$PM_{2.5}$ and $PM_{10\text{-}2.5}$ Chemical Speciation Monitoring for CASTNET

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Introduction

CASTNET IV will include monitoring and reporting of chemically speciated $PM_{2.5}$ and $PM_{10\text{-}2.5}$ consistent with the $PM_{2.5}$ Chemical Speciation Network (CSN) and new methods currently under development by EPA. RTI International currently supports the $PM_{2.5}$ Chemical Speciation Network (CSN) under contract to EPA/OAQPS and has been subcontracted to provide CASTNET IV with chemical analysis for $PM_{2.5}$ and $PM_{10\text{-}2.5}$ and other support such as quality assurance audits, installation of new equipment, training, and installation and analysis for ammonia denuders.

The CSN was established by EPA to monitor concentration trends and to assist state and local air monitoring agencies with meeting the National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$. The IMPROVE network, which was initiated in the late 1980s to assess and help address visibility impairment in Class I areas, includes a $PM_{2.5}$ speciation component that is similar to CSN's.

Chemical Species Monitored

Some of the chemical species monitored by CSN and IMPROVE are identical to those that are being monitored by CASTNET (e.g., sulfate, nitrate, chlorine/chloride, calcium, magnesium, ammonium). However, there are significant differences in the sampling technologies, size fractionation, and sampling duration used by CASTNET as compared to CSN and IMPROVE. The table below summarizes the PM species currently monitored by the three networks, along with species that might be measured under CASTNET IV.

Species	IMPROVE	CSN	CASTNET Dry Network
Mass	$PM_{2.5}$, PM_{10}	$PM_{2.5}$	total PM (open face sampler)
Ions	$PM_{2.5}$	$PM_{2.5}$	total PM (open face sampler)
SO_2, HNO_3 (filter-based)	--	--	weekly
Visibility (various methods)	✓	--	--
Ozone	--	--	continuous
Meteorology	--	--	continuous
Trace elements (by XRF)	$PM_{2.5}$	$PM_{2.5}$	*proposed* $PM_{2.5}$ and $PM_{10\text{-}2.5}$
$PM_{2.5}$ carbon (by OC/EC)	$PM_{2.5}$	$PM_{2.5}$	*proposed* $PM_{2.5}$ and $PM_{10\text{-}2.5}$
Ammonia (by quantitative denuder)	--	*proposed*	*proposed*
Carbonate Carbon	--	--	*proposed*
Biologicals (by electron microscopy and other methods)	--	*proposed*	*proposed*

Sampling Characteristics

The next table compares sampling characteristics of the three networks. The CSN and IMPROVE $PM_{2.5}$ samplers employ cyclones to remove particles larger than 2.5 microns in aerodynamic diameter from the filter sample. Since the open-face CASTNET filter cassette has no size-selective inlet, larger particles are included on the filter deposits. As will be illustrated later, this can cause significant differences in the proportion of chemical species, particularly those associated with coarse particles.

	CSN		IMPROVE	CASTNET Dry Network
Sampler Type Filter Type(s)	MetOne Teflon & Nylon	URG 3000N Quartz	IMPROVE Teflon, Nylon, Quartz	Open Face Teflon
Flow rate, Lpm	6.7	21.7	21 - 23	1.5
Sampling Time, hr	24	24	24	168
Sampled Volume, m^3	9.6	32	32	15

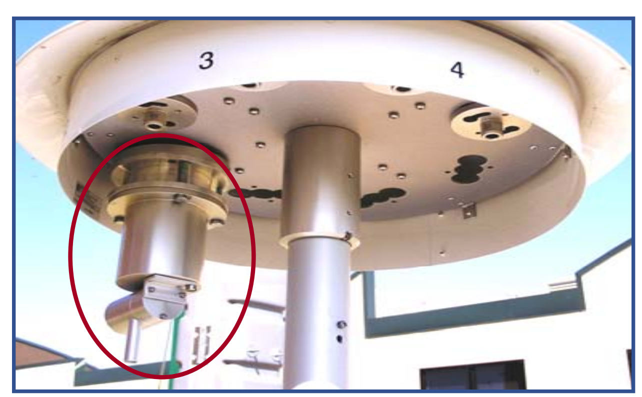
URG 3000N and CSN (MetOne SASS) samplers currently used on CSN

The MetOne sampler shown in the photo below is currently used at almost all of the CSN sites. The URG 3000N sampler, whose design is based on the current IMPROVE sampler, is currently being phased into the CSN program for sampling carbon so that results will be more comparable to those from the IMPROVE network. This will enable the intercomparison of data from the two networks going forward. The URG 3000N samples began operation at 57 CSN sites in May 2007, and a second set of 3000N samplers is currently being installed.

Current CSN Samplers: URG 3000N (left) and MetOne SASS (right). *Photo: RTI International*

Ammonia Sampling

RTI is working with researchers at Colorado State University, Met One, MACTEC, and EPA to evaluate and deploy a denuder system to quantify ambient ammonia gas. It will be compatible with the SASS sampler used for $PM_{2.5}$ sampling and will be used at selected CASTNET and/or CSN sites. This photo shows a prototype ammonium denuder module under development at Colorado State University.



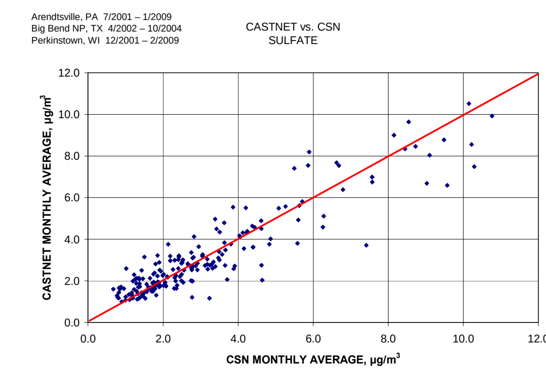
Prototype Ammonia Denuder and PM2.5 cyclone mounted on SASS Sampler. *Photo provided by MACTEC.*

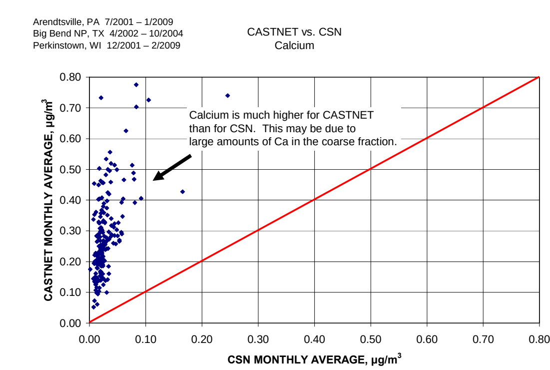
Data Intercomparison: CASTNET vs. CSN

A few of the same species are sampled and reported by CASTNET (open face sampler) and by CSN and IMPROVE ($PM_{2.5}$ sampler). These two figures show data from from three pairs of sites where CASTNET and CSN samplers were either collocated or located within a few miles of each other. Each plotted point represents a monthly average. For CASTNET, these were computed as averages from weekly filters (typically 4 per month), while the CSN averages were calculated using data from 24-hour samples taken on a 1-in-3 day schedule (approximately 10 per month). The difference in sampling periods is likely to contribute to the scatter in the data, but any bias should be minimal.

The first figure shows that for sulfate, which is known to exist mainly in the fine PM fraction, concentrations are very similar between CASTNET and CSN. However, the second figure shows that for calcium, which is associated with coarse crustal matter, the CASTNET concentrations are up to eight times higher than those from CSN, where only the fine fraction is sampled.

Data for sodium, potassium, and magnesium were also compared, but scatter was large due possibly to detection limit issues. Nitrate values were generally somewhat lower for CASTNET than for CSN. This might be attributed to volitalization of nitrate from the front Teflon filter in the CASTNET sampling cassette. CSN samples nitrate from the nylon filter, which minimizes nitrate loss.





Conclusions

Incorporating PM speciation measurements similar to those of CSN/IMPROVE at selected CASTNET sites will provide a database for establishing comparability between networks. Chemical speciation data collected at CASTNET sites on a coordinated schedule can also supplement the CSN and IMPROVE datasets to achieve more complete geographic coverage in the U.S.

It is expected that the addition of speciated $PM_{2.5}$ and $PM_{10\text{-}2.5}$ will supply researchers with important information about the distributions of different chemical species among the size fractions. In addition to providing information relevant to visibility and to human health ($PM_{2.5}$ and $PM_{10\text{-}2.5}$), the additional size/composition information can be used to improve source apportionment modeling inputs.

Routine gas-phase ammonia measurements at CSN and/or CASTNET sites should provide important information about sources of ammonia, which plays an important role in aerosol formation in the U.S.

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Recent RTI Publications

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