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Concentration and source origin of lanthanoids in the Canadian atmospheric particulate matter: a case study

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ABSTRACT

Ambient $PM_{2.5}$ and $PM_{2.5–10}$ samples collected at selected urban and rural sites within the Canadian National Air Pollution Surveillance (NAPS) $PM_{2.5}$ Speciation Program were analyzed for lanthanoids and other elements. The average concentrations of total lanthanoids (calculated as sum of concentrations of all elements) in $PM_{2.5}$ ranged from 0.059 to 0.334 ng m^{-3}. These concentrations were two times lower than in $PM_{2.5–10}$ samples and generally lower than values reported for industrial and urban areas around the world. The highest concentrations of lanthanoids were found in $PM_{2.5}$ samples collected at the Halifax NS site, located near a petroleum refining complex. In addition, La/Ce and La/Sm ratios at this site were significantly higher than their natural values. Increased La–enrichment factors were also found in Wallaceburg ON, which is located in a rural area, about 50 km downwind of two major petrochemical complexes. The results of this study demonstrate that La–enrichment factors are reliable tracers of emissions from oil refining industry.

Keywords:
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1. Introduction

Lanthanoid elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) have been traditionally used as tracers for a variety of geochemical processes in hydrosphere and lithosphere due to their very distinctive geochemical properties (Munksgaard et al., 2003; Borrego et al., 2005; Kamber, 2009). As a result of the lanthanoids contraction phenomenon, lighter lanthanoid elements are more abundant in the Earth's crust whereas heavier ones are more concentrated in the Earth's mantle. Also, concentrations of lanthanoids in the upper continental crust (UCC) follow the Oddo–Harkins rule whereby the odd–numbered elements are less abundant than their even–numbered neighbors (Oddo, 1914; Harkins, 1917). The chemical properties of these elements are so similar that their natural distribution pattern will not change by natural and anthropogenic processes unless material with already altered composition is released into the natural environment.

Today, the oil–refining industry extensively uses fluid catalytic cracking units (FCC) for the process of converting petroleum crude oils into gasoline or other commercial products. The FCC catalysts are zeolites that usually contain excessive amounts of La. Although the catalyst is re–cycled and re–used during the refining process, there is a small amount that is unintentionally released into the atmosphere which will change the natural concentration pattern of lanthanoids in air particulate matter (PM). In 1985, Olmez and Gordon suggested for the first time that the concentrations of lanthanoids in fine particulate matter ($PM_{2.5}$, particles smaller than 2.5 μm in aerodynamic diameter) can be used as unique tracers for emissions from oil refining industry (Olmez and Gordon, 1985). Since the concentration patterns are not affected by chemical and physical transformations that take place after emission and during transportation of particles in the atmosphere, these elements are ideal tracers for both long–range and point source emissions on an urban and a regional scale. Following this paper, several studies confirmed that the natural distribution patterns of lanthanoids in $PM_{2.5}$ were greatly distorted due to zeolite catalysts used in oil refining industry and released to the atmosphere either accidentally or during routine operations of petrochemical facilities (Kitto et al., 1992; Wang et al., 2001; Kulkarni et al., 2006; Kulkarni et al., 2007; Moreno et al., 2008a; Moreno et al., 2008b; Moreno et al., 2010).

Major sources for anthropogenic emissions of $PM_{2.5}$ in the atmosphere include the products of fossil fuels combustion used for industrial and domestic heating, power generation, transportation and other purposes, as well as emissions from oil refining industry. During 2009, the $PM_{2.5}$ released from fuel used for electricity, heating, transportation (road, rail, air, marine), and oil and gas industry accounted for 18% of total $PM_{2.5}$ emissions in Canada (Environment Canada, 2009b). Since fossil fuels are normally rich in Ni and V, PM emissions related to oil–based domestic and industrial applications have been traditionally traced by high levels and significant correlations of concentrations of Ni and V in $PM_{2.5}$ (Celo and Dabek–Zlotorzynska, 2010 and references therein). The inclusion of lanthanoids in source apportionment studies adds one parameter that can be used to distinguish oil combustion from oil refining sources.

In this study we report the concentrations and distribution patterns of lanthanoids in fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$, particles with aerodynamic diameter between 2.5 µm and 10 µm) atmospheric PM samples collected at selected sites across Canada as a part of the National Air Pollution Surveillance (NAPS) $PM_{2.5}$ Speciation Program. The objective of this research is to track the PM emission sources related to oil refineries by monitoring concentrations of lanthanoids at several sites located in urban areas that are affected by various anthropogenic sources of PM.

2. Experimental

2.1. Site location and description

The NAPS network sampling sites included in this study were selected to represent both urban and rural settings, and were located from East to West Coast of Canada as shown in Figure 1 and described in Table 1.

The Toronto, Montreal and Halifax sites are located in downtown areas of highly populated metropolitan cities that are heavily influenced by local transportation emissions. In addition to other industrial facilities and power plants located nearby, two oil refining complexes are situated about 15 km northeast of the Montreal site and a major facility operates less than 2 km southeast of the Halifax site. The Abbotsford sampling site is located less than 0.5 km north of one of the runways of the Abbotsford International Airport. The Windsor and Burnaby sites are both located in residential areas close to major traffic arteries. Windsor is one of the major industrial cities in Canada where air quality is heavily affected by industries (mainly automotive and metal processing) located on both sides of the border (Gilbertson and Brophy, 2001). This sampling site is located less than 2 km northwest of two power generation plants, less than 6 km west of several automotive manufacturing facilities and within 1 km from the Ambassador Bridge which is the busiest international border crossing between Canada and the US. Burnaby is a coastal city and major seaport, located close to the Port of Vancouver which is the largest and busiest port in Canada. The sampling site is located about 8 km south of a refinery and within 15 km from the Port of Vancouver. The Canterbury and Wallaceburg sites are both located in rural–undeveloped areas. While there is no industrial facility located close to the Canterbury site, the Wallaceburg site is situated about 50 km south of the industrial town of Sarnia where several industrial facilities of metal producing and processing, a power generation plant and two major petrochemical refining complexes operate.

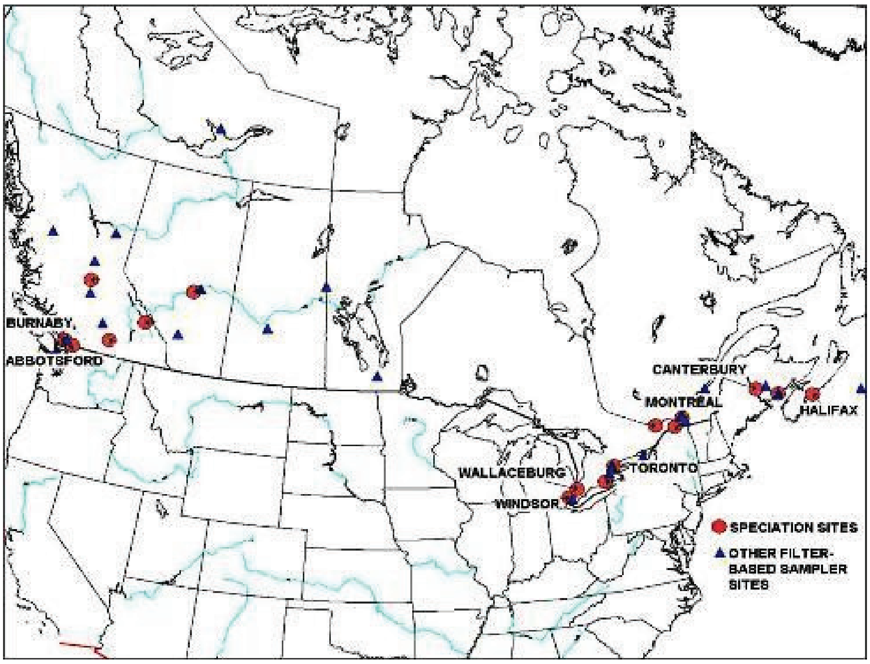

Figure 1. *Locations of the Canadian NAPS monitoring sites selected for this study.*

Table 1. *Brief description of the NAPS sampling sites (Dabek–Zlotorzynska et al., 2011)*

City (NAPS ID)	Province	Site Description	Major Source Influences	Sampling period
Halifax (30113)	Nova Scotia (NS)	Urban–core	Oil refining, oil–fired power plant, marine vessels, traffic	2006–2008
Canterbury (40801)	New Brunswick (NB)	Rural–undeveloped		2005–2007
Montreal (50104)	Quebec (QC)	Urban–core	Traffic, heating, oil refining	2005–2007
Windsor (60211)	Ontario (ON)	Urban–residential	Steel manufacturing, auto manufacturing, traffic	2005–2008
Toronto (60427)	Ontario (ON)	Urban–core	Traffic, heating	2005–2008
Wallaceburg (61902)	Ontario (ON)	Rural–undeveloped		2006–2008
Abbotsford (101004)	British Columbia (BC)	Suburban–residential	Traffic, heating, airport	2005–2008
Burnaby (100119)	British Columbia (BC)	Urban–commercial	Traffic, heating, oil refining, marine vessels	2006–2008