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Alkyl nitrates in outflow from North America over the North Atlantic during Intercontinental Transport of Ozone and Precursors 2004

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[1] This paper is based on alkyl nitrate measurements made over the North Atlantic as part of the International Consortium for Research on Atmospheric Transport and Transformation (ICARTT). The focus is on the analysis of air samples collected on the UK BAe-146 aircraft during the Intercontinental Transport of Ozone and Precursors (ITOP) project, but air samples collected on board the NASA DC-8 and NOAA WP-3D aircraft as part of a Lagrangian experiment are also used. The ratios between the alkyl nitrates and their parent hydrocarbons are compared with those expected from chemical theory. Further, a box model is run to investigate the temporal evolution of the alkyl nitrates in three Lagrangian case studies and compared to observations. The air samples collected during ITOP do not appear to be strongly influenced by oceanic sources, but rather are influenced by emissions from the N.E. United States and from Alaskan fires. There also appears to be a widespread common source of ethyl nitrate and 1-propyl nitrate other than from their parent hydrocarbons. The general agreement between the alkyl nitrate data and photochemical theory suggests that during the first few days of transport from the source region, photochemical production of alkyl nitrates, and thus ozone, had taken place. The observations in the more photochemically processed air masses are consistent with the alkyl nitrate production reactions no longer dominating the peroxy radical self/cross reactions. Further, the results also suggest that the rates of photochemical processing in the Alaskan smoke plumes were small.

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1. Introduction

[2] Alkyl nitrates are produced photochemically in the atmosphere through the oxidation of parent hydrocarbons [*Arey et al.*, 2001; *Atkinson and Arey*, 2003; *Atkinson et al.*, 1987; *Roberts*, 1990]. They are important tropospheric trace gas species, because their photochemical formation occurs through the same chemistry that also leads to the production of ozone. This chemistry is largely controlled by the availability of nitrogen oxides and alkyl nitrates can also act as reservoirs of these species. They can constitute a significant fraction of the total reactive odd nitrogen with the relative amount being greater remote from sources [*Blake et al.*, 2003; *Day et al.*, 2003; *Flocke et al.*, 1991, 1998; *Nowak et al.*, 2004; *Ridley et al.*, 1997; *Rosen et al.*, 2004; *Shepson et al.*, 1993; *Talbot et al.*, 1999, 2000, 2003]. Since the alkyl nitrates have atmospheric lifetimes ranging from several days to about a month, depending on the alkyl chain length, they can be transported over long distances [*Atherton*, 1989], and thus can be important for the redistribution of nitrogen oxides.

[3] Alkyl nitrate sources also include the ocean. Atmospheric data collected over the equatorial Pacific has shown this region to be strongly enhanced in the short-chain alkyl nitrates [*Atlas et al.*, 1993; *Blake et al.*, 1999, 2003]. Similarly the equatorial Pacific Ocean has been found to be supersaturated with respect to the atmosphere for methyl, ethyl, 1-propyl and 2-propyl nitrates [*Dahl et al.*, 2005]. However measurements made from 60°N to 60°S in the surface waters of the Atlantic show that, while large parts of the transect were found to be supersaturated in methyl and ethyl nitrates particularly between the

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equator and 40°S, the temperate regions, particularly in the Northern Hemisphere, were close to equilibrium with the overlying atmosphere suggesting this region not to be a major source and possibly even a sink [*Chuck et al.*, 2002]. Biomass burning has also been found to be a source of alkyl nitrates [*Friedli et al.*, 2001; *Simpson et al.*, 2002].

[4] This paper examines alkyl nitrate data collected over the North Atlantic. The field experiment and sampling and analytical techniques are described in section 2. In section 3 the concentration data are presented and examined in terms of the correlations between the different alkyl nitrates, and between the alkyl nitrates and carbon monoxide. The relationship between the alkyl nitrates and their parent hydrocarbons are explained with respect to the chemical production and loss reactions and the observations compared to the theory. The Lagrangian observations are compared to box model calculations. The conclusions drawn collectively from these different analytical approaches are presented in section 4.

2. Methodology

2.1. Aircraft Campaign

[5] The data presented in this paper were collected as part of the International Consortium for Research on Atmospheric Transport and Transformation (ICARTT) [*Fehsenfeld et al.*, 2006]. This paper focuses on data collected on board the UK BAe-146 aircraft during the Intercontinental Transport of Ozone and Precursors (ITOP) project [*Lewis et al.*, 2007], which was the UK contribution to ICARTT, but also uses data collected on board the NASA DC-8 and NOAA WP-3D aircraft as part of a Lagrangian experiment [*Methven et al.*, 2006].

[6] During ITOP the BAe-146 aircraft, which is operated by the Facility for Atmospheric Airborne Measurements (FAAM), was based at Horta (38°N, 28°W) on the island of Faial, part of the Portuguese Azores archipelago. Data from 10 flights are presented during the summer of 2004: B029 (15 July), B030 (17 July), B031 (19 July), B032 (20 July), B033 (22 July), B034 (25 July), B035 (28 July), B036 (29 July), B037 (31 July), B038 (1 August). For more details of the air masses sampled and meteorological conditions during each flight see the ITOP overview paper [*Lewis et al.*, 2007].

2.2. Sampling and Analysis

2.2.1. Alkyl Nitrates and Nonmethane Hydrocarbons

[7] Whole air samples (WAS) were collected on board the BAe-146 in 3L, stainless steel canisters, which were normally pressurized to 3 bar. The canisters were silco-treated by the manufacturers Restek, which involves spraying a thin layer of pure silica on the internal wall and electropolishing to minimize surface reactivity. The canisters are only used for aircraft samples and are never used in urban pollution. Occasionally they are cleaned by filling with humidified nitrogen and evacuating. During campaigns they are vacuum cleaned between samples using a rotary pump drawing air first via a mist filter and then a liquid nitrogen cold trap. The canisters are typically evacuated preflight to 1×10^{-2} torr over a period of 1–2 hours.

[8] Approximately 280 samples from 10 flights were analyzed for alkyl nitrates by gas chromatography/mass spectrometry (GC/MS) by the University of East Anglia (UEA) group. The WAS were connected by stainless steel tubing to a preconcentrator (Marks International Ltd), consisting of an Air Server and Unity™ thermal desorber. The air samples were dried by a Nafion dryer (Permapure™) before being trapped on a two bed packed cold trap (Carbograph 1TD and Carboxen 1000) at −10°C. The GC (Agilent 6890N) and MS (Agilent 5973) were from Agilent Technologies and a Restek 502.2 column (105 m, 0.32 mm ID, 1.8 μm film thickness) was used. The carrier gas was helium, (Research Grade, purity ≥99.99999%). The MS was operated in negative ion chemical ionization (NICI) mode using methane as reagent gas (purity ≥99.9995) and the selected ions were m/e 46 for all nitrates and for the RO fragments they were m/e 43, 57, 71 and 85 for C_2, C_3, C_4 and C_5 respectively. Concentrations of methyl, ethyl, 1-propyl, 2-propyl, 2-butyl, 2-methyl-3-butyl and the sum of 2- and 3-pentyl nitrates (hereafter referred to as 2 + 3-pentyl nitrate) are presented. The detection limit is <0.01 pptv and the precision error <5–10% on duplicate analyses. The accuracy is determined by that of the calibration standard provided by the Rosenstiel School of Marine and Atmospheric Science (RSMAS) group and measurement comparison (see below).

[9] C_2-C_9 NMHCs were determined from the same whole air samples as the alkyl nitrates, analyzed using capillary gas chromatography following the methodology of *Hopkins et al.* [2003] by the University of York (UoY) group. Briefly 1 L of air sample was taken from the canister, dried using a cold finger at −30°C and preconcentrated on a two stage carbon microtrap held at −20°C. On thermal desorption, the analytes were split approximately 50:50 between a 50 m 0.53 mm i.d. Al_2O_3 PLOT column for hydrocarbon analysis, and a 20 m 0.53 Lowox, PLOT column for carbonyl and C_7-C_9 NMHC analysis. Detection was via parallel Flame Ionization Detectors (FID). Regular calibration was made with reference to ppbv level compressed gas standards, and zero samples performed for each flight. The detection limit was structure-dependent, between 2 and 10 pptv. The accuracy, which comes from the gas standard is gravimetrically made, is 5% and the precision around 3% at concentrations above 50 pptv. Below this value an empirically derived power function defines both the accuracy and precision since other factors such as integration errors and uncertainty in the blank value become significant. As the concentrations reach 10 ppt uncertainty and precisions are ~20–30% and at 2 pptv level these have reached ~100%.

[10] A maximum of 168 evacuated two liter stainless steel canisters were filled to 40 psi using a metal bellows pump in each flight of the NASA DC-8 aircraft. The canisters were made by University of California Irvine (UCI) and not silco-treated. Prior to the flight they were evacuated to a pressure of 10^{-2} torr and filled to one atmosphere with purified UHP helium. They were then evacuated to 10^{-2} torr again after which about 20 torr of purified water vapor was added to reduce wall loss of some halocarbons and alkyl nitrates. After each flight the canisters were shipped back to the UCI home laboratory for analysis of methane, CO, C_2-C_{10} NMHCs, selected sulphur compounds, halocarbons and C_1-C_5 alkyl nitrates. Flame ionization, electron capture,

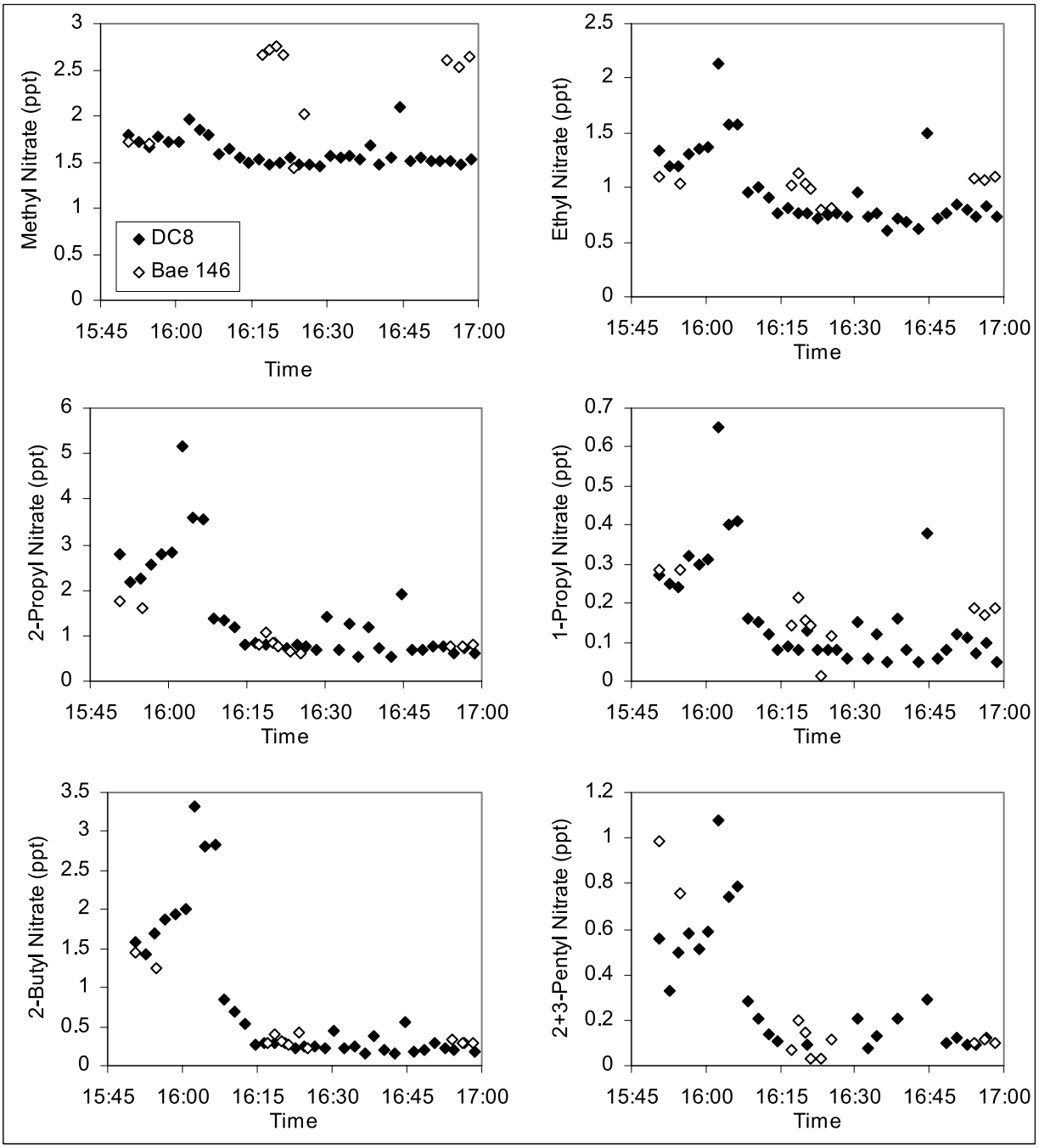

Figure 1. Time series of alkyl nitrate data from the BAe-146 and DC-8 aircraft during the in-flight comparison. The three time periods of data correspond to level runs at 22,000 ft, 12,000 ft and 1,000 ft.

and mass-spec detection were used for the analysis. The measurement precision for NMHCs is 1–3% and the absolute accuracy is between 2 and 10%. For alkyl nitrates the measurement precision is 2–4%. The accuracy is determined by that of the calibration standard provided by the RSMAS group (see below).

[11] Whole air samples collected on board the NOAA WP-3D were analyzed by the RSMAS group using GC-FID for C_1-C_5 NMHC, and by selected ion GC/MS for the alkyl nitrates. The WP-3D canisters were precleaned by repeated flushing with wet zero air at 60–80 C. The canisters were sent to the field with 1.5 atm of wet zero air. Prior to flight, the canisters were evacuated, flushed with pure N_2, and 3 torr of water vapor was added to each canister. The canisters were not silco-treated but the above treatment has been shown to be effective in stabilizing nitrates (up to C_5). Detection limits for the alkyl nitrates were 0.1–0.3 pptv, while the precision was approximately 5%. The accuracy of the calibration standard is under investigation. This calibration standard was used by all three groups (the UCI group from the start and the UEA group following the comparison exercise described below). For the hydrocar-

Table 1. Alkyl Nitrate Data From the In-Flight Comparison Between the BAe-146 and DC-8 Divided Into the Three Altitude Runs[a]

	Methyl	Ethyl	2-Propyl	1-Propyl	2-Butyl	2 + 3-Pentyl
			22,000 ft			
DC8, pptv						
Mean	1.73	1.25	2.40	0.25	1.57	0.46
stdev	0.07	0.08	0.34	0.02	0.14	0.12
BAe, pptv						
Mean	1.70	1.07	1.70	0.29	1.35	0.87
stdev	0.02	0.04	0.10	0.00	0.15	0.16
Difference, pptv	−0.02	−0.18	−0.72	0.03	−0.22	0.41
Difference, %	−1.3	−17.0	−43.1	11.3	−15.9	46.7
			12,000 ft			
DC8, pptv						
Mean	1.49	0.76	0.79	0.09	0.26	0.09
stdev	0.03	0.03	0.05	0.02	0.02	NA
BAe, pptv						
Mean	2.31	0.95	0.78	0.13	0.32	0.10
Stdev	0.57	0.15	0.18	0.07	0.09	0.06
Difference, pptv	0.81	0.19	−0.01	0.04	0.06	0.01
Difference, %	35.2	20.2	−0.8	29.2	18.5	10.0
			1,000 ft			
DC8, pptv						
Mean	1.53	0.79	0.70	0.08	0.26	0.12
stdev	0.04	0.02	0.06	0.02	0.02	NA
BAe, pptv						
Mean	2.62	1.10	0.77	0.19	0.32	0.11
stdev	0.61	0.16	0.21	0.08	0.10	0.07
Difference, pptv	1.09	0.31	0.07	0.10	0.06	−0.01
Difference, %	41.7	28.3	9.6	55.6	19.0	−8.4

[a]Presented are the means and standard deviations (stdev) for the samples collected on each run and the absolute and relative difference between the data from the two aircraft.

bons the detection limits were <3 ppt for C_2 and C_3 and <1 ppt for C_4 and higher, with an accuracy of better than 15–20% and a precision of 3–5%.

2.2.2. Nonmethane Hydrocarbon and Alkyl Nitrate Measurement Comparison

[12] Thirty two sample canisters were filled simultaneously to 40 psi with air collected from a remote Southern California research site. Four canisters were sent to six different research groups involved in VOC analysis from various platforms for the ICARTT program. Three of the laboratories were involved in hydrocarbon and alkyl nitrate measurements as part of the Lagrangian experiment. The agreement between the three laboratories (UoY, UCI, and RSMAS) for the alkyl nitrate parent hydrocarbons was ±3% for ethane, ±1% for propane, ±1% for n-butane, ±5% for i-pentane and ±15% for n-pentane. For the alkyl nitrates, the UCI and RSMAS groups had both used a standard calibrated in the RSMAS lab and the difference between the measurements for the comparison canisters were less than 1% for methyl and 1-propyl nitrate, 3% for ethyl nitrate, 9% for 2-propyl nitrate, 4% for 2-butyl and 3-pentyl nitrate, and 5% for 2-pentyl nitrate. The UEA calibration scale was adjusted through this comparison exercise to agree with the scale used by the other two labs, with the exception of 3-methyl-2-butyl which was not reported for the comparison. The ratios of the UEA value to the mean of the other two labs before adjustment were as follows: methyl nitrate 0.71; ethyl nitrate 0.84; 2-propyl nitrate 0.92; 1-propyl nitrate 0.70; 2-butyl-nitrate 0.74; 2 + 3-pentyl-nitrate 0.61.

2.2.3. In-Flight Comparison Between the DC-8 and BAe-146

[13] Flight B035 on 28 July 2004 included a period of comparison with the NASA DC-8, part of a coordinated plan devised by both INTEX and ITOP science teams. The aircraft rendezvoused west of the Azores (~38°N, ~38°W) and both planes flew in wing-tip to wing-tip formation for approximately 70 min, performing level runs at 22,000 ft, 12,000 ft and 1,000 ft in cloud free air. This allowed both aircraft to sample the same air masses and compare the common measurements quantitatively over an altitude range of 21,000 ft. The concentrations of pollutants were generally low throughout the comparison. This led to low concentrations of alkyl nitrates, which did not extend over a wide range of concentrations (Figure 1). The highest concentrations were observed during the high-level run at 22,000 ft. In general the agreement between the measurements on the BAe-146 and DC-8 are good, with absolute differences mostly less than 0.2 pptv and often less than 0.1 pptv (Table 1). This equates to relative differences of mostly less than 20% and often less than 10% (Table 1). The main exception was methyl nitrate data, where a number of BAe-146 samples collected on the midlevel (12,000 ft) and low-level (1,000 ft) runs had relatively high values compared to the DC-8 (i.e., 1 pptv (40%) greater).

2.2.4. Other Measurements

[14] On the BAe-146 CO was measured using an aerolaser UV monitor [*Gerbig et al.*, 1999] with 10 s integration and 2 ppbv detection limit, with an overall measurement uncertainty at 95% confidence of 3% plus 1 ppbv. O_3 was measured by a thermo environmental (TECO 49) UV photometric instrument with an overall measurement uncertainty at 95% of 5% plus 2 ppbv. NO was measured by chemiluminescence [*Brough et al.*, 2003] with an accuracy of ±8% and precision of 2–4% depending on the flight.

3. Results and Discussions

3.1. Alkyl Nitrates and Concentrations

[15] Figure 2 shows the alkyl nitrate data from the ITOP flights (B029 to B038). The data are presented as a series of data points sequential in time between 15 July and 1 August, with the division between each flight indicated by the vertical dashed lines. In general methyl nitrate was the most abundant alkyl nitrate, followed by 2-propyl, 2-butyl, ethyl, 2 + 3-pentyl, 2-methyl-3-butyl and 1-propyl, however the absolute concentrations and the relative concentrations of the alkyl nitrates varied between different air masses.

[16] The air masses sampled were divided into "marine" (O_3 < 40 ppb, CO < 90 ppb, H_2O > 10,000 ppm, around 40 samples), "fire plumes" (CO > 250 ppb, ethane > 1600 ppt, benzene > 140 ppt, 10 samples) and "other" (around 200 samples). Although the criteria for defining "fire plumes" are not specific to biomass burning, analysis of back trajectories confirmed that such high concentrations of these tracers were only encountered when it was clearly indicated that air came from the fire burning regions of Alaska and Canada. The mean concentrations in "other" air masses exhibit the relative order of concentrations described above (Figure 3). In the "marine" air masses methyl nitrate shows a slightly

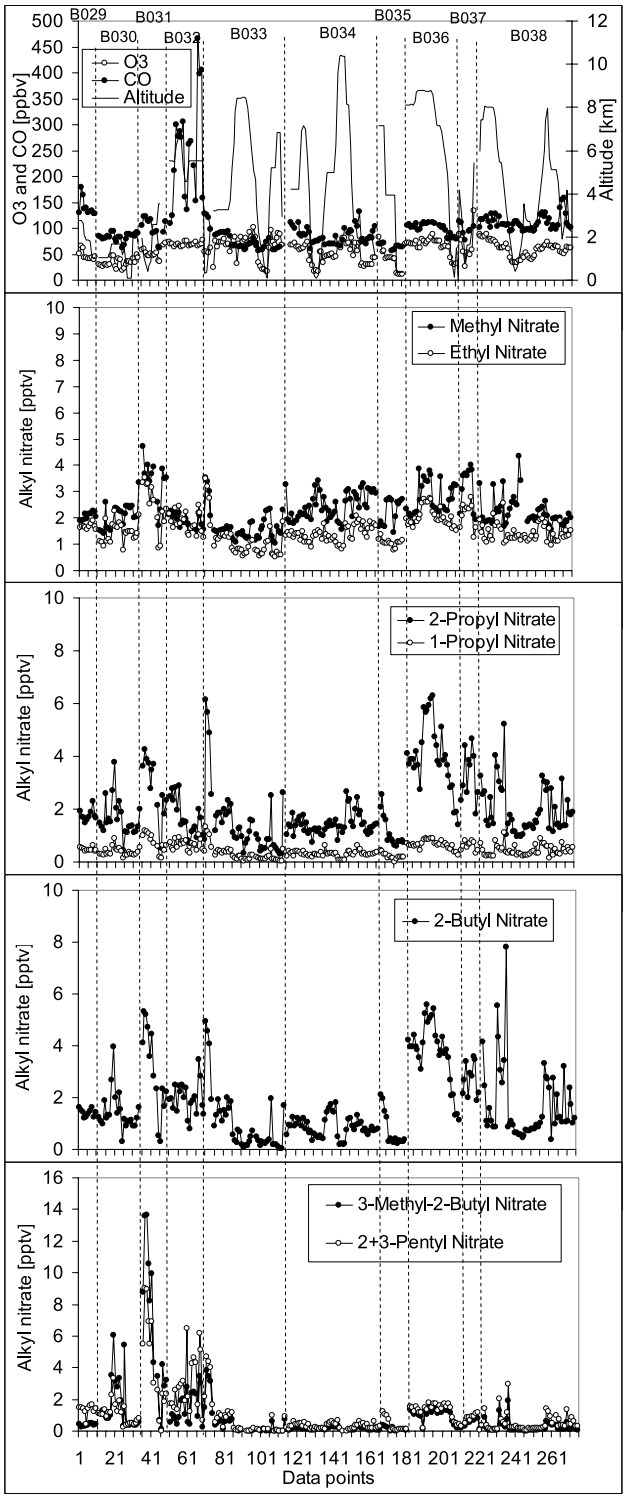

Figure 2. Alkyl nitrate data from the ITOP flights (B029 to B038). The data are presented as a series of data points sequential in time between 15 July and 1 August, with the division between each flight indicated by the vertical dashed lines. In the top plot are the ozone and carbon monoxide concentrations along with the altitude of the BAe-146 at the time of the WAS samples.

higher mean concentration to "other" air masses (2.40 compared to 2.29 ppt), but the concentrations of the other alkyl nitrates are lower by around 30–50% with the exception of ethyl nitrate which is lower by about 15% (1.33 compared to 1.57 ppt), such that it becomes the second most abundant alkyl nitrate. This suggests that the methyl nitrate may have been influenced by an oceanic source, but the predominant source of the other alkyl nitrates observed during ITOP was terrestrial.

[17] With the exception of methyl nitrate ("other" and "marine") and 2-propyl nitrate ("other"), the mean concentrations of the alkyl nitrates in the "fire plumes" (flight B032) were greater than in the other air masses, with 2 + 3-pentyl nitrate being the most abundant (Figures 2 and 3). This is in general agreement with observations of C_1-C_5 alkyl nitrates being emitted from wild fires in North America (California, Montana and Colorado) [*Friedli et al.*, 2001] and C_1-C_4 alkyl nitrates from Australian savanna burning [*Simpson et al.*, 2002]. However, where as *Simpson et al.* [2002] observed methyl nitrate to dominate alkyl nitrate emissions during the flaming stage of the savanna burning, methyl nitrate was not found to dominate in the ITOP "fire plume" data. This is similar to the observations of *Blake et al.* [1999, 2003] who did not observe evidence for enhanced concentrations of methyl nitrate in air influenced by tropical biomass burning. None of the previous studies reported a dominance of the pentyl nitrates in biomass burning plumes as observed in the ITOP data.

[18] The minimum and maximum values for the "other" air masses demonstrate that there are a number of different air masses assigned to this category, some of which contained very low concentrations of the alkyl nitrates and others which were clearly impacted by terrestrial emissions of VOCs (anthropogenic or biogenic) giving higher concentrations of alkyl nitrates than observed in either the "marine" or "fire plume" air masses. The highest alkyl nitrate concentration was observed during flight B031 (air from New York) for 2-methyl-3-butyl nitrate (13.7 ppt), when the maximum concentration of 2 + 3-pentyl nitrate (9.0 ppt) was also measured. It is quite possible that some of the "marine" maximum concentrations of the alkyl nitrates were impacted by terrestrial emissions (e.g., 5.4 pptv of 2-methyl-3-butyl nitrate and 1.7 pptv for 2 + 3-pentyl nitrate observed during flight B030).

[19] The alkyl nitrate concentrations observed during ITOP over the mid-North Atlantic are typical of those observed a few days downwind of a precursor source region. They are generally slightly higher than those observed over the Pacific during the PEM-Tropics A and B north of 10°N between 2 and 8 km altitude [*Blake et al.*, 2003], with the exception of methyl nitrate, while those during TRACE-P which studied Asian outflow [*Simpson et al.*, 2003] are slightly higher. This reflects the relative proximity to anthropogenic sources. Similarly measurements made at Chebogue Point, Nova Scotia during NARE-93 [*Roberts et al.*, 1998] and over the western North Atlantic in pollution outflow from North America during NARE-97 [*Stroud et al.*, 2001] tend to be slightly higher than observed during ITOP. Data from over the North American [*Bertman et al.*, 1995; *O'Brien et al.*, 1997; *Ostling et al.*, 2001; *Stroud et al.*, 2001] and European

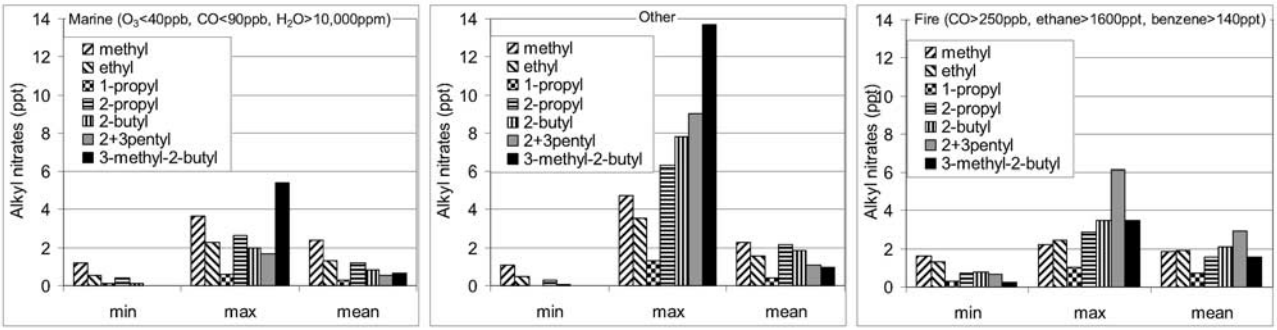

Figure 3. Minimum, maximum and mean concentrations of the alkyl nitrates for three types of air mass category: (left) "marine," (middle) "other," and (right) "fire plumes." The definitions of these air mass types are described in the text.

[*Flocke et al.*, 1998] continents and Hong Kong [*Wang et al.*, 2003] are much higher.

3.2. Relationship Between Alkyl Nitrates

[20] The correlation coefficients (r) and the gradients of the linear relationships between each pair of alkyl nitrates were calculated (Table 2) for 4 flight groups: B031, which is believed to have sampled air from the N. York region and showed elevated concentrations of the alkyl nitrates, in particular the pentyl nitrates; B032 which was highly influenced by Alaskan fire plumes with CO concentrations up to 600 ppb; B036, B037 and B038, which are thought to

Table 2. Correlation Coefficients (r) and Slopes (in Parentheses) of the Linear Relationships Between Each Pair of Alkyl Nitrate for the Four Flight Groups: B031; B032; B036, B027 and B038; and B029, B030, B033, B034 and B035

	Methyl	Ethyl	2-Propyl	1-Propyl	2-Butyl	3-Methyl-2-Butyl	2 + 3-Pentyl
				B031			
Methyl	. . . (. . .)	0.82 (0.74)	0.81 (0.52)	0.73 (1.67)	0.68 (0.32)	0.58 (0.10)	0.55 (0.14)
Ethyl	0.82 (0.92)	. . . (. . .)	0.98 (0.71)	0.98 (2.50)	0.97 (0.51)	0.91 (0.17)	0.91 (0.26)
2-propyl	0.81 (1.25)	0.98 (1.36)	. . . (. . .)	0.96 (3.39)	0.94 (0.69)	0.88 (0.23)	0.88 (0.35)
1-propyl	0.73 (0.32)	0.98 (0.39)	0.96 (0.27)	. . . (. . .)	1.00 (0.21)	0.96 (0.07)	0.96 (0.11)
2-butyl	0.68 (1.43)	0.97 (1.83)	0.94 (1.29)	1.00 (4.80)	. . . (. . .)	0.98 (0.35)	0.98 (0.54)
3-methyl-2-butyl	0.58 (3.37)	0.91 (4.75)	0.88 (3.30)	0.96 (12.81)	0.98 (2.71)	. . . (. . .)	1.00 (1.52)
2 + 3-pentyl	0.55 (2.12)	0.91 (3.12)	0.88 (2.17)	0.96 (8.42)	0.98 (1.78)	1.00 (0.66)	. . . (. . .)
				B032			
Methyl	. . . (. . .)	0.91 (0.84)	0.98 (0.35)	0.80 (1.63)	0.88 (0.45)	0.53 (0.25)	0.31 (0.10)
Ethyl	0.91 (0.99)	. . . (. . .)	0.89 (0.35)	0.97 (2.15)	0.95 (0.53)	0.66 (0.34)	0.54 (0.19)
2-propyl	0.98 (2.70)	0.89 (2.28)	. . . (. . .)	0.79 (4.48)	0.87 (1.23)	0.50 (0.66)	0.26 (0.23)
1-propyl	0.80 (0.39)	0.97 (0.43)	0.79 (0.14)	. . . (. . .)	0.94 (0.24)	0.74 (0.17)	0.67 (0.11)
2-butyl	0.88 (1.71)	0.95 (1.70)	0.87 (0.61)	0.94 (3.78)	. . . (. . .)	0.80 (0.74)	0.61 (0.39)
3-methyl-2-butyl	0.53 (1.12)	0.66 (1.28)	0.50 (0.38)	0.74 (3.21)	0.80 (0.86)	. . . (. . .)	0.90 (0.62)
2 + 3-pentyl	0.31 (0.94)	0.54 (1.53)	0.26 (0.28)	0.67 (4.20)	0.61 (0.96)	0.90 (1.30)	. . . (. . .)
				B036, B027, and B038			
Methyl	. . . (. . .)	0.71 (1.02)	0.50 (0.24)	0.49 (1.64)	0.42 (0.18)	0.38 (0.52)	0.34 (0.38)
Ethyl	0.71 (0.49)	. . . (. . .)	0.92 (0.31)	0.88 (2.02)	0.83 (0.25)	0.79 (0.74)	0.76 (0.59)
2-propyl	0.50 (1.03)	0.92 (2.74)	. . . (. . .)	0.86 (5.86)	0.94 (0.83)	0.90 (2.50)	0.86 (1.97)
1-propyl	0.49 (0.15)	0.88 (0.39)	0.86 (0.13)	. . . (. . .)	0.87 (0.11)	0.82 (0.33)	0.85 (0.28)
2-butyl	0.42 (0.97)	0.83 (2.77)	0.94 (1.05)	0.87 (6.62)	. . . (. . .)	0.93 (2.90)	0.94 (2.41)
3-methyl-2-butyl	0.38 (0.28)	0.79 (0.84)	0.90 (0.32)	0.82 (2.02)	0.93 (0.30)	. . . (. . .)	0.96 (0.79)
2 + 3-pentyl	0.34 (0.31)	0.76 (0.99)	0.85 (0.38)	0.85 (2.56)	0.94 (0.36)	0.96 (1.17)	. . . (. . .)
				B029, B030, B033, B034, and B035			
Methyl	. . . (. . .)	0.67 (1.04)	0.24 (0.26)	0.35 (1.49)	0.10 (0.10)	−0.05 (−0.05)	−0.09 (−0.11)
Ethyl	0.67 (0.43)	. . . (. . .)	0.77 (0.51)	0.88 (2.27)	0.68 (0.42)	0.35 (0.14)	0.56 (0.37)
2-propyl	0.24 (0.22)	0.77 (1.17)	. . . (. . .)	0.86 (3.39)	0.87 (0.81)	0.46 (0.30)	0.72 (0.73)
1-propyl	0.35 (0.08)	0.88 (0.34)	0.86 (0.22)	. . . (. . .)	0.88 (0.21)	0.47 (0.07)	0.78 (0.20)
2-butyl	0.10 (0.09)	0.68 (1.10)	0.87 (0.93)	0.88 (3.72)	. . . (. . .)	0.62 (0.41)	0.88 (0.96)
3-methyl-2-butyl	−0.05 (−0.08)	0.35 (0.86)	0.46 (0.72)	0.47 (3.03)	0.62 (0.92)	. . . (. . .)	0.75 (1.23)
2 + 3-pentyl	−0.09 (−0.07)	0.56 (0.84)	0.72 (0.70)	0.78 (3.05)	0.88 (0.80)	0.75 (0.45)	. . . (. . .)

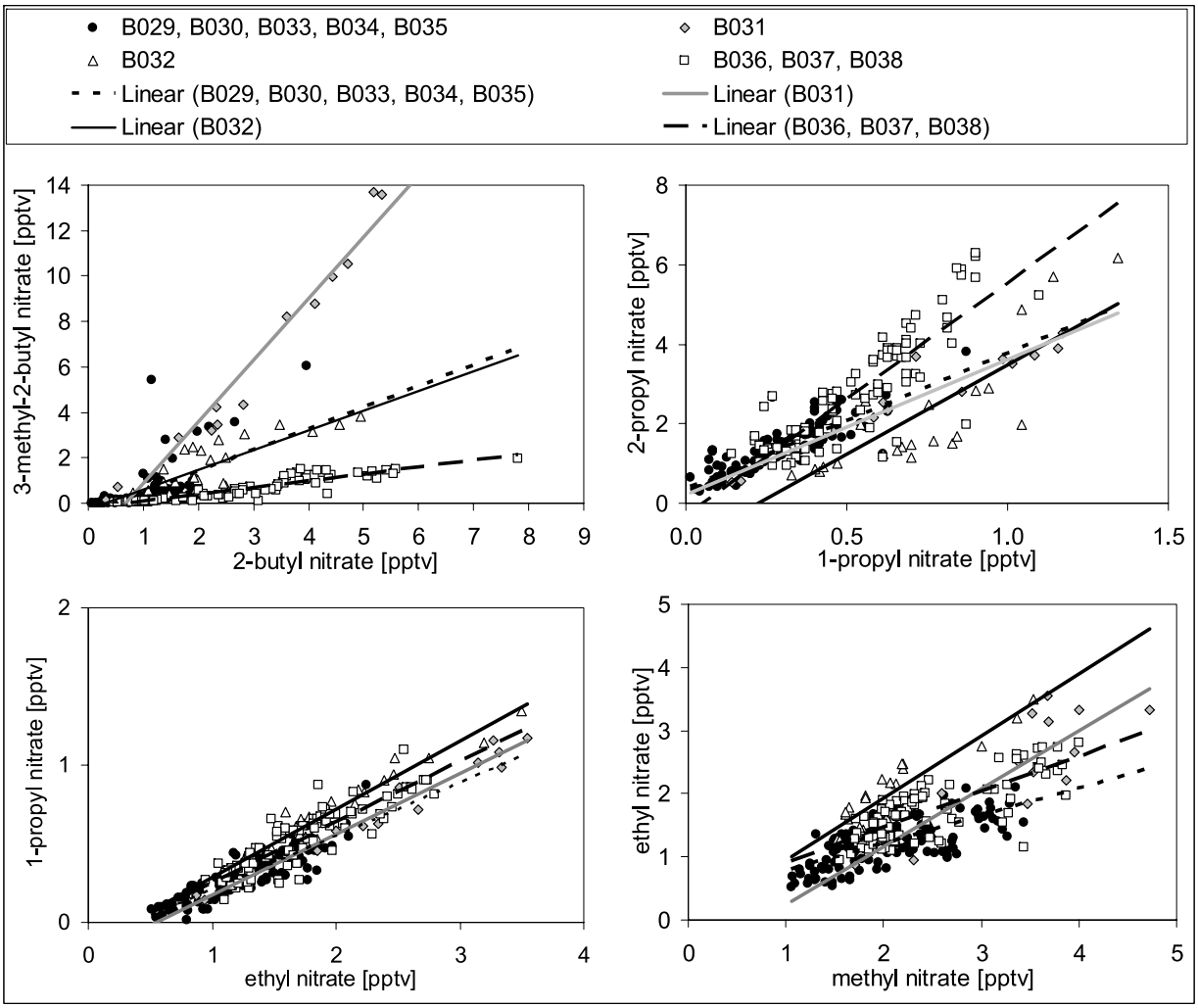

Figure 4. Relationships between pairs of alkyl nitrates for four sets of ITOP flights.

have sampled air from the N.E. United States and showed elevated alkyl nitrate concentrations in particular those of 2-propyl nitrate and 2-butyl nitrates; and B029, B030, B033, B034 and B035, the remaining flights, which predominantly sampled air with low concentrations of alkyl nitrates and contained most of the air classified above as "marine" (see Figure 2).

[21] The poorest correlation coefficients were found for flights B029, B030, B033, B034 and B035. This may be because more samples are included in this group possibly giving a larger variety of air masses, or because the concentrations of alkyl nitrates were generally low in these flights.

[22] For flight B032 (Alaskan fire plume) on the whole there were good correlations between methyl, ethyl, 1-propyl, 2-propyl and 2-butyl nitrates ($0.79 \leq r \leq 0.98$). The pentyl nitrates were well correlated with each other ($r = 0.90$), but exhibited weaker correlations with the other alkyl nitrates (e.g., $r = 0.31$ and 0.26 for 2 + 3-pentyl nitrates with methyl nitrate and 2-propyl nitrate, respectively).

[23] For flight B031 (N. York plume) there was a very good correlation between all alkyl nitrates ($0.88 \leq r \leq 1.00$) except for methyl nitrate. The pentyl nitrates and 2-butyl nitrate were highly correlated with each other ($0.96 \leq r \leq 1.00$).

[24] Flights B036, B037 and B038 exhibited a similar pattern of correlation to flight B031, with very good correlations between all alkyl nitrates ($0.76 \leq r \leq 0.96$) except for methyl nitrate, although the correlation coefficients were slightly poorer, presumably because of the wider range of air masses sampled and mixing with surrounding air masses. The pentyl nitrates and 2-butyl nitrate were highly correlated with each other ($0.93 \leq r \leq 0.96$).

[25] Although the correlation patterns between the alkyl nitrates were similar for B031 and for B036, B037 and B038, the ratios between the alkyl nitrates were sometimes very different (Figure 4) (Table 2). The most obvious difference is between the pentyl nitrates and the other nitrates, illustrated by the relationships between 3-methyl-2-butyl nitrate and 2-butyl nitrate (Figure 4, top left), with a gradient of 2.71 for B031 and only 0.30 for flights B036, B037 and B038. This clearly suggests that although the precursor species for the pentyl nitrates and the C_2-C_4 alkyl nitrates may be strongly related, their ratio may be different in some source regions within the N.E. of the United States. There is little NMHC data with which to confirm this, because for flight B031 for which there are measurements of alkyl nitrates all but 1 sample was below the detection limit for i-pentane. However, this one data point does agree

Table 3. Kinetic Data Relating to the Formation of Alkyl Nitrate Precursor Peroxy Radicals From Parent Hydrocarbon

RH	k_1^a ($\times 10^{-12}$ cm^3 molecule^{-1} s^{-1})	RO_2	α_1	α_3	k_5^a ($\times 10^{-12}$ cm^3 molecule^{-1} s^{-1})	j_4^b ($\times 10^{-6}$ s^{-1})
Ethane	0.248	ethyl	1	0.014[c,d]	0.18	0.73[e,f,g]
Propane	1.09	2-propyl	0.727[h]	0.042[i]	0.29	1.10[e,f,g]
Propane	1.09	1-propyl	0.272[h]	0.02[d,i]	0.58	0.77[e,g]
n-butane	2.36	2-butyl	0.855[j]	0.084[k]	0.86	0.91[e,f]
n-pentane	3.8	2-pentyl	0.568[l]	0.106[k]	1.7	1.2[f]
n-pentane	3.8	3-pentyl	0.349[l]	0.126[k]	1.0	1.2[f]
i-pentane	3.6	3-methyl-2-butyl	0.285[l]	0.141[m]	1.7	1.2[n]

[a]*Atkinson and Arey* [2003].
[b]Photolysis rates are for 40°N, 5 km altitude, 1 July and 24 hour averages.
[c]*Ranschaert et al.* [2000].
[d]*Atkinson et al.* [1982].
[e]*Clemitshaw et al.* [1997].
[f]*Roberts and Fajer* [1989].
[g]*Zhu and Kellis* [1997].
[h]*Droege and Tully* [1986a].
[i]*Carter and Atkinson* [1989].
[j]*Droege and Tully* [1986b].
[k]*Arey et al.* [2001].
[l]*Kwok and Atkinson* [1995].
[m]Master Chemical Mechanism [*Jenkin et al.*, 1997; *Saunders et al.*, 1997, 2003].
[n]Assumed the same photolysis rate as for the 2- and 3-pentyl nitrates.

with the above conclusion since the ratio between i-pentane and n-butane was 0.99 compared to an average of 0.33 for flights B036, B037 and B038.

[26] Since 1-propyl nitrate and 2-propyl nitrate both have the same parent hydrocarbon (propane), they should exhibit good correlations with each other. Further the ratio of 2-propyl nitrate to 1-propyl nitrate close to source should be around 5.6 on the basis of the abstraction ratios for the reaction of OH with propane and the branching ratios of the subsequent reactions of the peroxy radicals with NO (α_1 and α_3 in Table 3). The data from ITOP exhibit reasonably good correlations (Table 2 and Figure 4, top right). The gradient for flights B036, B037 and B038 is 5.9, very similar to that predicted from the kinetics, while the gradients for some of the other flight groups are as low as 3.4. This could be explained by an additional source of 1-propyl nitrate other than propane.

[27] Interestingly 1-propyl nitrate is correlated more strongly with ethyl nitrate than with 2-propyl nitrate and the ratios between 1-propyl nitrate and ethyl nitrate are more consistent between flights (Table 2 and Figure 4, bottom left). This suggests similar emission ratios of precursor species (e.g., ethane and propane) from different sources (e.g., automobile exhaust or biomass burning) or a single widespread source, perhaps a common precursor species.

[28] The correlation between ethyl nitrate and methyl nitrate shows reasonably good agreement, but the ratio between these nitrates varies between flights (Figure 4, bottom right). This is consistent with some commonality in sources, but with different sources having different emission characteristics (e.g., from the ocean or from precursor species emitted in automobile exhaust or biomass burning). Variations in ratios of ethyl nitrate to methyl nitrate have been used to distinguish between marine air and urban/industrial air [*Blake et al.*, 2003; *Simpson et al.*, 2003]. Flights B029, B030, B033, B034 and B035 had the lowest gradient (ethyl nitrate/methyl nitrate) (although poorest correlation coefficient), which is consistent with the fact that most of the marine air sampled in ITOP was during these flights. On occasions (e.g., flights B033 and B034) methyl nitrate was also observed at greater concentrations in the marine boundary than in the free troposphere. This suggests that while the oceanic source may have had an influence on the methyl nitrate, its impact on ethyl nitrate (and by correlation, 1-propyl nitrate) is less clear. The ITOP data suggest that the air sampled during the campaign was not strongly influenced by an oceanic source of alkyl nitrates. This is consistent with concentrations of alkyl nitrates in the temperate waters of the North Atlantic being close to equilibrium with the overlying atmosphere [*Chuck et al.*, 2002].

3.3. Relationship Between Alkyl Nitrates and Their Parent Alkane

[29] *Bertman et al.* [1995] derived a simple relationship between alkyl nitrates and their parent alkanes (RH). The alkanes react with OH to form alkyl radicals (R·), which rapidly react with oxygen to form an alkyl peroxy radical (ROO·).

$$RH + \cdot OH \rightarrow R\cdot + H_2O \quad (1)$$

$$R\cdot + O_2 \rightarrow ROO\cdot \quad (2)$$

When the alkyl peroxy radical reacts with NO it can either lose an oxygen atom to form an alkoxy radical (RO·) or bond with the NO to form an alkyl nitrate ($RONO_2$).

$$ROO\cdot + NO \rightarrow RO\cdot + NO_2 \quad (3a)$$

$$ROO\cdot + NO \rightarrow RONO_2 \quad (3b)$$

The alkyl nitrates are lost through photolysis and reaction with OH

$$RONO_2 + h\nu \rightarrow RO\cdot + NO_2 \quad (4)$$

$$RONO_2 + OH \rightarrow \text{ products} \quad (5)$$

Assuming that the only source of the alkyl nitrate is from its parent hydrocarbon, that the reaction of the alkane with OH (reaction 1) is the rate determining step in the formation of the alkyl nitrate and that no peroxy radical self reactions take place (i.e., NO rich atmosphere) then the rate of formation and loss of the alky nitrates can be summarized as the following:

$$\mathrm{RH} \rightarrow \mathrm{RONO2} \quad \text{at rate } \beta k_A \text{ where } k_A = k_1[\mathrm{OH}], \beta = \alpha_1.\alpha_3 \tag{6}$$

$$\mathrm{RONO2} \rightarrow \text{ products} \quad \text{at rate } k_B \text{ where } k_B = j_4 + k_5[\mathrm{OH}] \tag{7}$$

where k_1 is the rate of reaction 1, α_1 represents the proportion of the alkane that forms the particular alkoxy isomer, [OH] is the molecular density of OH, α_3 is the branching ratio of reaction 3 that forms the alkyl nitrate, j_4 is the photolytic loss rate of the alkyl nitrate and k_5 the rate of reaction 5. A relationship between the alkyl nitrates and their parent hydrocarbon concentrations as a function of time (t) can be described by the following equation [*Bertman et al.*, 1995]:

$$\frac{[\mathrm{RONO_2}]}{[\mathrm{RH}]} = \frac{\beta k_A}{(k_B - k_A)} \cdot (1 - e(k_A - k_B)t) + \frac{[\mathrm{RONO_2}]_0}{[\mathrm{RH}]_0} \cdot e(k_A - k_B)t \tag{8}$$

where $[\mathrm{RONO_2}]_0$ and $[\mathrm{RH}]_0$ are the initial concentrations of the alkyl nitrate and parent hydrocarbon respectively. Further, if it is assumed that the concentration of the alkyl nitrate is initially zero (i.e., no direct emissions), then the relationship between the alkyl nitrates and their parent hydrocarbon can be simplified as follows [*Bertman et al.*, 1995]:

$$\frac{[\mathrm{RONO_2}]}{[\mathrm{RH}]} = \frac{\beta k_A}{(k_B - k_A)} \cdot (1 - e(k_A - k_B)t) \tag{9}$$

Note that mixing with surrounding air is ignored in equations (6) and (7). This simplification is made on the assumption that when looking at ratios in equations (8) and (9) mixing will affect the alkyl nitrate and parent hydrocarbon similarly.

[30] Using the kinetic data in Table 3, the ratio between the parent hydrocarbon and the alkyl nitrate can be calculated with equation (9) for various times of t, assuming an average concentration of OH. By plotting ratios of alkyl nitrate to parent hydrocarbon concentrations against each other the observed data can be compared to the values derived from the kinetic data (Figure 5). On the basis of a study of the ICARTT Lagrangian experiment [*Arnold et al.*, 2007] a value of 2×10^6 molecules cm^{-3} has been assumed for [OH] for curves in Figure 5 and the points that equate to values of 1 day and 10 days for t are marked. The overall position of the line is not sensitive to the value of OH, but processing times are shifted along the line.

[31] In general, the observed data agrees reasonably well with the kinetic curves, which is somewhat surprising given the various assumptions made above and the uncertainties in the measurements. The main difference between the ITOP data set and that of previous studies is that it spans a greater extent of the kinetic curve, such that the agreement or deviations can be examined over a wider range of photochemical ages (from <1 day to nearly 10 days given the value of OH used). The mean NO concentration observed during ITOP (20 ± 31 pptv [*Lewis et al.*, 2007]) is below the limit of 100–200 pptv at which the efficiency of the alkyl nitrate formation is reduced because of competition between the reaction of ROO· with NO and ROO· self/cross reactions [*Roberts et al.*, 1998]. Also the concentrations of the hydrocarbons were often close to the detection limit, particularly for the longer-chain hydrocarbons, thus increasing the uncertainty in the calculated ratios. In fact the concentrations of the larger parent hydrocarbons were often below the detection limit, hence the reduced number of data points for these compounds.

[32] In all but one of the plots in Figure 5, the ratio of 2-butyl nitrate to n-butane is used on the *x* axis, because it is thought that the only significant source of butyl nitrate is from n-butane [*Roberts et al.*, 1998]. In such plots many of the data points for the ratios of ethyl nitrate and 1-propyl nitrate to their parent hydrocarbons (Figure 5, top) are above the theoretical curves, particularly those points with ratios that are indicative of less photochemically processed air. This is consistent with studies over N. America [*Bertman et al.*, 1995; *Roberts et al.*, 1998; *Stroud et al.*, 2001], which have suggested that this could be explained by sources of the alkyl nitrates other than from the parent hydrocarbon. *Simpson et al.* [2003] observed this for ethyl nitrate, but not 1-propyl nitrate, in Asian outflow over the Pacific. As discussed above (Figure 4), these alkyl nitrates exhibited a strong correlation with each other. If the ratio of these alkyl nitrates to their parent hydrocarbons are plotted against each other (Figure 5, middle left), there is also a very good correlation, showing that both these nitrates were often simultaneously enhanced relative to their parent hydrocarbon concentrations. This could be due to a common precursor, other than one of their parent hydrocarbons, for both these nitrates. This could be the fragmentation of a longer-chained hydrocarbon giving rise to a number of smaller peroxy radicals and subsequently smaller chain alkyl nitrates (e.g., a C_5 hydrocarbon leading to C_2 and C_3 alkyl nitrates). This finding appears to apply to all of the 4 different groups of flights, suggesting a widespread source of this precursor.

[33] A similar behavior is also seen for 2-propyl nitrate in that there are also a number of data points above the kinetic curve for the short photochemical processing times when plotted against the ratio of 2-butyl nitrate to n-butane (Figure 5, middle right), suggesting another source other than propane. Again this is consistent with previous studies elsewhere [*Bertman et al.*, 1995; *Roberts et al.*, 1998; *Simpson et al.*, 2003; *Stroud et al.*, 2001]. As discussed above the ratio of 2-propyl nitrate to 1-propyl nitrate, based simply on their relative formation rates from propane, should be around 5.6 close to source. Equation (9) also considers their loss rates and using the kinetic data in Table 3 and an OH concentration of 2×10^6 molecules cm^{-3} gives values for the ratio of 2-propyl nitrate to 1-propyl nitrate of 5.7 after 1 day of processing increasing to 6.3 at 10 days. Using an OH concentration of 1×10^6 molecules cm^{-3} leads to a ratio that barely changes such that by 10 days it is at a value of 5.5. Photochemical processing is therefore not expected to lead to a decrease in the ratio, closer to the value

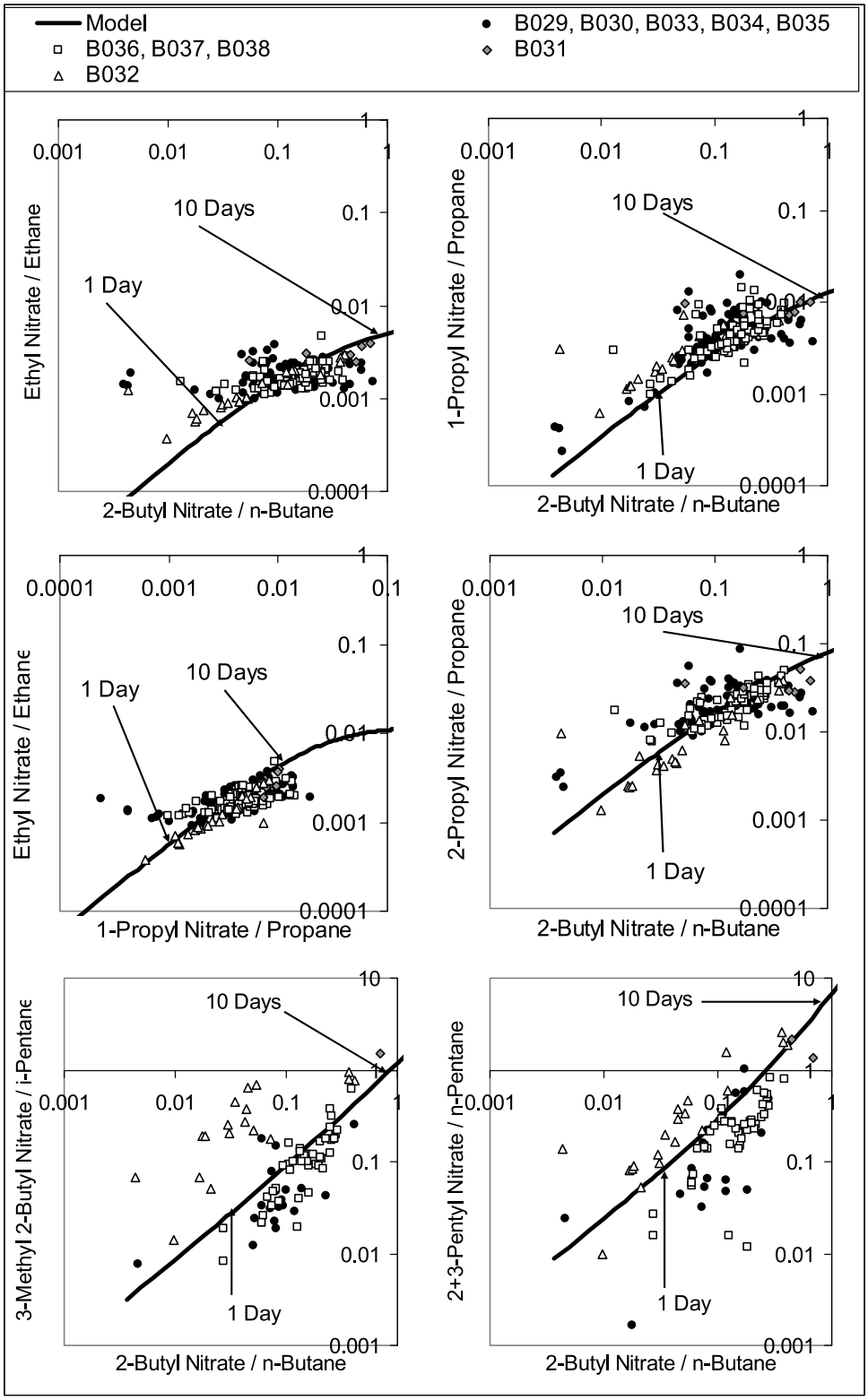

Figure 5. Relationships between various ratios of alkyl nitrates to their parent hydrocarbons. The observations are divided into four sets of flights. The model line is calculated using equation (9), data from Table 1 and an assumed concentration of OH of 2×10^6 molecules cm^{-3}. The points on the model curve that correspond to 1 and 10 days of photochemical processing are marked.

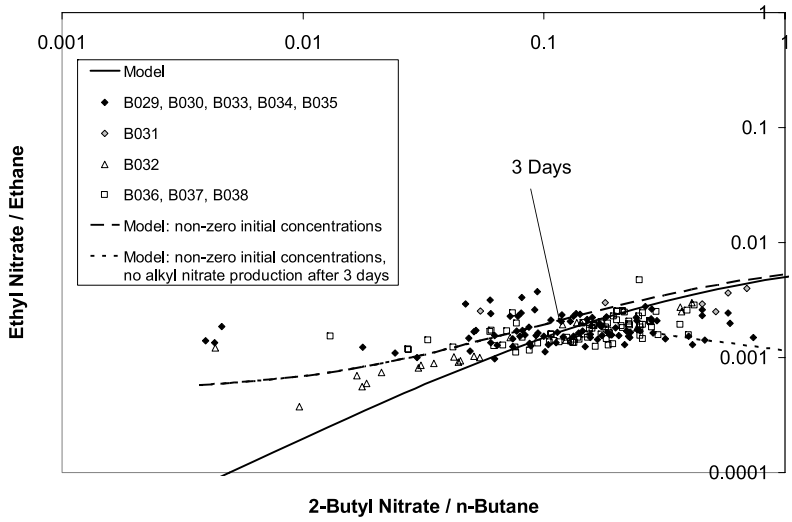

Figure 6. Relationships between the ratios of ethyl nitrate to ethane versus 2-butyl nitrate to n-butane. The observations are divided into four sets of flights. The model lines are calculated using equation (8) and data from Table 1 and an assumed concentration of OH of 2×10^6 molecules cm^{-3}. The solid model line assumes initial concentrations of the alkyl nitrates are zero (i.e., equation (9)). The dashed model line assumes that the initial ratio between ethyl nitrate and ethane is 0.05%. The dotted model line assumes that the initial ratio between ethyl nitrate and ethane is 0.05% and that no alkyl nitrate production occurs after 3 days (i.e., $\beta = 0$).

of 4 often observed. Thus plotting the ratios of 2-propyl nitrate and 1-propyl nitrate to propane against each other (not shown), which is essentially the same as plotting the ratios of the two propyl nitrates together, gives fairly good correlation, but with ratios of 2-propyl nitrate/propane to 1-propyl nitrate/propane that are often low compared to the kinetic curve. This is particularly so for flight B032 which sampled mostly fire plumes and for which the 2-propyl nitrate to 1-propyl nitrate ratio was often as low as 2. This is again consistent with an additional source of 1-propyl nitrate other than propane.

[34] Another reason for the deviations from the curve at the short photochemical processing times could be the presence of small initial concentrations of the alkyl nitrates. This is illustrated in Figure 6 for ethyl nitrate where an additional model line has been added that corresponds to an initial ratio between ethyl nitrate and ethane of 0.05% (equation (8)). This certainly improves the fit to the observed data prior to 3 days of photochemical processing and the same can be said for the 1-propyl and 2-propyl nitrates. This is consistent with these shorter-chain nitrates having lifetimes such that they are almost always observed to have concentrations significantly above zero (i.e., above detection limit) (Table 1). It could also indicate a primary source of these alkyl nitrates [*Bertman et al.*, 1995].

[35] It is also noticeable for the ethyl, 1-propyl and 2-propyl nitrates that at the longer processing times their ratios to their parent hydrocarbons are often below the theoretical curves (Figure 5, top). It should be noted that equation (8) and (9) assume that there is sufficient NO present for the rate determining step of the formation of the alkyl nitrate to be the loss of the parent hydrocarbon. In Figure 6 there is a third model line calculated from equation (8) but with β set to zero on the basis of the assumption that the formation of the alkyl nitrate ceases after 3 days of processing. The observed data tends to be spanned by the model lines suggesting reality is somewhere in between depending on the relative importance of the reaction of the peroxy radicals with NO (reaction 3) or themselves.

[36] As described above, equation (9) assumes mixing will affect the alkyl nitrate and parent hydrocarbon similarly. However, for the short-chain alkyl nitrates (e.g., ethyl), where the lifetime of the alkyl nitrate is shorter than for the parent hydrocarbon (i.e., $k_B > k_A$), mixing in of older air masses will cause a decrease in the ratio of alkyl nitrate to parent hydrocarbon [*Roberts et al.*, 1998]. Since $k_A > k_B$ for 2-butyl nitrate, when ethyl nitrate/ethane is plotted against 2-butyl nitrate/n-butane (Figure 6), mixing could also explain points being below the kinetic curve at the longer processing times. For 1-propyl nitrate and 2-propyl nitrate the relative sizes of k_A and k_B are sensitive to the OH value and assumed photolysis loss rates for the alkyl nitrates. Using the rates in Table 3, an OH concentration equal to 1×10^6 molecules cm^{-3} leads to $k_B > k_A$, where as for OH equal to 2×10^6 molecules cm^{-3} $k_A > k_B$. Thus the sign of the change in the ratio of the propyl nitrates to propane is dependent on the concentration of OH.

[37] The concentrations of the C_4 and smaller alkyl nitrates are not particularly elevated in the smoke plumes of flight B032, despite their parent hydrocarbons (ethane, propane and n-butane) being significantly elevated above background concentrations. This gives low alkyl nitrate to parent hydrocarbon ratios suggesting that the smoke plumes are not well processed photochemically. This is consistent with the observations of ozone, which are not elevated in these samples while the CO concentrations are very high (Figure 2), and with high concentrations of ethylene persisting in these plumes [*Lewis et al.*, 2007]. On the other hand the pentyl nitrates are elevated in concentration along with the pentanes in these samples. This gives rise to ratios above

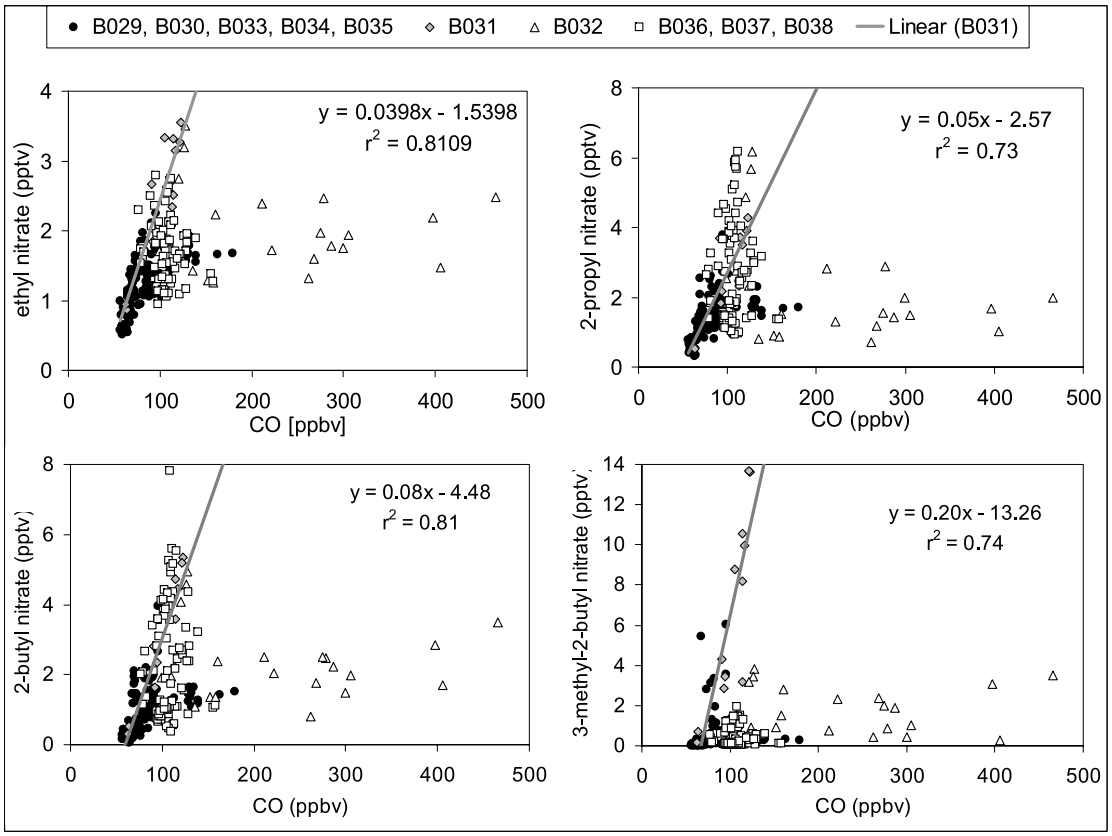

Figure 7. Relationships between various alkyl nitrates and CO for four sets of ITOP flights. The trend lines and r^2 values are for flight B031 only.

the kinetic curve when plotted against the ratio of 2-butyl nitrate to n-butane (Figure 5, bottom). Since the parent hydrocarbon is expected to be the only source of the pentyl nitrate, it is not clear why the pentyl nitrates appear to be being produced more efficiently in these plumes than the smaller alkyl nitrates.

[38] While the pentyl nitrate data for flight B032 is mostly elevated relative to the pentanes, the reverse is true for the data from the other flights with data points falling below the kinetic curve in Figure 5. This cannot be explained by low NO concentrations leading to no or insignificant formation of the alkyl nitrates. This is because, if there is no further formation of the alkyl nitrates, then their ratios to their parent hydrocarbons is simply a function of the relative lifetimes of the alkyl nitrates to those of their parent hydrocarbons (i.e., k_B relative to k_A). Since the lifetimes of the pentyl nitrates relative to their parent hydrocarbons are greater than that of 2-butyl nitrate to its parent, this would lead to higher ratios of the pentyl nitrates to the pentanes relative to the ratio of 2-butyl nitrate to n-butane. One possible explanation for the data falling below the kinetic curve might be the fragmentation of the pentanes leading to smaller chain peroxy radicals and subsequently smaller chain alkyl nitrates, instead of the pentyl nitrates.

[39] Unfortunately only a few of the air samples collected during flight B031 were analyzed for both hydrocarbons and alkyl nitrates. For those that exist the alkyl nitrate to parent hydrocarbon ratios are often relatively large suggesting photochemically processed pollution. In theory, using equation (9), calculated ratios of alkyl nitrate to parent hydrocarbon will either continue to increase indefinitely if $k_A > k_B$ (i.e., the lifetime of the alkyl nitrate is greater than the lifetime of the parent hydrocarbon) or increase toward a constant value ($\beta k_A/(k_B - k_A)$) if $k_B > k_A$ (i.e., the lifetime of the parent hydrocarbon is greater than the lifetime of the alkyl nitrate). However, the concentrations of the hydrocarbons decrease to a point where they become below the detection limit of the analytical system. Thus, in practice the samples that appear to be the most photochemically processed, may be those that initially contained the highest burden of parent hydrocarbons.

3.4. Relationship Between Alkyl Nitrates and CO

[40] When the ITOP campaign is considered as a whole the alkyl nitrates showed poor correlations with CO (Figure 7). This differs from that which was observed at Chebogue Point, Nova Scotia on the west coast of the Atlantic, where the r^2 value for the correlation between CO and $\Sigma RONO_2$ was 0.81 [*Roberts et al.*, 1998]. *Stroud et al.* [2001] observed good correlation between the CO and alkyl nitrates in pollution plumes as they were transported from North America to the North Atlantic. Similarly, flight B031, which targeted pollution from the New York region, showed good correlation with CO. It is notable that in flight B032 when the CO concentration reached up to 600 ppb in an Alaskan fire plume that the alkyl nitrates did not show any corresponding increase. This is in agreement with the lack

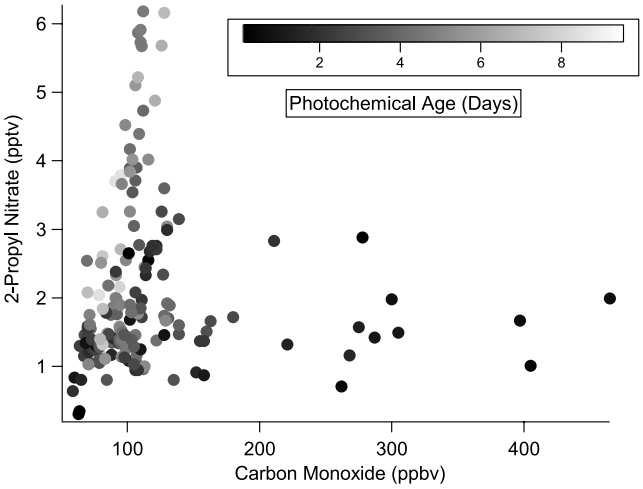

Figure 8. Relationship between 2-propyl nitrate and CO, shaded according to photochemical age as calculated from the ratio of 2-butyl nitrate to n-butane.

of a positive relationship between CO and ozone in these fire plumes.

[41] Using equation (9), one can calculate a photochemical age t from the observed ratios of the alkyl nitrate to its parent hydrocarbon. Figure 8 shows the relationship of 2-propyl nitrate to CO shaded by the photochemical age calculated from the 2-butyl nitrate to n-butane ratio. There is a tendency for the data points which exhibit a lower 2-propyl nitrate to CO ratio to be the less photochemically aged air, which partially explains the scatter seen in the alkyl nitrate to CO plots. It is probable that the age of air sampled at Chebogue Point was less variable than that sampled during ITOP, and hence the better correlation of the alkyl nitrates with CO.

3.5. Lagrangian Experiment

[42] Part of the ICARTT project was aimed at carrying out a Lagrangian experiment (ICARTT Lagrangian-2K4 Experiment). *Methven et al.* [2006] describes how this was done and defines several Lagrangian connections that involved the BAe-146 aircraft sampling air previously sampled by either the NOAA WP-3D or the NASA DC-8 aircraft. *Arnold et al.* [2007] used the concentrations of the nonmethane hydrocarbons in several of these cases to estimate the mean OH and the air mass dilution rates. Following this a box model has been set up to examine the evolution of the alkyl nitrates and their parent hydrocarbon with time. It essentially uses equation (6) and (7) to describe the loss of the parent hydrocarbon and the formation and loss of the alkyl nitrates, along with OH as estimated by *Arnold et al.* [2007]. In addition equation (10) is used to take account of the mixing with background air.

$$dX/dt = -\mathrm{K}(\mathrm{X} - \mathrm{X_b}) \tag{10}$$

where X is the concentration of the alkyl nitrate or hydrocarbon, X_b is the background concentrations of X, and K is the mixing rate (s^{-1}) for each case study as determined by *Arnold et al.* [2007]. Each model run was initialized by concentrations of the alkyl nitrates and parent hydrocarbons as observed by the upwind aircraft. X_b was taken to be the median concentrations observed by the BAe-146 for all flights.

[43] Figures 9–14 compare the observed concentrations of the various alkyl nitrates, their parent hydrocarbons and the ratio between the alkyl nitrates and their parents with those calculated in various model runs for Lagrangian cases 1, 2 and 5 as defined by *Methven et al.* [2006]. *Arnold et al.* [2007] used a "concentration" method to estimate the mean OH, which also considered the rate of mixing of the air mass with surrounding air. Thus optimum values for both OH and K were determined, along with uncertainty ranges represented by the 25th and 75th percentiles. Cases 1 and 5 both involved sampling of the air mass by the BAe-146 on two different days. *Arnold et al.* [2007] treated these as separate Lagrangian connections and thus determined OH concentrations and mixing rates for each case separately (i.e., case 1a, case 1b, case 5a and case 5b). For cases 1 and 5, the alkyl nitrate model was run using the values of OH and K from 1a and 5a, respectively. The values for 1b and 5b did not differ greatly from these.

[44] Case 1 involved sampling an air mass on three occasions: the DC-8 on 15 July (day 197), the BAe-146 on 19 July (B031, day 201) and again on 25 July (B034, day 207). The air mass received emissions from the New York region. By 25 July it had almost reached the Portuguese coast before returning westward toward the Azores. Figures 9 and 10 show that, within the uncertainty range of the optimum values of OH and K as determined for case 1a, the downwind concentrations of propyl nitrate and 2-butyl nitrate observed on day 201 (case 1a) can be reproduced. By day 207 (case 1b) the observed concentrations of propyl nitrate are lower than calculated, although the observed and calculated concentrations of 2-butyl nitrate are in reasonably good agreement. The model does a good job of reproducing the parent hydrocarbon concentrations and these concentrations are not very sensitive to the uncertainty in the values of OH and K (given by the 25th and 75th percentile ranges). These results suggest that the overprediction of the propyl nitrate on day 207 is not likely to be due to unaccounted mixing. A possible reason for this overprediction could be that the production rate of the alkyl nitrates might have been reduced by the concentration of NO falling to a level at which the reaction of peroxy radicals with NO do not dominate the self/cross reaction of the peroxy radicals. This is entirely consistent with the mean concentration of NO observed by the BAe-146 in the Lagrangian air mass on days 201 and 207 being only 23 pptv and 6 pptv, respectively. To illustrate this, a model run was performed in which it was assumed that the concentration of NO went to zero on day 201 and the production of the alkyl nitrates stopped. This captures the 1-propyl nitrate concentration and its ratio to propane on day 207. The concentration of 2-butyl nitrate was little affected by this change since n-butane had reached sufficiently low concentrations by day 201 that, even assuming that all the peroxy radicals reacted with NO, the production of 2-butyl nitrate was small compared to its loss rate. The calculated ratio of 2-butyl nitrate to n-butane is larger than observed, but this really illustrates that when the concentrations of alkyl nitrates and their parent hydrocarbons become low, small absolute errors can lead to large errors in the ratios.

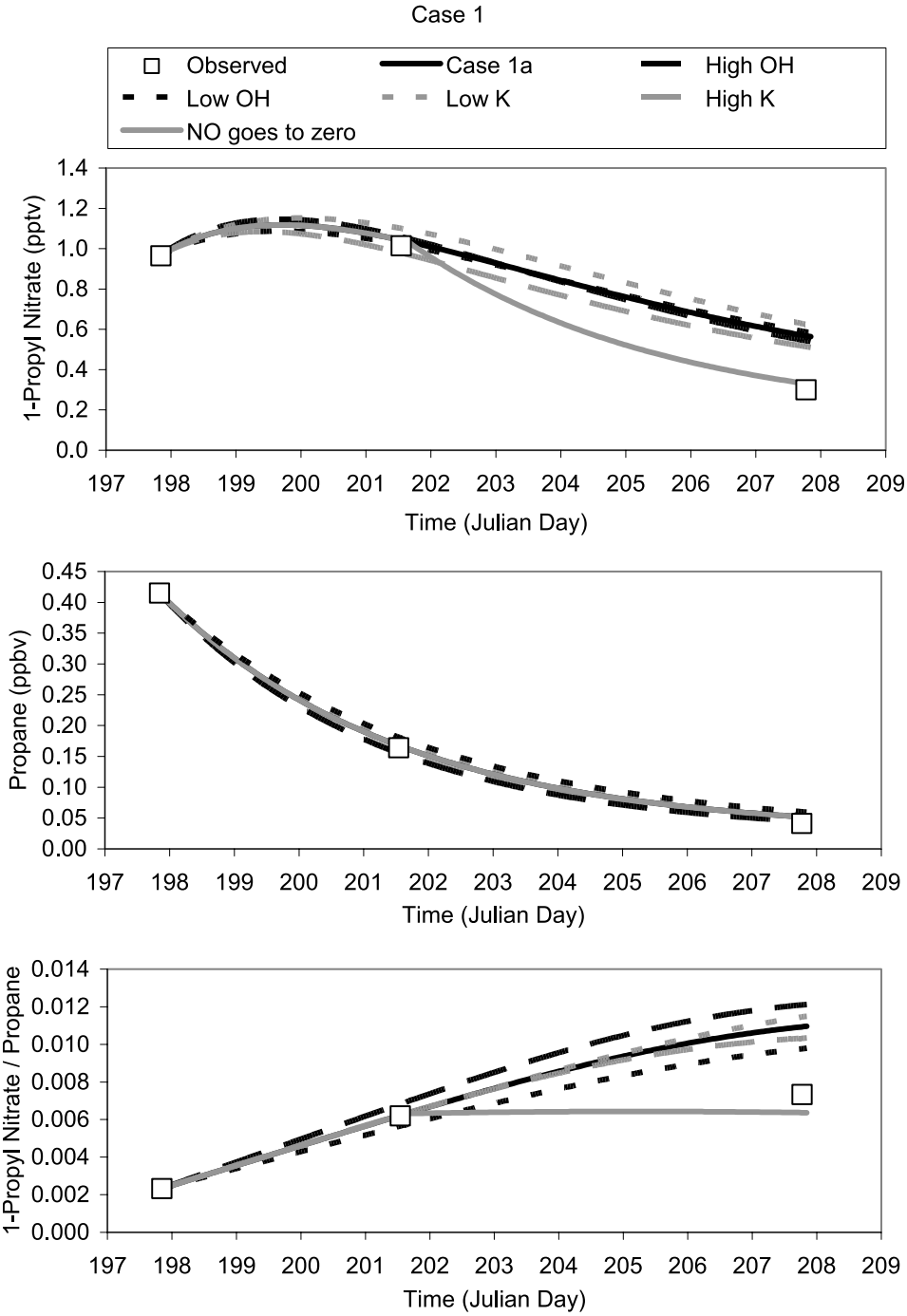

Figure 9. Time evolution of 1-propyl nitrate, its parent hydrocarbon (propane), and the ratio between them for the Lagrangian case 1. Case 1a uses the median of the optimum values of OH and K [*Arnold et al.*, 2007], high OH uses the 75th percentile for OH, low OH uses the 25th percentile for OH, high K uses the 75th percentile for K, low K uses the 25th percentile for K, and NO goes to zero assumes zero NO from day 201 onward. The observed data represent the mean for the WAS samples taken during the time period identified as a Lagrangian match.

The agreement between the calculated and observed concentrations for ethyl and 2-propyl are qualitatively the same as described above for 1-propyl nitrate and those for 2 + 3-pentyl nitrates are similar to 2-butyl nitrate.

[45] Case 5 also involved the sampling of an air mass on three occasions: the WP-3D on 28 July (day 210), the BAe-146 on 31 July (B037, day 213) and again on 1 August (B038, day 214). The air mass received emissions from the eastern United States and was transported at low level by a frontal system. Figures 11 and 12 show the plots for case 5 for ethyl and 2-butyl nitrate. The observed concentrations for these two nitrates, and for 1-propyl, 2-propyl and 2 +

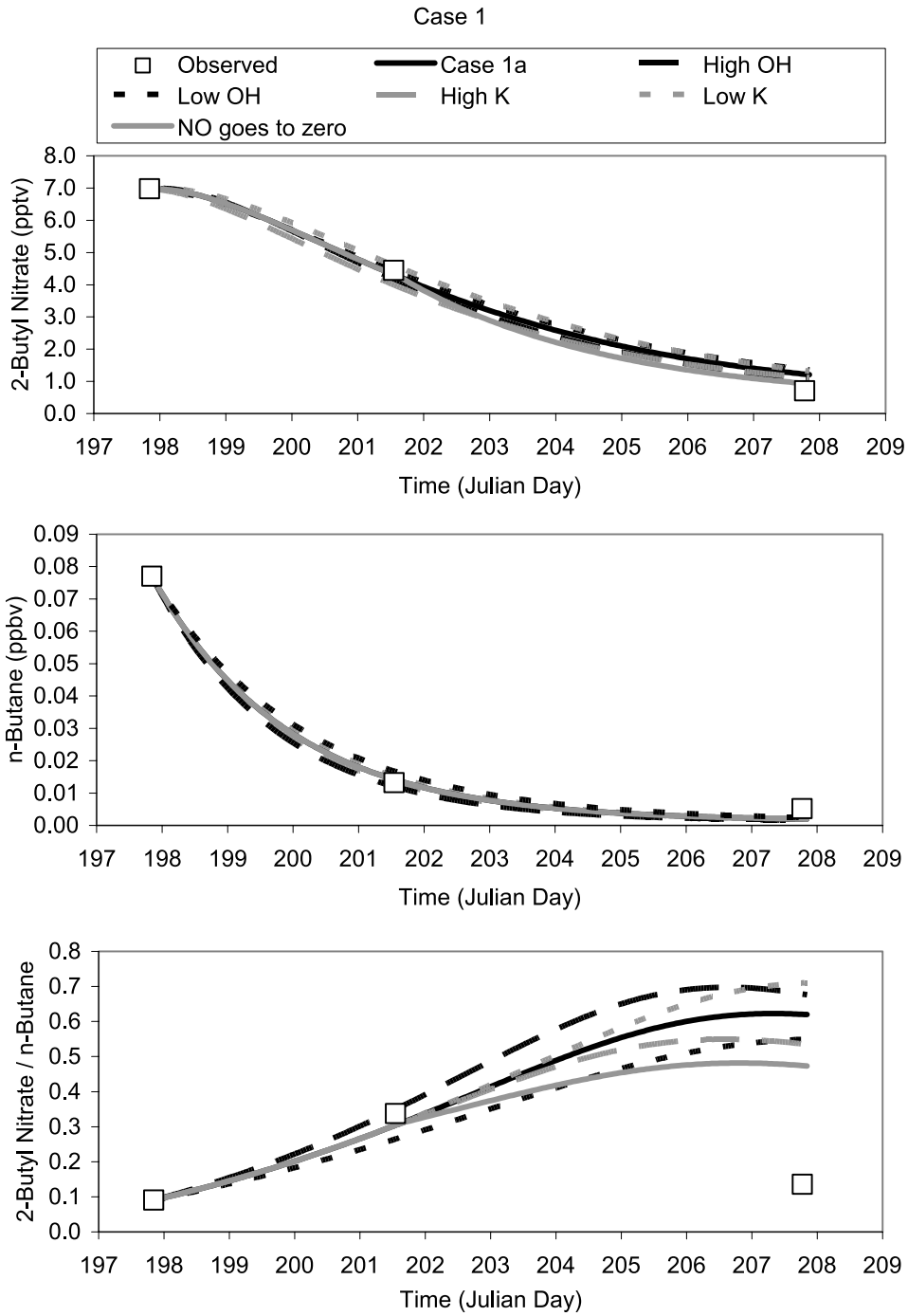

Figure 10. Time evolution of 2-butyl nitrate, its parent hydrocarbon (n-butane), and the ratio between them for the Lagrangian case 1. Case 1a uses the median of the optimum values of OH and K [*Arnold et al.*, 2007], high OH uses the 75th percentile for OH, low OH uses the 25th percentile for OH, high K uses the 75th percentile for K, low K uses the 25th percentile for K, and NO goes to zero assumes zero NO from day 201 onward. The observed data represent the mean for the WAS samples taken during the time period identified as a Lagrangian match.

3-pentyl nitrates, are qualitatively the same as case 1, in that the concentrations dropped rapidly between the second and third times of sampling. The concentrations of ethyl, 1-propyl and 2-butyl nitrates increased between days 210 and 213, but then fell considerably by day 214. Using the values of OH and K determined for case 5a the model captures the observed increase in ethyl nitrate and it produces an increase in 1-propyl nitrate, but slightly less than observed. It does not, however, simulate the increase in 2-butyl nitrate, the reason for which is unclear given that the model does a good job of reproducing the n-butane. Switching off the production of the alkyl nitrates by

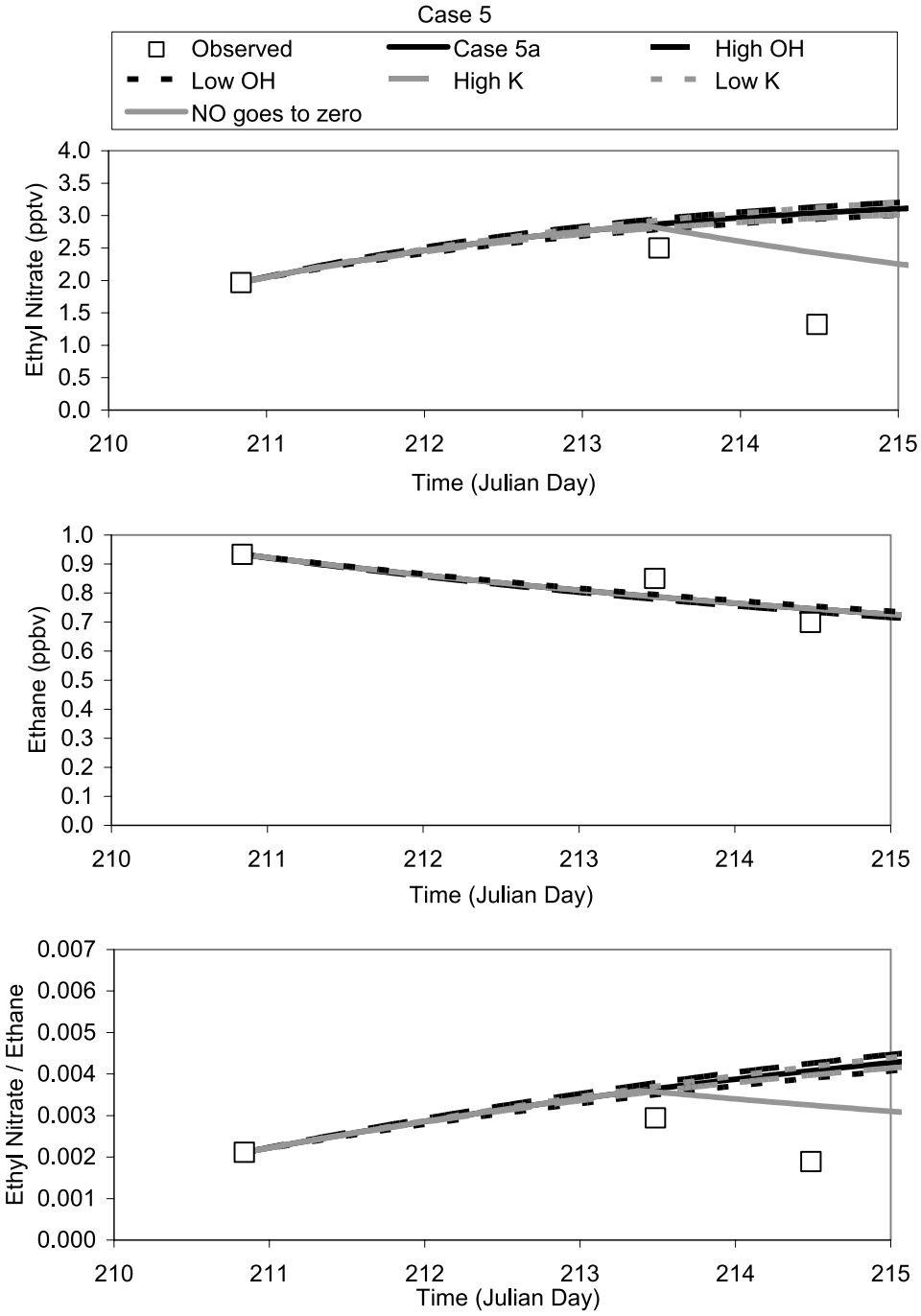

Figure 11. Time evolution of ethyl nitrate, its parent hydrocarbon (ethane) and the ratio between them for the Lagrangian case 5. Case 5a uses the median of the optimum values of OH and K [*Arnold et al.*, 2007], high OH uses the 75th percentile for OH, low OH uses the 25th percentile for OH, high K uses the 75th percentile for K, low K uses the 25th percentile for K, and NO goes to zero assumes zero NO from day 213 onward. The observed data represent the mean for the WAS samples taken during the time period identified as a Lagrangian match.

assuming NO goes to zero can also lead to a sharp decline in concentration between days 213 and 214. The mean concentration of NO observed by the BAe-146 in the Lagrangian air mass on day 213 and day 214 was only 14 pptv and 4 pptv, respectively, well below the 100–200 pptv level at which the efficiency of the alkyl nitrate formation is reduced [*Roberts et al.*, 1998].

[46] Case 2 involved the sampling of an air mass on two occasions: the DC-8 on 18 July (day 200), and the BAe-146 on 20 July (B032, day 202). The air mass sampled in this case was an Alaskan smoke plume with relatively high concentrations of hydrocarbons, some of which were greater in downwind samples. These plumes tended to be quite narrow and a small error in the Lagrangian matching is the

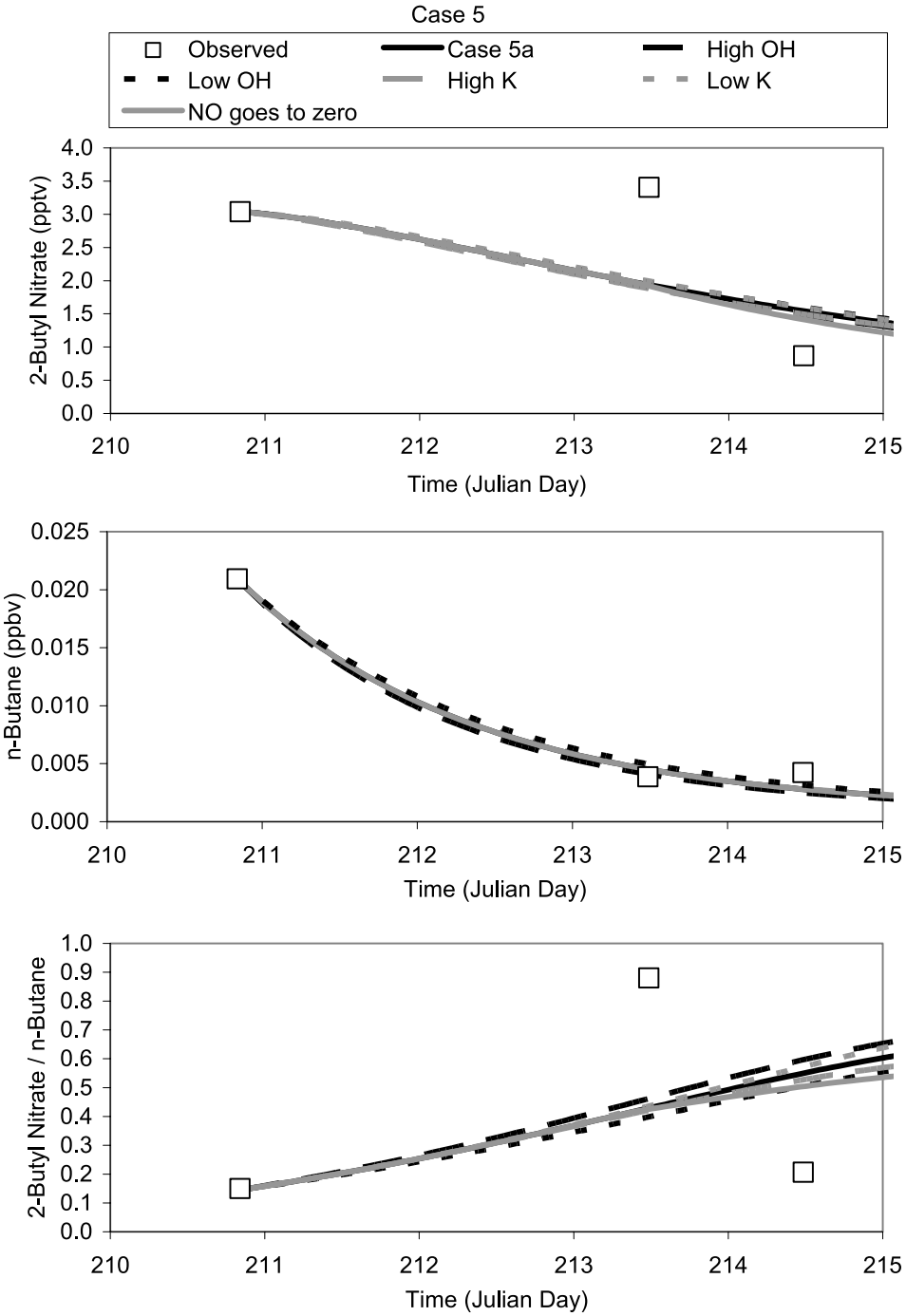

Figure 12. Time evolution of 2-butyl nitrate, its parent hydrocarbon (n-butane) and the ratio between them for the Lagrangian case 5. Case 5a uses the median of the optimum values of OH and K [*Arnold et al.*, 2007], high OH uses the 75th percentile for OH, low OH uses the 25th percentile for OH, high K uses the 75th percentile for K, low K uses the 25th percentile for K, and NO goes to zero assumes zero NO from day 213 onward. The observed data represent the mean for the WAS samples taken during the time period identified as a Lagrangian match.

most likely cause of this discrepancy. Despite some of the hydrocarbons increasing in concentration the alkyl nitrates all decreased in concentration. Using the values of OH and K determined for case 2 leads to an increase in alkyl nitrate concentrations, where as assuming no NO and switching off the alkyl nitrate production leads to a decline in concentration similar to that observed (Figures 13 and 14). Higher concentrations of parent hydrocarbons, similar to those observed, would only increase the calculated alkyl nitrate concentrations.

[47] Although the uncertainties in the values of OH and K are quite large [*Arnold et al.*, 2007] and thus so are the

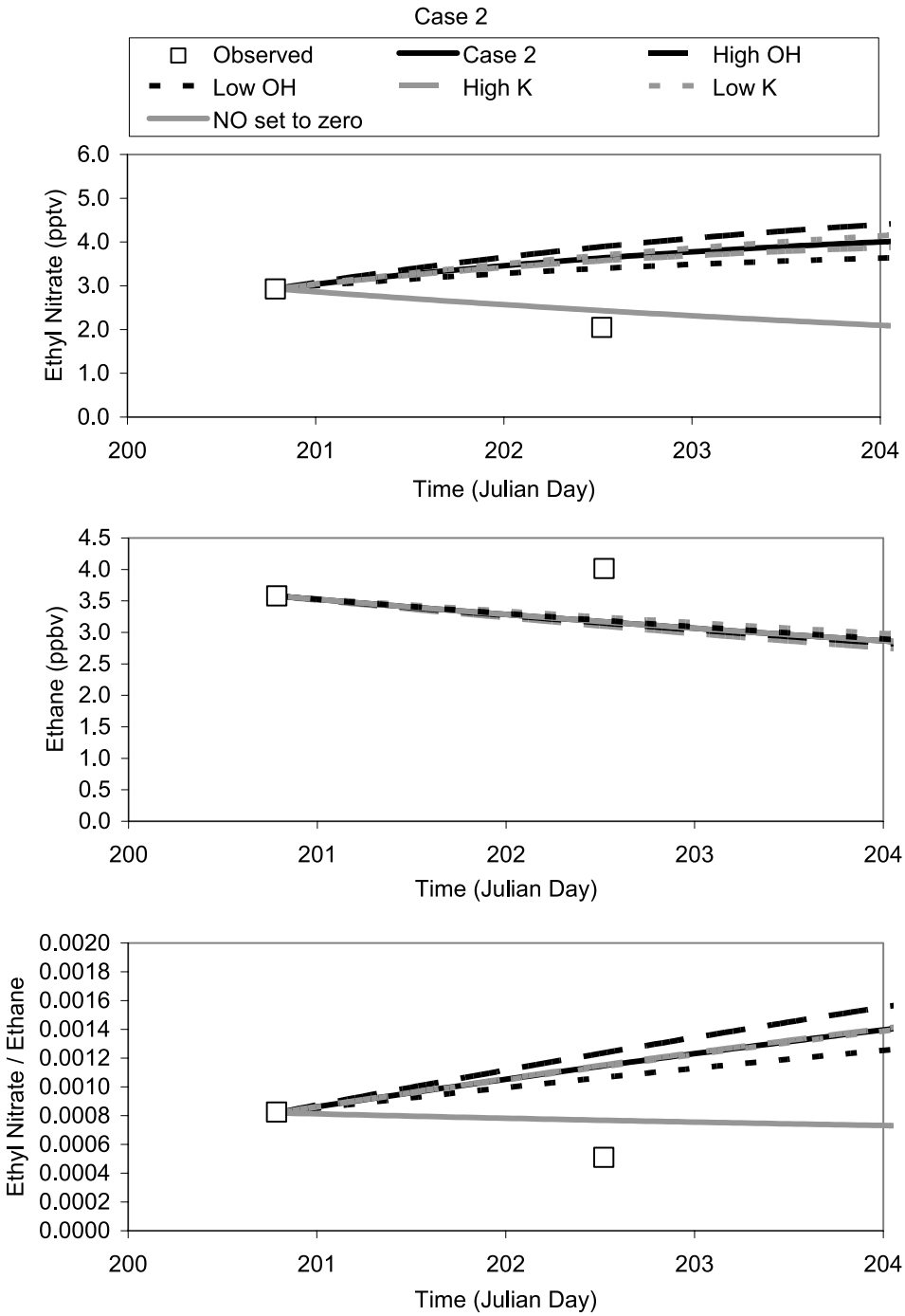

Figure 13. Time evolution of ethyl nitrate, its parent hydrocarbon (ethane) and the ratio between them for the Lagrangian case 2. Case 2 uses the median of the optimum values of OH and K [*Arnold et al.*, 2007], high OH uses the 75th percentile for OH, low OH uses the 25th percentile for OH, high K uses the 75th percentile for K, low K uses the 25th percentile for K, and NO set to zero assumes zero NO. The observed data represent the mean for the WAS samples taken during the time period identified as a Lagrangian match.

uncertainties in the calculated alkyl nitrate concentrations, these model runs produce results which corroborate some of the findings discussed above. Over the first few days of cases 1 and 5 the results suggest that the alkyl nitrates had been photochemical produced. This is consistent with the general agreement between the kinetic data and the hydrocarbon ratios (Figure 5), particularly at the shorter photochemical processing times. This implies that ozone had also been produced since one branch of the alkyl nitrate forming reaction (3) produces NO_2 (3a), which when photolyzed leads to ozone. However, after about 3 days the results suggest that the production of the alkyl nitrates may have

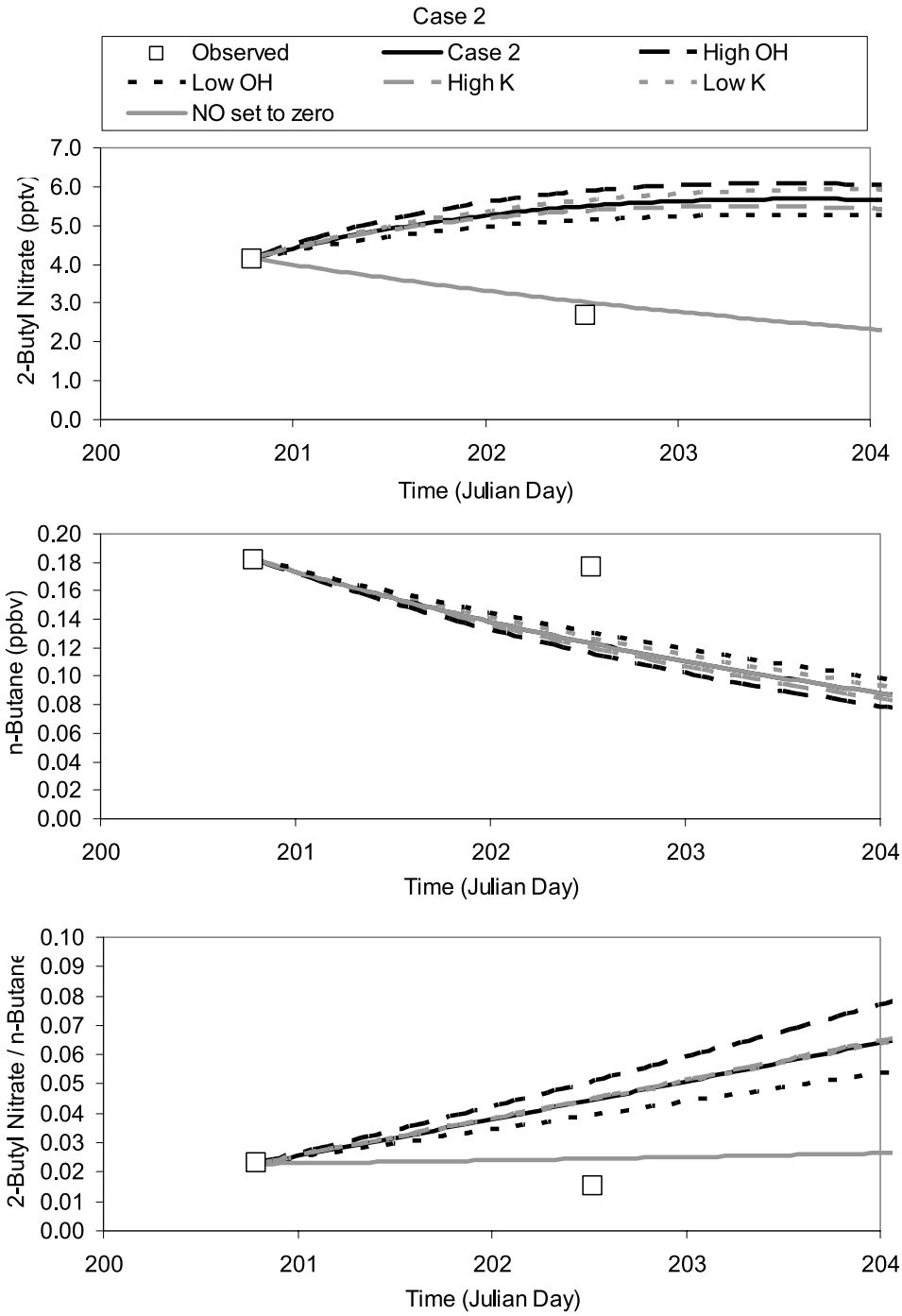

Figure 14. Time evolution of 2-butyl nitrate, its parent hydrocarbon (n-butane) and the ratio between them for the Lagrangian case 2. Case 2 uses the median of the optimum values of OH and K [*Arnold et al.*, 2007], high OH uses the 75th percentile for OH, low OH uses the 25th percentile for OH, high K uses the 75th percentile for K, low K uses the 25th percentile for K, and NO set to zero assumes zero NO. The observed data represent the mean for the WAS samples taken during the time period identified as a Lagrangian match.

been considerably reduced, again consistent with the relationship between the kinetic data and the alkyl nitrate to hydrocarbon ratios at the longer photochemical timescales (Figures 5 and 6). If these reductions in alkyl nitrates concentrations were due to net photochemical loss, as opposed to mixing, then the alkyl nitrates would have been a source of NO_X. Although the rate of ozone production may be low, in these remote regions of the N. Atlantic, where the NO concentrations are low, the balance between ozone production and destruction is highly sensitive to NO_X [*Reeves et al.*, 2002]. The mean NO observed during the ITOP flights was 20 pptv. Assuming an NO/NO_2 ratio of 1, typical of 5 km altitude over the mid-Atlantic [*Reeves et al.*, 2002], this equates to approximately 40 pptv of NO_X, which

coincidently was the NO_X compensation point for ozone production previously calculated for this altitude [*Reeves et al.*, 2002]. The mean concentration of the sum of the alkyl nitrates reported during ITOP is 10 pptv, which equates to an additional 25% of the observed NO_X. Thus the alkyl nitrate source of NO_X, albeit small, could contribute to maintaining ozone levels as the air undergoes long-range transport. The lack of photochemical production of the alkyl nitrates, and thus ozone, in case 2 is consistent with the alkyl nitrate to hydrocarbon ratios being small and the lack of correlation between the alkyl nitrates and CO in the smoke plumes (Flight B032).

4. Conclusions

[48] The alkyl nitrate concentrations observed during ITOP are typical of those found a few days downwind of precursor source regions. Although there is some evidence for an oceanic source of methyl nitrate, for the most part the air samples collected during ITOP do not appear to be strongly influenced by oceanic sources of the alkyl nitrates. Elevated concentrations were observed in air masses which have been influenced by emissions from the N.E. United States and from Alaskan fires. The large variations in ratios between the C_5 and C_2-C_4 nitrates suggest that emission ratios for the parent hydrocarbons vary between different regions of the N.E. United States.

[49] In general the alkyl nitrate data agrees well with photochemical theory. This suggests that at least during the first few days of transport from the source region photochemical production of alkyl nitrates had taken place. This implies that ozone production had also occurred. There also appears to be a widespread common source of ethyl nitrate and 1-propyl nitrate other than from their parent hydrocarbons. This might be from longer-chain hydrocarbons, possibly pentanes.

[50] The observations in the more photochemically processed air masses are consistent with the concentration of NO dropping to a point where the rates of the alkyl nitrate production reactions no longer dominate the peroxy radical self/cross reactions. However, in these low levels of NO, where the balance between ozone production and destruction is highly sensitive to NO_X, the alkyl nitrates might contribute to maintaining the ozone levels in air as it undergoes long-range transport.

[51] The observed patterns of the alkyl nitrates also suggest that the rates of photochemical processing in the Alaskan smoke plumes were small and that the rates of ozone formation in these air masses were low.

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