Behavior of Fine-Particle Elemental Data Near the Detection Limit

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PAPER #24

EXTENDED ABSTRACT

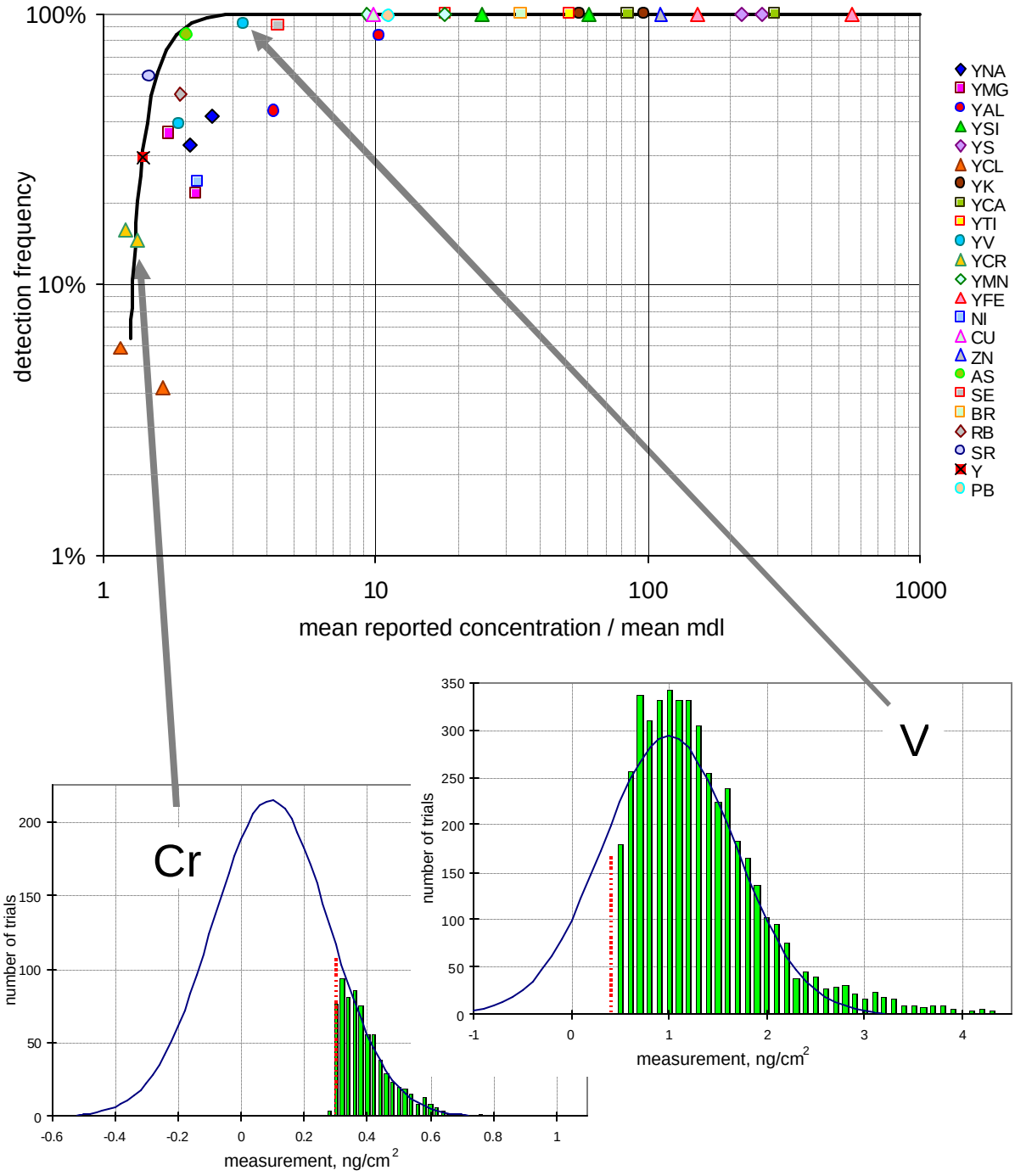
The IMPROVE (Interagency Monitoring of Protected Visual Environments) network uses XRF analysis to monitor most trace elements between Na and Br, along with Pb. The concentration and analytical uncertainty are reported for each detected element, along with minimum detectable levels for all elements, whether detected or not. Some of the elements of most interest for source apportionment, such as Na, Al, Ni, and As, are not always detectable. Others, such as V and Se, are often within an order of magnitude of the detection limit and determined with correspondingly limited precision. Uncertainties and detection limits can thus rank with concentrations in their importance as inputs to source apportionment modeling.

Uncertainties and detection limits are estimated for individual samples from details of the observed spectra, based on statistical theory and various assumptions. It is accordingly desirable to have some experimental confirmation of these estimates. Unlike concentrations, however, which are observable in individual samples, uncertainties and detection limits are observable only as statistics of multiple samples. Near the detection limit, moreover, these statistics are distorted by the associated censoring of undetected concentrations. To generate more-controlled data sets in which uncertainties and detection limits can be more easily characterized, we have undertaken a program of additional measurements.

This paper describes recent experiments in which the non-destructive character of XRF analysis was exploited to analyze selected samples hundreds of times, filling in the full distribution of potential analytical outcomes from which only one realization would normally be reported. Three lightly loaded (~1 $\mu g/m^3$ gravimetric mass) routine network samples were examined in this way, two by Cu-anode XRF and one by Mo-anode XRF. Theoretical counting statistics provide a framework for interpreting the multiple outcomes, which Figures 1 and 2 show to be distributed about as expected.

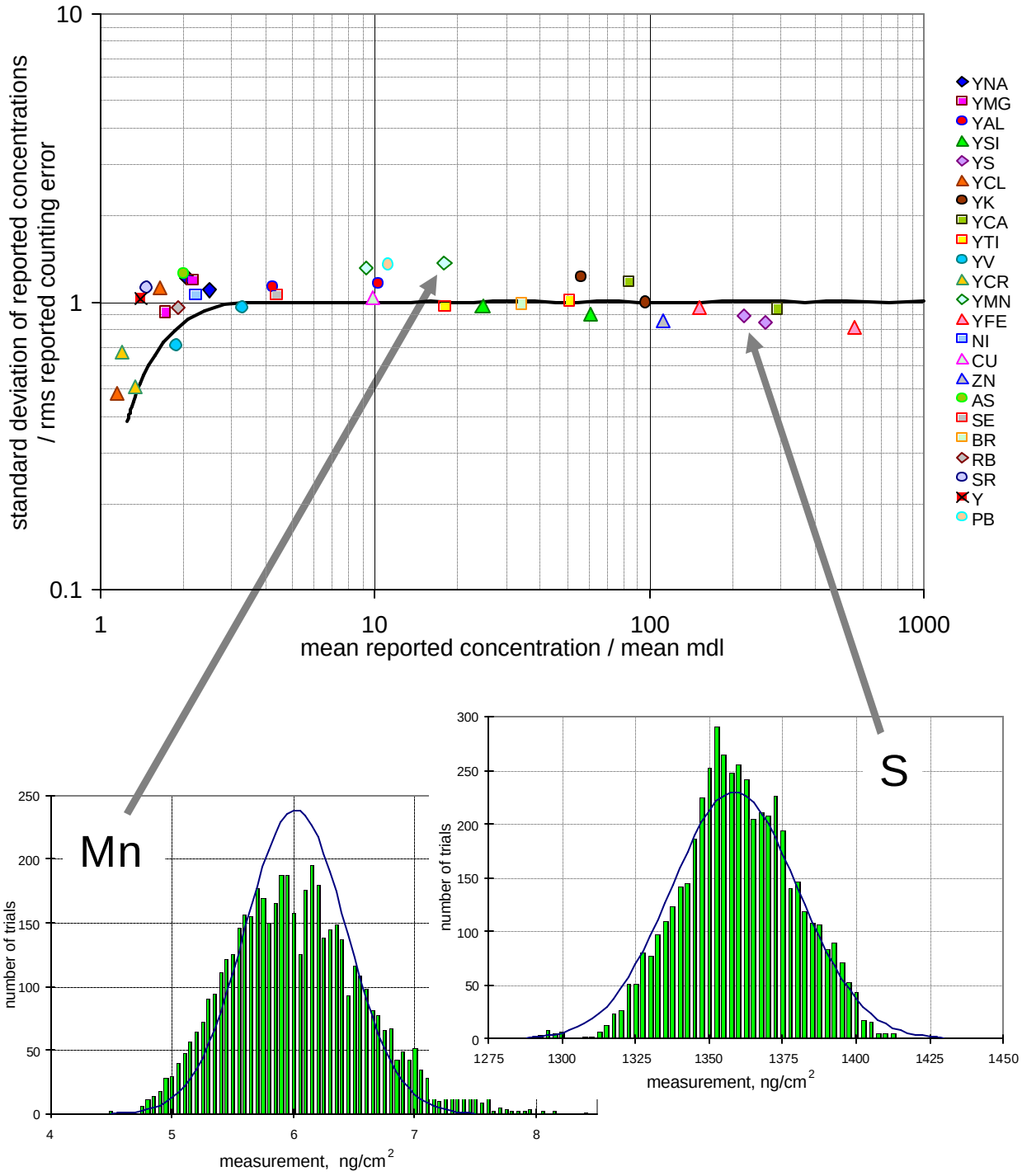
Paper No. 24, Behavior of fine-particle elemental data near the detection limit. Regional and Global Perspectives on Haze: Causes, Consequences and Controversies – Visibility Specialty Conference, Air & Waste Management Association, Asheville, NC October 25-29, 2004

Figure 1. Behavior of measurements near the minimum detection limit (mdl).



The multi-element graph at top plots observed detection frequencies against elements' concentrations relative to their minimum detection limits. The two Cu-anode analyses are distinguished from the Mo-anode analysis by Y prefixes in the element listing on the right. The smooth curve shows theoretical rates expected from truncation of large negative counting errors at reported detection limits. Histograms below show the distributions of measured concentrations observed for individual examples, together with reported detection limits (dotted red lines) and predicted distributions based on theoretical counting error (blue Gaussian curves).

Figure 2. Agreement of observed variation with theoretical counting uncertainty.

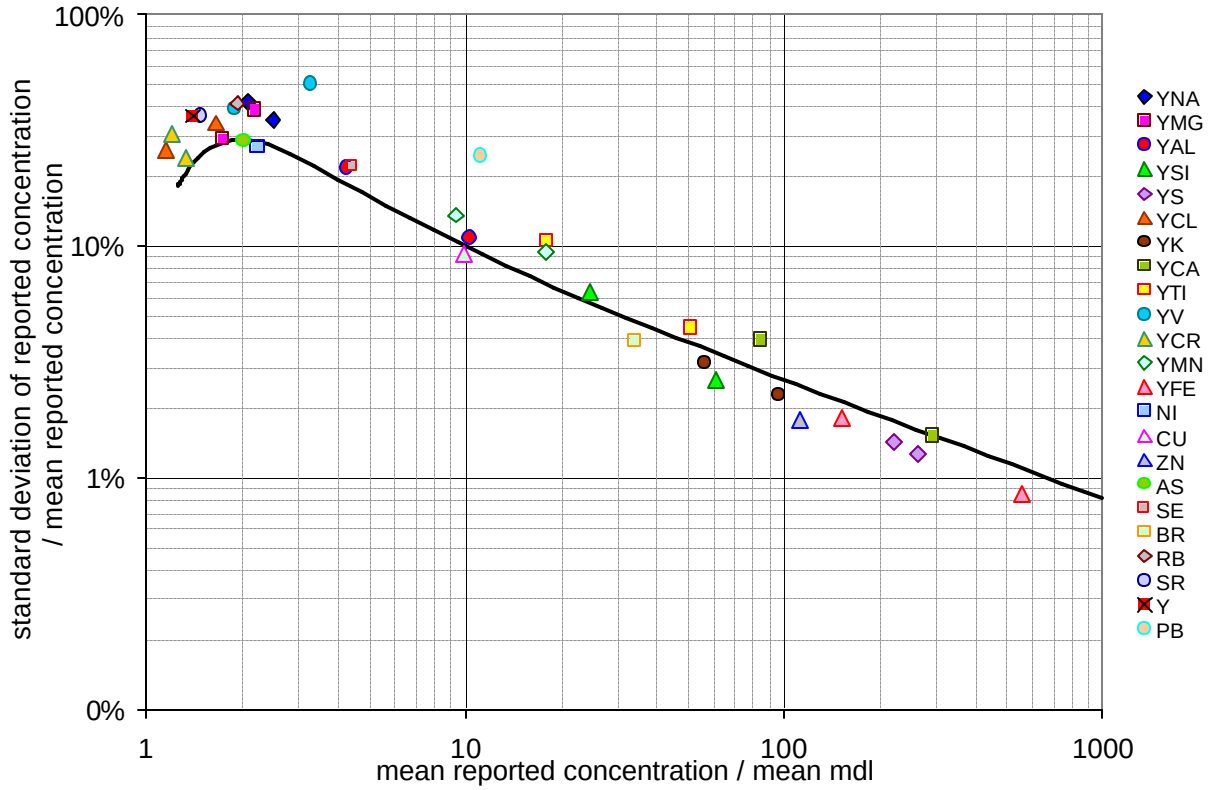


The multi-element graph at the top of Figure 2 plots observed concentration variation relative to estimated counting error, as a function of relative concentration. The smooth curve shows the censoring of observed variation at low concentrations that results from the non-reporting of large negative errors. Histograms below show the distributions of measured concentrations observed for example elements, together with predicted distributions based on theoretical counting error (blue Gaussian curves).

Figure 2 shows theoretical and observed counting uncertainties to compare rather well. The counting error grows roughly with the square root of concentration, and thus decreases in relative importance with increasing concentration. The one-sigma error at the mdl is about 60% of the concentration, but the variation of reported concentrations is diminished by non-detection of the most negative errors. The minimum detection limit is less well-determined, as both a theoretical concept and a descriptive statistic, and Figure 1 shows it to be an uncertain predictor of detection rates at marginal concentrations. It is best interpreted as scaling factor that normalizes concentrations with respect to data quality, as shown in Figure 3.

Figure 3 summarizes the precisions observed in our replicate analyses as a function of observed concentrations. The minimum quantifiable level (MQL) is often defined as the lower limit of concentrations measured with precisions of 10% or better. Figure 3 indicates that the theoretical MQL imposed by counting statistics is generally about ten times the reported mdl. The smooth curve indicates the generic dependence of observed replicate precision on concentration; the exact relationship depends on details of the elements' spectral peaks.

Figure 3. Observed concentration variation as a function of observed concentration relative to the mdl.



ACKNOWLEDGMENT

This analysis was supported by the National Park Service under Contract C2350990001.