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Time variations in the concentration of pollutants in the atmosphere over Moscow and estimation of their emissions

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Abstract. Data on the surface NO, NO₂, CO, SO₂, CH₄, and PM₁₀ concentrations measured at 46 stations from 2005 to 2014 in Moscow have been used in studying the characteristic features of their distribution over the city area and their time variations. Both seasonal and interannual variations in pollutant concentrations, as well as their 10-year trends, are closely related with variations in the urban infrastructure and weather conditions. The weekly cycle of the pollutants has been analyzed. Its largest amplitude is 18.9±5.6% for NO. For CO, NO₂, and PM₁₀, the amplitudes amount to 9.3±3.2%, 13.6±2.8%, and 10.9±5.5%, respectively. The weekly variations in CH₄ and SO₂ concentrations are not significant for such large-scale territorial averaging. The emission fluxes of CO, NO_x, SO₂, and CH₄ and their integral emissions from the Moscow megacity have been estimated from multiyear measurements of their surface concentrations and both vertical air-temperature and wind stratifications. During 2005—2014, the annual integral emissions of CO, NO_x, and CH₄ decreased with a rate of -1.9±0.3, -1.7±0.4, and -7.8±3.1 %·yr⁻¹, respectively, and that of SO₂ increased with a rate of 3.3±2.3 %·yr⁻¹. The means of integral annual pollutant emissions from Moscow differ slightly from those for other world megacities. The CO emissions coincide with their EDGAR v4.2 inventory values interpolated to the territory of Moscow. However, the EDGAR v4.2 values of NO_x, SO₂ and CH₄ significantly exceed their calculated values.

1. Introduction

Megacities have aroused considerable interest in studying both temporal and spatial variations in the atmospheric composition due to a large number of different air-pollution sources. Simulation is one of the most actively developing lines of investigation in this area. Both initial and boundary conditions—meteorological parameters and estimates of pollution sources—are necessary for chemical transport models. It is not a simple problem to describe urban sources, because data on pollutant emissions obtained from different inventories may significantly differ [1], which results in large errors in model results. In this work, a few methods were used to obtain emission estimates, whose comparison and analysis made it possible to specify urban emissions with a time step of 10 min, for each model cell



located on the territory of the Moscow megacity. The results obtained are an important step towards the development of on-line forecast of air pollution in megacities.

2. Spatial and temporal variations in pollutant concentrations

Both temporal and spatial distributions of pollution were estimated on the basis of data on pollutant concentrations measured at 46 uniformly spaced Mosekomonitoring (MEM) stations from 2005 to 2014. The NO, NO₂, CO, CH₄, SO₂, and (aerosol) PM₁₀ concentrations with a time step of 20 min were averaged over 10 years for each station. In this case, only the values, whose deviations did not exceed three sigma from the mean for each station, were taken into account. The results were used in constructing the dependence of mean concentration on the distance to the city center (Fig. 1). The nonuniform distribution of the pollutants over the city demonstrates that the CO, NO, and NO₂ concentrations are two times lower on the outskirts of Moscow than in its center. Maximum CH₄ concentrations were recorded in the residential zone of Moscow at a distance of 8 to 18 km from the center. Maximum SO₂ concentrations were recorded at stations located in the vicinity of the Third Ring Road (TRR) with a radius of about 5 km and the Moscow Automobile Ring Road (MARR) with a radius of 13 to 18 km, which is characterized by heavy traffic and in the vicinity of which most of heat and power plants are located. The concentration of aerosol within Moscow varies uniformly with its increase over and beyond the MARR.

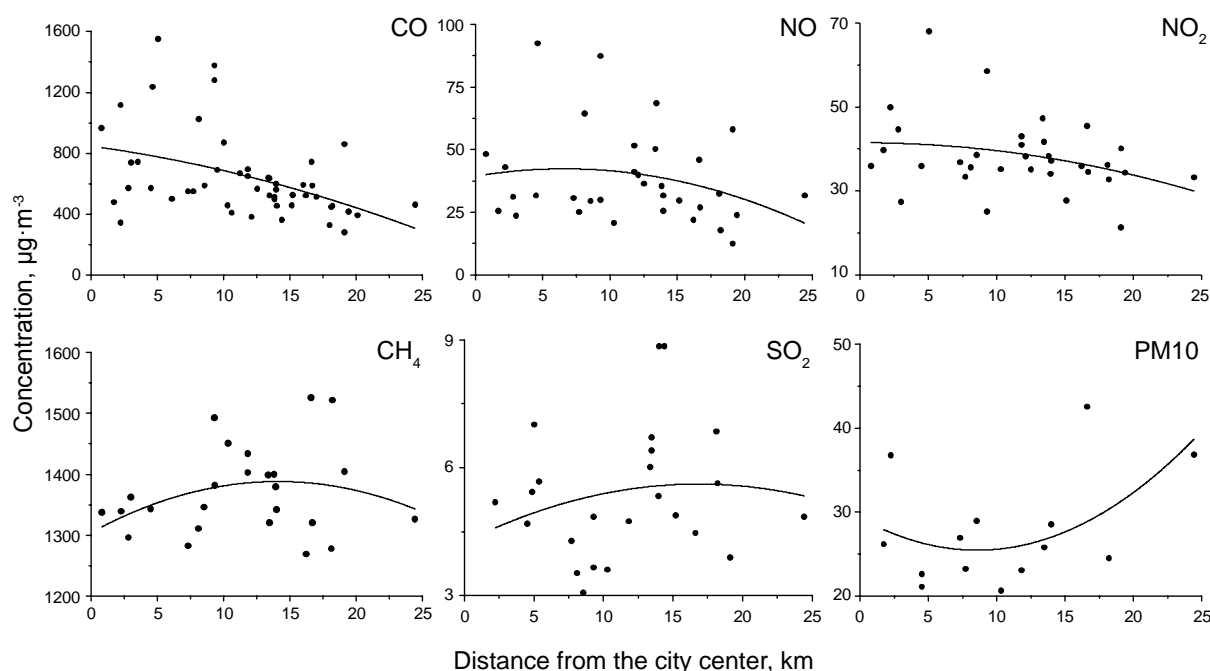


Figure 1. Mean surface pollutant concentrations for 2005-2014 with respect to the distance to the Moscow center and their second-degree trends.

The CO, NO, and NO₂ concentrations measured from the Ostankino TV tower at heights of 10, 130, 248, and 348 m in 2007–2014 made it possible to calculate their mean vertical profiles. As a result, the vertical distribution of carbon oxide has its local maximum concentration at a height of 248 m, which may be caused by the pollutant accumulation at this level during temperature inversions and by emissions from the pipes of factories and heat and power plants. The difference between the vertical profiles of NO and NO₂ concentrations is explained by the fast reaction of NO with ozone and its transition to NO₂. On the whole, one can conclude that both NO_x and CO emissions from urban sources exert their influence up to heights of 230–260 m [2].

The annually mean concentrations averaged over the whole area of Moscow were calculated to characterize time variations in the content of the pollutants in the atmospheric surface layer (see Table

1, 95% confidence interval). The surface CO, NO, CH₄, and PM₁₀ concentrations decreased from 2005 to 2014, and the NO₂ and SO₂ concentrations slightly increased over the same period, however, their positive temporal trend is insignificant.

Table 1. Annually mean pollutant concentrations and their temporal trends for the whole area of Moscow for 2005-2014.

Year	Concentration, $\mu\text{g}\cdot\text{m}^{-3}$					
	CO	NO	NO ₂	CH ₄	SO ₂	PM ₁₀
2005	740 ± 63	49.1 ± 4.2	40.6 ± 3.5	1405 ± 20	7.2 ± 0.8	28.6 ± 5.1
2006	700 ± 93	42.1 ± 5.8	41.0 ± 5.7	1445 ± 40	5.2 ± 1.3	32.9 ± 5.1
2007	610 ± 77	43.7 ± 5.1	38.9 ± 4.5	1450 ± 40	5.0 ± 0.5	36.9 ± 4.7
2008	559 ± 34	38.4 ± 2.7	36.6 ± 2.6	1335 ± 25	2.5 ± 0.6	31.8 ± 4.0
2009	564 ± 37	35.6 ± 3.4	37.9 ± 3.6	1350 ± 15	4.3 ± 1.9	32.3 ± 3.8
2010	653 ± 56	38.3 ± 4.2	41.1 ± 4.5	1305 ± 30	5.1 ± 0.7	35.1 ± 5.0
2011	531 ± 42	28.3 ± 2.4	39.3 ± 3.3	1270 ± 20	5.8 ± 1.8	23.1 ± 3.9
2012	496 ± 31	28.6 ± 2.4	41.6 ± 3.5	1320 ± 20	5.6 ± 0.9	22.1 ± 2.4
2013	482 ± 35	28.7 ± 2.3	42.6 ± 3.4	1315 ± 20	7.1 ± 1.4	22.7 ± 3.4
2014	483 ± 31	26.3 ± 2.2	39.1 ± 3.3	1325 ± 15	5.7 ± 0.4	27.9 ± 4.2
Trend, %·yr ⁻¹	-3.6 ± 0.7	-5.0 ± 0.6	0.3 ± 0.5	-1.1 ± 0.3	-1.1 ± 2.1	-3.7 ± 1.7

Seasonal variations in pollutant concentrations averaged over 10 years from 2005 to 2014 for the whole area of the megacity noticeably differ. Both CH₄ and SO₂ concentrations vary slightly during a year. The SO₂ concentration increases in February due to the use of liquid fuel in the urban heating system under the conditions of extremely low air temperatures, mainly in the first half of the period under consideration. The highest NO concentration was observed during the cold season. A few factors determine such a seasonal effect: first, heat and power plants operate at ultimate load; second, the atmospheric boundary layer over the city is most stable and the mixing-layer thickness is minimum; and third, low levels of UV solar radiation and low concentrations of volatile organic compounds (VOCs) and ozone slow down the transition of NO to NO₂ and the transition of NO_x to NO₃, N₂O₅, and HNO₃. The spring maximum concentration of NO₂ due to the reaction of NO with O₃ coincides with the spring ozone maximum concentration, and its decrease during fall coincides with the fall ozone minimum. The seasonal cycle of the concentration of CO demonstrates its minimum in November—December and significant variations during other months, which is characteristic of Moscow [3].

To determine the weekly variability, the superposed-epoch method was used, in which all Sundays of the time series under analysis served as fixed points. Preliminarily, at each MEM station, linear trends and variations with a period of longer than 8 days were eliminated from data on each pollutant concentration using the inverse Fourier transform method. The variations obtained were expressed in relative units through the point-by-point dividing by the absolute difference between them and the original data. The weekly cycles in relative units for each pollutant at each station were obtained using the superposed-epoch method. The weekly cycles averaged over Moscow, which characterize variations in the (averaged over the Moscow area) concentrations of the pollutants during the mean

(over 10 years) week with their increased values from Tuesday to Friday and decreased values from Saturday to Monday.

Table 2 gives the amplitudes of the (averaged over Moscow) weekly variations in the pollutants according to multiyear daytime, nighttime, and daily mean data. The amplitude is the relative deviation of the concentration value on Saturday, Sunday or Monday from the average value over the working days from Tuesday to Friday. The amplitudes, which are significant and at the significance level, and their 95% confidence intervals, which do not cross the zero line are denoted by bold type.

Table 2. Daytime, nighttime, and daily mean weekly-cycle amplitudes averaged over the area of Moscow and the 2005—2014 observation period.

Air pollutant	Amplitude, %											
	Daytime			Nighttime			All time					
CO	13.6	±	3.3	Su	2.2	±	4.8	Mo	9.3	±	3.2	Su
CH ₄	0.1	±	0.2	Mo	0.1	±	0.3	Sa	0.1	±	0.2	Mo
NO	23.9	±	5.8	Su	6.4	±	10.0	Mo	18.9	±	5.6	Su
NO ₂	16.7	±	2.8	Su	7.5	±	3.9	Mo	13.6	±	2.8	Su
SO ₂	7.6	±	6.5	Su	8.1	±	8.6	Mo	7.0	±	6.9	Su
PM ₁₀	14.5	±	5.1	Su	8.6	±	7.2	Mo	10.9	±	5.5	Su

The greatest decrease in the concentrations of CO, NO, NO₂, and PM₁₀, whose sources are auto transport, is observed on Sundays. The SO₂ concentrations depend on auto transport to a lesser degree. They are significantly affected by emissions from industrial and heat and power plants.

Since only a few percent of cars use natural gas as a fuel, the time cyclicity of vehicular traffic in the city almost does not affect weekly methane variations. The main sources of CH₄ – gas leakage in the urban gas-supply system — also slightly depend on the day of week. Therefore, the small amplitudes of the weekly cycle for CH₄ are observed by day and at night; however, they are not significant.

The amplitudes of weekly variations in all the measured pollutants are not constant in time and vary with season [4]. Figure 2 shows the deviations of daytime, nighttime and daily mean pollutant concentrations for every day of week from their mean values over the same time periods, with respect to which the week-cycle amplitudes given in Table 2 were determined. Variations in pollutant concentrations were calculated for each season and year in the mean. The daytime CO, NO, and NO₂ concentrations demonstrate a clearly pronounced weekly cycle in all the seasons. The highest deviations are observed on Sunday. The maximum Sunday decrease for CO and NO concentrations is observed in winter, and for NO₂ – in summer. It is equal 14.8±6.3% for CO, 28.0±14.7% for NO, and 18.8±9.1% for NO₂. The weekly-cycle amplitudes for SO₂ and PM₁₀ are maximum in fall and amount to 15.2±11.5% and 21.2±8.9%, respectively.

In nighttime data series, the weekly cycle is completely absent or at the significance level for all pollutants except NO₂ and PM₁₀. They annually mean amplitude reaches 7.5±3.9% и 8.6±7.2%, respectively. The Sunday effect is most noticeable in the cold season, when the dissociation of NO₂ and the transition of NO_x to NO₃ and N₂O₅ are hindered. The highest NO and NO₂ concentrations are observed from Thursday to Friday and from Friday to Saturday nights. The cleanest nights are from Saturday to Sunday and from Sunday to Monday. The night activity of auto transport during a week is reflected in such variability. The similar effect is also observed in other megacities [5].

The weekly cycle is pronounced in different districts of Moscow in different ways. The high weekly-cycle amplitudes for CO, NO, and NO₂, which amount to 21.0±1.6%, 25.1±2.5%, and 17.8±1.6%,

respectively, are characteristic of the central part of Moscow, in which there is a business center whose office buildings are mostly empty on Saturday and Sunday. Correspondingly, the traffic – the main source of CO and NO_x in the city center – is least active on these days. Small amplitudes of CO and NO_x are characteristic of the southeastern sector of Moscow. Here, the main portion of emissions is contributed by both industrial and heat and power plants continuously operating.

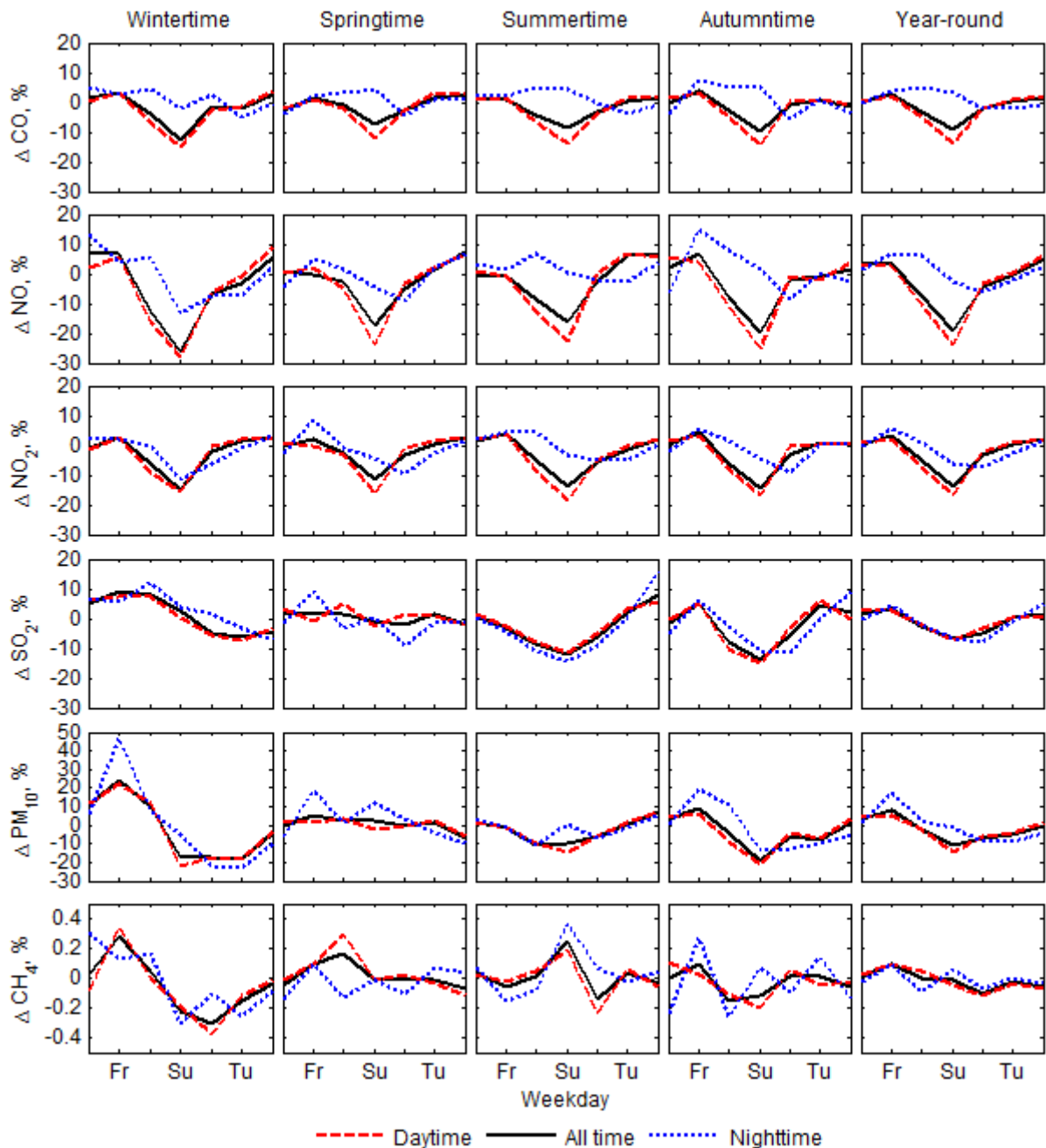


Figure 2. Weekly variations in the surface pollutant concentrations averaged over the Moscow area and over seasons (2005–2014 observational data). Daytime, nighttime, and daily mean variations – deviations from the mean values over Tuesday–Friday.

The forest zone occupies a significant part in the northeastern sector of Moscow. Here the traffic is least intensive, which results in minimum weekly-cycle amplitude for CO. The weekly cycle of the

PM₁₀ concentration slightly varies throughout the city area, however, its largest weekly-cycle amplitude is observed in the southwestern sector of Moscow with heavy traffic.

The character of variations in surface pollutant concentrations within the green belt around Moscow during a week significantly differs from that within the city. The Sunday effect is completely absent in CO, CH₄, and SO₂ variations. The weekly-cycle PM₁₀ amplitude is at the significance level, and only the NO and NO₂ concentrations demonstrate their significant decrease on Sunday (14.1±2.5% and 20.1±3.7%, respectively). Six stations, which are located at a distance of 30 to 70 km from the city center, operate within the green belt in small-populated areas.

3. Estimating pollutant emissions

A simple box model, which is usually used for solving inverse problems, is used as the first method to obtain anthropogenic emissions [6]. The following formula was used in calculating emissions:

$$F = \frac{\Delta C_i \cdot H}{\tau}, \quad \tau = \frac{\sqrt{\pi \cdot S}}{2 \cdot V}, \quad Q = F \cdot S, \quad (1)$$

where F is the pollution flux per unit area per unit time, Q is the total amount of pollutants emitted from the whole city surface during time τ , V is the mean wind velocity, S is the city area, H is the mixing-layer height, and ΔC_i is the difference between pollutant concentrations measured within the city and at a regional background station located outside the city. The annually mean emissions from the Moscow megacity and their time trends were obtained with consideration for both temperature and wind-velocity profiles measured at the Ostankino TV tower (see Table 3).

Table 3. Annually mean pollutant emissions in Moscow for 2005—2014 and their time trends.

Year	Q(CO), Gg·yr ⁻¹			Q(NO _x), Gg·yr ⁻¹			Q(SO ₂), Gg·yr ⁻¹			Q(CH ₄), Gg·yr ⁻¹		
2005	760	±	167	42.3	±	10.4	9.9	±	2.9	206	±	79
2006	767	±	173	43.6	±	10.8	7.2	±	2.3	289	±	107
2007	719	±	159	42.0	±	10.4	7.1	±	2.1	299	±	113
2008	695	±	154	40.7	±	10.0	3.8	±	1.2	121	±	47
2009	718	±	156	38.7	±	9.3	6.7	±	1.9	156	±	56
2010	732	±	172	39.8	±	9.8	7.5	±	2.2	90	±	39
2011	678	±	147	36.3	±	8.6	9.0	±	2.3	189	±	67
2012	649	±	144	37.2	±	8.7	9.9	±	2.5	113	±	38
2013	639	±	135	39.3	±	9.1	11.7	±	3.1	115	±	39
2014	638	±	136	36.8	±	8.6	9.5	±	2.5	133	±	45
Trend, %·yr ⁻¹	-1.9	±	0.3	-1.7	±	0.4	3.3	±	2.3	-7.8	±	3.1

Significant negative trends Q were obtained for CO and NO_x, which is the result of car-fleet replacement during the period under consideration. A noticeable CH₄ concentration decrease due to the modernization of the gas-supply system in the early 2000s may also be noted [7]. Unlike the other pollutants, the SO₂ emissions had a positive time trend because the total number of cars, including those running on diesel fuel, increased (Figure 3).

Using the gradient method of estimating emissions from vertical concentration profiles makes it possible to noticeably improve time resolution, when compared to the box method described above. In

this case, it is assumed that, under weak-wind and weak-convection conditions, the integral pollutant content in a vertical atmospheric column is bound to linearly increase with time, and the rate of this increase is determined only by emissions. The mean daily cycles of CO and NO_x concentrations at the four levels of the Ostankino TV tower were calculated for the days with weak winds. These daily cycles show the presence of morning maximum concentrations due to increased auto transport activity during this period and the absence of developed convection. The integral content of both CO and NO_x in a layer 350 m thick was calculated for each hour and, then, was averaged over all days with appropriate weather conditions. As a result, the curves of the mean integral content of CO and NO_x were constructed, on which a region with their maximum increase was chosen and approximated by a linear function (see [8]). The obtained linear rate of increase in the integral concentration of the pollutants corresponds to their fluxes per unit area during the morning hours specified.

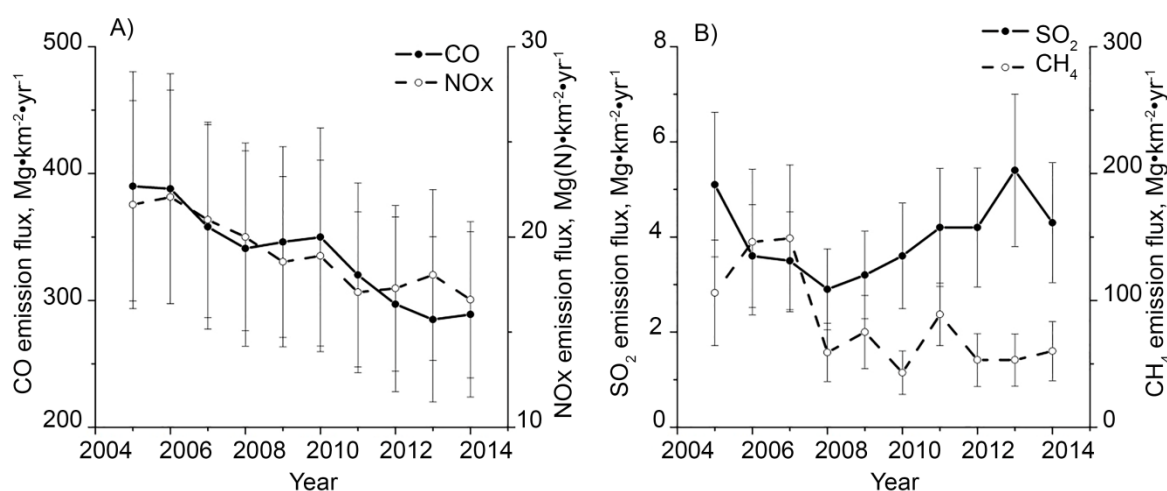


Figure 3. Integral annually mean pollutant emissions from the whole Moscow area.

The annually mean and monthly mean CO, NO_x(N), SO₂, and CH₄ emissions were calculated. The annually mean values are in good agreement with the results of the box method. The seasonal variations in the emissions of CO and NO_x(N) are identical: maximum in September and minimum in July. Integral emissions, as a balance between the sources and sinks of CO and NO_x depend on auto transport, heat and power industry, UV solar radiation level, and concentrations of VOCs and ozone. If the intensity of auto traffic, as a main source, does not depend on season, the sinks have a clearly pronounced seasonal cycle: the concentration of surface ozone is minimum in fall and VOC concentrations and UV radiation intensity are maximum in summer. Therefore, seasonal variations in the emissions of CO and NO_x are in good correlation with seasonal variations in their sinks.

4. Simulation

The emission values obtained in this work for the Moscow megacity were used as input parameters in the SILAM chemical transport model developed at the Finnish Meteorological Institute (URL: <http://silam.fmi.fi>). The SILAM model is a meso-global dispersion model operating in both Eulerian and Lagrangian coordinates [6]. Both initial and boundary conditions were specified for a rectangle with coordinates 55.4—56°N and 37.2—38°E. The TNO-2011 (URL: <http://www.tno.nl/emissions>) and MACC-III (URL: <http://www.gmes-atmosphere.eu>) inventory data were used to specify emissions for the territory outside the megacity. Meteorological parameters were specified using on-line data of the HIRLAM prediction model (URL: <http://hirlam.org/>).

January 15—31, 2014, the period, when the wind velocity did not exceed 2 m/s, was chosen for simulation. Such weather conditions are of prime interest, because they result in the accumulation of pollutants within the megacity and a significant increase in their daily mean concentrations.

The annually mean emission values previously obtained were interpolated in time using weighting coefficients obtained from seasonal variations in pollutant concentrations, their weekly cycle, and diurnal emission variations taken from the TNO inventory. The integral emission of each pollutant from the whole megacity area was distributed over the model cells with consideration for the two weighting coefficients: the first one was determined from the dependence of mean pollutant concentration on the distance to the megacity center and the other was determined from the concentration distribution over five sectors of the megacity (center, NE, NW, SE, and SW).

In order to minimize standard deviations in simulation results from observational data, calculations of an optimal emission distribution over the model cells were performed. Student's test is used as a criterion of estimating results.

To compare simulation results with observational data, calculations were performed, when specified emissions were taken only from the TNO-2011 inventory. Figure 4-A-B shows the mean difference between calculated and observed CO-concentration fields over the simulation period. Unlike the scenario with emissions taken only from the TNO-2011 inventory (Fig. 4-B), in the case of optimal emission distribution (Fig. 4-A) over the model cells, there is no increased mean carbon-oxide concentrations for the megacity.

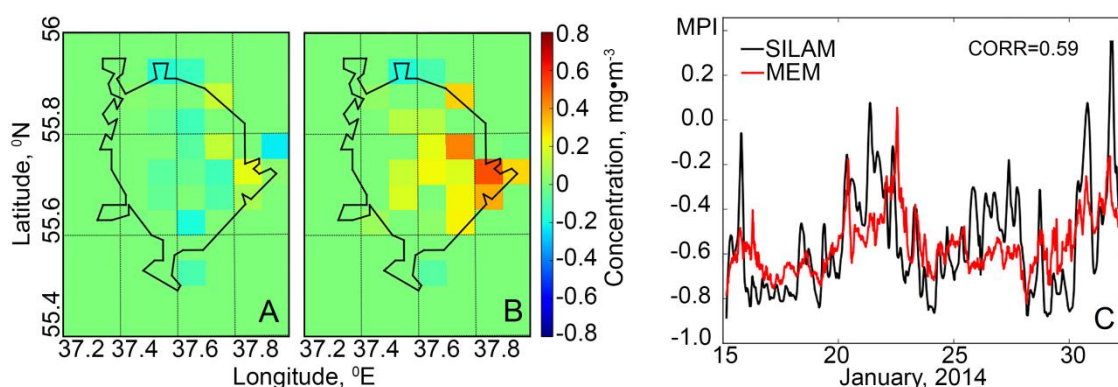


Figure 4. Mean differences between CO concentrations (for January 15—31, 2014) obtained from the SILAM model using IFA (A) or TNO (B) emission estimates and measured at the MEM stations and time MPI variations (C) over the same period for the Moscow megacity.

The CO, NO₂, SO₂, and PM₁₀ concentration fields made it possible to calculate the distribution field for the multiplicative pollution index (MPI) from the formula

$$MPI = \frac{1}{n} \cdot \sum_{i=1}^n \frac{AC_i - GC_i}{GC_i}, \quad (2)$$

where n is the number of pollutants, in this case $n=4$; AC_i is the annually mean concentration for the i -th pollutant, which is averaged over all stations; GC_i is the daily mean maximum permissible concentration (MPC) for the i -th pollutant according to WHO recommendations (2000).

The MPI mean over the calculation period amounted to -0.75, and the correlation coefficient between the calculated (from simulation results) and measured values of the MPI amounted to 0.59 (Fig. 4-C).

5. Conclusions

A complete observational data file obtained at the MEM stations over the 2005—2014 period was used to analyze the time variability and distribution of the NO, NO₂, CO, SO₂, CH₄, and PM₁₀ concentrations in the atmospheric surface layer over the Moscow megacity. The characteristic features of diurnal and seasonal variations in pollutant concentrations were revealed and their dependence on local sources and meteorological parameters was shown. The highest variability is characteristic of pollutant concentrations measured at stations located in the vicinity of motorways. The CO, NO, CH₄,

and PM_{10} concentrations averaged over the megacity demonstrate their significant negative trends. The MPI of the urban air shows a significant increase in the air quality over the indicated 10-year period. The complete volume of observational data obtained at 46 MEM stations from 2005 to 2014 was first used in determining both temporal and spatial features of weekly cycle. The weekly-cycle amplitudes for all the indicated pollutants and their dependence on local sources were estimated. The integral pollutant emissions from Moscow were calculated using the following two approaches: (1) from data on surface pollutant concentrations and vertical temperature and wind stratifications; and (2) from the rate of variations in pollutant concentrations in a vertical atmospheric column during the first half of days. Both the approaches yielded similar results. Comparison of the calculated emission values with data from the EDGAR v 4.2 global inventory yielded ambiguous results. On the one hand, the CO emission values almost coincided, and, on the other hand, the inventory data for NO_x , SO_2 , and CH_4 proved to be significantly higher. It follows from an analysis of contributions made by some sources that the emissions from enterprises of metallurgical and chemical industries are significantly overestimated in this inventory (especially SO_2 emissions during house heating). The emission values obtained were used in the SILAM regional chemical transport model to study the influence of Moscow on the composition and state of the regional atmosphere. The pollutant fields obtained are closer to observational data obtained at the MEM stations than the pollutant fields constructed based on data from both EDGAR v 4.2 global and European TNO inventories.

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