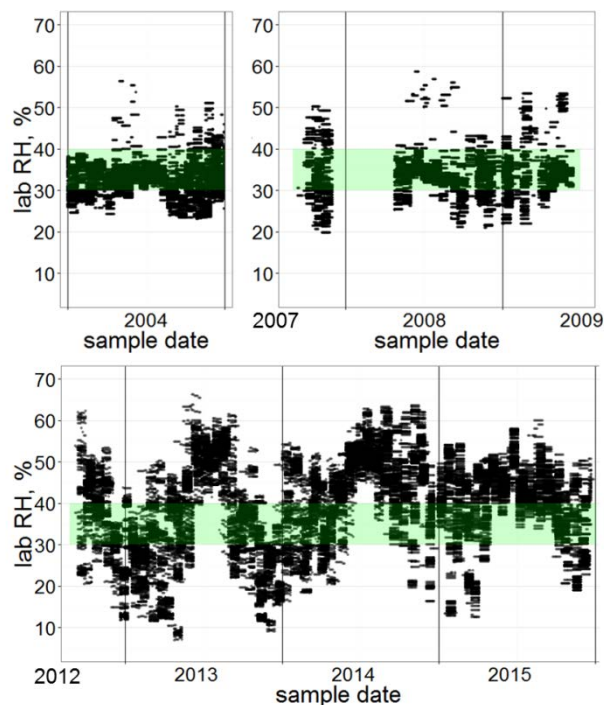


<b>Posting type</b>	Advisory
<b>Subject</b>	Increased variation of humidity in the weighing laboratory
<b>Module/Species</b>	A/ MF, D/ MT
<b>Sites</b>	All
<b>Period</b>	2011 and later
<b>Recommendation</b>	Recognize that gravimetric measurements are not FRM-compliant
<b>Submitter</b>	W.H. White, <a href="mailto:whwhite@ucdavis.edu">whwhite@ucdavis.edu</a> ,

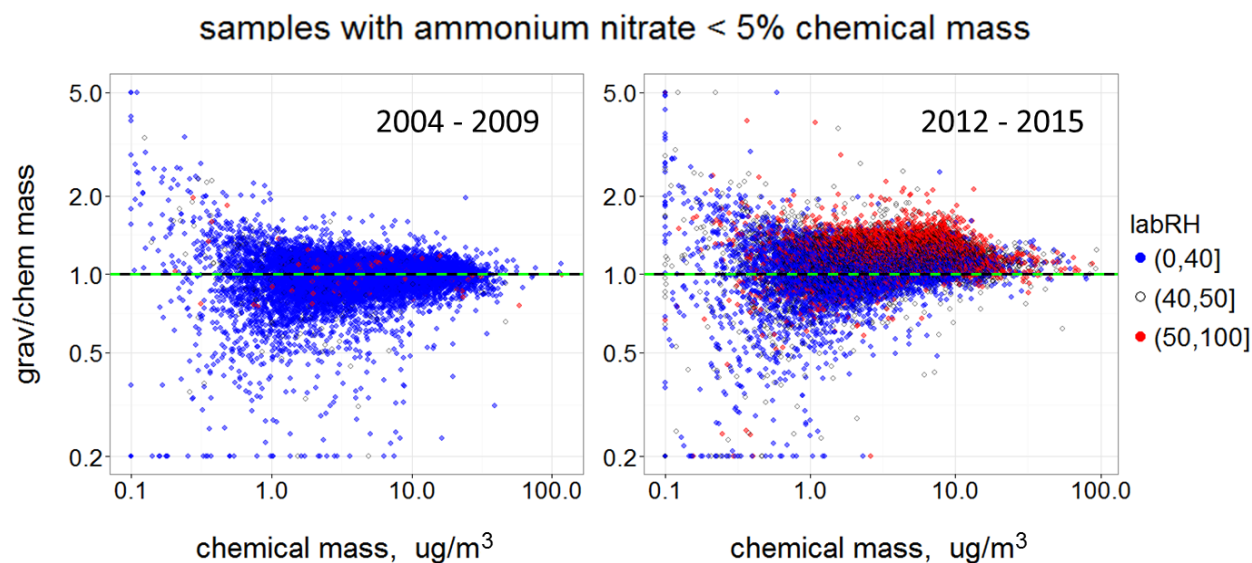
### Supporting information

IMPROVE gravimetric measurements have never complied with [EPA requirements](#) for the Federal Reference Method (FRM) determination of PM<sub>2.5</sub>. Samples are routinely weighed well beyond 10 days after collection, and the relative humidity (RH) in the conditioning and weighing laboratory can range well outside the regulatory limits of 30-40%. Starting with samples collected in 2011, IMPROVE filter-handling and weighing operations were relocated from a separate room in the Annex of Crocker Nuclear Laboratory (CNL) to a larger space in the main CNL building. Temperatures in the new facility are maintained by the building's central HVAC unit, which the [IMPROVE QAPP](#) (section 5.5.2) notes does not provide for independent regulation of RH. Statistical analyses of gravimetric vs. chemical data were reviewed at the 2015 IMPROVE Steering Committee meeting. Slides 14-16 from the [2015 presentation](#) showed some marked increases for 2011 and subsequent years in the mass regression coefficients for chloride and sulfate concentrations, which associate mass with the generally hygroscopic chloride and sulfate salts. This advisory examines the historical records of balance room humidity available from intermittent quality assurance monitoring. Early monitoring was not rigorously calibrated and cross-checked, and was intended more to give an indication of whether 30 – 40% humidity limits were achievable in the existing location with available HVAC systems.

**Figure 1.** Laboratory humidities at which IMPROVE samples were weighed. Exposed filters are shipped from each sampling site at 3-week intervals, and are analyzed as they arrive at CNL. The samples from a site's 3-week batch are weighed in quick succession, giving rise to the plot's general grouping of seven weights at about the same humidity.



Laboratory RH can vary significantly within a few hours, so samples cannot be assumed in equilibrium with the particular RH recorded when they are weighed. Lacking FRM-compliant measurements for comparison, we therefore cannot quantify the effects of nonstandard lab RH on IMPROVE mass concentrations. We can, however, compare gravimetric mass  $MF_{grav}$  with “dry” estimates obtained by scaling chemical measurements according to [standard assumptions](#) that neglect any unbound water:  $MF_{chem} \equiv 1.8Cl^- + \frac{80}{62}NO_3^- + \frac{132}{96}SO_4^{=2} + fine\_soil + 1.8OC$ . Ammonium nitrate is subject to substantial post-sampling loss from the weighed PTFE filter, so Figure 2 restricts comparisons to samples which collected minimal nitrate to begin with. For the 2012–2015 period, 21319 (39%) of the 54755 samples for which RH was monitored survive this restriction. The comparisons in Figure 2 indicate that the ratios  $MF_{grav}/MF_{chem}$  have been running higher since the 2011 laboratory move, with the increase most apparent at higher laboratory humidities.



**Figure 2.** Mass ratios  $MF_{grav}/MF_{chem}$  at three levels of laboratory RH (%) for samples collected with minimal ammonium nitrate. Off-scale values are plotted at the appropriate boundaries; striations evident at the lowest masses are associated with granularities in reporting.

**Data notes:** Sean Raffuse and Chuck McDade helped to assemble the laboratory RH data. Sample lab RH values are based on logged times of weighing, matched to 5-minute readings for 2004 and 2012-2015 and to 1-hour maxima for 2007-2009. Two anomalous sampling sites are excluded from the gravimetric/chemical comparisons, HAVO1 (Hawaii) and BYIS1 (Korea).