Monitoring of carbon isotope composition of snow cover for Tomsk region

P A Akulov¹, Y V Volkov¹²,3, D A Kalashnikova¹², V N Melkov¹, G V Simonova¹² and V A Tartakovskiy¹

¹Institute of Monitoring of Climatic and Ecological Systems SB PAS, Russia, 634055, Tomsk, Akademicheskiy av. 10/3,
²National Research Tomsk State University, Russia, 634050, Tomsk, Lenina av. 36
³National Research Tomsk Polytechnic University, Russia, 634050, Tomsk, Lenina av. 30

E-mail: galina_simonova@inbox.ru

Abstract. This article shows the potential of using δ¹³C values of pollutants in snow pack to study the human impact on the environment of Tomsk and its surroundings. We believe that it is possible to use a relation between the isotope compositions of a fuel and black carbon for establishing the origin of the latter. The main object of our investigation was dust accumulated by the snow pack in the winter of 2015-2016. The study of dust samples included the following steps: determination of the total carbon content in snow pack samples of Tomsk and its surroundings, extraction of black carbon from the dust, as well as the determination of δ¹³C values of the total and black carbon accumulated in the snow pack. A snow survey was carried out on the 26th of January and on the 18th of March. The relative carbon content in the dust samples was determined by using an EA Flash 2000 element analyzer. It varied from 3 to 24%. The maximum carbon content was in the dust samples from areas of cottage building with individual heating systems. The δ¹³C values of the total and black carbon were determined by using a DELTA V Advantage isotope mass spectrometer (TomTsKP SB RAS). The isotope composition of black carbon corresponded to that of the original fuel. This fact allowed identifying the origin of black carbon in some areas of Tomsk.

1. Introduction

The snow cover is a unique environment which deposits contaminants emitted into the atmosphere and then fed into the soil and surface water. The study of the chemical composition of the snow cover allows for a rapid geo-ecological assessment of urbanized areas. Observations of the snow cover are made by regional centers for monitoring environmental pollution of the Russian Hydro-Meteorological Centre, as well as by units of stationary networks for monitoring precipitation and background biosphere reserves. Control is performed mainly over 32 impurities [1]. This list does not include «black» carbon which is the main component of soot, i.e. a product of incomplete combustion of hydrocarbon fuels and biomasses. According to numerous recent studies [2], [3], it is «black» carbon that has a significant impact on public health and the climate through the process of changing the albedo of snow. «Black» carbon is released into the atmosphere as a result of forest fires, vehicle...
operation, activities of industrial enterprises and housing and communal services. One of the problems associated with the assessment of «black» carbon emissions is to determine the sources of its origin prevailing over a particular territory. We believe that, in order to solve this problem, it is possible to use the relation between the isotopic composition of a fuel and that of «black» carbon.

2. Materials and methods
The selection of snow samples was carried out on January 26 and in the period of the maximum snow accumulation on March 18, 2016. The samples were taken at 17 points (Fig. 1), six of them being background and located outside the city, and the rest being located in the areas with varying degrees of the anthropogenic load.

![Figure 1. Location of points for selection of snow cover samples.](image)
⊗ - background areas; О - areas with different degrees of anthropogenic load.

The process of sampling was carried out according to the procedure presented in [1] within areas of the size 5×5m using the envelope method. Snow cores were selected over the whole snow depth with the help of a plastic pipe with a diameter of 10cm and then packed in double sealed plastic bags. Melting of snow occurred under laboratory conditions in the packaged form. During the sampling, at each point, the average height of the snow cover was determined. The resulting melted water was filtered through the paper filter "blue ribbon". The weight of the dust deposited on the filters was determined as the difference in the weights of the clean pre-dried filter and the filter with the settling.

The dust load $P_n$ on the snow cover was calculated by the formula [4]:

$$P_n = \frac{P_0}{S \cdot t}$$

(1)

where $P_n$ is the dust mass in the snow sample (mg); $S$ is the area of the cross section of the pit or the sampler which was used for sampling (m$^2$); $t$ is the starting time point of the snow cover formation prior to the day of sampling. Calculations were performed for two periods: from the date of completed snow cover formation to 01.26.2016 and from 01.27.2016 to 03.18.2016. The difference between the mass of dust samples (accumulated since the formation of snow cover until 18.3.2016 and 26.1.2016), was used as the mass of dust for estimating dust load on the snow cover of the second period.

In the analysis and interpretation of the research results we used the average daily temperature and the daily precipitation calculated according to the monitoring data of the Hydro-Meteorological
Observatory of the Institute of Monitoring of Climatic and Ecological Systems SB RAS. The starting date of the completed snow cover formation was accepted as November 1, 2015.

In the dust samples we determined the relative carbon content (%) and the ratio of its stable isotopes $^{13}\text{C}/^{12}\text{C}$ in the form:

$$\delta^{13}\text{C} = \left[\frac{R_s - R_w}{R_w}\right] \cdot 1000 \text{ppm}$$

where $R_s$ is the ratio of $^{13}\text{C}/^{12}\text{C}$ in the sample and $R_w$ is the ratio of $^{13}\text{C}/^{12}\text{C}$ in the standard, i.e. carbon of the Belemnitella americana fossil clam (referred to as PDB) [5].

It appeared possible to separate pyrogenic «black» carbon from some of the dust samples. For the purpose of this, we used the method of samples preparation described in [6]. The dust samples were rectified of carbonates, silicon compounds, organic substances and kerogens by a sequential treatment with three-mole hydrochloric HCl acid (3M), a mixture of hydrofluoric acid and hydrochloric acid HF (10M)/HCl(1M) and oxidizing solution containing 0.1M $\text{K}_2\text{Cr}_2\text{O}_7$ solution in 2M $\text{H}_2\text{SO}_4$ at 55°C during 60 hours. For the samples containing 500 micrograms of “black” carbon or more, we determined the ratio $\delta^{13}\text{C}$.

The relative content and the isotopic composition of carbon in the dust samples were determined using the elemental analyzer EA Flash 2000 and the isotopic mass spectrometer DELTA V Advantage, respectively (Tomsk Centre for Collective Use SB RAS).

3. Results and discussion

According to the observations of the Hydro-Meteorological Observatory of the Institute of Monitoring of Climatic and Ecological Systems SB RAS (HMO IMCES SB RAS), the permanent snow cover was formed by November 1, 2015. The greatest part of winter precipitation equal to 106.4 mm occurred in November and December. In these months, the increase in thickness of the snow cover showed the maximum rate (Fig. 2a, b). In January, the amount of precipitation was minimal for the current winter (only 5.8mm), precipitation being observed during 5 days. The increase in thickness of the snow cover was minimal. At the time of the first snow survey the average snow depth was 39.2cm. Within the study area, this value changed in the range of 27.6 – 47.4cm (Table 1). In February and March there appeared about 42mm of precipitation and the snow depth increased by an average of 5.6cm. At the time of the snow surveys on 03.18.16 the average height value was 44.9cm, the territory of the snow depth ranging from 31.6 to 63.6cm.

![Figure 2](image_url)

**Figure 2.** Monthly average temperatures and precipitation from November 2015 to March 2016 (a) and daily values of snow depth (b) according to HMO IMCES SB RAS.

The dust load on the snow cover corresponds to the presumed distribution of the anthropogenic load within the study area. Within the city, the dust load on the snow cover is significantly higher. In the text bellow the values of dust load are given for two investigated periods accordingly. The minimum values were observed within the background areas. There are 1.3 – 12.6 mg/(m²•d) and 4.3 – 19.2 mg/(m²•d). The maximum values correspond to the areas located along the roads with heavy
traffic, including cargo transport, and in the areas of industrial facilities concentration (P8, P9, P10, P14): 114 – 1055 mg/(m²•d) and 40.9 – 2374 mg/(m²•d). An abnormally high value of the dust load in the P4 area in the second period is, apparently, due to the occurrence of temporary point source of pollution. The dust load on the areas located along busy roads mainly for cars and passenger vehicles (P11, P13, P15, P16) was 24.5 – 68.3 mg/(m²•d) and 6.7 – 36 mg/(m²•d) and in the areas of cottage building with individual heating systems (P7, P12, P17) – 14.7 – 30.4 mg/(m²•d) and 13.5 – 137 mg/(m²•d).

Table 1. Measured properties of snow cover.

| Point of sampling | Height of snow cover (cm) | Dust load (mg•m⁻²•d⁻¹) | Total carbon content (%) | δ¹³C_carbon (‰) | δ¹⁴C_black carbon (‰) |
|-------------------|---------------------------|-------------------------|--------------------------|-----------------|--------------------------|
| P1                | 40.6 51.4                 | 12.6 19.2               | 12 13                    | -28.60 -27.29   | -27.78                   |
| P2                | 33.6 36.2                 | 40.5 15.48              | 6                        | -28.22 -27.82   | -28.78                   |
| P3                | 37.0 51.0                 | 9.03 18.8              | 7 9                      | -26.87 -27.26   | -26.23 -27.26           |
| P4                | 27.6 31.6                 | 2.6 91.8               | 11                       | -29.16 -28.72   | -29.16 -28.72           |
| P5                | 53.0 63.6                 | 1.3 15.9               | 35                       | -28.32 -27.88   | -29.16 -28.72           |
| P6                | 31.8 32.4                 | 11 4.33                | 16                       | -26.67 -17.47   | -26.40 -17.47           |
| P7                | 37.2 32.4                 | 30.4 13.5              | 22                       | -26.30 -27.88   | -26.40 -27.88           |
| P8                | 45.2 38.2                 | 1055 2374              | 11 5.2                   | -21.90 -21.25   | -30.27 -29.77           |
| P9                | 38.2 48.2                 | 114 40.9               | 5 7.9                    | -26.73 -28.80   | -27.83 -28.36           |
| P10               | 38.3 39.8                 | 232 344                | 3 2.8                    | -26.90 -27.22   | -28.29 -29.52           |
| P11               | 45.8 56.8                 | 24.5 22.6              | 15 14                    | -25.40 -26.14   | -25.40 -26.14           |
| P12               | 41.2 49.6                 | 19.9 49                | 21 26                    | -26.40 -28.79   | -26.40 -28.79           |
| P13               | 39.4 36.8                 | 39.2 36                | 16 8.5                   | -25.50 -28.59   | -25.50 -28.59           |
| P14               | 39.4 36.6                 | 51.3 109               | 12 4                     | -26.00 -29.33   | -26.00 -29.33           |
| P15               | 39.4 49.8                 | 68.3 -                | 13 16                    | -27.10 -17.46   | -27.10 -17.46           |
| P16               | 38.0 47.7                 | 42.1 6.73              | 11 10                    | -28.80 -27.26   | -28.80 -27.26           |
| P17               | 47.7 61.0                 | 14.7 134.6             | 18 5                     | -26.80 -26.09   | -26.80 -26.09           |

* The measurement error of three replicates did not exceed ± 0.15 ‰.

Pollution of snow cover occurs as a result of capture and deposition of aerosols and fine dust particles by precipitation and direct deposition of pollutants from the atmosphere by gravity [1]. The ratio of the contributions made by these two mechanisms in the general contamination depends on many factors such as: the duration of the winter period, the frequency and intensity of precipitation, the size of aerosol or dust particles, the distance from the examined areas to local pollution sources and other. In the first period, the dust washout with precipitation was minimal, which was, apparently, reflected in the calculation of the dust load for two periods: 01.11.15 - 26.01.16 and 27.01.16 - 18.03.16. Within the second period the load was in most cases several times higher (Table 1).

Considering the carbon content in the dust samples obtained from the snow, we can roughly assess the contribution made by carbonaceous combustion products in the total pollution of the snow cover. In the obtained samples the relative content of carbon is small, varying between 3-24% in the samples from 26.01.16 and 6-86% in the samples from 18.03.16. The highest values were observed in the areas of cottage building for the first period 01.26.16 - 18-24% and for the second period 18.03.16 - 26-86%. In the dust samples carbon is present in the carbonates, organic substances (humic acids and plant materials) and in the form of soot. Under laboratory conditions, we determined a connection between carbon isotope relationships of different fuels and their combustion products (Table. 2) [7].
### Table 2. Isotopic composition of $\delta^{13}$C wood, peat, coal, kerosene and soot produced after combustion.

| Sample       | Pinus Sylvestris $\delta^{13}$C (‰) | Betula $\delta^{13}$C (‰) | Coal $\delta^{13}$C (‰) | Kerosene $\delta^{13}$C (‰) |
|--------------|------------------------------------|--------------------------|-------------------------|-----------------------------|
| Original sample | -27.33±0.1                       | -26.62±0.05              | -24.05±0.08             | -31.74±0.07                 |
| Charcoal     | -28.65±0.09                       | -28.72±0.12              | –                        | –                           |
| Soot         | -29.27±0.06                       | -25.12±0.1               | -24.20±0.05             | -30.02±0.06                 |

Considering the isotopic composition of the total carbon contained in the dust samples obtained from the snow, it is difficult to make a conclusion about a particular source of carbon origin (Tables 1 and 2). However, the isotopic composition of «black» carbon can be used to assess the original substance - fuel. Particularly, if within the investigated area «black» carbon is formed primarily as a result of combustion of one certain fuel. For example, the value $\delta^{13}$C=–24.7‰ of «black» carbon in the sample from the site located within a cottage area P7 corresponds to the value of coal soot. The isotopic composition of the P2 and P9 samples is the closest to the isotopic composition of soot resulting from burning wood. In case of furnace heating, the most commonly used wood is birch, pine being used less frequently. The isotopic composition of «black» carbon from the sample P8 (a road with heavy traffic of cars and trucks, located in the vicinity of a tank farm) corresponds to the isotopic composition of soot resulting from combustion of petroleum products.

### 4. Conclusions

The dust samples obtained from the snow cover formed in the winter 2015-2016 were investigated. As it was expected, the dust load was significantly higher in the city than outside. The maximum values of it were observed within the areas of industrial facilities concentration and in the areas located along the roads with heavy traffic, including cargo transport. However, the total carbon content was the highest in the dust samples from the areas of cottage building with individual heating systems. It was able to separate the sufficient amount of black carbon only from several dust samples. It turned out that in some areas of the city the carbon isotopic composition corresponds to supposed source of its origin. In the areas of cottage buildings with individual heating systems, the isotopic composition of black carbon corresponds to the coal and wood. In the vicinity of rural settlements the isotopic composition of black carbon corresponds to the wood. In the north of the city along the highway with heavy truck traffic near the oil depot the isotopic composition of black carbon corresponds to the fuel, obtained in the processing of petroleum products.

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