

The Role of Air Humidity in Variations of Near-Surface Ozone Concentration

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Abstract—Measurements at the Tropospheric Ozone Research (TOR) station in the Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, in 1994–2017 are used to study the dependence of variations in ozone concentration in the near-surface air layer on the absolute humidity. We found a neutral dependence at positive temperatures and surprisingly strong and sign-alternating variability at negative temperatures. The absolute air humidity negatively affects the ozone formation in the near-surface air layer, leading to decreased ozone concentration at temperatures of 0 to –30°C. At very low (below –30°C) temperatures the effect becomes positive, i.e., the ozone concentration increases with the growing absolute humidity.

Keywords: atmosphere, gas, humidity, air, ozone

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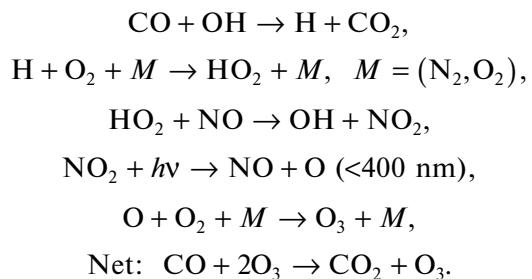
INTRODUCTION

Specific physicochemical properties of ozone (high toxicity for biological organisms and plants, ability to oxidize almost all materials, and contribution to the radiation budget of the planet [1, 2]) motivate the study of patterns of ozone formation in the troposphere and especially in the near-surface air layer. It is argued [3] that meteorological parameters affect appreciably the ozone production near the Earth's surface. At present, ozone formation is known to be associated with air temperature [4–6], UV-B radiation and radon [7], air pressure, wind speed, and solar radiation [8]. The information about interrelation with air humidity is contradictory.

For instance, the authors of work [9] concluded that increased ozone concentration was recorded at low relative humidity, high temperatures and values of solar radiation, and in the absence of clouds. Analysis of situation with intense fires in the Moscow region [10] revealed a negative correlation coefficient (–0.66) with relative humidity. Passage to the absolute humidity, with elimination of its temperature dependence, showed the absence of correlation in 2010 and a significant negative correlation (–0.48) in 2011. The negative interrelation with the concentration was also found in [11].

If we turn to the mechanism of ozone formation in the troposphere, the role of water vapor will become more evident. In background regions, ozone production begins with the photolysis of troposphere-residing

ozone itself [12]: $O_3 + h\nu \rightarrow O(^1D) + O_2 (<310 \text{ nm})$. Then, an excited atom $O(^1D)$ reacts with water vapor H_2O to give the hydroxyl $O(^1D) + H_2O \rightarrow 2OH$ which is shown in [13] to attack almost all gases residing in the atmosphere. For instance, carbon may oxidize to give ozone according to the pathway [12]:



Therefore, water vapor can be expected to participate in hydroxyl formation, thereby determining the oxidation rate of ozone-forming substances in the atmosphere and the amount of ozone formed. In this case, the constraining characteristic for the process is not the absolute, but rather relative, humidity. The authors of work [11] tried to determine the interrelation between ozone variations and specific humidity and found a negative dependence. However, they verified their study for different regions in United States and explained this result by geographic differences.

Thus, there are prerequisites to search for the form of the dependence of variations in ozone concentration on absolute humidity, and this is the subject of this work.

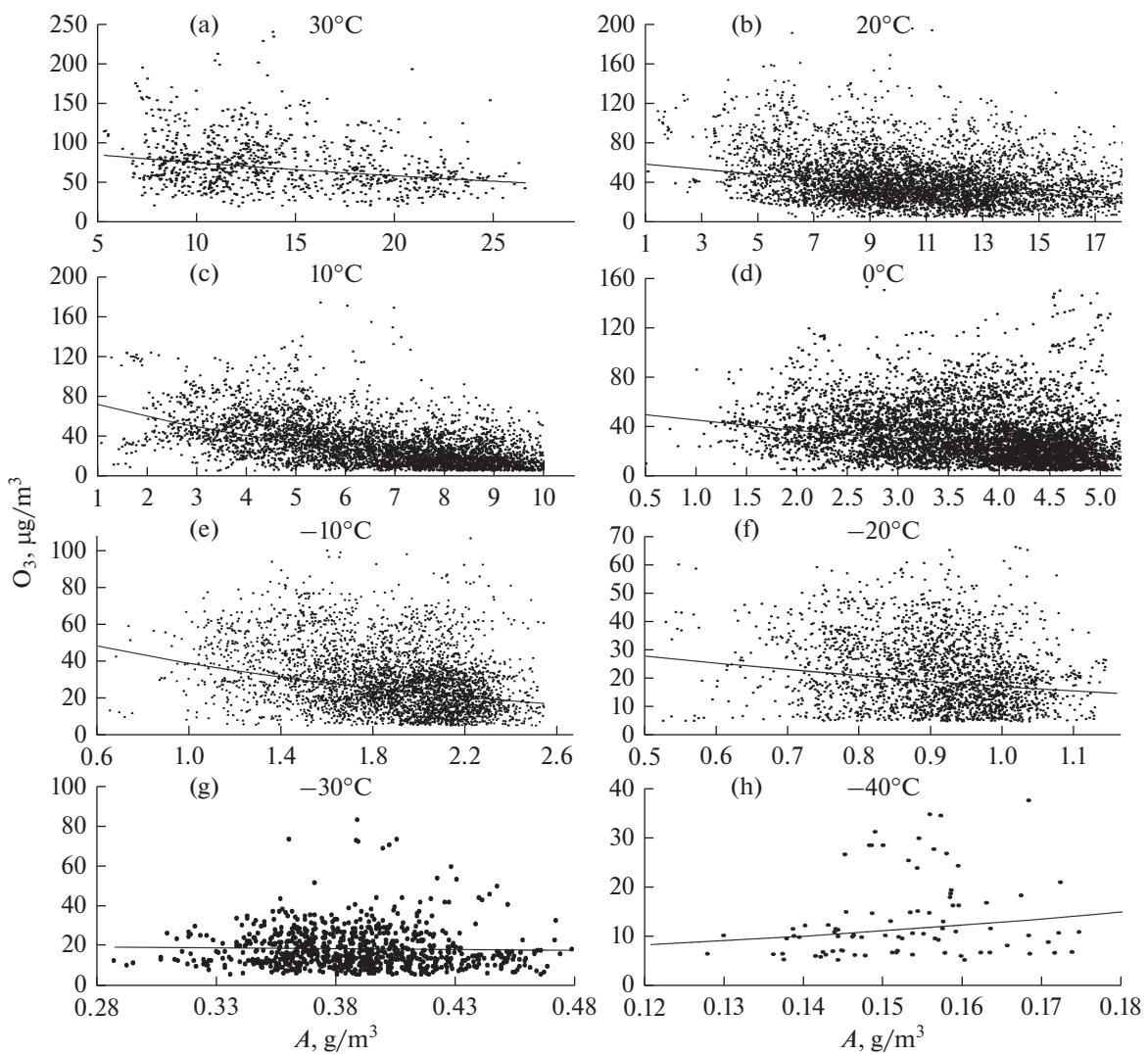


Fig. 1. Variations in ozone concentration versus the absolute air humidity for different air temperatures in the region of Tomsk.

INITIAL DATA AND METHODS USED

The studies were performed using data from monitoring of air composition in the region of Tomsk Akademgorodok from 1994 to 2017. The observations were performed using the Tropospheric Ozone Research (TOR) station at the Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences; the TOR location and the state-of-the-art measurement complex were described in [14].

The contribution of absolute humidity to ozone production was extracted using the following method. We performed a synoptic selection to eliminate the periods of passage of frontal divides and plumes from forest fires; then, the entire dataset was divided into subsets with the same air temperatures. This is required to eliminate the dependence of ozone production rate on temperature, which we found out earlier [15]. There had been eight subsets: -40 ± 1 ; -30 ± 1 ;

-20 ± 1 ; -10 ± 1 ; 0 ± 1 ; 10 ± 1 ; 20 ± 1 ; and $30 \pm 1^\circ\text{C}$. Within each subset we compared ozone concentration and absolute humidity for the same instant of time.

ANALYSIS AND DISCUSSION

From Fig. 1, it can be seen that ozone concentration stably tends to decrease with the growing water vapor content in the air temperature range from $+30$ to -10°C . At a temperature of -30°C the trend line becomes neutral. Surprisingly, at a temperature of -40°C the ozone production rate increases with growing water vapor concentration.

Importantly, the variability ranges of absolute humidity strongly differ among data subsets (air temperatures). For instance, the absolute humidity varies from 5.1 to 25.4 g/m^3 at a temperature of $+30^\circ\text{C}$ (Fig. 1a) and from 0.12 to 0.18 g/m^3 at -40°C .

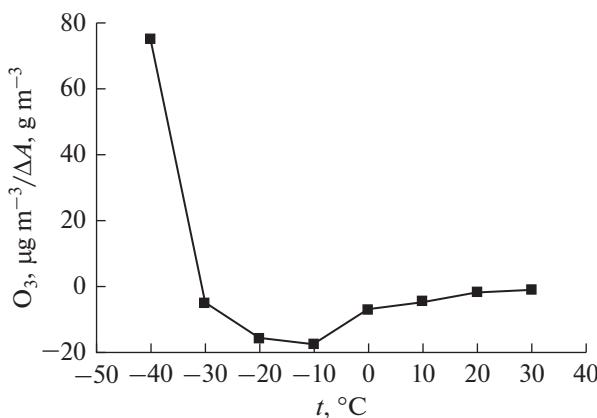


Fig. 2. Relative variations in ozone concentration versus the absolute air humidity for different air temperatures in the region of Tomsk from 1994 to 2017.

To compare variations in ozone concentration with absolute humidity at different temperatures, we normalize ΔO_3 (the difference between initial and final values of ozone concentration along trend lines in Fig. 1) by ΔA , i.e., the variability range of water vapor concentration at a given temperature. The dependence of this ratio on air temperature is presented in Fig. 2.

It can be seen that at positive air temperatures (0 to +30°C) variations in ozone as a function of absolute humidity are minor and close to zero. As humidity increases, ozone concentration decreases the most, by as much as $-17.3 \mu\text{g m}^{-3}/(\text{g m}^{-3})$, in the temperature range -20 to -10°C . At -40°C there is a convergence, so that an increase in the absolute humidity leads to the growth of ozone concentration at the relative rate of $77.3 \mu\text{g m}^{-3}/(\text{g m}^{-3})$.

CONCLUSIONS

Thus, our analysis of how ozone concentration varies as a function of absolute air humidity revealed that it shows a neutral behavior for positive air temperatures and surprisingly strong and sign-alternating variations for negative temperatures.

The absolute humidity has a negative effect on ozone formation in the near-surface air layer, reducing ozone concentration at 0 to -30°C .

At very low (below -30°C) temperatures the dependence becomes positive and the contribution of absolute humidity substantially increases.

These results turned out to be quite surprising and still unclear in many respects. Therefore, this requires further, more detailed analysis with a verification against data from other region.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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