Trace elemental composition of urban particulate matter (PM) is of interest from the standpoint of environmental and potential human health impacts. Due to their uniqueness to anthropogenic sources of PM, trace elements have been exploited as markers of pollution from different industrial processes in order to identify episodic releases of particles from local sources, to track the atmospheric transport of the released particles, and to study the health effects of exposure to metals. Monitoring of elemental composition of PM has become a crucial part of air quality programs in many countries around the world.

In Canada, the National Air Pollution Surveillance (NAPS) program, a joint program of the federal and provincial governments and territories, has been in operation for over 40 years. Since 1984, both fine (PM$_{2.5}$) and coarse (PM$_{10-2.5}$) particle mass measurements have been made using dichotomous samplers (often referred to as “dichots”). The Teflon filters from the dichotomous (both coarse and fine) and US EPA federal reference method (FRM) samplers are routinely analyzed for elements using energy dispersive X-ray fluorescence (EDXRF), and for anions and cations using ion chromatography (IC). As a part of the NAPS PM$_{2.5}$ Speciation program, initiated in 2003, trace metal concentrations are also determined using inductively-coupled plasma mass spectrometry (ICP-MS) combined with microwave-assisted acid digestion.

This work presents the EDXRF results for elemental composition of PM$_{2.5}$ and PM$_{10-2.5}$ collected at selected rural and urban NAPS sites over a 5-year period. The performance of various EDXRF instruments used during this time period is evaluated in respect to method detection limit, uncertainty and long term reproducibility. In addition, data obtained by independent methods will be discussed. In general, a good agreement between EDXRF and other techniques (ICP-MS, IC) was obtained.