



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.

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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 $2.5 \mu m$ and $10 \mu m$) 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 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.

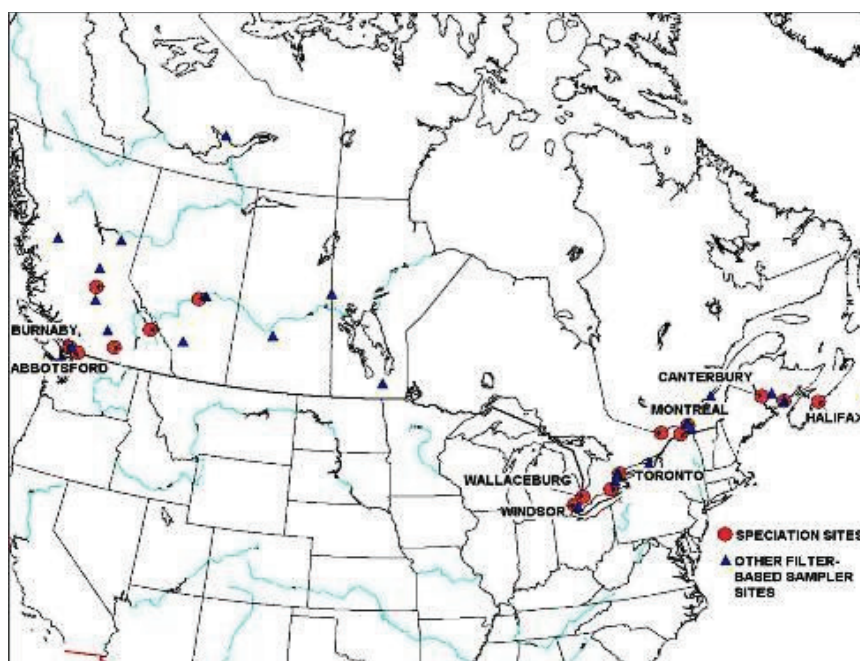


Figure 1. Locations of the Canadian NAPS monitoring sites selected for this study.

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

2.2. Sampling and chemical analysis

Samples were collected as a part of the NAPS PM_{2.5} Speciation program, following procedures described elsewhere (Dabek-Zlotorzynska et al., 2011; Jeong et al., 2011). Aerosol PM_{2.5} samples selected for this study were collected using the Partisol Model 2300 sequential speciation samplers and PM_{2.5-10} samples were collected simultaneously using R&P Partisol-Plus Model 2025-D sequential dichotomous samplers. Samples were collected over 24 hours on 47-mm PTFE filters (PALL Corporation, NY, USA). All filters were weighed before and after sample collection using a Mettler Microbalance (MT-5, Mettler-Toledo Inc., Highstown, NJ), under controlled relative humidity (40 ± 5%) and temperature (23 ± 3 °C). The data reported in this case study are from analysis of about thirty PM_{2.5} and ten PM_{2.5-10} samples collected at each site during the 2005–2008 sampling period. There is no data reported for PM_{2.5-10} samples from the Canterbury and Halifax sites because they were either not collected or not available for analysis.

Both fine and coarse PM samples were treated and analyzed by ICP-MS following a previously reported method (Celo et al., 2011). Briefly, samples were digested for 20 min at 200 °C with a HNO₃/H₂O₂/HF/HCl mixture using a MARS Xpress microwave oven (CEM Corporation, Matthews, NC). After digestion, samples were evaporated to almost dryness in presence of concentrated HCl and diluted to 15 mL with 4% (v/v) HNO₃ prior to ICP-MS analysis. Reagent blanks, filter blanks and other QA/QC samples were prepared in the same manner. Standard reference materials 1648a (Urban Particulate Matter) and BRC estuarine sediment reference material 667 (Institute for Reference Materials and Measurements, Geel, Belgium) were used for validation of analytical results. Recoveries ranged from 85 to 115% for La to Ho, from 75 to 85% for the heavier lanthanoids, and from 80 to 120% for other elements. All measurements were performed using an Agilent Technologies 7500ce ICP-MS system (Agilent Technologies, Wilmington, DE, USA), equipped with a high matrix introduction (HMI) system, MicroMist nebulizer, an octopole collision/reaction system (ORS), a Peltier cooled (2 °C) quartz Scott-type double pass spray chamber and an Agilent I-AS integrated autosampler. The HMI system was used to minimize the oxide and hydroxide interferences associated with the analysis of lanthanoids (Celo et al., 2011). The ORS was pressurized with He gas for analysis of V, As and Cr, and with H₂ for analysis of Fe and Se. Internal standardization with 1 mg L⁻¹ solution of ¹⁰³Rh and ¹¹⁵In was used

to correct for the instrumental drifts and non-spectral interferences.

2.3. Limits of detection and statistical data analysis

Limits of detection (LOD) were determined as 3 times standard deviation of 30 filter blanks, which were digested and treated through all the steps of analysis as samples. The LOD for analysis of PM samples ranged from 1–30 pg m⁻³. Typically, the heavier lanthanoids had the lowest LOD. In general, concentrations of La, Ce and Pr were above their respective LOD in 70–100% of PM_{2.5} samples, Nd, Dy, Er, Gd and Yd were above LOD in 10–70% and the other elements were detected at less than 25% of analyzed samples from each site. The percentage of PM_{2.5-10} samples with concentrations of lanthanoids above LOD was 70–100% for La, Ce, Pr and Nd, 50–80% for Sm, Gd, Dy, Er and Yb and less than 25% for the other elements.

STATISTICA ver. 8 software (StatSoft Inc., Tulsa, OK, USA) was used for statistical analyses. Summary statistics were calculated by substitution of concentrations below LOD with half of LOD. Unless otherwise stated, median with interquartile range (IQR) were reported.

3. Results and Discussion

3.1. PM_{2.5} and PM_{2.5-10} concentrations

The median PM_{2.5} mass concentration for samples included in this study was 11.8 µg m⁻³ (IQR 7.7 to 17.1 µg m⁻³) (see the Supporting Material, SM, Tables S1A and S1B), with the highest values recorded at the Toronto, Windsor and Montreal sites. This result agrees with previous reports of PM_{2.5} concentration in Canadian cities, and is consistent with the fact that these sites are affected by a number of anthropogenic emission sources, mainly manufacturing industries and transportation (Dabek-Zlotorzynska et al., 2011; Jeong et al., 2011). The rural site of Canterbury had the lowest concentration of PM_{2.5} whereas relatively high levels were recorded at the Wallaceburg rural site. Spatial distribution of PM_{2.5-10} concentrations showed a similar pattern, with the lowest values recorded at the rural sites (median 3.4 µg m⁻³ at the Wallaceburg site) and the highest at the urban sites (see the SM, Table S2). Median PM_{2.5-10} concentration was 5.1 µg m⁻³ (IQR 3.4 to 7.6 µg m⁻³).

Table 2. Median^a concentrations of lanthanoids (pg m⁻³) in PM_{2.5} samples (N = 30 for each site)

	LOD	Burnaby	Abbotsford	Windsor	Toronto	Wallaceburg	Montreal	Canterbury	Halifax
La	20	86 (56–163)	24 (10–58)	53 (38–85)	49 (35–62)	50 (25–104)	44 (25–94)	15 (10–32)	227 (96–270)
Ce	30	115 (91–194)	47 (27–61)	70 (49–110)	71 (57–91)	36 (18–68)	64 (38–101)	18	44 (18–67)
Pr	2.2	6.3 (3.8–10)	2.7 (1.1–3.4)	4.3 (2.9–6.3)	4.6 (2.8–6.5)	3.8 (3.0–8.5)	4.2 (3.0–7.0)	1.1 (1.1–3.5)	2.8 (1.1–5.2)
Nd	15	19 (8–27)	8	8 (8–23)	8 (8–20)	8 (8–26)	13 (8–26)	8	8 (8–17)
Sm	8.9	4.5	4.4	4.5 (4.5–7.5)	4.4 (4.4–7.1)	4.4 (4.4–6.0)	4.4	4.4	4.7 (4.4–4.8)
Eu	2.9	1.5	1.4	1.4	1.4	1.4 (1.4–2.5)	1.4	1.4	1.4
Gd	5.0	2.5	2.5	3.0 (2.5–6.1)	2.5	3.0 (2.5–5.3)	2.5	2.5	3.0 (2.5–5.1)
Tb	1.9	0.9	0.9	0.9	0.9	0.9 (0.9–3.1)	0.9	0.9	0.9
Dy	2.8	1.4	1.4 (1.4–3.5)	3.4 (1.4–4.3)	3.3 (1.4–3.4)	1.4 (1.4–3.4)	2.3 (1.4–3.4)	1.4 (1.4–3.3)	2.2
Ho	4.7	2.3	2.3	2.3	2.3	2.3 (2.3–21)	2.3	2.3	2.3
Er	2.1	1.1	1.1	1.1 (1.1–2.5)	1.1 (1.1–2.5)	1.1 (1.1–2.0)	1.2 (1.1–2.3)	1.1 (1.1–2.4)	1.1 (1.1–1.5)
Tm	1.4	0.7	0.7	0.7	0.7	0.7 (0.7–2.9)	0.7	0.7	0.7
Yb	3.1	1.6	1.6	1.6	1.6	1.6 (1.6–5.3)	1.6	1.6	1.6
Lu	1.2	0.6	0.6	0.6	0.6	0.6 (0.6–1.5)	0.6	0.6	0.6
Sum		244	99	155	152	116	144	59	300

^a Values in brackets are IQR, which are reported only when the number of samples with concentrations above LOD was more than 30%

Table 3. Median ^a concentrations of lanthanoids (pg m⁻³) in PM_{2.5-10} samples (N = 10 for each site)

	Burnaby	Abbotsford	Wallaceburg	Toronto	Windsor	Montreal
La	193 (97–257)	57 (55–58)	57 (71–105)	60 (14–52)	93 (81–146)	107 (96–140)
Ce	350 (114–639)	86 (83–87)	86 (39–104)	188 (54–240)	146 (92–200)	192 (141–228)
Pr	11 (7–17)	5.6 (5.6–5.7)	7 (2–9)	14 (1–20)	9 (6–13)	18 (11–23)
Nd	39 (18–53)	21 (20–23)	24 (18–21)	45 (5–81)	44 (26–65)	62 (50–72)
Sm	6 (6–19)	5 (4–8)	6 (4–6)	6	6 (6–18)	11 (6–12)
Eu	3.5 (1.3–6.1)	1.5 (1.4–1.8)	1.5	1.3 (1.3–5.7)	1.3	3.2 (2.5–4.2)
Gd	9.5 (2.6–13.2)	5.5 (4.8–5.2)	3.2 (2.1–3.6)	6.8 (2.6–15)	5.0 (2.6–11)	12.3 (9.6–16)
Tb	1.5	0.6	1.6	1.7	1.6	1.7 (1.0–2.4)
Dy	7.3 (4–9.8)	3.8 (3.7–3.9)	1.7 (1.7–3.8)	6.7 (1.7–14)	5.9 (2.9–7.2)	7.5 (5.9–10)
Ho	2.5	0.7	2.5	3.3 (2.5–6.6)	3.7	2.2 (1.4–2.5)
Er	3.7 (3.7–8)	2.8 (2.7–2.9)	3.0 (2.4–3.2)	3.5 (1.0–5.9)	4.0 (2.4–5.0)	4.1 (2.2–6.1)
Tm	1.4	0.2	1.5	1.5	1.5	0.6 (0.3–1.1)
Yb	2.7 (2.7–7.3)	2.3 (2.0–2.7)	2.7 (2.7–3.1)	2.7 (2.7–6.5)	2.7	3.5 (1.8–5.8)
Lu	0.7	0.7	0.7	0.7	0.7	0.6
Sum	774	192	212	354	432	434

^a Values in brackets are IQR, reported only when the number of samples with concentrations above LOD was more than 30%

The contribution of PM_{2.5} to the mass concentration of PM₁₀ (which includes particles with diameter ≤ 10 μm) is one parameter that is used frequently as an indicator of the PM origin (Querol et al., 2001; Charron and Harrison, 2005; Wojas and Almquist, 2007; Morawska et al., 2008; Moreno et al., 2008a; Perez et al., 2008). It is generally agreed that the fine portion of PM usually originates from various local and regional anthropogenic sources such as emissions related to industrial and vehicle combustion and few mechanical processes. The coarse portion is mostly derived from sea spray aerosol formation processes, re-suspension of local sediments and soils into the atmosphere by wind or vehicular traffic, and by mechanical processes such as wear and tear of materials, grinding, milling, mining, and construction industries. As a result, a high PM_{2.5}/PM₁₀ ratio signifies an important contribution of anthropogenic sources to PM emissions whereas lower ratios are expected for areas where the main PM input is dust re-suspension. In this study, the PM_{2.5}/PM₁₀ ratios were calculated as PM_{2.5}/(PM_{2.5}+PM_{2.5-10}) for each sample. The average ratio for all samples was 0.612 ± 0.14 indicating a significant contribution of fine particulates to total particulate mass at all sites. The Windsor and Abbotsford urban sites had the highest PM_{2.5}/PM₁₀ ratios (0.68 and 0.67 respectively) which suggest a significant contribution of anthropogenic particles to total particulate matter emitted at these sites. This result was expected for the Windsor site which is located close to several industrial facilities and high traffic roads that contribute to PM_{2.5} emissions. High PM_{2.5}/PM₁₀ ratios found at the Abbotsford site are most probably due to aviation emissions that are typically the major source of NO_x and PM_{2.5} air pollution in the vicinity of airports (Arunachalam et al., 2011; Kurniawan and Khadi, 2011; Mazaheri et al., 2011; Woody et al., 2011). Contribution of PM_{2.5} to PM₁₀ was slightly lower at the Toronto and Halifax sites where this ratio was ca. 0.60 which is typical for urban environments that are influenced by vehicular traffic (Charron and Harrison, 2005; Morawska et al., 2008). At the Burnaby and Montreal sites the average PM_{2.5}/PM₁₀ ratio was ca. 0.5 indicating that, compared to other urban sites included in this study, the contribution of coarse particles in the mass concentration of PM was higher.

The mass concentration, particle size fractionation and chemical composition of particulate matter at a given site, were also affected by the wind speed and prevailing direction (Charron and Harrison, 2005). As PM_{2.5-10} is less easily transported in the atmosphere than PM_{2.5}, high PM_{2.5}/PM₁₀ ratios are expected at rural sites where, compared to local sources, the contribution of regional scale emissions is significant. Hence, the elevated PM_{2.5}/PM₁₀ ratios at the Wallaceburg site (average 0.69 ± 0.15) are

most probably related to the fine particles emitted from the industrial facilities operating in the city of Sarnia, and transported at this site by the northerly winds which were typical for the sampling days included in this study (Environment Canada, Weather Office, 2011).

3.2. Concentrations and spatial distribution of lanthanoids

The median concentrations of total lanthanoids (calculated as sum of La to Lu concentrations) in PM_{2.5} samples analyzed in this study ranged from 59 to 300 pg m⁻³ (Table 2).

Maximum total concentrations were found at the Halifax (300 ± 15 pg m⁻³) and Burnaby sites (244 ± 12 pg m⁻³). It is worth noting that concentrations of lanthanoids in PM_{2.5} at all Canadian sites included in this study were lower than values reported for other regions around the world. For example, typical background concentration of total lanthanoids reported for urban areas around Houston, Texas was ca. 1.6 ng m⁻³ (Kulkarni et al., 2007). Moreno et al. (2008a) reported average total lanthanoids concentration in PM_{2.5} ranging from 0.47 to 1.39 ng m⁻³ for a site that is close to several industrial facilities in Puertollano, Spain, and from 1 to 10 ng m⁻³ for PM_{2.5} collected during a sampling campaign in Mexico City (Moreno et al., 2008b). More recently, total lanthanoids concentrations reported for PM_{2.5} samples collected at five industrial towns in Spain varied from 0.64 to 3.62 ng m⁻³ (Moreno et al., 2010). For comparison, the maximum total concentration of lanthanoids in this study was 1.5 ng m⁻³ recorded at the Halifax site.

As expected, the most abundant lanthanoids in all PM samples were La and Ce. These elements were above respective LODs in more than 90% of analyzed samples and accounted for 60 to 80% of total lanthanoids in both PM_{2.5} and PM_{2.5-10}. The highest median concentrations of La in PM_{2.5} were 227 pg m⁻³ (IQR 96 to 270 pg m⁻³) and 86 pg m⁻³ (IQR 56 to 163 pg m⁻³) at the Halifax and Burnaby sites, respectively. Burnaby site had also the highest concentration of Ce (115 pg m⁻³) followed by the Toronto, Montreal, Windsor and Halifax sites which had similar concentrations, at ca. 70 pg m⁻³.

Concentrations of total lanthanoids in PM_{2.5-10} samples were typically two times higher than PM_{2.5} at each site (Table 3), with the highest levels present at the Burnaby site where the median value was 774 pg m⁻³ (with IQR 284 to 969 pg m⁻³). At the other sites, total lanthanoids concentrations in PM_{2.5-10} ranged from 192 to 434 pg m⁻³.

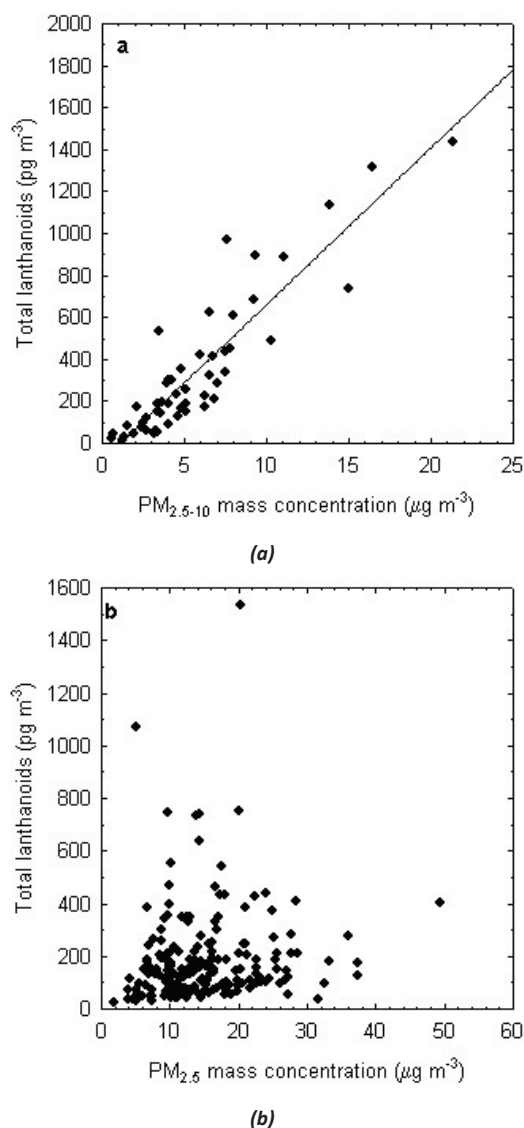


Figure 2. Total lanthanoids concentrations vs. PM mass for (a) $PM_{2.5-10}$ and (b) $PM_{2.5}$ samples.

Also, the concentrations of lanthanoids in $PM_{2.5-10}$ showed a significant correlation with particulate mass concentration (Spearman rank correlation 0.86, $p < 0.05$) (Figure 2a), which suggests that the natural and/or anthropogenically induced re-suspension of local soils and sediments, and various mechanical processes that contribute to $PM_{2.5-10}$ emissions have a considerable effect on the presence of lanthanoids in the coarse fraction of air particulate matter. In contrary, the lack of correlation for $PM_{2.5}$ samples (Figure 2b) implies that the emission sources of lanthanoids do not have a significant impact on the mass of fine particles.

3.3. Concentration patterns of lanthanoids and La enrichment factors in FCC and air particulate samples

Fluid catalytic cracking is the major conversion process used in oil refineries to produce valuable hydrocarbons from crude oil fractions. Fluid cracking catalysts (FCC) commonly contain La-enriched zeolites and there is evidence showing the presence of La-enriched particles in the flue gas emitted from the refineries, despite attempts to minimize the loss of FCC through the process (Niccum, 2010). As a result, concentration patterns of lanthanoids and especially La-enrichment factors (ratios of La to other lanthanoids, mainly Ce and Sm) are often used as reliable indicators for tracing emissions of oil-refining industries (Table 4). Several studies have demonstrated that PM emitted by such

sources had La-enrichment factors that were significantly higher than natural distribution values and showed distorted concentration patterns of lanthanoids.

The concentration patterns of lanthanoids for the Upper Continental Crust (UCC) composition (Taylor and McLennan, 1986) and for PM samples analyzed in this study are depicted in Figure 3.

Unlike the commonly used PM_{10} fraction, $PM_{2.5-10}$ reflects the chemical composition of coarse particles with minimal contribution from the finer fraction. Since the coarse particles are mainly related to re-suspension processes and cannot travel in long distances in the atmosphere (Charron and Harrison, 2005), lanthanoid patterns of $PM_{2.5-10}$ typify the local soil and sediments composition and consequently can be considered as the background pattern for each site. As shown in Figure 3b, the $PM_{2.5-10}$ samples analyzed in this study had natural distribution patterns at each site. Median and IQR of La/Ce and La/Sm ratios for all samples were 0.57 (0.44–0.78) and 5.9 (3.9–6.9) with no significant differences between sites (Kruskal–Wallis test at $p < 0.05$) (Kruskal and Wallis, 1952). Although the Burnaby site had the highest concentrations of lanthanoids in $PM_{2.5-10}$, the distribution patterns and the insignificant La-enrichment factors suggest that the oil-refining facility located nearby has no significant impact on $PM_{2.5-10}$ emissions and its chemical composition.

The distribution patterns of lanthanoids for $PM_{2.5}$ samples at the Abbotsford, Windsor, Toronto, Montreal and Canterbury sites were similar and quite close to the UCC distribution patterns (Figure 3c). La enrichment factors at these sites were not significantly different from each other (Kruskal–Wallis test at $p < 0.05$). Median and IQR values for La/Ce and La/Sm ratios were respectively, 0.69 (0.54–0.83) and 5.0 (3.9–7.9). Although slightly higher than what is expected for natural composition of particles in the atmosphere, these values are very close to ratios found for the $PM_{2.5-10}$ composition and are much lower than what is reported for $PM_{2.5}$ emissions that were influenced by FCC-oil-refining operations (Table 4). This implies that the oil-refining industry does not have a significant effect on the $PM_{2.5}$ emissions at these sites during the sampling periods of this study. While these results were expected for the Abbotsford, Windsor, Toronto and Canterbury sites, this was not the case for the Montreal site which is located about 15 km southwest of two major oil refining facilities. However, most of the sampling days at the Montreal site were either calm (wind speed below 30 km h^{-1}) or characterized by southwesterly winds (Environment Canada, Weather Office, 2011) which explains why the oil refineries located north of the sampling site did not show any significant effect on the chemical composition and concentration of $PM_{2.5}$ -lanthanoids at this site.

The concentrations of lanthanoids in $PM_{2.5}$ samples collected at the Halifax, Burnaby and Wallaceburg sites showed a different pattern (Figure 3d). The enrichment factors of La compared to Ce, and Sm at Halifax were 4.9 (2.1–6.9) and 39 (21–51), respectively. These values are much higher than natural ratios and similar to what is reported for $PM_{2.5}$ emissions related to the loss of zeolite catalysts from the FCC units (Kulkarni et al., 2006; Kulkarni et al., 2007; Moreno et al., 2008a). Hence, the refinery which is located about 2 km southeast of the Halifax site is a major source of $PM_{2.5}$ -lanthanoids. Actually, this facility processes about 82 000 barrels of crude oil per day (Dartmouth Refinery, 2011) and releases about 210 tonnes of $PM_{2.5}$ per year (Environment Canada, 2009), which explains its significant contribution to the composition of $PM_{2.5}$ at this site. La/Ce and La/Sm ratios at the Burnaby site were 1.7 (0.5–2.1) and 26 (14–42), which are lower than values found at the Halifax site but still much higher than the natural enrichment factors. It is worth noting that the petrochemical complex located close to the Burnaby site processes 50 000 to 55 000 barrels per day (Chevron in Canada, 2011) and releases not more than 25 tonnes of $PM_{2.5}$ per year (Environment Canada, 2009a). As a result, a less prominent effect of these

emissions was found at the Burnaby site as compared to the Halifax site. La enrichment factors at the Wallaceburg site were 1.3 (0.7–1.6) and 9 (6–21) for La/Ce and La/Sm, respectively. These results are consistent with values reported for urban areas where the emissions of lanthanoids are partly due to oil-refining sources (Wang et al., 2000; Moreno et al., 2006; Kulkarni et al., 2007).

Since this site is located about 50 km south of two major oil-refining complexes, the contribution of PM_{2.5} emissions from these facilities is less significant than at the Halifax and Burnaby sites, albeit remaining quite distinguishable from other natural and/or anthropogenic sources of PM at this rural site.

Table 4. Enrichment factors reported for PM_{2.5} and PM₁₀ composition in different regions of the world

Sampling site	La/Ce	La/Sm	Reference
PM₁₀ samples coming from non-refinery sources			
Beijing, China	0.44 – 0.51	6.0 – 6.9	Wang et al. (2001)
Puertollano, Spain	0.63 – 1.07	7.7 – 12.8	Moreno et al. (2008a)
Mexico City, Mexico	0.81 – 0.93	14.0 – 20.0	Moreno et al. (2008b)
Bailen, Spain	0.58	NR	Moreno et al. (2010)
Algeciras, Spain	0.74	NR	
PM_{2.5} samples coming from non-refinery sources			
Camden, NJ	0.51	5.2	Olmez and Gordon (1985)
Houston, TX	0.70	3.9	Kulkarni et al. (2006)
Puertollano, Spain	0.73 – 1.37	10.2 – 16.4	Moreno et al. (2008a)
Mexico City, Mexico	0.67	11.6	Moreno et al. (2008b)
Bailen, Spain	0.59	NR	Moreno et al. (2010)
Algeciras, Spain	0.79	NR	
PM₁₀ samples coming from refinery sources			
Delft, The Netherlands	1.11	12.6	Wang et al. (2000)
Puertollano, Spain	2.33	40.9	Moreno et al. (2008a)
Puertollano, Spain	0.77	NR	Moreno et al. (2010)
La Linea, Spain	0.85	NR	
PM_{2.5} samples coming from refinery sources			
Camden, NJ	1.25	20.0	Olmez and Gordon (1985)
Philadelphia, PA	1.23 – 1.62	17.4 – 32.0	Kitto et al. (1992)
Houston, TX	2.90	53.7	Kulkarni et al. (2006)
Puertollano, Spain	1.09 – 5.38	14.6 – 35.0	Moreno et al. (2008a)
Mexico City, Mexico	1.56	20.4	Moreno et al. (2008b)
La Linea, Spain	0.98	NR	Moreno et al. (2010)
Puertollano, Spain	0.93	NR	
Comparison/reference values			
Fluid Cracking Catalysts (FCC)	1.22	19.4	Kitto et al. (1992)
	4.30	55.2	Kulkarni et al. (2006)
	4.54	63.0	This study
Upper Continental Crust (UCC)	0.59	5.5	Taylor and McLennan (1986)

NR–Non reported

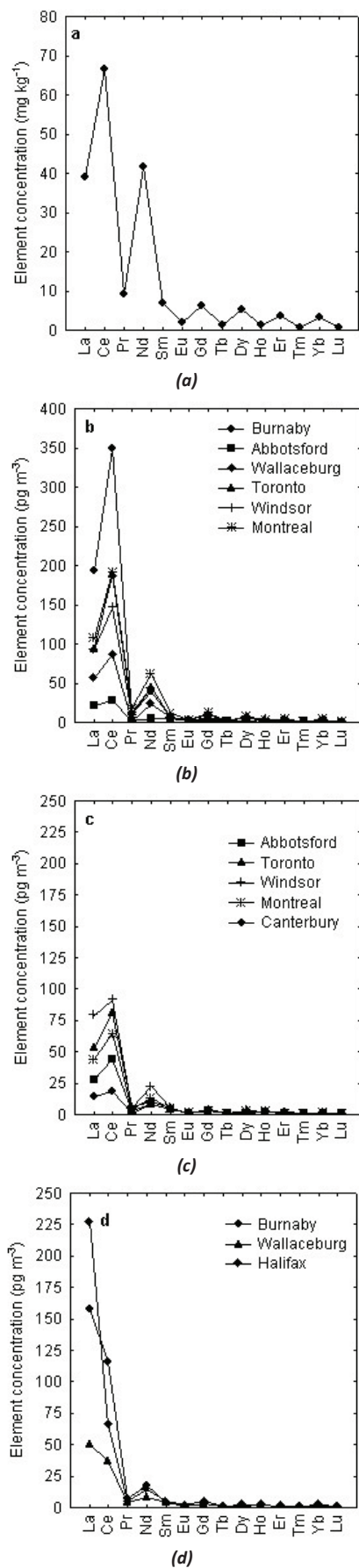


Figure 3. Distribution patterns of lanthanoids for (a) Earth's Crust; (b) $PM_{2.5-10}$ Samples; (c) $PM_{2.5}$ at the Abbotsford, Toronto, Windsor, Montreal and Canterbury sites; (d) $PM_{2.5}$ at the Burnaby, Wallaceburg and Halifax sites.

3.4. Vanadium, nickel and lanthanoids

V and Ni are known to be reliable tracers of emission sources that are related to fossil fuels combustion and/or processing in the refining facilities. The concentrations of these elements at sites where $PM_{2.5}$ composition is affected by such sources are high, and are strongly correlated with slopes of linear regression lines (or V/Ni ratios) that can be used to typify the fossil fuels (Lopez et al., 1995; Saganic and Gilroy, 2002; Moreno et al., 2010; Jeong et al., 2011). In addition, V-rich emissions coming from oil and petroleum coke combustion usually have La/V ratios less than 0.1, which is much lower than what is expected by the uncontaminated crustal materials ($La/V = 0.2$ to 0.3), whereas $La/V > 1$ values are expected for $PM_{2.5}$ coming by FCC emission sources (Kulkarni et al., 2006; Moreno et al., 2008a; Danadurai et al., 2011). Since most of the industrial areas with petrochemical complexes involve multiple air emission sources, using La/V ratio as the single marker of FCC-related emissions is not sufficient and using other parameters such as concentration of Ce and the three-component La-Ce-V diagram, is needed.

Median and IQRs for concentrations of V and Ni in $PM_{2.5}$ samples analyzed in this study were 1.37 ng m^{-3} ($1.21-3.03$) and 0.87 ng m^{-3} ($0.80-1.48$), respectively, with the Burnaby, Toronto and Halifax sites having the highest levels (5.2 , 4.9 and 3.9 ng m^{-3} V, and 1.7 , 2.6 and 1.9 ng m^{-3} Ni, respectively) (see the SM, Table 1S). In addition, V and Ni concentrations at these sites were strongly correlated (Spearman rank correlation 0.75 , 0.90 and 0.95 , $p < 0.05$, respectively), suggesting that the fossil fuels used for domestic, transportation or industrial processes, have a significant contribution to the chemical composition of $PM_{2.5}$ emitted at these sites (Kulkarni et al., 2006; Moreno et al., 2008a; Moreno et al., 2008b; Moreno et al., 2010). Further on, the slopes of V vs. Ni linear regression lines at Burnaby and Halifax sites were 2.7 ± 0.2 and 2.9 ± 0.2 , respectively which are comparable with average V vs. Ni ratios that are typical for PM emissions from combustion of heavy fuel oil used by marine transportation vessels (Querol et al., 2007; Moreno et al., 2010; Jeong et al., 2011). Hence, V and Ni emissions at these sites are related to the burning of heavy oils by marine vessels operating in the harbors located close to these sites. The slope of V vs. Ni linear regression line at the Toronto site, was 1.9 ± 0.1 which is similar to values reported for $PM_{2.5}$ emitted close to high traffic roadways (Saganic and Gilroy, 2002). Compared to $PM_{2.5}$, V and Ni median concentrations in $PM_{2.5-10}$ for all sites were about 5 times lower and did not show any correlation.

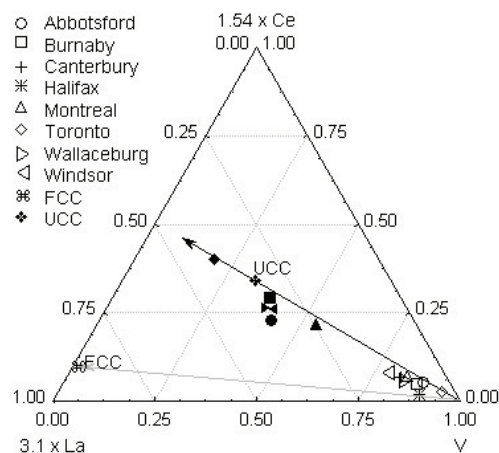


Figure 4. LaVtCe tertiary plots for $PM_{2.5-10}$ (closed symbols), $PM_{2.5}$ (open symbols) samples. The FCC sample was provided from one supplier of FCC catalysts in Canada. The V-UCC and V-FCC lines represent La/Ce ratios for UCC and FCC respectively; the arrows show the direction of increasing La/V ratio.

The La/V ratios in all PM_{2.5} samples were not higher than 0.04, implying that a significant amount of V in this fraction of PM is coming from combustion processes. In contrary, the median La/V ratio for PM_{2.5-10} was 0.28 (with IQR 0.15–0.39) which is very close to the uncontaminated crustal material composition (Moreno et al., 2008a). The three-component diagrams (or ternary plots) which are traditionally utilized by geologists to illustrate the compositional variations in minerals and rocks, have also been used to show geochemical patterns in atmospheric PM (Moreno et al., 2008a; Moreno et al., 2010). In the ternary La–V–Ce plot shown in Figure 4, La and Ce concentrations are adjusted so that the UCC point is placed in the center of the triangle. This plot shows a distinctive grouping of PM_{2.5} samples close to V–apex and PM_{2.5-10} samples close to UCC composition point.

Further on, the PM_{2.5} samples were clustered in two groups: the Halifax site is plotted closer to V–FCC line and the other sites are plotted closer to the V–UCC line. These results imply that the presence of V in PM_{2.5-10} samples is mostly due to fugitive dust suspended in the atmosphere while the emissions of V-rich fine aerosols are coming mainly from fossil fuel combustion processes. Unlike the other sites, emissions from petrochemical industrial complexes close to Halifax show some contribution to the presence of V in PM_{2.5}.

4. Conclusion

The data presented in this study support the previous reports that the distribution patterns of lanthanoids in air PM_{2.5} are sensitive and reliable tracers for emissions related to oil-refining industry. The average concentrations of total lanthanoids in PM_{2.5} samples from the Canadian urban and rural sites included in this study, ranged from 59 to 334 pg m⁻³ and were typically two times lower than PM_{2.5-10}. The lowest concentrations of lanthanoids were found at the Canterbury site which has a minimal anthropogenic impact. Compared to this site, concentrations of lanthanoids at the Windsor, Toronto and Montreal urban sites were 2.5 to 4 times higher. However, the La enrichment factors were comparable to the natural composition and to the PM_{2.5-10} values indicating that the main source of lanthanoids present in PM_{2.5} at these sites is the wind and/or traffic induced re-suspension of local road dust. The highest concentrations of all lanthanoids were found at the Halifax site which is located less than 2 km southeast of a major petrochemical complex. La/Ce and La/Sm ratios at this site were respectively 4.1 and 39 which indicate that the oil refining facility has a significant effect on the emissions of lanthanoids at this site. The second highest concentrations and enrichment factors were found at the Burnaby site, which is located close to a smaller petrochemical complex, which results in less significant contribution of this facility on PM_{2.5} composition. Compared to urban sites included in this study, concentrations of lanthanoids at the Wallaceburg site were about 2 times lower whereas La-enrichment factors were almost double and consistent with values reported for areas where the emissions of lanthanoids are partly due to oil-refining sources. These results confirm that the lanthanoids distribution patterns and La enrichment factors are useful indicators for tracking PM emissions from oil-refining facilities located as far as 50 km from the sampling site.

Finally, our results show that La, Ce and V can be used to identify three classes of particles: particles of crustal origin which are mostly found in the coarse fraction of PM, fine particles highly enriched in La which are related to the refinery emissions, and V-enriched fine particles originating from heavy oil combustion.

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Supporting Material Available

Median mass and trace metal concentrations for PM_{2.5} samples from urban sites (Table S1A), Median mass and trace metal concentrations for PM_{2.5} samples from rural sites (Table S1B), Median mass and trace metal concentrations for PM_{2.5-10} samples from urban and rural sites (Table S2). This information is available free of charge via Internet at <http://www.atmospolres.com>.

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