

Intermittent Contamination of Chromium and Nickel

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Posting Type: Advisory

Module/Filter: MetOne SASS / Polytetrafluoroethylene (PTFE)

AQS Parameter Codes: 88112 (Chromium), 88113 (Cobalt), 88114 (Copper), 88126 (Iron), 88136 (Nickel)

Sites: Entire CSN network

Period: Entire period of Met One SASS operation

Recommendation: Consider sampler contamination as a possible source of Cr and Ni. Apply threshold tests to remove most contaminated samples.

Overview

During analysis of elemental data from collocated CSN samplers, poor agreement between concentrations of chromium (Cr) and nickel (Ni) was observed; contrary to expectations, the agreement degraded as the concentrations increased, suggesting contamination. The contamination is difficult to identify, but becomes apparent in comparisons with the IMPROVE network and when viewed in the context of other elements. The rate of severe, identifiable contamination is about 2%.

Figure 1 compares CSN and IMPROVE paired measurements for select elemental species. Concentrations of Cr and Ni from CSN are sometimes much higher than measured at collocated IMPROVE samplers. Similar high concentrations are not seen for other species.

High concentrations of Cr are often accompanied by high concentrations of both Ni and iron (Fe), as seen in Figure 2. Furthermore, there are consistent Cr/Ni and Fe/Cr ratios for those high values. This is suggestive of a single contaminant material from a common source; the ratios are consistent with stainless steel.

Stainless steel has a variety of compositions. The ratios found in the high concentration Cr data (Cr/Ni ~ 3 and Fe/Cr ~ 3.5) are similar to common stainless steel types such as 301, 302HQ and 304L (Source: Specialty Steel Industry of North America).

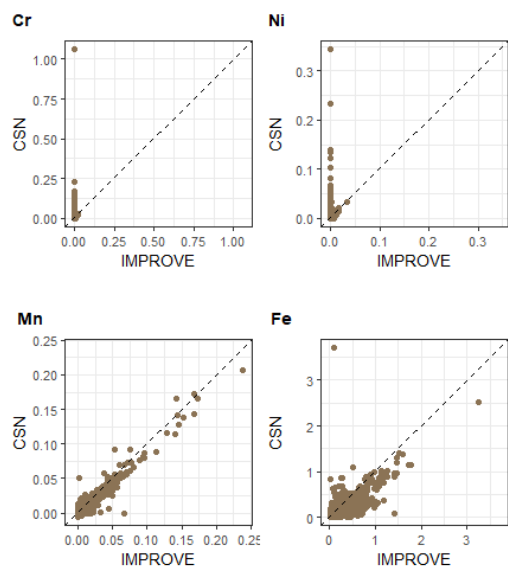


Figure 1: Concentration pairs ($\mu\text{g}/\text{m}^3$) of select elements for all CSN-IMPROVE collocated sites, 2001-2017

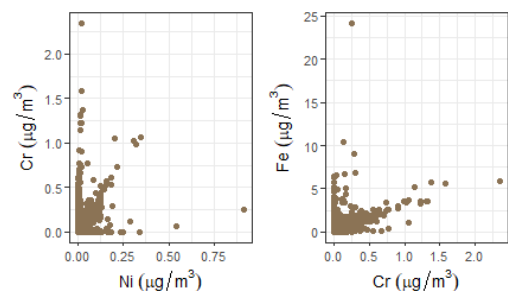


Figure 2: Cr and Ni (left) and Fe and Cr (right) concentrations for all CSN sites, 2002 - 2018

Source

Several exploratory analyses to determine the specific cause have been conducted. The specific source of the contamination has not been identified, but is likely related to the Met One SASS/Super SASS sampler. The majority of CSN sites used the Met One for PTFE and nylon filter sampling since their inception, and the entire network converted to the Met One between 2001 and 2015. Cr concentrations for the Seattle – Beacon Hill site are shown in Figure 3 on a log scale. This site has collocated IMPROVE and CSN samplers and switched from the URG MASS400 to the Met One in 2006. Very high Cr concentrations are only seen in the CSN data after the sampler was changed.

Paired high Cr and Ni concentrations are also seen on the monthly field blanks in Figure 4. The bulk of concentrations are tightly distributed near zero, but a few high outliers are seen on many months. The high points can be seen in both the Cr and Ni data with similar ratios as the ambient exposed samples. However, similar high values are not seen on laboratory blanks.

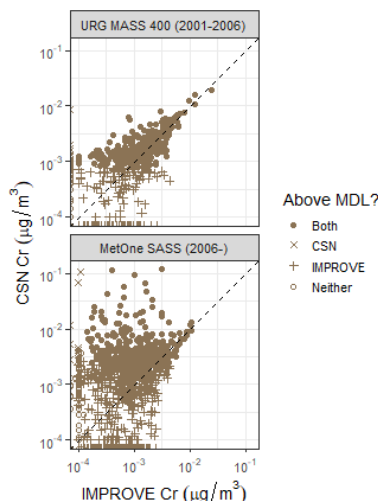


Figure 3: Cr concentration pairs for CSN-IMPROVE collocated site at Seattle - Beacon Hill (AQS Id: 53-033-0080), segregated by sampler

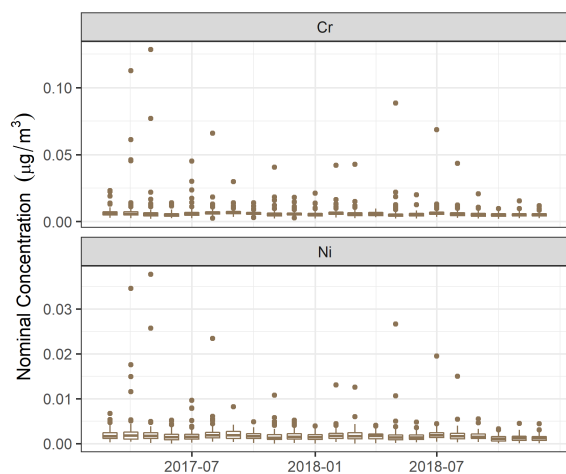


Figure 4: Monthly field blank box plots for Cr and Ni

Looking at the network more broadly, no evidence of contamination is seen in the elemental data from other samplers, including those that were previously used in CSN (Anderson RAAS, R&P Model 2025 and 2300, URG MASS400) and those used in IMPROVE. The Met One SASS and Super SASS are not distinguished from each other in the CSN metadata, but both samplers show similar patterns. Figure 5 shows the Cr and Ni

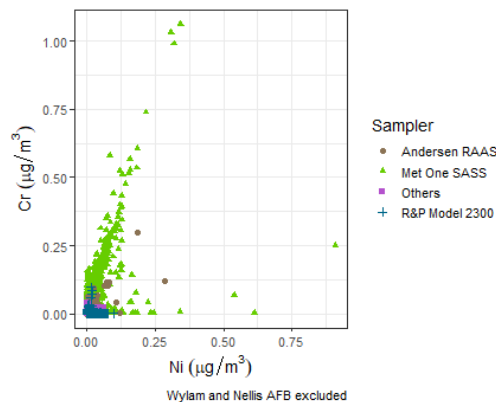


Figure 5: Cr vs Ni concentration for all CSN sites excluding Wylam (01-073-2003) and Nellis AFB (32-003-0020, no longer active), segregated by sampler type

CSN data colored by sampler type. Two CSN sites with frequent high observed Cr concentrations (and no complimentary high Ni concentrations) have been excluded to focus on suspected contamination. See Figure 7 below for details.

Identification of contaminated samples and co-contaminants

Although there appears to be a continuum of contamination, highly contaminated samples can be positively identified by examining the two characteristic ratios: Cr/Ni and Fe/Cr. The following three tests are used to identify likely contamination:

$$\begin{aligned} Cr &> 0.01 \mu\text{g}/\text{m}^3 \\ 1.5 &< Cr/Ni < 6 \\ 1.75 &< Fe/Cr < 7 \end{aligned}$$

This concentration of Cr is at least 3-5 times the minimum detection limit. Figure 6 shows concentrations of Cr compared to four other species. Samples that were true for all three of the above tests are highlighted in green. Though only Cr, Ni, and Fe are used in the tests, cobalt (Co) and copper (Cu) also appear to be involved in the contamination, as evidenced by the consistent positive slope of the samples identified as contaminated.

There are high Cr concentrations measured in the CSN network that are not associated with contamination. They are distinguishable from contaminated samples based on their relatively lower Ni concentrations. Currently, the vast majority of those samples come from the Wylam, Alabama site. The other site excluded from Figure 5 (Nellis Air Force Base) is no longer in operation. Figure 7 highlights the Wylam samples, showing that the tests are able to discriminate between likely contamination and likely uncontaminated samples with high Cr loading.

Frequency and pattern of contamination

The likely contamination is intermittent, relatively infrequent, and present throughout the network and throughout time. Figure 8 shows that the contamination began with the widespread adoption of the Met One SASS

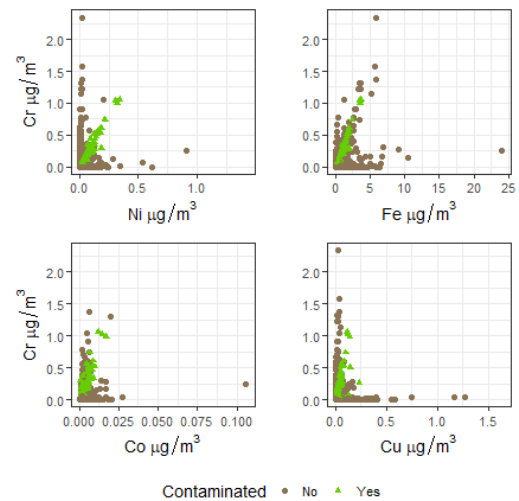


Figure 6: Comparison of Cr with four suspected co-contaminants

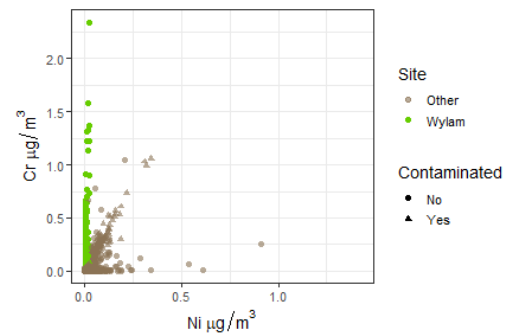


Figure 7: High Cr concentrations at Wylam, Alabama

samplers, starting in 2001-2002. Since 2005, the monthly proportion of samples above detection for Cr and Ni that we identify as likely contaminated has hovered between 1 and 3%, with an unexplained spike from late 2016 through late 2017. The CSN analysis lab, along with the instrument used for measuring elements, changed in November 2015. The issue exists both before and after the lab change, suggesting that the source of the contamination is not a specific lab or instrument. In the most recent years, the contamination rate has been 2-3%.

The spatial pattern of likely contaminated samples over all time is shown in Figure 9, both in proportion of total above detection samples and in raw counts. These samples are not limited to any particular region or type of site. The distribution appears random. Of the 340 sites in the CSN database with at least 100 samples with Cr and Ni valid and above detection, 273 sites (80) have at least one likely contaminated sample. Figure 10 provides the count of CSN sites binned by the fraction of likely contaminated samples.

Flagging future data

Starting with samples collected January 1, 2020 and going forward, UC Davis will apply the contamination tests to all elemental data. Samples identified as likely contaminated will be reviewed by the validator. After review, the Cr, Ni, Fe, Co, and Cu parameters will be assigned the SC null data qualifier (“Sampler contamination”) prior to delivery to DART.

Recommendation

Because of the ubiquitous nature of this contamination, we suggest caution when using CSN Cr or Ni from the Met One SASS. For data prior to January 1, 2020, which have not been prescreened or flagged, we suggest applying the threshold tests above to remove the most contaminated samples. Fe, Co, and Cu are also co-contaminants, but the relative impact on those elements is significantly smaller.

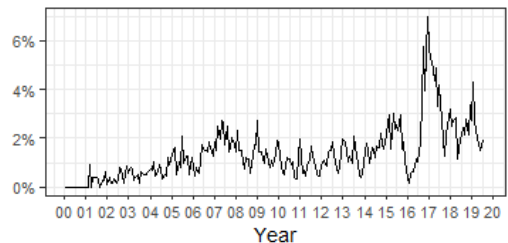


Figure 8: Monthly proportion of above detection samples satisfying likely contamination criteria

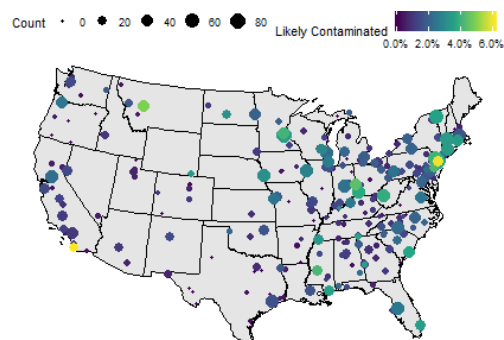


Figure 9: Spatial distribution of likely contaminated samples

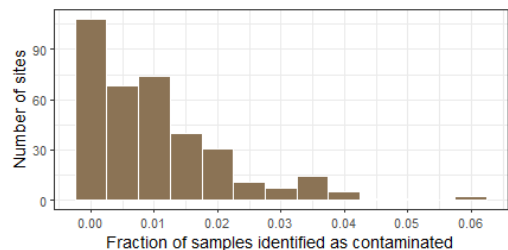


Figure 10: Frequency distribution of site contamination rates