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MEMORANDUM

TO: Mike Koerber, Lake Michigan Air Directors Consortium (LADCO)

FROM: Charles Stanier, Assistant Professor of Chemical and Biochemical Engineering
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DATE: February 13, 2012

RE: Data analysis and thermodynamic sensitivity analysis of Ashland, WI and Cassville, WI filter data (July 1, 2010 – June 30, 2011)

I have completed data analysis of the filter data sent to me during fall 2011 (with corrections sent for Ashland on January 12, 2012). In this memo and all supporting documents, the Cassville variables are taken from the file "biomass_daily_av_obs_Jul10_Jul11_final_14Nov2011.xls." All Ashland variables taken from the file "ASH_biomass_daily_av_obs_Jul10_Jul11_final_25Oct2011.xls" except for OC, EC, and TC. These three variables are taken from "Biomass Speciated Results 1-13-12 fix.xls." The January 12, 2012 fix addresses an error discovered and corrected by Jason Treutel (Jason.Treutel@wisconsin.gov) based on concerns that Stanier had over the Ashland mass closure and lack of variability in Ashland OC concentrations.

The summary of the result is that there are two distinct periods for inorganic thermodynamic sensitivity. During winter, ammonium nitrate concentrations are relatively high, and the system appears sensitive to reductions in total ammonia and total nitrate at both locations, although the specific balance depends on the site and whether average or episode PM_{2.5} conditions are under consideration. During non-winter periods, the aerosol has a majority fraction of organic aerosol, and inorganic controls are likely not very efficient for PM_{2.5} control. Of the inorganic species, sulfate is most effective, followed by nitrate (during spring and fall only).

The overall descriptive statistics for these datasets, in my analysis, can be found in Table 1.

Table 1. Descriptive statistics for data on Cassville and Ashland sites.

Variable	Units	Cassville mean	Cassville n (days)	Ashland mean	Ashland n (days)
PM _{2.5} (24 hour filter-based)	µg m ⁻³	11.4	115	7.04	115
SO ₂	ppb	2.39	362	0.51	355
NO	ppb	5.6	365	1.88	343
NO ₂	ppb	6.8	365	3.98	341
NO _x	ppb	12.5	365	4.79	341
Wind Speed	mph	5.6	364	5.42	357
Temperature	°F	48.3	365	43.2	357
RH	%	70.0	365	67.2	357
NO ₃ (p)	µg m ⁻³	2.19	117	0.76	115
SO ₄ (p)	µg m ⁻³	1.93	117	1.07	115
OC	µg m ⁻³	2.78	115	3.13	118
EC	µg m ⁻³	0.43	115	0.27	118
TC	µg m ⁻³	3.21	115	3.40	118
NH ₃ (g)	ppb	3.4	110	1.2	107
HNO ₃ (g)	ppb	0.13	110	0.07	107
HSO _x (g)	ppb	1.18	110	0.13	107

The final 3 variables in the table were by denuder measurements. NH₄ aerosol was not measured and was estimated using ISORROPIA version 1.7 (Nenes, Pandis et al. 1998). ISORROPIA was called numerous times with guessed values for total ammonia. The guess of total ammonia that returned (in the ISORROPIA model output) the measured value of gas phase ammonia was retained and used to calculate the estimated NH₄(p) concentration by difference between the guessed total ammonia value and the measured gas phase ammonia. One caution in this is that the modeled partitioning of nitrate vs. nitric acid may be different from the measured partitioning. Blank corrections were not used in the data analysis. This would have the biggest impact on the analysis during low concentration periods.

Figure 1 shows mass closure in the two datasets. Figure 2 shows fractional composition during the months of January – March (allowing comparison to the Winter Nitrate Study).

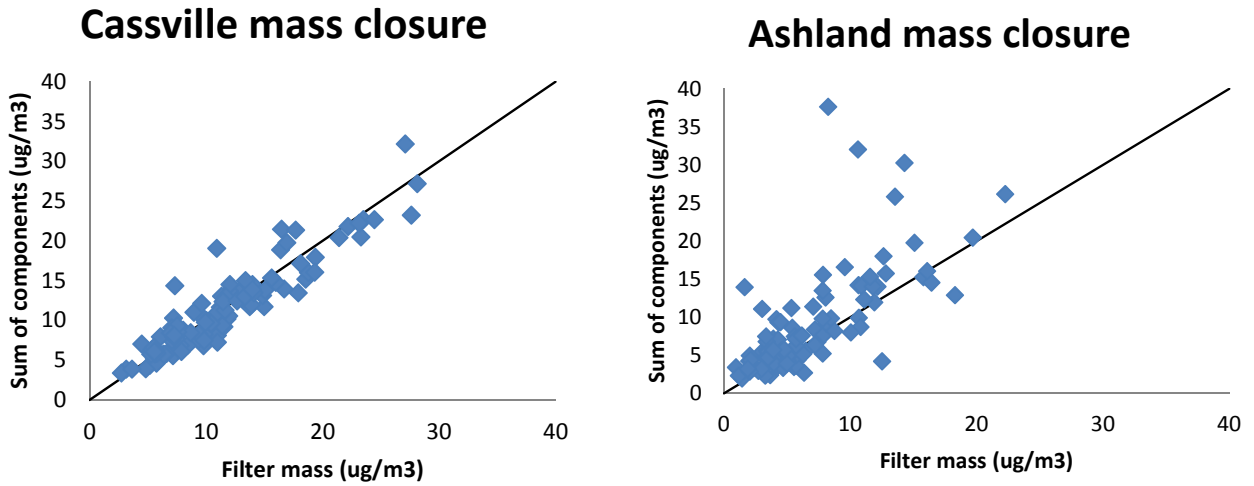


Figure 1. Mass closure using an OM/OC ratio of 2.0.

The study PM_{2.5} time series for the two sites is shown in Figure 2.

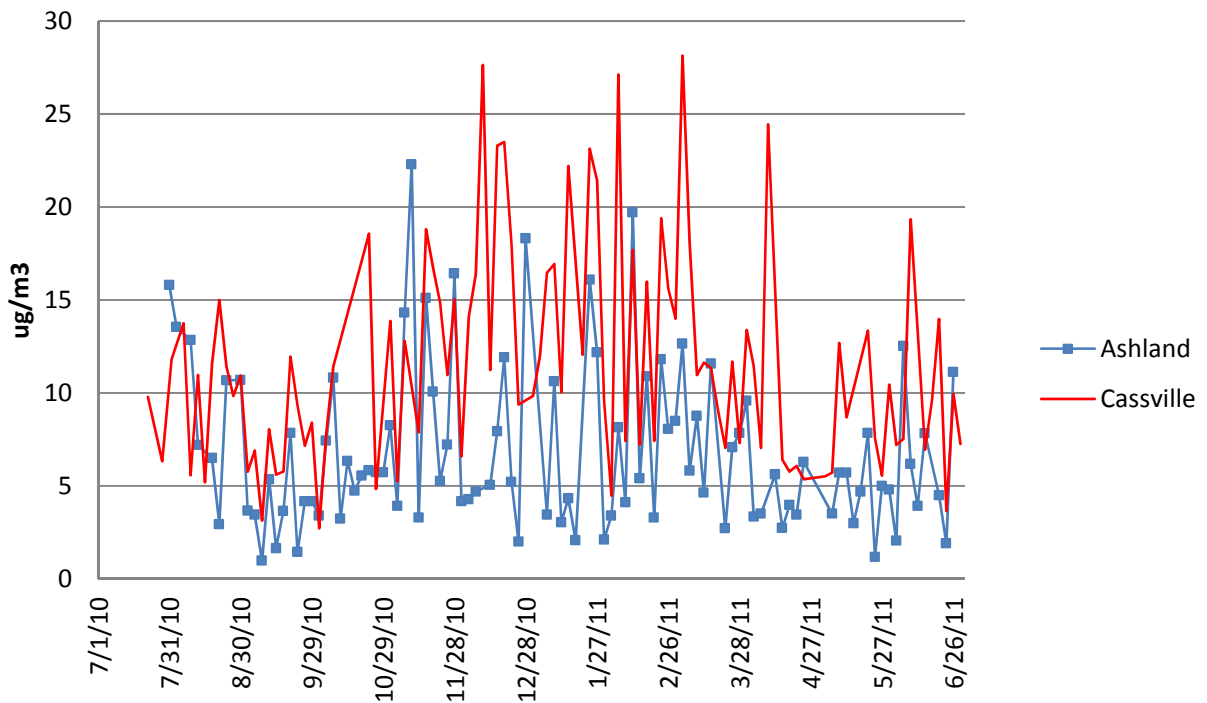


Figure 2. PM_{2.5} Time series for the two sites in question, showing minima during September and April, and peak concentrations from November – March.

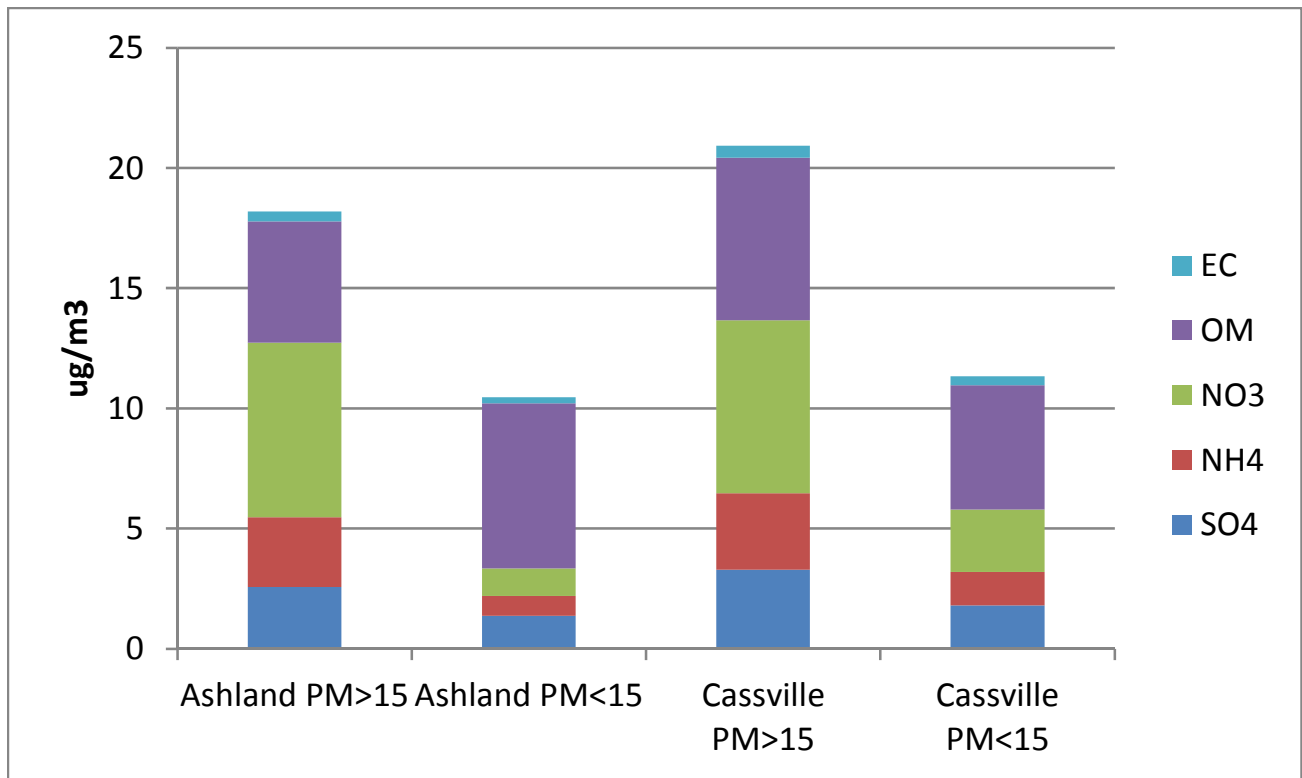


Figure 3. January – March component masses by chemical component, segregated by $PM_{2.5}$ concentration (with a threshold of $15 \mu g m^{-3}$ separating less and more polluted samples).

As figure 3 shows, the concentration during winter during low concentration periods is dominated by organic aerosol. However, during higher concentration periods, ammonium nitrate and, to a lesser extent, sulfate play important roles in concentrations. The relative sensitivity of the system to nitrate and ammonia reductions can often be predicted by knowing the gas ratio. The gas ratio is a measure of ammonia availability (Ansari and Pandis 1998), with gas ratio values above one indicating free gas phase ammonia. The formula for the gas ratio is

$$\frac{TA - 2xTS}{TN}$$

where TA, TS, and TN are molar concentrations of total ammonia, total sulfate, and total nitrate, respectively. Gas ratios for Cassville and Ashland are graphed in Figure 4.

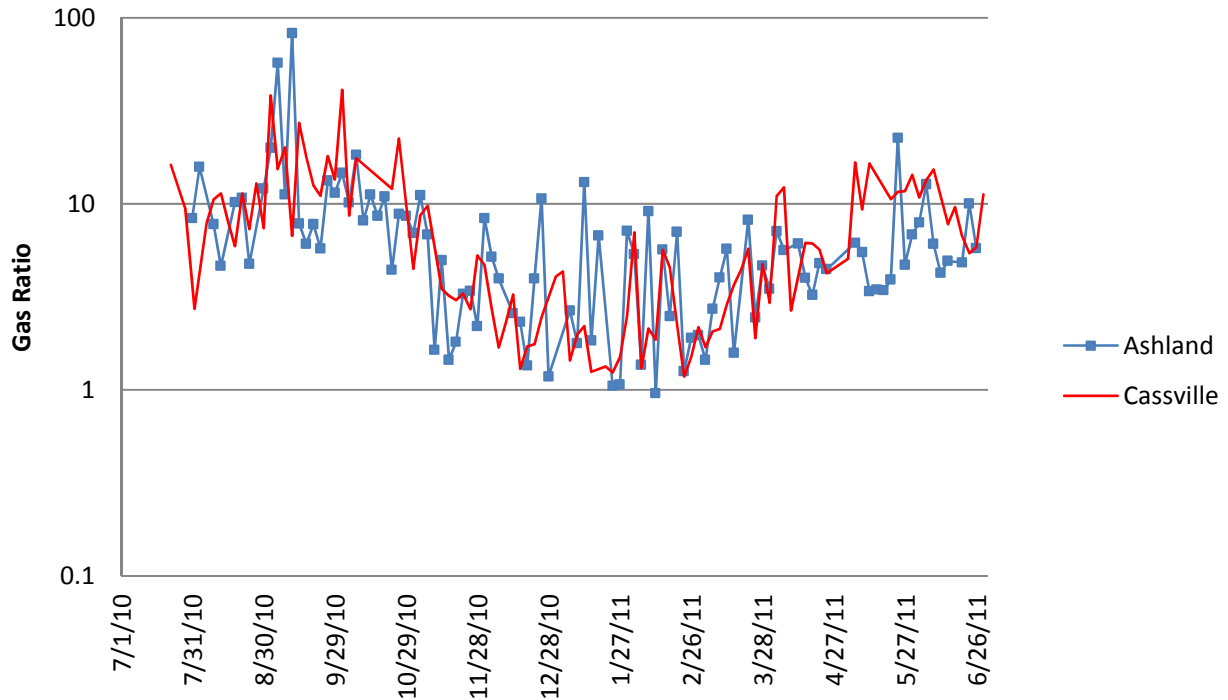


Figure 4. Gas ratio time series. Gas ratio is high (>5) during summer, but approaches 1 during winter months.

Gas ratios are compared to the LADCO WNS (Baek, Carmichael et al. 2010) in Table 2.

Table 2. Comparison of gas ratios from the LADCO WNS to the Cassville/Ashland study

Variable	Milwaukee	Mayville	Cassville	Ashland
Mean Gas Ratio, all samples Jan-Mar	2.5	2.1	2.7	4.0
Mean NH ₃ (g) in ppb - all samples Jan – Mar	2.27	2.40	2.1	0.65
Mean Gas Ratio “non-episode” hours for WNS, days with PM<15 for Cass/Ash study	3.1	2.2	3.4	4.2
Mean Gas Ratio “episode” hours for WNS, days with PM>15 for Cass/Ash study (only 2 samples for Ashland)	1.5	1.2	1.8	1.0

Table 2 shows that mean winter gas ratios are comparable at the LADCO WNS sites and Cassville and Ashland, and that measured gas ratios fall, reaching nearly 1, during higher concentration winter periods. From Figure 4 and Table 2, we can predict the relative sensitivity of nitrate and ammonia at Cassville and Ashland will be as follows:

- Spring, summer and fall periods. High gas ratios. Ammonia in excess, and very little sensitivity to modest percentage ammonia reductions. Low ammonium nitrate concentrations, and aerosols dominated by organics and ammonium sulfate. With ammonia in excess, sensitivity to sulfate > sensitivity to ammonia.
- Winter, PM_{2.5} daily average < 15 µg m⁻³. Ammonia in excess, and little sensitivity to modest percentage ammonia reductions. Aerosols dominated by organics, with non-negligible contributions from both ammonium sulfate and ammonium nitrate. With ammonia in excess, sensitivity to nitrate > sensitivity to ammonia.
- Winter, PM_{2.5} daily average > 15 µg m⁻³. Ammonia and nitrate balanced. Aerosols sensitive to both total nitrate and total ammonia reductions. Aerosols majority comprised of ammonium nitrate.

As shown in the LADCO WNS Phase II report (Spak, Baek et al. 2012), sensitivity to total nitrate (which is established by thermodynamic box modeling such as in this work) and sensitivity to NO_x can be quite different because of the long time required to NO_x to nitrate conversion. Observationally-constrained sensitivity modeling with CMAQ shows that for episodes in Milwaukee during winter (which have similar gas ratio to Cassville wintertime conditions), ammonia reductions are ~4 times more effective than NO_x reductions at PM_{2.5} control, even though thermodynamic modeling predicts balance sensitivity to total nitrate reductions compared to total ammonia reductions. It is likely that CMAQ or other 3D modeling would show a similar result for NH₃ vs. NO_x sensitivity at Cassville and Ashland, relative to the NH₃ vs. TNO₃ sensitivity examined by the thermodynamic box model in this work.

Thermodynamic sensitivity was calculated using the same procedures as described in the Phase I WNS report (Baek, Carmichael et al. 2010). In fact, the code to do the box modeling and plotting for this report was adapted from the Phase I report codes.

The season-to-season sensitivity is summarized in Figure 5. The variable plotted is the sensitivity to fractional reduction as defined in Baek, Carmichael et al. (2010). For example, the nitrate fractional sensitivity (S_{NO₃-f} in Baek, Carmichael et al.) is calculated as

$$\frac{\Delta PM_{2.5, inorg} / PM_{2.5, inorg}}{\Delta TNO_3 / TNO_3}$$

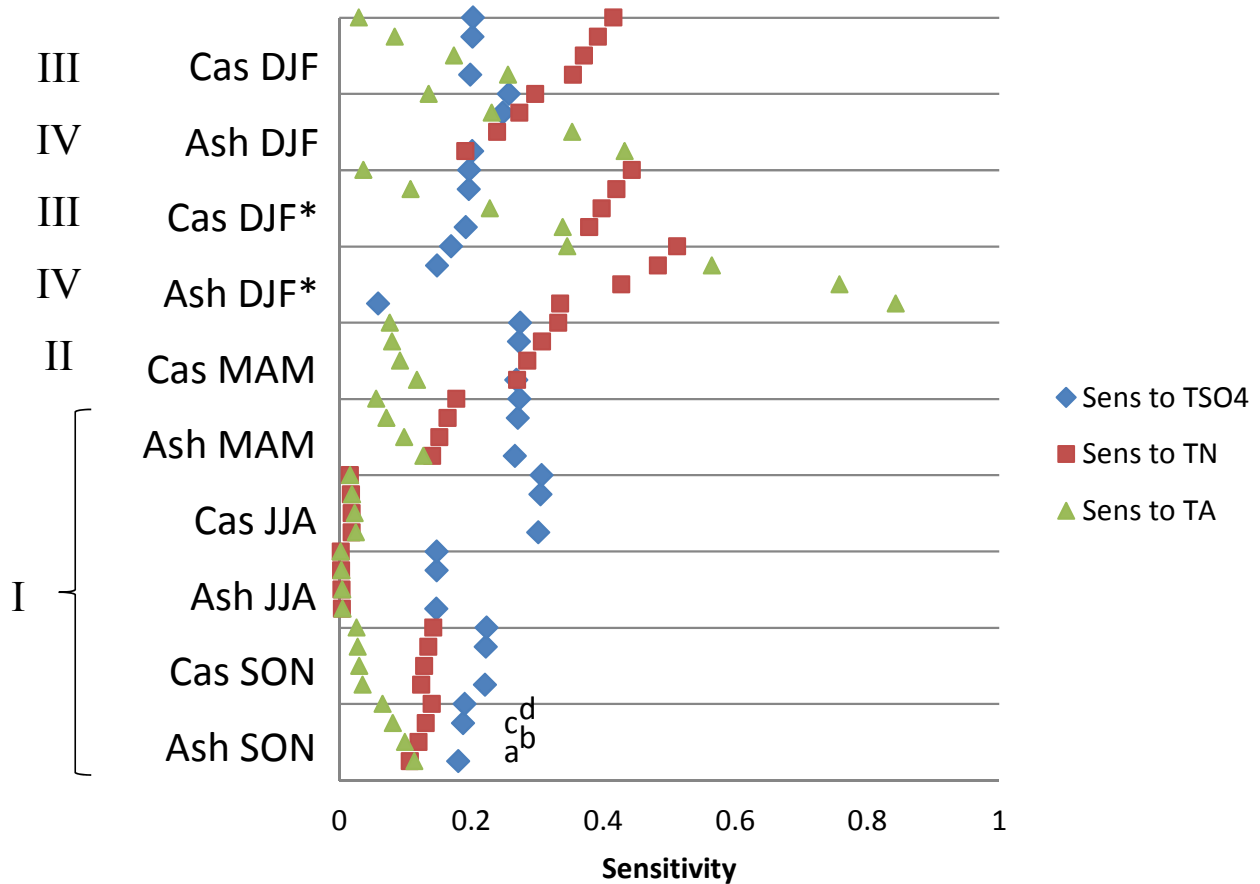


Figure 5. Fractional sensitivity of PM_{2.5} to 30% reductions in total sulfate (blue), total nitrate (red) and total ammonia (green). A sensitivity of 1 means that a 1% reduction (increase) in the species causes a 1% reduction (increase) in PM_{2.5}. For example, pure ammonium sulfate aerosol would have a fractional sensitivity to sulfate reduction of 1.0. Also, pure organic aerosol would have a fractional sensitivity of 1.0 with respect to reduction to total organics. Within each grouping of 4 cases, there are four subcases (e.g. a, b, c, and d). The subcase closest to the bottom (a) is at 120% of measured sulfate, followed by subcases at 100%, 75% and 50% of measured sulfate. Nitrate sensitivity typically increases as sulfate drops, and ammonia sensitivity decreases. DJF* cases are calculated using only days with PM_{2.5} > 15 µg/m³. Types of behavior are indicated by Roman numerals and specific behavior types are discussed in the text.

Group I consists of cases where inorganic aerosols are most sensitive to sulfate. This includes summer, fall, and spring at Ashland (but not at Cassville). Spring at Cassville is sensitive to both sulfate and nitrate. Because inorganic aerosols are not a majority component of the aerosol during these times, the sensitivity of all the inorganic precursors is limited in groups I and II, and PM_{2.5} will be most sensitive to organic aerosol concentrations. Group III is characterized by the highest sensitivity to total nitrate. This is the case for Cassville in wintertime. The change in the ammonia sensitivity across the four subcases (a-d) is due to the changing ammonia availability as sulfate concentrations are reduced. As sulfate is reduced, ammonia availability increases and the fractional sensitivity to ammonia controls decreases.

Group IV describes Ashland in wintertime. The sensitivity is greatest to ammonia and nitrate, with ammonia sensitivity greater at current sulfate levels, and nitrate sensitivity greater under hypothetical cases at 75% and 50% of measured sulfate levels.

The overall concentration isopleths are shown in Figure 6 (Cassville) and Figure 7 (Ashland).

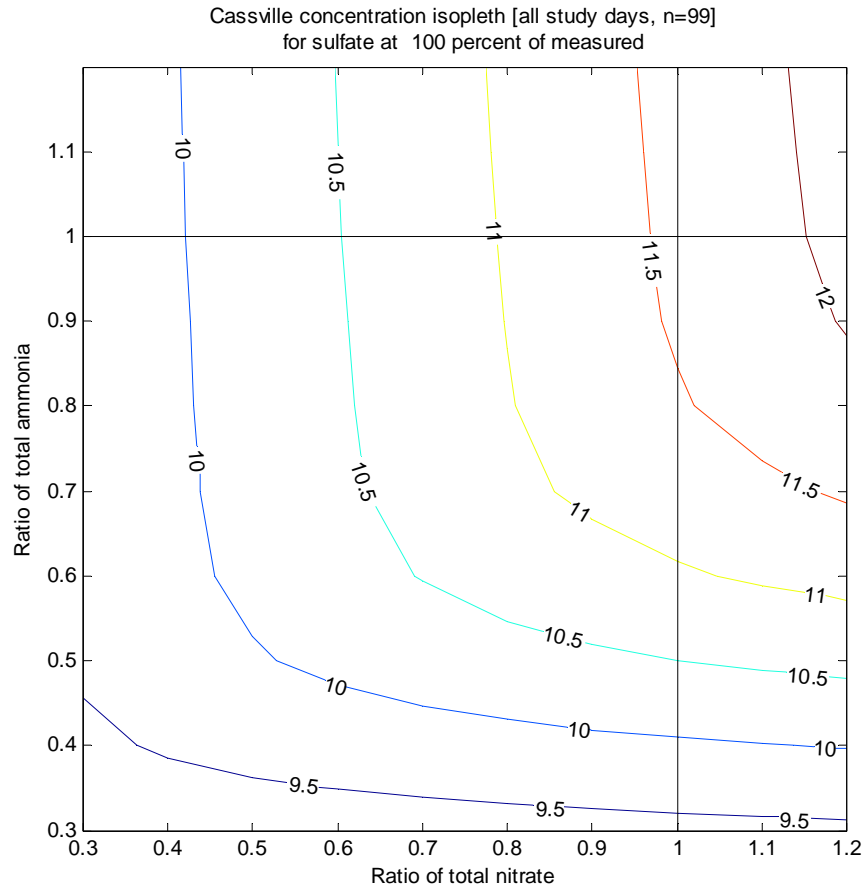


Figure 6. Concentration isopleth for total nitrate and total ammonia reduction as Cassville, assuming total sulfate at 100% of measured levels. Starting from the [1 1] position, reductions in total nitrate are predicted to have more dramatic reductions in PM_{2.5} than reduction in total ammonia. This is consistent with the gas ratio, which is high during non-winter periods and during low PM_{2.5} winter periods. The fact that large reductions in ammonia and nitrate do not take mean PM_{2.5} concentrations below 9 µg/m³ is due to the high organic fraction in these aerosols.

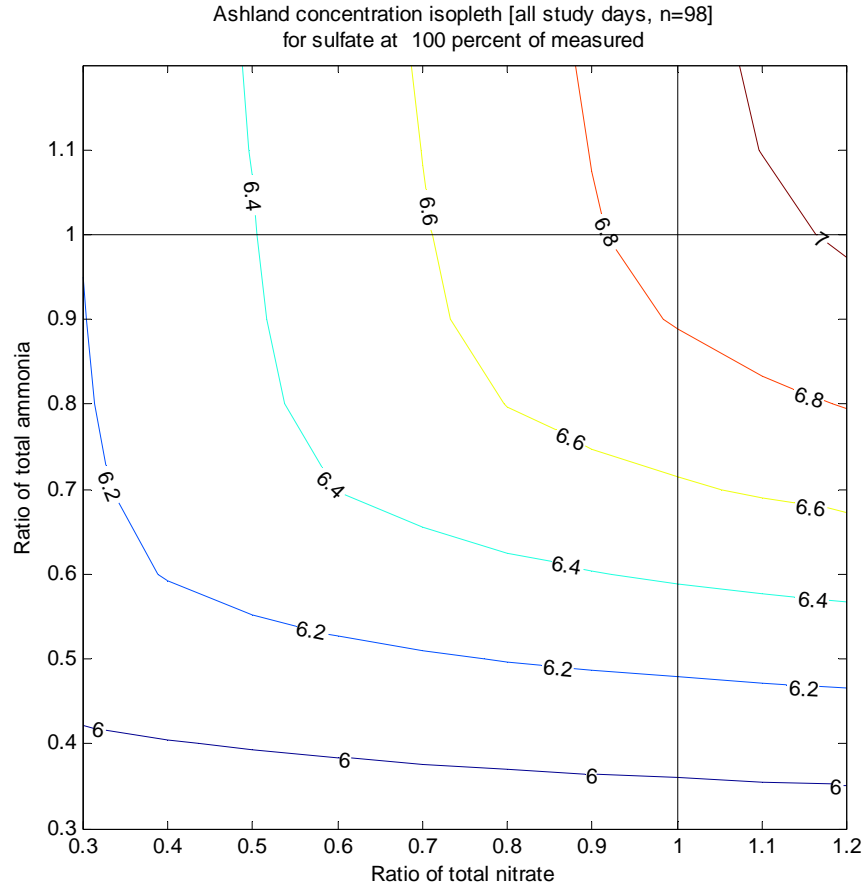


Figure 7. Concentration isopleth for total nitrate and total ammonia reduction as Ashland, assuming total sulfate at 100% of measured levels. Starting from the [1 1] position, reductions in total nitrate are total ammonia are approximately balanced. The fact that large reductions in ammonia and nitrate do not take mean $PM_{2.5}$ concentrations below $5.8 \mu\text{g}/\text{m}^3$ is due to the high organic fraction in these aerosols.

Table 3 tabulates the sensitivity modeling results from a subset of the large database of box modeling runs.

Table 3. Tabulated box modeling results for selected model cases.

				Concentrations in $\mu\text{g}/\text{m}^3$				Changes in concentration from base case ($\mu\text{g}/\text{m}^3$)			
Site	Season	PM2.5 filter ¹	Sulfate Level ²	Modeled PM2.5 at measured	Modeled PM2.5 (TNO3 ↓30%)	Modeled PM2.5 (TNH3 ↓30%)	Modeled PM2.5 (TNO3 & TNH3 ↓30%)	Modeled PM2.5 at measured	Modeled PM2.5 (TNO3 ↓30%) ^{3,4}	Modeled PM2.5 (TNH3 ↓30%) ^{3,4}	Modeled PM2.5 (TNO3 & TNH3 ↓30%)
				TNO3 and TNH3				TNO3 and TNH3 ³			
Ash	SON	none	100	6.72	6.47	6.52	6.37	0.00	-0.25	-0.20	-0.35
Ash	SON	none	50	6.08	5.82	5.96	5.74	-0.64	-0.90	-0.76	-0.98
Cass	SON	none	100	9.74	9.37	9.65	9.31	0.00	-0.37	-0.09	-0.43
Cass	SON	none	50	8.65	8.28	8.59	8.24	-1.09	-1.46	-1.15	-1.50
Ash	DJF	none	100	7.40	6.87	6.69	6.57	0.00	-0.53	-0.71	-0.83
Ash	DJF	none	50	6.45	5.87	6.20	5.83	-0.95	-1.53	-1.20	-1.57
Cass	DJF	none	100	15.23	13.53	14.47	13.43	0.00	-1.70	-0.76	-1.80
Cass	DJF	none	50	13.68	11.97	13.56	11.95	-1.55	-3.26	-1.67	-3.28
Ash	DJF	> 15	100	18.04	15.73	14.70	14.59	0.00	-2.31	-3.34	-3.45
Ash	DJF	> 15	50	16.51	13.97	14.96	13.91	-1.53	-4.07	-3.08	-4.13
Cass	DJF	> 15	100	20.32	17.90	19.02	17.74	0.00	-2.42	-1.30	-2.58
Cass	DJF	> 15	50	18.32	15.88	18.12	15.85	-2.00	-4.44	-2.20	-4.47
Ash	MAM	none	100	5.75	5.49	5.59	5.41	0.00	-0.26	-0.16	-0.34
Ash	MAM	none	50	4.97	4.70	4.88	4.65	-0.78	-1.05	-0.87	-1.10
Cass	MAM	none	100	10.73	9.81	10.44	9.65	0.00	-0.92	-0.29	-1.08
Cass	MAM	none	50	9.62	8.33	9.05	8.20	-1.11	-2.40	-1.68	-2.53
Ash	JJA	none	100	8.14	8.13	8.13	8.12	0.00	-0.01	-0.01	-0.02
Ash	JJA	none	50	7.54	7.53	7.53	7.53	-0.60	-0.61	-0.61	-0.61
Cass	JJA	none	100	9.90	9.84	9.83	9.79	0.00	-0.06	-0.07	-0.11
Cass	JJA	none	50	8.38	8.33	8.33	8.31	-1.52	-1.57	-1.57	-1.59

¹none means that all samples were used. >15 means that only samples in excess of 15 $\mu\text{g}/\text{m}^3$ were used.

²100 refers to total sulfate at measured level. 50 refers to total sulfate at 50% of measured levels.

³Yellow shading indicates the single inorganic reduction (50% sulfate, 30% total nitrate, or 30% total ammonia) with the largest modeled impact.

⁴Italic indicates which had a larger impact, the 30% TNO3 reduction, or the 30% TNH3 reduction.

An appendix contains additional figures.

REFERENCES

- Ansari, A. S. and S. N. Pandis (1998). "Response of inorganic PM to precursor concentrations." Environmental Science & Technology **32**(18): 2706-2714.
- Baek, J., G. R. Carmichael, et al. (2010). Episodic Air Pollution in Wisconsin (LADCO Winter Nitrate Study) and Georgia (SEARCH Network) During Jan-Mar 2009, Lake Michigan Air Directors Consortium.
- Nenes, A., S. Pandis, et al. (1998). "ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols." AQUATIC GEOCHEMISTRY **4**(1): 123-152.
- Spak, S., J. Baek, et al. (2012). Episodic Air Pollution in Wisconsin (LADCO Winter Nitrate Study) and Georgia (SEARCH Network) During Jan-mar 2009. Phase II Report. Three Dimensional Modeling and Process Analysis. Rosemont, IL, Lake Michigan Air Directors Consortium.

Ashland and Cassville WI Analysis of Daily Filters Appendix

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January 2012

Figure A1. OC (not OM) time series. Ashland OC time series appears much more episodic.

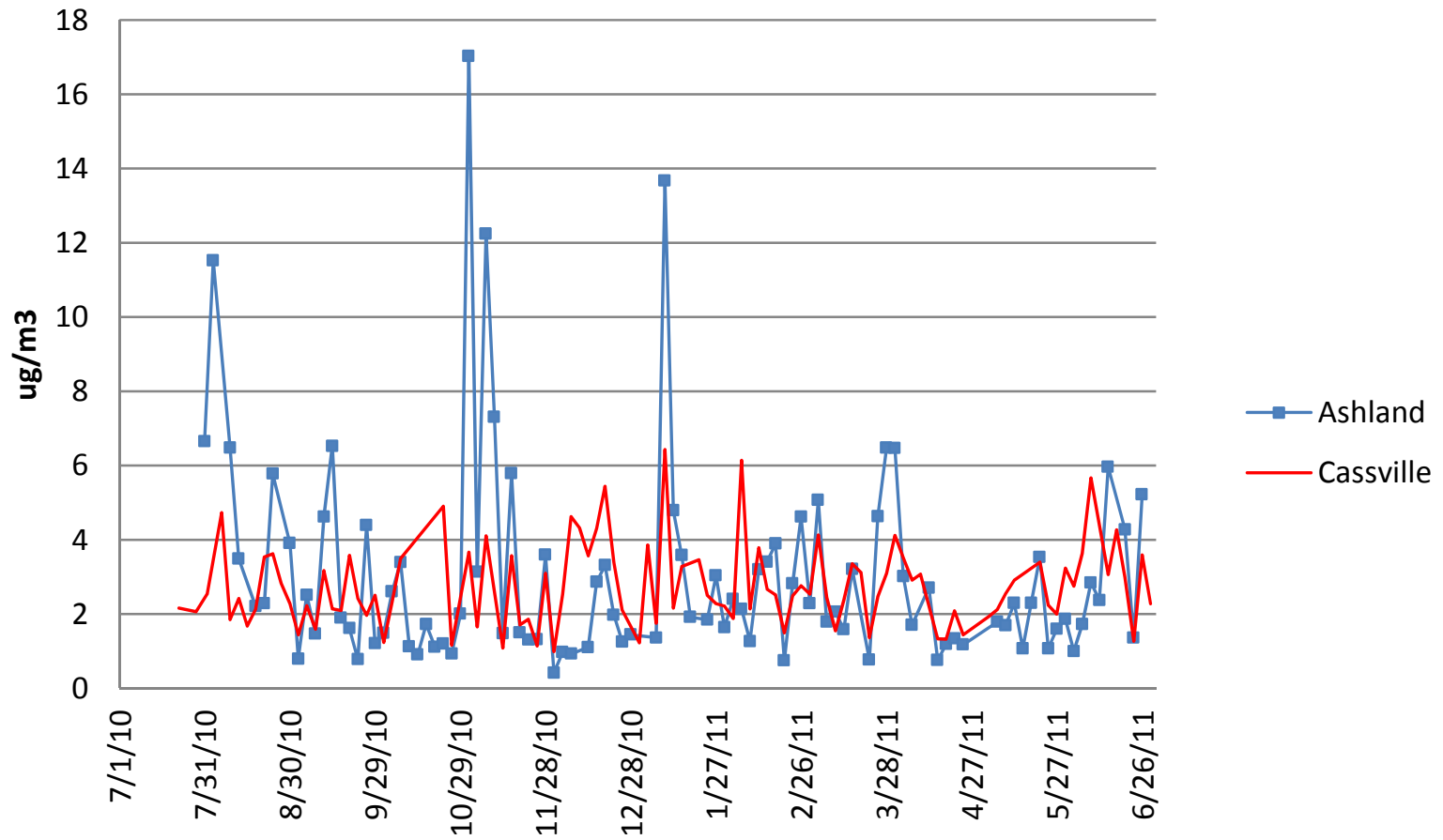


Figure A2. Sulfate time series shows elevated winter levels at both sites.

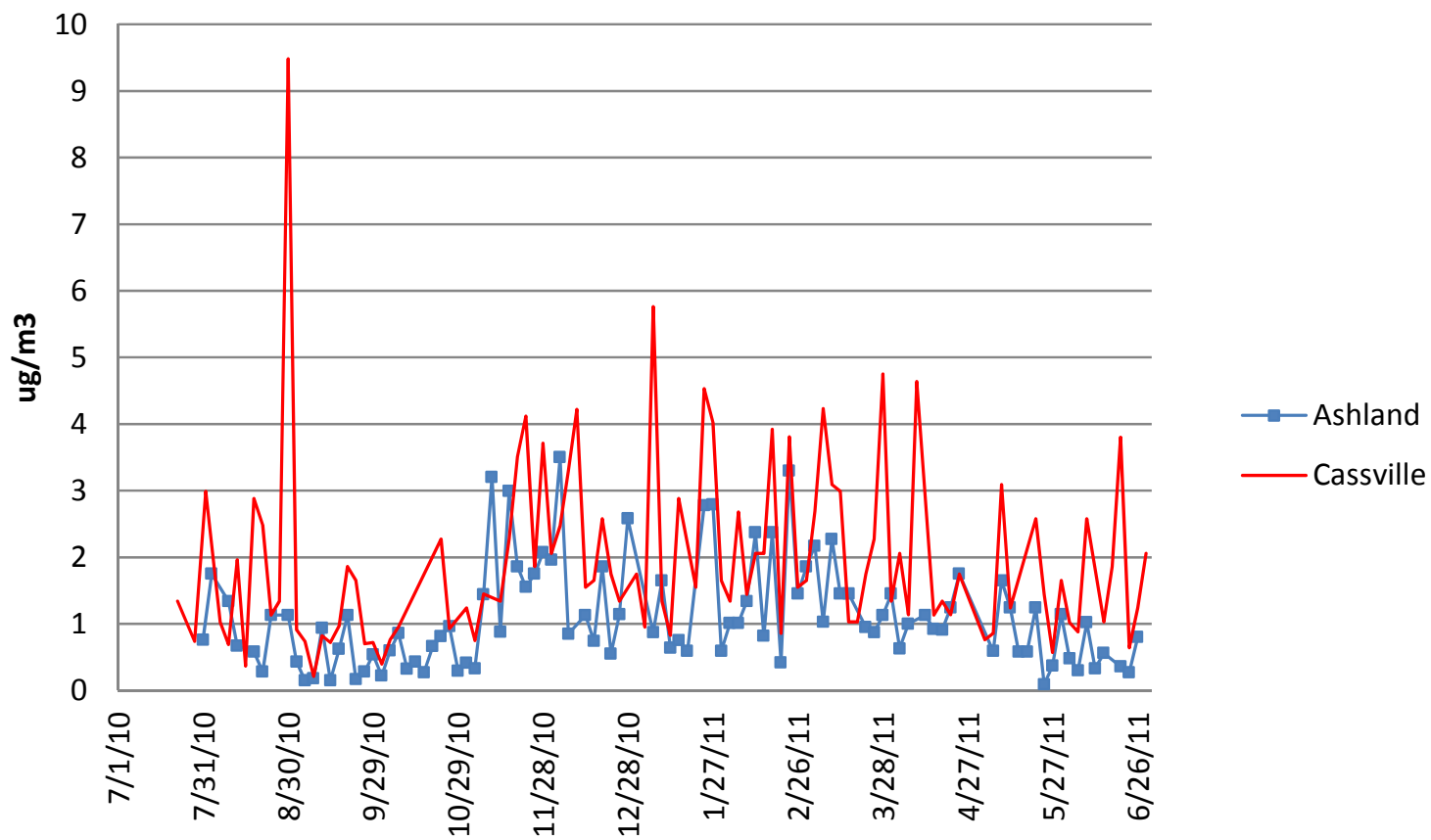


Figure A3. Nitrate time series. Shows nitrate only during cold season. Cassville nitrate is higher than Ashland nitrate.

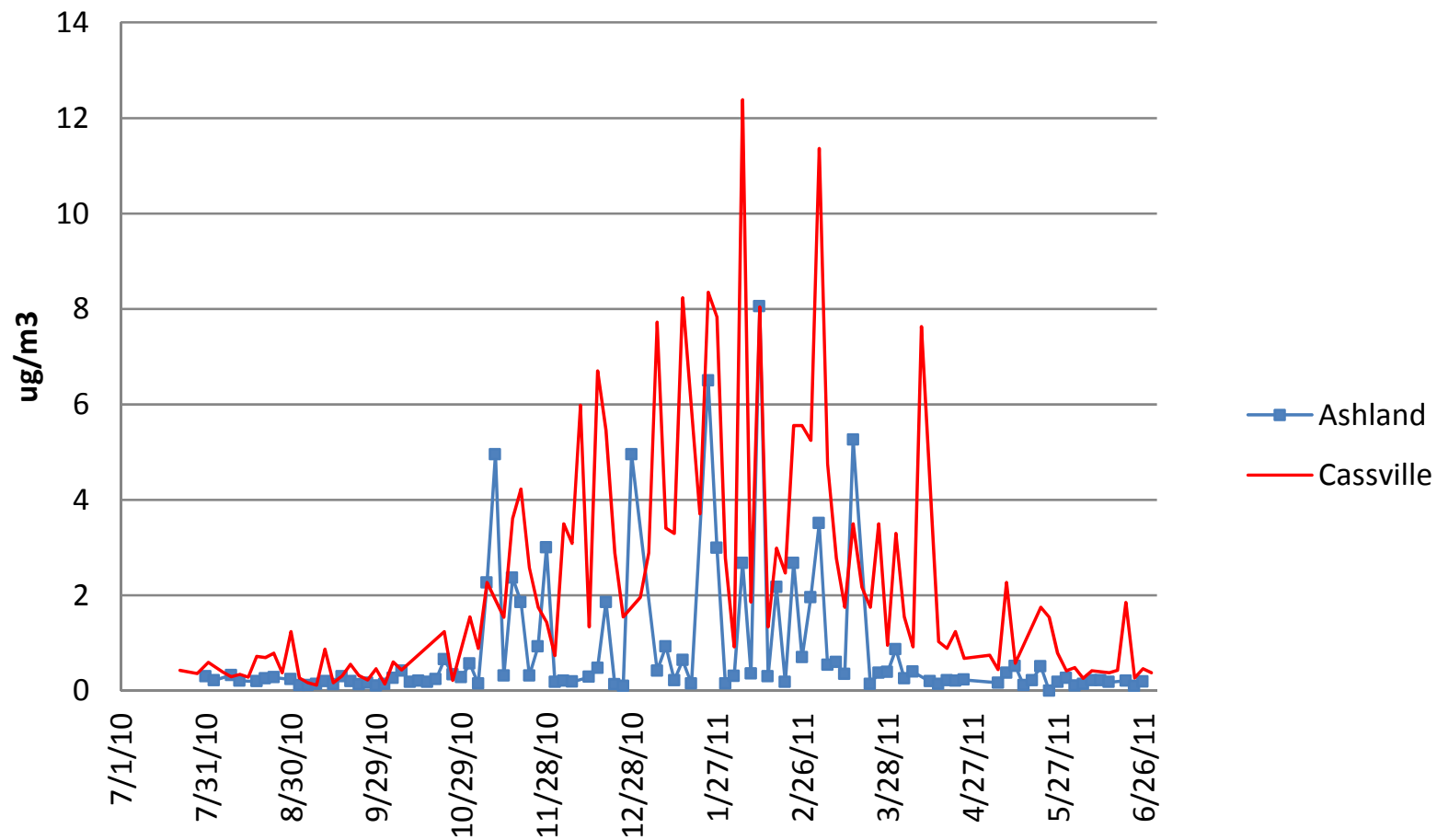


Figure A4. Ammonium time series. Ammonium is estimated using the thermodynamic model because it was not measured.

Estimated NH₄(p) - no blank corrections

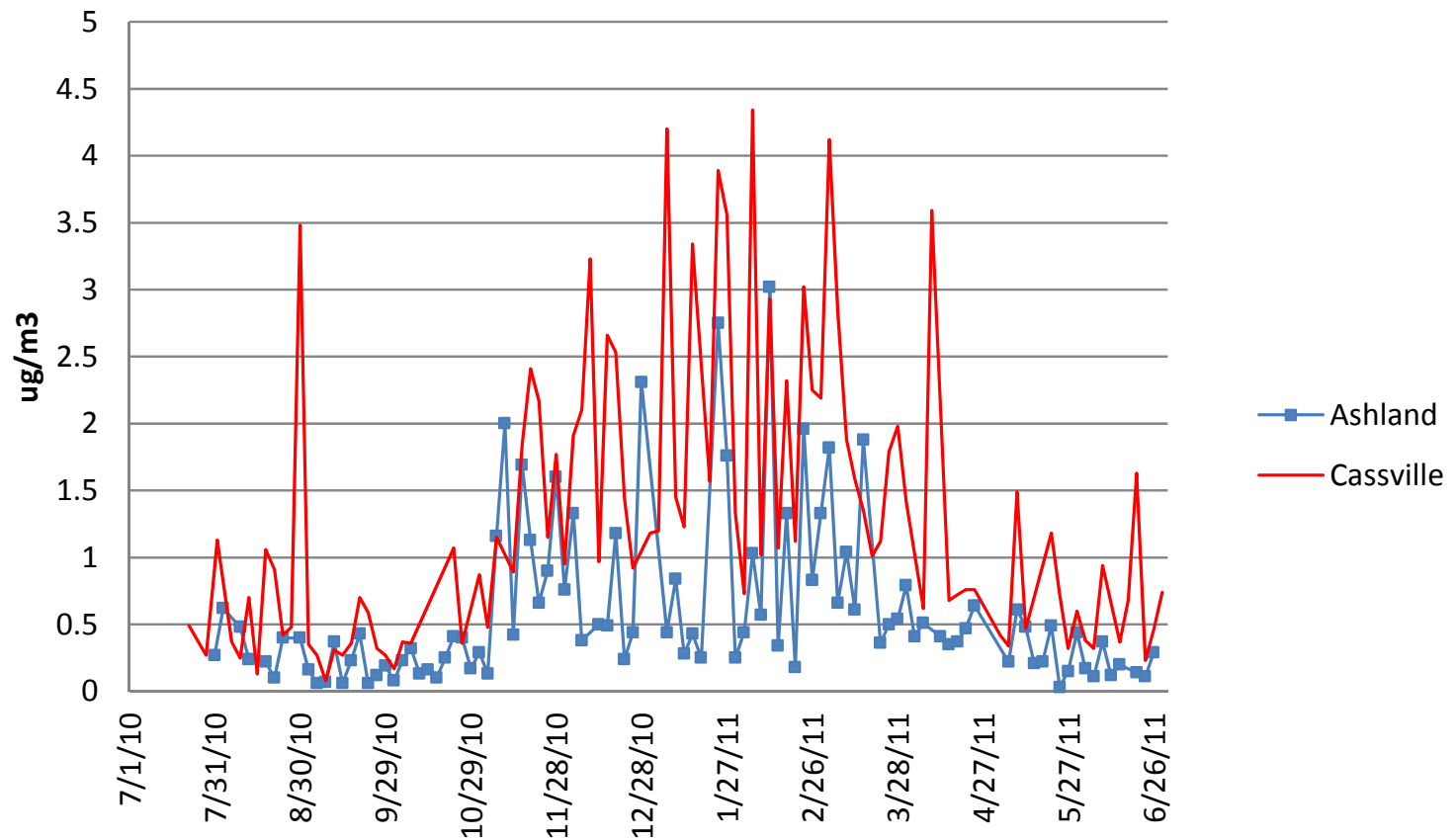


Figure A5. EC time series.

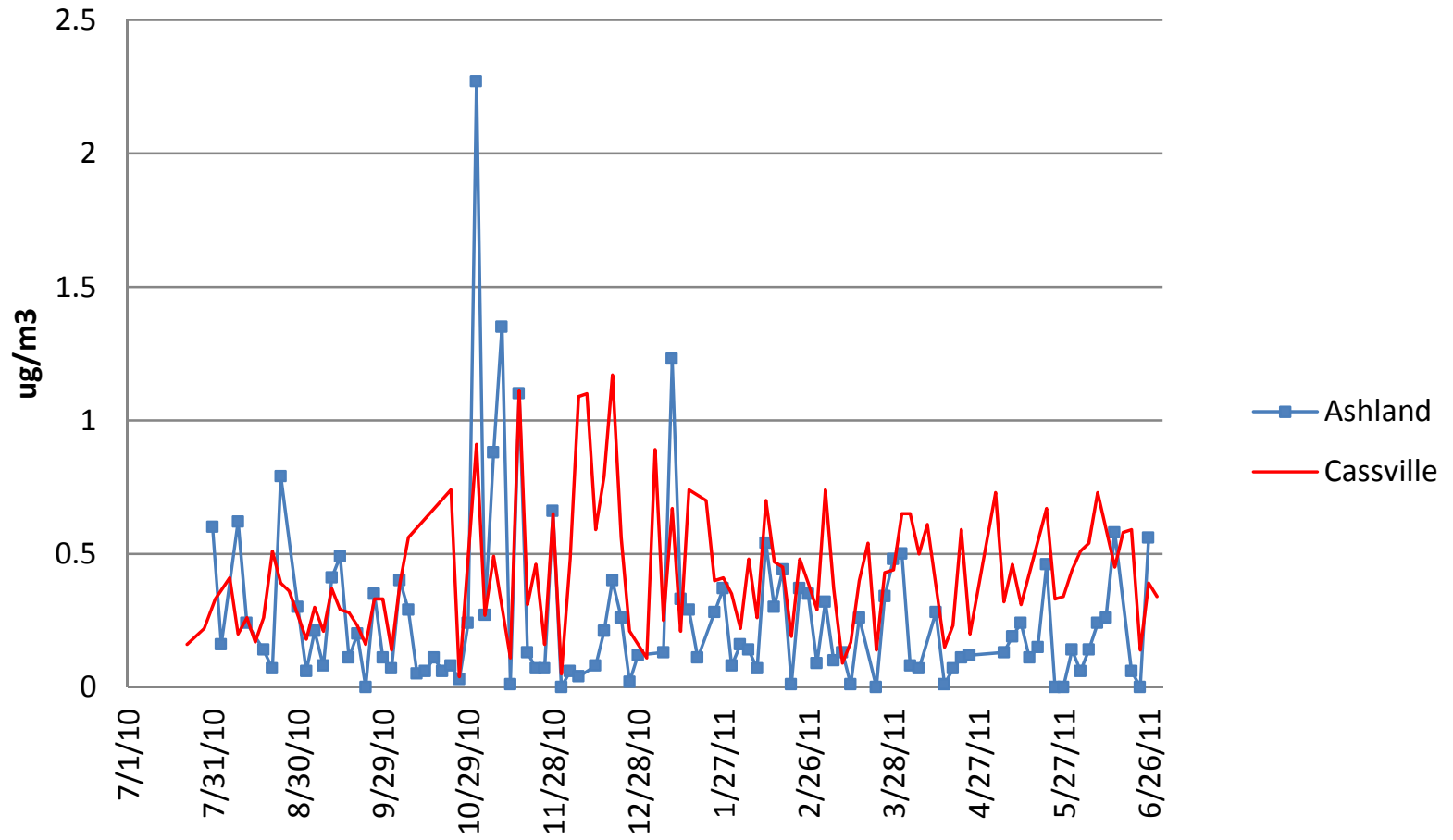


Figure A6. HNO₃(g) time series.

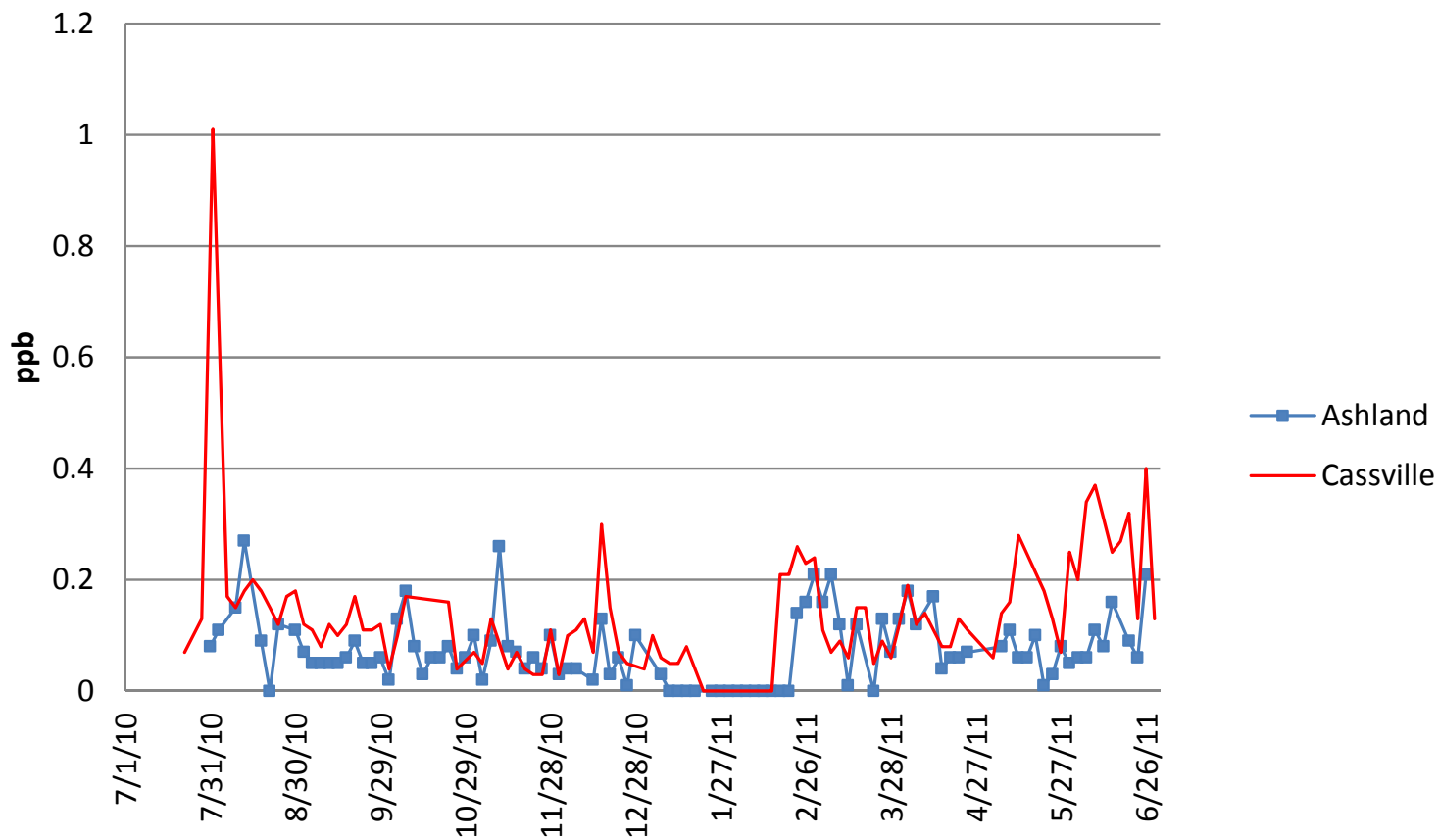


Figure A7. NH₃(g) time series. NH₃(g) is significantly higher at Cassville. Cassville shows a spring NH₃ elevation as well as a fall NH₃ elevation.

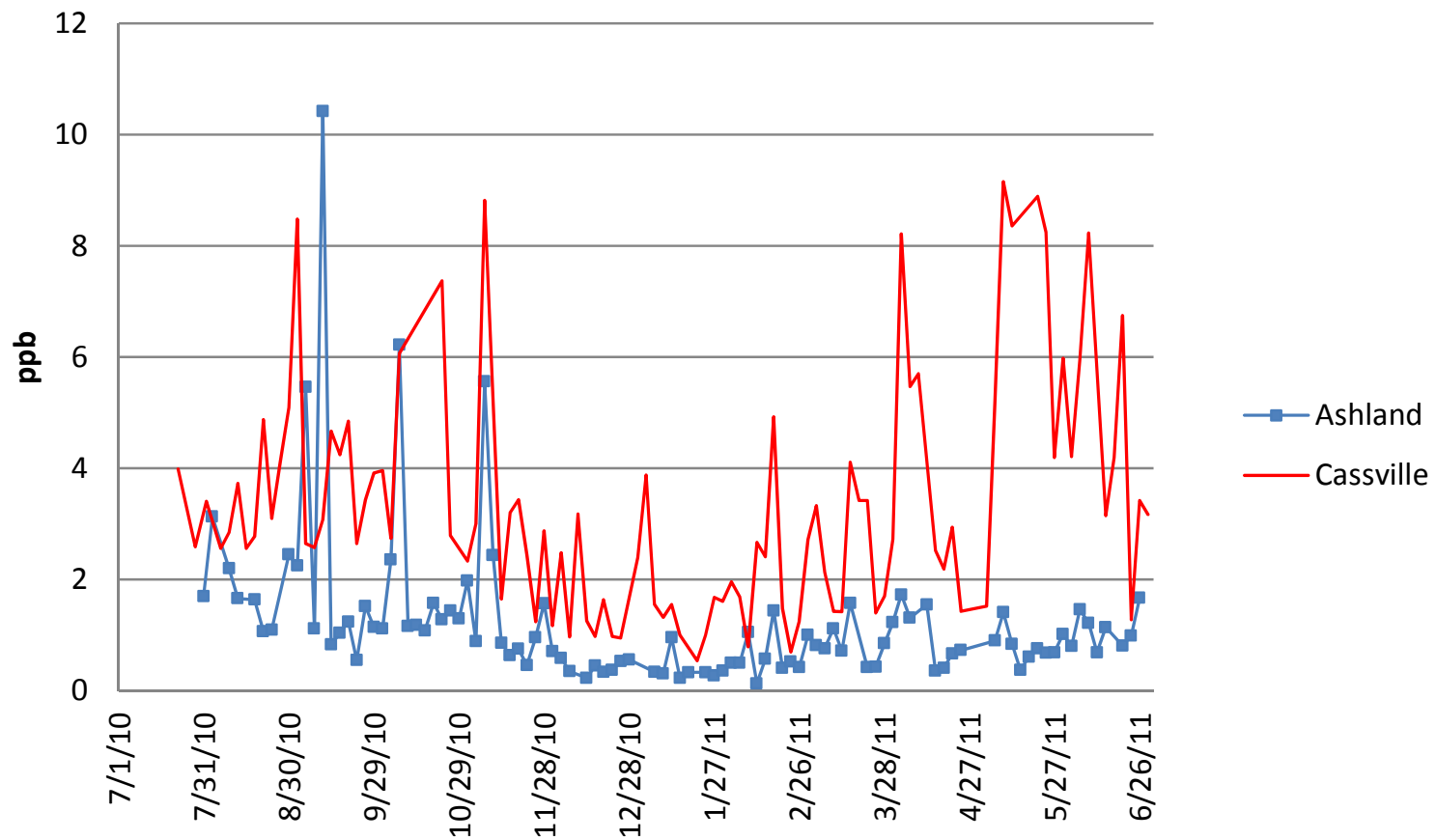


Figure A8. Total ammonia time series.

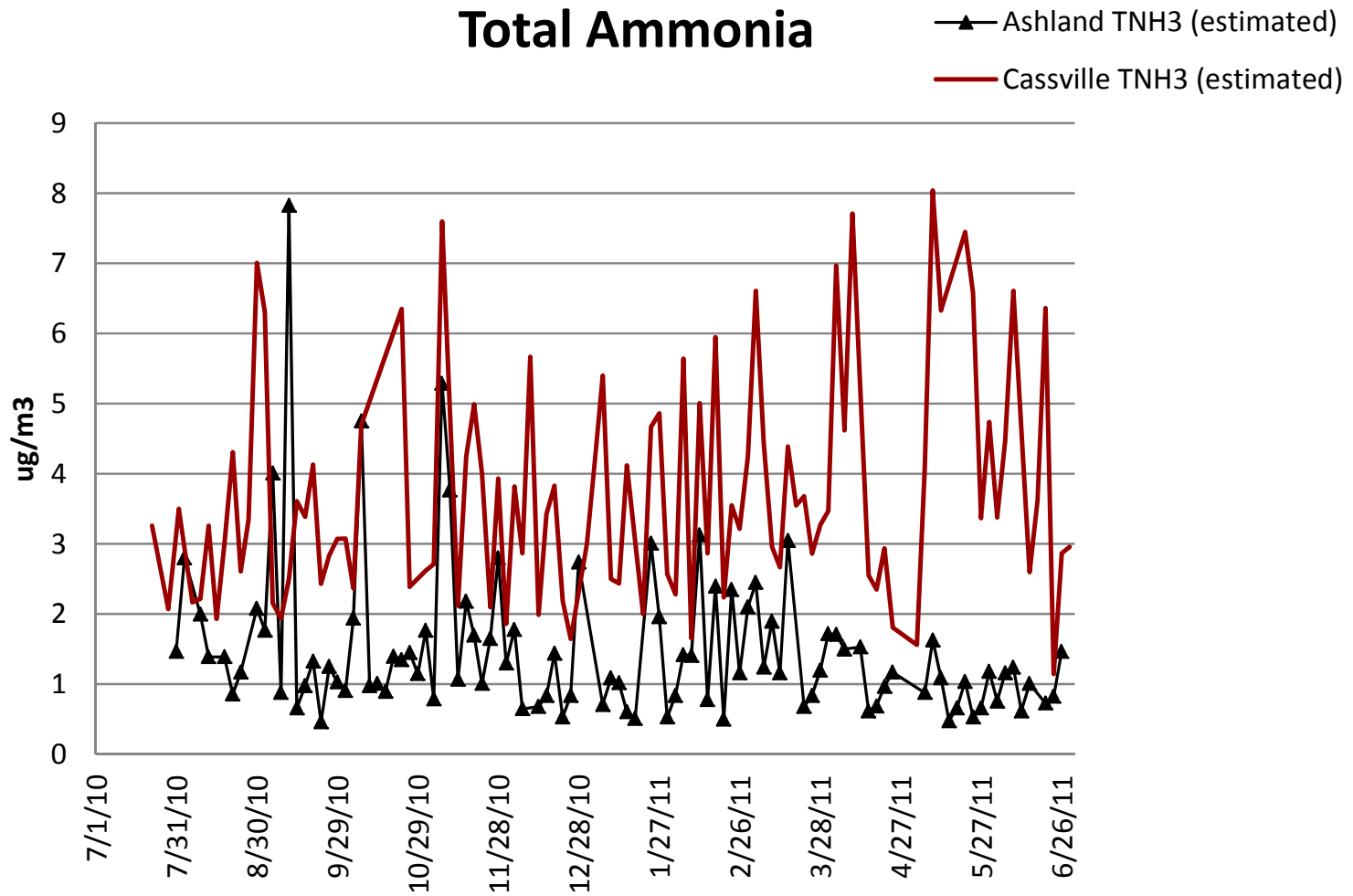


Figure A9. Ammonia Partitioning (Modeled) – Cassville
Nearly all gas phase except Nov - Mar

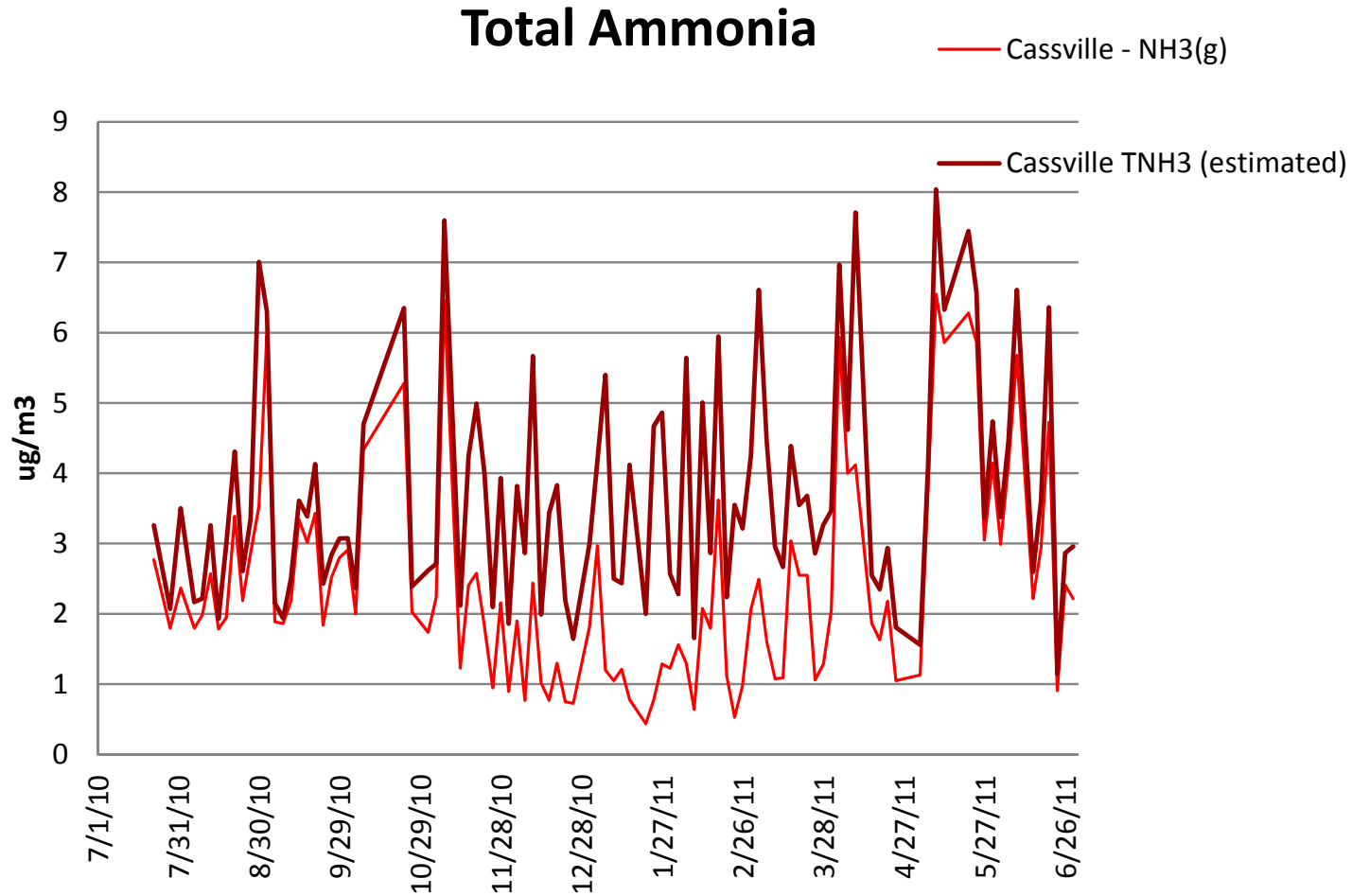


Figure A10. Ammonia Partitioning (Modeled) – Ashland
Nearly all gas phase except Nov - Mar

Ashland Ammonia Partitioning

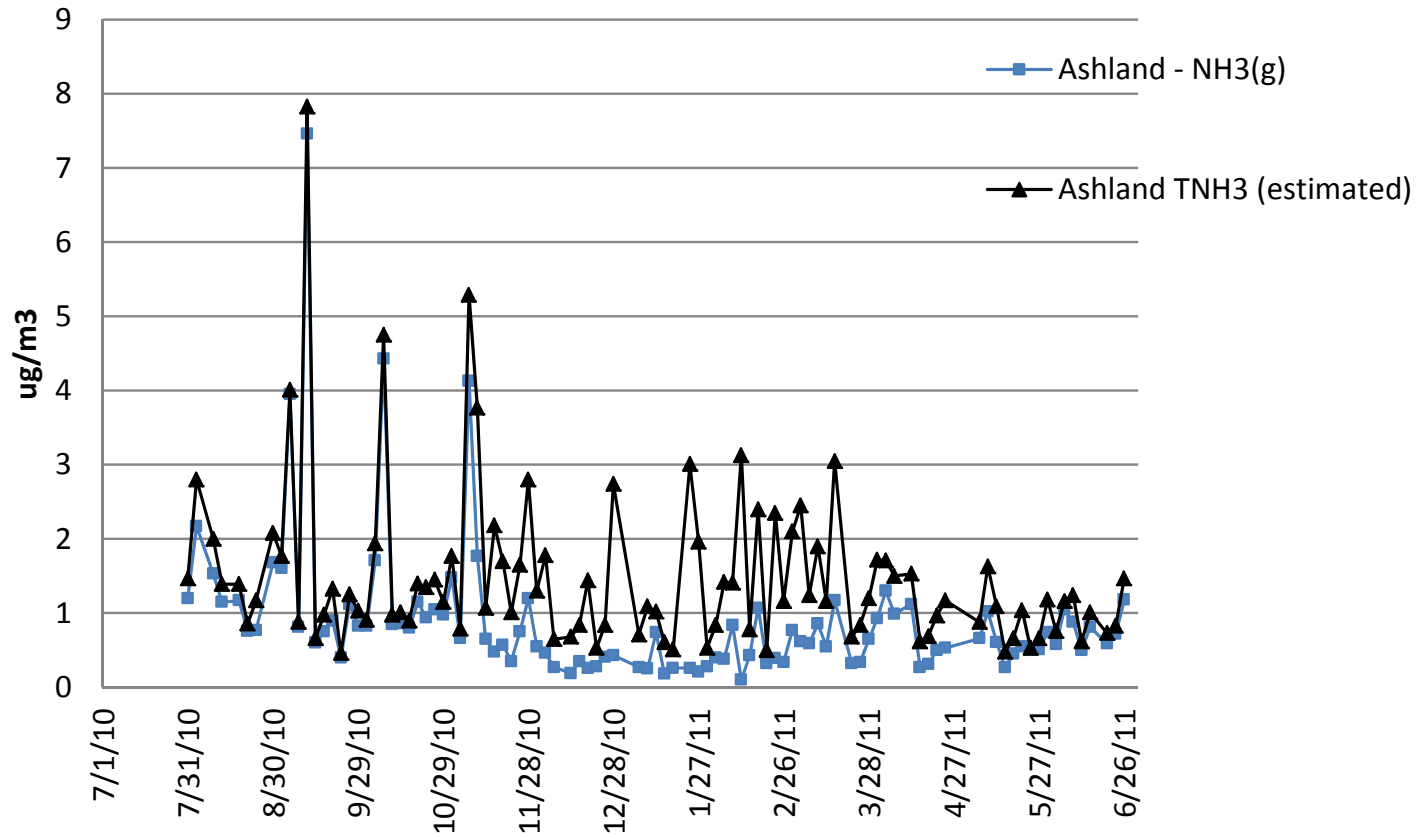


Figure A11. Degree of Sulfate Neutralization
[moles NH₄(p) – moles NO₃(p)] / [moles SO₄]]
Note that NH₄(p) is modeled.

Estimated DSN - no blank corrections

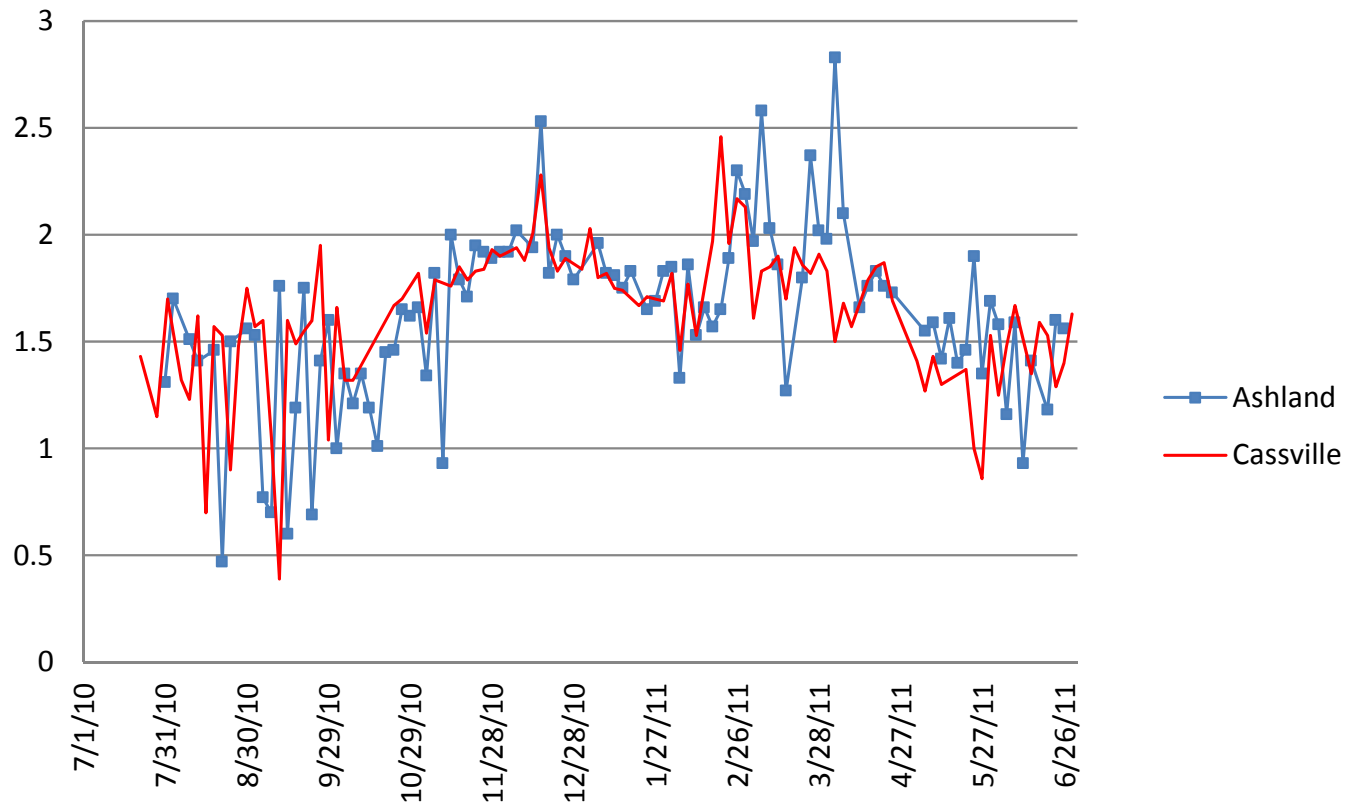


Figure A12. OC/EC Ratio time series. Ashland OC/EC ratio higher.

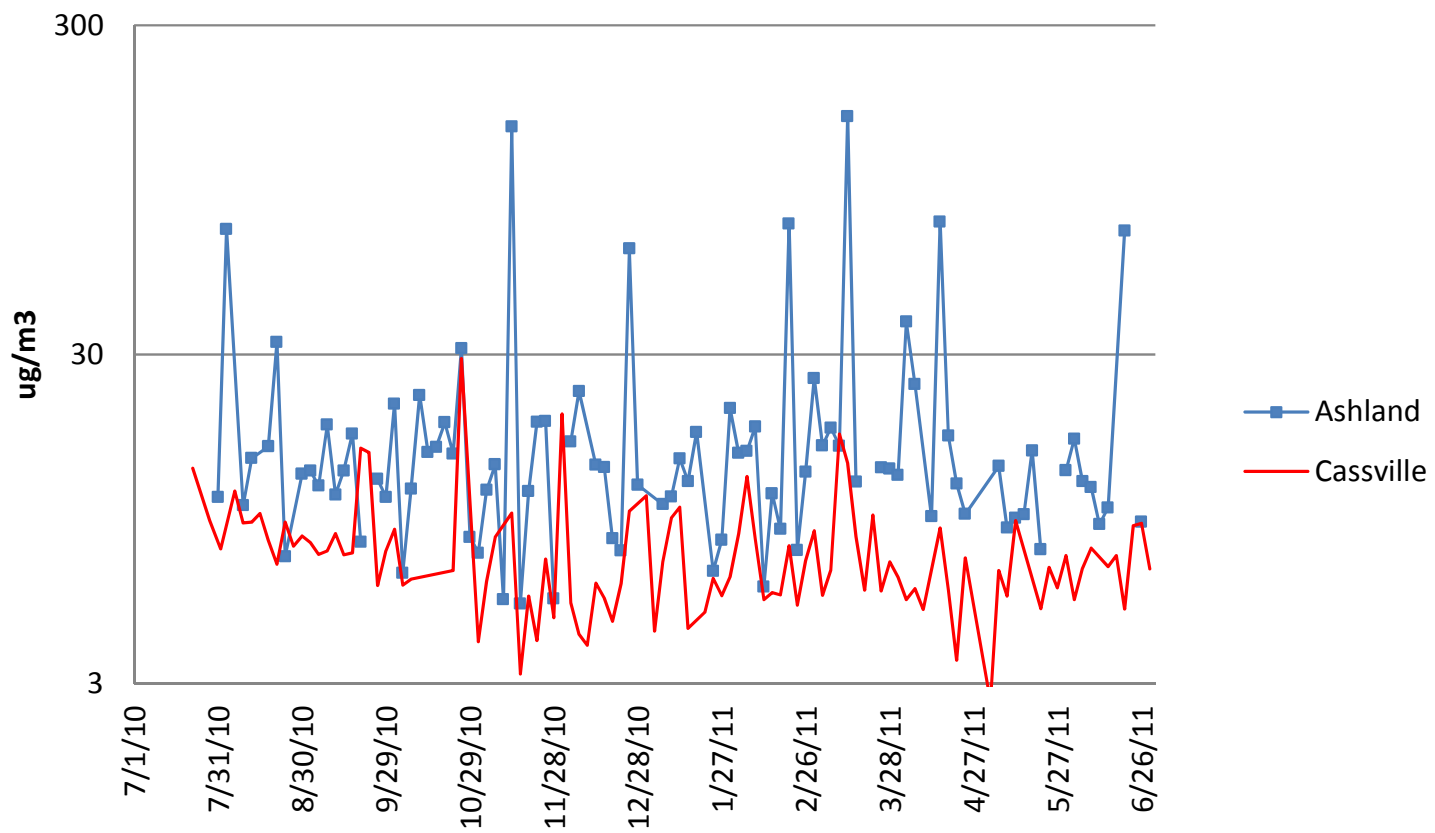


Figure A13. Gas Ratio vs. PM2.5

In the winter nitrate study (right hand plot), a decrease was seen in gas ratio as PM2.5 increased, especially at Mayville (rural site). This seems to be replicated in the Ashland/Cassville data. Analysis only for the Jan-Mar months to match the WNS.

PM2.5 vs Gas Ratio during same months as WNS

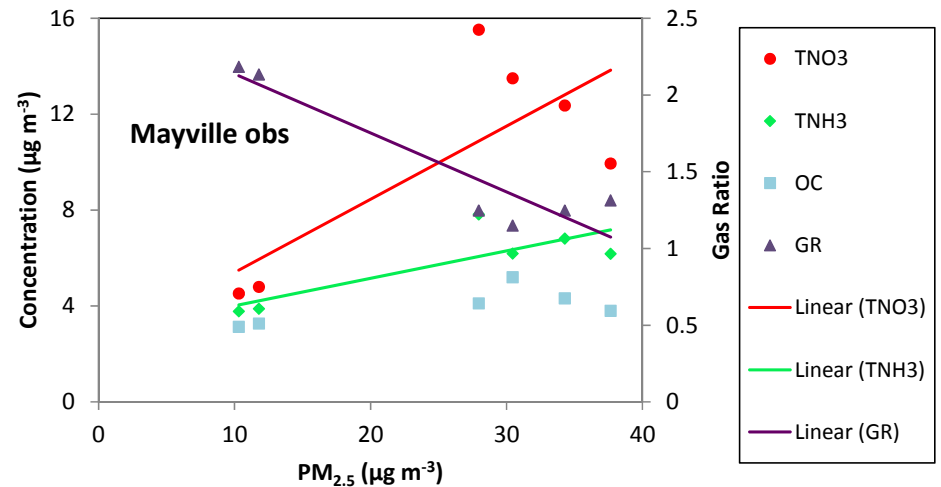
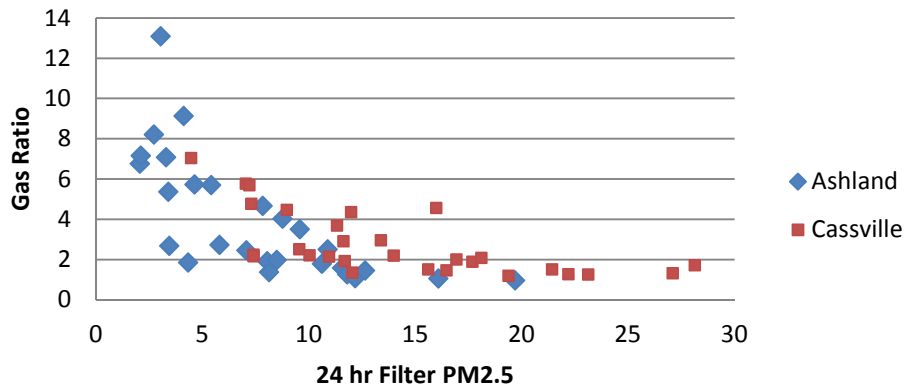


Figure A14. During non-winter periods, the measured gas ratios are higher and consequently, the sensitivity to NH₃ will be less during the non-winter periods. A check shows the gas ratios do not decrease during high PM periods during the warm season. This is not surprising given that the gas ratio has total nitrate in the denominator.

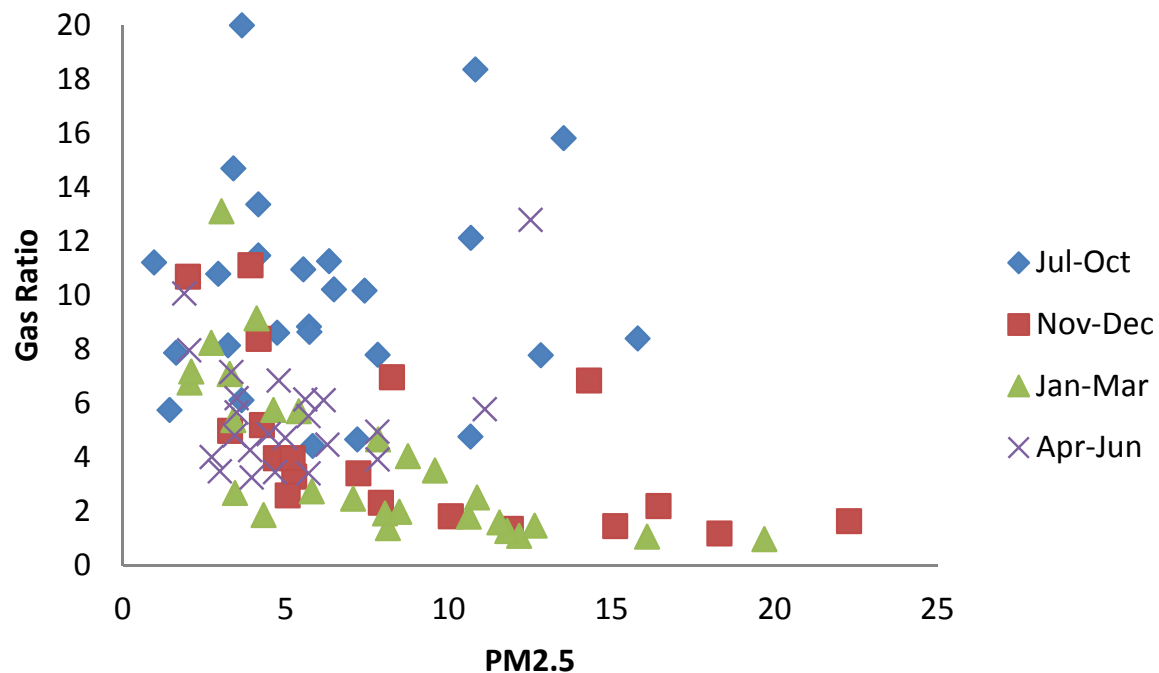


Figure A15. Ashland, all study days.
Sensitivity to TNH_3 and TNO_3 reductions
(balanced, but sensitivity is low overall due to high organic fraction)

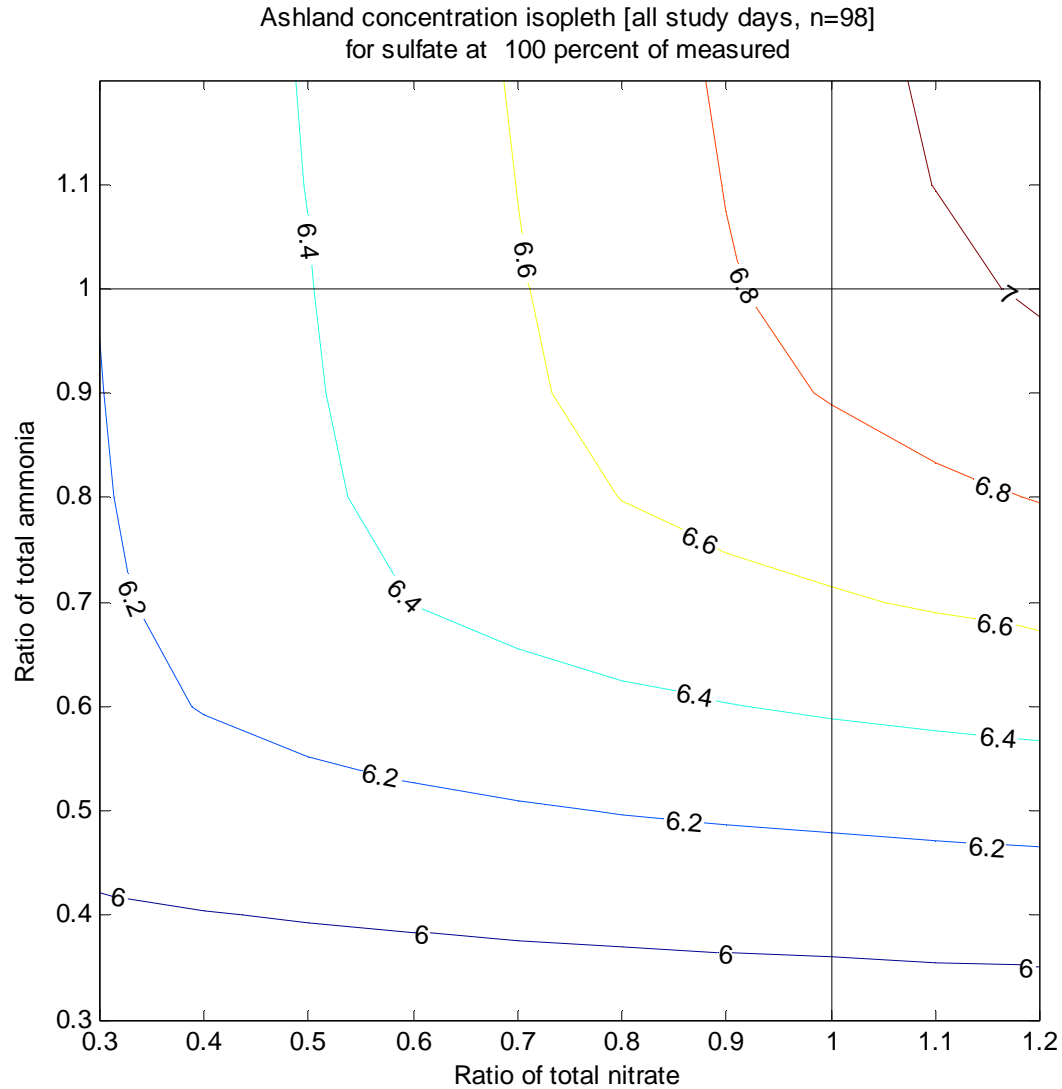


Figure A16. Cassville, all study days.
Sensitivity to TNH_3 and TNO_3 reductions
(TNO_3 reduction slightly more effective)

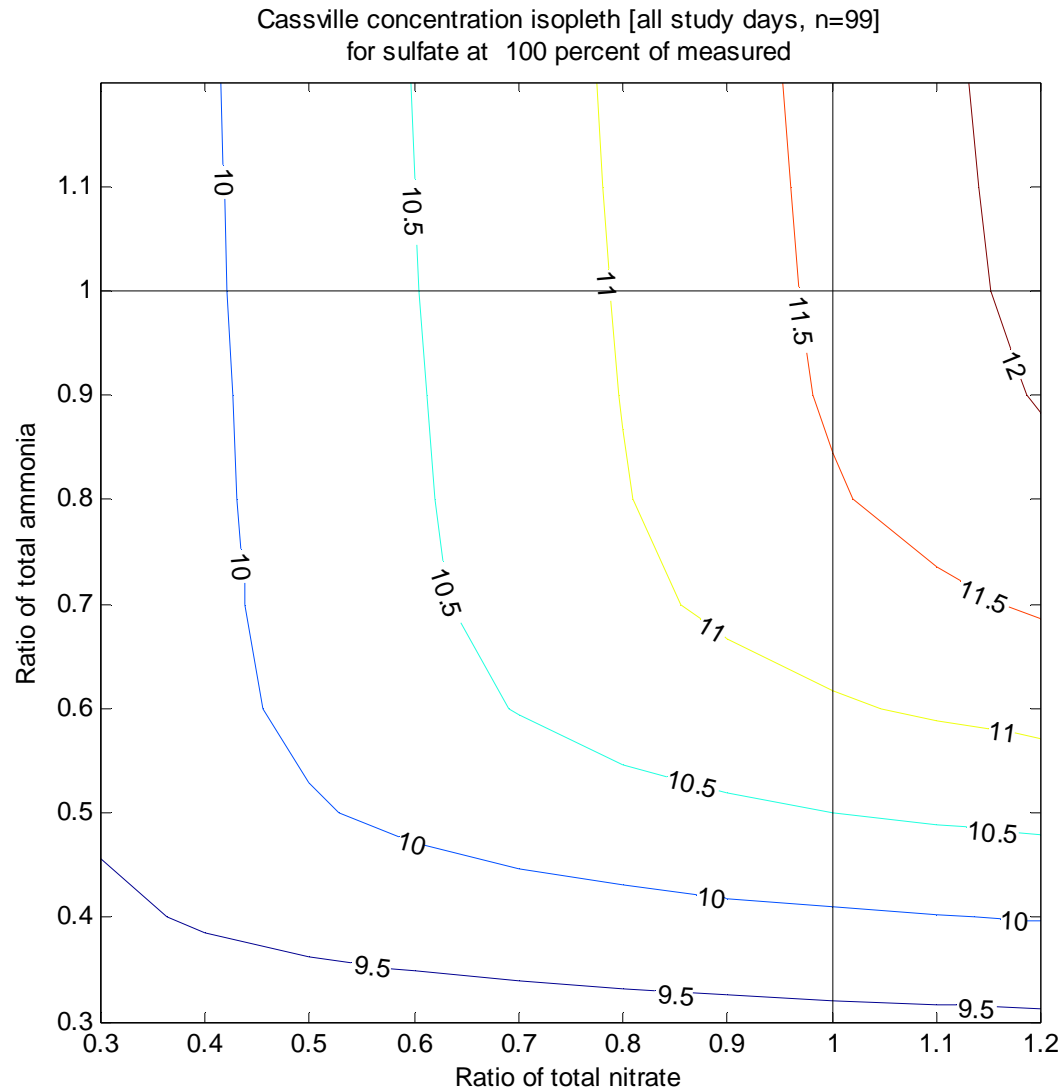


Figure A17. Ashland, all study days with $PM_{2.5} > 15$
Sensitivity to TNH_3 and TNO_3 reductions
(balanced, with TNH_3 reduction slightly more effective)

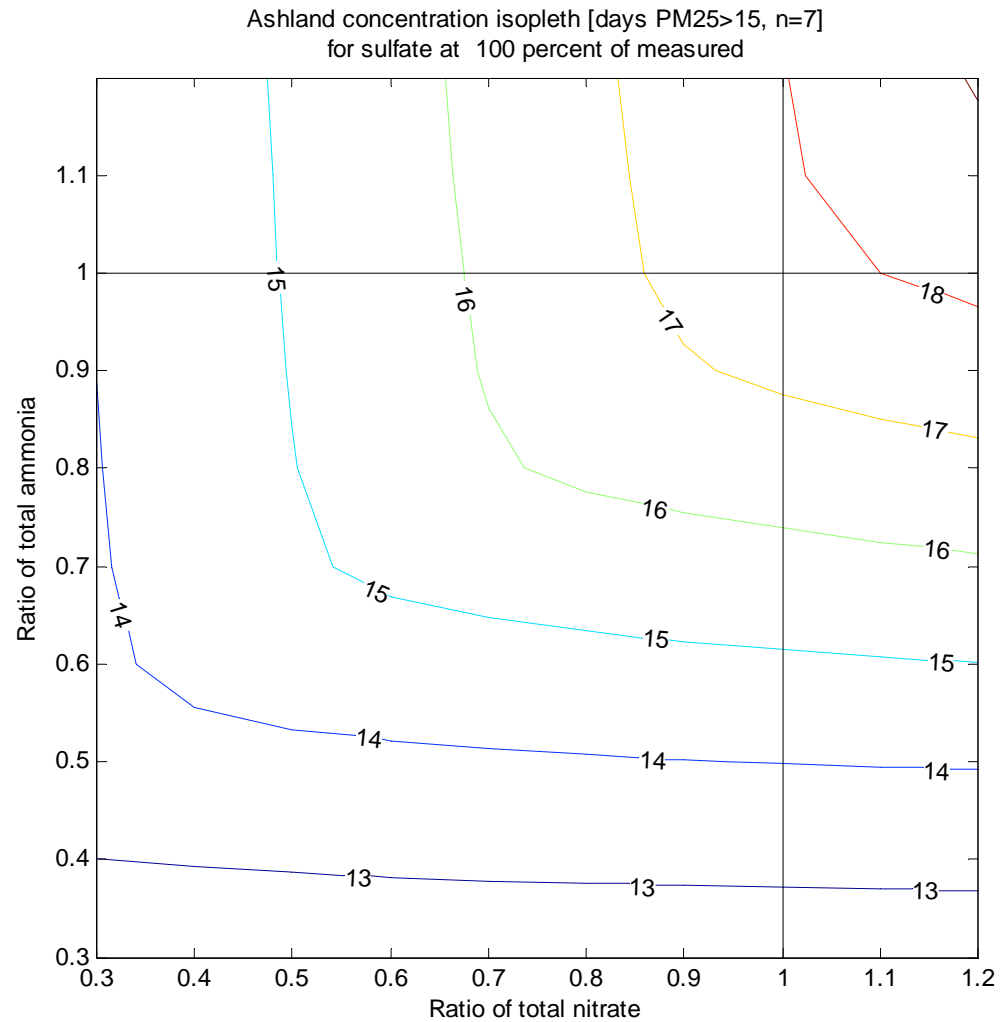


Figure A18. Cassville, all study days with $PM_{2.5} > 15$
Sensitivity to TNH_3 and TNO_3 reductions
(slightly more sensitive to TNO_3)

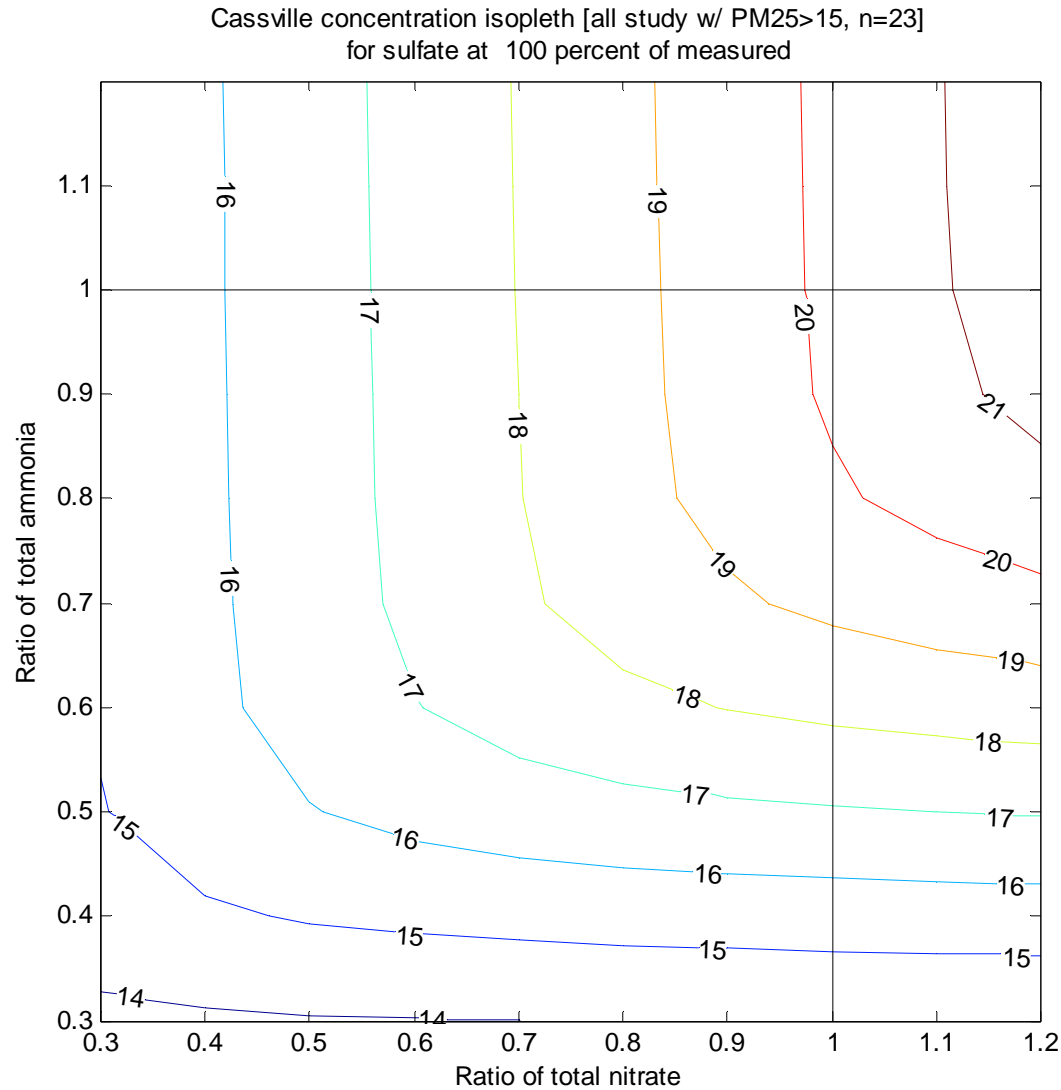
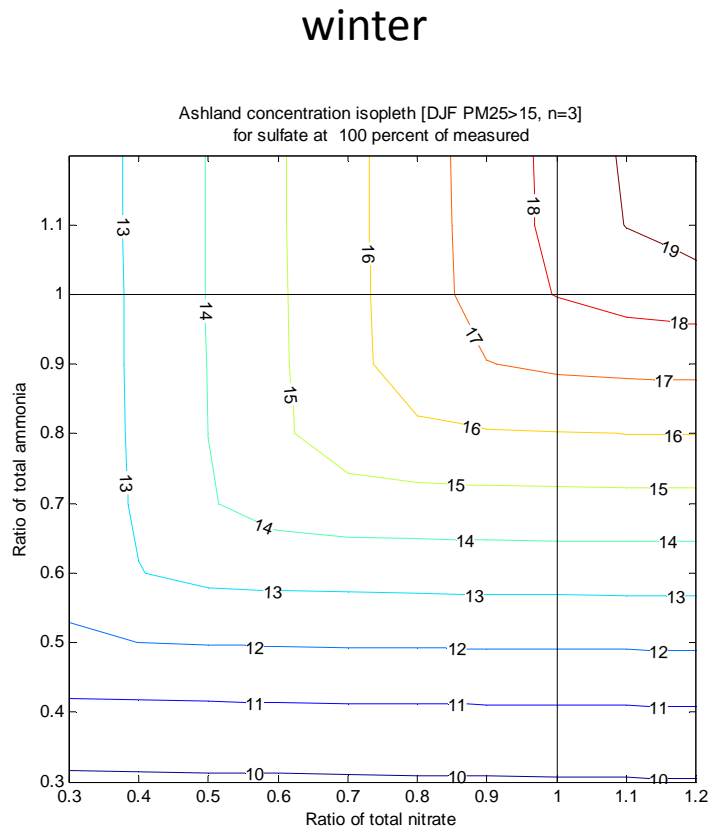


Figure A19. Ashland, Winter (DJF) vs. Summer (JJA) Comparison, High PM_{2.5} Days. Sensitivity to TNH₃ and TNO₃ reductions



No summer samples
with PM_{2.5} > 15 and all
needed inorganic species
at Ashland

Figure A20. Cassville, Winter (DJF) vs. Summer (JJA) Comparison, High PM_{2.5} Days. Sensitivity to TNH₃ and TNO₃ reductions

