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ISOPRENE AND MONOTERPENES OVER RUSSIA AND THEIR IMPACTS IN TROPOSPHERIC OZONE FORMATION

ABSTRACT. Ground-based levels of important biogenic volatile organic compounds (BVOCs), isoprene and monoterpenes, as well as NO_x and O_3 measured simultaneously along the Trans-Siberian railway on a mobile railway laboratory in TROICA-12 campaign in summer 2008 are analyzed. It was shown that the highest isoprene (≥2.5 ppb) concentration was observed in the daytime in the Far East region where several favorable factors for its emissions occurred: a large amount of deciduous forests, high temperatures (>28°C) and light conditions. Maximum levels of monoterpenes (up to 3-9 ppb) along the Trans-Siberian railway were observed during the nighttime in the Ural region and in Central Siberia where coniferous vegetation is located. To evaluate the relative importance of isoprene and monoterpenes in ground-level ozone formation in Russian cities along the Trans-Siberian railway, where high NO_x concentration leads to tropospheric ozone generation, daytime ozone-forming potential (OFP) was calculated. The chemical losses of the studied BVOCs during their transport from sources to the measurement point were taken into account. Calculated OFPs due to isoprene (OFP_{iso}) and monoterpenes (OFP_{mono}) along the Trans-Siberian railway are in average 15±13 and 18±25 ppbv of ozone, respectively. The highest OFP_{iso} (up to 40 ppbv) were estimated in Central Siberia and in the Far East. OFPmono was the highest in the regions of coniferous vegetation, Ural and Central Siberia, and reached 80 ppbv. In the most cities along the Trans-Siberian railway, where high NO_x concentration (10-20 ppbv) along with high daytime temperatures (>25°C) were observed, monoterpenes made a main contribution to tropospheric ozone formation. Only in the Far East cities, where the largest deciduous vegetation area of the Trans-Siberian railway is located, isoprene played the main role in tropospheric ozone generation. It was also noted that OFP_{iso} increases with the population-size of the cities. It can be either due to the greater proportion of deciduous vegetation in the large cities along the Trans-Siberian railway or due to the impact of anthropogenic isoprene source. OFP_{mono} was the lowest in the medium cities and the highest in the small ones.

KEY WORDS: isoprene, monoterpenes, tropospheric ozone, biogenic volatile organic, ozone-forming potential, Trans-Siberian railway, mobile laboratory, TROICA

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INTRODUCTION

One of the important consequences of human activity on the atmosphere is an increase in tropospheric ozone level. Environmental changes, higher temperature, in combination with higher concentrations of specific anthropogenic pollutants lead to higher tropospheric ozone concentration. The highest ozone levels are often observed in urban environment, which is not only characterised by higher temperatures (heat islands), but also by higher levels of ozone precursors, nitrogen oxides (NOx), carbon monoxide (CO), methane (CH_4) and volatile organic compounds (VOCs). CO, CH_4 and VOCs are mainly oxidized in the troposphere by OH radicals, and at high air temperature and solar radiation in NO_x-polluted conditions can cause the formation of high ozone levels which pose a threat to human health (Sillman 1999). Thus, the proper estimates of ozone precursors impact on its ground-based production are very important for the diagnostics of the atmospheric photochemical system (APS) state and for extreme ecological situations forecasting. Atmospheric oxidation of CH_4 and CO is significantly slower (atmospheric lifetimes for CH_4 and CO are about 10 years and 1-2 month, respectively), and can cause mainly global and regional ozone increase. However, the oxidation of many VOCs occurs in the daytime and causes ozone increase near their local pollution sources as it takes place in urban environment.

Biogenic volatile organic compounds (BVOCs) constitute approximately 90% of global volatile organic compound (VOC) emissions, with the isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) being the most abundant (Guenther et al. 2012), and have significant effects on atmospheric chemistry and physics. Due to high reactivity of BVOCs, they are rapidly oxidized by OH radicals (Fan and Zhang 2004; Bowman and Seinfeld 1994; Sillman 1999; Wagner and Kuttler 2013), thus significantly influencing the oxidizing capacity of the atmosphere and thereby impacting the residence time of air pollutants and the most reactive greenhouse gases. The simulations of chemical-transport models showed that the impact of biogenic VOCs on tropospheric ozone formation can vary from 40 to 70% of the impact of all nonmethane hydrocarbons (NMHCs), with isoprene (C_5H_8) playing the major role (Guenther et al. 2000). As BVOC emissions increase with ambient light and temperature (Penuelas and Staudt 2010), the expected progression of climate change may affect BVOC emissions and contribute to regional changes of atmospheric composition. The atmospheric composition measurements over Russia along the Trans-Siberian railway in the unique TROICA (TRanscontinental Observations Into the Chemistry of the Atmosphere) experiments on a mobile laboratory in summer 2008 allowed the detailed analysis of the main BVOCs levels, isoprene and monoterpenes, over Russia and the estimation of their impact in tropospheric ozone formation.

Monitoring of the most important ozone precursors is carried out on the Global Atmospheric Watch (WMO GAW) network stations. In Russia, the ozone precursors are measured occasionally at the stations of the State air pollution control network existing only in large cities with population of over 100 thousand people. The transcontinental measurements of atmospheric composition on a mobile laboratory carried out in the international experiments TROICA in 1995-2010 are filled the deficit of the information on ozone levels in the atmosphere over continental Russia significantly (Elansky et al. 2009). In particular, a tendency to an increase of ozone formation in urban air was revealed especially in stagnant air conditions.

Along the Trans-Siberian railway, 87 cities are located, which are different in urbanization and anthropogenic load intensity. The measurements of BVOCs by PTR-MS method simultaneously with other atmospheric compounds along the Trans-Siberian railway in summer 2008 (TROICA-12) allowed the detailed analysis of the contribution of the main tropospheric ozone precursors to its production in differently populated Russian cities.

MATERIALS AND METHODS

TROICA experiments

TROICA experiments over Russia on a mobile laboratory were carried out regularly from 1995 to 2014 (Elansky et al. 2009). About 10 inorganic compounds as well as aerosols and meteorological parameters were measured continuously and simultaneously by a specially constructed automated system. The system was built on a railway carriage with air inlets at the height of about 4 m above the ground. VOC concentrations have been measured routinely since 2008. The TROICA carriage–laboratory is equipped in accordance with the measurement requirements of the Global Atmospheric Watch (WMO), and is located just after the electric locomotive to minimize various effects of near-surface air perturbations due to moving train (Skorokhod et al. 2017). The possible impact of oncoming trains as well as human activities in the train (all conveniences were placed at the end part of the train) on the measurements is expected to be generally non-significant as demonstrated previously in Crutzen et al. (1996), Elansky et al. (2000) and Panin et al. (2001).

This paper is a continuation one from Skorokhod et al. (2017), where benzene and toluene were investigated. Thus, it describes the data from the same experimental period and setup.

In present study, the data from the summer campaign TROICA-12 (21.07.2008 – 04.08.2008) along the Trans-Siberian railway (Fig. 1) are analyzed. The train covers the total length of the route from Moscow to Vladivostok (~ 9288 km) for approximately 6 days, so the total duration of a single campaign is about two weeks. (Henceforth, we denote forward path from Moscow to Vladivostok, and return path from Vladivostok to Moscow, as east and west segments of the whole route, correspondingly).

Undoubtedly, the results of the observations at each particular location performed from the moving carriage are strongly influenced by specific weather conditions (synoptic patterns), as well as by complex interplay of local pollution sources and atmospheric transport by turbulent eddies on a variety of scales, the latter being considered as a source of random noise in the measurement data. Generally, straightforward quantification of the effects of atmospheric dilution and absolute strength of the associated nearby emission sources is inhibited in data analyses. Yet, the passage of each location twice (in the forward and return paths of the TROICA campaign) allows for some qualitative assessment of the impact of weather conditions, since the time between the two subsequent measurements is of the order of one week, which is comparable to the characteristic time of the boundary layer ventilation in mid-latitudes (Skorokhod et al. 2017).

Various types of meteorological conditions along the railroad can be generalized into three distinctive weather patterns when traversing mountain area adjacent to Baikal Lake (~110° E) in east and west segments. There was clear and warm (>20° C at noon) weather on the route from Moscow to Baikal, hot weather (>24° C at noon) between Baikal Lake area and Vladivostok (east and west segments), and cool (daytime temperatures of 15 – 20° C) and rainy weather between Baikal Lake and Moscow on the return west segment of the route. Nighttime surface temperature inversions and stagnant air conditions were common for the east segment, although light winds were typical for the both east and west segments of TROICA. This feature is clearly seen in Fig.1 where 2-day back trajectories along the TROICA route calculated with the use of NOAA HIGHSPLIT model (Stein et al. 2015; Rolph 2016) based on 3D wind fields are shown as averages of corresponding ensembles of trajectories originated within a height range from 0 – 400 m a.g.l. According to Fig.1, the characteristic distances of transport within a planetary boundary layer does not exceed 500 – 600 km in the two days preceding measurement time, so the measured chemical composition of the respective air masses can be considered as representative of the cumulative impact of pollutant sources at local to regional scales. The exception is the Far East Region where regional advection by southerly winds may contribute to measured pollutant concentrations from highly urbanized areas of the north-east China.

In the whole, in TROICA-12 experiment meteorological conditions was favorable to study chemical composition of fresh air masses from regional sources and ozone production from the emitted precursors due to high daytime surface air temperatures and solar radiation.

VOC measurements

Isoprene and monoterpenes concentrations were measured by a Compact Proton Transfer Reaction Mass Spectrometer (Compact PTR-MS) from Ionicon Analytik GmbH (Austria). Errors in instrument's calibration by the proper gas standard (Ionicon Analytic GmbH, Innsbruck, containing 17 VOCs) did not exceed 15%. For PTR-MS instrumental parameters (in particular, drift tube voltage, temperature and pressure) factory settings were used.

The Compact PTR-MS measurement range depends on the substances measured, integration time and system set-up. Its detection limits for the investigated VOCs are in order of pptv. Isoprene and monoterpenes were detected by the instrument at masses M69 and M137, and M81, respectively. In case of isoprene, other aldehydes and ketones are known to be detectable at this mass. However, isoprene has been found to be the dominant species at M69 within various kinds of air masses (de Gouw and Warneke 2007). Monoterpenes were analyzed as the sum of the M137 and M81 signals as total monoterpenes.

Other components and meteorology

NO and NO_2 concentrations were measured at different times with a TE42C-TL instrument (Thermo Electron Corp., USA) and with a M200AU instrument produced by Teledyne Corp. (USA). These instruments apply the chemiluminescent method. The minimum NO and NO_2 concentrations detectable with these instruments are equal to 0.05 ppb, which makes it possible to measure the so-called background con-

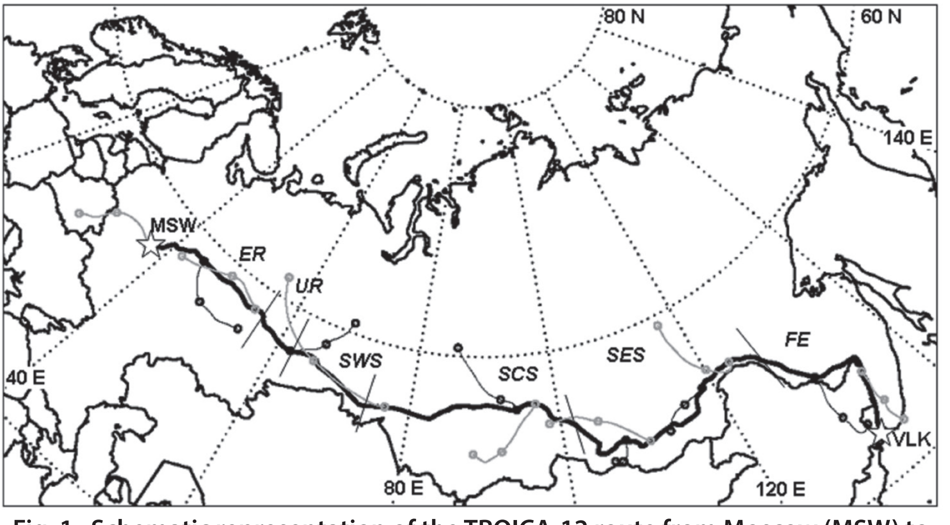

Fig. 1. Schematic representation of the TROICA-12 route from Moscow (MSW) to Vladivostok (VLK). Thin solid lines across the route represent approximate boundaries of various geographic regions: European Russia (ER), Ural mountain region (UR), southern parts of West (SWS), Central (SCS), and East (SES) Siberia, and Far East (FE). Back 2-day trajectories with endpoints at Trans-Siberian Railroad at local noon of each successive day of carriage movement are shown for East (black solid) and West (gray solid) routs of the campaign. Open circles mark air particles positions at 0, 24, and 48 hours along the each trajectory

centrations not influenced by the pollution sources. NO_x concentration is the sum of NO and NO_2 concentrations (Skorokhod et al. 2017).

Ozone concentration was measured with Dasibi 1008RS and 1008AH gas analyzers. These instruments are based on the photometric method (Skorokhod et al. 2017). They allow measuring the ozone concentration in the range from 1 to 1000 ppb with a total error of ±1 ppbv. These instruments undergo scheduled calibrations against the secondary standard, the O3-41M No. 1294 instrument, which undergoes in its turn annual calibrations against the SRP No. 38 standard owned by the Mendeleev Research Metrology Institute (Russia).

For measuring of atmospheric pressure, air temperature, relative air humidity, as well as wind speed and direction, the device of type ACAT-3M produced by "SPA Typhoon" (Russia) was used. This device included a sonic anemometer and proper pressure, temperature and relative humidity sensors. Additionally, air temperature and relative humidity were measured by HMP-233 device, and atmospheric pressure were measured by PTA-427 device. Both devices produced by Vaisala (Finland).

RESULTS AND DISCUSSION

Isoprene and monoterpenes along the Trans-Siberian railway

The areas adjacent to the Trans-Siberian railway are markedly different in amount of urbanization and anthropogenic load. Eighty-seven towns are located immediately on the railway, sixty-eight towns are in the Ural mountain region and West Siberia with the remaining ones located in the East Siberia and the Far East. Yet, it is in the area of first tens to hundreds of kilometers from the Trans-Siberian railway where the most significant regional anthropogenic sources are commonly located in all the regions considered. As mentioned above, the meteorological conditions during the most of the TROICA campaign were favorable for both studying chemical composition of fresh air masses contaminated by regional sources and for ozone production from the emitted precursors due to high daytime surface air temperatures and solar radiation.

The major problem of the TROICA data analyses is a correct elimination of screening effects (relative to regional scale pollution sources) produced by local pollution sources along the railroad. Except for small areas of biomass burning and smoldering in the vicinity of railway, such sources are mainly of anthropogenic origin and characterized by highly limited spatial extents (and, hence, an impact upon a chemical composition), so they can be effectively filtered out by applying some objective criteria based on the NO/NO_2 ratio to the original 10-second dataset as described in detail in Vasileva et. al. (2011) and in Skorokhod et al. (2016). The filtered data (~75% of the dataset) were used to calculate 10-min averaged dataset, which is analyzed hereafter.

The most important parameters of tropospheric ozone formation are VOCs and NO_x (NO_x =NO+NO_2) concentrations, temperature and solar radiation. For TROICA-12 measurements, NO_x–sensitive regime (NMHC/NO_x > 20, where NMHC is a sum of nonmethane hydrocarbons) was typical. Fig. 2 shows a subset ($[O_3]$≥24 ppbv) of 1-hour averages for O3 and NO_x(=NO+NO_2) along with the corresponding regression curve, which were measured under clear sky, high air temperature (>25°C), clear sky conditions favorable for rapid photochemical ozone production during the course of the day. According to Fig.2a, the ozone mixing ratio increases nonlinearly with NO_x, with the measured ozone and NO_x are broadly satisfying the dependence

$$\left[O_3\right]=\left[O_3\right]_b+\alpha\left[NO_x\right]^{\beta} \quad (1)$$

The large scatter of measurement points on the plot is due to different degree of photochemical processing of the measured air samples and variations in local vertical mixing conditions affecting near-surface ozone and NO_x abundances. We can also see that the discrepancy between the measurements and the fitted curve has a tendency to increase with $[NO_x]$ which may be explained by a high dependence of the O_3 production rate, $P(O_3)$, on NO_x and VOC abundances so that $P(O_3) \propto ([NO_x]^2/[VOC])^2$ (Kleinman et al. 2001).

The data shown on Fig. 2a may be viewed in a more systematic way by considering $[O_3]/[NO_x]$ as a proxy for the ratio of local ozone photochemical production, $P(O_3)$, to $[NO_x]$ by assuming a proportionality between the measured ozone concentrations and the rate of ozone production, $P(O_3)$, in the sampled air parcel en route to a measurement point. Then, $P(O_3) = c_1 \cdot [O_3]$, where a constant c_1 is a function of measured $[NO_x]$, air mass history, and meteorological conditions affecting boundary layer chemistry. We then obtain a non-linear fit $[O_3]/[NO_x] = \bar{\alpha}[NO_x]^{-\bar{\beta}}$, $\bar{\alpha}$ =29.08, $\bar{\beta}$ =0.87 (Fig.2b) which represents a uniformly valid approximation for a $[O_3]/[NO_x]$ ($[NO_x]$) dependence in the sampled air mass. The above relation can be rearranged to $d\ln[O_3]/d\ln[NO_x] = 1 - \bar{\beta}$, where the left hand side of the expression gives the relative sensitivity of O_3 production rate to $[NO_x]$ averaged over the whole set of measurements performed in the photochemically processed urban air masses encountered in the TROICA. Kleinmann et al. (1997, 2001) use the conservation equation for free hydrogen radicals (OH, HO_2, and organic peroxides RO_2):

$$Q = L_R + L_N \quad (2)$$

where Q is the radical production rate, and L_R and L_N are the loss rates due to radical-radical reactions and reactions of radicals with NO_x, to propose a functional relationship between $d\ln[O_3]/d\ln[NO]$ and L_N/Q:

$$dIn[O_3]/dIn[NO_x] = (1 - \frac{3}{2}L_N/Q)/(1 - \frac{1}{2}L_N/Q) \quad (3)$$

which is valid over a wide range of pollution levels. Using (3), one can obtain a regional average day time ratio for L_N/Q from the corresponding slope of the regression line shown on Fig.2b given the best-fit value for the $\bar{\beta}$ exponent: $L_N/Q = 2\bar{\beta}/(2+\bar{\beta})$ =0.6 ($\bar{\beta}$=0.87). The derived value for L_N/Q is slightly above the theoretically predicted threshold value of 0.5 separating between NO_x and VOC sensitive regimes of ozone production (see Fig. 1b from Kleinmann et al. (1997)). The final conclusion is that the average day-time conditions in the urban air masses measured in the TROICA campaign are somewhere in the transition from NO_x to VOC sensitive regimes so that the both anthropogenic emissions of NO_x along with the predominant biogenic VOC emissions play equally important role in controlling day-time ozone levels in the towns along the Trans-Siberian Railroad during the weather conditions favorable for intence ozone photochemistry.

Fig. 3 shows isoprene and monoterpenes derived from the filtered 10-second dataset for the east and west segments of the TROICA-12 experiment. Simultaneous measurements of O_3, NO_x, meteorological parameters and altitude a.s.l. along the Trans-Siberian railway are also shown in the figure. To clarify the time of day, the times

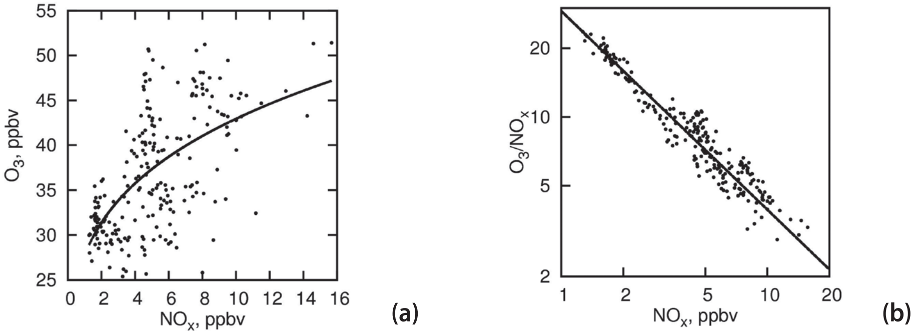

Fig. 2. Day-time (10:00–17:00 local time) correlations of O_3 and NO_x along with the fitting curves for $[O_3]$≥25 ppbv: $[O_3] = [O_3]_b + \alpha[NO_x]^{\beta}$, $[O_3]_b$ =24 ppbv, α =4.4 ppbv, and β =0.62 (a) and $[O_3]/[NO_x] = \bar{\alpha}[NO_x]^{-}$, $\bar{\alpha}$ =29.08, $\bar{\beta}$ =0.87 (b)

of local noon (12:00 LT) are presented by white circles in Fig. 3. The whole path from Moscow to Vladivostok is divided into 6 lengthy segments according to climatological conditions and anthropogenic load intensity: European Russia (ER), Ural mountain region (UR), southern parts of West (SWS), Central (SCS), and East (SES) Siberia, and Far East (FE).

Maximum levels of NO_x (> 20 ppb), were observed in large cities (with population size of 0.25 – 1 million people: Perm, Ekaterinburg, Tumen, Omsk, Krasnoyarsk, Irkutsk, Ulan-Ude, Chita, Khabarovsk) along the Trans-Siberian railway (see Fig. 3). It was shown in Skorokhod et al., 2017 that motor vehicle exhausts were the most significant anthropogenic source of air pollution in the cities along the Trans-Siberian railway, even though in some cities (Khabarovsk, Birobidzhan, Skovorodino, Tulun, Tajshet, and Tyumen) the contribution from other sources (including industrial emissions, coal burning and gasoline evaporation) was also important. Ozone had a pronounced daily cycle, with a maximum concentration being observed in the daytime (see Fig. 3). The absence of clearly defined peaks in ozone distribution points to the essential role of horizontal advection and regional photochemical processes in its spatial distribution in the developed ABL conditions.

Isoprene and monoterpenes depended significantly on temperature and solar radiation during the experiment (Fig. 3). In this regard, the highest isoprene (≥2.5 ppb) concentration was observed in the daytime (10:00-19:00 LT) in the FE region where several favorable factors for their emissions occurred: a large amount of deciduous forests, high temperatures (>28°C) and light conditions (see Fig. 3). Monoterpenes can emit from coniferous vegetation both during the day and at night with their night concentration increasing due to accumulation of monoterpenes in a stable atmosphere. Maximum levels of monoterpenes along the Trans-Siberian railway (up to 3-9 ppb) were observed during the nighttime (19:00 – 02:00 LT) in UR region, in SCS and ECS where coniferous vegetation is located.

Estimation of ozone forming potential in Russian cities

To evaluate the relative importance of VOCs in ground-level ozone formation, in

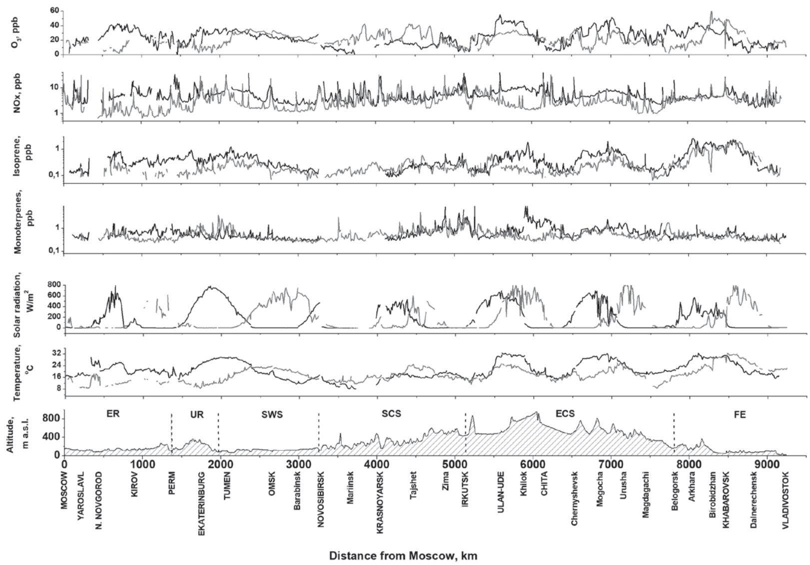

Fig. 3. 10-minute isoprene and monoterpene concentrations derived from the filtered 10-sec dataset for the east (black line) and west (gray line) segments of the TROICA-12 experiment. Simultaneous measurements of O_3, NO_x, meteorological parameters and altitude a.s.l. along the Trans-Siberian railway are also shown

numerous studies (Xie et al. 2008; Wagner et al. 2014) ozone-forming potential (OFP) is employed. OFP is defined as:

$$OFP_{VOC}\left[\mu g / m^3\right] = C_{VOC} \times MIR_{VOC} \qquad (4)$$

where C_{VOC} is a VOC concentration having the dimension of μg/m^3, MIR_{VOC} is a maximum incremental reactivity (Carter 1994). The latter is a dimensionless quantity defined as gram of O^3 produced per gram of the VOC, which defines the maximum ozone concentration formed from chemical destruction of the given VOC.

We used this method to evaluate the contribution of the studied ozone precursors to its production in the Russian cities along the Trans-Siberian railway. Taking into account the fact that all VOCs studied, especially reactive isoprene, can have significant chemical losses during the time before the train will pass the mixed air mass in the measurement point, we calculated their initial concentrations preliminary.

Initial isoprene concentrations was derived from simultaneous measurements of its products, MVK and MACR, and isoprene concentration following Xie et al. (2008). The calculations are based on isoprene reaction with OH radicals, which is the main photochemical loss for isoprene in the atmosphere (Stroud et al. 2001). Since this method is valid in the daytime, only daytime measurements (10:00 – 19:00 LT) were used for calculations of initial isoprene concentrations in this study.

For monoterpenes, atmospheric oxidation by ozone and nitrate radical (NO_3) is also very important (Perakyla et al. 2014). However, monoterpene loss due to the reactions with NO_3 is more important during the night. The evaluations based on ozone oxidation is a problem at this stage of the study and expected to be taken into account in future work. Thus, we estimated initial daytime concentration of monoterpenes basing only on their reaction with OH radicals following the method of Wiedinmyer et al. (2001).

The derived initial concentrations of isoprene and monoterpenes are 4 and less than 1.5 times higher on average, respectively, than the measured ones. The OFPs were calculated from the initial concentrations of isoprene and monoterpenes for differently populated Russian cities along the Trans-Siberian railway during the daytime (10 – 19 LT (local time)). This period is characterized by the most active photochemical ozone formation due to VOCs reactions with OH radicals.

Contribution of isoprene and monoterpenes to ozone formation in Russian cities

Calculated OFP_{iso} and OFP_{mono} along the Trans-Siberian railway are in average 15±13 and 18±25 ppbv of ozone, respectively. The highest OFPs due to isoprene (up to 40 ppbv) were estimated in Central Siberia and in the Far East. OFPs due to monoterpenes were the highest in the regions of coniferous vegetation, Ural and Central Siberia, and reached 80 ppbv. Significant OFPs due to BVOCs (16±12 and 28±34 ppbv of ozone due to isoprene and monoterpenes, respectively) were obtained in the cities along the Trans-Siberian railway, where high NO_x concentration (10-20 ppbv) along with high daytime temperatures (>25°C) were observed. Fig.4 shows that monoterpenes mainly contribute to tropospheric ozone formation in most Trans-Siberian cities. Only in the Far East cities, where a large deciduous vegetation area of the Trans-Siberian railway is located, isoprene plays the main role in tropospheric ozone generation (see Fig. 4).

Table 1 shows that OFPiso increases with the population-size of the cities. It can be due to either the greater proportion of deciduous vegetation in the large cities along the Trans-Siberian railway or the impact of anthropogenic isoprene sources (transport exhausts, power plants etc.), which can fluctuate in summer urban air between 10-50% (Borbon et al. 2001; Starn et al. 1998). An impact of monoterpenes on ozone formation is generally the lowest in the medium-sized cities and the highest in the small-sized ones.

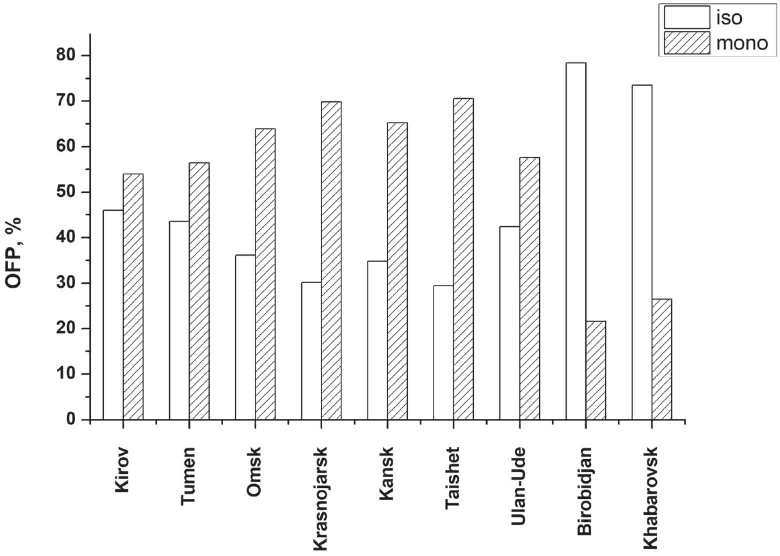

Fig. 4. Contribution of isoprene and monoterpenes to ozone formation potential (OFP) in the cities along the Trans-Siberian railway (OFP_{iso} + OFP_{mono} in each city gives 100%)

Table 1. The percentiles of OFPs and NO_x (P_{10} - P_{90} (P_{50})) in all cities along the Trans-Siberian railway (in ppb)

Population, thous. (number of cities crossed in daytime)	OFP_{iso}	OFP_{mono}	NO_x
<50 (2)	5.65-17.35 (9.67)	6.32-54.45 (18.99)	1.99-10.74 (5.12)
50-250 (4)	7.19-37.65 (11.02)	4.45-23.19 (10.53)	2.48-13.61 (4.89)
>250 (5)	5.43-54.02 (24.49)	6.89-40.35 (16.19)	2.65-16.29 (9.71)

CONCLUSION

Due to a lack of information about the impact of the most important ozone precursors on its production in Russian cities, ground-based levels of important BVOCs, isoprene and monoterpenes, as well as NO_x and O_3 measured simultaneously along the Trans-Siberian railway on a mobile railway laboratory in TROICA-12 campaign in summer 2008 were analyzed. Meteorological conditions during the most of the TROICA campaign were favorable for both studying chemical composition of fresh air masses contaminated by regional sources as well as for ozone production from the emitted precursors due to high daytime surface air temperatures and solar radiation.

It was shown that the highest isoprene (≥2.5 ppb) concentration was observed in the daytime in the FE region where several favorable factors for their emissions occurred: a large amount of deciduous forests, high temperatures (>28°C) and light conditions. Monoterpenes also emitted from coniferous vegetation during the night with their concentration increasing due to accumulation in a stable atmosphere. Maximum levels of monoterpenes along the Trans-Siberian railway were observed during the nighttime measurements (up to 3-9 ppb) in UR region, in SCS and ECS where coniferous vegetation is located. Thus, biogenic ozone precursors are dependable on the parameters of atmospheric boundary layer (ABL).

Maximum levels of NO_x (> 20 ppb), were observed in large cities (with population size of 0.25 – 1 million people: Perm, Ekaterinburg, Tumen, Omsk, Krasnoyarsk, Irkutsk, Ulan-Ude, Chita, Khabarovsk) along the Trans-Siberian railway. To evaluate the relative importance of BVOCs in ground-level ozone formation in Russian cities along the Trans-Siberian railway, daytime ozone-forming potential (OFP) was calculated. Taking into account that all VOCs studied can have significant chemical losses during their transport from sources to the measurement point, calculated initial concentrations of isoprene and monoterpenes were used for OFPs evaluation. Initial concentrations of isoprene and monoterpenes is about 4 and up to 1.5 times higher than the measured concentrations.

Calculated OFP_{iso} and OFP_{mono} along the Trans-Siberian railway are in average 15±13 and 18±25 ppbv of ozone, respectively. The highest OFP_{iso} (up to 40 ppbv) was estimated in Central Siberia and in the Far East. OFP_{mono} was the highest in the regions of coniferous vegetation, Ural and Central Siberia, and reached 80 ppbv. In the most cities along the Trans-Siberian railway, where high NO_x concentration (10-20 ppbv) along with high daytime temperatures (>25°C) were observed, monoterpenes made a main contribution to tropospheric ozone formation. Only in the Far East cities, where the largest deciduous vegetation area of the Trans-Siberian railway is located, isoprene played the main role in tropospheric ozone generation. It was also noted that OFP_{iso} increased with the population-size of the cities. It can be either due to the greater proportion of deciduous vegetation in the large cities along the Trans-Siberian railway or due to the possible impact of anthropogenic isoprene source. OFP_{mono} was the lowest in the medium cities and the highest in the small ones.

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REFERENCES

Borbon A., Fontaine H., Veillerot M., Locoge N., Galloo J. C., and Guillermo R. (2001). An investigation into the traffic-related fraction of isoprene at an urban location. Atmos. Environ., 35, 3749–3760.

Bowman F. M. and J. H. Seinfeld (1994). Ozone productivity of atmospheric organics. Journal of Geophysical Research Atmospheres 99(D3):5309-5324.

Carter W. P. L. (1994). Development of ozone reactivity scales for volatile organic compounds. J. Air Waste Manage. Assoc., 44, 881–899.

Carter W. P. L. (2010). Updated Maximum Incremental Reactivity Scale and hydrocarbon reactivities for regulatory applications. California Air Resources Board Contract 07-339, January 28, 2010.

Crutzen P.J., Elansky N.F., Hahn M., Golitsyn G.S., Brenninkmeijer C.A.M., Scharffe D., Belikov I.B., Maiss M., Bergamaschi P., Rockmann T., Grisenko A.M., and Sevastyanov V.V. (1996). Trace gas measurements between Moscow and Vladivostok using the Trans-Siberian Railroad. J. Atm. Chemistry, No 29, 179–194.

de Gouw J. and Warneke C. (2007). Measurements of volatile organic compounds in the Earth's atmosphere using proton-transferreaction mass spectrometry. Mass Spectrom. Rev., 26, 223–257. doi:10.1002/mas.20119

Duan J.C., Tan J.H., Yang L., Wu S.X., and Hao J.M. (2008). Concentration, Sources and Ozone Formation Potential of Volatile Organic Compounds (VOCs) during Ozone Episode in Beijing. Atmos. Res. 88: 25–35.

Elansky N.F., Belikov I.B., Berezina E.V. (2009). Atmospheric composition observations over Northern Eurasia using the mobile laboratory: TROICA experiments, edited by N.F. Elansky, Moscow, 73 p.

Elansky N.F., Golitsyn G.S., Vlasenko T.S., and Volokh A.A. (2000). Volatile organic compounds observed in the atmospheric surface layer along the Trans-Siberian Railroad. Dokl. Akad. Nauk, V. 373, No 6, 816–821.

Fan J. and Zhang R. (2004). Atmospheric oxidation mechanism of isoprene. Environ. Chem. 2004, 1, 140–149. doi:10.1071/EN04045

Guenther A., Geron C., Pierce T., Lamb B., Harley P., Fall R. (2000). Atmospheric Environment, 34, pp. 2205–2230.

Kleinman L.I., Daum P.H., Lee J.H., Lee Y.-N., Nunnermacker L.J., Springston S.R., Newman L., Weiristein-Lloyd J.b., Sillman S. (1997). Dependence of ozone production on NO and hydrocarbons in the troposphere. GRL. 24:2299–2302.

Kleinman L.I., Daum P.H., Lee Y.-N., Nunnermacker L.J., Springston S.R., Weinstein-Lloyd J., Rudolph J. (2001). Sensitivity of ozone production rate to ozone precursors. Geophysical Research Letters 28, 2903–2906.

Panin L.V., Elansky N.F., Belikov I.B., Granberg I.G., Andronova A.V., Obvintsev Yu.I., Bogdanov V.M., Grisenko A.M., and Mozgrin V.S. (2001). Estimation of Reliability of the Data on Pollutant Content Measured in the Atmospheric Surface Layer in the TROICA Experiments. Izvestiya, Atmospheric and Oceanic Physics, V. 37, Suppl. 1, 81-91.

Penuelas J. and Staudt M. (2010). BVOCs and global change. Trends Plant Sci., 15, 133–144. doi:10.1016/j.tplants.2009.12.005

Peräkylä O., Vogt M., Tikkanen O-P., Laurila T., Kajos M.K., Rantala P.A., Patokoski J., Aalto J., Yli-Juuti T., Ehn M., Sipila M., Paasonen P., Rissanen M., Nieminen T., Taipale R., Keronen P., Lappalainen H.K., Ruuskanen T. M., Rinne J., Kerminen V-M., Kulmala M., Back J. and Petaja T. (2014). Monoterpenes' oxidation capacity and rate over a boreal forest. Boreal Environment Research, 19, suppl. B, pp. 293-310.

Sillman S. (1999). The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments. Atmos. Environ., 33, 1821–1845. doi:10.1016/S1352-2310(98)00345-8

Skorokhod A.I., Berezina E.V., Moiseenko K.B., Elansky N.F., Belikov I.B. (2017). Benzene and Toluene in the surface air of North Eurasia from TROICA-12 campaign along the Trans-Siberian railway. Atmos. Chem. Phys., 17, 5501-5514. doi: 10.5194/acp-17-5501-2017

Starn T.K., Shepson P.B., Bertman S.B., White J.S., Splawn B.G., Riemer D.D., Zika R.G., and Olszyna K. (1998). Observations of isoprene chemistry and its role in ozone production at a semirural site during the 1995 Southern Oxidants Study. J. Geophys. Res., pp. 103, 22, 425-22, 435.

Stroud C.A., Roberts J.M., Goldan P.D., Kuster W.C., Murphy P.C., Williams E. J., Hereid D., Parrish D., Sueper D., Trainer M., Fehsenfeld F.C., Apel E.C., Riemer D., Wert B., Henry B., Fried A., MartinezHarder M., Harder H., Brune W.H., Li G., Xie H., and Young V.L. (2001). Isoprene and its oxidation products, methacrolein and methylvinyl ketone, at an urban forested site during the 1999 Southern Oxidants Study. J. Geophys. Res.: Atmos. 106 (D8), 8035–8046.

Vasileva A.V., Moiseenko K.B., Mayer J.-C., Jurgens N., Panov A., Heimann M., Andreae M.O. (2011). Assessment of the regional atmospheric impact of wildfire emissions based on CO observations at the ZOTTO tall tower station in central Siberia. J.Geophys. Res., 116, D07301. doi:10.1029/2010JD014571

Wagner P. and Kuttler W. (2014). Biogenic and anthropogenic isoprene in the near-surface urban atmosphere–A case study in Essen, Germany. Sci. Total Environ., 475, 104–115. doi:10.1016/j.scitotenv.2013.12.026

Wiedinmyer C., Friedfeld S., Baugh W., Greenberg J., Guenther A., Fraser M., Allen D. (2001). Measurement and analysis of atmospheric concentrations of isoprene and its reaction products in central Texas. Atmospheric Environment 35 (6), 1001–1013.

Xie X., Shao M., Liu Y., Lu S., Chang C.C., and Chen Z.M. (2008). Estimate of initial isoprene contributions to ozone formation potential in Beijing, China. Atmos. Environ., 42, 6000–6010.

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