

## Investigating sources of particulate emissions from copper smelting using single particle ICP-Time-of-Flight MS

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Nonferrous metal smelting emits airborne particulate matter (PM) containing toxic metals including arsenic, lead, and cadmium. Knowledge of the chemical composition of smelter-associated PM is needed to assess its impact on communities surrounding smelters, and to develop effective pollution mitigation strategies. To help close this knowledge gap, we collected air samples in the vicinity of a copper smelter in Quebec and used single particle ICP-Time-of-Flight-MS (spICP-ToF-MS) to measure the composition and concentration of metal-containing particles. From time-resolved sampling, we determined that metal-containing emission events of PM generally occurred on <1 hour time scales. During some emission events, up to 25% of the total arsenic was held in sub-micron particles, which has significant implications for bioavailability. The most common particle types detected in air were aluminosilicate minerals, and Cu-Fe particles with approximately a 1:1 ratio, likely representing chalcopyrite or other copper ore minerals. To determine whether these particles were mobilized from transport or handling of copper concentrate, we analyzed road dust and air along a truck route where the road was both dry and wetted to mitigate dust. Road dust was comprised mainly of copper ore minerals, these particle types increased 10x in air when the road was dry. However, trace element concentrations including As, Pb, and Cd were higher when the road was wet (although this location was closer to the smelter). This suggests that although copper ore particles may indeed contribute to the total emission, they may not be dominant carriers of As, Pb, and Cd. Moreover, trace elements including As-In-Sn-Sb-Bi were found to co-occur in higher frequencies in the air, compared to road dust. In road dust samples, 95% of As-bearing particles contained copper, whereas in the air samples, 53% occurred with Cu, suggesting a source other than suspended copper concentrate. The co-occurrence of As-In-Sn-Sb-Bi in individual particles is unlikely to be of mineralogical origin, as these elements are typically not present in the same minerals. We hypothesize that these particles are formed via condensation of volatilized species during the smelting process. Ultimately more work is needed to relate specific smelting processes to the multi-element chemistry of emitted particles.