Tropospheric Aerosol Dynamics: Temporal and Spatial analysis of aerosol chemical properties and distributions from both Anthropogenic and Natural sources.

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Abstract

The lower troposphere sampled during KORUS was often characterized by impressive aerosol loading, mainly sulfates, nitrates, and organic aerosol. Near Seoul the contributions from inorganic ions, especially nitrate, frequently dominated. We examine the relationships between time of day, synoptic meteorology, gas phase precursors (e.g., SO_2, NO_x, HNO_3), O_3, and the aerosol-associated ions to explain the large variations of nitrates and sulfates in space and time that were observed throughout the KORUS study region. Long range transport of dust in the mid to upper troposphere often resulted in significant coarse nitrate, but it is less clear whether dust at lower altitudes similarly impacted the partitioning between HNO_3 and aerosol nitrate. Biomass burning smoke encountered on several flights caused a marked reduction in aerosol acidity, though simultaneous increases in concentration of all measured cations (Ca^{2+}, Mg^{2+}, Na^+, NH_4^+, and K^+) suggest that smoke may have mixed with dust in some cases. Aerosol collected in the polluted marine boundary layer were generally strongly acidic but some samples with enhanced seasalt outside of Asian outflow had higher pH.

Objectives

- Investigate the pH of atmospheric particles derived from filter based measurements on the DC-8 aircraft using the Isorropia II Thermodynamic Model (Fountoukis & Nenes, 2007).
- Determine the general and specific properties of pH anomalies; in general it has been found that atmospheric particles are highly acidic (pH 0-3)(Bougiatioti et al., 2016; H. Guo et al., 2015; Hongyu Guo et al., 2016; Weber, Guo, Russell, & Nenes, 2016).
- Investigate the temporal and spatial patterns in Ozone production along the Seoul Stereo-route.

Particle Acidity Results

Particle acidity was calculated using the Isorropia II Thermodynamic Model run in the forward mode. Because ammonia was not measured during KORUS calculations were based solely on aerosol composition. Hennigan et al. (2015) suggest this approach when incomplete data on gaseous precursors is available. Average particle pH for all samples collected on the Korean local flights was 2.87 with standard deviation of 2.25 (N = 964). Strong impact from crustal dust during flights on the 4th ,5th, and 7th of May resulted in significantly higher flight average pH values of 5.06, 5.08, and 7.04, respectively (Table 1).
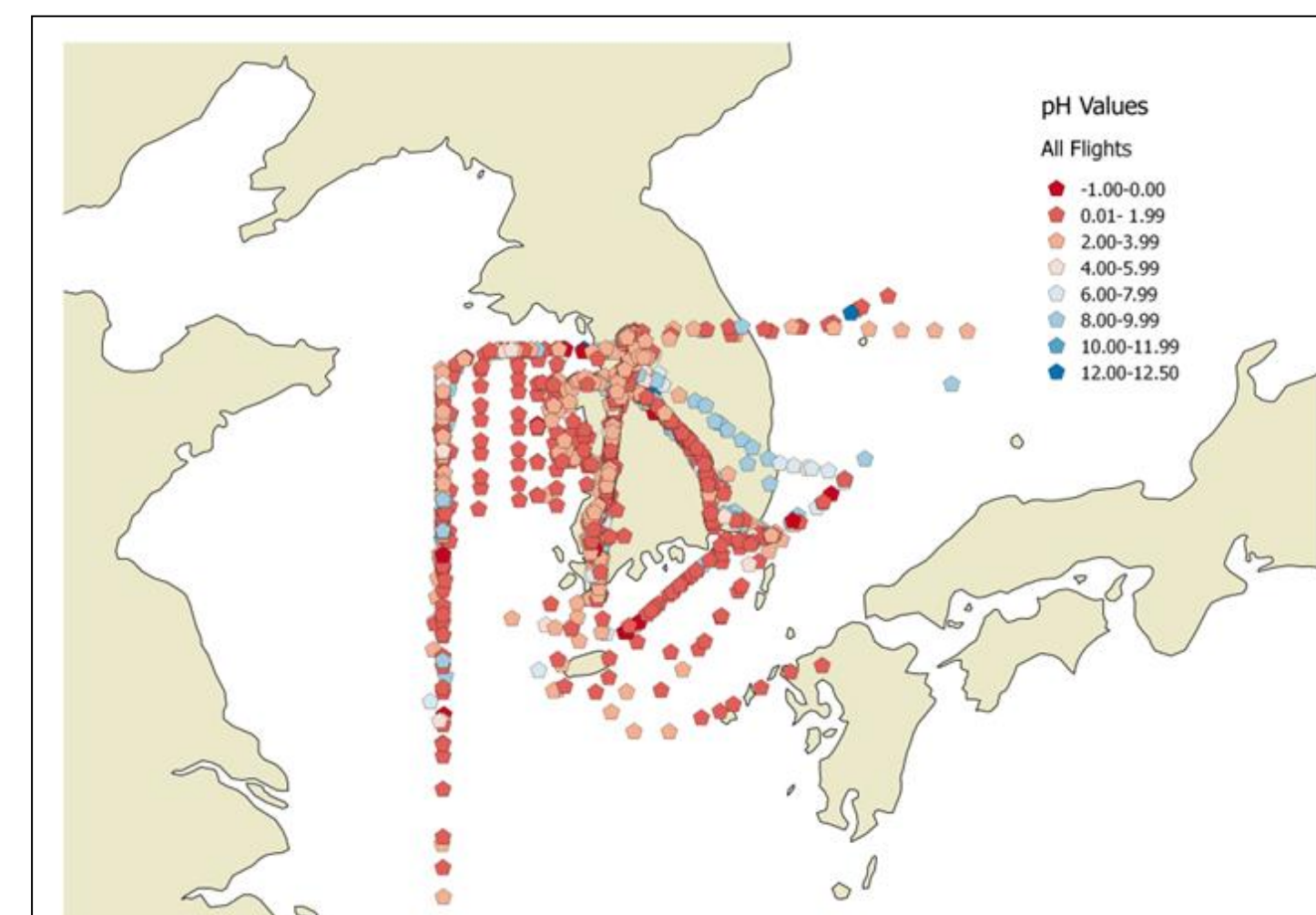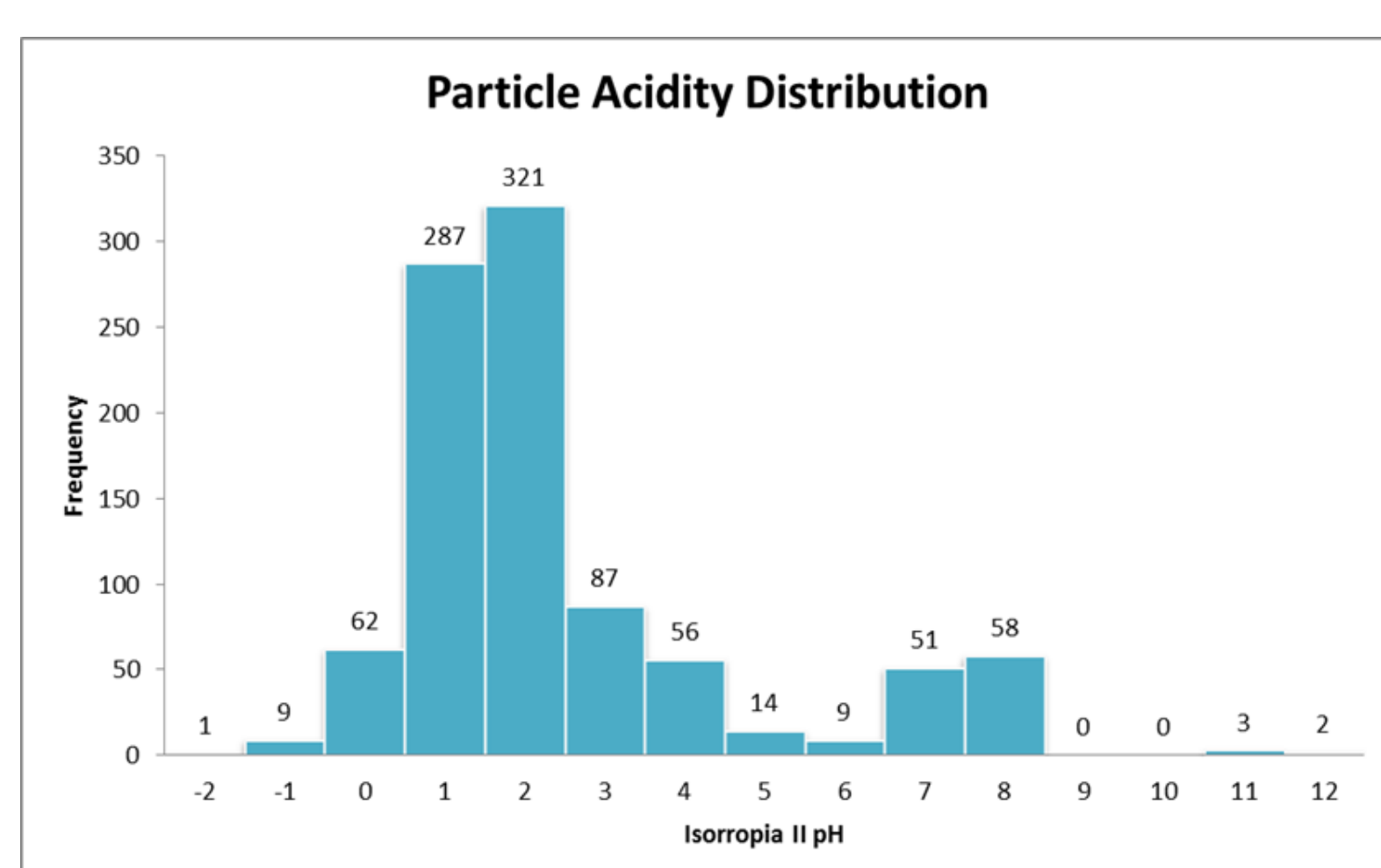

Figure 1
Isorropia II generated pH values for all aerosol filter data (Flights 2-21). Average pH is 2.87 and is driven up by neutralizing dust species (Ca^{2+}, Mg^{2+}) impacting flights 3-5.

Figure 2
Spatial distribution of pH values derived for all aerosol filters (Flights 2-21).

Table 1
Average bulk filter aerosol concentrations (ug/m³) highlighting flights 3-5 which are significantly less acidic than the other flights. Average pH of all flights removing the aforementioned is 2.382 with standard deviation of 1.827. Flights with higher pH have enrichment of Ca^{2+}, Mg^{2+}, integrated particle size and volume (Anderson: TSI Aerodynamic Particle Sizer). Flight 5 is heavily impacted by a dominance of large particles. Flights 3 and 4 have similar large particle presence but these impacts are not as dominant or as spatially ubiquitous.

| Flight/s	N		Cl⁻	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	pH	Temp K	Relative Humidity %	Integrated Number 500 - 5000nm	Integrated Volume 500 - 5000 nm
5	54	Average	0.311	3.533	2.763	0.303	1.341	0.300	0.280	2.215	7.038	280	41	7.58	74.85
		St.Dev	0.222	2.467	1.668	0.208	0.781	0.185	0.198	1.426	1.222	11	16	6.39	62.50
3	53	Average	0.749	2.259	2.222	0.421	1.001	0.171	0.142	0.959	5.060	277	29	3.03	15.83
		St.Dev	0.951	3.329	2.116	0.507	1.012	0.163	0.147	0.957	2.345	14	15	3.65	11.93
4	28	Average	0.228	1.577	2.391	0.189	0.976	0.099	0.123	1.063	5.083	280	27	2.86	18.77
		St.Dev	0.221	2.080	0.997	0.148	0.619	0.070	0.073	0.610	3.069	13	13	2.52	13.69
All - (3-5)	829	Average	0.120	3.792	5.600	0.157	2.899	0.217	0.073	0.474	2.382	284	51	13.71	11.40
		St.Dev	0.436	4.321	5.018	0.256	2.587	0.203	0.076	0.466	1.827	13	24	15.82	8.57
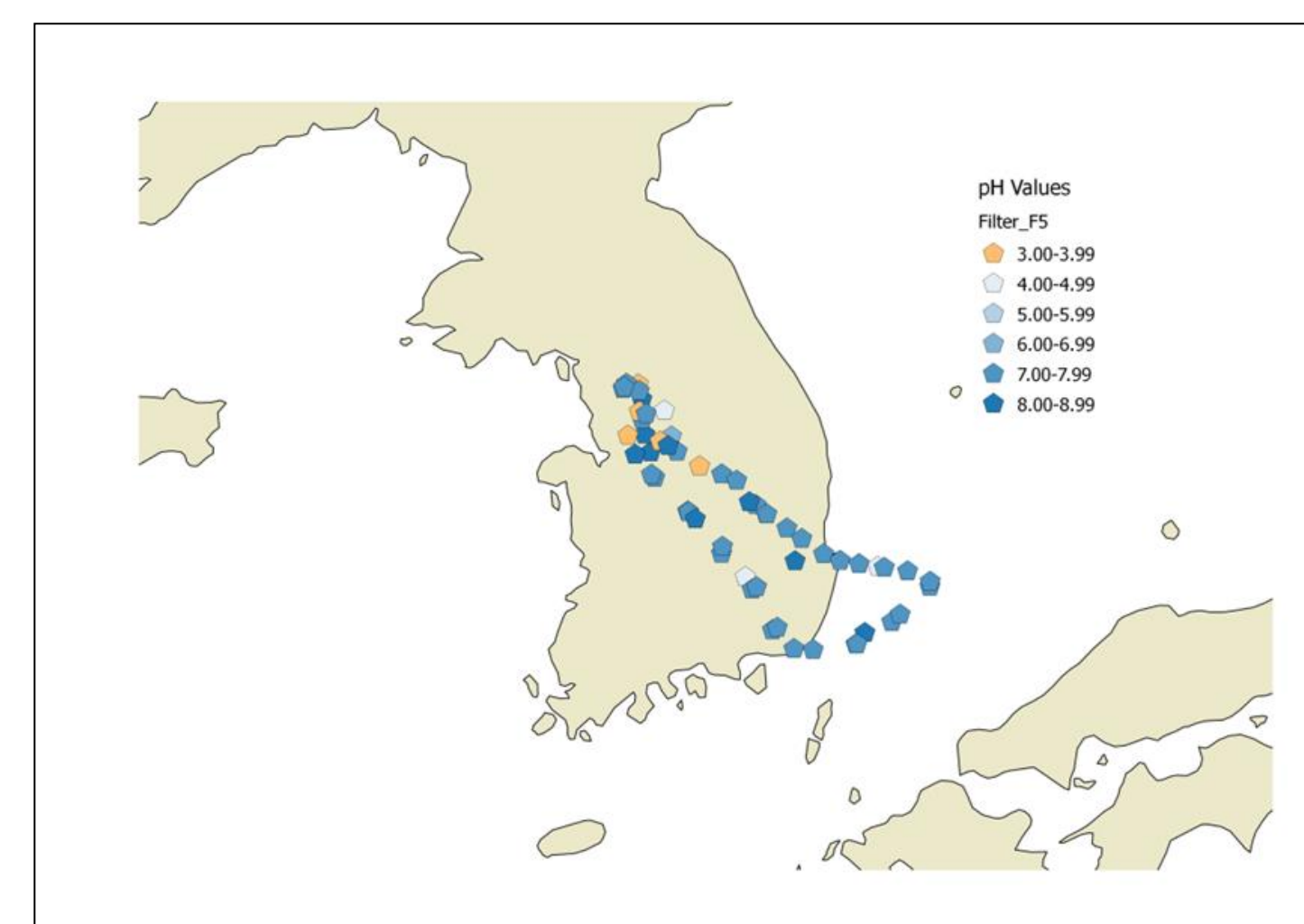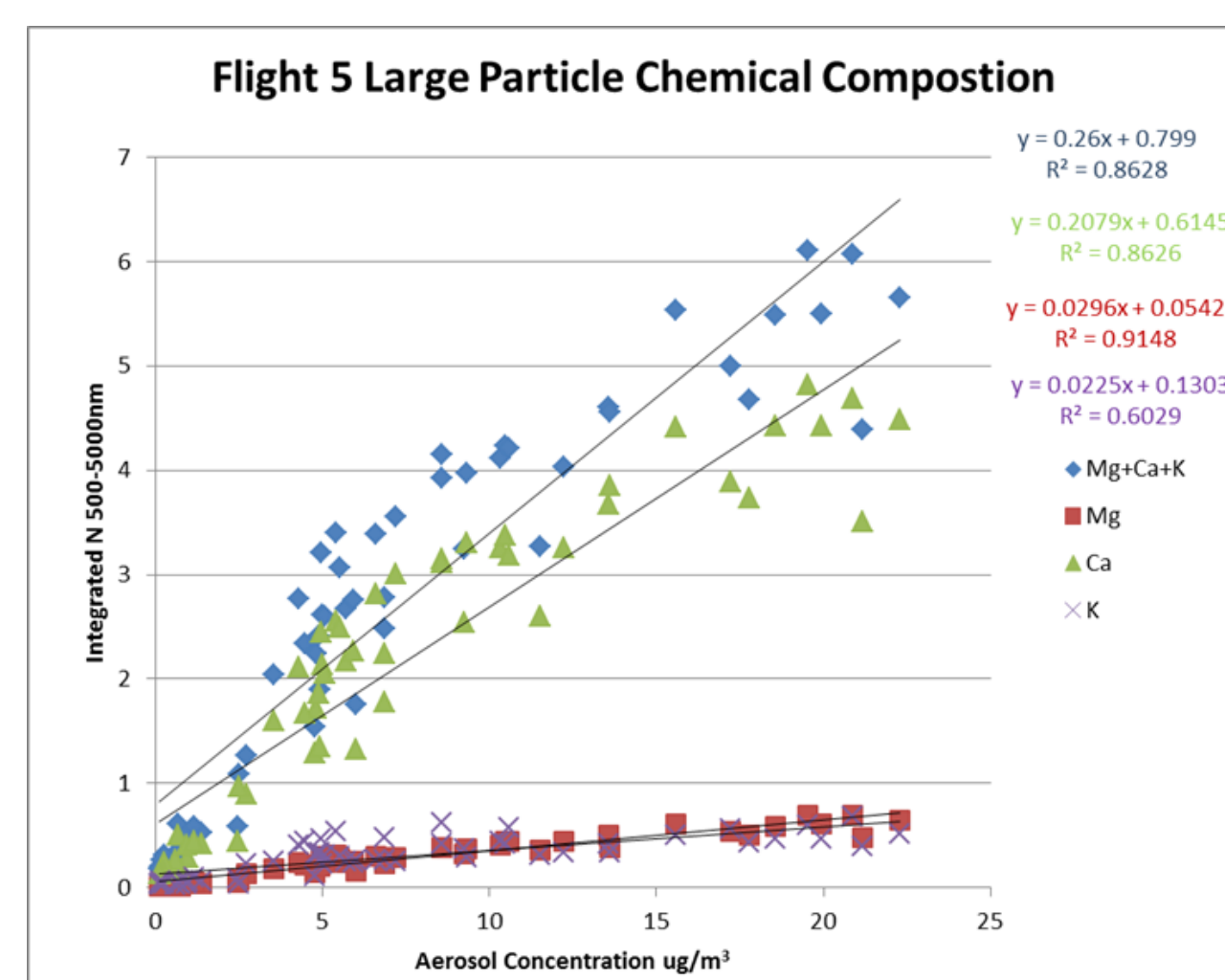
Figure 3
Flight 5 integrated large particle number vs. the aerosol filter concentrations of crustal species Mg^{2+}, Ca^{2+}, and K^+. Good agreement exists between increases of large particle abundance and increasing crustal species.
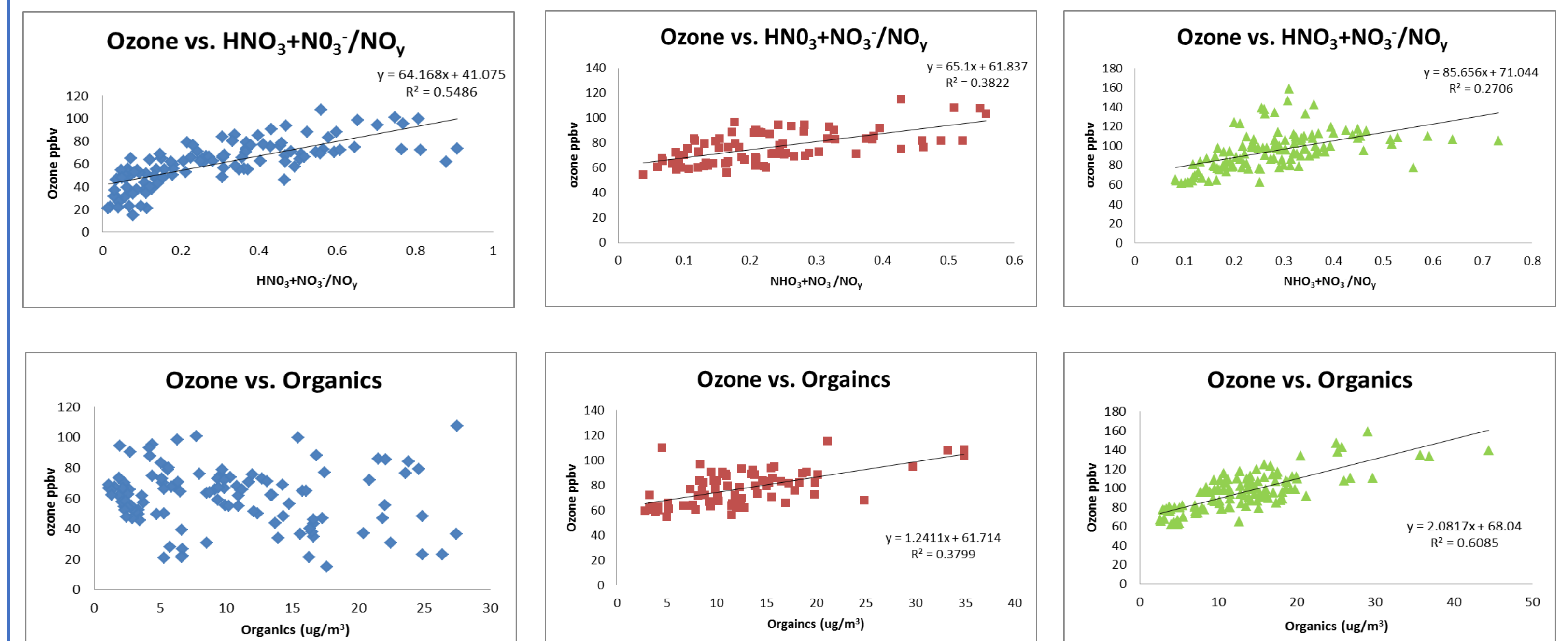

Figure 4
Flight 5 spatial distribution of particle pH values generated from Isorropia II. Altitude: max = 7.29km, min = 0.17km, average = 1.91km. pH: max = 8.48, min = 3.25, average =6.97.
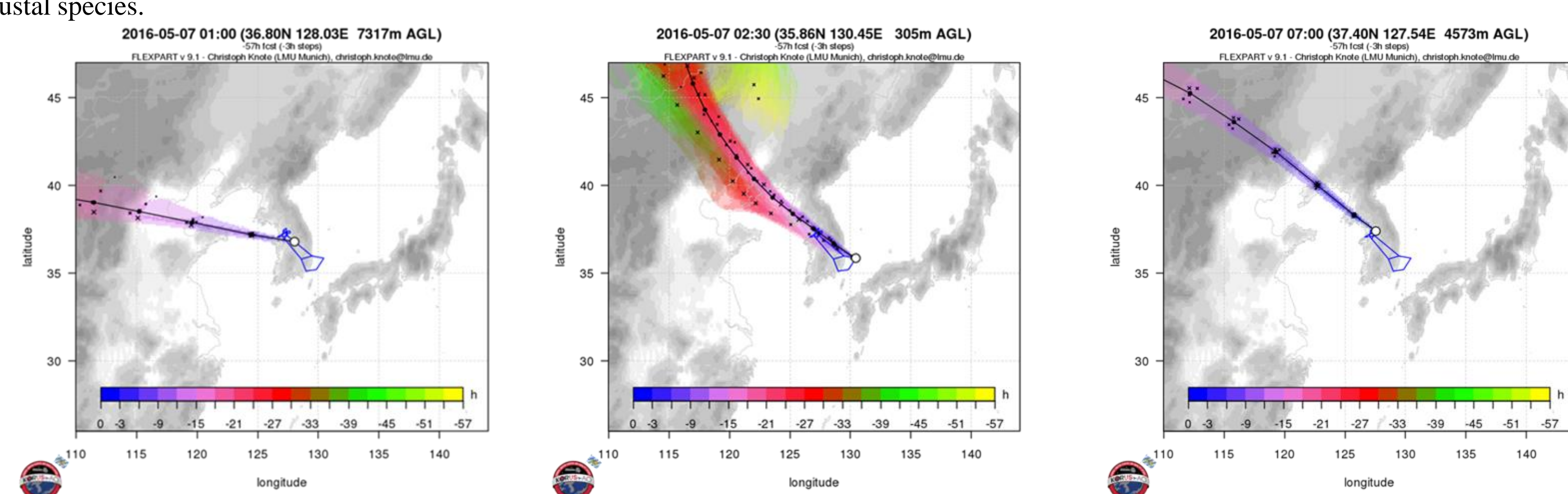
Figures 5,6,7
Generated back trajectories forecasts from Knote utilizing the FLEXPART 9.1 model. These plots are for the DC-8 during flight 5 (2016-05-07) at times 1:00, 2:30, and 7:00. The model indicates that particle source was dominated from north central China and Mongolia.

Seoul Stereo Route

The Seoul Stereo route is located between the missed approach at Dunjeon-dong and the Seoul Spiral. It's low altitude, repeated temporal stamps, and transect from urban to forested offers an attempt to further review the impact of both natural and anthropogenic aerosols on Ozone processes. Across all sampling it appears that HNO_3 loading throughout the day and Organics at midday and late best generalize ozone formation for the stereo route.
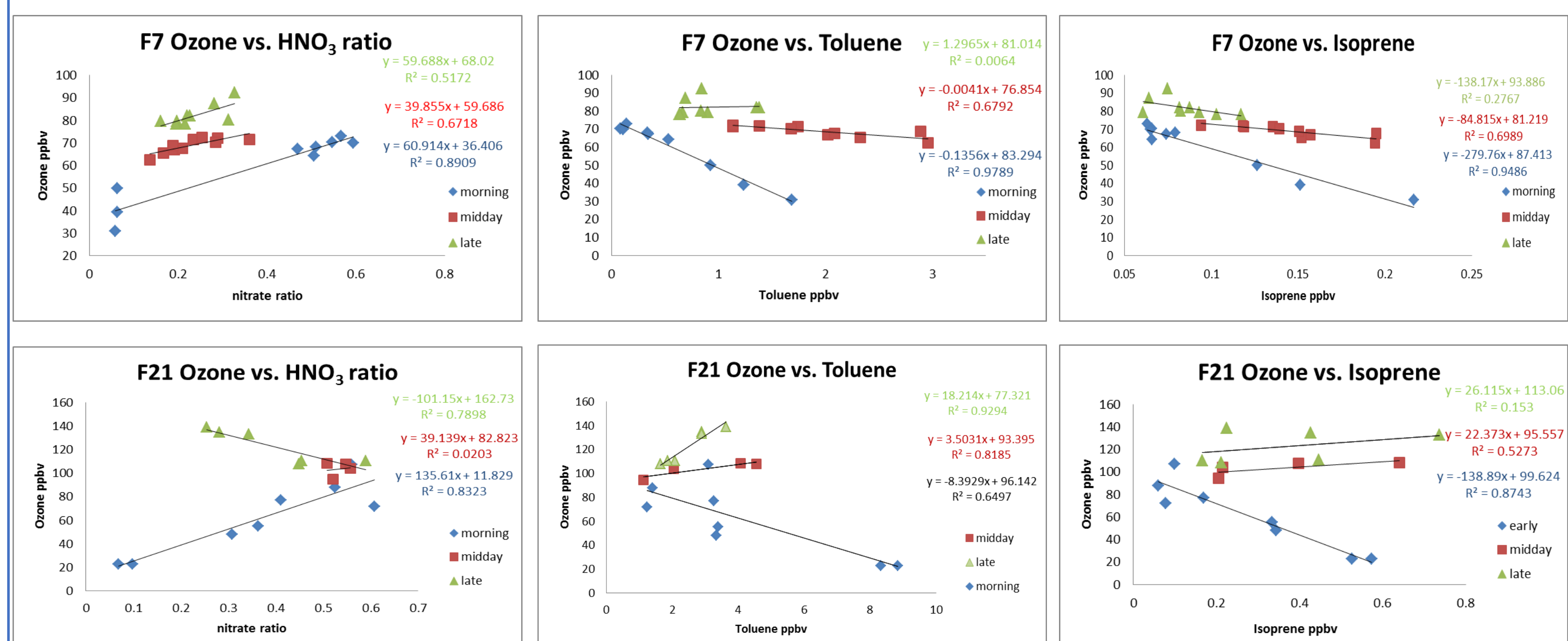

Figures 8,9: Morning ozone concentrations vs. Organics and HNO_3.+submicron Nitrate.

Figures 10,11: Midday ozone concentrations vs. Organics and HNO_3.+submicron Nitrate.

Figure 12, 13: Late ozone concentrations vs. Organics and HNO_3.+submicron Nitrate.

Trend Comparison Flights 7 and 21

Figures 14-19
Comparison of temporal variance in Ozone trends within the Seoul stereo route for flights 21 and 7. Flight 21 has some of the highest ozone observations of the mission where flight 7 is nominal. Note HNO_3 ratio is (HNO_3+Submicron Nitrate)/NO_y.

Discussion:

1. In general atmospheric particles collected during the Korus-AQ mission were highly acidic (pH = 2.87 +/- 2.26 N=964)(Figures 1, 2).

2. Enhanced dust during 3 days in early May resulted in higher concentrations of cations in aerosol, and an increase in the abundance of super micron particle. This event increased average aerosol pH by ~2.0 units for flights 3 and 4 and ~ 4.0 units during flight 5. Dust was ubiquitous in flight 5 (pH min = 3.25, max = 8.48, average = 6.97, Figure 4) while only portions of flights 3 and 4 were impacted.

3. Back trajectories suggest that the dust over Korea during flights 3 through 5 originated from North Central China and Mongolia, this input to the Korean troposphere has been reported for thousands of years (Chung, 1992). How do these neutralizing events affect acid catalyzed dynamics in the Korean troposphere?

4. Temporal and climatic variances throughout the mission make constraining Ozone dynamics within the stereo route difficult. The strongest widespread indicator is Organic aerosol abundance during peak sunlight (Figure 13). The ratio of HNO_3/NO_y has decreasing strength of relationship from morning to late afternoon but is still a relatively useful indicator for majority processes (Figures 8,10,12).

5. Strong correlations between OA and HNO_3/NO_y versus O_3 were seen for most repeats of the Seoul stereo route, but the slopes varied widely with time of day and between days with different synoptic conditions.

Acknowledgements

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