



Natural and anthropogenic inputs of trace elements to the surface- and ground-waters in the Athabasca Bituminous Sands region, Alberta, Canada

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It has been suggested that open pit bitumen mining and upgrading activities in the Athabasca Bituminous Sands (ABS) deposit in northern Alberta, Canada, contribute significant amounts of priority pollutants (i.e. Ag, Be, Cd, Cu, Ni, Sb, Tl and Zn) to the Athabasca River (AR), one of the largest rivers in Canada. To distinguish natural and anthropogenic inputs of trace elements (TEs) to the AR, metal-free analytical protocols developed for polar snow and ice were used to collect surface- and ground-water samples in the vicinity of industrial activities and downstream, in two consecutive years (October 2014 and 2015).

The surface water results show that the concentrations of potentially toxic TEs (Ag, Bi, Cd, Co, Cu, Ni, Sb, Tl and Zn) in the dissolved ($< 0.45 \mu\text{m}$) and total fractions of samples showed no discernable trend from upstream to downstream of industrial activities. For the TEs that are enriched in bitumen (V, Ni, Mo and Re), only the concentration of Re was significantly greater downstream compared to upstream, but this increase was apparent in both dissolved and total fractions. The majority of TEs (63 to 96 %) were present in the particulate fraction (i.e. total – dissolved), and the TE content of the suspended solids ($> 0.45 \mu\text{m}$) in surface waters were similar downstream and upstream of industry. The concentrations of TE in these particles were proportional to those of conservative, lithophile elements (Al, La, and Th), but well below their corresponding abundance in crustal rocks. The groundwater results show that the average dissolved concentrations of elements known to be enriched in bitumen were significantly ($P < 0.05$) greater in the groundwaters near industrial activities and tailing ponds compared to the groundwaters far downstream from industry. The dissolved concentrations of potentially toxic TEs (i.e. As, Cd, Cu, Pb, Se and Zn) in groundwaters were not significantly different near and far from industry. Moreover, the dissolved concentrations of some potentially toxic TEs (e.g. Pb) appeared to follow conservative lithophile elements (such as Al), particularly at sites near industry, reflecting the importance of colloids.

Taken together, these findings suggest that: 1) Contributions of particulate matter from natural processes such as physical weathering and erosion are the primary sources of TEs in the AR, both upstream as well as downstream of industry; 2) The inputs of TEs from groundwaters to the AR are insignificant compared to inputs from surface waters upstream, and; 3) The TEs which are enriched in bitumen (particularly Re) appear to be the most obvious indicators of possible industrial contributions to the AR.