



## Origin Identification of Carbonaceous Aerosol Particles by Carbon Isotope Ratio Analysis

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### ABSTRACT

We applied stable carbon isotope ratio ( $^{13}\text{C}/^{12}\text{C}$ ) and radiocarbon ( $^{14}\text{C}$ ) analysis for the quantification of three main aerosol sources (coal, biomass and liquid fossil fuel derived aerosol emissions). Submicron aerosol samples ( $\text{PM}_{10}$ ) were collected from 27<sup>th</sup> October, 2014 to 19<sup>th</sup> January, 2015 at a suburban site of Vilnius city (Lithuania). To determine fossil and non-fossil contributions to submicron carbonaceous aerosol particles,  $^{14}\text{C}$  measurements of total carbon (TC) were performed using single stage accelerator mass spectrometer (SSAMS, NEC, USA). The concentrations of TC and  $\delta^{13}\text{C}$  in  $\text{PM}_{10}$  fraction were measured using elemental analyzer interfaced to isotope ratio mass spectrometer (EA-IRMS).

The TC concentration during measurement period ranged from 1.3 to 9.6  $\mu\text{g m}^{-3}$ . The variation of TC concentrations can be explained by the influence of long-range transport and dispersion properties of the boundary layer (mixed layer depth).

We found that biomass-derived aerosol sources are prevailing in Vilnius during wintertime and ranged from 57% to 84% of total carbonaceous aerosol fraction. Applying isotope mass balance calculations the traffic emissions were estimated to be  $15 \pm 7\%$  and coal combustion made up  $14 \pm 9\%$  in  $\text{PM}_{10}$ . To provide better information about the pollution sources, the carbon isotope analysis along air mass transport pattern was performed. Our results demonstrated that the high contribution to  $\text{PM}_{10}$  from coal burning (up to 40%) was observed for air masses transported from highly industrialized Western Europe regions. Combination of stable carbon isotope ratio with the radiocarbon data allow to distinguish coal from liquid fossil fuel in the aerosol particle emissions.

**Keywords:** Aerosol particles; Stable carbon isotopic ratio; Radiocarbon analysis.

### INTRODUCTION

Fine aerosol particles (particles having the aerodynamic diameter  $< 1 \mu\text{m}$ ,  $\text{PM}_{10}$ ) have a significant effect on the climate change, direct and indirect radiative forcing, visibility and human health (Watson, 2002; Forster *et al.*, 2007; Mauderly and Chow, 2008).  $\text{PM}_{10}$  contain a substantial fraction (up to 70%) of carbonaceous species (Zhang *et al.*, 2007). Carbonaceous aerosol in  $\text{PM}_{10}$  arising largely from anthropogenic sources includes all types of combustion activities (motor vehicles, biomass burning, power plants and industrial processes) (Cheng *et al.*, 2011; Crippa *et al.*, 2013). Fine carbonaceous aerosol particles are currently an important area of study due to a continuous increase in their concentration due to anthropogenic activities. Therefore, the development of methods to identify contributions of natural and anthropogenic sources gains great importance.

Furthermore, distinguishing fossil fuel and biomass burning sources is necessary to develop abatement strategies for more efficient control of carbonaceous aerosol particle pollution.

During the last decade, significant progress has been made in the characterization of carbonaceous aerosol sources using specific tracers. Different aerosol sources have a specific stable carbon isotopic composition ( $^{13}\text{C}/^{12}\text{C}$ ). The  $\delta^{13}\text{C}$  of total carbon (TC) has been successfully used to identify the origin of pollution sources (Widory *et al.*, 2004; Kelly *et al.*, 2005; Ulevicius *et al.*, 2010) and to assess the anthropogenic input (Górka *et al.*, 2009; López-Veneroni, 2009; Górka *et al.*, 2012). Therefore, it is often difficult to distinguish fossil, biogenic and biomass burning emissions by measuring  $\delta^{13}\text{C}$  of TC alone, due to overlapping  $\delta^{13}\text{C}$  values between major pollution sources such as fossil and non-fossil fuel burning emissions (Cao *et al.*, 2011; Kundu and Kawamura, 2014). Nevertheless, recent studies demonstrated significant difference in  $\delta^{13}\text{C}$  values between coal ( $\delta^{13}\text{C}_{(\text{coal})} = -24.5\text{‰}$ ) and liquid fossil fuel ( $\delta^{13}\text{C}_{(\text{liquid fossil fuel})} = -28\text{‰}$ ) (Górka *et al.*, 2009; Garbaras *et al.*, 2015;). This isotope ratios differences can be used for identification of specific aerosol particle sources.

Radiocarbon ( $^{14}\text{C}$ ) analysis allows distinguishing between

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fossil and non-fossil (biomass burning and biogenic emissions) sources of carbonaceous aerosol (Szidat *et al.*, 2006; Schichtel *et al.*, 2008; Sun *et al.*, 2012; Buchholz *et al.*, 2013). Most radiocarbon measurements have been performed on the PM<sub>2.5</sub> and PM<sub>10</sub> carbonaceous aerosol samples (Gelencsér *et al.*, 2007; Schichtel *et al.*, 2008; Fushimi *et al.*, 2011; Glasius *et al.*, 2011; Dusek *et al.*, 2013). However, <sup>14</sup>C analysis of PM<sub>1</sub> is not so common (Endo *et al.*, 2004; Minguillón *et al.*, 2011; Zhang *et al.*, 2013). Taking into account that PM<sub>1</sub> fraction is combustion-derived aerosol particles the <sup>14</sup>C analysis in PM<sub>1</sub> samples could give more conclusive information on the sources of carbonaceous aerosol particles. The limitation of the radiocarbon analysis is that this method does not allow distinguishing coal-derived aerosol particles from the emissions of diesel and gasoline.

Dual isotope (<sup>14</sup>C and <sup>13</sup>C) analysis of carbonaceous aerosol has only been reported in a few previous studies (Ceburnis *et al.*, 2011; Kirillova *et al.*, 2013). Authors demonstrated that <sup>14</sup>C/<sup>12</sup>C and <sup>13</sup>C/<sup>12</sup>C ratios provide valuable information concerning both the sources and atmospheric processes of carbonaceous aerosol. Ceburnis *et al.* (2011) used a dual isotope (<sup>14</sup>C and <sup>13</sup>C) method for quantifying biogenic marine and terrestrial organic aerosol sources. Kirilova *et al.* (2013) established water soluble organic carbon (WSOC) sources in Indian region.

Our main objective was to distinguish coal, biomass and liquid fossil fuel-derived PM<sub>1</sub> aerosol particles in the Vilnius city applying the stable carbon isotope ratio and radiocarbon analysis.

## MATERIALS AND METHODS

### Sampling

The measurements were performed from 10/27/2014 to 01/19/2015 in Vilnius, the capital of Lithuania. The sampling site is located in the vicinity of Vilnius at the State Research Institute Center for Physical Sciences and Technology (54°64'N, 25°18'E, about 156 m above the sea level and 5 m above the ground level). The sampling location is situated in a grove and surrounded by the grassland about 10 km west of the city centre. The sampler was located 300 m in the west direction from the highway Vilnius-Kaunas with the intensity 10,000 vehicles per day. The power station was located 3 km in the north from sampling site. Small houses which use biomass and coal for domestic heating purpose were located in the vicinity (more than 300 m) of the sampling site. Local sources of aerosols in the area includes biomass and solid fossil fuel burning for the domestic heating, C3 type grass burning in the fields, traffic-related emissions. During measurement period the average of relative humidity, temperature and wind speed were 80 ± 13%, 4 ± 3°C and 7 ± 3 m s<sup>-1</sup>, respectively. The wind direction was mainly from east and south.

Backward air mass trajectories were calculated using a hybrid single particle Lagrangian (HY-SPLIT) model from the National Oceanic and Atmospheric Administration (NOAA), <http://www.arl.noaa.gov/hysplitarc-bin/traj1file.pl?metdata=FNL>. Trajectories were calculated for every 3 or 6

h (depending on the period) with a total of 48 h duration at 500 m altitude AGL (Above Ground Level).

Atmospheric aerosol particles of PM<sub>1</sub> were collected using the high volume aerosol sampler (Digitel AG, DH-77), the flow rate was 500 L min<sup>-1</sup>. The calibration of the sampler was performed using Calibration Unit (Digitel AG). The 2–3 days samples were collected from 10/27/2014 to 01/19/2015 on the 150 mm diameter quartz-fiber filters (pre-baked at 600°C for 3 h to remove organic impurities before sampling). The filters were changed in the sampler at 5 p.m. The exact time for the filter loading/unloading and the sampled volume was registered by the sampler automatically. Obtained filter samples were stored in a freezer until analysis. For the proper collection of long-range transport particles the PM<sub>1</sub> sampler was used. It allowed to eliminate the interference with the aerosol particles of the local origin, which in principle can have distinct isotopic signature comparing to the long-range origin particles.

### Sample Preparation

For the analysis of the total carbon (TC) concentration and stable carbon isotope ratio about 1.42 cm<sup>2</sup> of the aerosol filter was used. The part of the filter was wrapped in the tin capsule and stored in the freezer until δ<sup>13</sup>C analysis. The rest of the filter was used for the preparation for radiocarbon measurements.

Samples were prepared for the radiocarbon (<sup>14</sup>C) analysis using an elemental analyzer (EA, Vario Isotope Select, Elementar, GmbH) connected to the Automated Graphitization Equipment AGE-3 (IonPlus AG). CO<sub>2</sub> from the sample is produced in the EA and passes to the AGE-3 system. In AGE-3 system CO<sub>2</sub> is adsorbed in a column filled with zeolite material. Consequently graphite is produced by reducing the CO<sub>2</sub> with hydrogen on an iron catalyst (Wacker *et al.*, 2010). Punches of 1.9 cm in diameter were used for graphitization of the aerosol filters before <sup>14</sup>C analysis. From 3 to 14 punches of the filter were used for making one graphite sample. The quantity of punches depended on the carbon content on each filter. AGE-3 system is capable of graphitizing the sample with the carbon amount exceeding 0.2 mg. Each punch was packed into the tin capsule and combusted in EA. CO<sub>2</sub> formed from several punches of one filter was collected in one of the reactors of AGE-3 and graphitized to get graphite samples.

### Measurements

Aerosol samples were analyzed for the total carbon content and their stable carbon isotopic compositions using an elemental analyzer (EA, Thermo FlashEA 1112) connected to the isotope ratio mass spectrometer (IRMS, Thermo Delta V Advantage). For broader description of the equipment parameters see Garbaras *et al.* (2008).

Stable carbon isotopic ratio data presented here are expressed as δ<sup>13</sup>C relative to the Pee Dee Belemnite (PDB) standard as follows:

$$\delta^{13}\text{C} = \left[ \left( R_{\text{sample}} - R_{\text{standard}} \right) / R_{\text{standard}} \right] \times 1000 \text{ (‰)} \quad (1)$$

Here  $R_{sample}$  and  $R_{standard}$  are the ratios of  $^{13}\text{C}$  to  $^{12}\text{C}$  in the sample and the standard (referred to as PDB), respectively. As standards caffeine IAEA-600 ( $\delta^{13}\text{C} = -27.771 \pm 0.043\text{‰}$ ) and oil NBS-22 IAEA ( $\delta^{13}\text{C} = -30.031 \pm 0.043\text{‰}$ ) were used. As a laboratory working standard, EMA P2 (Elemental Microanalysis,  $\delta^{13}\text{C} = -28 \pm 0.1\text{‰}$ ) was used.  $\delta^{13}\text{C}$  analysis included filter blank analysis. Sampling was performed during relatively high concentration of aerosol particles, sometimes during smog conditions. The signal intensity of blank filters was much smaller comparing to the loaded filters, but we took into account the blank filter influence on the stable carbon isotope ratio value. Based on the inter-laboratory trials, the accuracy of the IRMS system is better than 0.2‰.

The  $^{14}\text{C}/^{12}\text{C}$  ratios in the graphitized aerosol samples were measured using the 250 kV single stage accelerator mass spectrometer (SSAMS, NEC, USA). An accuracy of the measured  $^{14}\text{C}/^{12}\text{C}$  ratio was better than 0.3%. The ion beam was calibrated using Alfa Easer Black Carbon powder. The latter standard is good for estimation of the instrument background value. In this way the estimated SSAMS background was  $6.69 \times 10^{-4} f_M$  (fraction of modern carbon). The graphitized phthalic acid was used for estimation of the background of analysis. It was determined to be  $2.45 \times 10^{-3} f_M$ . OxII (NIST SRM 4990c, USA) standard was used as a reference material (percent of modern carbon (pMC) value of 134.07). For the isotopic fractionation correction the ratio of  $^{13}\text{C}$  to  $^{12}\text{C}$  was used.

$^{14}\text{C}$  results are reported as fraction of modern carbon ( $f_M$ ), the fraction of the measured  $^{14}\text{C}/^{12}\text{C}$  ratio related to the  $^{14}\text{C}/^{12}\text{C}$  ratio of the reference year 1950 (Stuiver and Polach, 1977) is calculated by a following equation:

$$f_M = \frac{(^{14}\text{C}/^{12}\text{C})_{sample}}{0.749(^{14}\text{C}/^{12}\text{C})_{OxII}} \quad (2)$$

Four aerosol samples were measured at Lund radiocarbon laboratory (Geocentrum II Lund University, Sweden). Later  $^{14}\text{C}$  analysis was performed in all 11 aerosol samples (including four earlier samples) at National Electrostatics Corporation (NEC, USA). Data of these four samples showed a good match in a range of expanded uncertainty of  $k = 2$ . The comparison between two laboratories is shown in Table 1.

$^{14}\text{C}$  excess from nuclear bomb tests due to thermonuclear weapons tests during 1950s and 1960s needs to be corrected. Other authors have indicated that the present-day value of atmospheric  $\text{CO}_2$  is around 1.04 (Levin et al., 2010; Genberg et al., 2011). Fraction of modern carbon of carbonaceous aerosol particles derived from wood combustion is in the

range of 1.08–1.30 depending on the age of the wood (Szidat et al., 2006; Szidat et al., 2009; Genberg et al., 2011; Minguillón et al., 2011). Szidat et al. (2009) suggested  $f_M$  value of 1.16 for carbonaceous aerosols from residential wood burning using 30–50-year-old plants. Minguillón et al. (2011) recommended  $f_M = 1.083$  corresponding to emissions from the burning of 25 years-old trees.  $f_M$  of biogenic primary and secondary organic aerosol are close to  $f_M$  of contemporary biomass (around 1.04). Carbonaceous aerosol particles derived from fossil fuel have  $f_M = 0$ . As suggested by Heal et al. (2011), a correction factor of 1.08 was used in this study. The value 1.08 was chosen as being within the range 1.04 (recent-grown crops and biogenic volatile organic compounds (VOCs) emissions) and 1.16 (tree wood 30–50 years-old), based on the expectation that the majority of non-fossil carbon in these samples is derived from truly contemporary sources rather than from 50 years-old biomass. The fraction of contemporary carbon ( $f_c$ ) and the fraction of fossil carbon ( $f_f$ ) in aerosol filters are estimated as follows (Levin and Hesshaimer, 2000):

$$f_{c(sample)} = \frac{f_{M(sample)}}{1.08} \quad (3)$$

$$f_f = 1 - f_c \quad (4)$$

The same principle of analysis will be used in the results and discussion chapter.

## RESULTS AND DISCUSSION

### TC Concentration and Temporal Variation

The measurements of the total carbon concentration in submicron aerosol particles ( $\text{PM}_{10}$ ) were performed in the vicinity of Vilnius during 10/27/2014–01/19/2015. To identify potential region sources of carbonaceous aerosol particles we calculated 2–3 days backward air mass trajectories and a mixed layer depth (MLD) for each aerosol sample using the NOAA Hysplit model (Draxler and Rolph, 2013).  $\text{PM}_{10}$  samples have been selected for analysis according to four geographical sectors. Sector 1 represents air masses coming from the North Atlantic Ocean, the Northern Sea and Scandinavia and classified as „clean“ sector. Sector 2 is characterized by air masses coming from Western Europe. Sector 3 describes air masses passing over Central and Southern Europe and southern Belarus. Sector 4 represents eastern air masses coming from Belarus, northern Ukraine and Russia. 2–4 sectors were classified as “polluted” sectors characterized by various types of carbonaceous pollution sources such as petrol and diesel emissions, oil

**Table 1.** Results of four aerosol filters which were measured in USA and Lund radiocarbon laboratories.

Sampling period	USA-SSAMS, $f_M$	LUND-SSAMS, $f_M$
10/30/2014–10/31/2014	$0.74 \pm 0.01$	$0.72 \pm 0.01$
11/05/2014–11/07/2014	$0.79 \pm 0.01$	$0.80 \pm 0.01$
11/14/2014–11/17/2014	$0.87 \pm 0.01$	$0.87 \pm 0.01$
12/23/2014–12/26/2014	$0.76 \pm 0.01$	$0.74 \pm 0.01$

and coal combustion, and biomass burning. Coal is used as a fuel in neighboring Poland during cold season. In the Western Europe the fossil fuel is used in the industry and transportation. In the eastern part of the Europe wood is used for the domestic heating. Typical backward trajectories showing different air mass transport pathways are given in Fig. 1.

Filter samples, which could not be attributed to any of the sectors, are labeled as “undefined” and were not analyzed. Thus, 11 aerosol samples representing different regional sources were selected for analysis.

The concentration of total carbon in  $PM_{10}$  is presented in Fig. 2. Results showed a significant variation of TC concentration in the range  $1.3$  and  $9.6 \mu\text{g m}^{-3}$ . The average for the whole measurement period was  $4.47 \mu\text{g m}^{-3}$ . The changes in TC concentrations may be explained by the influence of long-range transport of carbonaceous aerosol particles and meteorological parameters.

The lowest TC concentrations ( $1.32 \mu\text{g m}^{-3}$ ) were registered during northerly air flow. The highest levels of TC concentration (up to  $9.6 \mu\text{g m}^{-3}$ ) were registered in the most polluted southern air masses. The TC concentration ranges are significantly lower ( $3.6 \pm 1.3 \mu\text{g m}^{-3}$ ) in western and eastern sectors. However, the range of the TC

concentration during clean periods (30–31 October 2014) overlaps somewhat with that during polluted air masses. This would imply that the difference in TC concentration levels is based not only on the strength of emission sources, long-range transport, but also on the dispersion properties of the boundary layer (mixed layer depth). This suggests that meteorological conditions (low mixed layer depth) and local pollution sources during 30–31 October 2014 outweigh the long-range transport effect at the urban site.

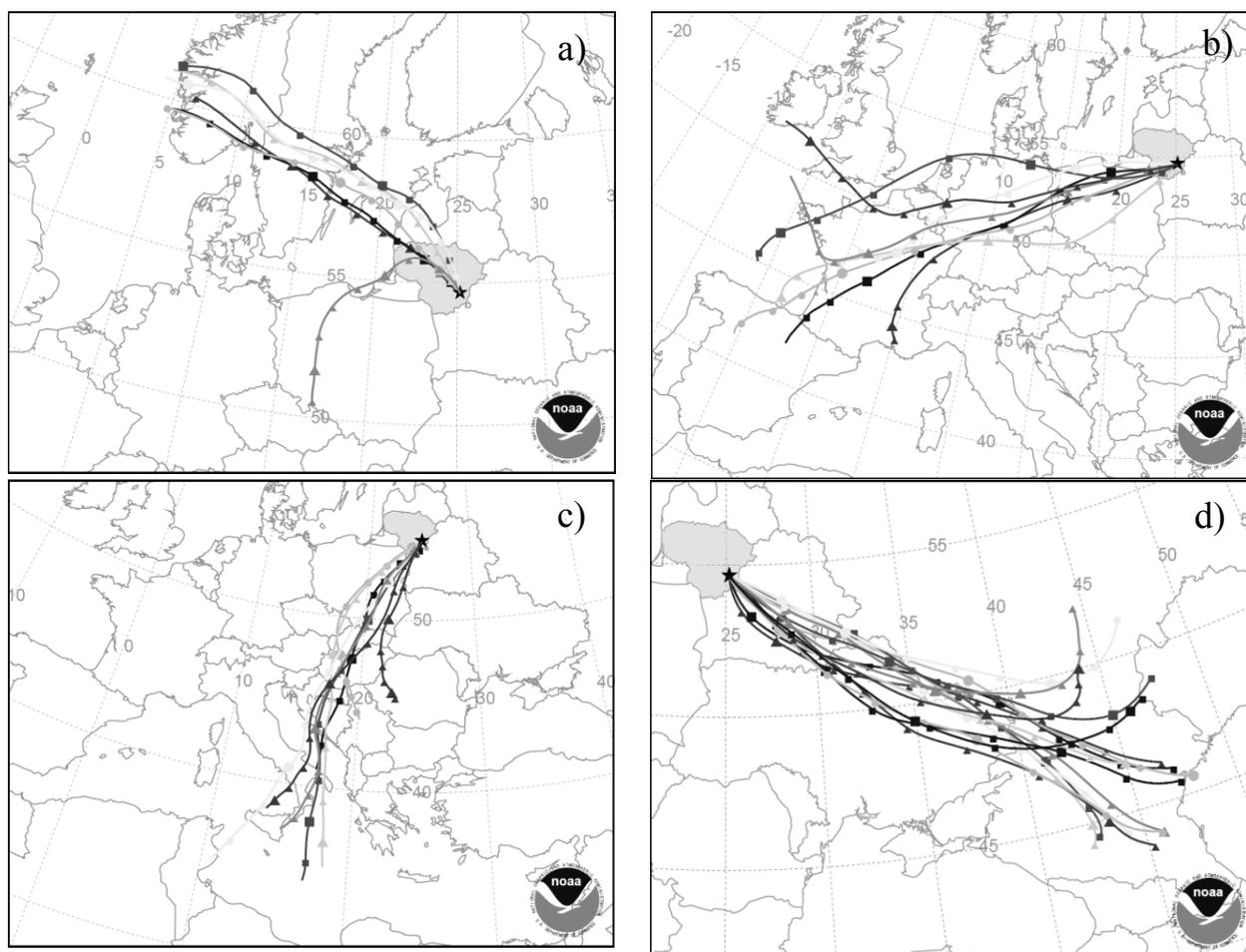
We found no correlation of temperature with TC concentration. As mentioned above (section 2.1) the wind direction was prevailing from south and east (regions without intensive local pollution sources). This finding suggested that TC concentration is not associated with the wind direction, but more related with long-range transport.

It can be concluded that, in addition to the air mass origin, the meteorological conditions such as the mixed layer depth can influence TC concentrations.

#### Quantification of Fossil and Non-Fossil Sources

We measured radiocarbon in the aerosol filters in order to distinguish modern (biomass) aerosol sources from the fossil fuel (coal, diesel and gasoline) emitted particles.

The fractions of contemporary carbon ( $f_c$ ) values in Vilnius



**Fig. 1.** Typical air mass backward trajectories for a) sector 1; b) sector 2; c) sector 3; d) sector 4. Description of four geographical sectors is given in the text.

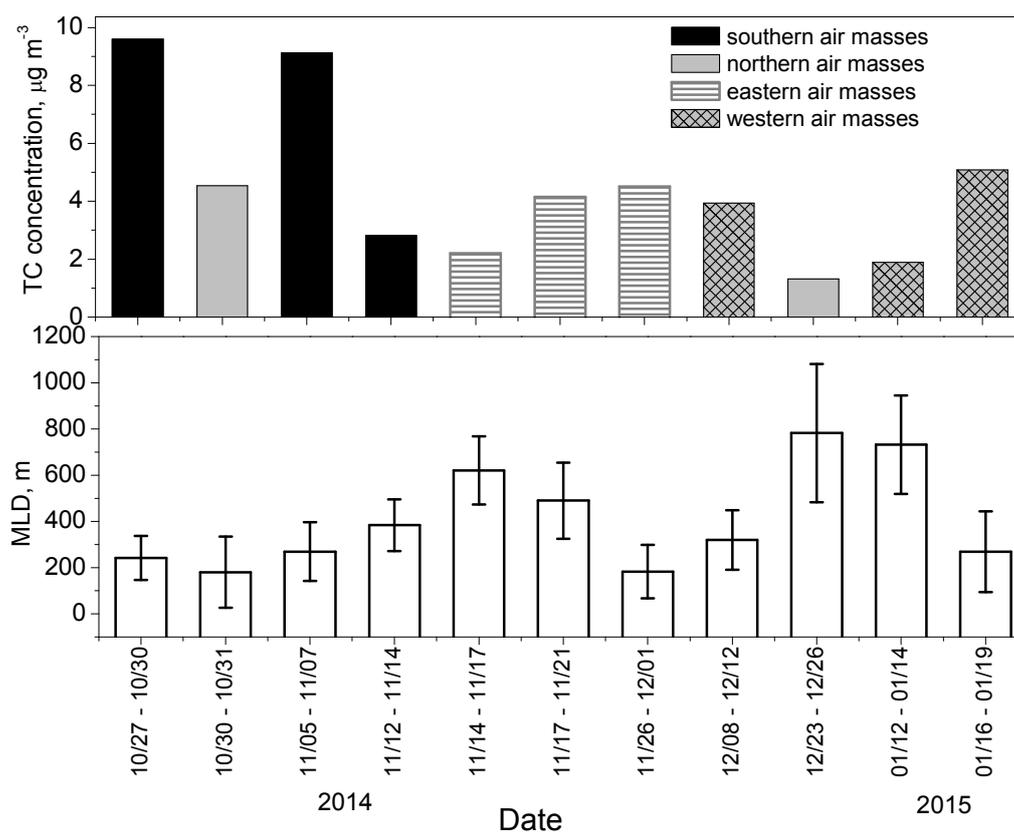


Fig. 2. TC concentrations and mixed layer depth (MLD) during 10/27/2014–01/19/2015 in Vilnius.

are presented in Table 2.  $f_c$  ranged from 0.57 to 0.84, indicating that contemporary sources are prevailing in Vilnius during wintertime. Similar values have already been found at other urban sites in Europe (Szidat *et al.*, 2006, 2009; Minguillón *et al.*, 2011). Tanner *et al.* (2004) demonstrate that contemporary carbon in winter was mainly from residential wood burning activities and agricultural waste incineration. The biogenic-derived carbonaceous aerosol content is expected to be small in winter because of the reduced biogenic primary aerosol emission as well as reduced secondary organic aerosol (SOA) formation from biogenic VOCs at lower temperature (Jordan *et al.*, 2006). In this study, the high average  $f_c$  value ( $0.71 \pm 0.08$ ) in winter exhibited biomass-dominated carbon signatures, which demonstrated that biomass burning for residential heating had the high impact on air quality at the Vilnius site.

Fig. 3 shows a scatter plot of  $f_c$  and TC concentration. There is no significant correlation ( $r^2 = 0.17$ ) between  $f_c$  and the TC concentration. Our observation demonstrated (section 3.1) that TC concentrations were influenced not only by source emissions but also by the meteorology. The weak correlation between  $f_c$  and the TC concentration has been observed in previous studies (Buchholz *et al.*, 2013; Dusek *et al.*, 2013). This would imply that anthropogenic fossil pollution is quantified much precisely with the  $^{14}\text{C}$  content rather than with the absolute TC concentration.

As shown in Fig. 4, the variation of the contemporary and fossil carbon content of  $\text{PM}_{10}$  depended on the air mass origin. As seen in Fig. 4 the  $f_c$  value amounted to 0.77 in

southern and eastern air masses. The western air masses have much lower value of  $f_c$  (0.6). The west European region has been considered as the most severely polluted area and industrial emissions, coal burning and automobile emissions are considered as major contributors. The more pronounced fossil signal in Vilnius ( $f_f = 0.4$ ) suggested that the anthropogenic emission from west European industrialized areas (Germany, Poland) had a major impact on the regional air quality.

#### $^{14}\text{C}$ and $^{13}\text{C}$ Based Sources Apportionment

We applied the isotope mixing model for the determination of sources of aerosol particles during cold season in the suburban site of the Vilnius city. We assumed that main sources for the aerosol particles during the investigation period were biomass burning, traffic and coal combustion emissions. The measured  $\delta^{13}\text{C}$  value represents a mix of all sources and can be expressed as follows:

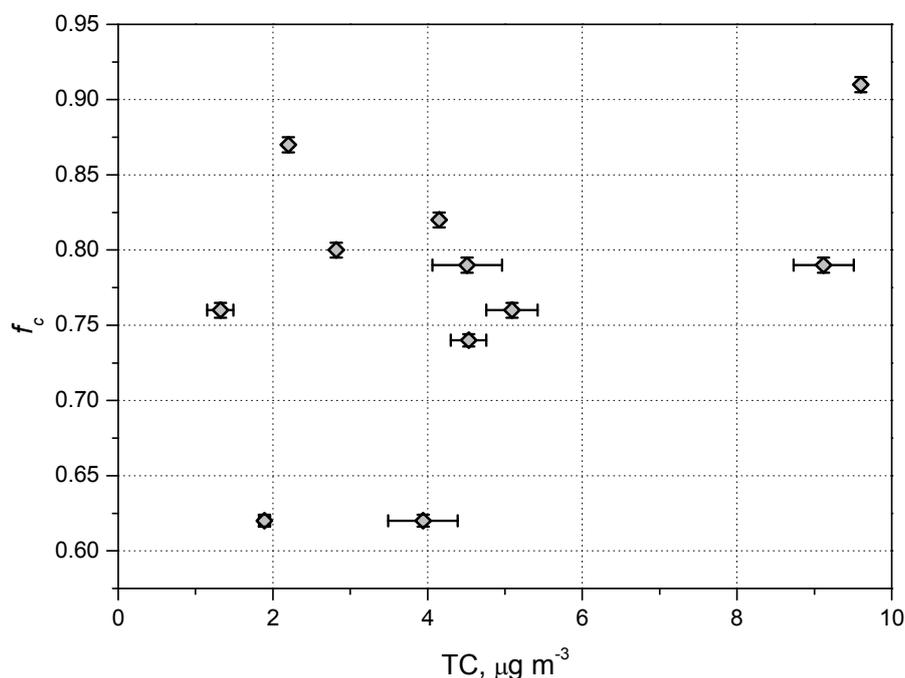
$$\delta^{13}\text{C} = \delta^{13}\text{C}_{\text{biomass}} \times k_1 + \delta^{13}\text{C}_{\text{coal}} \times k_2 + \delta^{13}\text{C}_{\text{traffic}} \times k_3 \quad (5)$$

where  $\delta^{13}\text{C}_{\text{biomass}}$ ,  $\delta^{13}\text{C}_{\text{coal}}$ ,  $\delta^{13}\text{C}_{\text{traffic}}$  are stable carbon isotope ratio values of biomass, coal and traffic emissions, respectively. The coefficients  $k_1$ ,  $k_2$ ,  $k_3$  are relative contributions of biomass burning, coal combustion and traffic related aerosol sources, respectively, and can be expressed as:

$$k_1 + k_2 + k_3 = 1 \quad (6)$$

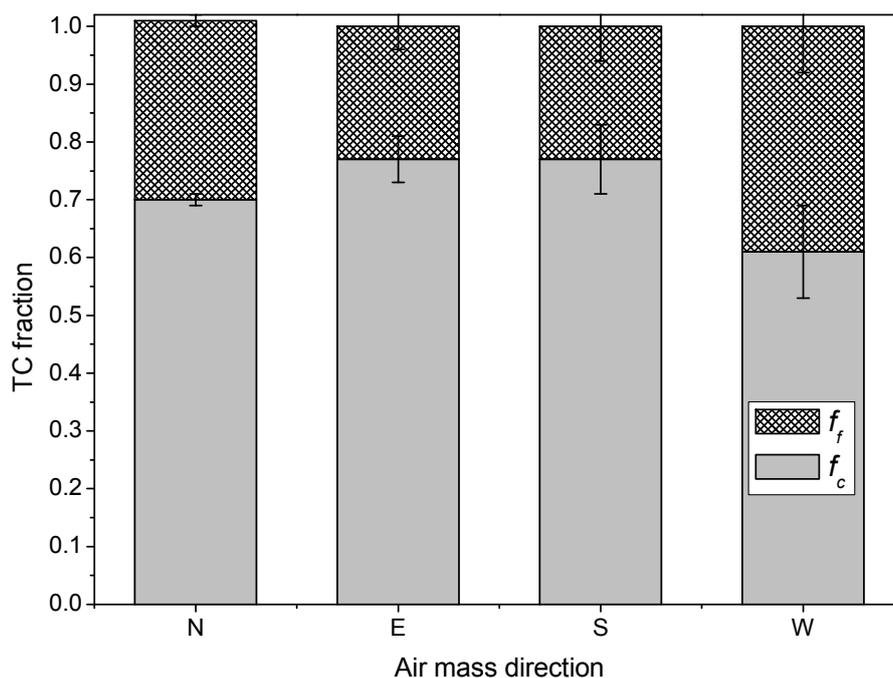
**Table 2.** The values of  $f_c$  in TC for the samples in different air mass origin.

Date	$f_c$	$f_f$	Air mass trajectory
10/27/2014–10/30/2014	0.84	0.16	S
10/30/2014–10/31/2014	0.69	0.31	N, NW
11/05/2014–11/07/2014	0.73	0.27	S
11/12/2014–11/14/2014	0.74	0.26	S
11/14/2014–11/17/2014	0.81	0.19	E
11/17/2014–11/21/2014	0.76	0.24	E
11/26/2014–12/01/2014	0.73	0.27	E
12/08/2014–12/12/2014	0.57	0.43	W
12/23/2014–12/26/2014	0.70	0.30	N, NW
01/12/2015–01/14/2015	0.57	0.43	W
01/16/2015–01/19/2015	0.70	0.30	W, SW

**Fig. 3.** Dependence of the fraction of contemporary carbon ( $f_c$ ) on the total carbon concentration in the  $PM_{10}$  aerosol filters at Vilnius background site, Lithuania.

The main biomass species used for domestic heating include pine, spruce, birch, and alder. From the controlled biomass burning experiment it was established that during burning of the mentioned species only small isotopic fractionation (0.6–0.9‰) was observed between original material and produced aerosol particles (Garbaras *et al.*, 2015). Relying on these burning experiments we assume that in Lithuania and neighboring countries aerosol particles from the biomass burning have  $\delta^{13}C$  values in the range from –26 to –27‰.  $\delta^{13}C$  of coal emission is about  $-24.5 \pm 0.5\text{‰}$  (Górka *et al.*, 2014). The  $\delta^{13}C$  values of diesel and gasoline fuel in Lithuania are about  $-31.6 \pm 0.1\text{‰}$  (Mašalaitė *et al.*, 2012). Taking into account fractionation ( $\sim 2.7\text{‰}$ ) during burning of diesel and gasoline in internal combustion engines (Widory, 2006), we can expect  $\delta^{13}C$  values for the traffic-derived aerosol to be in the range of –28 to –29‰. Generally it is assumed that aerosol aging changes the carbon isotope ratio in the aerosol particles. Usually particles become more

isotopically enriched comparing to the precursor gasses due to ongoing photochemical reactions. Rudolph (2007) has demonstrated that isotope fractionation can occur during reactions of volatile organic compounds with oxidants. Few studies have examined isotope fractionation during SOA formation (Irei *et al.*, 2006; Fisseha *et al.*, 2009; Irei *et al.*, 2011). Wang and Kawamura (2006) showed that aging removes lighter carbon isotopes from particulate phase in the atmospheric oxidation processes. Kirillova *et al.* (2013) demonstrated that aerosol transported longer distances in India have larger differences in  $\delta^{13}C$  signature between WSOC and total organic carbon. We used TC isotope ratio measurement values as input for the mass balance equation. It means that the extent of fractionation due to aging is unknown because samples contain both organic and elemental carbon. More laboratory aging studies are needed for expanding the list of individual compounds and their fractionation factors due to aerosol aging. The uncertainties for the source



**Fig. 4.** The fraction of contemporary ( $f_c$ ) and fossil ( $f_f$ ) carbon in the aerosol filters in northern (N), eastern (E), southern (S) and western (W) air masses.

definition by using stable carbon isotope ratio are within the range of one permil and these uncertainties are bigger than the accuracy of the measurement itself. The reason for the scatter of  $\delta^{13}\text{C}$  values in the source material is that specific sources are not of the same origin (for example different tree types), and also photochemical transformation can occur.

$\delta^{13}\text{C}$  values in  $\text{PM}_{10}$  fraction ranged from  $-26.22$  to  $-27.36\text{‰}$  during the investigated period (Fig. 5). The variation of carbon isotope ratio between  $\text{PM}_{10}$  samples was relatively small, but it does not reflect the aerosol source distribution, because mixture of all three sources makes up the measured  $\delta^{13}\text{C}$  values.

We included radiocarbon analysis in the model which allows estimating the input from modern (biomass) and fossil sources (coal and traffic emissions). We assume that in winter the relative contribution of biomass burning is equal to  $f_c$  ( $k_1 = f_c$ ) and in this modern fraction there is no input from the vegetation. Combining (5) and (6) it follows that:

$$k_2 + k_3 = 1 - k_1 = 1 - f_c = f_f \quad (7)$$

$$k_3 = f_f - k_2 \quad (8)$$

$$\delta^{13}\text{C} = \delta^{13}\text{C}_{\text{biomass}} \times f_c + \delta^{13}\text{C}_{\text{coal}} \times k_2 + \delta^{13}\text{C}_{\text{traffic}} \times (f_f - k_2) \quad (9)$$

We solve Eq. (9) to find coefficient  $k_2$ , while coefficients  $k_1$  and  $k_3$  are found from the Eqs. (7) and (8).

The stable carbon isotope ratio from biomass and traffic related emissions can overlap, but it differs for the coal related emissions. By combining the stable carbon and radiocarbon analysis we were able to quantify the input from the biomass

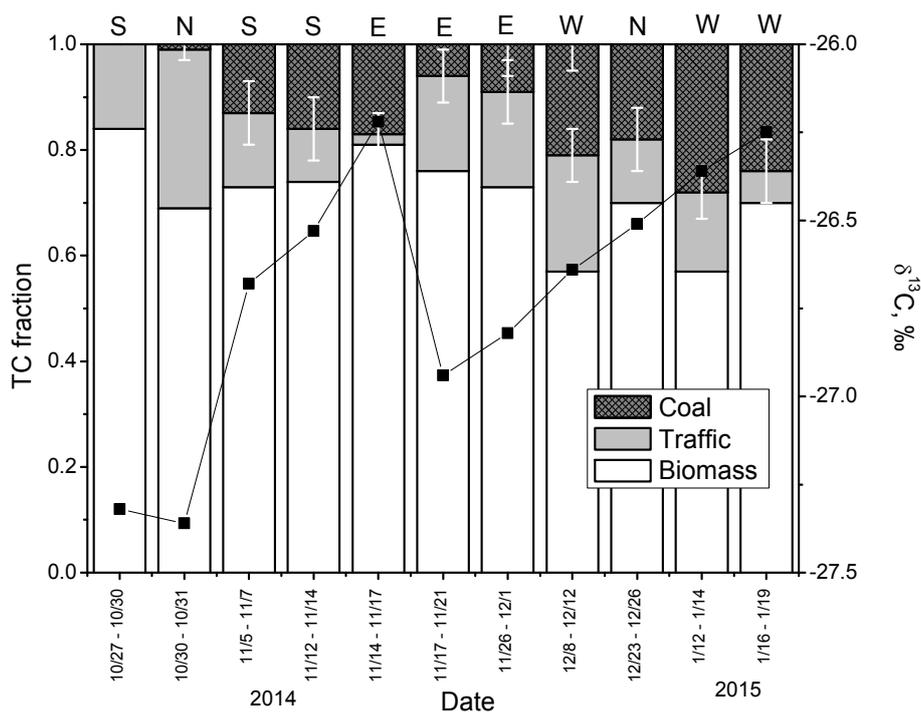
burning, coal and traffic emissions (Fig. 5).

The largest coal input to the aerosol particles was registered during western air mass transport. It can be due to the air mass transport from Poland, where coal is widely used for the energy production. Górká et al. (2014) using isotope mass balance equations found that in Wrocław city (Poland) coal-derived aerosol particles comprise up to 41% of elemental carbon fraction and are comparable to the traffic related emissions.

Aerosol sources of biomass burning were dominant during atmospheric inversion events and can be attributed to the local domestic heating. In the end of the October (30–31 October) favorite meteorology conditions (low mixing layers depth and small wind) for the accumulation of the aerosol particles were observed. Environmental Protection Agency of Lithuania registered hourly  $\text{PM}_{10}$  concentration up to  $250 \mu\text{g m}^{-3}$  in these days. As shown in Fig. 5, the main aerosol fraction during smog was from biomass combustion ( $77 \pm 10\%$ ), and there were almost none coal combustion. Traffic emissions contributed about  $15 \pm 7\%$  during all investigated episodes (except 14–17 November 2014), and it shows almost constant input of this source to the total emission inventory. In the mid of the November (14–17 November 2014) mixing layer depth and air mass transport from the east were notably high. The relative small input from the traffic could be explained by these circumstances.

## CONCLUSIONS

Radiocarbon and stable carbon isotope investigation of  $\text{PM}_{10}$  were performed at suburban site of the Vilnius city ( $54^\circ 64'\text{N}$ ,  $25^\circ 18'\text{E}$ ) during a period of 10/27/2014–01/19/2015.



**Fig. 5.** Estimated fraction of biomass burning, traffic emissions and coal combustion in the aerosol particles in Vilnius. Air masses directions are indicated on the top of the figure.

Concentrations of total carbon in  $\text{PM}_{10}$  fraction were in the range of  $1.3\text{--}9.6 \mu\text{g m}^{-3}$ , with an average of  $4.47 \mu\text{g m}^{-3}$ . Our observation has demonstrated that a temporal variation of TC concentrations is determined by regional emissions and boundary layer dynamics (mixed layer depth).

Measurements of  $^{14}\text{C}$  revealed large contribution of contemporary carbon ( $f_c$ ) in  $\text{PM}_{10}$  ranging from 0.57 to 0.84. The high  $f_c$  values in cold season indicated that biomass burning for residential heating had the high impact on air quality at the Vilnius site. The variation of the contemporary and fossil carbon content of  $\text{PM}_{10}$  can be attributed to different air mass origin. The highest  $f_c$  values (0.77) were registered in southern and eastern air masses. However, the  $f_c$  were significantly lower (0.6) in the westerly air masses, implying that the fossil fuel emission from west European industrialized areas contributed to regional air pollution.

Employing the isotope mass balance model we determined that the contribution of traffic emissions was almost constant ( $15 \pm 7\%$ ) during all investigated episodes, while the content of coal-derived aerosol particles depended on air mass transport. The largest coal input (up to 40%) to the aerosol particles was observed during western air masses.

The combination of  $\delta^{13}\text{C}$  values with radiocarbon data is a powerful tool in the studies of the aerosol particle source apportionment because in addition to distinguishing fossil and non-fossil aerosol sources it allows the quantification of the amount of coal-derived aerosol particles.

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