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Assessing the Comparability of Ammonium, Nitrate and Sulfate Concentrations Measured by Three Air Quality Monitoring Networks

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Abstract—Airborne fine particulate matter across the United States is monitored by different networks, the three prevalent ones presently being the Clean Air Status and Trend Network (CASTNet), the Interagency Monitoring of PROtected Visual Environment Network (IMPROVE) and the Speciation and Trend Network (STN). If combined, these three networks provide speciated fine particulate data at several hundred locations throughout the United States. Yet, differences in sampling protocols and samples handling may not allow their joint use. With these concerns in mind, the objective of this study is to assess the spatial and temporal comparability of the sulfate, nitrate and ammonium concentrations reported by each of these networks. One of the major differences between networks is the sampling frequency they adopted. While CASTNet measures pollution levels on seven-day integrated samples, STN and IMPROVE data pertain to 24-hour samples collected every three days. STN and IMPROVE data therefore exhibit considerably more short-term variability than their CASTNet counterpart. We show that, despite their apparent incongruity, averaging the data with a window size of four to six weeks is sufficient to remove the effects of differences in sampling frequency and duration and allow meaningful comparison of the signals reported by the three networks of concern. After averaging, all the sulfate and, to a lesser degree, ammonium concentrations reported are fairly similar. Nitrate concentrations, on the other hand, are still divergent. We speculate that this divergence originates from the different types of filters used to collect particulate nitrate. Finally, using a rotated principal component technique (RPCA), we determined the number and the geographical organization of the significant temporal modes of variation (clusters) detected by each network for the three pollutants of interest. For sulfate and ammonium, the clusters' geographical boundaries established for each network and the modes of variations within each cluster seem to correspond. RPCA performed on nitrate concentrations revealed that, for the CASTNet and IMPROVE networks, the modes of variation do not correspond to unified geographical regions but are found more sporadically. For STN, the clustered areas are unified and easily delineable. We conclude that the possibility of jointly using the data collected by CASTNet, IMPROVE and STN has to be weighed pollutant by pollutant. While sulfate and ammonium data show some potential for joint use, at this point, combining the nitrate data from these monitoring networks may not be a judicious choice.

Key words: Air quality, particulate matter, monitoring networks, moving average, principal component analysis.

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1. Introduction

Depending on its size, air-borne particulate material is commonly divided into two classes: fine and coarse. The fine particles are those whose diameter is less than or equal to 2.5 micrometers (μm), justifying the acronym '$PM_{2.5}$'. The particles exceeding this threshold but whose diameter is less than or equal to 10 μm constitute the coarse class size ('$PM_{coarse} = PM_{10} - PM_{2.5}$'). $PM_{2.5}$ is mostly composed of secondary particles, i.e., particles that are not directly emitted in the atmosphere but are formed from primary gaseous emissions. Among the important $PM_{2.5}$ constituents are sulfates, nitrates and ammonium. Sulfate has its origins in SO_2 emissions from power plants and industrial facilities; nitrates are formed by the oxidation of the nitrous oxides (NOx) emitted from power plants, automobiles and other types of combustion sources, and ammonium predominantly originates from human and animal wastes and agriculture (fertilizer application). New research shows that, while air-borne particulate sulfate and ammonium are indeed mostly present in the fine particle class ($PM_{2.5}$), a substantial portion of nitrate can be found in the coarse class size (PM_{10}), especially in coastal areas (ZHUANG *et al.*, 1999; CAMPBELL *et al.*, 2002). Growing concerns about the adverse effects of particulate matter on human health and the visual quality of the environment justify the recently promulgated particulate matter National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$ and PM_{10} (see http://www.epa.gov/ttn/naaqs). Should a NAAQS be violated, it is important to know the chemical composition of particulate material so as to identify its origin and develop meaningful emission control strategies to attain the NAAQS for $PM_{2.5}$.

Currently, speciation information is provided by several networks; the three prominent ones being the Clean Air Status and Trend Network (CASTNet), the Interagency Monitoring of PROtected Visual Environment Network (IMPROVE) and, more recently, the Speciation and Trend Network (STN). In addition to these three networks, there are other smaller networks, such as the Atmospheric Integrated Research Monitoring Network developed by the National Oceanic and Atmospheric administration (see http://www.arl.noaa.gov/research/programs/airmon.html) that collect the same type of information. Combining as many air quality data as possible to obtain the most accurate and aerially extensive representation of the atmosphere would be helpful for evaluation of the performance of regional-scale air quality models, primary tools used for designing control strategies aimed at meeting and maintaining the above-mentioned NAAQS. If combined, all networks provide speciated air quality data at several hundred locations throughout the United States. However, differences in network sampling protocols and samples handling may not allow their joint use. With these concerns in mind, the objective of this study is to assess the spatial and temporal comparability of the sulfate, nitrate and ammonium concentrations reported by the three prominent networks (CASTNet, IMPROVE and STN). Although some authors have investigated differences between CASTNet and IMPROVE observations (Ames and Malm, 2001), to our knowledge, no study of the comparability of these three networks (CASTNet, IMPROVE and STN) is available yet. Our objective is to uncover similarities and differences among the reported observations. By doing so, we hope to inform about the difficulties ahead when blending data from multiple networks with different sampling protocols. It is not our goal to provide a universal recipe for performing this task.

While the concentrations reported by IMPROVE and STN reflect one-in-three days 24-hour air samples, CASTNet observations describe one-week integrated samples. Since a shorter sampling interval leads to a higher amount of short-term variability in the time series of measurements and *vice versa*, the data from the different networks need to be somehow harmonized before they can meaningfully be combined. One means of harmonizing the data is by calculating temporal averages so that the averaged data from all networks contain similar information regarding temporal changes. We intend to determine the shortest averaging time interval after which fluctuations of data gathered by the three networks may become comparable. Second, a rotated principal component analysis (RPCA) will be used to summarize the regional organization of each contaminant, as can be assessed with each network. Finally, the temporal patterns recorded by each network in corresponding geographical areas will be compared.

2. *Brief Description of Monitoring Networks and their Sampling Protocols*

Created in 1990 to measure dry deposition fluxes, CASTNet now comprises over 70 monitoring sites in the United States, located mostly in rural areas. The air sampler at a CASTNet site is a non size-selective three-stage filter pack located 10 m above ground level, continuously supplied with a 1.5 l/min flow rate in the eastern United States (U.S.) and 3 l/min in the western U.S. Unlike the IMPROVE protocols, filters are not equipped with any particle size limiting device. Yet, the flow rate utilized and the height of the instrument are thought adapted to limit the entrance of coarse particles into the filter (Finkelstein, 2003, personal communication). Filters are changed every week; measured concentrations, therefore, are seven-day average estimates. The nitrate, sulfate and ammonium ions, collected on the first of the three consecutive filters, composed of teflon, are interpreted as particulate species. Nitrate and sulfate are quantified by ion chromatography and ammonium concentrations are estimated by the indophenol method. Presently, all CASTNet concentrations are standardized to a temperature of 25°C and a pressure of 1013 mb before being reported. A new database providing CASTNet concentrations in ambient conditions is currently being built (FINKELSTEIN, 2003, personal communication).

Initiated in 1985, the IMPROVE network essentially aims at monitoring air quality conditions in Class I areas, i.e., in national parks and wilderness areas that receive special protection from adverse air quality impacts through the U.S. Environmental Protection Agency's Prevention of Significant Deterioration (PSD) program (U.S. EPA, 1980). The air sampler at IMPROVE sites consists of 4 modules located 3 m above ground level and equipped with a device that stops particles larger than 2.6 μm. Sulfate concentration is calculated by stoichiometry from the mass of sulfur extracted from a teflon filter and analyzed for by X-Ray fluorescence. Nitrate is determined from particles extracted from a nylon filter preceded by an acidic vapor diffusion denuder which eliminates nitric acid vapor (non-particulate nitrate). Nitrates are determined by ion chromatography. Ammonium concentrations at IMPROVE sites are not determined directly but are calculated by stoichiometry, assuming that all the sulfates and nitrates in the particulate phase have been neutralized by ammonium. A 24-hour integrated air sample is collected every three days. Measured concentrations are reported at ambient temperature and pressure conditions, in contrast to CASTNet.

Established by the USEPA to supplement $PM_{2.5}$ mass estimates provided by the Federal Reference Method (FRM) network, the STN network began operation in late 1999. Contrary to CASTNet and IMPROVE, STN sites are located in urban, suburban, and rural environments. The data they provide will allow, among other things, assessment of trends in fine particles in urban areas across the country. Eventually, the number of STN sites will surpass the combined number of IMPROVE and CASTNet sites. At this early stage of its development, the network is not as simply describable as CASTnet and IMPROVE networks. A variety of air samplers and sampling protocols has been approved for use in the STN while the other networks use identical equipment at all their sites and standard analytical techniques. It appears, though, that the STN sampling methodology resembles that of IMPROVE. As with IMPROVE, a one-in-three days sampling schedule has been adopted. Nitrates are extracted from a nylon (or quartz filter), as is the case at IMPROVE sites, rather than the teflon filter used at CASTNet sites. Nitrates are determined by ion chromatography. Depending on the sampling equipment, sulfates are extracted from a teflon, nylon or quartz filter and analyzed by ion chromatography. Unlike IMPROVE sites, ammonium is determined directly via ion chromatography from the same filter used to determine sulfates. Measured concentrations are reported at ambient temperature and pressure conditions.

Further details about the sampling protocols utilized by each network, as well as the data they provide, are available at http://vista.cira.colostate.edu/IMPROVE/, http://www.epa.gov/CASTNet and http://www.epa.gov/oar/oaqps/pm25 for the IMPROVE, CASTNet, and STN, respectively.

3. Methods

3.1. Evaluation of an Appropriate Averaging Time Interval for Removal of the Effects of Distinct Sampling Frequency and Duration

As stated earlier, the frequency and duration of air sample collection at CASTNet sites are different from those used at IMPROVE and STN sites. While the latter two provide non-consecutive (one-in-three days) 24-hour samples, CASTNET data represent seven-day averages. Consequently, the corresponding contaminant time series are very distinct, with the IMPROVE and STN data exhibiting more short-term variability than these of CASTNet. Using an interative moving average filter such as described in RAO *et al.* (1997) and HOGREFE *et al.* (2000) to separate variation at frequencies less than 2.5 $months^{-1}$ from those at frequencies greater than 2.5 $months^{-1}$, GEGO *et al.* (2003) showed that, despite their apparent incongruity, the low frequency signals embedded in the sulfate time series reported by CASTNet and IMPROVE are comparable.

We propose to extend the results of GEGO *et al.* (2003) by identifying the shortest temporal averaging interval that minimizes the effects of different sampling durations and frequency. After identification of the shortest averaging interval and construction of the temporally averaged signals, we believe that the remaining differences between the three networks are no longer attributable to differences in the sampling frequency, but result from differences in site locations, instrumentation used or analytical techniques employed. There is no indicated method for precisely determining that shortest averaging time interval. In this study, we calculated, for each contaminant and network, the variance of the measurement averages corresponding to window sizes of 1, 2, 4, 6 and 8 weeks. Averaging may be considered sufficient when the variance of the IMPROVE and STN average signals no longer exceed that of CASTNET average signals. We also calculated, for each pair of networks and each window size, the correlation coefficient, the slope of the regression line, and the average and maximum difference between signals. The slope of the regression line between a pair of networks is not expected to vary as the window size increases, as it indicates systematic differences caused by differences in sampling location or instrumentation. On the other hand, increasing the averaging time is expected to increase the strength of the correlation between the respective signals and reduce the amplitude of their differences by reducing the differences in the amount of short-term variability introduced by their respective sampling frequencies.

3.2. Rotated Principal Component Analysis

Principal component analysis (PCA) is a multivariate technique designed to facilitate interpretation of large data sets involving numerous mutually dependent variables. By summarizing the correlations (i.e., identifying the redundancies) between all variables, PCA allows determination of the 'true' dimensionality of a data set. It also allows building of a new data set (the principal components data set) whose dimensions reflect the true dimensionality of the original data set and whose variables are mutually orthogonal. EDER (1989) provided insights on how to use PCA to analyze and summarize the temporal correlation of time series of a given air contaminant measured at numerous monitored sites. In EDER's (1989) approach, a sample individual corresponds to a sampling event (date) and a variable is a monitoring site. PCA used in this framework allows classification of all monitoring sites into a limited number of categories, each of which corresponds to a specific contaminant's temporal evolution (specific succession of rises, falls and plateaus), i.e., a specific mode of variation.

Practically speaking, PCA begins with the construction of the correlation (or covariance) matrix summarizing the site-to-site correlation between all pairs of sites. For this study, all observations at a given site were standardized to zero mean and unit variance before evaluation of the correlation matrix. This procedure is thought to limit the impact of heteroscedasticity (inequality of variances) and facilitate interpretation of results (PALM, 1999).

After determination of the eigenvectors and eigenvalues of the correlation matrix (KENDALL *et al.*, 1983), the principal components were calculated. The first principal component (PC) is obtained by multiplying the original set of variables by the first eigenvector of the correlation matrix. Its orientation is such that it maximizes the part of the variance of the original data that can be explained by a single variable. The second and higher order PCs are defined in similar fashion. The second PC, for instance, is obtained by multiplying the original variables by the second eigenvector of the correlation matrix. The variance of the second PC is the second eigenvalue of the correlation matrix, and so on. Since higher order eigenvalues are progressively smaller, successive PCs explain less and less of the variance of the original data.

One may consider that the information included in the original data set can be reasonably described by a limited number of PCs. The number of PCs retained is representative of the true dimensionality of the original data set. In our case, it also represents the number of 'distinct modes of variations' or the number of clusters we wish to differentiate in the data set. There are several methods for deciding the number of PCs to retain, among them the "Rule N" method (OVERLAND and PREISENDORFER, 1982), and the Scree test (CATTELL, 1966; WILKS, 1995). No one approach is thought superior to the others. In this study, the number of clusters retained for each air pollutant and network is the number of eigenvalues greater than 1 (EDER, 1989).

Orthogonally rotating the PCs retained so as to increase their correlation with the original data, a procedure often referred to as varimax (KAISER, 1958), has been shown to facilitate interpretation of the principal components (HOREL, 1981). We, therefore, chose to use it as well. The successive use of PCA to determine the number of PCs to retain and of varimax to better segregate the variables (in this case, the monitoring sites) is often referred to as rotated principal component analysis

(RPCA). Monitoring stations where nitrate, sulfate or ammonium concentrations fluctuate in a similar manner (i.e., that are grouped in the same cluster) are those that are more correlated with a given rotated principal component than with the others.

4. Data

This study utilizes the nitrate, sulfate and ammonium concentrations reported by IMPROVE, CASTNet and STN at sites located east of 100° longitude west (eastern U.S.), from July 1st, 2001 to July 31st, 2002. Only those sites with less than 20% missing values were retained. Because RPCA cannot handle missing data, missing data at a given site were substituted for using a temporal linear interpolation scheme. Although not exceeding the number of missing data threshold, several clustered STN sites in the urban corridor between Pennsylvania to Massachusetts were excluded from the analysis to reduce overrepresentation of the urban corridor in the principal component analysis. Also, due to the unavailability of pertinent meteorological information (pressure), the concentrations reported by CASTnet were not converted into 'ambient conditions', a condition that would simplify their comparison with IMPROVE and STN data. A total of 51 CASTNet sites, 39 IMPROVE sites and 26 STN sites were utilized in the RPCA. Sites used in the study are presented in Figure 1.

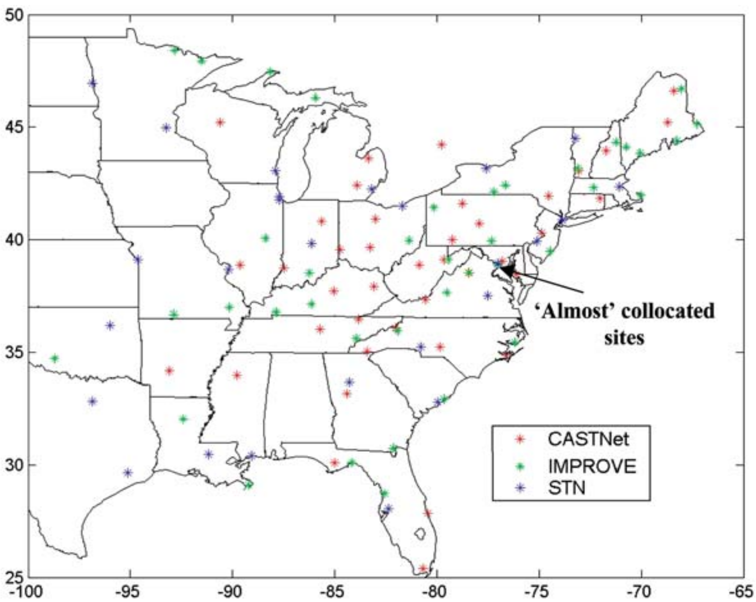

Figure 1
Location of the monitoring sites.

5. Results

5.1. Evaluation of an Appropriate Averaging Time Interval

Ideally, the appropriate averaging time interval for the removal of short-term variability linked to their specific sampling frequencies should be determined by analysis of signals recorded by the three networks at collocated sites. In this case, indeed, the differences between the signals are only attributable to dissimilarities in sampling frequency and sampling equipment, and not to spatial variability. While there are instances of collocated IMPROVE and CASTNet sites, presently there are no sites where all three networks are represented. As the best alternative, for this study, we identified the set of the three closest CASTNet, IMPROVE and STN stations and used the data collected at these stations to evaluate an appropriate averaging time. See Figure 1 for the location of these sites and Table 1 for specification of their respective names and coordinates.

Justifying the need for averaging the information reported by all networks, Figure 2 depicts a scatter plot of weekly nitrate, sulfate and ammonium concentrations at the almost collocated CASTNet, IMPROVE and STN sites during the time period studied. Weekly IMPROVE and STN estimates were obtained by averaging

Table 1

Names and locations of the 'quasi-collocated' sites

Network	Station name or number	Location	Longitude	Latitude
CASTNet	BEL116	Beltsville, Maryland	−76.8172	39.0284
IMPROVE	WASN1	District of Columbia	−77.0343	38.8761
STN	110010043	District of Columbia	−77.0125	38.9188

The distance between the CASTNet and IMPROVE sites is 25 km;
the distance between the STN and IMPROVE sites is five km.

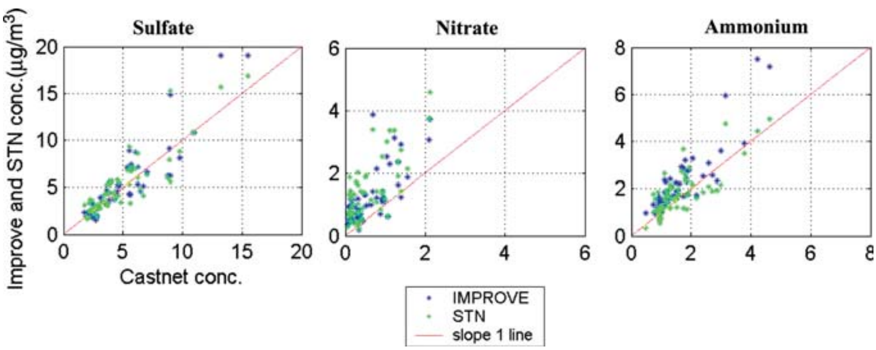

Figure 2
Scatter plots of IMPROVE and STN weekly average concentrations (μg/m^3) versus CASTnet concentrations (μg/m^3).

Table 2

Evolution of the variance (μg/m^3)^2 of the moving averaged signals for different averaging intervals

Network	**Averaging interval**				
	1 wk	**2 wk**	**4 wk**	**6 wk**	**8 wk**
			Sulfate		
Castnet	8.25	6.23	5.37	4.42	3.47
Improve	12.81	10.27	8.07	6.26	4.82
STN	10.05	7.76	6.00	4.76	3.64
			Nitrate		
Castnet	0.27	0.19	0.17	0.16	0.15
Improve	0.62	0.51	0.44	0.38	0.35
STN	1.45	1.17	0.87	0.38	0.63
			Ammonium		
Castnet	0.73	0.52	0.43	0.34	0.25
Improve	1.65	1.27	0.95	0.69	0.50
STN	0.80	0.55	0.37	0.26	0.18

the 24-hour observations that fall within a given CASTNet week. The significant dispersion observable in Figure 2 proves that, at the time scale of a week, the three networks provide different information and that this information needs to be harmonized if the networks are to be jointly used. Table 2 shows the effects of averaging on the variances of the signals reported by the three networks. It is obvious that averaging tends to homogenize the variability in the data from all networks.

In the case of sulfate (Tables 3a and 3b), the CASTNet signals tend to be slightly less than those of STN, which are themselves slightly less than IMPROVE (Table 3a). These differences may be the result of different local environments. Indeed, although close in space, the local settings of these monitors are quite different. While the CASTNet site is in range-land, the IMPROVE site is in Washington D.C. and the STN station is classified as 'Urban and Center City'. Differences between recorded signals are therefore to be expected. Despite the various local environments, for averaging intervals of 4 weeks and longer, the mean relative difference between all observations is less than 15% and the correlation (R) more than 95% (Table 3b). Since our estimation is supported by examination of only

Table 3a

Slope of the regression lines of sulfate concentrations recorded by each pair of networks

Networks	Slope of the regression line
Improve vs Castnet	1.10
Stn vs Castnet	1.05
STN vs Improve	0.95

Table 3b

Absolute values of the mean and the largest relative differences (%) between sulfate concentrations recorded by each pair of networks, as a function of the averaging time interval

Network	**Averaging interval**				
	1 wk	2 wk	4 wk	6 wk	8 wk
	Absolute value of the mean relative difference (%)				
Improve vs Castnet	22	17	15	11	12
Stn vs Castnet	23	17	13	11	11
STN vs Improve	15	13	12	8	5
	Absolute value of the largest relative difference (%)				
Improve vs Castnet	68	46	31	22	20
Stn vs Castnet	80	51	30	28	25
STN vs Improve	86	45	29	20	10
	Correlation coefficient				
Improve vs Castnet	.90	.95	.96	.97	.96
Stn vs Castnet	.88	.98	.99	.99	.99
STN vs Improve	.97	.98	.98	.99	.99

a single set of 'quasi-collocated' sites, our results are quite uncertain and should be reconfirmed with additional sets of collocated sites, when available.

The encouraging sulfate results seen for 4-week averaging do not apply to nitrate. Although the correlation between signals is quite high after averaging the observations, CASTNet nitrate estimates are always much less (50%) than their STN and IMPROVE counterparts, regardless of the averaging interval (Tables 4a and 4b). We believe that such extreme differences do not solely result from the local settings of the monitors but are mostly due to the different collection devices utilized by the networks. In CASTNet, the nitrate interpreted as particulate material is collected on a teflon filter (nitrate is also collected from a nylon filter but the latter is assumed to represent nitric acid concentrations). It has been shown that volatilization of ammonium nitrate from teflon filters may cause substantial loss of nitrate and considerable underestimation of nitrate concentration (HERRING and CASS, 1999). At IMPROVE and STN sites, nitrates are collected on a nylon filter preceded by an acidic vapor diffusion denuder placed in the system to eliminate all nitric acid vapor. The nitrates present on the nylon filter are therefore interpreted as particulate matter.

Table 4a

Slope of the regression lines of nitrate concentrations recorded by each pair of networks

Networks	**Slope of the regression line**
Improve vs Castnet	1.68
Stn vs Castnet	2.12
STN vs Improve	1.29

Table 4b

Absolute values of the mean and the largest relative differences (%) between nitrate concentrations recorded by each pair of networks, as a function of the averaging time interval

Network	**Averaging interval**				
	1 wk	2 wk	4 wk	6 wk	8 wk
			Absolute value of the mean relative difference (%)		
Improve vs Castnet	229	202	182	169	166
Stn vs Castnet	323	290	261	247	236
STN vs Improve	37	33	31	33	32
			Absolute value of the largest relative difference (%)		
Improve vs Castnet	845	820	479	529	468
Stn vs Castnet	1804	1290	844	550	472
STN vs Improve	140	107	62	62	51
			Correlation coefficient		
Improve vs Castnet	.74	.77	.84	.89	.94
Stn vs Castnet	.59	.68	.87	.88	.94
STN vs Improve	.89	.92	.97	.99	.99

In this kind of apparatus, the reliability of the vapor remover has occasionally been questioned. It has been shown that high humidity may cause some nitric acid vapor to return to the sample stream, causing an overestimation of the estimated particulate nitrate concentrations (HICKS, 2003, personal communication). AMES and MALM (2001) provide a rather thorough review of the respective strengths and weaknesses of teflon vs. nylon filters for determination of nitrate concentrations. Their article also refers to different studies aimed at quantifying the biases between techniques. Since our investigation focuses on a single set of nearby stations (not strictly collocated), we did not attempt to quantify these biases, although their existence seems unquestionable. As mentioned in the introduction of this paper, our only intention at this time is to alert the reader of the difficulties ahead when blending data from the three networks considered, however providing solutions to effectively deal with this problem will require further effort.

Examination of ammonium signals tends to show that the concentrations calculated by IMPROVE, under the assumption that ammonium is the only cation used for the neutralization of sulfate and nitrate, are overestimated by about 30% and 20% in comparison to CASTNet and STN signals, respectively (Tables 5a

Table 5a

Slope of the regression lines of ammonium concentrations recorded by each pair of networks

Networks	Slope of the regression line
Improve vs Castnet	1.37
Stn vs Castnet	1.07
STN vs Improve	0.78

Table 5b

Absolute values of the mean and the largest relative differences (%) between ammonium concentrations recorded by each pair of networks, as a function of the averaging time interval

Network	**Averaging interval**				
	1 wk	2 wk	4 wk	6 wk	8 wk
	Absolute value of the mean relative difference (%)				
Improve vs Castnet	41	40	39	36	39
Stn vs Castnet	34	28	25	25	24
STN vs Improve	22	19	17	13	14
	Absolute value of the largest relative difference (%)				
Improve vs Castnet	115	89	68	68	57
Stn vs Castnet	138	100	70	69	45
STN vs Improve	64	43	41	25	31
	Correlation coefficient				
Improve vs Castnet	.88	.90	.93	.94	.93
Stn vs Castnet	.78	.83	.82	.84	.90
STN vs Improve	.90	.90	.91	.94	.95

and 5b). These results suggest that the assumption used in the IMPROVE network to calculate ammonium concentrations (all the sulfates and nitrates in the particulate phase are neutralized by ammonium) may not always be valid.

Based on the preceding results, it appears that an averaging window size between 4 and 6 weeks might be appropriate for harmonization of the short-term variability of all signals and, therefore, removing the effect of the different sampling frequencies. Hence, for the rest of this study, we chose to present the results relative to a 5-week window size rather than the raw information when plotting a contaminant time series. Since that window size is large enough to eliminate the short-term effects of synoptic forcings, any time series constructed by applying a 5-week moving average filter is hereafter referred to as a 'longer-term' signal.

Note that in the case of sulfate, a window size as little as 2 or 3 weeks may be judged sufficient for network blending. A shorter window leads to slightly lesser correlation and larger mean relative difference between networks, but preserves more temporal details. Depending on the study at hand, shorter intervals may be found more pertinent. In this case, we chose to apply the same 5-week window to all three species considered.

Figure 3 depicts scatter plots of IMPROVE and STN versus CASTNet signals, averaged by blocks of successive 5-week intervals over the period considered (Panel A) and the long-term signals of sulfate, nitrate and ammonium observations (Panel B). The close agreement between sulfate estimates is rather obvious (Fig. 3, upper graphs). As obvious is the divergence between nitrates estimated by CASTNet and by the two other networks. Regularly but mostly in the high concentration season, CASTNet's concentration is less than a third that of IMPROVE or STN (Fig. 3, middle graphs). Ammonium concentrations correspond fairly well for all networks,

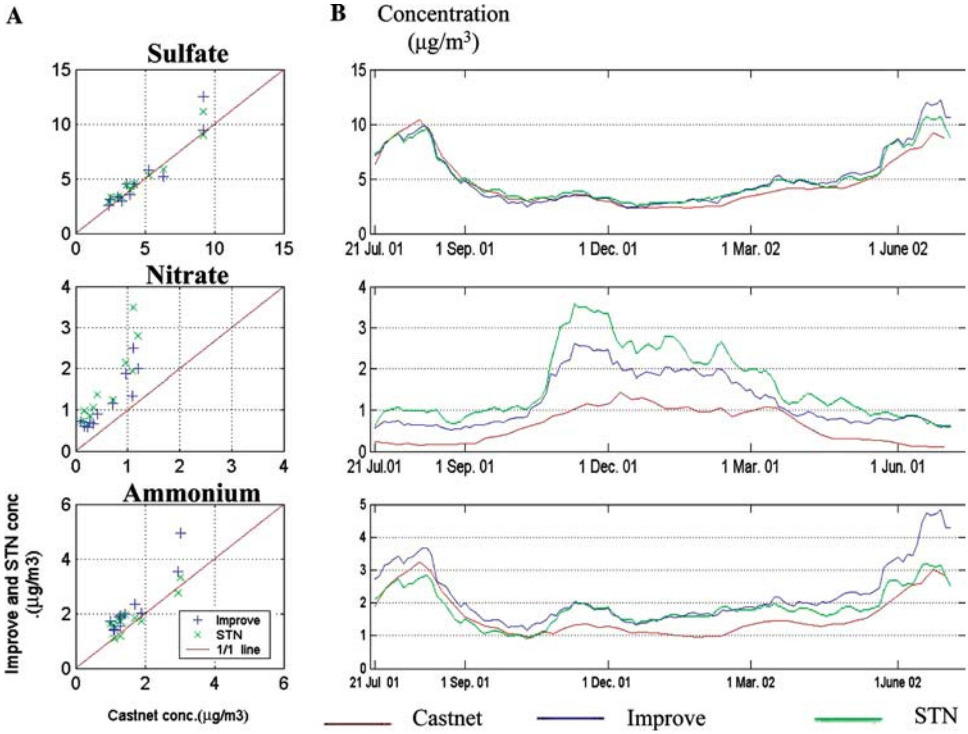

Figure 3
Panel A — Scatter plots of the block average concentrations calculated for STN and IMPROVE vs the block average concentrations calculated for CASTNet (window: 5 weeks), Panel B — time series of the longer-term signals (5-week moving average) of STN, IMPROVE and CASTNet.

with, again, a tendency for CASTNet estimates to be lowest. The differences between STN and IMPROVE estimates are minor at low concentrations but IMPROVE estimates significantly exceed that of STN at higher concentrations (greater than 2 $\mu g/m^3$).

5.2. Rotated Principal Component Analysis

5.2.1. Organization of monitoring sites into distinct ‘modes of variation’

RPCA allows regrouping in a single category (cluster) all sites in a given network responding to the same mode of variation, i.e., where undulations (changes) occur simultaneously and with a reasonably similar amplitude (in terms of standardized scores). It was performed on the raw data (not temporally averaged) collected by each network individually. Attempts to perform RPCA on all networks simultaneously (on the weekly averages, the longer-term signals or the differences between weekly averages and longer-term signals) proved unsuccessful.

Figure 4
Identification of sites where sulfate concentrations present the same mode of variation (each mode of variation is represented by a different marker and color).

Sulfate

RPCA of the sulfate concentrations measured at the 51 CASTNet sites included in this study indicates the presence of seven distinguishable modes of variation (seven eigenvalues greater than 1). Performed on IMPROVE sites, PCA suggests the existence of eight groups, two of them constituted of a single site. Similarly, the correlation matrix of sulfate concentrations at STN sites has six eigenvalues greater than 1 (six modes of variations). Varimax rotation of the principal component axes and computation of the correlation coefficient between the original time series and the rotated principal component allows identification of sites (clusters) exhibiting the same mode of variation.

Figure 4 displays the location of sites corresponding to each one of the modes of variation identified for sulfate at CASTNet, IMPROVE and STN sites. In the three networks, each mode of variation corresponds to a distinct and unified geographical region. The number of IMPROVE and STN sites is too limited to clearly identify the geographical boundaries of each cluster. Yet, it appears that the limits delineated for CASTNet are somehow compatible with those of IMPROVE and STN. To facilitate that comparison, identical colors have been chosen to identify corresponding clusters in each network.

Nitrate

RPCA of the nitrate concentrations at the CASTNet sites indicates nine distinguishable modes of variation (nine eigenvalues greater than 1), suggesting formation of nine homogeneous clusters (or groups); IMPROVE and STN data suggest the existence of nine and five nitrate clusters, respectively. The clusters identifying location of the different nitrate modes of variations in the CASTNet, IMPROVE and STN networks are presented in Figure 5. Neither the CASTNet nor

Figure 5
Identification of sites where nitrate concentrations present the same mode of variation (each mode of variation is represented by a different marker and color).

the IMPROVE network allows clear delineation of the limits of each cluster. Several modes of variation are occasionally observed in a limited geographical area, as seen by the classification of sites in New England and in the mid-Atlantic States, for CASTNet and IMPROVE, respectively. For STN , each cluster forms a unified geographical area.

Ammonium

RPCA performed on ammonium concentrations led to fairly sharp clustering in the three networks, with all modes of variation corresponding to unified areas (Fig. 6), despite some anomalies. Among the anomalies are the central Florida IMPROVE site that is grouped with one site in Vermont; and the Michigan, Pennsylvania and Vermont sites that are grouped together in CASTNet, although separated by two widespread modes of variation. There are strong similarities between the ammonium and sulfate clusters in the IMPROVE network (compare Figs. 6 and 4, middle panel), an obvious situation that was expected since

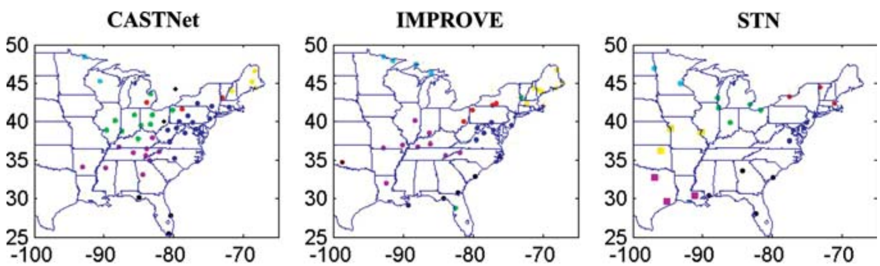

Figure 6
Identification of sites where ammonium concentrations present the same mode of variation (each mode of variation is represented by a different marker and color).

ammonium concentrations at IMPROVE sites are calculated (by stoichiometry) from sulfate and nitrate concentrations.

5.2.2. Assessment of the similarities between the average longer-term signals of each network in corresponding zones

RPCA of the sulfate data collected at CASTNet sites led to delineation of seven modes of variation corresponding to distinct regions whose limits seem compatible with IMPROVE and STN classifications. This finding suggests the possibility of jointly using the sulfate measurements reported by the three networks. Although the boundaries of some clusters seem to agree, it is possible that the mode of variation they bound are substantially different. For instance, the time series of the data collected by one network in a given area may hypothetically represent mostly seasonal variation while the data collected by another network in the same area may reflect synoptic processes. In such a case, combining data from the two networks is not advised.

To address this concern, we identified for each clustered area the spatially averaged longer-term signals of each network and simply compared these signals. Since monitoring sites are not collocated and the networks monitor different environments (CASTNet sites are located in rural areas, IMPROVE sites are predominantly in pristine areas, STN monitors are placed in urban and rural sites), the average concentrations they measure may be different. The most relevant comparison, therefore, is of the synchronism and direction (increase or decrease) of the change reported. Synchronous changes would indicate that the information reported by the different networks is correlated; another clue of their potential joint use.

RPCA and temporal characterization of each mode of variation are valuable tools for a global comparison of networks because they involve all monitoring sites. However, they only allow assessment of the correlation between long-term signals but not of other important parameters for joint use of all data, such as biases between networks, the latter being only identifiable through comparison of data at collocated sites.

Because of the numerous disagreements between the cluster boundaries assessed for nitrate with the three networks, there is insignificant purpose in providing comparisons of the longer-term nitrate signals from the three networks. Therefore, the proposed technique was only applied to sulfate and ammonium data, and then only for those areas where there is reasonable agreement in the geographic boundaries of the clusters by all three networks.

Sulfate

Figure 7 shows the average longer-term signals calculated for the three networks in five corresponding clusters. Each line on the figure represents the spatially

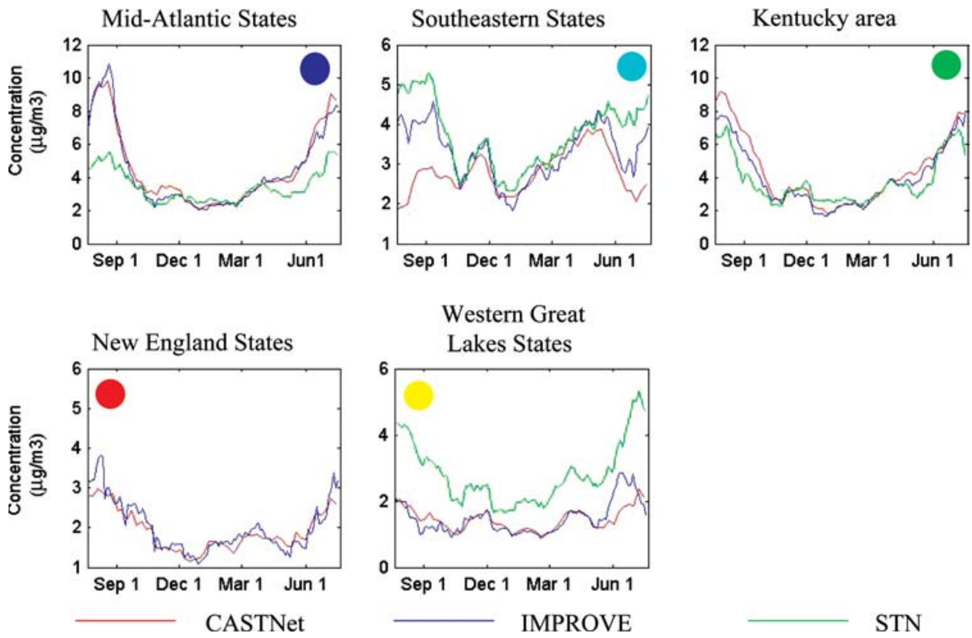

Figure 7
Longer-term signal (5-week moving average) of sulfate concentrations measured by CASTNet, IMPROVE and STN in 5 homogenous areas – average of all stations in each cluster.

averaged longer-term signals of all sites in a given network that are grouped in the same cluster, i.e., that are identified by the same marker. In the case of the cluster overlapping the mid-Atlantic States (dark blue cluster), for instance, the CASTNet line is the average of longer-term signals from all 22 CASTNet sites within the blue cluster. The corresponding IMPROVE line is the average of the eight IMPROVE sites within that cluster, and the STN line is the average of the five sites in the dark blue cluster.

The average longer-term signals in all three networks are very similar, not only in terms of the timing of the changes they report, but their amplitudes as well in the cluster overlapping the mid-Atlantic States (dark blue), the New England cluster (red) and that centered on Kentucky (green). Sulfate fluctuations in the Western Great Lakes States (yellow) are synchronous, but STN concentrations are higher than those reported by CASTNet and IMPROVE, probably because the former pertain to an urban environment while the other networks are located in rural areas or National parks. In the case of the Southeastern States (cyan), the timing of major breaks in the longer-term signals is synchronous. All networks report a local maximum around November 15, 2001, and again around May 1, 2002. Yet, the CASTNet signal is lower than those of STN and IMPROVE, perhaps because the former are exclusively located along the Florida shoreline and not further inland.

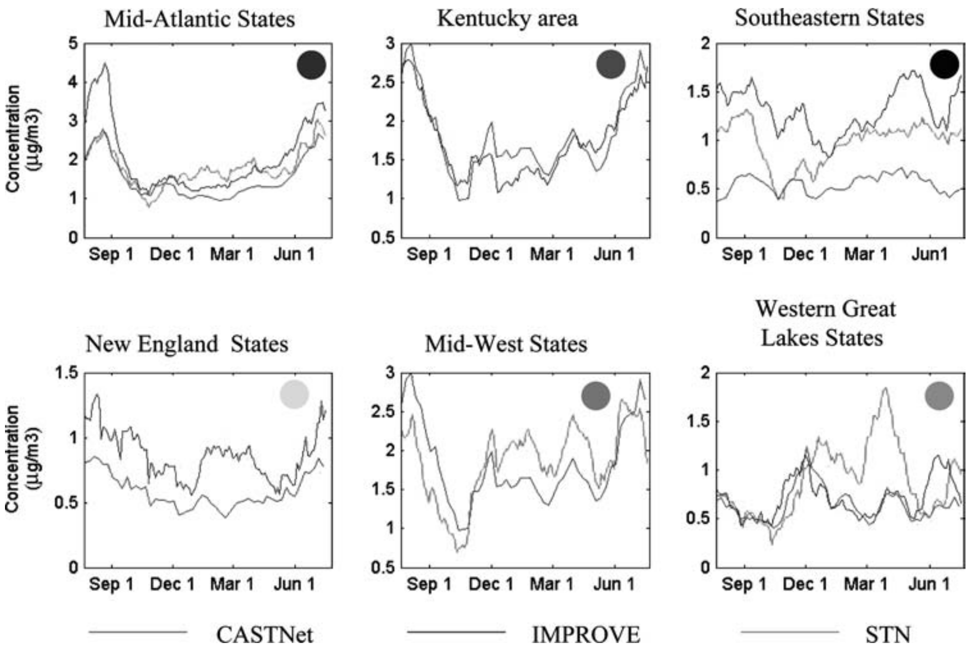

Figure 8
Longer-term signal (5-week moving average) of ammonium concentrations measured by CASTNet, IMPROVE and STN in 6 homogenous areas – average of all stations in a cluster.

Ammonium

As observed with sulfate, the spatially averaged longer-term signals of all three networks in the mid-Atlantic States (dark blue cluster) are very similar, both in terms of the timing of the changes and their amplitudes (Fig. 8). In New England (yellow) the longer-term signal in IMPROVE always exceeds that of CASTNnet, suggesting that the calculated IMPROVE concentrations may be overestimating reality. Yet, this discrepancy between CASTNet and IMPROVE signals is not visible in the cluster centered on Kentucky (magenta), nor that centered on the Western Great Lakes States (cyan). These findings illustrate once again a limitation of the RPCA technique, as it is not sensitive to systematic biases between networks. Notice that, presumably because they monitor urban environments, the STN signals indicate higher concentrations in the Western Great Lakes States (cyan) than those of CASTNet and IMPROVE. Still, the timing of major changes is reproduced. The same observation applies to the comparison of the CASTNet and STN signals in the cluster centered in the Midwest States of Illinois, Indiana and Ohio (green). The signals reported in the Southeastern States (black) show few similarities. If indulgent, one may see some synchronism in the CASTNet and STN signals, although the IMPROVE signal is clearly not correlated with the other two.

Since similar modes of variation are recorded by all networks in several corresponding zones, both for sulfate and ammonium concentrations, it appears that, for these contaminants at least, jointly using different networks may be possible. However, one needs to keep in mind that the actual observations may need some adjustment for biases, an issue not resolvable using RPCA.

6. Summary

The objective of this study is to compare some spatio-temporal characteristics of the particulate nitrate, sulfate and ammonium concentrations reported by the CASTNet, IMPROVE and STN networks. While CASTNet collects weekly-integrated samples, IMPROVE and STN have opted for one-in-three day sampling frequency and produce non-continuous results pertaining to 24-hour air samples. Due to these differences in sampling, the weekly-average concentrations calculated for STN and IMPROVE show manifest variability than their CASTNet counterpart.

Averaging the observations (in time) reduces the variability of STN and IMPROVE signals and enhances inter-network compatibility. Using a set of nearly collocated sites, we estimated the shortest moving average interval needed for comparing the three networks to be between four and six weeks. After such averaging, the inter-network correlations of sulfate, nitrate and ammonium time series become high. In addition, the longer-term sulfate concentrations reported by the three networks become very similar, possibly indicating that no systematic biases were introduced by the different sampling locations nor the instrumentation used at the sites studied. This interpretation has to be considered with caution because it relies on a single set of three nearly co-located sites. On the other hand, even after averaging the data within eight- or ten-week intervals, the nitrate concentrations reported by CASTNet are still very different and substantially less than those reported by the IMPROVE and STN. The differences were thought attributable to the distinct air sampling equipment used in the CASTNet program. Nitrate estimates are determined from the material collected on a teflon filter in the CASTNet protocol and from a nylon filter in the IMPROVE and STN protocols. Ammonium estimates seem rather consistent at low concentrations. At high concentrations, though, the IMPROVE signal exceeds those of CASTNet and STN. We speculated that the assumption used in the IMPROVE network to calculate ammonium concentrations (all the sulfates and nitrates in the particulate phase are neutralized by ammonium) may not always be valid.

RPCA was used to identify the distinct modes of variations (clusters) identified for each pollutant in a given network and their boundaries. It was shown that, for sulfate, the clusters formed for all three networks have clear geographical boundaries that seem to correspond. It was also shown that the average longer-term signals defined by each network within corresponding zones are very similar. In the case of nitrate, the clusters formed for the CASTNet and the IMPROVE networks cannot be clearly delineated but appear more mingled. Both networks, for instance, indicated that several modes of variation were occasionally coexisting in a limited geographical area. RPCA performed on ammonium concentrations led to fairly sharp clustering for the three networks, with the spatial limits of each cluster reasonably coinciding for the three networks. As for sulfate, we demonstrated that the modes of variation within a given cluster are very similar between the networks.

In summary, the results of this study indicate that sulfate and ammonium present some potential for networks integration. However, before blending the data from the three networks, basic issues such as that of the biases between networks first need to be resolved. A direct means to resolve network biases is by comparing data at collocated sites. Since there are presently no truly collocated sites, we were precluded from further investigating this issue. In the perplexing case of nitrate, severe incompatibilities between the observations reported by CASTNet and the other two networks prevent us from recommending any type of joint type use of the data from the three networks.

Whether for model evaluation purposes or for the generation of spatial maps depicting the most accurate and aerially extensive representation of the atmosphere, blending data from different sources is theoretically a beneficial option. Yet, as this study shows, that operation needs to be considered cautiously. While apparently possible for some species, the prospect of merging data sets is very uncertain for others. In fact, the extreme divergences between networks for some contaminants are bound to foster debate on the pertinence of the diverse sampling protocols utilized, and the representativeness of the measurements performed.

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