Posting Type	Informational, Historical
Date Submitted	January 10, 2025
Subject	Overestimated Al due to Cl interference
Projects	CSN, IMPROVE
Sites	Strongly affects samples with high Cl concentrations, mostly coastal sites with sea salt aerosols
Sample Period	4/3/2020 – 6/30/2021 for IMPROVE 8/25/2020 – 1/29/2022 for CSN
Parameters	PM$_{2.5}$ Aluminum
Recommendation	Download latest data to obtain corrected data, FED and AQS data was updated in November 2024
Submitters	Jason Giacomo jagiacomo@ucdavis.edu Nicole Hyslop, nmhyslop@ucdavis.edu

Supporting Information

Introduction

During routine validation of the IMPROVE January and February 2021 sample data, some samples with anomalously high aluminum (Al) concentrations were identified. Upon investigation by the XRF lab, we discovered that a correction for the overlap of the Cl K$_\alpha$ escape peak on the Al K$_\alpha$ line was not correctly calculated in the calibration of one of the X-ray fluorescence (XRF) instruments. Further investigation provided evidence that this problem impacted more instruments/calibrations across IMPROVE and CSN data.

Background

When analyzing samples containing multiple elements, some of the elements' fluorescence lines overlap (i.e., have similar energy). There are many types of overlaps, but typically, the ones that need extra attention are due to elements that are not next to each other on the periodic table, so are not expected to have peaks close to each other in energy (which is mostly accounted for by deconvolution algorithms). This is most common in the low energy region where the K$_\alpha$ line of a light element may be similar in energy to an L line of a heavier element. For instance, the S K$_\alpha$ line with an energy of 2.309 KeV overlaps the Mo L$_\alpha$ line of energy 2.292 KeV. These overlaps must be accounted for to quantify one element in the presence of a significant concentration of the other.

There are also overlaps that depend on the detector system employed in a particular XRF instrument. The Panalytical Epsilon 5 EDXRF spectrometers use a germanium (Ge) detector, which can cause what is referred to as an escape peak. An escape peak occurs when an X-ray incident on the detector causes fluorescence of an atom in the detector. This escape X-ray interferes with the measurement of the original X-ray, and the energy measured by the detector is equal to the energy of the original incident X-ray minus the energy of the detector atom fluorescence X-ray. For the Ge detector the most probable escape peak is caused by the release of a Ge L_α X-ray with an energy of 1.188 KeV. Specifically, when a chlorine (Cl) atom releases a Cl K_α X-ray at 2.622 KeV, it can produce an escape peak (Cl K_α - Ge L_α) of 2.622 KeV - 1.188 KeV, or 1.434 KeV, which is nearly the same as the Aluminum (Al) K_α energy of 1.486 KeV; this escape peak erroneously inflates the Al measurement.

Usually, escape peaks have a low probability, and therefore, low intensity relative to the K and L lines of the elements. The exception occurs when the element producing the interfering escape peak has a high concentration compared to the element of interest. There are a few cases where the escape peaks are accounted for in the calibration. In this case, it is known that Cl can have a very high concentration relative to Al in natural aerosol samples (e.g., coastal sites with high sea salt aerosol concentrations), so an overlap correction is added to the calibration to correct Al for escape peaks.

The XRF software calculates an escape peak correction factor using reference materials which include both the interfering elements together and each of the interfering elements separately. When properly added to the calibration curve, the software will calculate a correction factor which will reduce the calculated Al concentration when significant concentrations of Cl are present in the sample (by using the Cl K_α intensity to theoretically calculate the Cl K_α escape peak intensity and applying the correction factor). The calculation with the correction factor, $f_{Al/Clesc}$, is:

$$C_{Alcorr} = E_{Al}(R_{Al+Clesc} - f_{Al/Clesc}R_{Clmeas}) \tag{1}$$

where C_{Alcorr} is the concentration of aluminum corrected for the overlap, E_{Al} is the calibration coefficient for Al, $R_{Al+Clesc}$ is the combined peak intensity of the Al K_α and Cl K_α escape peaks, and R_{Clmeas} is the peak intensity of the Cl K_α line.

It is not feasible to have calibration standards for every range of possible interferences in ambient aerosol samples. For our calibrations, a few standards with only Cl, only Al, and both Al and Cl are utilized. Under normal circumstances, the correction factor is relatively small and positive (~ 0.001). In the case of the calibration with the anomalously high Al results, the correction factor was large and negative (-0.15). As can be seen from Equation 1, a negative correction factor will have a net additive effect on the primary element's calculated concentration, which is incorrect.

Scope and Impact

We plotted the overlap correction factors for several years to investigate whether similar anomalous overlap corrections had occurred in other calibrations. Figure 1 shows the Al-Cl overlap correction factor plotted by XRF application (calibration). From this plot we can see which overlap correction factors are negative and relatively large.
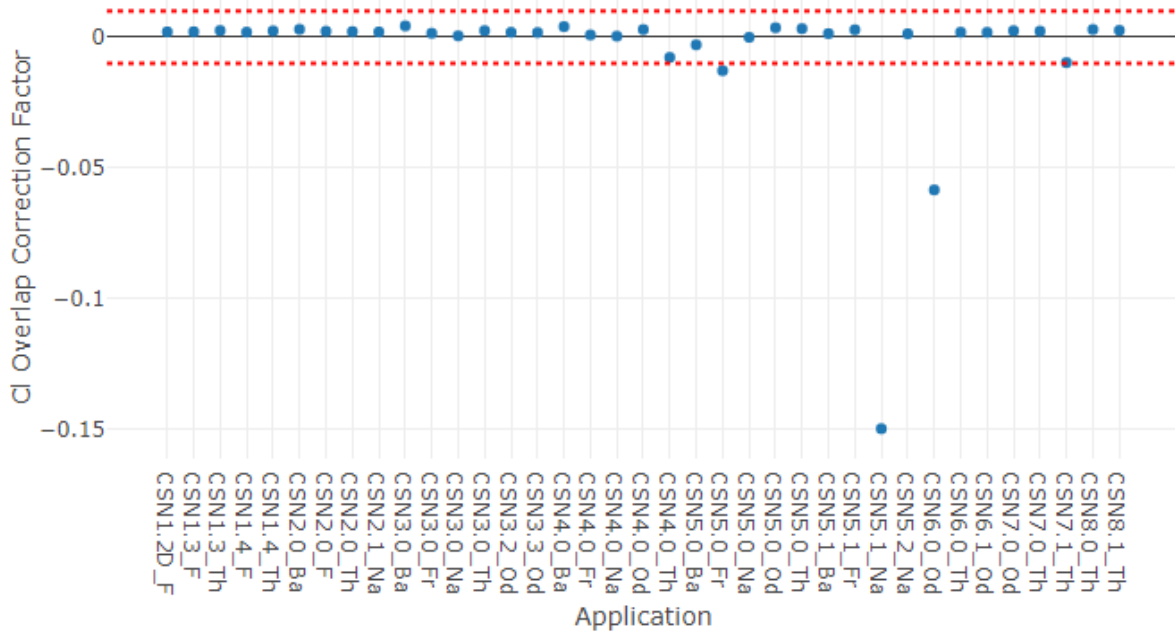

Figure 1. Al-Cl line overlap correction factors for all CSN calibrations between 2019 and 2023 on the five XRF instruments. The red dashed lines indicate ± 0.01. Samples analyzed using the three calibrations with correction factors below the red line (CSN5.0_Fr, CSN5.1_Na, and CSN6.0_Od) were reprocessed and redelivered.

There are no overly large, positive overlap correction factors in Figure 1. The issue is the negative overlap correction factors. In Figure 2, the Al areal densities are plotted against the Cl areal densities to look for correlations with small correction factors. As seen in Figure 2, the negative overlaps create a positive sloping "floor" value for the Al concentrations, indicating that even small negative correction factors will have an impact on Al concentrations. We determined it was not worth the effort to reprocess the data for these small interferences and focused our efforts on the larger correction factors in Figure 3.
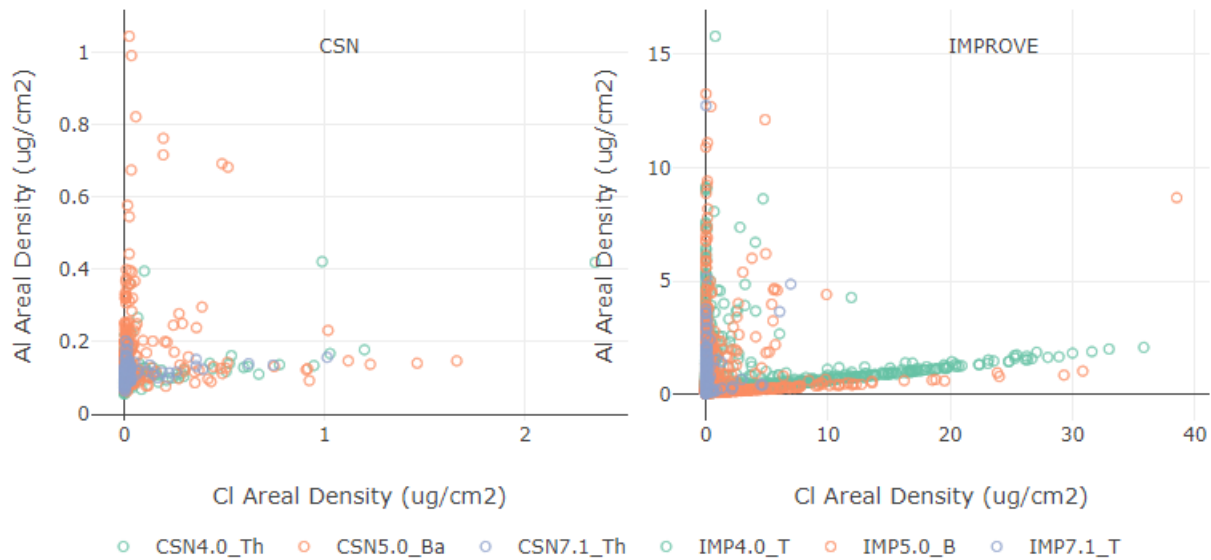
Figure 2. Al and Cl areal densities for applications with small negative overlap correction factors.

Figure 3 plots the Al versus Cl areal densities for applications with larger negative overlap corrections. As expected, Figure 3 shows a stronger upward sloping floor value for aluminum with increasing chlorine concentration. Also note, the stronger dependence for the CSN network samples even at lower chlorine concentrations. Aluminum clearly has a strong dependence on the chlorine concentration caused by the large negative overlap correction factors from these XRF calibrations. Due to the interdependence of aluminum on the chlorine concentration and the lack of *a priori* knowledge of the actual aluminum concentration in the sample it is not possible to predict the amount of error introduced.
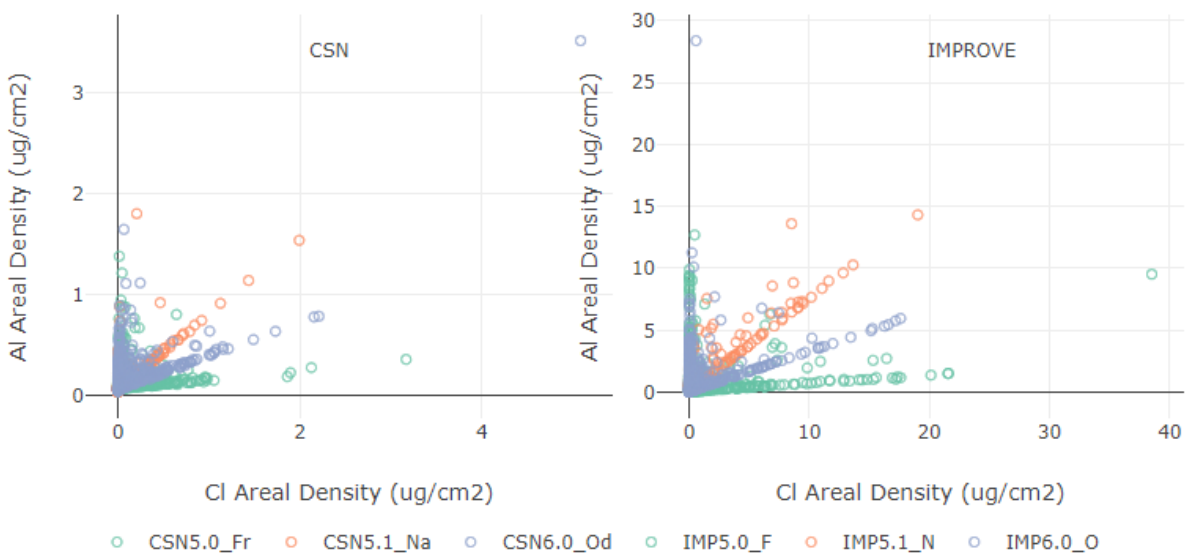

Figure 3. Al and Cl areal densities for applications with large negative overlap correction factors.

Root Cause and Corrective Action

Procedures do not exist to test for appropriateness of overlap correction factors, though some guidelines are provided in lab documents not directly related to our SOPs. Additionally, this problem occurred because we did not realize that when updating a calibration from one year to the next, any standards (or overlap correction standards) that were excluded in the previous calibration will also, automatically, be excluded in the new calibration.

A new procedure will be added to the SOP to ensure this doesn't happen again. First, at the beginning of a new calibration, all interfering standards will be reset to be included in the calibration regressions. Second, limits for appropriate ranges of the overlap correction factors will be set.

Remedy

To remedy this problem, the calibrations with negative correction factors were recalculated after adjusting the standards used to calculate the overlap correction factor. Three calibrations each for CSN and IMPROVE were updated: CSN5.0_Fr, CSN5.1_Na, CSN6.0_Od, IMP5.0_F, IMP5.1_N, and IMP6.0_O. The Al concentrations were recalculated using these new calibrations, and the updated concentrations were delivered to the respective databases (FED and AQS) in November 2024. A total of five XRF instruments are used to analyze the IMPROVE and CSN samples, so not all samples from 2020 and 2021 were affected. This problem only impacts a subset of 2020 and 2021 data downloaded prior to November 2024. A total of 5,147 Al concentrations were updated for IMPROVE and a total of 19,943 Al concentrations were updated for CSN. Figure 4 shows the original and updated Al concentrations by application for IMPROVE and CSN in log scale. Figure 5 plots the original and updated Al concentrations for IMPROVE and CSN in linear scale, respectively. Most concentrations did not change significantly as shown in Figure 5: 13% of the changes in the measurements were greater than their reported uncertainties for both CSN and IMPROVE. Blue points lying on the 1:1 line indicate reprocessed data that were essentially identical to the original data, while red points indicate reprocessed concentrations that were lower than the originally reported concentrations by more than the value of the uncertainty associated with the concentration.
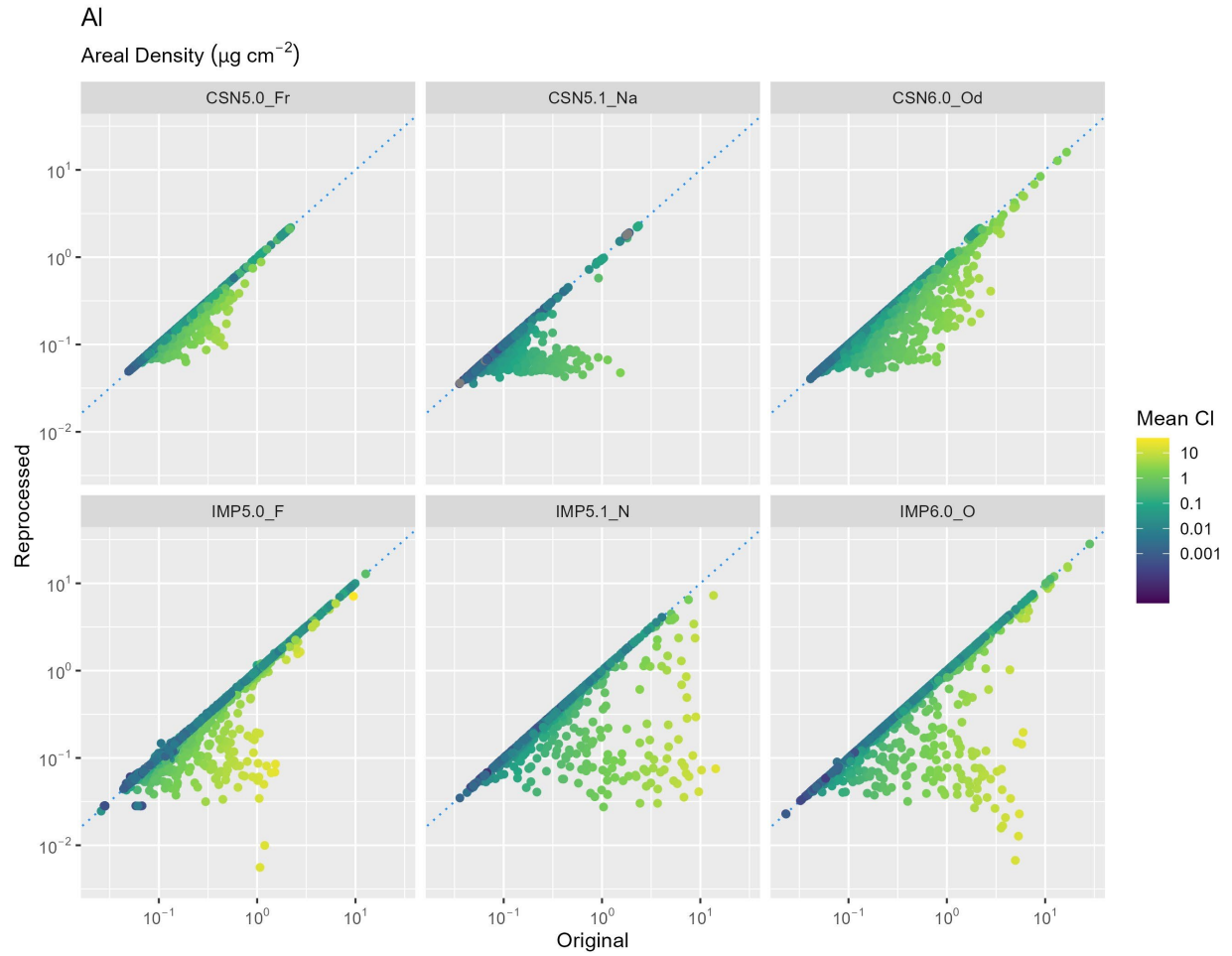
Figure 4. Updated versus originally reported Al concentrations for the six updated calibrations in log scale. CSN data are shown in the top row of plots, and IMPROVE data are shown in the bottom row of plots. The points are shaded according to the Cl concentration on the samples; higher Cl concentrations resulted in larger changes.
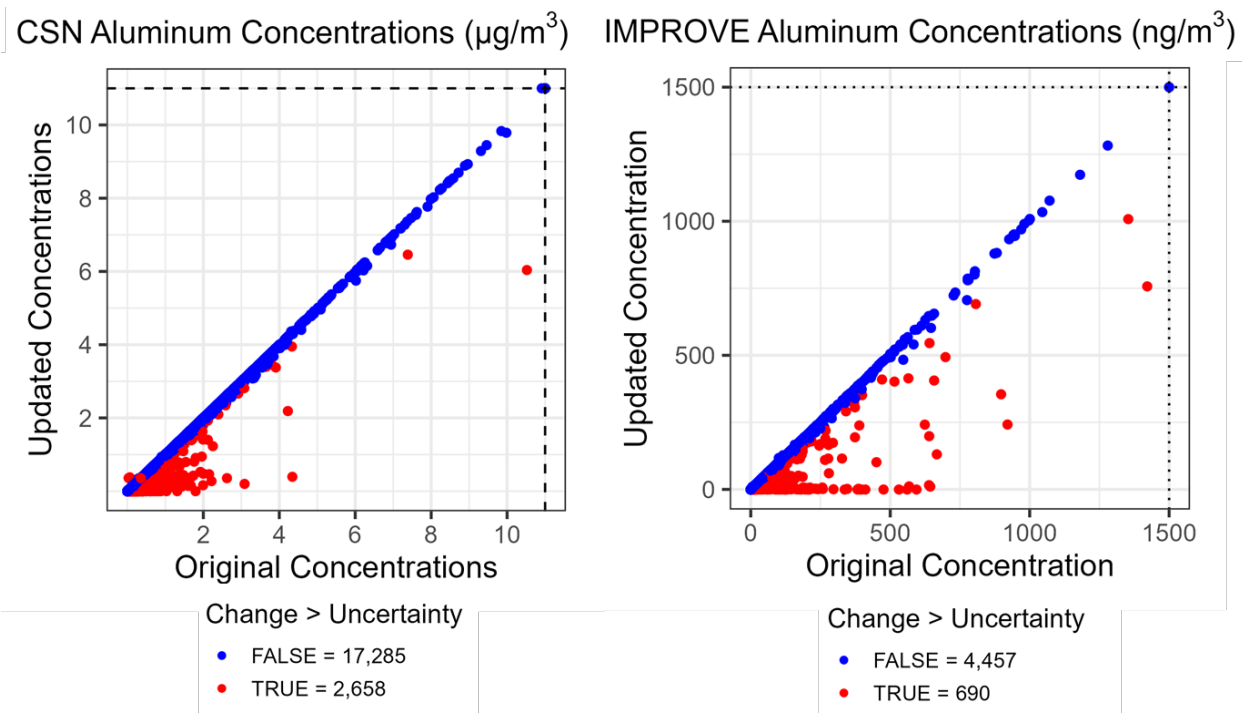
Figure 5. Updated versus originally reported Al concentrations for CSN and IMPROVE in linear scale.

Summary and Conclusions

We discovered an error in the XRF processing and fixed it. Corrected Al data were updated in the public AQS and FED databases in November 2024. Al is used in the estimated soil and reconstructed mass concentrations so these parameters were also corrected. Some Al concentrations from the affected periods downloaded from AQS and FED prior to 2024 will be biased high. The bias will be highest at sites with high Cl concentrations, typically coastal sites with sea salt and some northern sites with wintertime road salt.