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Application of AF4-ICP-MS to identify natural versus industrial sources of trace elements to the Athabasca River in Alberta, Canada

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The Athabasca River (AR) is the second largest river in Alberta and the largest undammed river. Industrial activities such as mining and upgrading of bitumen from bituminous sands have been criticized as a potential source of trace elements (TE) to the AR, but evidence is limited. Seasonal changes in flow rates and concentrations of suspended solids, on the other hand, have been associated with extreme variation in the concentrations of TE, especially between spring and fall. To quantify spatiotemporal variation in the concentrations of TE in the AR, we gathered water samples across transects upstream, alongside and downstream from the industrial region, in fall and spring, using novel, metal-free sampling methods.

We measured the concentrations of total and dissolved (i.e. < 0.45 μm) TE of environmental concern (Ag, Cd, Pb and Tl), TE that are enriched in bitumen (V, Ni, Mo), and those that are found mainly in colloidal forms (Al, Co, Cu, Fe, Mn, U, Th, La and Ce), in the ultraclean metal-free SWAMP laboratory at the University of Alberta, using inductively coupled plasma mass spectrometry (ICP-MS). In order to distinguish industrial from natural sources of TEs, element concentrations were normalized to Th, and the ratios compared to the corresponding values for the Earth's Upper Continental Crust. Moreover, to help assess the sources of TE's, we also measured the distribution amongst mainly ionic species and small molecules < ca. 300 Da, organic colloids, and larger inorganic colloids (e.g. Fe oxyhydroxides) using asymmetrical flow field-flow fractionation (AF4) coupled online to a UV-Visible spectrophotometer (UV) and ICP-MS.

The results showed that the total concentrations of some of the investigated TEs were more abundant of upstream of industry, compared to downstream in spring. This finding suggests that the natural contribution of soil and sediment particles from erosion might be the primary sources of TE to the AR in spring. In fall, the total concentrations were not significantly more abundant downstream of industry. Likewise in fall, the dissolved concentrations were not significantly different upstream from downstream. Clearly, to identify anthropogenic inputs to the river, natural inputs and their seasonal variation must be known. Further studies of seasonal and spatial variation in TE concentrations, and their distribution amongst these major colloidal species in the Athabasca River, are underway.