Applied Geochemistry xxx (2016) 1–10

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

# Characterization of the $\delta^{13}C$ signatures of anthropogenic $CO_2$ emissions in the Greater Toronto Area, Canada☆

Stephanie C. Pugliese [a], Jennifer G. Murphy [a, *], Felix Vogel [b], Douglas Worthy [c]

[a] University of Toronto, Department of Chemistry, 80 St. George St., Toronto, ON, M5S 3H6, Canada
[b] Laboratoire des Sciences du Climat et de L'Environnement, CEA-CNRS-UVSQ, Université de Paris-Saclay, France
[c] Environment Canada, Climate Research Division, 4905 Dufferin St., Toronto, ON, M3H 5T4, Canada

ARTICLE INFO

*Article history:*
Received 19 August 2016
Received in revised form
2 November 2016
Accepted 3 November 2016
Available online xxx

*Keywords:*
Anthropogenic carbon dioxide
Carbon isotopes
Source apportionment
Urban pollution
Keeling plots
Mass balance

ABSTRACT

In urban environments, carbon dioxide ($CO_2$) is emitted from a variety of anthropogenic and biogenic sources. The isotopic ratio $\delta^{13}CO_2$ has been widely used to source apportion $CO_2$ as different sources have distinct isotopic fingerprints; the disadvantage of this technique is that $\delta^{13}CO_2$ signatures are often spatially and temporally specific. We present a study characterizing the $\delta^{13}CO_2$ signatures of the dominant anthropogenic sources of $CO_2$ in the Greater Toronto Area (GTA). Refined gasoline and diesel fuel were sampled from various stations around the GTA in three separate campaigns (April, July and November 2015) to assess the variability of their $\delta^{13}CO_2$ signatures. Mean winter $\delta^{13}CO_2$ signatures for refined gasoline were measured to be $-27.58 \pm 0.52$ ‰ and $-28.12 \pm 0.43$ ‰ (uncertainties represent the standard deviation in sample signatures) in April and November respectively while the mean summer signature was measured to be $-28.09 \pm 0.34$ ‰. Diesel fuel samples $\delta^{13}CO_2$ signatures from the same campaign periods were measured to be $-29.09 \pm 0.34$ ‰, $-29.47 \pm 0.29$ ‰, and $-29.28 \pm 0.21$ ‰, respectively. We hypothesize that inter-seasonal variability in signatures is likely a result of the use of different parent crude petroleum. We found no significant impacts from octane grade, fuel distributor or municipality the fuel was purchased from on the measured $\delta^{13}CO_2$ signatures. Other transportation fuels that were measured include dyed-diesel ($\delta^{13}CO_2$ signature $= -29.3 \pm 0.20$ ‰) and jet fuel ($\delta^{13}CO_2$ signature $= -29.5 \pm 0.20$ ‰), which were both different than measurements made for the same fuels in other locations globally. To account for emissions from residential and commercial heating and electricity production, a variety of fuels were characterized in this study. The primary heating fuel used in the GTA, natural gas, was measured to have a $\delta^{13}CH_4$ signature of $-44.2 \pm 0.20$ ‰. Anthracite coal (a fuel that was used prior to 2014 for electricity) was measured to have a $\delta^{13}CO_2$ signature of $-23.8 \pm 0.20$ ‰, which is fairly consistent with coal samples measured elsewhere. With the transition in Ontario from coal to biomass-fueled power generation, softwood, hardwood and mixed wood pellets were sampled from two distributors in the GTA and measured $\delta^{13}CO_2$ signatures were $-25.0 \pm 0.20$ ‰, $-26.8 \pm 0.20$ ‰, and $-25.8 \pm 0.20$ ‰, respectively. Using these measured signatures, we performed a sensitivity analysis to quantify the precision required for continuous ambient measurements to separately identify fuel type using $\delta^{13}CO_2$ as the sole tracer. The local signatures were also used in a mass balance calculation to quantify the relative contribution of two end-members (with the signatures of $-44$ ‰ and $-28$ ‰) to total measured $CO_2$ in the GTA in 2014.



## 1. Introduction

Over the last three centuries, concentrations of atmospheric carbon dioxide ($CO_2$) have been increasing, primarily as a result of fossil fuel combustion and deforestation (Hartmann et al., 2013). In response to international treaties, such as the Kyoto Protocol, Copenhagen Accord and the Paris Agreement, there has been a recent drive to reduce or offset emissions of $CO_2$ and other greenhouse gases (GHGs). However, even in heavily urbanized areas, $CO_2$ is derived from a variety of biological (e.g. respiration from humans, soil and plants) and anthropogenic (e.g. residential and commercial

☆ This paper has been recommended for acceptance by Prof. M. Kersten.

* Corresponding author.
*E-mail address:* jmurphy@chem.utoronto.ca (J.G. Murphy).

http://dx.doi.org/10.1016/j.apgeochem.2016.11.003
0883-2927/

heating, electricity production, vehicle exhaust) sources and is atmospherically transported across regional and national borders. Therefore, to independently evaluate whether regulations are being properly implemented, there is an increasing need to not only monitor ambient concentrations of $CO_2$ but also identify the major sources and sink processes and quantify their relative contributions. Several tracers, such as carbon monoxide (CO), have been used in an effort to address this challenge, as combustion processes yield CO and $CO_2$ in specific ratios according to fuel type and engine efficiency (Djuricin et al., 2010). Using CO as a tracer for anthropogenic $CO_2$ is a relatively inexpensive technique, however analyses can be complicated by the fact that there are biogenic sources of CO as well as unrelated sink processes (Gamnitzer et al., 2006; Vogel et al., 2010). An alternate approach to identify the sources of atmospheric $CO_2$ is the use of its isotopic composition. The most useful isotope to investigate the fossil fuel contribution of atmospheric $CO_2$ is radiocarbon, $^{14}C$, as fossil fuel combustion emits $CO_2$ with no $^{14}C$ because its half-life (5730 years) is much shorter than the age of fossil fuels (Djuricin et al., 2010). Conversely, present day background and biogenic $CO_2$ is enriched in $^{14}C$, enabling the ability to easily trace fossil fuel-derived $CO_2$. However, analysing even small samples for $^{14}C$ is time-consuming and costly, making it impractical for continuous monitoring. An alternate approach is to use the stable isotope composition of $CO_2$ ($^{13}CO_2$ and $^{12}CO_2$) where their ratio (relative to a known standard, Equation (1)) can be used to identify the source as long as the unique end-member signatures are known.

$$\delta^{13}C = \left( \left( \frac{\frac{^{13}C_{sample}}{^{12}C_{sample}}}{\frac{^{13}C_{standard}}{^{12}C_{standard}}} \right) - 1 \right) \times 1000\,‰ \quad (1)$$

The isotopic end-members of various $CO_2$ sources are typically different enough that partitioning between various fossil fuel combustion activities as well as biological activities has been achieved successfully (Djuricin et al., 2010; Gorka and Lewicka-Szezebak, 2013; Kuc and Zimnoch, 1998; Pataki et al., 2003; Widory and Javoy, 2003; Zimnoch et al., 2012). A study demonstrating the utility of $\delta^{13}C$ analyses was performed in 2013 by Gorka and Lewicka-Szczebak in Wroclaw, in southern Poland. In the two heating seasons of 2011 (January–March and October–December), they were able to identify the influence of coal in the first heating season (with a source $\delta^{13}CO_2$ of −25.7 ‰) and the influence of diesel and gasoline in the second heating season, following the opening of a new highway (with a source $\delta^{13}CO_2$ of −27.6 ‰) (Gorka and Lewicka-Szezebak, 2013). The primary difficulty associated with using $\delta^{13}C$ to source apportion $CO_2$ is that isotopic signatures exhibit geographic variability and therefore a prerequisite of this analysis is to characterize local emissions (Bush et al., 2007; Widory and Javoy, 2003). However, there have been only a few studies globally that have considered the spatial and temporal variability of anthropogenic $\delta^{13}CO_2$ signatures with even fewer, if any, exhaustive studies characterizing the $\delta^{13}CO_2$ signature of sources in a Canadian metropolitan area.

In an effort to address this gap, this study was focused on evaluating the spatial and temporal variability of carbon isotopic signatures of fossil fuel combustion processes in the Greater Toronto Area (GTA) and southern Ontario. We characterized the carbon isotope ratio of locally supplied fuels for transportation (gasoline, diesel, dyed-diesel and jet fuel) and heating/electricity generation (natural gas, kerosene, stove oil, coal and wood pellets). Samples of gasoline and diesel fuel were collected from different municipalities within the GTA as well as in different seasons to evaluate the extent of spatial and temporal variability of the isotopic signatures. To our knowledge, this is the first attempt at characterizing the $\delta^{13}CO_2$ signatures of anthropogenic $CO_2$ sources in the GTA as well as the first characterization of $\delta^{13}CO_2$ signatures of dyed diesel, kerosene, stove oil and wood pellets globally. Through a mass balance approximation, we demonstrate the utility of using these local carbon isotope signatures to quantify the contribution of different end-members to total $CO_2$ annually. Currently, estimates of anthropogenic $CO_2$ emissions in the GTA are made available by the EDGAR v.4.2 (EDGAR, 2010) and the FFDAS (FFDAS, 2010) inventories, which have very different annual totals ($1.42 \times 10^8$ and $6.04 \times 10^7$ tonnes $CO_2$, respectively). Furthermore, the EDGAR inventory provides estimates of sectoral contributions in the GTA (~41% natural gas and ~32% gasoline + diesel) which is different from a locally derived estimate (~31% natural gas and ~48% gasoline + diesel, with gasoline accounting for ~73% of that combined fraction) (Greening Greater Toronto, 2012). Therefore, we expect the results of this work will improve our ability to quantify the relative contributions of anthropogenic sources of $CO_2$ in the GTA and help in reducing discrepancies between bottom-up inventories and top-down atmospheric calculations.

## 2. Methods

### 2.1. Study region

The GTA is located in southern Ontario on the northwest shore of Lake Ontario and is the largest urban area in Canada, as well as one of its most densely populated regions (945.4 persons per square kilometre) (Statistics Canada., 2012b). The GTA comprises four municipalities, Halton, Durham, Peel and York, which together have a population exceeding 6 million (Statistics Canada., 2012b). The majority of residences in Ontario are heated by natural gas furnaces (~64%) with the rest reliant primarily on electricity (~25%) and minimally by propane (~3%) and kerosene and stove oil (<1%) (Statistics Canada, 2007; Statistics Canada, 2012a). Prior to 2014, ~22% of electricity in Ontario was derived from coal combustion (Ontario Ministry of Energy (2015)). When considering the GTA only, coal combustion accounted for an even larger fraction (~50%), most of which was produced at the Nanticoke Generating Station, ~130 km south-west of Toronto (Independent Electricity System Operator (IESO), 2015). Following Ontario's coal phase-out action plan, requiring all coal-fired power plants in the province to be decommissioned or transitioned into biomass-fueled power plants by 2014, electricity is now primarily produced via nuclear (~62%), hydro (~22%) and natural gas (~12%) (Ontario Ministry of Energy (2015)).

### 2.2. Transportation fuels sample collection

Refined gasoline and diesel samples were collected from 38 different stations across the GTA (Section 3.1). Three campaigns were carried out to ensure both winter- and summer-grade gasoline were sampled (the transition between the two grades usually occurs in June and September of each year (U.S. Energy Information Agency, 2016)). Campaign #1 sampled winter-grade gasoline and diesel fuel from all stations on April 1 & 8, 2015 (hereafter referred to as “Winter, 2015-A”), campaign #2 sampled summer-grade gasoline and diesel fuel from all stations on July 17 & 22, 2015 (hereafter referred to as “Summer, 2015”), and campaign #3 sampled winter-grade gasoline and diesel fuel from a limited subset of stations on November 19, 2015 (hereafter referred to as “Winter, 2015-B”). During each campaign, 0.25–0.50 L of fuel was sampled into amber glass bottles from stations in Downtown Toronto as well as five suburban regions (Mississauga, Vaughan, Scarborough, Oakville and Brampton). In each region, grade 87 gasoline and diesel fuel were sampled from the three top

Please cite this article in press as: Pugliese, S.C., et al., Characterization of the $\delta^{13}C$ signatures of anthropogenic $CO_2$ emissions in the Greater Toronto Area, Canada, Applied Geochemistry (2016), http://dx.doi.org/10.1016/j.apgeochem.2016.11.003