Chapter 11. Ammonia and Ammonium Measurements from Passive, Modified IMPROVE and CASTNET Samplers.

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11.1 INTRODUCTION

Ammonia, NH_3, is a ubiquitous component of the ambient atmosphere, and although its lifetime in the atmosphere generally ranges from only a few hours to a few days, its impacts can be significant. Ammonia, a strong base, will react quickly with atmospheric acids to form fine particulate matter. Two common reactions, whose products are ammonium salts, are depicted by equations 11.1 and 11.2 below:

$$NH_{3(g)} + H_2SO_{4(g)} \rightarrow NH_4HSO_{4(s)} + NH_{3(g)} \rightarrow (NH_4)_2SO_{4(s)} \quad 11.1$$

$$NH_{3(g)} + HNO_{3(g)} \leftrightarrow NH_4NO_{3(s)} \quad 11.2$$

In the first reaction, NH_3 reacts with sulfuric acid (H_2SO_4) to produce particulate ammonium sulfate ($(NH_4)_2SO_4$). In the second reaction, NH_3 reacts with nitric acid (HNO_3) to produce particulate ammonium nitrate (NH_4NO_3). Note that the second reaction is reversible; hence, an equilibrium exits between the solid and gas phases that is dependent upon temperature, relative humidity (RH), and the concentrations of the precursor gases. These fine aerosol particles efficiently attenuate radiation through the atmosphere, thereby contributing to visibility-reducing haze and climate forcing. The small particles also penetrate deep into lungs, negatively impacting human health by stressing the respiratory, pulmonary, and immune systems, causing increased morbidity and mortality rates.

Ammonia gas deposits directly from the atmosphere onto terrestrial and aquatic ecosystems (dry deposition). Ammonia also dissolves readily into the aqueous phase and will subsequently be washed out of the atmosphere as ammonium ion (NH_4^+) in precipitation (wet deposition). When deposited, either as ammonia or ammonium ion, eventually ammonia causes an over enrichment of nitrogen (N) in the environment. The effects of deposition are numerous and include eutrophication of surface water, with a consequent decrease in biodiversity. In the terrestrial environment, excess NH_3 deposition leads to increased soil acidity, alteration of the soil's chemical balance, and crop damage, and affects ecosystems by favoring species that require higher nitrogen concentrations.

A large fraction of ammonia is emitted from concentrated animal feeding operations (CAFO). Over the past several decades animal husbandry practices have undergone a significant shift from small family farms to much larger factory-type operations. For example, from 1982 through 1997 total livestock production increased by about 10%, while the total number of feeding operations decreased by more than 50%. The remaining CAFO became more geographically concentrated. This combination of larger and more geographically concentrated operations has led to significant regional sources of ammonia emissions. The extensive cultivation of nitrogen-fixing legumes and the use of various types of ammonia-based fertilizer also contribute substantially to reactive forms of nitrogen entering the environment. On a global basis, it is estimated that agriculture practices such as animal husbandry and farming contribute

60–80% of the total ammonia emission budget. Other important sources of ammonia include the oceans, biomass burning, humans and their pets, and natural ecosystems.

Despite the clear importance of the NH_3/NH_4^+ system to atmospheric chemistry and deposition to aquatic and terrestrial ecosystems, there have been relatively few studies performed to understand ammonia emission inventories, atmospheric transport, or ammonia deposition velocities, all of which are needed to model and predict the concentration and effects ammonia might have if concentrations continue to increase. Furthermore, there are no national networks performing routine measurements of ammonia gas to discern the spatial and temporal distribution of ammonia. This study was designed to investigate the feasibility of modifying existing aerosol samplers currently used in various national networks for monitoring the NH_3/NH_4^+ system and evaluating passive samplers for NH_3 measurement.

11.2 INSTRUMENTATION

There are several networks currently operating across the country that monitor various aspects of ambient air quality. Each network utilizes a sampling system designed to monitor the parameters of interest for that particular network. In this study the IMPROVE and Clean Air Status and Trends Network (CASTNET) samplers were modified by adding an acid-impregnated filter for the measurement of ammonia and ammonium ion. The concentration obtained from these samplers is then compared with a denuder-based URG (URG Corporation) sampler and with passive samplers. Each of these sampling systems is described below. In conjunction with the aerosol sampler measurements, meteorological measurements of wind speed and direction, temperature, relative humidity, and solar radiance were also made. The aerosol samplers used in this study were operated on the roof of a trailer located in a somewhat isolated part of the Foothills Campus at Colorado State University. The inlet of the CASTNET sampler, which houses the filter pack, and the IMPROVE, URG, and passive samplers are shown in Figure 11.1 from left to right.

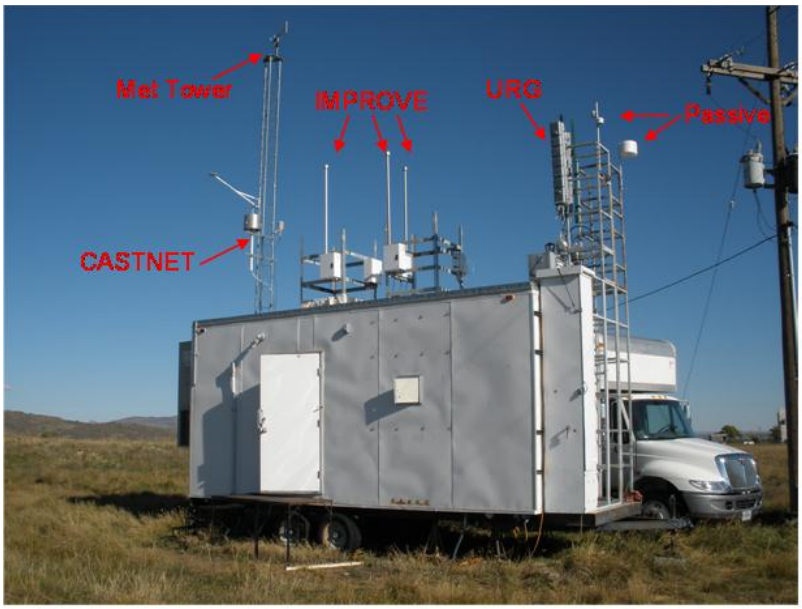

Figure 11.1. Study trailer showing aerosol sampling equipment. The CASTNET, Met tower, IMPROVE, URG, and passive samplers are shown from left to right.

11.2.1 URG Sampler

The URG samplers were configured as follows, in order of sample air flow: a 2.5 μm size-cut, Teflon®-coated cyclone, a sodium carbonate (Na_2CO_3) coated denuder to capture acidic gases (HNO_3 and sulfur dioxide, SO_2), a phosphorous acid (H_3PO_3) coated denuder to capture ammonia, a Nylasorb filter to remove particulate material, and finally a second H_3PO_3-coated denuder to capture any NH_3 from NH_4NO_3 particles that have volatilized from the filter (see Figure 11.2). The samplers operated at a flow rate of 10 LPM; the sample volume was measured using a dry gas meter. This system has been shown to minimize sampling artifacts; therefore, the URG denuder/filter-pack sampler is considered the "field standard" for this study. Two URG samplers operating side by side were used for comparison purposes. One sampler operated on a 24-hour sample collection period. This sampler was used to compare with the 24-hour sampling cycle of the IMPROVE sampler. The other URG sampler operated on a weekly sample collection period to compare with the weekly sampling cycle of the CASTNET sampler. Previous studies have shown the minimum detection limits (MDL) of sulfate, nitrate, and ammonium ion concentrations from the URG are 0.05, 0.07, and 0.03 μg m^{-3}, respectively. The precision (expressed as relative standard deviation, RSD) for these species is 5.2%, 6.7%, and 4.5%, respectively (Yu et al., 2006). Similar results for MDL and RSD are reported by Lee et al. (2004).

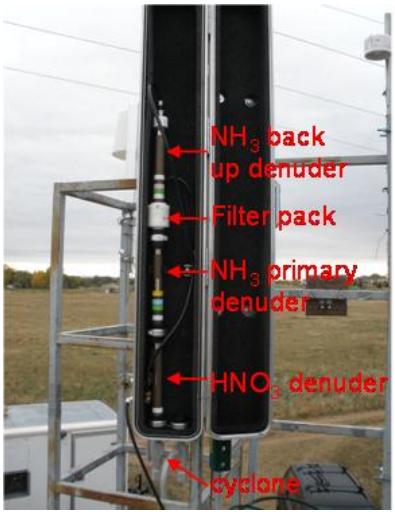

Figure 11.2. URG sampler with the NH_3 backup denuder at top and filter pack, NH_3 primary denuder, HNO_3 denuder, and $PM_{2.5}$ cyclone at bottom. Note the top of the sampler is the outlet and the bottom of the sampler is the inlet.

11.2.2 IMPROVE Sampler

Visibility-impairing particulate matter is monitored within selected national parks and other Class I visibility areas by the IMPROVE network (Malm et al., 1994). This network uses a sampling system which consists of four modules (channels A, B, C, and D). Each module has a separate size selective inlet, filter medium, flow control, and pump, but are connected to a single control unit. Each module utilizes a cassette, which holds four filters allowing the sampler to operate 1–2 weeks unattended. The unmodified Channel B utilizes a Nylasorb filter to collect aerosol samples that are analyzed by ion chromatography (IC) for sulfate and nitrate ion concentrations. However, Channel B was modified for this work by adding a phosphorous-acid-

impregnated cellulose fiber filter to collect NH_3 gas. Figure 11.3 shows the arrangement of the IMPROVE sampler filter cassette. The cellulose fiber filter was placed between the cassette filter holder and the Teflon spacer, while the Nylasorb filter was placed between the Teflon-coated support grid and the top of the cartridge assembly. Figure 11.4 shows the filter cassette in the channel B module ready for sample collection.

Figure 11.3. IMPROVE sampler filter cassette with additional screen and spacer for NH_3 collection. The sampler includes 1) cassette filter holder, 2) Teflon spacer, 3) Teflon-coated support grid, and 4) top of cartridge assembly.

Figure 11.4. IMPROVE sampler channel B with sample cassette installed.

11.2.3 CASTNET Sampler

The CASTNet filter pack uses a Teflon filter to collect the following particulate species: sulfate, nitrate, ammonium, calcium, magnesium, sodium, and potassium. A nylon filter collects nitric acid and some of the SO_2, and dual potassium-carbonate-impregnated cellulose filters collect the remaining SO_2. The CASTNET sampler collects weekly samples at a flow rate of 1.5 LPM in the eastern United States, where aerosol concentrations are higher, and 3 LPM in the western United State, where aerosol concentrations are generally lower. Total aerosol concentrations are collected, as CASTNET does not use a size-selective cyclone. The sampler flow rate is calibrated to standard conditions; thus, volumes were corrected for ambient pressure and temperature before comparing to other samplers. The CASTNET filter packs were prepared at MacTech (MacTech Engineering and Consulting, Inc., Gainesville, Florida) and shipped in

sealed plastic bags as per network protocol. For this study the filter pack was modified to accommodate another filter (citric-acid-impregnated cellulose fiber filter) for the collection of ammonia gas. Figure 11.5 shows a disassembled CASTNET filter pack and a filter pack ready for deployment. Figure 11.6 shows regular and modified CASTNET filter packs in the sampler holder.

Figure 11.5. CASTNET filter pack ready for deployment (left) and a disassembled filter pack (right).

Figure 11.6. Regular (left) and modified (right) CASTNET filter packs in the sample holder.

11.2.4 Passive Samplers

The Radiello (Sigma-Aldrich, St. Louis, Missouri) and the Ogawa (Ogawa & Co. USA Inc., Pompano Beach, Florida) passive samplers were also deployed during this study. These passive samplers work by the simple diffusion of NH_3 through the atmosphere and across a diffusive body surface and, finally, deposition onto a cartridge impregnated with acid. Passive samplers have some advantages over conventional sampling systems: they are self-contained units, relatively inexpensive, and simple to operate, and they have zero power requirements. The Radiello passive sampler was operated in triplicate throughout this study, while two Ogawa

passive samplers were operated side by side. Figure 11.7 shows the passive samplers deployed in the field.

Figure 11.7. Passive samplers deployed in the field. The Ogawa sampler is on the left, and the Radiello sampler is on the right.

11.3 COMPARISONS OF DATA FROM CASTNET, URG, AND IMPROVE SAMPLERS

Although NH_3 was the primary species of interest during this study, other aerosol species such as sulfate and nitrate are also compared. The comparison of other species serves to evaluate the overall quality of analytical procedures, provides estimates of uncertainty, and allows for the evaluation of changes to the samplers caused by the addition of the cellulose fiber filter.

11.3.1 IMPROVE versus URG

The IMPROVE and URG samplers were operated in August–October 2008 for a 24-hour sampling duration starting at 9:00 a.m. Samples were collected each Monday, Tuesday, Thursday, and Friday, while filter blanks were obtained on the non-sampling days. IC analyses were performed at the Atmospheric Chemistry Laboratory at Colorado State University. Figure 11.8 shows a comparison between sulfate ion concentrations from the regular IMPROVE, modified IMPROVE, and URG samplers. The timeline and the scatter plot show some scatter between data points; however, in general, there is good agreement in the concentrations from each sampler. On average there is ~1% difference between concentrations from the two IMPROVE samplers and ~ 5% difference between concentrations from the IMPROVE and the URG samplers. This comparison suggests the addition of the cellulose fiber filter to the IMPROVE Channel B sampler has no adverse effect on the measurement of sulfate ion concentrations and demonstrates good agreement in the data obtained with the URG and IMPROVE samplers.

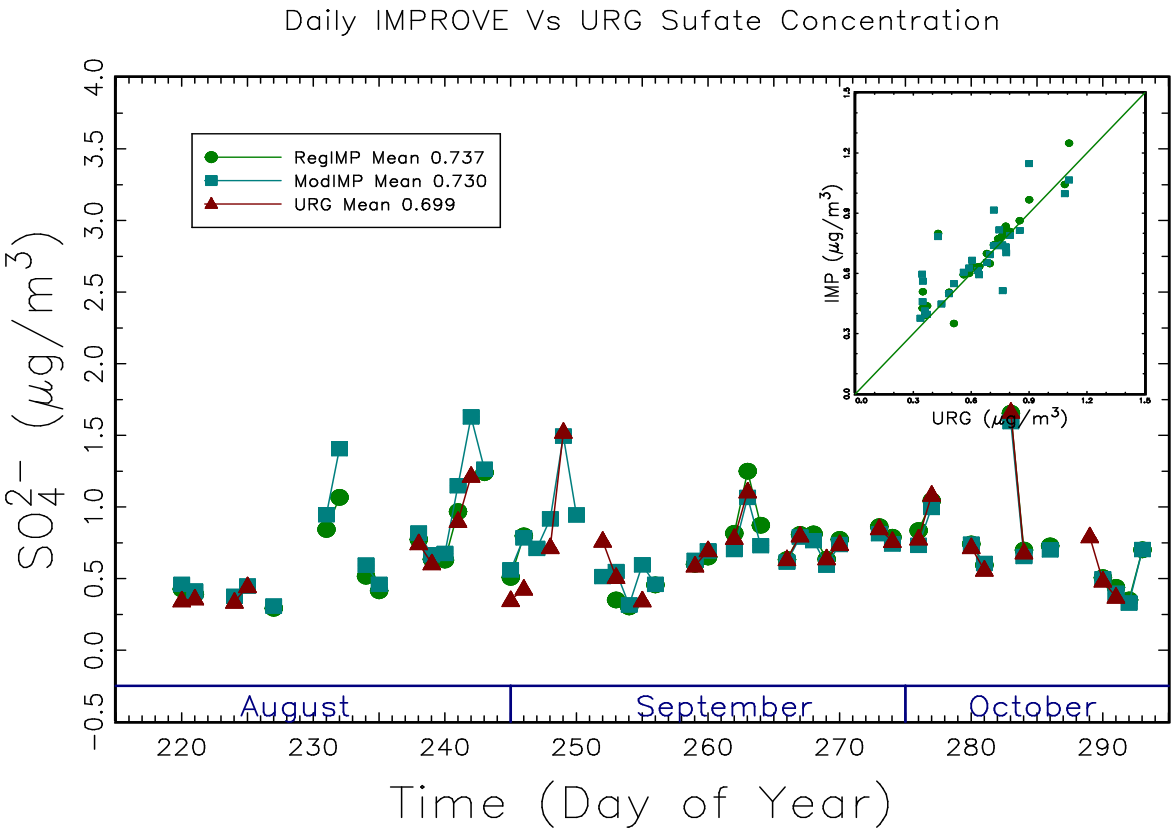

Figure 11.8. Comparisons of sulfate ion (SO_4^{2-}) concentrations from the regular IMPROVE (RegIMP), modified IMPROVE (ModIMP), and URG samplers during fall 2008. Mean sulfate ion concentrations (μg m^{-3}) for each sampler are reported.

A comparison of nitrate ion concentrations between the samplers shows results similar to that of sulfate ion comparisons. Nitrate ion concentrations from the two IMPROVE samplers were nearly identical, and they were both ~5% higher than nitrate ion concentrations obtained from the URG sampler. A timeline and scatter plot of nitrate ion concentrations from the three samplers are shown in Figure 11.9.

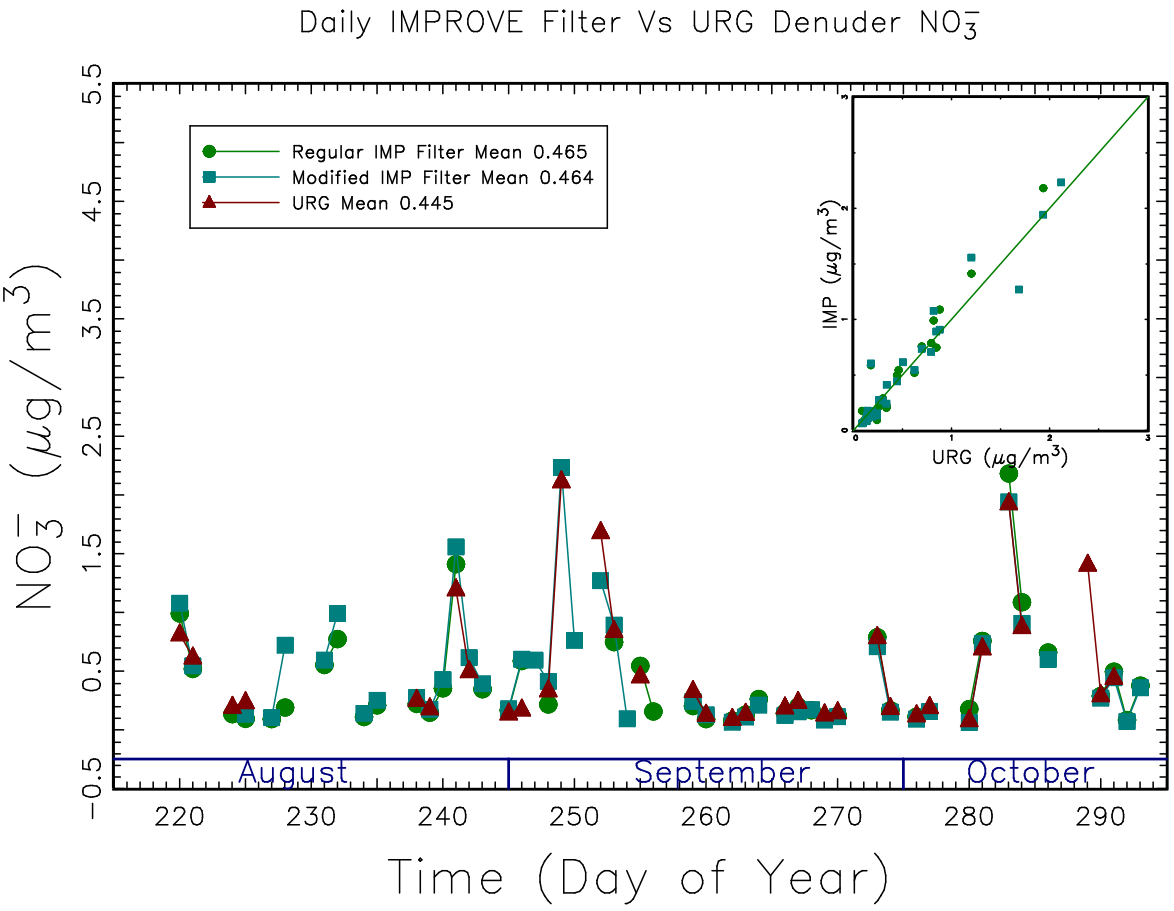

Figure 11.9. Comparisons of nitrate ion (NO_3^-) concentrations from the regular IMPROVE (RegIMP), modified IMPROVE (ModIMP), and URG samplers during fall 2008. Mean nitrate ion concentrations (µg m^{-3}) for each sampler are reported.

Concentrations of ammonium ion are shown below in Figure 11.10. As expected, the concentrations obtained from both of the IMPROVE samplers are lower than those from the URG sampler. Although NH_4NO_3 can be volatilized and NH_3 lost from the Nylasorb filters of both the IMPROVE and the URG samplers, the URG sampler captures the volatilized NH_3 with a backup denuder, thereby mitigating any bias from this dissociation. On average the ammonium ion concentrations were approximately 25–30% less from the IMPROVE sampler compared to the URG sampler. The loss of ammonium ion would of course vary with the concentration of NH_4NO_3, ambient temperature, and RH.

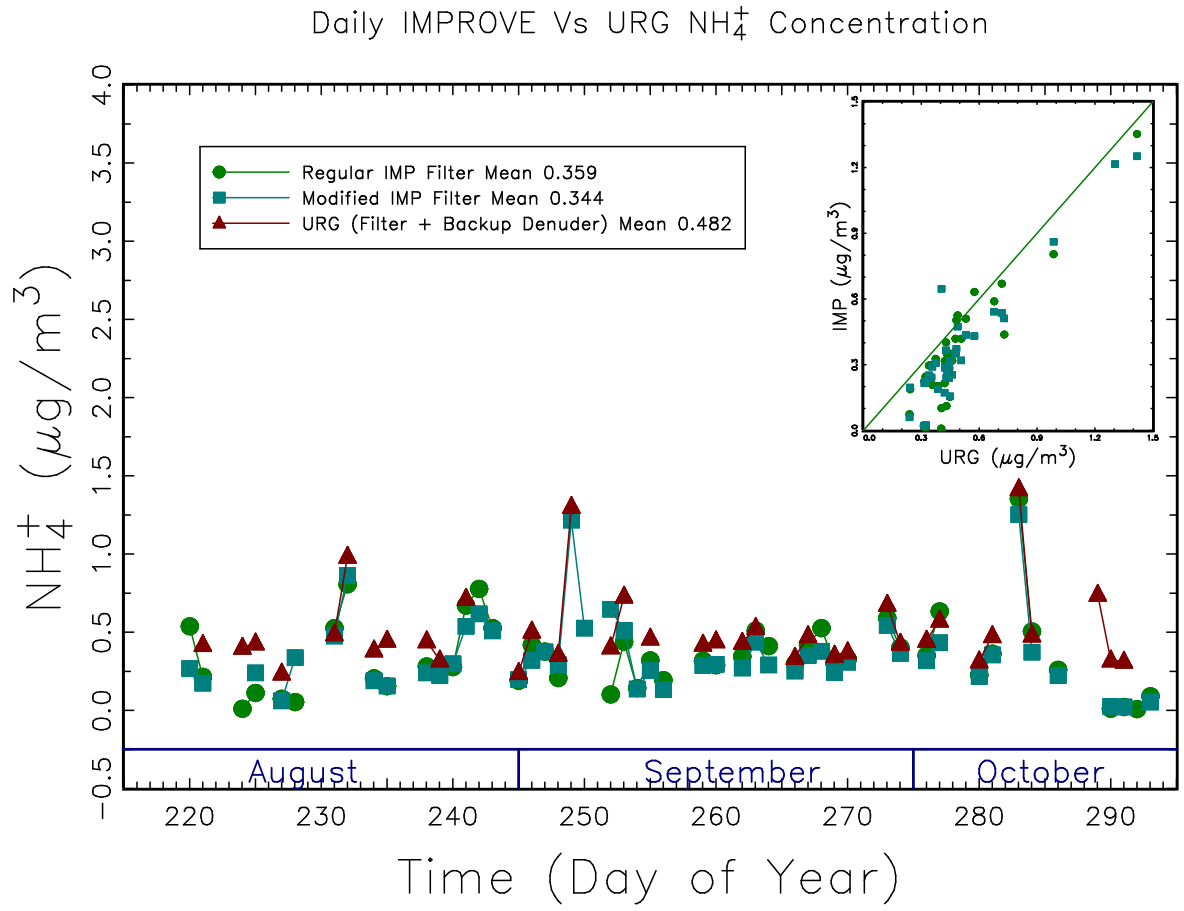

Figure 11.10. Comparisons of ammonium ion (NH_4^+) concentrations from the regular IMPROVE (Regular IMP), modified IMPROVE (Modified IMP), and URG samplers during fall 2008. Mean ammonium ion concentrations (µg m^{-3}) for each sampler are reported.

A comparison of ammonia concentrations from the URG and the modified IMPROVE samplers is shown below in Figure 11.11. The mean ammonia concentration from the IMPROVE sampler was 1.2 times higher than the mean ammonia concentration from the URG sampler. It is expected that concentrations from the IMPROVE sampler would be higher because the acid-impregnated cellulose filter is behind the nylon filter and would therefore collect the ammonia dissociated from ammonium nitrate volatilized from the nylon filter. Clearly, measurements with the IMPROVE sampler will result in some bias in the ammonia and ammonium ion concentrations. The dissociation of ammonium nitrate is the primary reason; however, other acid/base reactions can also occur on the filter to further complicate the interpretation.

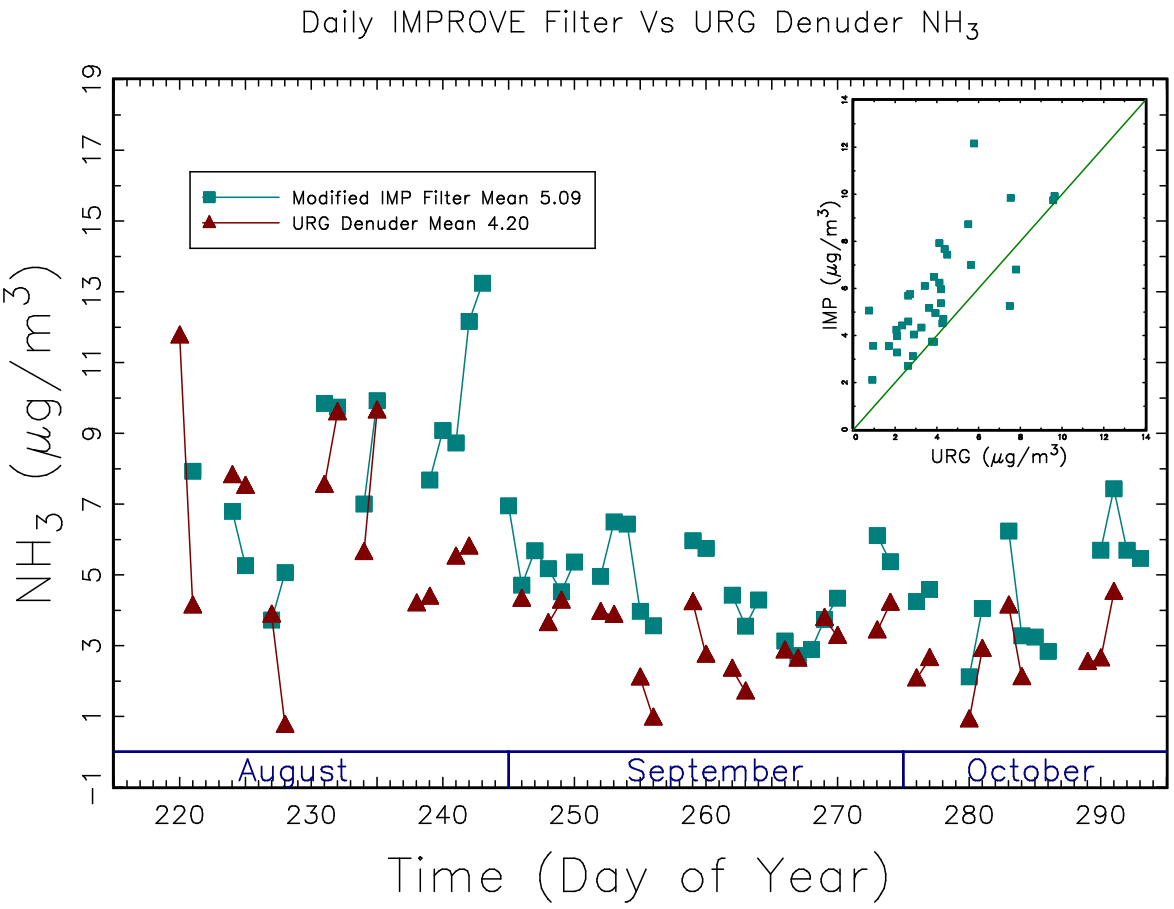

Figure 11.11. Comparisons of ammonia (NH_3) concentrations from the modified IMPROVE (Modified IMP) and URG samplers during fall 2008. Mean ammonia concentrations (µg m^{-3}) for each sampler are reported.

Because of these biases, a comparison of total reduced inorganic nitrogen (NH_x = NH_3 + NH_4^+) was also performed. Figure 11.12 shows a comparison of NH_x concentrations from the modified IMPROVE and URG samplers. The mean concentration from the IMPROVE sampler was 1.15 times higher than the mean concentration from the URG sampler. The bias was lower than when comparing NH_3 or NH_4^+ concentrations individually.

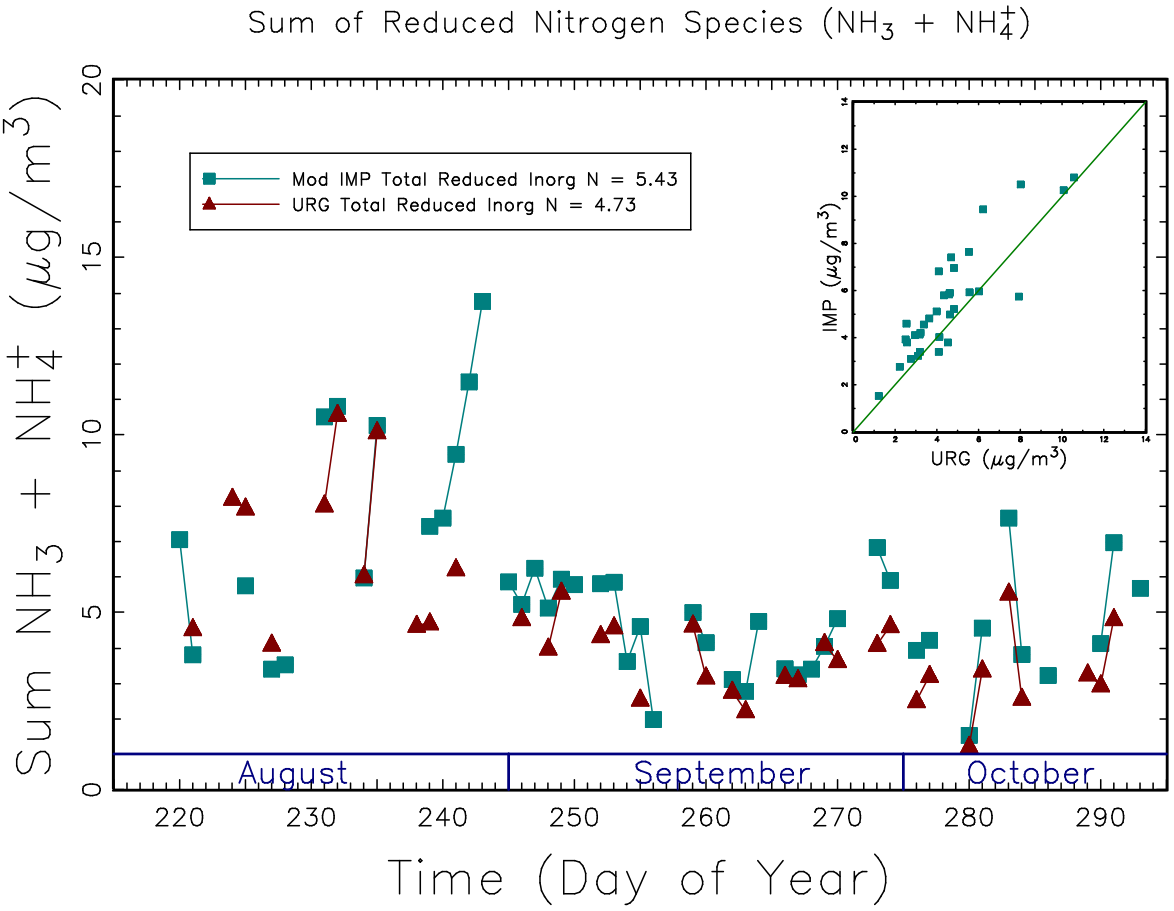

Figure 11.12. Comparisons of NH_x (NH_3 + NH_4^+) concentrations from the modified IMPROVE (Mod IMP) and URG samplers during fall 2008. Mean NH_x concentrations (µg m^{-3}) for each sampler are reported.

Further testing of the IMPROVE NH_x measurements revealed ammonia was coming off the nitric acid denuder. The denuder was removed, the inlet stack was cleaned, and another comparison was performed during spring 2010, using only the acid-impregnated cellulose fiber filter. The results of this comparison are shown in Figure 11.13. The comparison of total NH_x from the modified IMPROVE and URG samplers improved significantly.

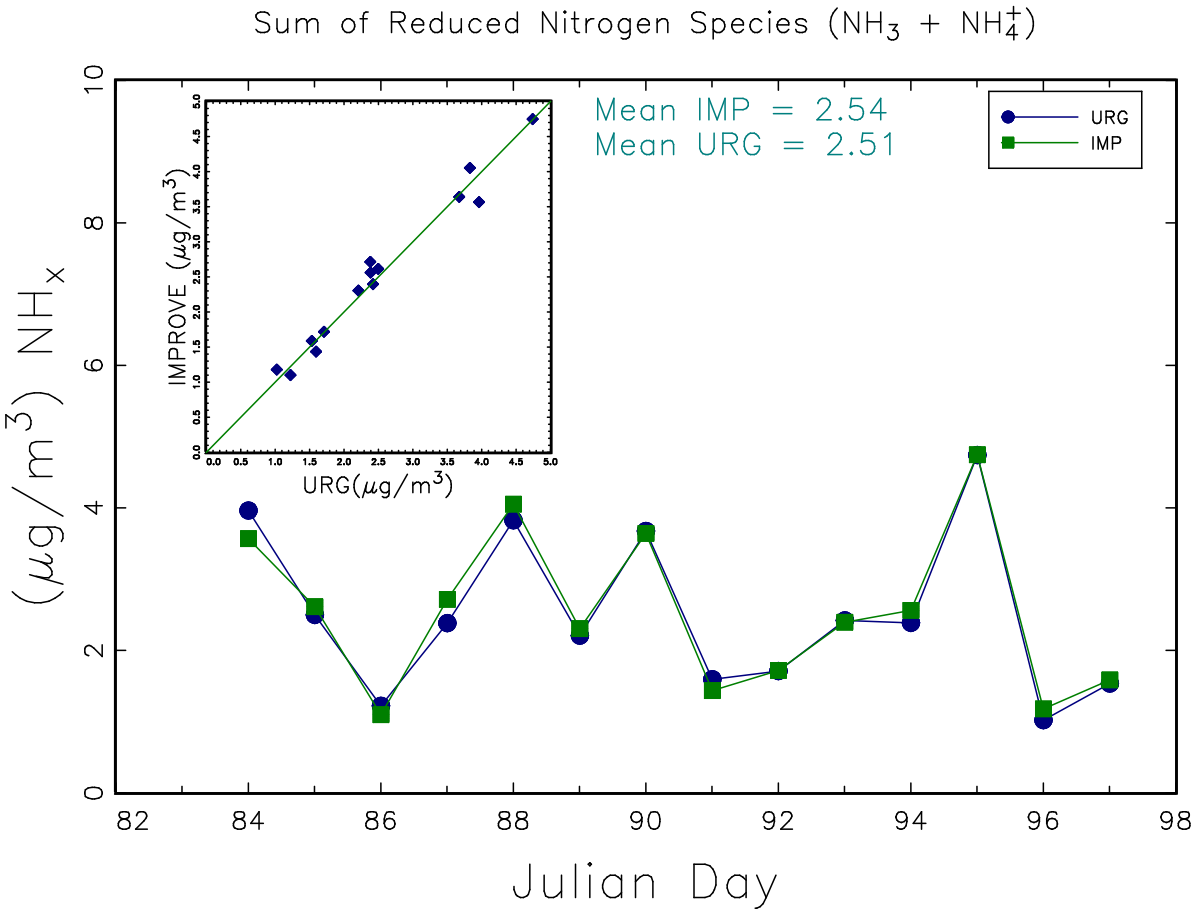

Figure 11.13. Comparisons of NH_x (NH_3 + NH_4^+) concentrations from the modified IMPROVE (IMP) and URG samplers during spring 2010. Mean NH_x concentrations (µg m^{-3}) for each sampler are reported.

11.3.2 CASTNET versus URG

Weekly samples from the URG and CASTNET samplers are compared in this section. Data from the regular and modified CASTNET samplers are compared to investigate if the addition of another filter for NH_3 collection had any impact on the measurements of other species.

Figure 11.14 shows a comparison of sulfate ion concentrations between the regular CASTNET, modified CASTNET, and URG samplers during fall 2008. Concentrations from the regular and modified CASTNET samplers agreed well and were within 3% difference on average. In general, the agreement between data from the URG and CASTNET samplers was within 10% difference on average; however, most of this difference was due to three data points (day of year 232, 239, and 267). Elevated values of Ca, Mg, and NO_3 were also observed for these time periods; thus, it seems possible this discrepancy is due to dust, which would contribute coarse material to the CASTNET sampler but not the URG sampler because of the 2.5 µm size-selective cyclone.

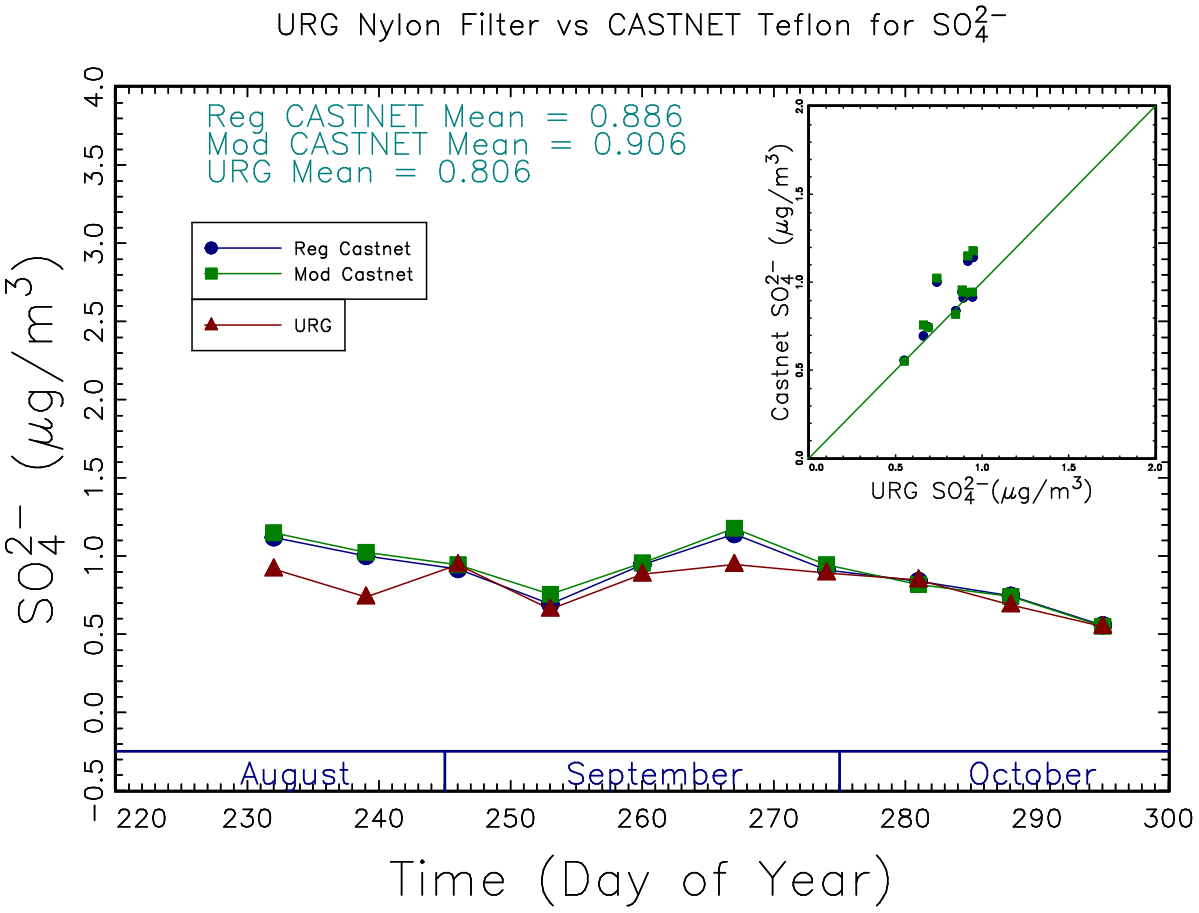

Figure 11.14. Comparisons of sulfate ion (SO_4^{2-}) concentrations from the modified CASTNET (Mod CASTNET), regular CASTNET (Reg CASTNET), and URG samplers during fall 2008. Mean sulfate ion concentrations (µg m^{-3}) for each sampler are reported.

Particulate nitrate ion concentrations are shown in Figure 11.15 for fall 2008 weekly samples. Mean concentrations from the modified and regular CASTNET samplers agreed to within ~2% but were approximately 30% higher than concentrations from the URG sampler. As previously discussed, this could be the result of coarse aerosol particles being sampled by the CASTNET sampler and not the URG sampler (see day of year 232, 239, and 267).

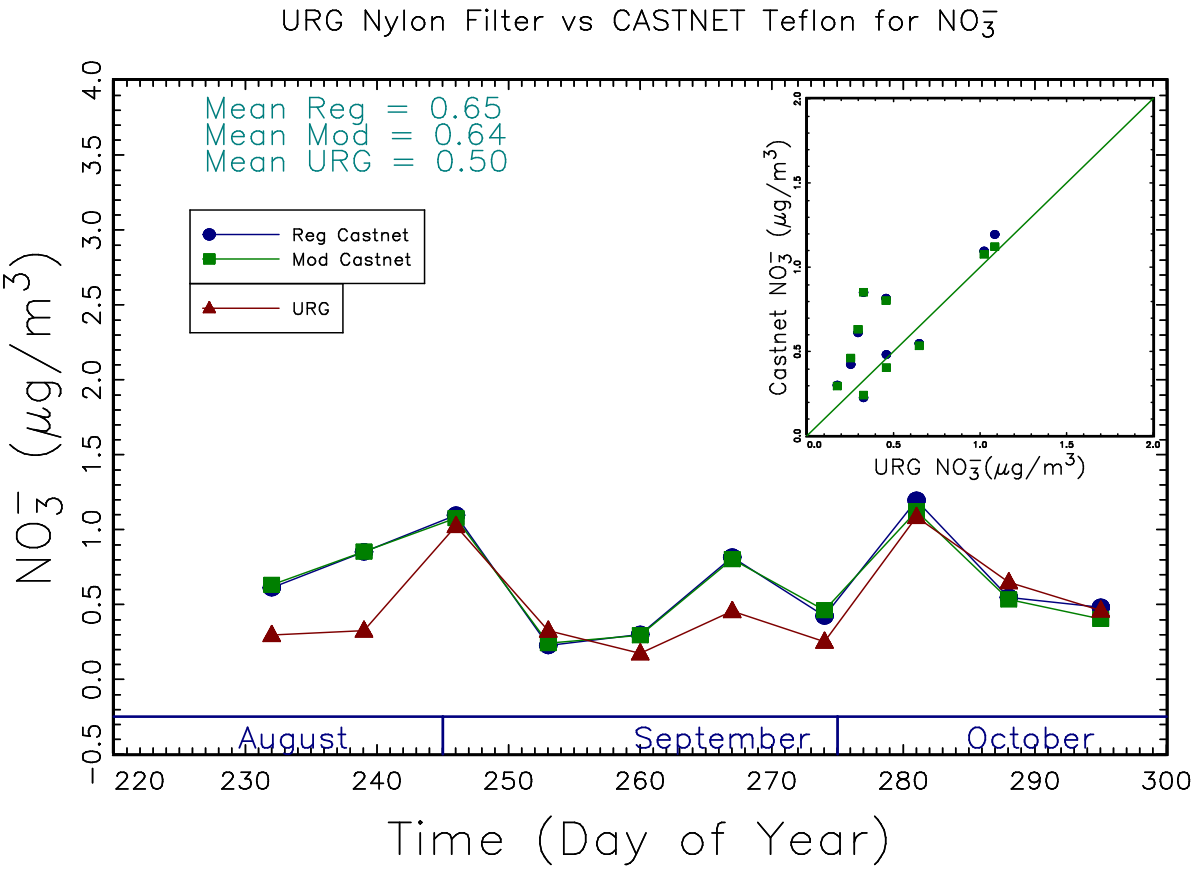

Figure 11.15. Comparisons of nitrate ion (NO_3^-) concentrations from the modified CASTNET (Mod CASTNET), regular CASTNET (Reg CASTNET), and URG samplers during fall 2008. Mean nitrate ion concentrations (µg m^{-3}) for each sampler are reported.

Figures 11.16 and 11.17 show nitric acid (HNO_3) concentrations and total oxidized nitrogen (NO_3^- + HNO_3) concentrations, respectively, from the two CASTNET and the URG samplers. Concentrations of both nitric acid and total oxidized nitrogen from the CASTNET samplers agree to within a few percent; however, they are about 30% higher than concentrations from the URG sampler.

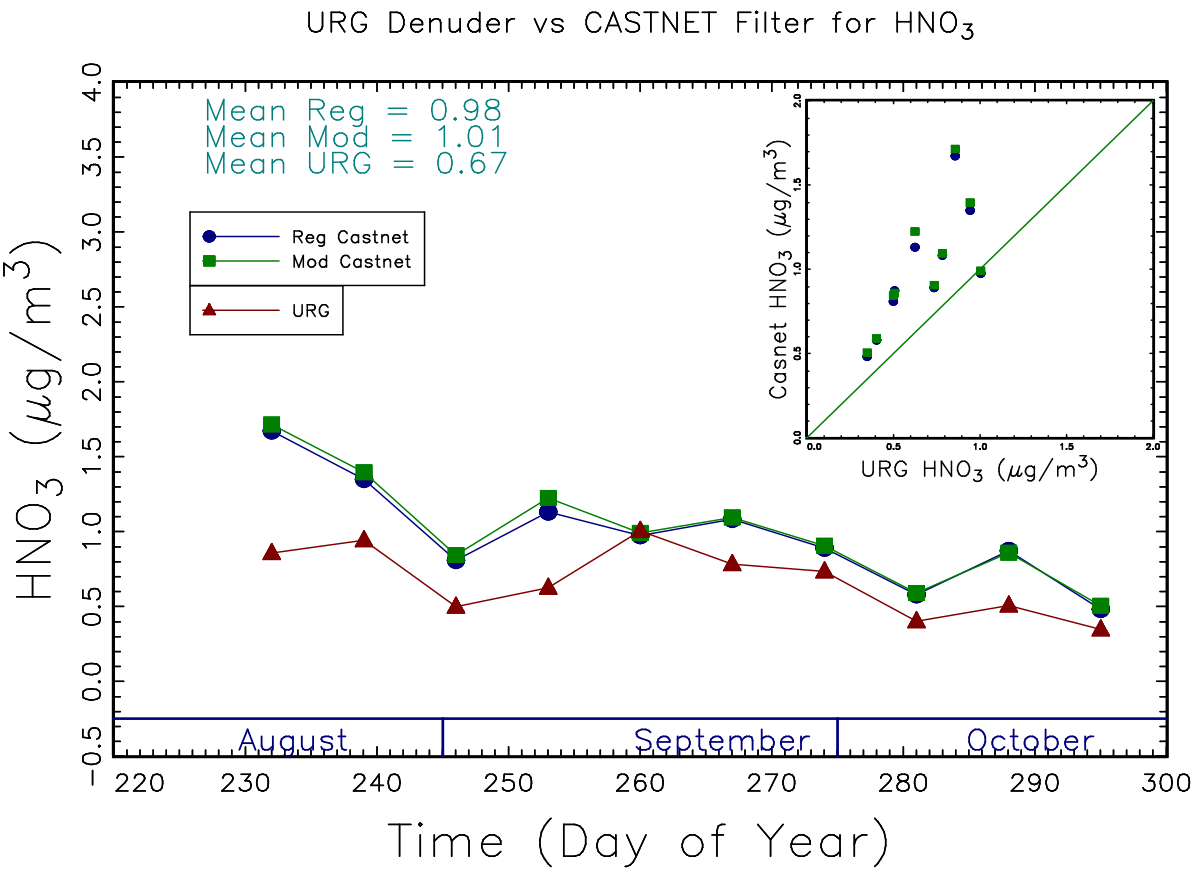

Figure 11.16. Comparisons of nitric acid (HNO_3) concentrations from the modified CASTNET (Mod CASTNET), regular CASTNET (Reg CASTNET), and URG samplers during fall 2008. Mean nitric acid concentrations (µg m^{-3}) for each sampler are reported.

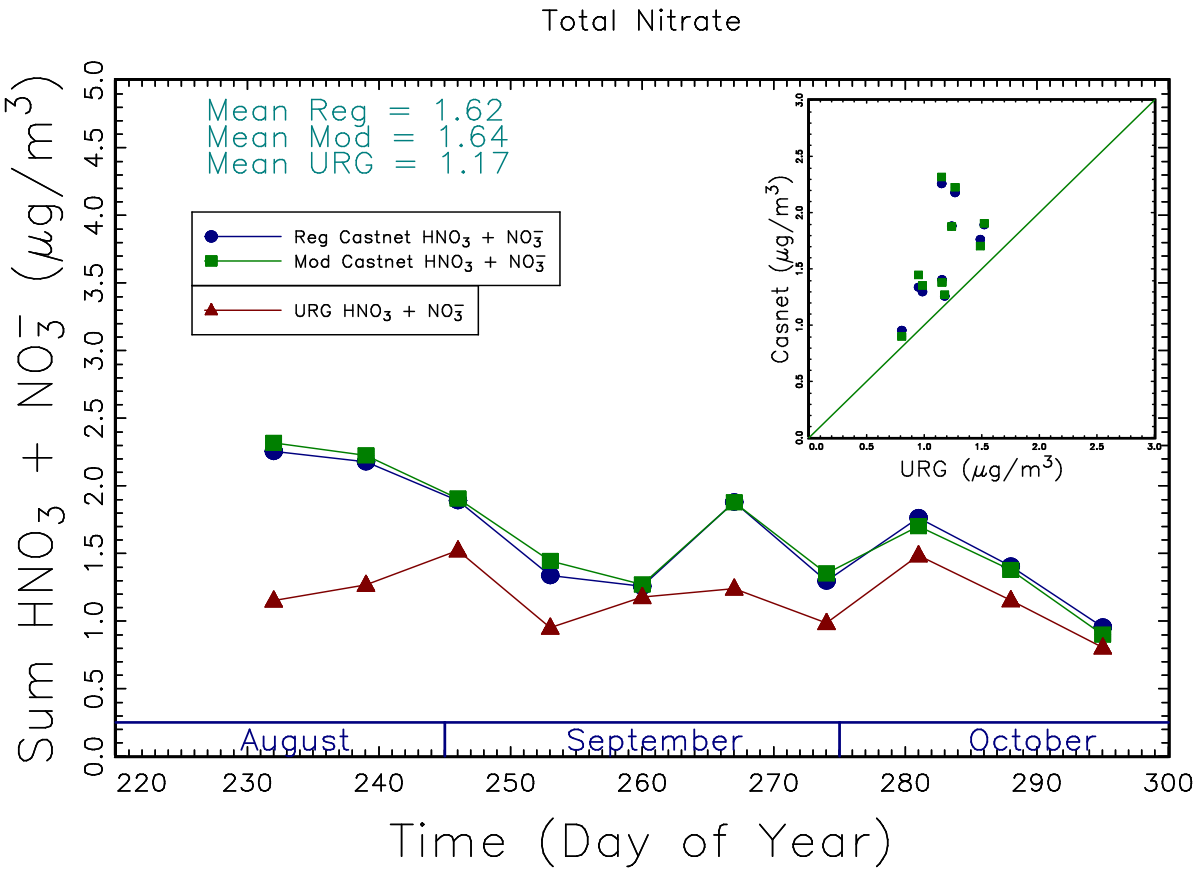

Figure 11.17. Comparisons of total oxidized nitrogen concentrations (NO_3^- + HNO_3) from the modified CASTNET (Mod CASTNET), regular CASTNET (Reg CASTNET), and URG samplers during fall 2008. Total oxidized nitrogen concentrations (μg m^{-3}) for each sampler are reported.

A comparison of particulate ammonium ion concentrations is shown in Figure 11.18 Concentrations from the two CASTNET samplers agreed to within 7% on average. Concentrations from the URG sampler were about 30% higher than the average of the CASTNET samplers. This result is not surprising because there is volatilization of NH_4NO_3 from the filters as equilibrium conditions vary over the week-long sample collection period. The ammonia volatilized from the URG filter is subsequently captured by the backup NH_3 denuder and added back to the concentration of particle NH_4^+; however, the ammonium lost from the CASTNET filter is collected by the backup NH_3 filter and reported as NH_3 gas. The CASTNET sampling system thus shows a negative bias for ammonium ion concentrations.

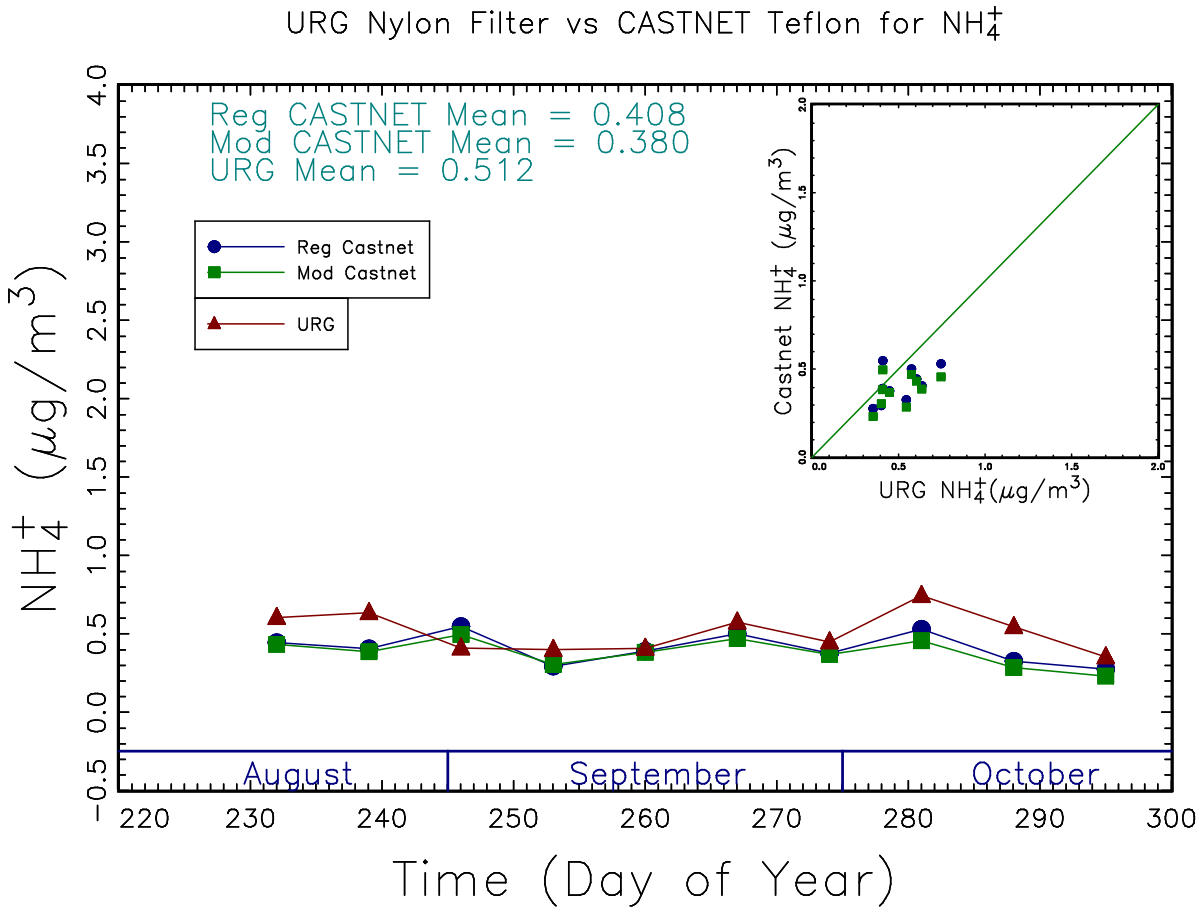

Figure 11.18. Comparisons of ammonium ion (NH_4^+) concentrations from the modified CASTNET (Mod CASTNET), regular CASTNET (Reg CASTNET), and URG samplers during fall 2008. Ammonium concentrations (µg m^{-3}) for each sampler are reported.

Figures 11.19 and 11.20 show ammonia and NH_x concentrations, respectively. As expected, the CASTNET ammonia concentrations are higher (by about 9%) than the URG ammonia concentrations, in part due to the captured NH_3 volatilized from the filter. The NH_x concentrations are expected to be the same, and, indeed, the concentrations from the CASTNET sampler are only about 5–6% higher than the concentrations from the URG sampler. This is well within the estimated uncertainty for these measurements.

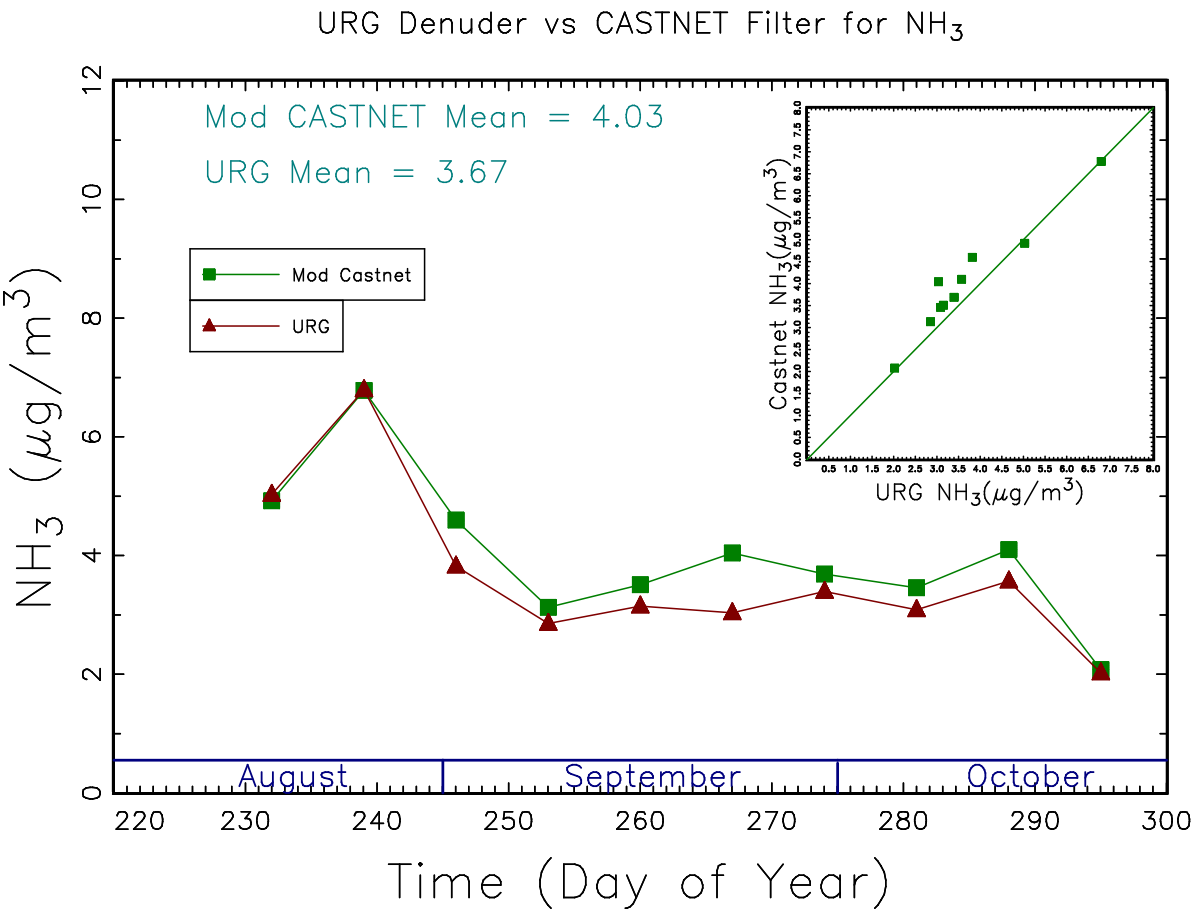

Figure 11.19. Comparisons of ammonia (NH_3) concentrations from the modified CASTNET (Mod CASTNET), and URG samplers during fall 2008. Ammonia concentrations (µg m^{-3}) for each sampler are reported.

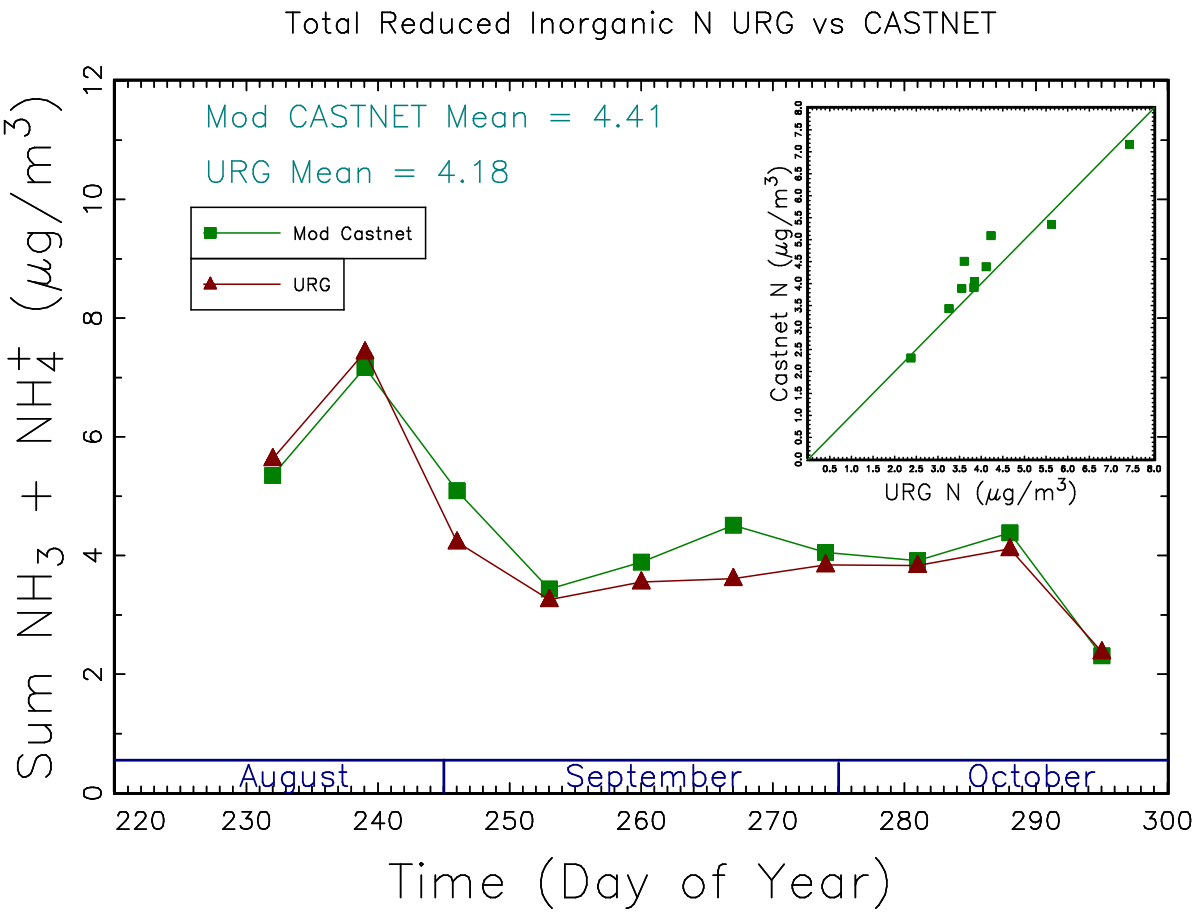

Figure 11.20. Comparisons of total reduced inorganic nitrogen ($NH_x = NH_3 + NH_4^+$) concentrations from the modified CASTNET (Mod CASTNET) and URG samplers for 2008. NH_x (µg m^{-3}) for each sampler are reported.

11.3.3 Ammonia Comparisons from CASTNET, Passive, and URG Samplers

Figure 11.21 shows the comparison of ammonia concentrations from 2-week samples from the Radiello and Ogawa passive samplers during 2008. In addition, weekly samples from the CASTNET and the URG samplers during fall months are also shown. In general, the concentration of NH_3 obtained from all the samplers is in good agreement.

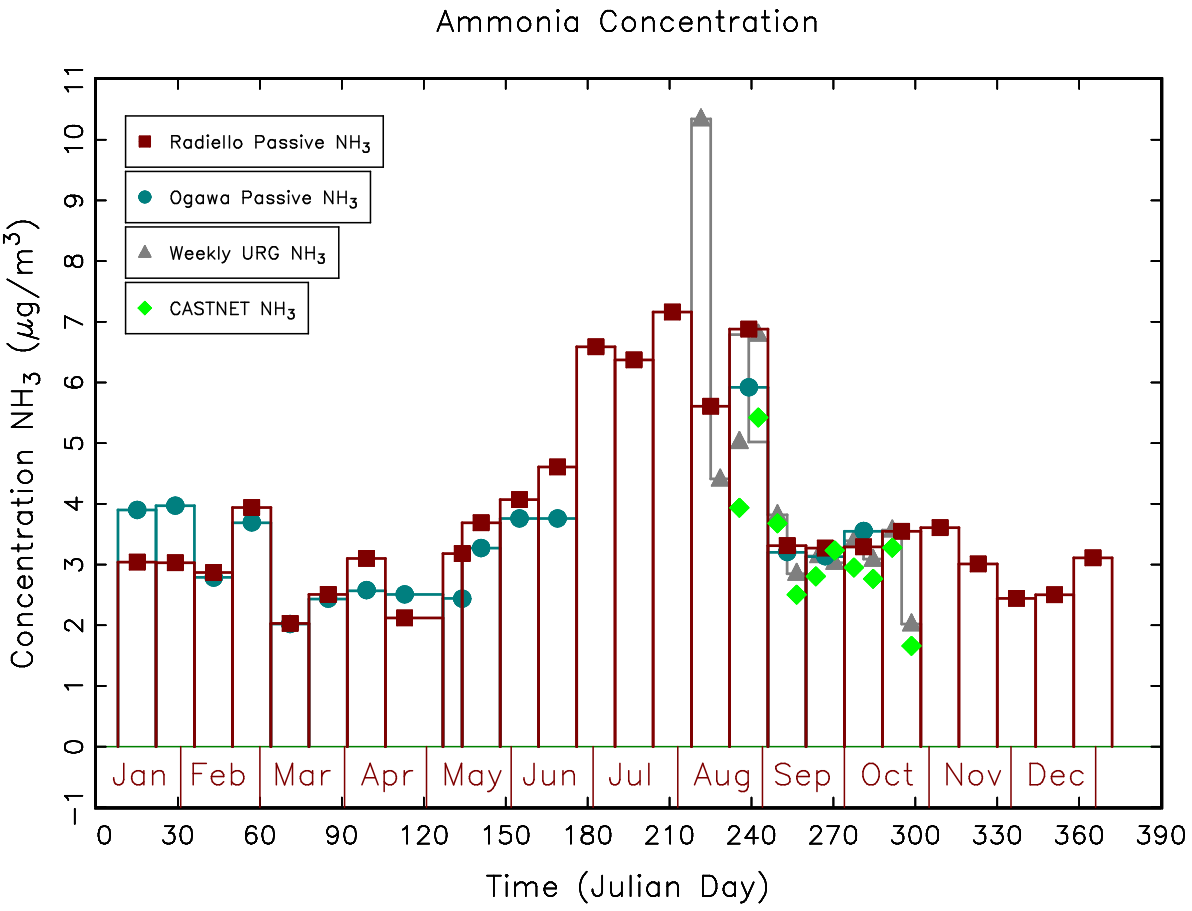

Figure 11.21. Comparison of weekly ammonia (NH_3) concentrations (µg m^{-3}) from URG and CASTNET samplers and 2-week concentrations from the Radiello and Ogawa passive samplers during 2008.

11.4 SUMMARY

The NH_x system plays an important role in atmospheric chemistry, contributing to particle formation and reactive nitrogen deposition. To measure the NH_x system, the IMPROVE and CASTNET samplers have been modified by the addition of an acid-impregnated cellulose fiber filter. Comparisons of concentrations from these modified samplers to data from the URG sampler show agreement within the estimated uncertainty of the samplers, except where known biases are present. These results suggest that modifications to the IMPROVE and CASTNET samplers do not appear to significantly alter the concentration of other species measured by each sampler, which is an important consideration because maintaining consistency with the historical dataset of each sampling network is of critical importance. As observed in this and other

datasets, the sampling of ammonia gas and ammonium ion concentrations using acid-impregnated filters is subject to artifacts. The most significant artifact comes from the dissociation of ammonium nitrate from the Nylasorb filter. This artifact decreases the concentration of ammonium ion and increases the concentration of gaseous ammonia measured.

Because of these biases, we found closer agreement in NH_x concentrations between the URG and IMPROVE or CASTNET samplers. A reasonable approximation of the ammonia and ammonium concentrations could be derived by a simple charge balance calculation. Assuming species concentration in moles and fully neutralized ammonium sulfate and that ammonium ion is the only cation of consequence, the concentrations of NH_3 and NH_4^+ can be approximated from the following equations:

$$2[SO_4^{2-}] + [NO_3^-] = [NH_4^+] \quad 11.3$$

$$[NH_3] = [NH_x] - [NH_4^+] \quad 11.4$$

The concentrations of ammonia measured either with the passive samplers or the CASTNET sampler have been shown to be comparable to the field standard URG sampler. These multiday integrated samples, while acceptable for seasonal and temporal information, are not adequate for source apportionment analyses, which the IMPROVE sampling system, operating for 24 hours every third day, is better suited to address.

ACKNOWLEDGEMENTS

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