Atmospheric pollution in Tallinn: levels of priority pollutants

Dedicated to the 65th birthday of Professor Toomas Tenno, Chair of Colloid and Environmental Chemistry, University of Tartu

Gary Urb[a,b*], Erik Teinemaa[a,c], Antonius Kettrup[d], Istvan Gebefügi[d], Margit Laja[a,b], Janek Reinik[a], Eduard Tamm[e], and Uuve Kirso[a]

[a] National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia; margit@kbfi.ee, jreinik@kbfi.ee, uuve@kbfi.ee
[b] Institute of Physical Chemistry, University of Tartu, Jakobi 2, 51014 Tartu, Estonia
[c] Estonian Environmental Research Centre, Marja 4d, 10617 Tallinn, Estonia; erik@klab.envir.ee
[d] GSF-National Centre for Environment and Health, Institute of Ecological Chemistry, D-85764 Neuherberg, Germany
[e] Institute of Environmental Physics, University of Tartu, Tähe 4, 51010 Tartu, Estonia

Abstract. The levels of priority air pollutants (NO_x, CO, SO_2, O_3, particulate matter) were investigated at three sites in Tallinn (Estonia). The concentration of particles with diameters less than 2.5 μm (PM2.5), reaching human alveoli in lungs, was also measured. The collected samples of particulate matter were extracted with the accelerated solvent extraction method and analysed with high performance liquid chromatography. The chemical analysis indicated the occurrence of polycyclic aromatic hydrocarbons in the airborne particulate matter samples. The data received were grouped into four categories for annual, seasonal, diurnal, and day-of-the-week trends. The winter concentrations of NO_x and CO in the urban area were twice as high as in the summer period. Annual and diurnal variations were studied to find out the main sources of pollution. Increasing traffic intensity and industrial activity were suggested to be associated with changes in air quality.

Key words: ambient air, gaseous pollutants, particulate matter, air quality, PAH.

INTRODUCTION

Ambient air in urban conditions contains a large amount of different gaseous compounds and particulate matter (PM). It is well known that SO_2, NO_x, CO, organics, and combustion-generated PM are primary atmospheric pollutants [1]. The so-called secondary pollutants are formed during chemical reactions from

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* Corresponding author, urb@kbfi.ee

primary pollutants in the air. The term NO_x, oxides of nitrogen, indicates in current use the sum of $NO + NO_2$. Typically more than 90% of the NO_x emitted could be in the form of NO [1]. Globally it is estimated that the contribution of on-road vehicles to the total anthropogenic NO_x emissions is about 30%, that of non-road engines and vehicles 19%, and energy production is even more significant, 46% [2, 3]. Carbon monoxide is produced by incomplete combustion of fossil fuels (5%) and by light-duty motor vehicles (60%). Sulphur compounds are emitted mainly during combustion of fossil fuels in the form of sulphur dioxide (SO_2) [1].

In the air quality standard PM is characterized with a concentration of total suspended particulate matter (TSP). However, the airborne PM comprises particles of extremely diverse sizes. The smallest freshly formed particles are less than 5 nm in diameter and contain only tens of molecules. Particles in the ranges 3–50 nm are highly abundant in the urban air as a result of vehicle emissions [1]. On the other hand, airborne particles can be as large as 100 μm, a significant proportion of particle mass (but not in number) may well be in the size range close to 10 μm [1]. Particles of smaller size fraction than 2.5 μm are capable of penetrating to the alveolar region of the respiratory system of human lungs more effectively than coarse particles [4]. Epidemiological studies have proved a connection between total mortality and exposure to PM10 [4]. Therefore, the mass of suspended particulate matter less than 10 μm (PM10) and less than 2.5 μm (PM2.5) in size is more important to monitoring than the total concentration of suspended particles [5].

In urban conditions, various pollutants are emitted by mobile and stationary sources. Chemical components present in PM are highly diverse. They range from nearly neutral and highly soluble substances such as ammonium sulphate, ammonium nitrate, and sodium chloride to sooty particles, made up of elemental carbon, coated in organic compounds, and essentially insoluble minerals such as particles of clay [4].

Air pollution problems are well studied in many cities in the world including in the European Union. What is the situation regarding the air quality in Estonia? The Estonian Environmental Research Center (EERC) has since 1994 performed continuous monitoring of ambient air in the country within international and national programmes [6].

The focus of this study was on extending and generalizing the experimental material on gaseous pollutants and PM, received during national monitoring programmes by EERC. In addition, several sampling episodes were performed on PM10 and PM2.5 during the research work. The aim of the study was to characterize air pollution in relation to the annual, seasonal, and diurnal variation in the capital city of Estonia, Tallinn, and to assess the impact of different pollution sources on air quality.

EXPERIMENTAL

Collection of aerosol samples

The monitoring sites are situated in Tallinn (ca 400 000 inhabitants). Locations of the sampling sites are shown in Fig. 1.

Fig. 1. The location of the sampling sites in Tallinn.

- Viru is situated in the city centre, in the area of the highest traffic intensity;
- Kopli (Rahu) is located in an industrial area, close to railway and cargo port transportation, NW from the city centre;
- The third monitoring site is situated in a suburban residential area of Õismäe (approx. 40 000 inhabitants), SW from the city centre.

The air samples were taken as a rule in the human breathing zone, height 1.5–3 m.

Instrumentation

The EERC used the following equipment for continuous monitoring during the study:
- Fluorescence analyser Horiba APSA 360 CE (0.5–500 ppm) for SO_2;
- Chemo luminescence analyser Horiba APNA 360 CE (0.5–1000 ppb) for NO, NO_2, and NO_x;
- UV absorption analyser Horiba APOA 360 CE (0.5–1000 ppb) for O_3;
- IR analyser Horiba APMA 360 CE (0.05–100 ppm) for CO;
- β-Radiation absorption analyser FH 62-I-R (0.5–1500 μg/m^3) for PM10.

The monitoring data were collected, verified, and primarily saved on half an hour average results basis and sent to the EERC server. EERC performs the apparatus maintenance, calibration, and data inspection. The measurement accuracy corresponds to international requirements for gaseous pollutants i.e., SO_2, NO_2, NO_x, NO, CO, and $O_3 \pm 15\%$ and PM $\pm 25\%$ [6].

In addition to automatic continuous measurement, EERC collected samples of TSP (24 h) with glassfibre filters in the city centre (Viru). The mass was quantified in the EERC analytical laboratory.

Additional instrumentation and facilities for the monitoring of the PM10 and PM2.5 size solid particles of urban aerosols were installed in the sites of continuous monitoring. Sampling episodes for the quantification of the particles were performed during 2003 and 2004.

Sampling of PM10 and PM2.5 was carried out with a GSF (National Research Center for Environment and Health, Germany) mobile air monitoring laboratory, equipped with the following instruments:

- Andersen PM10 Sampler (HVS) on 20×25 cm quartz filters at 1800 m^3/24 h for high-volume samples;
- Two parallel Andersen Dichotomous Samplers model 241 with fine and course quartz filters (diameter 37 mm) at total operational flow rate 16.7 L/min for PM10 and PM2.5.

The fine particles (PM2.5) were collected with an IMPROVE aerosol sampler, which is similar to the device described by Ruuskanen et al. [7]. For the separation of coarse particles, the IMPROVE sampler has a cyclone with 50% cut point at 2.5 μm particle diameter before the inlet. A critical orifice and a vacuum pump Model N0135 AN18 (KNF Neuberger, Germany) produced a stable sample flow rate of 23 L/min, necessary for proper operation of the cyclone. Teflo™ membrane filters R2P1025 (Gelman Laboratory, USA) with 3 μm pore size were used for sampling. The minimum sampling time period was 24 h. Pressure drop on the filter measured by Magnehelic® differential manometer (Dwyer Instruments, USA) was used as an indicator of the filter clogging.

Chemical analysis

The collected PM samples were analysed for the bulk composition of hazardous organic compounds, i.e., polycyclic aromatic hydrocarbons (PAHs). From the hazardous organic compounds, the set of US Environmental Protection Agency (EPA) 16 priority PAHs were determined. These include acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, chrysene, dibenz[ah]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, pyrene, some of which are considered highly mutagenic and/or carcinogenic [8, 9].

Each aerosol filter was extracted with acetone in an Accelerated Solvent Extractor (ASE). The ASE extracts (ca 30 mL) were filled in a 100 mL reduction flask and 200 μL dimethylformamide (DMF) was added. DMF prevents the volatile PAH such as naphthalene, fluorene, acenaphtene, phenanthrene, and anthracene from evaporating. The extracts were reduced to 2 mL in a rotary evaporator at 40 °C and 500–510 mbar. The residual solvent was filled in a 2 mL volumetric flask and concentrated down to the DMF content under a gentle steam of nitrogen in a vapotherm (Barkley mobil S). The volumetric flask was filled to the mark with acetone and the sample was transferred into an auto sampler vial for analysis by high performance liquid chromatography (HPLC).

The HPLC system HP 1100 (Hewlett-Packard, USA) consisted of a vacuum degasser, a gradient pump, an auto sampler, a column thermostat, a diode array detector, a fluorescence detector, and a computer workstation (Agilent Technologies, Germany). The HPLC analyses employed a MZ-PAH C-18, 5 μm, 250 mm analytical column manufactured by MZ Analysetechnik (Germany). Acetonitrile and water were used as the mobile phase. The PAHs were separated with an acetonitrile gradient at 308 K and 0.5 mL/min. The separation started with 58% acetonitrile, the organic solvent content was increased to 100% in 35 min, and finally held at 100% acetonitrile for the last 12 min. Within the next 2 min the initial eluent composition was reached and the system equilibrated for 15 min. The injection volume was 10 μL. Detection and quantification of the PAHs was carried out with time programmed fluorescence detection.

During the analysis of real samples, internal calibration of standards was carried out regularly and the calibration curve was renewed if necessary. The detection limits of 1–22 pg/μL were low enough to determine PAH concentrations in the range of pg/m^3 for quartz and Teflon® filter samples.

RESULTS AND DISCUSSION

Continuous monitoring

The air quality parameters, i.e., mean annual concentrations of SO_2, NO, NO_2, NO_x, O_3, CO, and PM in the ambient air of Tallinn (Table 1) are strongly related to the monitoring site. The concentrations of CO and NO_x are many times higher in the city centre (Viru) than in the industrial (Kopli) and residential (Õismäe) areas. At the same time the SO_2 pollution was more pronounced in the Kopli monitoring site than elsewhere. The concentration of NO in the Viru site was abnormally high compared to the other sites, which could indicate permanent light-vehicle emissions in the city centre.

Table 1. Annual average concentrations ($μg/m^3$) of gaseous pollutants and particulate matter in the ambient air of Tallinn in three locations of continuous monitoring

Pollutant	Viru			Kopli			Õismäe*		
	2001	2002	2003	2001	2002	2003	2001	2002	2003
SO_2	3.14	1.63	2.06	2.26	3.50	3.22	1.65	1.35	0.98
NO	30.20	25.49	31.05	4.89	8.44	10.21	2.35	2.70	3.19
NO_2	35.94	36.32	37.37	16.67	19.13	20.42	11.94	13.29	13.59
NO_x	82.08	75.26	84.74	24.14	32.03	36.02	15.49	17.41	18.46
O_3	38.51	36.84	32.74	54.34	49.84	45.26	60.93	59.48	49.65
CO	570	450	430	270	310	330	250	280	280
PM10	29.86	40.84	38.11	20.97	28.26	25.60	18.23	20.88	19.23

* January and February 2001 not included.

Table 2. Monthly averages (μg/m^3) of PM10 in the ambient air of three sites in Tallinn (2003)

	Viru	Kopli	Õismäe
Jan	30.61	24.15	18.12
Feb	37.59	29.61	23.27
Mar	54.93	39.84	29.07
Apr	50.19	29.72	24.21
May	32.36	25.71	19.57
Jun	34.11	27.03	17.92
Jul	48.42	25.79	22.69
Aug	42.59	23.75	13.11
Sep	37.21	20.72	17.91
Oct	27.60	17.99	12.16
Nov	33.10	20.73	17.49
Dec	28.44	20.70	14.57

It is well known that PM10, PM2.5, and PAHs have a strong impact on air quality associated with urban health problems. The concentration of ambient particles depended on monitoring site. The highest concentrations of particles were observed in the Viru site. Seasonally the values showed increasing trends in all the sites studied in March–April (Table 2). The high concentration of particulate matter in spring could be due to sanding streets and the use of studded tires, which abrade asphalt and release particulate matter from its surface. In spring the traffic and wind raise particulates into the air.

The concentration of PM2.5 in Tallinn was found to be in the range 4–22 μg/m^3 (2003). The total content of fine particles (PM2.5) made up 4–18% of the mass of PM10 particles. Annual average concentrations of PM10 and PM2.5 in the residential area were close to the corresponding data in the centre of Helsinki (Finland), only 80 km away from Tallinn [10].

Semivolatile organic compounds, such as PAHs, demonstrate significant partitioning between the gas and particle phases under ambient conditions. However, under certain conditions, e.g., cold temperatures and high concentration of particles, many PAH compounds can be expected to concentrate in particulate matter. This is the case in Estonian meteorological conditions. That is why the content of PAH compounds was quantified in fractions of particulate matter. The total concentration of these PAHs was in the range 3–6 ng/m^3 in the PM2.5 fraction.

The data received from three monitoring sites of Tallinn were grouped into four categories for annual, seasonal, diurnal, and day-of-the-week trends.

Annual variations

During the three years of monitoring (Table 1), the concentration of NO$_x$ in the city centre (Viru) remained approximately at the same level, whereas PM10 concentration increased over 27%. The increase in the PM10 concentration may be due to the intensive construction work that started close to the Viru site in 2002. The CO and O$_3$ concentrations show decreasing trends in the Viru site. The average concentration of CO was 32% smaller in 2003 than in 2001.

In the Kopli site, a significant increase of NO, SO_2 and PM10 could be observed (50%, 40%, and 20%, respectively) in the studied period of time. The heating intensity should not have changed during the period of investigation. The increase in the concentrations could be explained by traffic intensity at the cargo port, which is suggested to be the main source of technogenic emission in this area.

In the Õismäe residential area the concentration levels of none of the compounds studied changed significantly during the monitoring period. The small variations (Table 1) would not refer to traffic intensity rise or any other considerable development in this area.

Seasonal variations

The winter concentrations of NO_x and CO in the urban area were twice as high as in the summer period (Fig. 2, for 2002). Strong seasonal variations for NO_x concentrations were also estimated in 2003. The mean concentrations of NO_x were found to be very high in the winter, 131.27 μg/m^3, compared with spring, summer, and autumn (99.4, 86.67, 81.8, respectively).

The average weekly concentrations estimated for SO_2 in 2003 were measured as follows: 2.4 μg/m^3 in winter, 4.07 μg/m^3 in spring, and 1.3 μg/m^3 in autumn.

In addition to the direct dispersion and transport of pollutants, the meteorological factors play a role in tropospheric chemistry; these include temperature, sunlight intensity and snow, rain, and fogs [11]. For estimating the role of meteorological factors on levels of gaseous pollutants in ambient air, the ratio of NO concentration to its oxidized form, NO_2, was calculated. The results demonstrated the seasonal variation in the terms of NO/NO_2 ratio, illustrated in Fig. 3. The oxidation of nitrogen monoxide is most pronounced in the warm period of the year with high solar irradiation ($NO/NO_2 < 1$), whereas nitrogen remains mainly in monoxide form in the winter period ($NO/NO_2 > 3$).
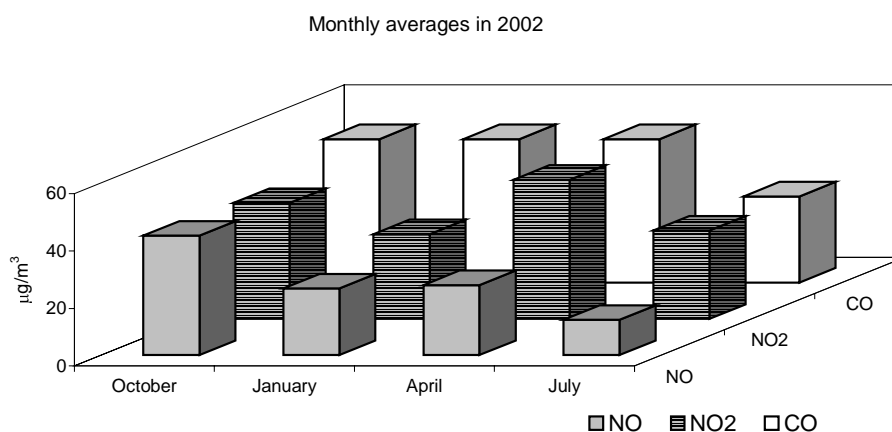

Fig. 2. Monthly average concentrations of NO, NO_2, and CO (×0.1) in the Viru site (2002).
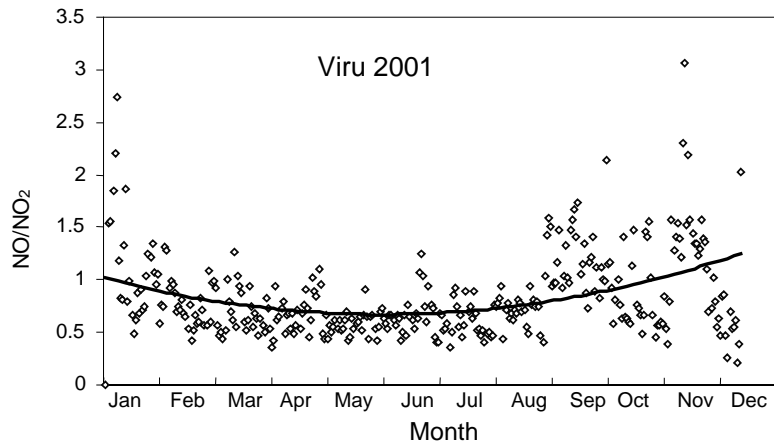
Fig. 3. Seasonal variations of the NO/NO$_2$ ratio in the Viru site (2001).
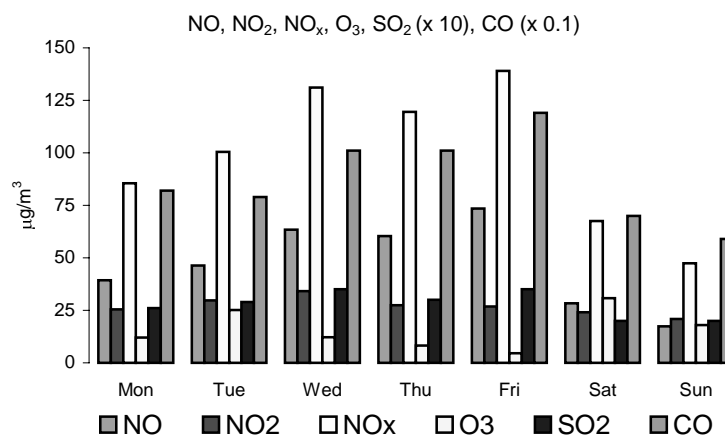

Fig. 4. Weekly trends of gaseous pollutants in the Viru site (winter 2001).

The concentrations of NO$_x$ and CO had significantly higher values in the winter period compared to summer, especially in the middle of the week (Fig. 4). At the same time, the O$_3$ concentration in the summer period was twice as high as that in wintertime.

Days-of-the-week variations

The difference in NO$_x$ and CO concentrations between workdays and weekends (Table 3) could be explained by the changes in traffic intensity. The concentrations of SO$_2$, mainly caused by heating, are much higher in the Kopli than in the Viru site. In the Kopli area domestic heating is dominating, while in the Õismäe and Viru sites central heating systems are used. No extensive conclusions can be made on the basis of daily SO$_2$ concentrations. The values vary in a large scale.

Table 3. Daily averages ($\mu g/m^3$) of NO_x, O_3, SO_2, CO in winter (1–7 Jan) and summer (2–8 July) in the Kopli site (2001)

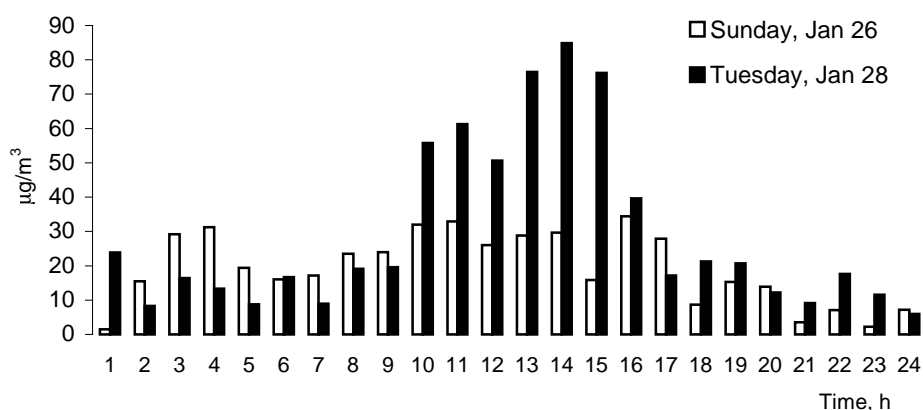|	NO	NO₂	NOₓ	O₃	SO₂	CO
Winter						
Mon	8.6	23	36.2	11.8	4.5	480
Tue	5.9	22.1	31.1	29.3	4.4	410
Wed	7.4	24	35.3	17.2	7.2	480
Thu	13.7	23	44	8.6	5.3	560
Fri	37	23.9	80.4	4.9	2.7	800
Sat	2.8	13.8	18	39.1	2.4	380
Sun	3.2	11.4	16.3	26.2	4.5	370
Summer						
Mon	2.8	9.4	13.7	60.6	0.8	200
Tue	3.7	12.7	18.3	60.7	1.3	170
Wed	2.8	14.4	18.6	67	1.7	170
Thu	2.7	19.3	23.4	62.9	3.1	170
Fri	4.2	25.1	31.6	56.9	3.1	290
Sat	2.1	18.2	21.5	79.8	2.4	180
Sun	1.6	25.3	27.8	67.4	4.6	190

Fig. 5. Diurnal variation of PM10 in the Viru site (January 2003).

In Õismäe, the higher concentrations of NO_x can be observed on Fridays and Saturdays as well as in summer and autumn. In spring, however, the highest concentration was recorded in the middle of the week.

Ambient particle concentrations were found to be on different levels, depending on the season and day of the week (Fig. 5).

Diurnal variations

High differences were observed in the levels of PM pollution over the day (see Fig. 5, Viru monitoring site). As a rule, the concentration of PM10 increased

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after the morning rush hour of automobile traffic and reached a maximum just before midday. During the rush hour in the afternoon high concentration levels occurred again. The maximum diurnal average concentration of PM10 was 142.7 $\mu g/m^3$ in 2003, which was much higher than in 2001. One possible explanation could be the increasing traffic intensity and construction work.

CONCLUSIONS

The levels of priority air pollutants (NO_x, CO, SO_2, O_3, particulate matter) were determined at three sites in Tallinn (Estonia) in 2001–2003:

- The average concentrations of CO and NO_x were many times higher in the city centre (Viru) compared to the industrial (Kopli) and residential (Õismäe) areas.
- A significant increase in the NO concentration (50%) was observed in the Kopli site.
- The concentration of PM10 increased 27% in the city centre (Viru), whereas the concentration of NO_x remained approximately at the same level.
- The average concentration of PM2.5 in the ambient air of Tallinn was in the range 4–22 $\mu g/m^3$.
- The average concentration of total PAH was in the range 3–6 ng/m^3.

ACKNOWLEDGEMENTS

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Õhusaastus Tallinnas, peamiste saasteainete tasemed

Gary Urb, Erik Teinemaa, Antonius Kettrup, Istvan Gebefügi,
Margit Laja, Janek Reinik, Eduard Tamm ja Uuve Kirso

On kirjeldatud Tallinna õhus mõõdetud saasteainete kontsentratsioonide eri-nevusi ja nende võimalikke allikaid. Kolme Tallinna (Viru, Kopli, Õismäe) seire-jaama andmete erinevus gaasiliste komponentide kontsentratsioonides on märki-misväärne, mis viitab erinevatele saasteallikatele neis piirkondades. Kesklinnas on CO kontsentratsioonid kõrgemad, mille põhjuseks on arvatavasti sõiduautode heitgaasid. Kopli piirkonnas toimub aktiivne transporditegevus, kus diiselkütuse põletamise tulemusena on NO_x kontsentratsioonid kõrgemad. Õismäe piirkond on eelnevate aastatega võrreldes jätkuvalt stabiilne nii aerosoolsete gaaside kui ka tahkete osakeste (PM) kontsentratsioonide poolest. PM10 kontsentratsioonid on Tallinnas siiski jätkuvalt kasvanud: näiteks Virus 2001. aastaga võrreldes koguni 27%.