurements shown were made in downslope air convincingly described as reflecting lower mid-tropospheric air very largely removed from surface influences. Periods with high inversion and local influence were treated separately (but often had relatively high ratios, 6–8!). Again, the average [HNO₃]/[NO_x] ratio is just over 4. The ratio also was seen to change slowly over days, on the time-scale in which large-scale weather and composition change, not rapidly in response to nearby emissions. The rarity of convection during downslope conditions in the fair-

weather Eastern Pacific puts most of these measurements hours, days, or weeks downwind of new sources. Figure 2 shows that these ratios appear to average 10-40% of theory, and that low ratios should be associated with rapid ratio change, and hence, great ratio variability. The Arctic summer data of the ABLE-3a, 3b campaigns are more complex to analyze, but Singh et al. [1993] and Fan et al. [1993] point out similar low ratios in the nitrogen budget in this region. The AASE-I data [Carroll et al., 1990] was also taken during the slow-photochemistry winter period, but fits in well with our discussion, and helps motivate it [Carroll, et al., 1992]. Slow timescales complicate the analysis in darker, cooler regions of the troposphere ($T < \sim 230$ K), and there could be effects on upper-tropospheric NO_x from aircraft [Kasibhatla, 1993].

Could the instruments be measuring wrongly?

Not wrongly enough, it appears: only some brief comments are appropriate here. Could NO₂ be measured too high? There is a complicating, necessary conversion step from NO₂ to NO in high sensitivity chemiluminescent and laser techniques [Gregory et al., 1990, and referenced work]. Our uncertainties regarding underconversion (e.g., incomplete NO₂ photolysis) and overconversion (e.g., conversion of abundant(?) pernitric acid) are necessarily limited by the fast photochemical steady state (see below). NO₂ may or may not be in excess of the value implied by known theory [Ridley et al., 1992, Chameides et al, 1990, and referenced work], but even ~100% excesses in NO₂ make only minor ~50% changes to the observed [HNO₃]/[NO_x] ratio, and higher values of [NO₂]/[NO_x] in equation (1) also imply a higher theoretical value. Could HNO₃ be underestimated? Experimental concerns with NO_y (all nitrogen which can interchange to become NO, in the air or in a reducing converter instrument) or one of its presumed major constituents, HNO₃, center on their removal on surfaces prior to detection. To some extent the measurements of NO_y and HNO₃ support each other due to the differences in the instruments. Measurements of HNO₃ are few, and often the discrepancy between theory and observations is large, as in the CITE-3 and AASE-2 measurements currently under analysis. It can be worthwhile to constrain [HNO₃]/[NO_x], the "N oxidation ratio," using [NO_x]/[NO_y], the "active nitrogen ratio."

$$(2) \quad \frac{[\text{HNO}_3]/[\text{NO}_x]}{\leq ([\text{NO}_y] - [\text{NO}_x]) / [\text{NO}_x]} = \frac{([\text{NO}_y] - [\text{NO}_x] - [\text{PAN}] - \dots) / [\text{NO}_x]}{([\text{NO}_x] / [\text{NO}_y])^{-1} - 1}$$

It should be possible to improve the HNO₃ estimate significantly by correcting the NO_y above for peroxyntic acid calculated using NO_x. PAN must be corrected by measurements when $T < 5^\circ\text{C}$, where it is determined by transport. In the Mauna Loa situation, [NO_y] - [NO_x] - [PAN] is highly correlated with measured [HNO₃], but is a bit higher; if that difference represents actual HNO₃, the average ratio rises to ~6, still a very low value [Carroll et al., 1992, Norton et al., 1992].

Discussion: Fast Cycles, Actual and Simulated

Fast-Cycles? In addition to equation (1), there is a budget equation for NO_x and HNO₃ (See again Figure 1).

$$(3) \quad S = r [\text{HNO}_3],$$

This equation should be valid for data averaged over times comparable to emission/rainout cycles for nitrogen; its simplicity makes applications requiring averaging simpler. It reminds us that explanations for the N oxidation ratio which deal with S , the source of nitrogen to the system imply corresponding effects for the sink, and vice versa. For example, an explanation which describes some ubiquitous sources of NO_x to raise [NO_x] must imply an acceleration of the nitrogen cycle and a larger sink, due either to proportionally higher [HNO₃] (which consequently doesn't solve the N oxidation ratio condition), or a faster removal rate, r . This will be called the "fast-cycle" (candidate) explanation. Other reservoirs of nitrogen like PAN or nitric acid aerosol can only seriously perturb either (1) or (3) when they interchange at the same one-half-to-three day timescale and when the contents of the reservoir change

significantly. In particular, small reservoirs will empty rapidly and cannot explain persistent, widespread deviations from the theoretical ratio described. Peroxyacetyl nitrate (PAN) forms a major constituent of the tropospheric nitrogen budget in the Arctic, and this complicates the analysis of ABLE-3 [Singh et al., 1992, Fan et al., 1993]. Its inclusion had little effect on our calculations of the N oxidation ratio, although it sometimes altered the ratio [HNO₃]/[NO_y].

What do the clocks imply? Hydrogen peroxide could provide an alternative chemical clock marking time since the last cloud event (Figure 2). During MLOPEX it was observed to rain out to near-zero values in air cleansed by precipitating clouds; non-precipitating clouds apparently lowered the values [Heikes, 1992]. The 0-1.8 ppb levels of hydrogen peroxide observed by Heikes would suggest that most of the air had passed through a cloud event 0.5-4 days before. Mean peroxide values of 1 ppb would correspond to about 1.5 days since a cloud event. It is a problem that simulations suggest higher peroxide values than observed [Liu et al., 1992]. However, H₂O₂ has well known activity in the liquid phase, and if it mostly oxidizes compounds like SO₂ rapidly, this might be invoked to explain low observed values.

Both the N oxidation ratio and the hydrogen peroxide shown in Figure 2 seem to argue for a 1.5-day residence time for nitric acid and peroxide against complete rainout at 3 km, a little longer in the upper troposphere. This "fast-cycling" timescale is extremely short compared to the mean times in the literature: and the Eastern Pacific was not a particularly rainy area during sampling. Giorgi and Chameides [1986] suggest rainout lifetimes of 5 days for the lower free troposphere up to 6 kilometers, rising to 15 days at 8.5 km. Balkanski et al. [1993] suggest an average of 15 days at 30 N, much longer than the 5 days they infer at 50 N. Also, as Stewart et al. [1989] show, the NO_x climatologies of the troposphere have a complex relationship to averaged rainout lifetimes; specifically longer dry periods tend to give high average [HNO₃]/[NO_x] ratios. In sum, it appears that rapid HNO₃ removal is a possible but not attractive explanation for the low N oxidation ratio.

Are there misrepresentations in models assessing tropospheric oxidizing capacity? Taken together, equations (1) and (3) make it clear that all one-, two-, and three-dimensional models that are run with simulated spatially averaged or continuous sources of NO_x are including a term that spuriously presses their [HNO₃]/[NO_x] ratios toward observed values. Sources are usually simulated as continuous, even in 3-d models, when the actual occurrence or statistics of occurrence of sources, e.g., of lightning, aircraft emissions, cloud venting, etc., are either unknown or inconveniently complex and expensive to simulate. Often, these are paired with continuous sinks e.g., a "rainout lifetime," which can be evaluated in (1) using the budget relation (3). One example of the large and pernicious effects of the model errors on the simulation of continuous emissions and cloud venting, effects on the simulated ozone budget, was demonstrated in Chatfield and Delany [1990]. These simulation errors need quantification. Clearly, there are ramifications for the sensitivity of correctly modeled global OH and ozone levels to increasing nitrogen inputs to the region above the boundary layer. If there is currently a fast cycle, that implies that additional NO_x should somehow also be lost quickly. Conversely, re-NO_x-ification explanations suggests that any new active nitrogen should have increased persistence and effects, and these now deserve some brief consideration.

Re-NO_x-ification?

In addition to the very slow re-NO_x-ification processed described in current-theory section, above, there are fascinating and little-explored processes that could explain the frequency of low oxidation ratios in the mid-troposphere. For example, formaldehyde could act to reduce nitric acid in appropriate solutions. One known process, addition, produces hydroxy-methyl nitrate or methyl dinitrate [Walker, 1965], and possible the di-nitrate form has been mentioned by Fan et al. [1994]. If this were a major reaction, there should be large

amounts of organic nitrate which have not been observed [Atlas et al., 1992]. Another reaction of formaldehyde and nitric acid in solution makes formic acid and reduced nitrogen, HONO or NO and NO₂. Horváth, et al. [1988] described one mechanism and rate for this redox reaction, which required [H⁺], [HNO₃], and some trace catalytic amount of reduced nitrogen in the same solution. Rate and mechanism information are hardly complete and trace catalysts can play important roles [Bazsa and Epstein, 1986].

We propose that conditions favoring an autocatalytic reaction might occur in background nitrate aerosol [Norton et al., 1992], high-humidity sulfate aerosols, or in non-precipitating cloud particles. All of these are much more ubiquitously present in the mid-troposphere than the rainout processes discussed above. Atmospheric parcels tend to oscillate a kilometer or so within tropospheric wave motions, especially outside the equatorial belt, allowing near-daily episodes of high humidities and clouds. Indeed, the organic nitrate products may serve to preconcentrate reactants for the redox reaction, e.g., in a nitrate aerosol particle incorporating ambient sulfuric acid by coagulation or from the gas phase. Simple computer simulations of the effect of such reactions have been made using hypothesized aerosol-transformation rates on the gas-phase chemistry. As one might expect, these easily reproduce the observed [HNO₃]/[NO_x] ratios observed at Mauna Loa and produce several hundred ppt of formic acid which tends to bring theory closer to observations [Norton, 1992]. Effects on HCHO are small; other reactions dominate. The formic acid observed may be considered a tracer of nitric acid which has been reduced; interpretations based on this tracer, which is itself reactive, may help reconcile the observed [HNO₃]/[NO_x] ratio to photochemical theory.

Summary and Conclusions

The ratio of measured [HNO₃]/[NO_x] is 0.25–0.5 of the values simulated using currently accepted theory. Simulations used to explain the present and future atmosphere will tend to get [HNO₃] or [NO_x] off. We have applied ratio and budget conditions which can characterize suggested solutions to this problem. If the observed nitrogen ratios are explained by a fast-cycle (pervasive-source) process, then the N cycle must be giving more N removal than current theoretical assessments suggest. Current averaged models of global chemistry contain a numerical effect similar to such a pervasive source. Liquid-phase reactions of HNO₃ and HCHO in aerosol or cloud droplets could conceivably be active enough to allow tropospheric re-NO_x-ification and perhaps also contribute to the observed levels of formic acid and NO_y.

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