IMPROVE-CSN Carbon PM Monitoring Workshop Notes
June 22-24, 2008 at UC-Davis

Notes adopted from those by Phil Lorang and Chuck McDade, and modified by Marc Pitchford. These are probably best read while also looking at each presentation (available on the IMPROVE web site in March 2008). No attempt has been made to convey the content of the presentations themselves.

Of particular interest are the writing assignments for the various components of the action plan listed in the last four pages of these notes.

Workshop Participants

Chuck McDade – UCD	Lowell Ashbaugh – UCD	Joann Rice – EPA
Max Peterson – RTI	James Flanagan – RTI	Bret Schichtel – NPS
Neil Frank – EPA	John Watson – DRI	Phil Lorang – EPA
Sherri Hunt – EPA	Mike Kleeman – UCD	Antony Chen – DRI
Judith Chow – DRI	Ashley Mefferd – UCD	Jay Turner – Washington U.
Warren White – UCD	William Malm – NPS	Marc Pitchford – NOAA

DAY 1

Introduction by Marc Pitchford (Presentation not given at the meeting)
Why are we here? Carbon is important, the most abundant PM species. It has the most uncertainty due to artifacts, sensitive methods, and matrix effects. We have obvious questions to answer, and we need to get our answers in order, hence this meeting.
Goals: Develop an action plan to get more information to answer these questions over the next 1-2 years. And, meanwhile, develop an interim plan to deal with artifact estimation, CSN data adjustment for comparability, and relate IMPROVE and IMPROVE_A data.
Meeting approach: For each of the items mentioned, we will review the available information, identify gaps, generate an action plan to get more data, and develop interim approaches.
Challenges: No new funding, so far. We are under the constraint that we can't stop ongoing monitoring. Need to honor the expectation that the networks will track "the Trend." We can't cut the number of sites way back, can't switch to much different instrumentation. No radical changes.

Discussion:
How much is being spent on the two PM2.5 speciation networks now? About $6 million each per year. About 20,000 samples/year. About $1 million in each program just for the carbon analysis.

REVIEW OF THE CARBON ARTIFACT ADJUSTMENT APPROACH FOR IMPROVE (Lowell Ashbaugh)
Discussion:

The conceptual model in the presentation slides may not be realistic, e.g., there could be a finite number of active sites on the quartz filter rather than a proportional retention.
Why those 6 monitoring sites for QBQ? Legacy decision, made when there were many fewer sites overall.
Of the 6 sites, Okefenokee Swamp is different than the others for organic carbon (higher values at Okefenokee).
IMPROVE can't switch QBQ sites around during the year, because of the lack of active flow. Would need to recalibrate flow rate each time. Active flow control would allow QBQ to be only sometimes.
Recent experiments show that matrix effects are present in the primary filter (i.e. inorganic material from the particles on the filter can influence the results of the carbon analysis), but secondary QBQ filter isn't subject to matrix effects because it has no particles, which may make its use for artifact adjustment wrong. There is also some small amount of EC on the QBQ filter which could be subtracted from total carbon.

REVIEW OF CURRENT ARTIFACT ADJUSTMENT APPROACH FOR CSN INCLUDING SAMPLER-SPECIFIC VARIATIONS (Jim Flanagan)
Discussion:
There was a discontinuity in OC fraction approach in July 2003.
Description of mechanics of blank exposure in the field.
There is a trend in blanks. 2001-2002 had greater OC on blanks than 2003+.
Filter lot change is roughly on an annual basis. Cassette cleaning procedure change could be responsible for some of the field and trip blank values.
A given sampler keeps its cassettes, so if cleaning is done incompletely and a cassette that off-gases organics is returned to the same sampler, a sampler will have a systematic bias effect. Jay Turner has seen differences in Detroit and elsewhere where a particular site is consistently higher than others. Could be a cleaning effect, or perhaps operator practice differences.
Clarification: UCD and RTI follow the same procedures for disassembling cassettes and repackaging the quartz filters for shipment to DRI for the IMPROVE and URG 3000 samplers.

EVIDENCE FOR POSITIVE AND NEGATIVE ARTIFACTS (John Watson)
Discussion:
There are old studies in the literature about positive and negative artifacts in carbon sampling: Dennis Fitz, SCENES and Peter Mueller should be contacted to see if they can provide documentation of their work. Meeting attendees should send old references to John Watson for his bibliography. IMPROVE was doing subtractions even before some of the published papers cited by Watson.
Slicing filters front-to-back sometimes gives inconsistent front-to-back comparisons.
IMPROVE QBQ filters can pick up OC from the face of the cassette, unlike when three filters are used to protect the middle one from touching.
There was a historical experience with baggies and O-rings causing artifact. Now being avoided.
Question: How and why were the 8 collocated CSN sites picked? Various factors, practical considerations, diversity, willingness of operators.

How are IMPROVE field blanks picked? There is a computer program that generates a random schedule. Details of its logic are apparently not transparent. All field blanks happen on the same day, when they happen.
There is more OC on passive blanks in summer than in winter. There are various plausible explanations.
Should one compare blanks on a ug/g of filter, or on ug per reactive are of filter, not the full filter area?
Could CSN extend the exposure period for its field blanks?
In summer, the difference between active QBQ and passive QBQ is larger than in winter. Could be that OC volatilized from the front filter collects on the back up filter. Could be a different type of OC in the summer atmosphere.
OC can condense on the PM caught on the front filter, e.g., when there is high PM from fires. OC on second filter may not be a good predictor of the non-PM OC caught on the front filter.
Antony Chen presented a slide arguing that IMPROVE negative artifact is small. There was some debate as to whether it is right to use OLS regression for this purpose. General agreement was that the evidence is inconclusive of the point claimed.
Point made: Need to be explicit about whether "truth" is what is in the air or what is collected and weighed on an FRM Teflon filter.
Front-to-back filter slicing studies have been too sparse and have had too varied results to allow generalizations.

PRELIMINARY ORGANIC ARTIFACT CONCEPTUAL MODEL (Marc Pitchford)
Discussion:
"VOC" as Marc defines it (never condenses or absorbs onto carbon) maybe very few. Even VOC with very low vapor pressure can absorb at active sites. Should change "VOC" to "nonabsorbing for practical purposes."
Even if saturated on the filter, there can be turnover of molecules.
One needs to consider and model what happens at the filter once sampling ends, not just what happens during the sampling period.
One can have alternative simplified conceptual models by assuming/proving that some factors or processes dominate over others. We may not be able to disprove alternate models with the type of data we have in hand.
OC on QBQ secondary filter might actually be liquid material that has been wicked off the PM caught on the front filter, rather than gas phase OC caught on active sites.
Not all PM in the atmosphere contributes to visibility degradation – very small PM may not matter much (ref: Delbert Eatough & George Allen).
PM caught and retained on FRM Teflon filter media may not be what affects health.
We need to understand relative properties of OC on the PM, versus the OC that is caught in the filter media.
Projects to compare water soluble OC to total OC may give insights. WSOC is too polar to volatilize. This will be investigated further by Collett & Weber. There could be other OC that also don't volatilize.

The agenda was changed at this point to continue with planned presentations, and then come back to discussion of conceptual models and gaps.

REVIEW OF EVIDENCE FROM CSN VS. IMPROVE (Warren White)

Discussion:

John's main point (see presentation slides): The high face velocity in IMPROVE samplers (compared to some CSN samplers) strips SVOC from the primary filter, creating a negative artifact for OC.

There was a discussion of additive vs. multiplicative differences in the model.

Question: Is it right to use the reported concentration of OC-IMPROVE as the estimate of actual OC?

If IMPROVE loses 20% of OC on the PM, wouldn't the visibility algorithm and/or the mass closure (1.4 vs. 1.8) adjustment in effect correct for the loss? Not the mass closure, since the Teflon filter would lose that mass also.

Losses don't happen just due to the face velocity. Other factors that can contribute include diurnal changes, non-cold shipping.

Is the relationship/model presented by John Watson what the health researchers need?

A reference was mentioned: Atmospheric Environment, Hyslip and White, 2007.

We need to be careful about whether old TOT continues to be done the same as in the past, if/when it becomes rare to use it. New measurements may not represent the past method. Neil offered the idea that if/when we only need a few TOT measurements maybe they could be done as some lab that has other customers who order TOT. Others pointed out that introducing a lab variable may not be a good idea.

We need to ask the health researchers if the relationship developed by John Watson (with its error term) is OK for their purposes. The health researchers use some pretty fancy statistical tricks for other factors that aren't constant or known in their samples.

Judy Chow is working for some health researchers to re-punch and test some old filters.

It may be possible to develop site-specific f and g factors in the Watson model. Bob Casey did the first punch/analysis on the filters in Judy's re-punching project.

EPRI is funding someone at Emory U. to re-analyze St. Louis's 2 data sets to see if the re-punched values affect the epidemiology conclusions.

MetOne should have a small negative artifact, given its low face velocity compared to IMPROVE.

Also, different CSN samplers will have relative differences, due to differences in face velocity.

We could pull some old IMPROVE filters and re-punch then for IMPROVE_A analysis, to get a richer data set to relate old and new IMPROVE.

INTERIM APPROACHES FOR COPING WITH ARTIFACTS (John Watson)

Discussion:

Should we keep or drop the trip blanks in the "new CSN" system? John has a slide with 3 ideas for special studies. Need to expand frequency of field blanks by site; perhaps focus field blanks on certain sites. Also, consider after filters at some collocated sites. Consider active flow control on some IMPROVE samplers so they can be used interchangeably for afterfilters.

IMPROVE vs. IMPROVE_A and IMPROVE vs. CSN (Warren White)

Discussion:
Warren White showed charts based on 2004-2006 replicates. Judy said there was replicate data from 2001-2003 also. 2004 was probably the worst period in terms of flaky data, because the old analyzers were not operating consistently. After 2004, only the best 2 of the old instruments were kept in operation and they were kept calibrated better.
Only 43 samples from March-May 2004, so we cannot be so certain that the distribution of EC/TC is different from 2005-2006.
Maybe the trend upwards in OC/TC from 2000 through 2005 could be due to network expansion, with newer sites being systematically different from the original sites? Alternately, were the old analyzers deteriorating, causing the apparent trend?
There are discontinuities in OC3 and EC in late 1994, which are not explained yet.
There is not much data comparing IMPROVE and IMPROVE_A the way that IMPROVE was done before 2005. To address this, one would have to re-punch old IMPROVE filters and re-analyze them with IMPROVE_A. We should not expect filters to have been much affected by their time in storage, based on Judy Chow's experience.

DAY 2

STN AND IMPROVE CARBON FIELD BLANK DATA EXPLORATION (Brett Schichtel)
Discussion:
Warren White lost the argument about whether Brett had correctly handled OC vs. OM in his equations, and graciously admitted defeat on that point.
There are lower intercepts in the East than in the West. Is the higher intercept in the West in "OC= A + B*PM.5" actually nitrate?
CSN regression intercepts may not mean much given the short exposure time [of the field blanks]. IMPROVE summer field blank correction may be too low. Evidence that liquids can migrate from the front filter to the backup.

TWO MONTHS OF COLLOCATION DATA FROM OLD CSN VS. NEW CSN (Joann Rice)
Discussion:
We should also look at the TC comparison – does it confirm Warren's estimate that 20% of the OC on PM gets lost in the IMPROVE sampler?
Filter type may be an influence, in addition to the flow, the area of the filter face, and TOR vs. TOT.
Need to be conscious of sampler type whenever using CSN data or trying to interpret it.
Lower flow rate samplers have more OC, implying less negative artifact.

IMPROVE SECONDARY FILTER vs. FIELD BLANKS (Warren White)
Discussion:
The point made is that QBQ is higher than the field blank.
Clarification of LNRC measurements, small variations over time.
Discontinuities in late 1994 were noted again.

CSN CARBON MEASUREMENTS AND ADJUSTMENTS (Neil Frank) and TRENDS IN CSN FIELD AND TRIP BLANKS (Jim Flanagan)

Discussion:
TOC by mass closure vs. applying 1.4 factor to OC and doing blank subtraction.
1.4 factor fits, if the blanks are assumed to be the true picture of the positive artifact. 1.4 is too low, if the true artifact is larger than indicated by the CSN field blank.
There was clarifying discussion about the manufacturer-recommended instrument software change at RTI on July 8, 2003. (Later, it was noted that RTI has the capability of re-presenting data after July 8 using the previous software's logic.)
Around 2003, there were also changes at RTI in how cassettes were cleaned, how work surfaces in the filter unloading/loading lab were cleaned, etc.
Jay Turner said that the CSN collocated precision data in Cleveland shows a change at July 8, 2003.

GOALS DISCUSSION

There are these data applications to consider:

- Visibility program (modeling, trends tracking, source attribution)
- Health effect studies
- Compliance
- Model evaluation
- Climate

The goal for the health effects researchers: give them a consistent data base with meta data note about special things to consider, e.g., changes in instrumentation, software, etc.
Discussion ensued about whether "we" should offer solutions and best practices for dealing with identified continuity and artifact issues. Should we post an official "fudged" data set? Most felt that we should do so, but that we need to make it clear to users what has been done to the data and why.
Top priority is to make data users aware of the issues.
Mike Kleeman – We should consider the epidemiology studies to be our most important data customers, because they help set the NAAQS. They need our help to get the best "fudged" data sets. Another view was that epidemiologists have sophisticated statistical methods, and can find their own way once they know the issues. Anyway, central monitors are an uncertain way to represent population exposure; monitoring issues are on top of that basic problem.
One participant noted his perception that epidemiologists don't take time to invite review by monitoring/atmospheric scientists, and if they did some problems would be avoided before publication.

John Watson listed 4 types of action items:

- Systematize what we already know, e.g., publish a paper that tells all we know about method changes and data discontinuities
- Figure out what more we can learn from more analysis of the data we have
- Figure out what more we can learn from re-analysis of old filters
- Figure out what new field experiments do we need?

Phil Lorang: EPA cannot/will not resist the expectation of the epidemiologist community that we will provide data sets with adjustments we believe in.

EC and OC are very important because of the linkage to diesels emissions and exposure.

Point made: Epidemiologists mostly care about urban area and CSN, so it may not be necessary to offer a "fudged" IMPROVE data set for them.

The IMPROVE program experts typically also are the experts on CSN, so they have a role helping to figure out how to "fudge" CSN data.

DISCUSSION OF ACTION STEPS

The text in bold is what was written on the white board during the meeting as the official list of action items and the persons who agreed to prepare a brief draft plan for review by others at the meeting. *The notes in italics are ones taken by Phil Lorang on the same action item, and may be useful as a supplement.* The draft plans should specifically indicate what is to be done, who is to do it and give an estimate of required resources and time to accomplish the plan. Authors (i.e. the names in parenthesis below) can contact anyone at the workshop for additional information or advice. Drafts are due to Marc Pitchford by the end of the 3rd week of February and will be circulated to all workshop participants for review, after which they will be revised. Revised plans will be the basis of proposed activities over the next year or more to gather the information that can help us better deal with carbon PM monitoring and data analysis for the IMPROVE and CSN programs.

<u>Re-analysis of Archived Filters</u>

- **Before and after new IMPROVE analyzer (pre2000+) (Warren White)**
- **Collocated IMPROVE/CSN – (16 sites) Old IMPROVE analyzer (Warren White)**
- **Pre & Post 1994 IMPROVE (Warren White)**
- **Re-analyze CSN samples using IMPROVE-A (for EC) (Joann Rice)**
- **CSN pre-July 2003 (re-process through new analyzer software) (Max Peterson)**

Re-punch some old pre-2005 (2003-2004) IMPROVE filters and retest with IMPROVE_A
Reanalyze CSN-IMPROVE collocation pre-2005 filters with IMPROVE_A
Explore the discontinuities in late 1994 some more
Consider all seasons
Re-punch old CSN filters and do IMPROVE_A for EC to get more relevant data set for an analysis of the type Warren White did with the currently available collocation data (Joann)
Do new IMPROVE_A on old IMPROVE filters from all 16 CSN-IMPROVE collocation sites, across more years prior to 2005.

<u>Information Exchange</u> **(Chuck McDade)**

- **Systematize changes in both networks (exclude data advisory)**

- **Publicly accessible database**
- **Monitoring Site MetaData**
- **Additional sampling information (sample change time, etc)**

John Watson suggested we systematize what we know in a paper for a health journal. Start by creating an outline. Include timeline of changes that we think are important for carbon measurement results. Paul Solomon is working on a paper that covers some of this information?
Should we assemble a common, comprehensive data base, or a repository for separate partial data bases, or at least a clear inventory of the available data and whom to get it from? VIEWS has an approach for holding data sets.
We should start a practice of data advisories for CSN, like IMPROVE already does.
We should start a practice of posting site histories for CSN sites, like IMPROVE already does.
Are the specifics of the field blank placement and retrieval (when was it placed, when was it retrieved and sealed) captured in the data base for CSN? For IMPROVE?
Post the QBQ values that are used to correct for IMRPOVE positive OC artifact for each month, retrospectively and then ongoing.
Ask health researchers to figure out how much an increment of added uncertainty in EC would degrade the certainty of the ambient concentration-health effect association. For example, start with a real ambient data set, do the health effect regression, then add simulated uncertainty to the data set and repeat the regression.
Find out what years and sites of CSN are being used in epidemiology studies (NCER is trying to do this now).

Data Analysis

- **Reanalyze CSN samples using IMPROVE_A (for EC) (Max Peterson)**
- **CSN pre-July 2003 (re-process through new software) (Max Peterson)**
- **Expand Warren's regression analysis (Warren White)**

Run new RTI software on pre-July 2003 samples.
Make more monitoring site meta data available.
Label sites by the degree of expected negative artifacts, e.g., whether there is a strong influence of fresh volatile VOC, to allow categorization in analyses of existence of negative artifact. (HEI collected this information on some sites, is it captured in AQS meta data?)
Repeat/expand Warren White's regression analysis, looking for coefficients representing positive and negative artifacts and CSN-IMPROVE relationships:

- *Repeat for the pre-2005 data, to explore the 2001-2002 vs., 2003+ discontinuity in CSN OC.*
- *Repeat for rural sites, including Big Bend which somehow was missing from the data set used by Warren so far.*
- *Repeat for the other urban collocation sites that are available, beyond the 6 cites used by Warren so far.*
- *Do the analysis directly on filter measurements, rather than post-correction IMPROVE reported values, to make things more explicit.*

John Watson had a slide with 3 suggested action items:

- *Identify the components in the OC fractions of QBQ and field blanks.*

- *Investigate whether the difference between TOR and TOT results can reveal what's in the filter material below the surface.*
- *Study saturation dynamics.*

Re-regress 2005-2006 IMPROVE vs. IMPROVE_A by season.
Make more use of Babs data as the indicator of EC trends across years.

Special Studies

- **Literature Review gathering of positive and negative artifact evidence (John Watson)**
- **Source specific sample testing for artifacts (Judy Chow)**
- **Look for differences between high and low face velocity (Jay Turner)**
- **Characterize OC capture by quartz filters (wrt Temp, Humidity, exposure length time) (Antony Chen)**
- **Better understanding of negative artifact (variability in time and space) (Mike Kleeman)**
- **Old CSN - Look at longer exposure of field blanks & secondary filters (Jim Flanagan**)

To convince skeptics, do a clean experiment to test for the existence of negative artifacts (or did SCENES settle this issue already?).
Some disagreement about whether it would be possible to conduct such a study, given site dependencies.
There was discussion about the value of doing a literature inventory and review, reach weight-of-evidence conclusions, a "meta analysis."
Someone at CalTech did a thesis along these lines recently?
John Watson keeps a literature inventory.
Kleeman: It is necessary to take a source-oriented perspective when considering negative artifacts, since some sources emit much more volatile OC than others, e.g., highway vehicles.
Schichtel: One could deploy 10-20 pairs of high and low flow samplers, to test for negative artifact, but is it worth it for visibility applications? If we want to do this, it needs to be done before MetOne samplers replace the other types in the CSN network.
Special study idea: characterize the physical dynamics of quartz filter absorption/desorption, e.g. 72 hours of exposure versus one week of exposure.
Design an experiment to tell whether QBQ or a 3-day or 7-day field blank is better for estimating the positive artifact.
Design an experiment to determine the diurnal pattern of gas-phase OC; understanding that might help understand the absorption/desorption during the sampling period.
Need to pay attention the dependency of artifacts on emission source types affecting the monitoring site.
Study quartz dynamics.
Do some lab experiments on negative artifacts, under tightly controlled conditions.
Do some experiments in the field at different exposure periods for field blanks.

Network Changes

- **Old CSN – fewer trip blanks (or none) (Joanne Rice)**
- **Old CSN – fewer field blanks (or none) (Joanne Rice)**

- **Continue collection of Old CSN to new CSN & to IMPROVE during CSN transition (Mike Kleeman)**
- **Get better spatial coverage for QBQ for IMPROVE. Also at urban collocated sites & urban/rural pairs (Marc Pitchford & Neil Frank)**

Drop CSN trip blanks? Neil says "No."
Drop the CSN field blanks that have short exposure time, add a variety of other blank types (long exposure field blanks, QBQ, etc.)?
General sentiment was that for the short remaining period of old CSN sampling, the field blank approach should remain as it has been.
General sentiment was that for the short remaining period of old CSN sampling, we should not add QBQ.
Do not stop collocated CSN-IMPROVE sites. Put the last 4 sites with old-CSN and IMPROVE into the Round 3 conversions, which will be 18-24 months from now.
There were some weak favorable feelings about keeping all 3 methods going, with Neil feeling the most positive (?).
Eventually, after all issues are settled, restore full IMPROVE to the 3 IMPROVE sites that now have only collocated carbon channels operating. Or, shut them down. It is too difficult to do good QA review of carbon data without the information that comes from the other channels.
When QBQ is collected, both filters must be analyzed, because otherwise there's too much risk that the filters will be confused. Measuring both makes it clear which was the primary.
Add QBQ to IMPROVE at the 6 rural sites that now have dual carbon channels.
Raised and discussed but then dismissed: Reduce the frequency of analyzing the QBQ filters, rather than doing on every sample from the 6 sites. Dismissed because of the risk of mixing up filters.
Do QBQ at the 6 urban collocated new CSN-IMPROVE sites, especially at urban areas that have a nearby rural dual carbon channel IMPROVE site.
Do IMRPOVE field blanks at fewer sites but for more days per year, to get enough data to study seasonal differences.
Do field blanks at the 6 IMPROVE QBQ sites, so that there is more robust data for comparing QBQ and field blank results.
Coordinate field blank schedules between IMPROVE and URG30000N sites at the 6 collocated urban CSN-IMPROVE sites, to be able to compare the results of the 3-day exposure in the URG3000N sampler to the 7-day exposure in the IMPROVE sampler.
Add Babs measurements and reporting to CSN.

<u>Interim Data Adjustments</u>
We need to decide how to adjust for artifacts in the new CSN. We can take a year or two to figure this out.

<u>Other Action Items</u>
Brett will collect all the presentations and post them on the IMPROVE website.
Presenters should send their files to Brett.

All participants should send relevant old references on carbon artifact issues to John Watson for his literature collection.

Marc will distribute the 2 draft DRI reports to all the participants, who should return comments to Judy Chow. Please pay particular attention to the accuracy of the descriptions of the details of the monitoring networks.