

IV.9 Pollutants without set limit values

IV.9.1 Volatile organic compounds

According to the Air Protection Act, a volatile organic substance is any organic compound or mixture of organic compounds, except methane, that has a vapour pressure of 0.01 kPa or more at 20 °C, or has a corresponding volatility under the specific conditions of its use. Volatile organic compounds (VOCs) play an important role in atmospheric chemistry and thus in the oxidation strength of the atmosphere, affecting the condition and quality of the air. Together with nitrogen oxides, VOCs play an important role in the process of formation of ground-level ozone and other photo-oxidation pollutants. Conversion and decomposition of VOCs is usually initiated by reaction with a hydroxyl radical (Viden 2005). Because of the range of differing length of reactivity of particular VOCs and their amount, pollution limit levels were not established for these substances.

Monitoring of VOCs was included in the EMEP programme on the basis of a decision by the EMEP Workshop on Measurements of Hydrocarbons/VOCs in Lindau in 1989 (EMEP 1990). Regular mea-

surement at the Košetice Observatory was launched during 1992 and three years later it was supplemented by the identical measurement at the Praha-Libuš station. In the framework of EMEP, measurements were initially made at five stations; however, over 20 years the number of stations and range of measured hydrocarbons has changed several times. A homogeneous series of measurements has well been maintained at the Košetice Observatory until now. Since 2011, the Košetice Observatory has been involved in the ACTRIS project, carried out in the context of the EU 7th Framework Programme INFRA-2010-1-1.1.16: Research Infrastructures for Atmospheric Research. The successor ACTRIS-2 project identified as H2020INFRAIA-20142015 followed on from this project and was implemented in the May 2015–April 2019 period. The subject of VOCs is part of the work of the Trace gases networking working group: Volatile organic carbon and nitrogen oxides, in an attempt to improve and harmonise VOC measurements in Europe. In the framework of the project, standard operational procedures were developed and the best measuring techniques for ensuring quality were tested. The CHMI laboratory regularly participated in a round robin test where the results of the analyses of VOCs confirmed that the laboratory has been complying with the recommended parameters of the GC system and has been meeting the required uncertainty values for all the substances in both standards and real samples. The ACTRIS-2 project was completed in 2019. VOCs monitoring and research activities continue within the pan-European ACTRIS research infrastructure which has been part of the European Strate-

Tab. IV.9.1.1 Average annual concentrations of VOC in the ambient air at stations Košetice and Prague-Libuš

Volatile organic compound		Annual average [$\mu\text{g}\cdot\text{m}^{-3}$]									
		Košetice					Pha4-Libuš				
		1995	2005	2010	2015	2019	1995	2005	2010	2015	2019
Alkane	Ethane	2.34	2.07	2.51	2.20	2.07	3.62	2.43	1.94	1.97	1.98
	Propane	1.80	1.21	1.28	1.10	0.95	2.15	1.65	1.82	1.06	1.12
	Butane	1.16	0.60	0.71	1.04	0.46	1.76	1.02	1.15	1.15	0.74
	2-methylpropane	0.68	0.37	0.47	0.32	0.28	1.14	0.80	1.03	0.45	0.56
	Pentane		0.29	0.35	0.30	0.22	1.21	0.52	1.74	0.32	0.38
	2+3 - methylpentane		0.03	0.06	0.06	0.12	0.90	0.47	0.31	0.22	0.34
	Hexane		0.09	0.11	0.07	0.09	0.60	0.16	0.18	0.09	0.23
	Heptane		0.03	0.06	0.06	0.08	0.30	0.07	0.14	0.08	0.11
	Octane		0.02	0.05	0.10	0.13		0.06	0.09	0.11	0.12
Alkene	Ethene	1.28	0.77	0.55	0.55	0.53	2.52	1.32	0.45	0.62	0.65
	Propene	0.32	0.15	0.16	0.12	0.11	0.68	0.34	0.30	0.14	0.15
	suma Butenes		0.14	0.20	0.18	0.19	0.87	0.42	0.38	0.26	0.37
	suma Pentenes		0.05	0.07	0.02	0.05		0.27	0.14	0.04	0.11
	Isoprene	0.14	0.09	0.13	0.17	0.32		0.38	0.47	0.37	0.72
Aromatic hydrocarbon	Benzene	1.05	0.42	0.58	0.41	0.44	1.51	0.62	0.72	0.42	0.44
	Toluene	0.99	0.31	0.40	0.30	0.34	2.07	0.86	0.94	0.53	0.99
	Ethylbenzene		0.06	0.06	0.19	0.28	0.42	0.19	0.18	0.27	0.43
	m,p-Xylene		0.78	0.55	0.55	0.71	1.42	0.55	0.57	0.71	1.02
	o-Xylene		0.05	0.04	0.29	0.45		0.16	0.14	0.35	0.58

gy Forum on Research Infrastructures (ESFRI) activities since 2016. The average annual VOC concentrations at the Košetice Observatory and the Praha-Libuš stations over 25 years of monitoring exhibit a statistically significant decreasing trend reflecting the decrease in VOCs emissions both in the Czech Republic and also in the entire European area (Tab. IV.9.1.1). The trend in ethane concentrations is much stronger at the suburban station of Praha-Libuš than at the background Košetice Observatory station. The only exception is isoprene which is of natural origin (emitted by deciduous trees), which exhibited an increasing trend at both stations. In general, it can be stated that the concentrations of the main VOCs at the suburban levels in the 1990's were approx. 50–100% higher than at the background station. The differences between the two stations have decreased substantially in the past decade.

The results obtained in 2019 do not in any way deviate from the long-term trends (Tab. IV.9.1.1). The annual variation in most VOC concentrations reflects the emission levels and thus maximum values in the winter and minima in the summer; the situation is the opposite only for isoprene (Fig. IV.9.1.1).

It follows from the report on VOC measurements in the context of EMEP (Solberg et al. 2018) that the VOC concentrations continuously decrease on a regional scale and thus reflect the decreasing

trend in emissions. The concentration level at the Košetice Observatory is comparable with those at the German, Swiss and French stations. The Czech station has long been characterised by lower annual average ethane concentrations. For most VOCs the concentrations measured in the winter are usually similar to those at German stations, while the values at the Košetice Observatory are slightly lower in the summer.

The Geneva Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Transmission was adopted in November 1991 and came into effect in September 1997 (UN-ECE 1991). The Protocol contained three options for reducing VOCs:

1. 30% reduction in VOC emissions by 1999, where the base values were those for 1984 and 1990;
2. The same reduction as under (1) and the provision that the overall national emissions in 1999 do not exceed the 1988 level;
3. Where 1988 emissions did not exceed the set limits, countries could adopt the 1999 level as the emission ceiling.

In 1999, the Göteborg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone was adopted and it came into effect on 17 May 2005 (UN-ECE 1999). The Protocol contains the emission ceilings for 2010 for four pollutants including VOCs. According to the Protocol, European VOC emissions were to be reduced

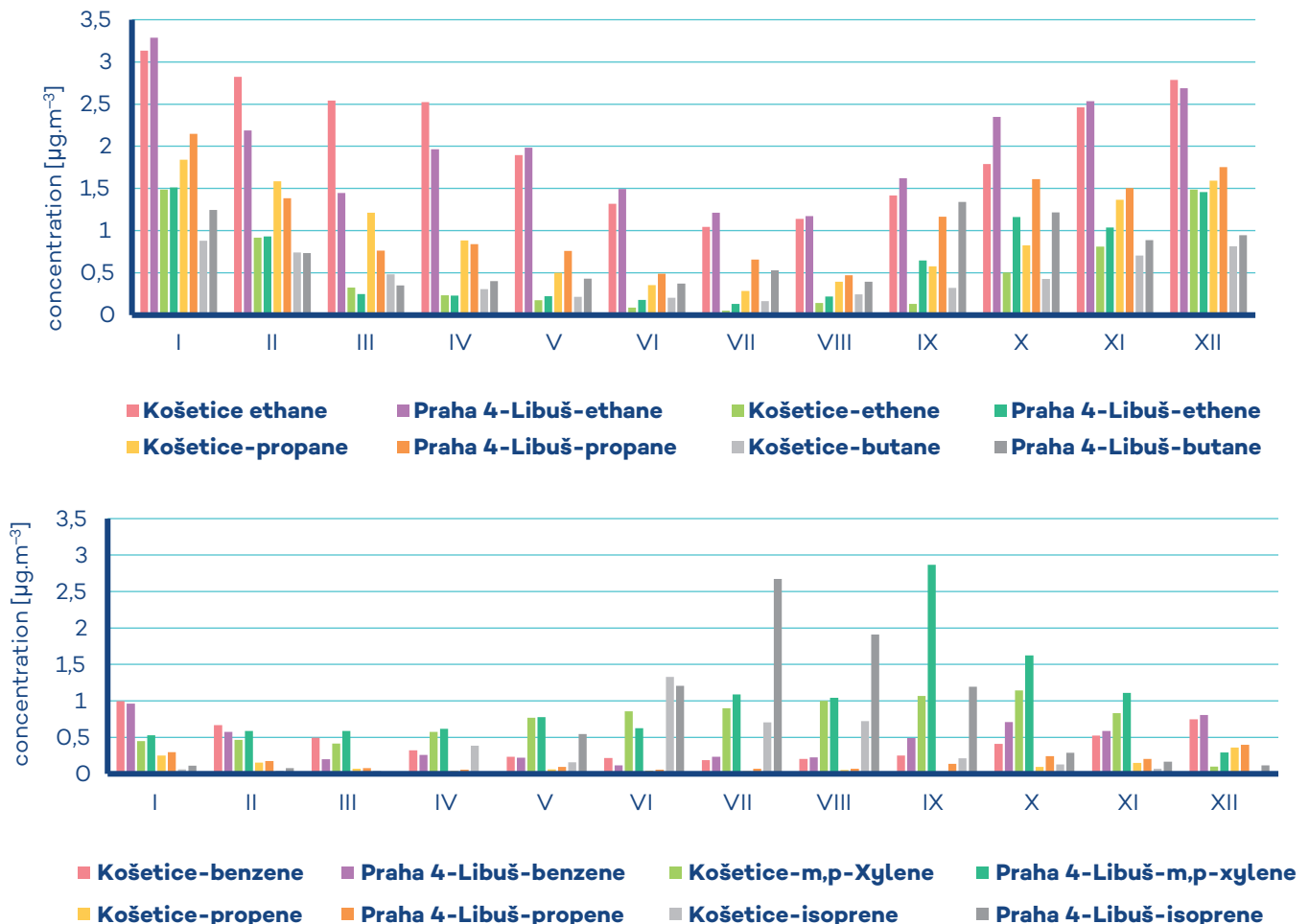


Fig. IV.9.1.1 Annual course of average monthly concentrations of VOC, 2019

by at least 40% compared to 1990. The Czech Republic, similarly to most Central European countries (except Poland), has fulfilled this limit – VOC emissions in the Czech Republic decreased by 51% in the 1990–2010 period (EEA 2013c).

Emissions of volatile organic compounds

Chemical products containing VOCs are used in a wide range of applications in households and industry as cleaning agents, solvents and degreasing agents. They can find use as components of coatings, varnishes, adhesives and pharmaceutical products.

VOCs are released during the storage and use of petroleum products. They are also formed in incomplete combustion.

In 2018, the largest amount of VOC emissions originated from the sector 1A4bi – Residential: Stationary (42.9%). Significant sources of VOC emissions in the Czech Republic belong to the sector of the use and application of organic solvents (NFR 2D3) which contributed by 29.3% to pollution of the air by these substances. This sector encompasses activities 2D3a – Domestic solvent use including fungicides (5.5%), 2D3d – Coating applications (11.7%), 2D3e – Degreasing (2.8%), 2D3f – Dry cleaning (0.03%), 2D3g – Chemical products (4.5%), 2D3h – Printing (1.6%) and 2D3i – Other solvent use (3.1%). Some of these emissions are released into the air in a controlled manner, but a substantial part of them escape into the air in the form of fugitive emissions which are difficult to control (Fig. IV.9.1.2). The share of transport, including evaporation from the fuel system of vehicles, was 7.3%. Livestock breeding contributed 8.9% to total VOC emissions, of which the largest share is from cattle breeding (6.9%).

Total VOC emissions in the 2008–2018 period exhibited a decreasing trend (Fig. IV.9.1.3), caused by the use of products with lower volatile organic compound contents, e.g. water-based coatings and plastic powders. Legislative regulations apply to retail packaging of coatings, limiting the maximum solvent contents in products placed on the market. The constant renewal of the vehicle fleet is leading to a continuous reduction in VOC emissions from transport.

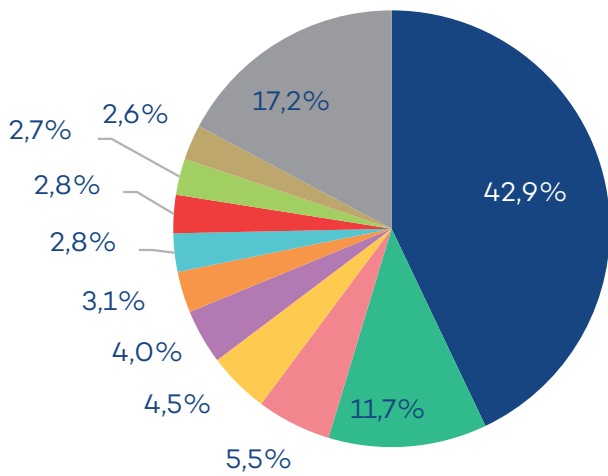


Fig. IV.9.1.2 Total emissions of VOC sorted out by NFR sectors, 2018

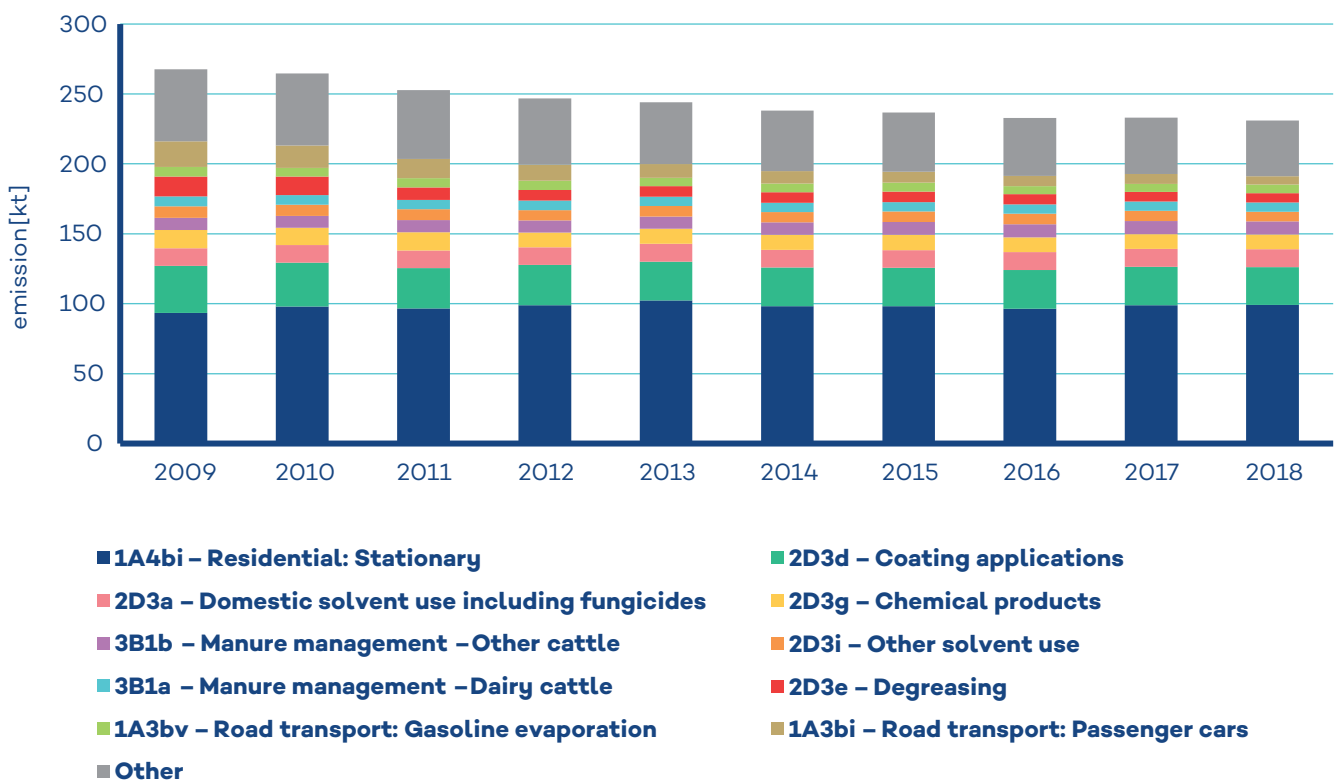


Fig. IV.9.1.3 The development of VOC total emissions, 2009–2018

IV.9.2 Measurement of the numerical size distribution of aerosol particles

The numerical size distribution of aerosol particles has been measured within the CHMI for several years at selected stations. Since 2019, the measurements described below have been extended by other regular measurements. Together, they form the basis of an emerging network of ultrafine particles.

The CHMI has a long-term cooperation with the Institute of Chemical Process Fundamentals of the Czech Academy of Sciences (ICPF CAS) which has been measuring the size distribution of aerosol particles at the Košetice Observatory since 2008. This measurement is part of the ACTRIS European Research Infrastructure monitoring network (Aerosols, Clouds, and Trace gases Research Infrastructure Network). Since 2016, these measurements have also been supported by the ACTRIS-CZ, the Czech part of the large research infrastructure project, which focuses on the Košice locality. For activities involving research activities of the CHMI, two institutes of the Academy of Sciences of the Czech Republic, and the Masaryk University, the collective designation of the locality is used, namely the National Atmospheric Observatory Košetice (NAOK).

In the daily spectra measured at four localities (Ústí nad Labem-city, Lom, NAOK and Ostrava-Fifejdy) it is possible to recognize at first sight the difference in the number of particles in different size categories which reflect the character of the localities. While the median spectra of stations in the Ústí nad Labem region are cha-

racterized by the influence of local sources (transport, industry), the median spectrum of the NAOK in the Vysočina region is rather affected by long-distance transport. The Ostrava-Fifejdy station has a different range of measurement sizes, so it is not possible to accurately characterize the predominant source of particles of the typical spectrum and compare it with other stations. In general, however, spectra can be described using common features. The highest concentrations of the number of particles are usually measured in the late evening, night and early morning hours. This phenomenon is probably associated with the development of the boundary layer of the atmosphere and its stability during the night hours. At night, there can be an accumulation of pollutants, and therefore aerosol particles. After sunrise, in some cases, an increase in photochemical reactions between accumulated substances can be observed, which can lead to the formation of secondary aerosols.

The median daily particle size spectrum in 2019 was, as in previous years, less distinct at NAOK compared to other considered measurements. Relatively constant concentrations of accumulation mode particles can be observed, which decrease during the day (between 7:00 and 16:00 UTC) due to atmospheric dilution. On the contrary, the numbers of nucleation mode particles (particle size up to 20 nm) increase from the morning and reach a maximum after 15 hours. The increase in the number of nucleation mode particles is probably associated with the process of particle formation and their subsequent growth to higher sizes. It is at NAOK where the effect of long-distance transport of particles in the form of relatively stable concentrations of the accumulation mode, and the effect of dilution and stability of the atmosphere on the concentrations of particles can be well observed (Fig. IV.9.2.1)¹.

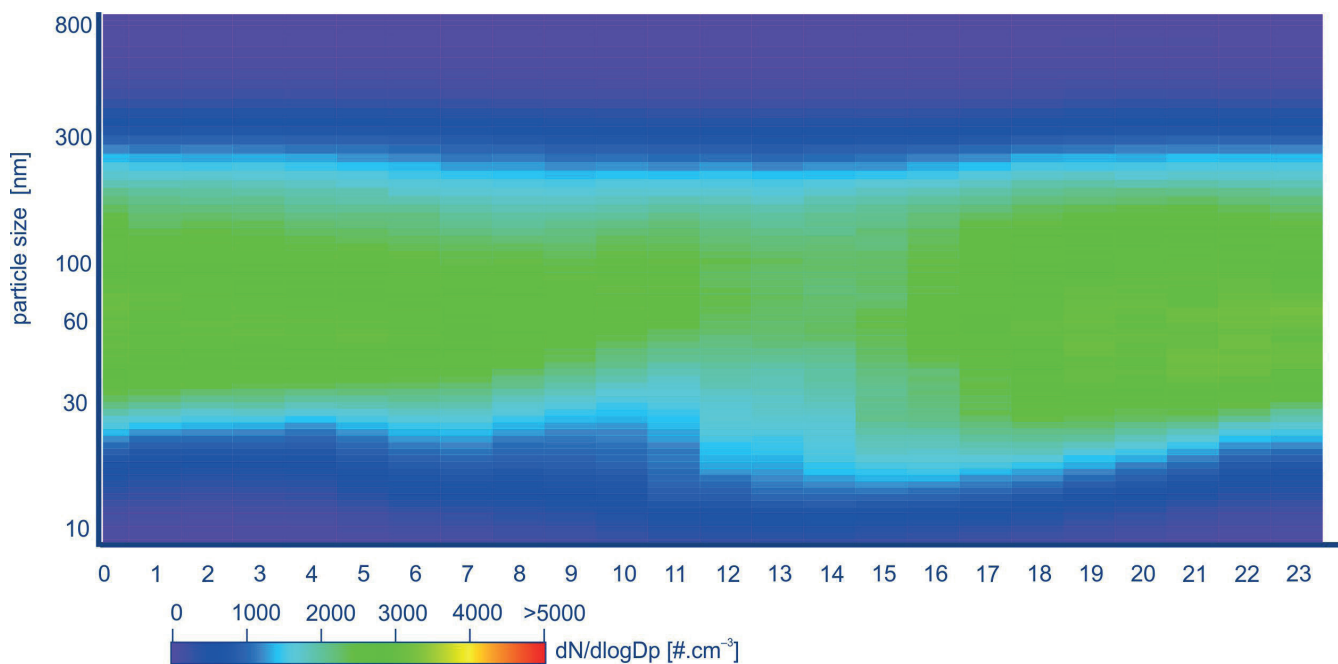


Fig. IV.9.2.1 Median spectrum of the daily progression of the number of particles, NAOK, 2019

1 The $dN/d\log D_p$ unit denotes the normalized number of particles in a given size category. The distribution of the number of aerosol particles does not correspond to a symmetrical normal distribution, therefore a logarithmic transformation is used to display the aerosol spectrum to obtain a log-normal distribution (Hinds 1999). The Y-axis indicates the nano-meter particle size categories of aerosol particles, the colour scale shows the number of particles in a given size category (the number of particles increases from cold to warm colours).

Daily variation of the number of particles at the Ústí nad Labem-city station is characteristic by an increase of the number of particles in all parts of the spectrum in the morning and afternoon hours, reflecting not only peak traffic conditions but also the increasing occurrence of combustion products from industrial sources. These sources are connected with elevated production of both particles and their gaseous precursors, from which secondary particles can be formed by photochemical processes. Increase of particles between 20 and 100 nm is the most distinct, reaching the

maximum between 6 and 9 hours in the morning (Fig. IV.9.2.2). As already mentioned earlier, changes in the counting concentration are affected by not only the sources but also by stability of the atmosphere. While during a day, the atmosphere is well mixed due to turbulent flow, in the evening when the turbulence ceases, the atmosphere gets stabilized (Stull 2003).

The Lom station in the Ústí nad Labem region started measuring the size distribution of aerosol particles in 2017. This background

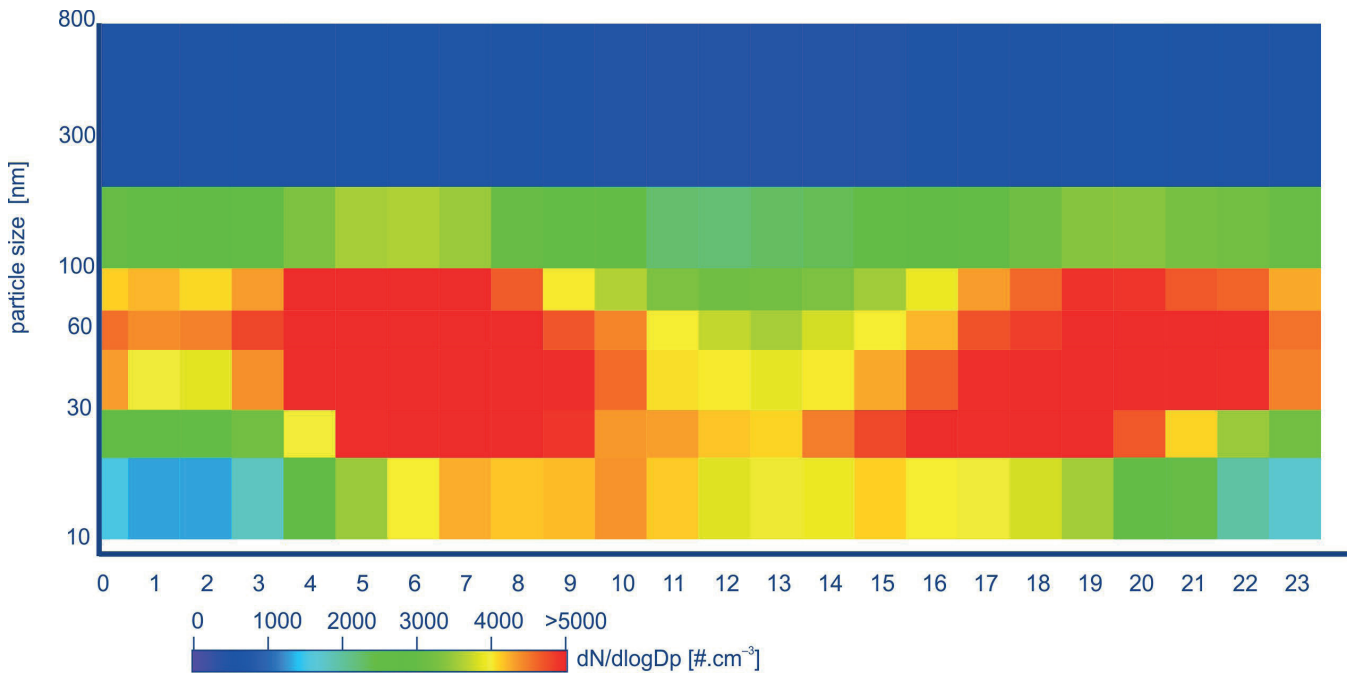


Fig. IV.9.2.2 Median spectrum of the daily progression of the number of particles, Ústí nad Labem-město, 2019

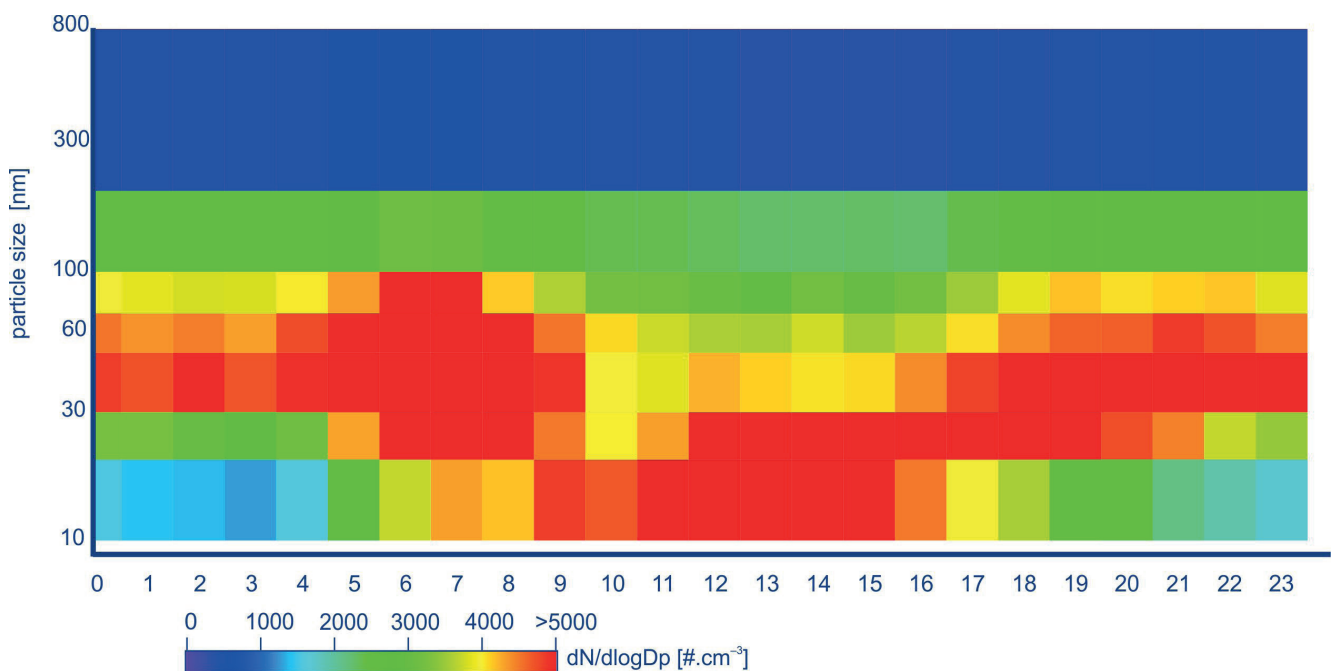


Fig. IV.9.2.3 Median spectrum of the daily progression of the number of particles, Lom, 2019

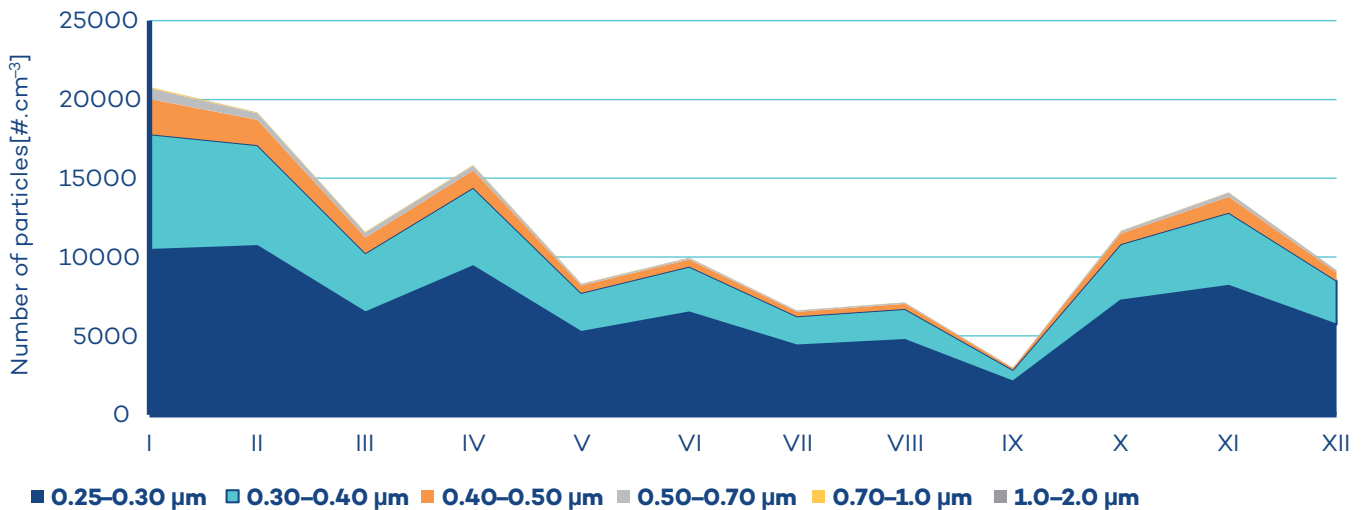


Fig. IV.9.2.4 Monthly variability of average particle numbers, Ostrava-Fifejdy, 2019

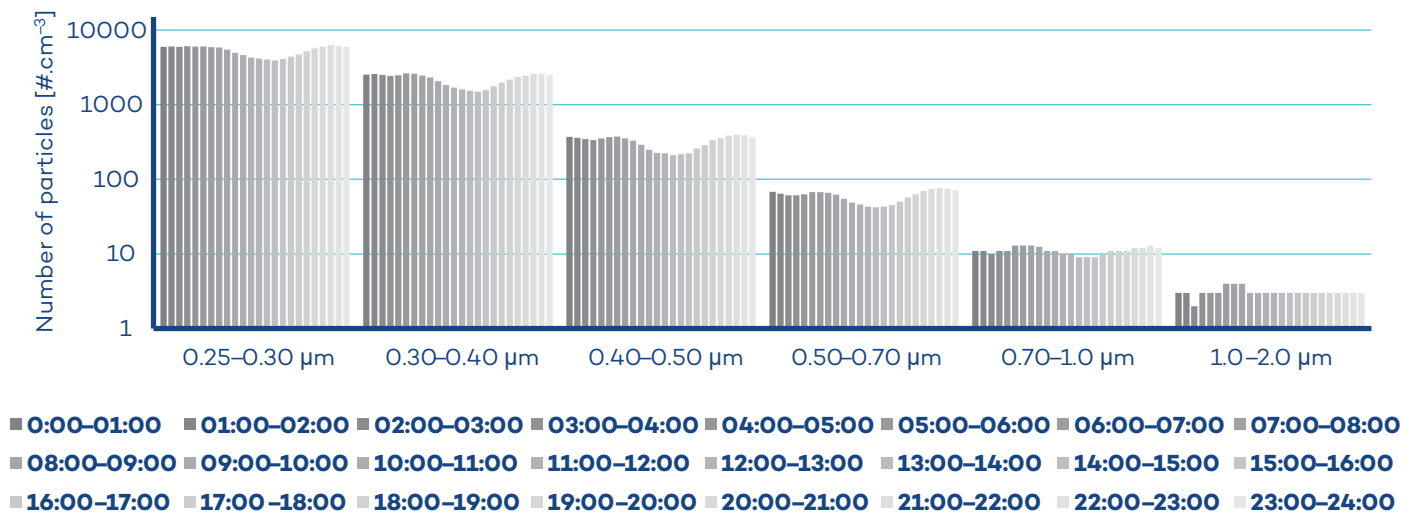


Fig. IV.9.2.5 Median spectrum of the daily progression of the number of particles, Ostrava-Fifejdy, 2019

industrial station is located approximately 4 km from the petrochemical complex and about 500 m from the town of Lom. In contrast to the other three stations, events of formation of new particles manifested by high concentrations of nucleation mode particles lasting from 9:00 to 15:00 accompanied by the transformation of nucleation mode particles into larger aerosol spectrum particles can be identified at this station in the year-round median spectrum. The described daily spectrum probably reflects the influence of industrial sources as well as transport and large cities in the vicinity (Fig. IV.9.2.3).

The Ostrava-Fifejdy urban background station is equipped with the GRIMM analyser which has been used to monitor the number of particles in 32 size fractions in the range of 0.25 to 3.20 μm since 2008. The number of particles was also monitored by the GRIMM analyser in the Moravian-Silesian region in the past at the background suburban Ostrava-Poruba locality (2012–2015) and

from 2016 to April 2018 at the background rural Věřňovice locality. The average number of monitored particles at the Ostrava-Fifejdy station was 11,400 in 2019.

The highest number of particles from the monitored size intervals is represented in smaller size fractions up to 0.30 μm and making about 67% of all measured particles at the Ostrava-Fifejdy locality. Particle numbers show significant differences during the year. The highest average number of particles is reached in January, February, April and November. The differences in the average numbers of particles between the hot (April to September) and cold (January to March and October to December) parts of the year in 2019 are 26% (Fig. IV.9.2.4).

The median daily course of the number of particles is more pronounced in smaller fractions up to 0.7 μm , in larger size fractions the daily course is more balanced (Fig. IV.9.2.5) and at

the same time it reaches the lowest values. During the day, the lowest values are reached in the afternoon, the highest during the evening, night and morning. There is no noticeable increase in the number of particles during daily rush hour. Therefore, there is no significant effect of traffic or this method is not able to follow this effect.

In the annual variability of the total number of particles, the highest values are reached at the Ostrava-Fifejdy station, even though it measures the number of particles of a size above 250 nm. During some months, the total number of particles is up to three times higher than at the other stations. There are different variations of the total number of particles between stations during the year. At the Ústí nad Labem-city station, the highest total concentrations were measured in February (10,700 particles per cm³), at

the Lom station in June (10,600 particles per cm³), at the NAOK in July (5200 particles per cm³), and at Fifejdy in January (20,800 particles per cm³). At all three compared stations, an increase in the number of particles caused by heating during the winter and more stable atmospheric conditions can be observed, as well as a secondary increase in concentrations in the spring and summer. The increase in the total number of particles is associated with the events of the formation of new particles, which are bound to the period with a high vegetation activity, and therefore an increased production of VOCs (a precursor of secondary particles). The described process is also supported by the increasing intensity of sunlight. The secondary increase in the total number of particles in October and November was not reflected at the NAOK station. Thus, the increase at the Ústí nad Labem-city and Lom stations may be caused by local influences (Fig. IV. 9.2.6).

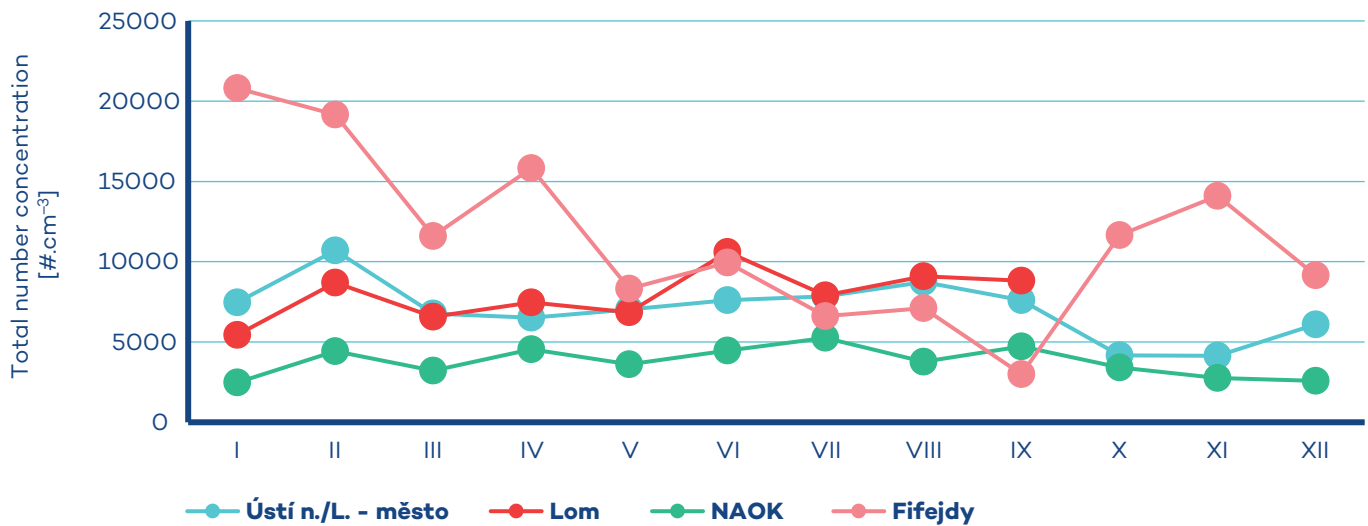


Fig. IV.9.2.6 Average monthly variability of the total particle number concentration, Ústí Labem-město, Lom, NAOK, Fifejdy, 2019

IV.9.3 Monitoring concentrations of elemental, organic and black carbon

The first regular measurement of EC/OC in the Czech Republic was launched in February 2009 at the Košetice Observatory (OBK). The average concentration of total carbon (TC) in 2009–2019 in the sampled $PM_{2.5}$ fraction was $3.4 \mu\text{g}\cdot\text{m}^{-3}$, of which the EC amounts to $0.4 \mu\text{g}\cdot\text{m}^{-3}$ and OC to $3.0 \mu\text{g}\cdot\text{m}^{-3}$. In 2019, the highest average concentration of TC ($3.8 \mu\text{g}\cdot\text{m}^{-3}$) was measured in January. January was the coldest month of 2019 at OBK (average temperature -1.9°C), and the results of carbon concentration measurements were probably affected by temperatures that were mostly below freezing for a month, which could increase the need for heating and the associated increase of these products of combustion. In 2019, the average concentration of TC

($2.8 \mu\text{g}\cdot\text{m}^{-3}$) was $0.6 \mu\text{g}\cdot\text{m}^{-3}$ higher than in 2018. This decrease was probably affected by higher temperatures in the winter of 2019 compared to the previous year. Adverse meteorological conditions together with increased production of carbon particles due to heating increase the measured TC concentrations. In the last two years, we have observed an increase in OC concentrations in the summer, which may be caused by higher temperatures, supporting the formation of secondary OC. The average annual EC concentration in 2019 was $0.3 \mu\text{g}\cdot\text{m}^{-3}$ and the OC concentration reached $2.5 \mu\text{g}\cdot\text{m}^{-3}$. Overall, considering the course of concentrations during the period of measurements, a slightly decreasing trend can be identified despite the increase in average annual concentrations in some years. While the EC concentration (2009 – $0.6 \mu\text{g}\cdot\text{m}^{-3}$) has been gradually decreasing since the beginning of the measurement, in 2012, 2013, and 2018, the concentrations increased again. After the renewal of the measurement in 2016, the annual average concentration

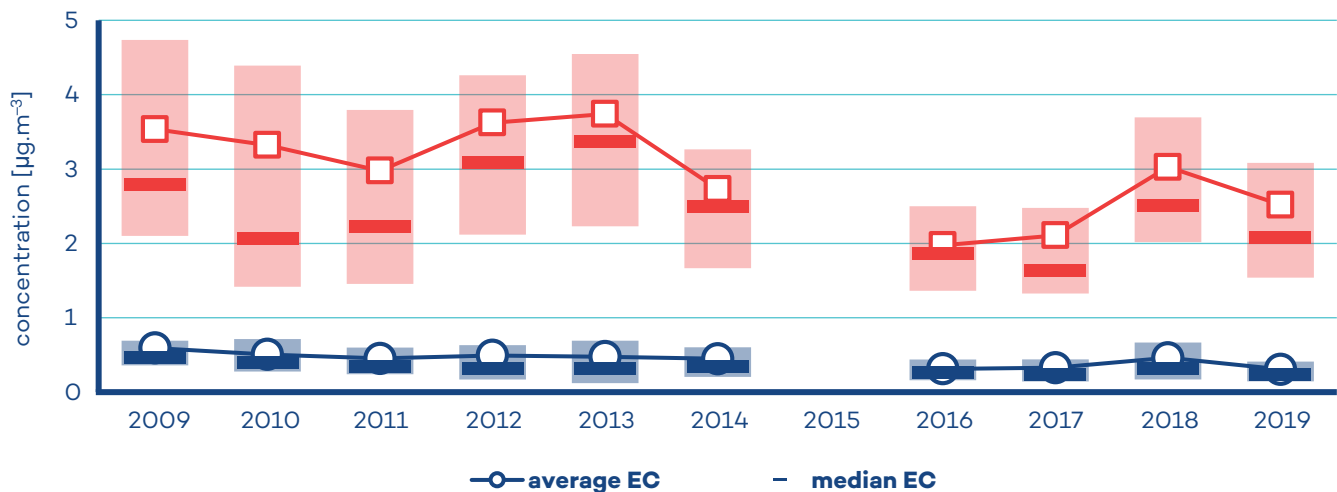


Fig. IV.9.3.1 Annual average concentrations of EC and OC, Košetice Observatory, 2009–2019

Note: The range of daily values is indicated by the top/bottom border of the boxes representing the value of 75th and 25th percentile respectively; the horizontal line indicates the median.

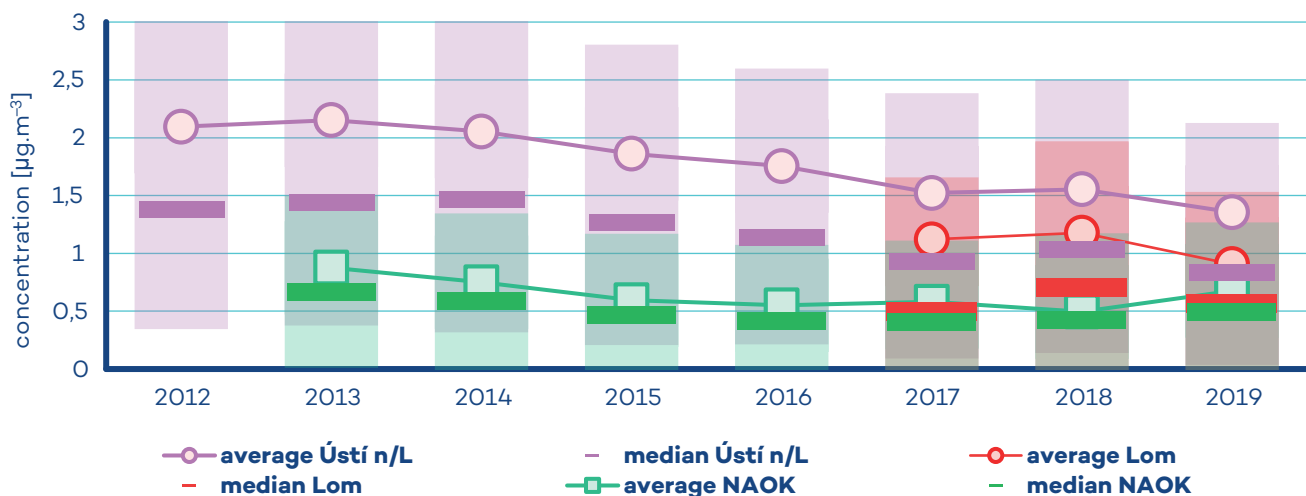


Fig. IV.9.3.2 Annual average concentrations of BC, NAOK, Lom, Ústí nad Labem-město. 2012–2019

Note: The range of daily values is indicated by the top/bottom border of the boxes representing the value of 75th and 25th percentile respectively; the horizontal line indicates the median.

rations were slightly above $0.3 \mu\text{g}\cdot\text{m}^{-3}$. Significant increase was recorded in 2018. Similar but more noticeable course was also observed for the OC. The highest average value was observed in 2013 ($3.7 \mu\text{g}\cdot\text{m}^{-3}$), while the lowest OC concentration was characteristic for 2016 ($2.0 \mu\text{g}\cdot\text{m}^{-3}$) (Fig. IV.9.3.1).

Measurements of concentrations of BC take place at three stations, namely the Ústí nad Labem-město, Lom, and NAOK (the core station is the Košetice Observatory). The Ústí nad Labem-město and NAOK stations measure BC since 2012, the station Lom since 2017.

The annual variability of concentrations of BC reflects higher amount of emissions produced during the heating season; increased values are recorded during the cold part of the year. Apart from the heating season, weekly maxima can be identified namely due to traffic. Another source of BC is barbecue taking place in the summer months.

The evaluation of BC concentrations at all three stations cannot be performed with a sufficient reliability in terms of the average annual concentration. Data coverage does not meet the required number of measurements. In addition, outages occurred mainly in the winter, which may have led to underestimation of the results. The annual average BC concentration of $1.4 \mu\text{g}\cdot\text{m}^{-3}$ at the Ústí nad Labem-město station is therefore probably underestimated. In the previous period, however, a declining trend was observed showing a decrease of the average annual concentrations in the period 2012–2018 since the beginning of the measurements by $0.6 \mu\text{g}\cdot\text{m}^{-3}$. During this period, variability of data also decreased reaching the peak in 2014. Although the levels of 1st and 3rd quartiles in 2014 reached 0.7 and $2.7 \mu\text{g}\cdot\text{m}^{-3}$ respectively, the 1st quartile of 2018 amounted to $0.5 \mu\text{g}\cdot\text{m}^{-3}$ and the 3rd quartile to $2.1 \mu\text{g}\cdot\text{m}^{-3}$. Insufficient data coverage also applies to the Lom station where the average annual concentration in 2019 was $0.9 \mu\text{g}\cdot\text{m}^{-3}$. This figure should also be considered as slightly underestimated. Although the Lom and Ústí nad Labem-město stations are located in an industrial region, lower concentrations of BC can be observed at the Lom station due to its location outside the traffic arteries. The long-term monitoring of BC concentrations at the NAOK station gives two to three times lower the values recorded at the Ústí nad Labem-město station. The annual average concentration dropped from the level of $0.9 \mu\text{g}\cdot\text{m}^{-3}$ in 2013 to $0.7 \mu\text{g}\cdot\text{m}^{-3}$ in 2019. The variability of measured data was the lowest in 2016 (1st and 3rd quartiles reached the values of $0.3 \mu\text{g}\cdot\text{m}^{-3}$ and $0.7 \mu\text{g}\cdot\text{m}^{-3}$ respectively) the following year the variability moderately increased, similarly to the average concentration. Compared to the previous year, a slight increase in BC concentrations was recorded in 2019 (from an annual average of 0.5 to $0.7 \mu\text{g}\cdot\text{m}^{-3}$). However, this increase does not necessarily mean deterioration in air quality. Last year, the NAOK renewed the monitoring device with a higher measurement frequency and more advanced measurement technology. This change in instrumentation, along with missing data, can cause slight changes in results. Despite the mentioned shortcomings in the measurement, it can be concluded in view of multiple years

of concentrations data that the overall course of concentrations at the mentioned stations is not quite identical. Despite the fact that since 2013 the BC concentrations have been decreasing, the NAOK has seen an increase in concentrations in 2017 and 2019, however, the slight increase in concentrations at the stations in the Ústí na Labem region was observed only in 2018. These differences may be associated with a different structure of sources, affecting BC concentrations (Fig. IV.9.3.2).

Based on the results of inventories in the Czech Republic in 2018, up to 46.9% of BC emissions originated from the transport sector, particularly from combustion of fuel in diesel engines. Of this, the following sectors contributed the most to the total BC emissions: Road transport: Passenger cars (1A3bi) by 16.7% and Agriculture, forestry, fishing: Off-road vehicles and other machinery (1A4cii) by 14.6%. Of stationary sources, the most BC emissions were produced by the Residential: Stationary sector (1A4bi) with a share of 51.1% to total emissions (Fig. IV.9.3.3). Developments in total BC emissions in the 2009–2018 period can be characterised by a decreasing trend, particularly due to measures in the transport sector (Fig. IV.9.3.4)¹.

1 The share of BC emission by sectors has recently been recalculated and the results given in previous years can therefore differ.

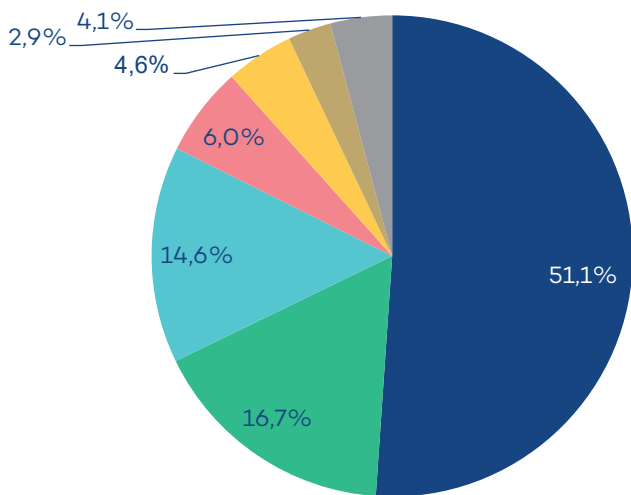


Fig. IV.9.3.3 Total emissions of BC sorted out by NFR, 2018

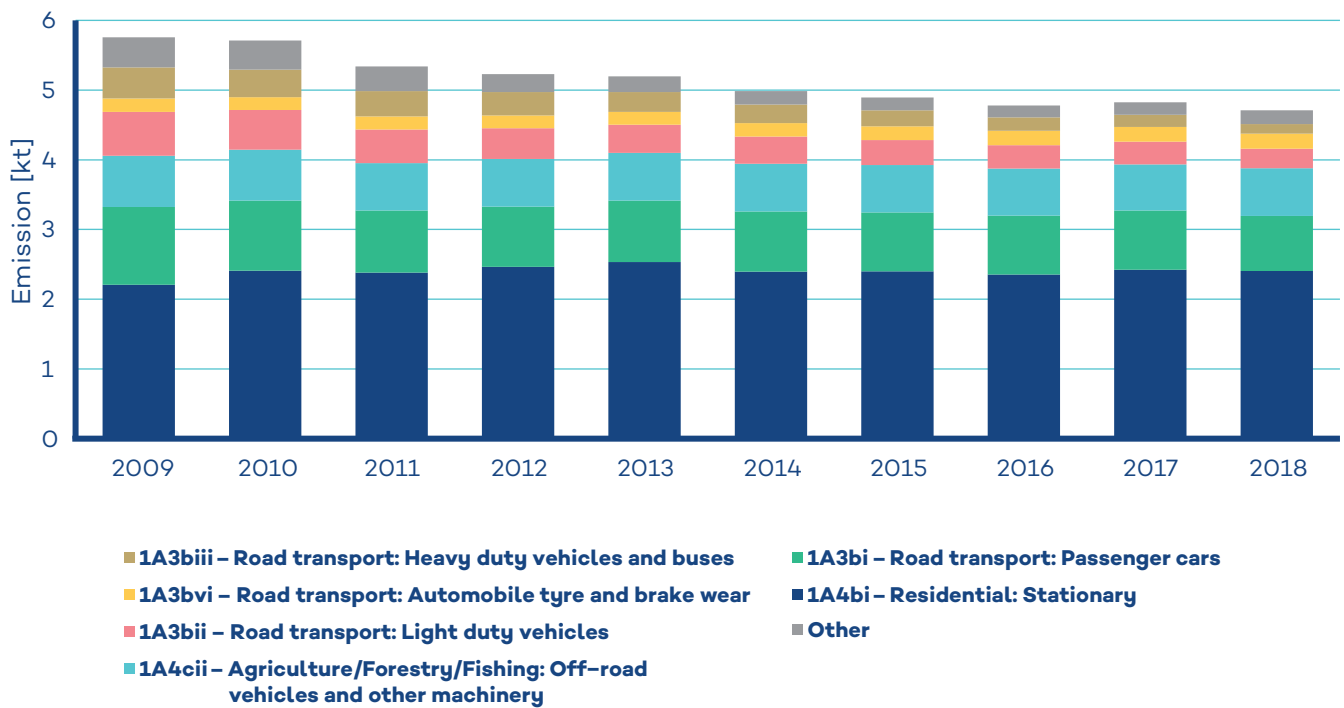


Fig. IV.9.3.4 The development of BC total emissions, 2009–2018