Identification of air pollution by macro-tracers for source apportionment

B Svedova1, J Ruzickova1, M Kubel1,2, H Raclavska1,3 and K Raclavsky1
1ENET Centre-Energy Units for Utilization of Non-traditional Energy Sources, VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic
2Institute of Environmental Engineering, Faculty of Mining and Geology, VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic
3Institute of Geological Engineering, Faculty of Mining and Geology, VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic

Abstract. Identification of air pollution sources in the city of Olomouc was performed during the heating and non-heating season 2016. The contributions of air pollution sources were determined by ratios and equations for organic carbon (OC), elemental carbon (EC), sulphates, nitrates, levoglucosan, etc. During the heating season, the concentration of EC was six times higher compared to the non-heating season.

1. Introduction
Atmospheric particles are generated through a variety of physical and chemical mechanisms from different sources, affecting the occurrence and representation of individual PM components [1]. Organic carbon (OC) and elemental carbon (EC) are products of incomplete combustion of fossil fuels, biomass and biofuels. Elemental carbon is only a primary product of imperfect combustion, whereas OC can also be of secondary origin, i.e. photochemical reactions of volatile organic compounds in the atmosphere [2]. OC and EC cannot be considered as typical “markers” but they can be successfully utilized to identify the type of combustion material [3]. The significance of EC increases during the winter months due to the greater extent of incineration in local furnaces [4]. Sulphates and nitrates can account for 30 to 60% of PM$_{2.5}$. By oxidizing precursor gases (SO$_2$) and nitrogen oxides (NO$_x$) in the atmosphere, sulphates and nitrates are generated as a product of some anthropogenic activities. The presence of sulphates in the aerosol is mostly the result of long-distance transmission, nitrates occur in local or regional sources [5]. Potassium is a water-soluble ion commonly used as a marker for the identification of biomass combustion [6], and it is present mainly in fine grain particles of diameter ≤ 1 µm [7]. Levoglucosan and mannosan are the main products of thermal decomposition of structural polysaccharides contained in biomass [8]. Levoglucosan is used as an indicator for wood burning emissions [9]. The ratio between the K$^+$/EC concentration is used as an indicator for biomass combustion. High K$^+$/EC ratios (range: 0.21-0.46) are typical for biomass combustion and low ratios (range: 0.025-0.09) for fossil fuel emissions [10]. The OC/levoglucosan ratio can be used to evaluate the contribution of OC emissions from biomass combustion [11]. According to Frey et al., 2006 [12], this ratio is 9.8 in the case of normal combustion of biomass, and 24.6 in the case of smouldering. The mean OC/levoglucosan ratio for biomass combustion is 14.2, but the ratio values for different types of wood ranged from 3.0 to 100 [13].

The EC/OC ratio for the exhaust gases from the combustion of diesel is around 1.2 and the ratio of EC/OC is 0.45 for the exhaust gas emissions from the combustion of petrol in cars with the catalyst.
Coal combustion has an EC/OC ratio of about 0.3, for wood combustion, the values range from 0.06 to 0.25, and ratio value for biogenic emissions is 0.03 [14].

The aim of the contribution was to research the chemical character of PM$_{10}$ and to assess the sources of air pollution at the localities of Olomouc Hodolany and Klášterní Hradisko during the summer and winter season 2016 based on information on the content of organic, elemental carbon and other components contained in PM.

2. Sampling site and methods
Dust particles (PM$_{10}$) were collected on quartz fibre filters using a high-volume sampler. PM sampling took place from 27th to 29th July 2016 (summer) and from 5th to 7th December 2016 (winter) at both localities at the same time. The sampling site Olomouc Klášterní Hradisko (1) is in front of a house; there is a field in the immediate surroundings. The site is in an area without direct industrial influence. The sampling site Olomouc Hodolany (2) is situated in a garden in front of a house, adjacent to a field and in vicinity there is a built-up area with houses, see figure 1.

![Figure 1. Sampling sites Klášterní Hradisko and Hodolany.](image-url)

For assessment of the impact of anthropogenic contamination, OC and EC measurements were made by thermo-optical analysis on an OC/EC analyser (SunSet Lab) using the EUSAAR 2 temperature protocol. Determination of water soluble sulphates, nitrates and potassium in PM was done by dissolving PM$_{10}$ particles in deionized water with subsequent determination of ions using the ion chromatography method on the Metrohm 850 Professional IC instrument [15] according to ISO 10304 Water quality - Determination of dissolved anions by liquid chromatography of ions and ISO 14911 Water quality - Determination of dissolved Li$^+$, Na$^+$, NH$_4^+$, K$^+$, Mn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ using ion chromatography. Determination of anhydrosaccharides and organic compounds was performed using pyrolysis gas chromatography mass spectrometry (Py/GC/MS).

3. Results
The OC, EC, OM and PM$_{10}$ concentrations for both localities during summer and winter sampling in 2016 are shown in table 1. During the heating season (winter season), the PM$_{10}$ daily limit (50 µg/m$^3$ according to the Act on Air Protection 201/2012 Coll.) was slightly exceeded at the Hodolany locality.

During the heating season, the PM$_{10}$ concentration was about twice as high at both localities. In the heating season, there was a 2.6 times higher increase in OC concentrations at both localities and a nearly 6-fold increase in EC concentrations compared to the non-heating season. The increase in OC and EC concentrations is due to a higher intensity of incineration processes during the winter months (combustion of fossil fuel and biofuels).
Table 1. OC, EC, and PM10 concentrations in heating and non-heating season.

| Locality                    | PM10 (µg/m³) | OC (%) | EC (%) | OM* (%) | OC/EC | EC/PM10 (%) | OM in PM10 (%) |
|-----------------------------|--------------|--------|--------|---------|-------|-------------|----------------|
| Hodolany- summer            | 28.46        | 8.22   | 0.80   | 11.51   | 41.83 | 8.80        | 58.57          |
| Hodolany - winter           | 50.93        | 21.31  | 4.48   | 29.83   | 28.90 | 2.80        | 40.50          |
| Klášterní Hradisko - summer | 22.77        | 6.23   | 0.77   | 8.72    | 36.02 | 9.92        | 50.43          |
| Klášterní Hradisko - winter | 45.06        | 16.23  | 4.47   | 22.72   | 27.30 | 3.40        | 38.30          |

OM value (organic matter) = OC concentration × 1.4. The value 1.4 is mostly used for both urban and rural areas [4].

In the winter season, 288 organic compounds were identified in the PM10 samples, which is about 3 times more than in the summer season (97 organic compounds). Sources of organic pollution include both anthropogenic activities and natural sources of biogenic compounds. The dominant group of organic compounds in the summer season were monocyclic arenes (aromatic hydrocarbons containing only one benzene nucleus) that are part of emissions from the transport. During the heating season, concentrations of all organic compounds with exception of monocyclic arenes (especially benzene compounds and BTEX group compounds) increased. Carboxylic acids (organic acids containing the carboxyl group -COOH) represented a dominant group in PM10 during the heating season at both locations. Anthropogenic sources of carboxylic acids are primarily the combustion of biomass and solid fossil fuels, or road transport. Also, polycyclic aromatic hydrocarbons (PAHs) showed significantly higher concentrations at both localities during the winter than other organic compounds. Sources of carboxylic acids, PAHs, sulphur-containing compounds, alkenes are primarily combustion processes (fossil fuel combustion and biofuels).

3.1. Identification of the origin of dust particles using diagnostic ratios

The value of the OC/EC ratio for Hodolany was 10.27 in the summer and 4.76 in the winter, and for Klášterní Hradisko the value was 8.09 during the summer campaign and 3.63 during the winter season. The values of the OC/EC concentration ratio for Hodolany and Klášterní Hradisko during the summer season correspond to emissions from biomass combustion. During the winter season, there is a significant decrease in emissions from biomass combustion and the effect of local heating is evident. EC/OC values were 0.1 for Hodolany and 0.12 for Klášterní Hradisko during the summer period and 0.21 (Hodolany) and 0.28 (Klášterní Hradisko) for the winter season, see figure 2. The EC and OC emissions in PM10 during the summer correspond mainly to biomass combustion, and in the winter period, the EC/OC ratio corresponds to coal and wood combustion (the EC/OC ratio for coal combustion is 0.3 and for wood combustion 0.06-0.25) [14]. OC also includes biogenic matter, therefore, the difference between the heating and non-heating season is not as significant as in the case of elemental carbon (EC), which is a direct indicator of combustion processes. The K'/EC ratio in Hodolany was 0.28 and in Klášterní Hradisko, the value was 0.29 during the non-heating season. These values indicate that both localities are affected by biomass burning or by biogenic mass during the summer period. In the winter season, the value of K'/EC= 0.13 (identical for Hodolany and Klášterní Hradisko) indicates fossil fuel combustion, which was also confirmed by chemical analysis carried out at these localities, see figure 2.

Nitrate are a major component of PM10 at both sites. In the winter season, nitrate concentrations in Hodolany increased about 10 times and in Klášterní Hradisko about 12 times compared to the summer, see table 2. The increase in nitrate concentrations in the winter season can be influenced by combustion processes (fossil fuels and some types of biomass), but also by environmental conditions affecting nitrate formation (low precipitation, humidity and temperature). The concentrations of sulphates in the winter period are almost identical for both localities. Sulphate concentrations in Olomouc correspond to the range of average sulphate concentrations for Central Europe (3 to 7 µg/m³ in Schaap et al., 2004 [16]). The sources of an increase in sulphate concentrations in the winter season are combustion processes. Some diagnostic ratios can be used...
to determine the origin of dust particles. For example, the \((\text{SO}_4^2-) / (\text{NO}_3^-) < 1\) ratio indicates the origin from transport sources, while \((\text{SO}_4^2-) / (\text{NO}_3^-) > 1\) refers to stationary sources of combustion, especially of coal [17]. On the basis of this ratio, surprisingly during the winter season, the influence of transport sources was demonstrated, and during the summer, the value of the ratio indicates partial influence from industrial sources.

![Figure 2. Diagnostic ratio EC/OC, OC/EC and K'/EC.](image)

Table 2 lists the concentrations of anhydrosaccharides (L - levoglucosan and M - mannosan) during both the summer and winter seasons. The L/M ratios are comparable during the summer and winter months at both localities. The L/M diagnostic ratio makes it possible to identify the type of combustion biomass. Based on the L/M ratio, the dominant species of combustion biomass is coniferous wood. The ratio L/M for coniferous wood ranges from 3.6 to 3.9 [18]. The study by Caseiro et al., 2009 [19] states that the L/K⁺ ratio in Austria ranged from 0.9 to 1.7 during the winter months and from 0.22 to 0.56 during the summer months, while the L/K⁺ ratios in Olomouc were lower. The L/K⁺ ratio ranged from 0.11 to 0.14 in the summer, and from 0.36 to 0.40 in the winter.

![Figure 3. Percentage contribution of individual sources.](image)

Table 2. Concentrations of selected water-soluble ions in the summer and winter season.

| Locality           | \((\text{NO}_3^-)\) (µg/m³) | \((\text{SO}_4^2-)\) (µg/m³) | K⁺ | L   | M   | \((\text{SO}_4^2-) / (\text{NO}_3^-)\) | L/M | L/K⁺ |
|--------------------|-----------------------------|-------------------------------|-----|-----|-----|--------------------------------------|-----|-------|
| Hodolany- summer   | 0.799                       | 3.289                         | 0.222 | 0.03 | 0.01 | 4.12                                 | 3.6 | 0.14  |
| Hodolany- winter   | 7.669                       | 4.552                         | 0.595 | 0.24 | 0.07 | 0.59                                 | 3.6 | 0.4   |
| Klášterní Hradisko- summer | 0.642             | 3.603                         | 0.221 | 0.03 | 0.01 | 5.61                                 | 3.7 | 0.11  |
| Klášterní Hradisko- winter | 7.818              | 4.566                         | 0.591 | 0.21 | 0.06 | 0.58                                 | 3.4 | 0.36  |

3.2. Contribution of OC from biomass and fossil fuel combustion using equations

The study by Caseiro et al. 2009 [19] reports that the L/M ratio for hardwood is 14.4-14.8 and for softwood 3.6-3.9. Using the L/M ratio, it is possible to determine the type of combustion wood using the following equation (1), and to determine the contribution of OC and PM from biomass combustion (equations (2), (3)):

\[
\% \text{ spruce wood} = \left( \frac{14.8 - R_{L/M}}{0.112} \right)
\]  

(1)

Information on the share of soft and hardwood (according to equation (1)) was used to calculate the conversion factor OC/levoglucosan. Foreign literature states the value of 7.35 as the general conversion factor OC/levoglucosan for the common European background environment [20]. The values of the OC/levoglucosan factor for both localities in Olomouc were 5. This calculated value of conversion factor (5) was used to calculate the contribution of the OC concentration from biomass combustion (OC_BB) using equation (2):

\[
OC_{BB} = \text{Levoglucosan} \cdot \text{conversion factor}
\]  

(2)
For calculation of dust particles contribution from biomass combustion (PM_{bb}) to total PM\(_{10}\), equation (3) with PM/levoglucosan conversion factor 11.2 (the recommended value for Central Europe) was used [20]:

\[
PM_{bb} = \text{Levoglucosan} \cdot \text{conversion factor}
\]

The OC contribution from fossil fuel combustion (OC\(_{FF}\)) was found using equation (4) [21]:

\[
OC_{FF} = 1.1 \cdot (EC - 4.2 \cdot \text{Levoglucosan})
\]

The average percentage contribution of PM from biomass combustion to total PM\(_{10}\) was 1.2% (Klášterní Hradisko) and 1.3% (Hodolany) during the summer season and 5.2% (Klášterní Hradisko) and 5.3% (Hodolany) during the winter. The percentage contribution of OC from biomass and fossil fuel combustion is shown in figure 3.

4. Conclusion
The proportion of organic matter in PM\(_{10}\) in the winter season was 58.6% for Hodolany and 50.4% for Klášterní Hradisko. During the summer months, the OM percentage in PM\(_{10}\) was about 0.7 times lower for both Hodolany and Klášterní Hradisko. The OC/EC and K'/EC ratios show that during the winter months the air quality at both localities is influenced by fossil fuel combustion, and by biomass combustion or transport during the summer months. The OC contribution from biomass combustion was 0.6% of PM for both localities during the non-heating season, and 2.3% (Klášterní Hradisko) and 2.4% (Hodolany) from PM during the heating season. Contribution of OC from fossil fuel combustion from PM was 2.5% (Hodolany) and 3.2% (Klášterní Hradisko) during the summer season, and 12.8% (Hodolany) and 17.4% (Klášterní Hradisko) during the winter season. In future, more attention will be paid to the EC and OC contributions caused by different kinds of fuel.

Acknowledgement
This work was supported by research projects of the Ministry of Education, Youth and Sports of the Czech Republic: National Sustainability Program LO1404 - TUCENET, SGS 2017/35 Research in Selected Areas of “Smart Energy” in the 21st Century and SP2017/185 Characteristics of Unburned Carbon from Local Furnaces.

References
[1] Pachauri T, Singla V, Satsangi A et al. 2013 Aerosol Air Qual. Res. 13 523-536
[2] Zhu CH S, Cao J J, Tsai CH J et al. 2014 Sci. of the tot. Environ. 466–467 203-209
[3] Oros D R, Abas M R , Omar M J N Y et al. 2006 Appl. Geochem. 21 919-940
[4] Pio C, Cerqueira M, Harrison R M et al. 2011 Atmos. Environ. 45 6121-6132
[5] Qin M, Wang X, Hu Y et al. 2015 Atmos. Environ. 112 81- 89
[6] Zhang T, Claey s M, Cachier H et al. 2008 Atmos. Environ. 42 7013-7021
[7] Duan F, Liu X, Yu T and Cachier H 2004 Atmos. Environ. 38 1275-1282
[8] Caseiro A, Marr I L, Claey s M et al. 2007 J. Chromatogr. 1171 37-45
[9] Simoneit B R T, Schauer J J, Nolte CG et al. 1999 Atmos. Environ. 33 173-182
[10]Andreae M O 1983 Science 2201148-1151
[11]Zdrahal Z, Oliveira J, Vermeylen R et al. 2002 Environ. Sci. Technol. 36 747-753
[12]Frey A, Virkkula A, Saarnio K et al. 2006 Rep. Ser. Aero. Sci. 83 325-329
[13]Fine P M, Cass G R and Simoneit B R T 2002 Environ. Sci. Technol. 36 1442-1451
[14]Zheng M, Hagler G S W, Ke L et al. 2006 J. Geophys. Res. 111 D20313
[15]Rogula-Kozłowska W, Sówka I, Mathews B et al. 2013 J. of Environ. Proc e 4 371-379
[16]Schaap M, van Loon M, Brink H M et al. 2004 Atmos. Chem. Phys. 4 857-874
[17]Xiu G, Zhang D, Chen J, Huang X, Chen Z, Guo H and Pan J 2004 Atmos. Environ. 38 227-236
[18]Ward T J, Hamilton R F, Dixon R W et al. 2006 Atmos. Environ. 40 7005-7017
[19]Caseiro A, Bauer H, Schmidl C, Pio CA, Puxbaum H 2009 Atmos. Environ. 43 2186-2195
[20]Cheng Y, Engling G, He K-B et al. 2013 Atmos. Chem. Phys. 13 7765-7781
[21]Pio C A, Legrand M, Alves C A et al. 2008 Atmos. Environ. 42 7530-7543