**Posting type** Advisory

**Subject** Shifts in Mo-anode XRF element calibration factors

**Module/Species** A/ Ni, As, Se, Br, Rb, Pb

**Sites** Entire network

**Period** Shift occurs between September and October 2005

**Recommendation** Consider calibration changes when interpreting trends

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## **Supporting information**

A molybdenum-anode XRF instrument is used to analyze the heavier elements (Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, and Pb). During the analysis of September 2005 samples, new calibration foils with lighter deposits were acquired and used in the Mo-anode XRF system. The new calibration foils resulted in changes to the calibration factors for the elements Ni, As, Se, Br, Rb, and Pb that could be observed in their effects on reported ambient concentrations.

The new foils represent an attempt to utilize reference foils that more closely match ambient samples in loading. These foils were used in preparing a calibration table that provides the reference points for converting the x-rays collected during analysis to elemental concentrations on filter samples collected in the atmosphere. The uncertainties quoted by the manufacturer for these new foils were +/-10% compared to +/-5% for the older, more heavily loaded foils. After a number of ambient samples had been analyzed it became apparent that these new foils resulted in ambient concentrations that were inconsistent with those observed in prior years.

Table 1 shows the percent change in the calibration factors with the old standards compared to the new standards. The percentages represent the differences between the last calibration performed with the old foils and the first calibration performed with the new foils. The calibration factors are multiplicative factors in the estimation of the reported concentration, that can introduce systematic biases between the previous and current data. The resulting shifts in concentration must be accounted for in any analysis of trends.

Table 1. Percent change in the calibration factors.

| Element | Energy<br>Line | Calibration<br>Change |
|---------|----------------|-----------------------|
|         | Line           | Change                |
| Ni      | $K_{\alpha}$   | 28%                   |
| Cu      | $K_{\alpha}$   | 4%                    |
| Zn      | $K_{\alpha}$   | -4%                   |
| As      | $K_{\alpha}$   | -76%                  |
| Se      | $K_{\alpha}$   | -27%                  |
| Br      | $K_{\alpha}$   | -19%                  |
| Rb      | $K_{\alpha}$   | -28%                  |
| Sr      | $K_{\alpha}$   | 0%                    |
| Zr      | $K_{\alpha}$   | 0%                    |
| Pb      | $L_{\alpha}$   | 4%                    |