Influence of air temperature on air composition in Moscow

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Abstract. Empirical relations between T and surface concentrations of CO₂ and five minor air gases have been studied on a base of hourly data during 12 years. In wide range -6…+15 ºC significant changes of minor gases are absent. Real tendencies are increase of O₃ and, vice versa, fall of NO and NO₂ with increasing T from +15…+17 to +38 ºC. Both effects are a consequence of unstable stratification that enhances vertical mixing. In cool weather -7…-18 ºC O₃ falls whereas nitrogen oxides grow with decreasing T due to frequent inversions and slowing down the NO oxidation rate. At an even lower temperature up to -30 ºC NO and NO₂, vice versa, decrease with decreasing T – probably, due to strong cold advection of clean Arctic air. Unlike minor gases, CO₂ decreases with increasing T up to 25 ºC due to photosynthesis intensification from winter to summer. Seemingly growth of CO at T>27 ºC is fully explained by smoky haze during heat waves in 2010 and 2002. The CO₂ growth in hot weather is also created by heat stress of trees. Thus, except only oxidation rate, any influence of T is indirect as a result of stratification, photosynthesis, smoky haze, advection, etc.

1. Introduction
As is known a ratio between major air gases (N₂, O₃ and Ar) in the atmosphere is constant everywhere up to 80+100 km heights. Changes in the dry air chemical composition relate to different content of CO₂ and minor air gases (ozone, nitrogen oxides, carbon monoxide, sulfur oxides, methane and others). In fact, carbon dioxide surface concentration in mid latitudes in the Northern hemisphere demonstrates clear annual course and geographical differences between dry land and oceans due to photosynthesis production by forests. Spatial distribution of minor air gases and their temporal changes depend on their main sources which are concentrated in big cities and industrial regions for NO, NO₂, CO₂ in wetlands and around gas pipelines for CH₄, etc. [1]. Studying the air composition in cities is important because of the strong influence of minor gases on human health. Topical issue is the relation between meteorological parameters and concentrations of minor gases. These relations have both scientific and practical importance, including their possible use for air pollution forecasting in big cities. Some examples of similar empirical relations are presented in the literature, but they are usually calculated on the basis of relatively short data series and for a limited range of considered parameters. Among others, positive formaldehyde function of the air temperature T in Beloyarsky city (Khanty-Mansi autonomous region of the Russian Federation) for one year is presented in [2]. The CO functions of the wind velocity V under the conditions of both the surface inversion and the elevated inversion are demonstrated in [3]. The dependences of the concentrations of CO₂ and minor gases in the air on V are presented by authors in [5].

The aim of this work was to obtain for the first time statistically significant empirical functions of T for various air gases based on long-term hourly data for 12 years. Preliminary results were published earlier in [6].

2. Data and methodology
The special ecological station was created jointly by the Obukhov Institute of Atmospheric Physics (IAP) and Lomonosov Moscow State University (MSU) on the territory of the MSU Meteorological Observatory in the south-west of Moscow at about 8 km from the centre of Moscow Kremlin (city centre). This area, located close to the Botanical Garden of Moscow State University, has low-density
urban development (only scientific buildings). No plants or other industrial objects operate in the vicinity of MSU area, and two of the three nearby major roads with heavy traffic are located 500 m from the Observatory. Another road (Michurinsky avenue) is closer (at only 200 m), but it was closed for several years due to the subway construction. Thus, the air quality is comparatively high here and represents the cumulative impact of all urban emissions (the so-called ‘urban background’ without any prevailing emission source). As a result, the air composition measurements there are representative and show real dynamics of air pollution.

The continuously measured surface concentrations of CO₂ and various trace gases, including O₃, NO, NO₂, CO and SO₂ were taken at this station. Ozone was measured using a Dasibi 1008-RS gas analyzer based on recording radiation attenuation with the 253 nm wavelength. Carbon monoxide was measured by infrared absorption using a TE48S analyzer. Nitrogen oxides were measured by the chemiluminescence method using a TE42C-TL gas analyzer. Sulfur dioxide was detected by the fluorescence method using a Horiba APSA-360 analyzer. The error in measuring of O₃ amount is ±1 ppb (by volume); in measuring NO and NO₂ is up to ±0.05 ppb; in measuring SO₂ is up to ±0.5 ppb; the errors in measuring CO and CO₂ are ±10 ppb and ±1 ppm, respectively. The measuring instruments used at the ecological station fully complied with the state standard and international requirements for measuring systems operating at the network of stations of the Global Atmosphere Watch of the World Meteorological Organization (GAW WMO) [5]. The height of all gas intakes at the station was 4 m above the ground.

The total sampling of all data from 2002 to 2014 for O₃ is 100,412 hours; for NO and NO₂ is 72,740 and 72,738 hours, respectively; for CO and CO₂ is 101,074 and 97,948 hours, respectively; for SO₂ is 79,773 hours (measurements of this gas started later, in 2004).

Hourly measurements of T are carried out at the MSU Meteorological observatory uninterruptedly using the classic thermograph records, the data of which are corrected according to the thermometer readings in the Stevenson box every 3 hours. Both liquid thermometers and a thermograph (supplied with a bimetallic sensor) are regularly tested and calibrated in accordance with [7] in the department of verification of the Russian Hydrometeorological Service. As is known, the accuracy of T measurements with a thermometer in the Stevenson box is ±0.2 °C. Both the thermometer and thermograph are installed at a height of 2 m.

It should be noted that this analysis represents the first step without separately considering the daily and annual courses of T. Evidently, any value of T can be detected at different seasons and at different times of the day (e.g., the value of +15 °C in mid-latitudes is typical both for summer nights and for mid-spring and early autumn midday). In fact, the response of the air composition to a certain value of T can be different depending on other factors (presence or absence of short-wave solar radiation, etc.). However, we do not study here the possible influence of other factors on the air composition.

3. Results of analysis

3.1. Air temperature

Let us discuss the main results of our studying. All continuous stationary data on T during the operation of gas analyzers from February 1st, 2002 to July 21st, 2014, were collected and analyzed. The total sample of T values is 109,287 hours during 4554 days. The histogram of T (close to the distribution function) is presented in figure 1. As is seen, it is bimodal. The main winter mode of 1 °C (i.e. from 0.5 to +1.4 °C) is sharp: 5079 hours. The secondary summer mode is wider and less: 3455 and 3459 hours for 15 and 16 °C, respectively. Evidently, the minimum between these maxima (2530 hours at 7 °C) means a comparatively fast transition of T in the annual course in spring and autumn. Distribution wings extend far in both directions: down to -30 and up to +38 °C, thus a range of the T values for 12.5 years is 68 °C. The coldest day was January 18th, 2006 due to strong cold advection of Arctic air [8], when the minimal T was -30.1 °C: it was 4 hours in the early morning of this day and another hour the next day January 19th with T≤ -29.4 °C. On the other hand, an extremely high air
temperature was detected during the intense heat wave in the summer of 2010: a total of 5 hours were detected with $T \geq 37.5 \, ^\circ \text{C}$ at midday: one hour – on July 26th, one hour – on July 29th, three more hours – on August 2nd. It should be noted that the maximal $T$ value for the entire history of meteorological observations at MSU since 1954 was observed on July 29th, 2010: +38.1 \, ^\circ \text{C} \, [9]. It is also important to note that the range from -25 \, ^\circ \text{C} (51 hours) to +35 \, ^\circ \text{C} (33 hours) is provided with sufficient sampling for statistical analysis (at least 30 separate values for each gradation).

![Figure 1. Air temperature T distribution function by hourly data from February, 2002 to August, 2014 in Moscow.](image)

3.2. Ozone

Empirical ozone function of $T$ based on the entire measurement period 2002-2014 is presented in figure 2. As one can see, there are no significant changes in the wide $T$ range from -7 to +15 \, ^\circ \text{C}. For higher air temperature, there is a clear tendency to an increase in $O_3$ with an increase in $T$. Evidently, such high $T$ values are mostly observed in mid latitudes under unstable stratification in midday in summer or late spring. Thus, the increase in $O_3$ is explained by both its chemical source (photochemical dissociation of $\text{NO}_2$ molecules in the presence of ultraviolet solar radiation with a wavelength $\lambda < 410 \, \text{nm}$), and the downward $O_3$ transport from upper air layers under conditions of intense thermal convection and vertical mixing. It should be noted that extremely high ozone values in strong heat ($T > 30 \, ^\circ \text{C}$) are mainly associated with two strong heat wave cases in the summer of 2010 and 2002. In both cases, there was a dense smoky haze from forest and peat fires around the Russian capital above the city. Therefore, in these conditions, additional ozone generation took place in these fire plumes [4]. Thus, at $T = 37 \, ^\circ \text{C}$ the average $O_3$ amount is extremely high: 84.7 ppb (data sampling for this $T$ value is 13 hours).

On the other hand, at low air temperature ($T < -7 \, ^\circ \text{C}$) there is a tendency for a gradual decrease in $O_3$ with a decrease in $T$ to at least -21 \, ^\circ \text{C}; at even lower $T$ this drop goes to nothing, so the $O_3$ level is stabilized with an extremely low amount (3-4 ppb only at $T$ from -25 to -29 \, ^\circ \text{C}). Probably, the decrease in the ozone content is due to the prevailing stable stratification, including frequent surface inversions, which prevent vertical mixing and downward $O_3$ transport from the upper air layers to the surface. Inside the inversion layer, the ozone content decreases due to the dry deposition of this gas on the surface. In addition, in late autumn and in winter, the incoming ultraviolet radiation is extremely low due to the low altitude of the Sun and frequent dense low clouds. Thus, the photochemical generation of $O_3$ in the lower atmosphere is almost absent at these seasons. As a result, on average the lower $T$, the less the surface ozone concentration. However, during severe strong frosts at $T < -21 \, ^\circ \text{C}$, this tendency is not clear.
3.3. Nitrogen oxide and nitrogen dioxide

Nitrogen oxide and dioxide, unlike other minor air gases, demonstrate significant changes in the middle of the T range (from about -7 to 20 °C for NO and from -7 to 16 °C for NO$_2$), but these changes are small and non-directional. At higher T, a clear and statistically significant tendency towards a decrease in NO and NO$_2$ with an increase in T is seen from figure 3. Evidently, this is due to the predominance of unstable stratification at midday in summer and late spring. Thermal convection leads to the upward dispersion of both gases which are mostly produced by low sources of fuel burning (moving cars). In contrast, at lower T (from -7 to -18 °C), both pollutants grow rapidly with decreasing T. Probably this is a result of both the prevailing stable stratification in winter, preventing dispersion, and the slowing down of NO oxidation rate to NO$_2$ under negative T values. Therefore, it is not surprising that at T < -10 °C the NO/NO$_2$ ratio becomes >1 whereas at any higher T it is less than 1.

![Figure 2](image2.png)
**Figure 2.** Dependence of the surface ozone concentration on air temperature T by the data from 2002–2014 in Moscow. Confidence intervals are calculated with a 0.95 confidence probability.

![Figure 3](image3.png)
**Figure 3.** Dependence of NO and NO$_2$ surface concentrations on air temperature T by the data from 2002–2014 in Moscow. Confidence intervals are calculated with a 0.95 confidence probability.
Finally, at extremely low T < -18 °C the opposite tendency towards a decrease in NO and NO2 with a decrease in T is evident. This is probably the result of strong cold advection of Arctic air with low background levels of NO and NO2.

3.4. Carbon oxide

The CO function of T is presented in figure 4. As with ozone, there are no significant changes in CO amount over the wide range of T from -6 to 27 °C. The sharp increase in CO with increasing T at an even higher air temperature, especially at T > 32 °C, requires an explanation. For this, we separately considered all cases of haze detected at the MSU Meteorological observatory from February 2002 to July 2014. As is known, haze is a meteorological phenomenon of strictly limited horizontal visibility (< 10 km) not due to the presence of small water droplets (like mist), but because of dry particles in the air: smoke, dust, soot particles, etc. Both mist and haze lead to limited visibility, but haze, unlike mist, is accompanied by grey or brown sky color and as a rule by low relative humidity [7]. Thus, in total during the operation of the station, there were 67 separate cases (total – 849 hours) of haze; mainly in extremely hot summers of 2010 and 2002, when forest and peat fires often occurred around Moscow. The longest episode of strong smoky haze (plumes from multiple fires) lasted 112 hours 15 min continuously from August 6th to August 11th, 2010. During these days, horizontal visibility dropped to only 100 m on August 7th and extremely high air pollution was detected.

Figure 4 b) shows a separate calculation of CO average surface concentrations during haze and at all other times. As one can see, the sharp CO growth under extremely high T, especially at T=34 °C, is fully explained only by the presence of haze. In the absence of haze, the CO function of T is smoothed to its highest 37 °C value (all 5 hours of CO measurements with T = 38 °C were detected during a strong smoky haze). Thus, the only significant tendencies of CO levels depending on T is their gradual increase with decreasing T from -6 to -26 °C and, vice versa, a fall under extremely low air temperature below -26 °C. The first tendency is the probable result of the prevailing stable stratification including frequent strong surface inversions which contribute to the accumulation of CO, as well as other fuel combustion products from low sources (mostly emitted by urban transport). In addition, the rate of CO oxidation as well as NO slows down under low T. The opposite tendency for CO to fall with decreasing T for T< -26 °C seems surprising but is apparently explained by the strong cold advection of continental Arctic air from the Arctic region. It should be noted that all 54 hours with T ranging from -27 to -30 °C took place in four days during just two synoptic periods: January 18th, 19th, 20th and February 06th, 2006. Clean Arctic air has a low background CO level and, due to its quick invasion into Moscow region, it did not have enough time to saturate the fuel combustion products above the city. In addition, thermal stratification during intense cold advection is unstable, which also leads to air cleaning due to upward dispersion of pollutants.

Thus, the influence of air temperature on surface CO concentrations, except for only a slowdown in the oxidation rate with decreasing T, is indirect through stratification, advection, smoky haze and other possible factors.

3.5. Carbon dioxide

Besides minor air gases, the surface CO2 concentration also was measured at the station. As is known, it has been continuously growing globally at almost the same rate, at least since the middle of the 20th century according to the well-known so-called ‘Keeling curve’ at the Mauna Loa Observatory – e.g., [10]. For the period 2002–2014, CO2 there has increased from 373 to 399 ppm. In European Russia (in Obninsk town in Kaluga region, 96 km south-west of the centre of Moscow, according to RPA ‘Typhoon’ measurements), the CO2 content is higher than in the Pacific Ocean and ranged from 380 ppm in 2002 to 400 ppm in 2014 [11]. In such a large city as Moscow, it is still slightly higher according to the measurements at IAP and MSU ecological station: from 386 ppm in 2002 (by the data of 11 out of 12 months) to 406 ppm in 2013.

Unlike minor gases, the CO2 function of T (see figure 5) demonstrates a steady decrease with increasing T over a wide range from -18 to +25 °C. The evident reason for this is the annual course of
carbon dioxide, which is especially clear in mid latitudes in the Northern hemisphere due to changes of photosynthesis intensity in different seasons. According to [11], the CO₂ annual course in Obninsk is characterized by minimal values in summer from June to August and maximal values in November and December. In Moscow, according to the data of IAP and MSU ecological station, the annual CO₂ course is similar: the minimum is the same from June to August (382±385 ppm), but the maximum is shifted forward in time to January and February (404±405 ppm). Thus, a decreasing function in figure 5 demonstrates a total transition from high winter CO₂ values to low summer ones with increasing T.

![Graph showing CO₂ concentrations versus air temperature]

**Figure 4.** Dependence of the CO surface concentrations on air temperature T in Moscow according to 2002±2014 data. Confidence intervals are calculated with the 0.95 confidence probability.
a) Whole data sampling;

b) Data separation based on the presence of haze.

Figure 5. Dependence of surface CO₂ concentrations on air temperature T in Moscow according to 2002-2014 data. Confidence intervals are calculated with the 0.95 confidence probability.

A sharp growth of CO₂ concentration for T from +33 to +37 °C relates to strong smoky haze, as well as for CO. Separate recalculation of all values, both during haze and in the absence of this phenomenon (figure 5 b), demonstrates that a sharp maximum of 406 ppm at T = +34 °C is fully explained by the increase of CO₂ as a product of combustion in fire plumes. Haze was detected during 22 out of 36 hours of CO₂ measurements at +34 °C, and the average value for this partial sampling is 422 ppm, whereas the average value for the rest 14 hours without haze at +34 °C is only 380 ppm.
a) Whole data sampling:

![Graph showing sulfur dioxide concentrations vs air temperature in Moscow over 2004-2014 data.](image)

*Figure 6.* Dependence of surface SO$_2$ concentrations on air temperature T in Moscow according to 2004-2014 data. Confidence intervals are calculated with the 0.95 confidence probability.

However, it should be noted that in the conditions of extremely hot weather, even in the absence of haze, the CO$_2$ levels are a bit higher than at lower air temperature. As one can see in figure 5 b), the average concentration at T from +28 to +33 °C is 376±377 ppm, whereas at T from +34 to +37 °C it is 380±381 ppm (at the highest air temperature of +38 °C, as well as for CO, all 5 hours of measurements were received during haze). The difference between the last two average values at +36 and +37 °C and any value between +28 to +33 °C is statistically significant with the 0.95 confidence probability as seen from the confidence intervals. The reason for this effect is the oppression of the activity of trees during strong heat wave, which leads to the slowing of photosynthesis rate [12]. Thus, the CO$_2$ growth in extremely hot weather is the result of at least two factors: both oppression of trees and a high concentration of this gas in plumes of fires during smoky haze. At low values T < -18 °C, the CO$_2$
function of T is not monotonous. In general, this gas decreases with decreasing T during severe frosts, which may be the result of low background values of CO$_2$ in the Arctic air.

3.6. Sulfur dioxide

One more minor air gas we are studying is sulfur dioxide. As can be seen in figure 6, it has the longest range of non-significant changes depending on T among other gases: from -16 to 33 °C. At higher T, the growth of SO$_2$ is weaker than that of CO and CO$_2$. Nevertheless, the effect of smoky haze is also detected for SO$_2$: a separate calculation without hours of haze demonstrates a smoothed SO$_2$ function. Thus, the plumes of fires during the catastrophic heat wave in summer 2010 contained sulfur dioxide along with other combustion products. A sharp increase with decreasing air temperature at T < -16 °C is explained not only by stable stratification, but also by an increase in urban heating – especially during severe frosts. As is known, in the extremely cold winter of 2006, reserve fuel (fuel oil and coal) with an increased sulfur content was used in Moscow [5,8]. Thus, unlike NO, NO$_2$ and CO, the SO$_2$ concentration in Moscow remained anomalously high even at extremely low T values.

Thus, almost any influence of air temperature on air composition, as a rule (except for only changes in the oxidation rate) is indirect and manifests itself in thermal stratification, smoky haze, photosynthesis activity, advection, the intensity of urban heating emissions, and other factors.

4. Conclusions

1. The influence of air temperature T on air content is usually relatively weak and, as a rule, indirect. In a wide range of T from -6/-7 °C for O$_3$, NO, NO$_2$ and CO to 15/-16 °C for O$_3$, NO$_2$, 20 °C for NO and 27 °C for CO, no significant changes or any direct tendencies were found. For SO$_2$ this range is even wider: from -16 to 33 °C. Unlike minor air gases, carbon dioxide demonstrates a gradual decrease with increasing T from winter to summer up to 25 °C due to its annual course connected with intensive photosynthesis during the summer growing season.

2. At high T values (>15 °C for O$_3$, >16 °C for NO$_2$, and >20 °C for NO), clear tendencies towards the growth of ozone and, vice versa, a decrease in nitrogen oxides are revealed. Both tendencies seem to be the consequence of unstable stratification, i.e. thermal convection, which enhances vertical mixing during daytime in summer and in late spring. More intense mixing leads to upward dispersion of NO and NO$_2$ and, on the contrary, to downward transport of O$_3$ to the surface from upper air layers. In addition, the incoming solar radiation also leads to an additional ozone increase due to its chemical generation.

3. At comparatively low T values (<-7 °C for O$_3$, from -7 to -18 °C for NO and NO$_2$, from -7 to -26 °C for CO and < -16 °C for SO$_2$) a fall of ozone and, vice versa, an increase in NO, NO$_2$, CO and SO$_2$ with decreasing T were detected due to prevailing stable stratification, including frequent surface inversions, which prevent vertical mixing of air dispersion of minor gases. This leads to O$_3$ decrease due to its dry deposition on the surface and to the accumulation of other minor air gases near the surface. Besides, slowing down the oxidation rate of NO to NO$_2$ also leads to increase of nitrogen oxide. The SO$_2$ growth is also the result of increased urban heating.

4. At extremely low T during severe frosts (<-18 °C for NO, NO$_2$ and < -26 °C for CO), an opposite tendency is revealed for a decrease in NO, NO$_2$ and CO with a decrease in T is detected as a result of strong and rapid cold advection of clean Arctic air with low a background of these gases to Moscow region. Unlike these gases, the SO$_2$ levels remain high during severe frosts due to the use of reserve oil fuel for urban heating.

5. The seeming growth of CO at high T (> 27 °C) is fully explained only by the influence of smoky haze from forest and peat forests as a result of strong heat waves in the summer of 2010 and 2002. The growth of CO$_2$ at high (> 25-28 °C) T is the result of both smoky haze, and the oppression of green trees. Smoky haze at extremely high T also affects SO$_2$ concentration.
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