Posting type	Information
Subject	Change in the XRF analytical protocol for CSN samples
Filter/Species	PTFE (Teflon®), elements
Sites	Entire network
Period	October 2018 and forward
Recommendation	None
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Supporting information

The element content of collected CSN samples is quantified by energy-dispersive X-ray fluorescence (EDXRF) analysis. Typical CSN mass loadings are close to the EDXRF detection limits for several elements, and it is challenging for EDXRF systems to provide good determinations. In November 2015, the contractor performing the EDXRF analysis changed from Research Triangle Institute (RTI) to University of California at Davis (UCD). The EDXRF instruments used by these two laboratories use different techniques for exciting the samples – direct excitation (RTI) with a single source spectrum at full intensity, versus secondary excitation (UCD) from intermediate targets providing a sequence of different spectra at lower intensities – and the two techniques are most advantageous for different elements. After analyzing CSN samples for several months, we determined that the detection limits for several elements, particularly heavier elements, had increased when the laboratory changed. More details on these changes can be found in the National Ambient Air Monitoring Conference presentation, https://projects.erg.com/conferences/ambientair/conf18/White_Warren_Speciation_8-15_1030_SalonF_POST_508.pdf.

To obtain lower detection limits for some elements reported in CSN (e.g. Pb), the analytical protocol for EDXRF analysis was modified and the overall analysis time was increased. The secondary targets and measurement times on each target were optimized to lower the detection limits. Table 1 below shows the protocol utilized before January 2019 and the modified protocol applied for all subsequent analysis starting in January 2019. All CSN samples collected in October 2018 and beyond are analyzed with the new EDXRF protocol.

Table 1. EDXRF secondary targets and measurement times for the two protocols. Only elements in **bold type** are affected by the protocol changes.

Old protocol for samples collected thru September 2018

Target	Analysis Time, s	Reported Elements
CaF_2	600	Na, Mg, Al, Si, P, S, Cl, K
Fe	400	Ca, Ti, V, Cr
Ge	300	**Mn, Fe, Co, Ni, Cu, Zn**
KBr	300	**As**
SrF_2	300	**Se, Br**
Mo	300	**Rb, Sr, Pb**
Al_2O_3	200	**Zr, Sn, Sb, Cs, Ba, Ce**
CsI	200	**Ag, Cd, In**

New protocol for samples collected October 2018 onward

Target	Analysis Time, s	Reported Elements
CaF_2	600	Na, Mg, Al, Si, P, S, Cl, K
Fe	400	Ca, Ti, V, Cr
Ge	400	**Mn, Fe, Co, Ni, Cu, Zn**
SrF_2	500	**As, Se, Br**
Zr	500	**Pb**
Mo	500	**Rb, Sr**
Al_2O_3	500	**Zr Ag, Cd, In, Sn, Sb, Cs, Ba, Ce**

The graphs below summarize the results of the changes to the XRF protocol with approximately one year of CSN samples analyzed prior to the change (October 2017 through September 2018) and one year of filters analyzed since the change (October 2018 through September 2019). The protocol changes only affect the heavier elements from Mn to Pb, so only those elements are plotted below. Figure 1 shows box and whisker plots of the monthly MDL for the old and new protocols; MDL are based on CSN field blank analysis results. Detection limits have improved for most elements. The number of network samples with elemental concentrations above the MDL under the old and new protocols is shown in Figure 2. Increases in the number of detectable samples are seen for Fe, Zn, Mn, Ni, Cu, and Pb. The small increases or decreases in detection rates for the other elements are indistinguishable from normal sample year variations, which result from natural variability in atmospheric concentrations. Overall, the XRF protocol changes have decreased the detection limits for at least Fe, Zn, Mn, Ni, Cu, and Pb.

Figure 1: Comparison of MDLs for old and new XRF protocols.

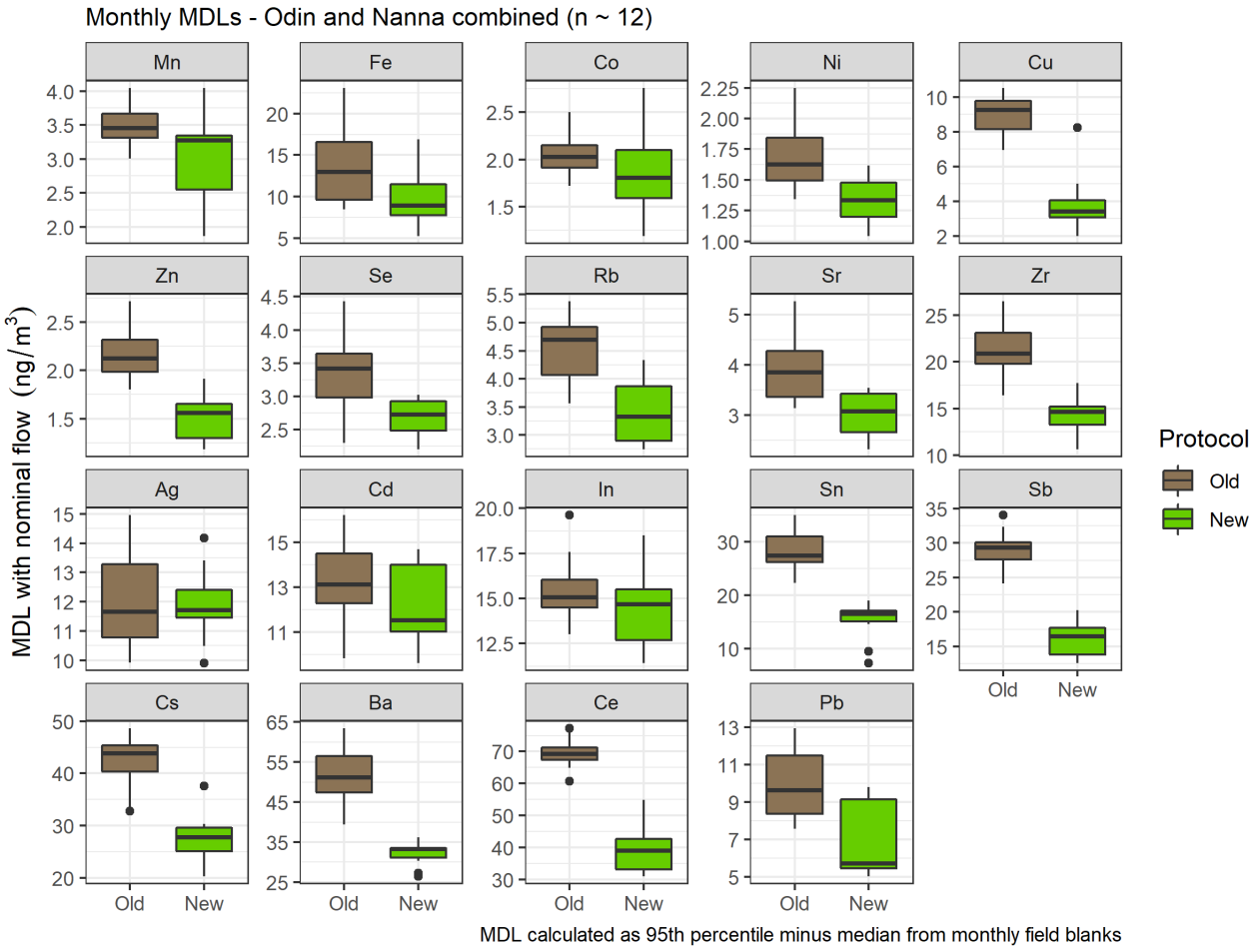

Figure 2: Impact on detection rates of elements within the network. For copper (Cu), approximately 28% of the samples analyzed after the protocol change were above the MDL in contrast to 18% prior to the protocol change.