The comparison between the isoprene, methyl vinyl ketone and methacrolein concentrations measured in the TROICA-12 expedition at Far East region

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Abstract. The spatial and temporal distribution of isoprene and its oxidation products, such as methyl vinyl ketone (MVK) and methacrolein (MACR) was investigated. The measurements were carried out using by the mobile observatory, placed on the railcar chassis. As the object was selected the vast area of deciduous and mixed forests in Far East, which is crossed by Trans-Siberian Railway. It was shown that the isoprene and MVK and MACR have pronounced daily variations. The isoprene growth at night was not observed. The isoprene and MVK+MACR concentrations are satisfy to a linear regress; the slopes (B) are close to the ~ 1 (0.93 and 1.04 for TROICA-12 East and West, accordingly). The correlation coefficients (R) are significant and equal to 0.68 and 0.79 for TROICA-12 East and West. The noise of initial 10 sec measured values of MVK+MACR-to-isoprene ratio (below ratio) is significant. The high ratios (> 5) are observed not only at night but also during the day. At night, the high values of ratio somewhat larger than in the daytime. The MVK+MACR and isoprene pair has a high correlation (R~0.60–0.86) and weak dependence of NOx, except the one case when the twilight emission of isoprene was dominated.

1. Introduction

As well-known isoprene produced within the chloroplasts of leaves, is the most abundantly plant emitted hydrocarbon to the atmosphere, with global carbon emissions reaching 500 to 750 Tg per year [1]. Isoprene biogenic emissions are correlated with sunlight and temperature, and as a result, most part of biogenic emissions occurs during the daytime [1], [2]. In the atmosphere, isoprene can react with hydroxyl radicals (OH), ozone (O3), and nitrate radicals (NOx), which lead to the formation of gases such as formaldehyde, methyl vinyl ketone (MVK), methacrolein (MACR), carbon monoxide (CO), and ozone (O3) [3]. As well-known at daytime isoprene oxidation is typically initiated by the addition of a hydroxyl radical (OH) and resulting in the production of a series of isomeric hydroxyl-substituted alkyl peroxy radicals (ISOPO2, HOCH2C(OO)CH=CHCH3). In atmospheric conditions the ISOPO2 react with the NO/NOx or hydroperoxyl radicals (HO2), which are the major pathways to sink down ISOPO2 and produced MVK and MACR. The isoprene NOx oxidation pathway generally have been categorized as either “high-NOx,” pathways [4],[5] or “low-NOx” experiments [5],[6]. For details about uncertainties in ISOPO2 reactions see discussion in [5].

Siberian forests usually have sufficiently low local NOx concentrations so the cross-section TROICA expedition is a good subject for such research. The goal of this work was differences of
MVK+MACR yields from isoprene photo-oxidation between this work and those in earlier works for conditions “low NOx” and “high NOx”. To solve this problem, we used NOx and isoprene data obtained in TROICA-12 expedition.

Also we paid attention on another problem: in summer during the daytime the ambient concentrations of isoprene were mixed in convective boundary layer. Some studies [7],[8] have reported increasing of isoprene just before the sunset. In the absence of NO3 radical chemistry isoprene concentrations at the surface can be quite large at night due to early evening emissions to a developing nocturnal boundary layer (NBL) [9]. Therefore at evening biogenic compounds was emitting into a ‘smaller volume’ of NBL. Therefore at evening in the presence of reduced sunlight and as result in presence of small amount of OH formation, isoprene was accumulated of within a shallow stable layer. Note that advection also plays role in observed isoprene increasing during nighttime. Nighttime isoprene decays interpretation is often complicated by the competing effects of chemistry and transport, particularly within shallow nocturnal boundary layers [10]. Furthermore, there are also large uncertainties in isoprene and NO3 oxidation nighttime chemistry [8],[10].

The second goal of this work was the investigation of duration cycle of isoprene and some isoprene oxidation products: methyl vinyl ketone (CH3C(O)CH=CH2, MVK) and methacrolein (CH2=C(CH3)CHO, MACR). The special attention was given to studying of evening and nighttime values of isoprene, MVK and MACR, which was received during our TROICA-12 expeditions.

2. Measurements and dataset description

As well-known Proton Transfer Reaction Mass Spectrometry (PTR-MS) provides on-line monitoring of volatile organic compounds (VOCs) with a low detection threshold and a fast response time [11],[12]. Used in this work the Compact Real-Time VOC Monitoring Station (Compact PTR-MS) was acquired from Ionicon Analytik. The instrument consists of an ion source, a drift tube reaction chamber and a quadrupole mass spectrometer (QMS). H3O+ ions were generated in the hollow cathode discharge and directed to the drift tube where H3O+ and VOC ion-molecule reactions take place. The determination of atmospheric VOCs by this method is possible only if the chemical compound has affinity to a proton above than to water. The basic VOCs components, studied in this work, such as isoprene and their oxidation products, have affinity to a proton above than to water and therefore they can be determined by using PTR-MS technique. However, the proton mass spectrometry method has lack in selectivity in case that chemical compounds have the same atomic weight and, hence, isomers do not separate during our measurements. In this work the PTR-MS method with H3O+ injector does not allow us to separate the oxidation products of biogenic emissions, such as MVK and MACR.

The reagent and product ions were detected by the QMS in the 1–300 amu (atomic mass unit) range with resolution < 1amu. The linearity range of measuring VOCs values is equal to 500 pptv – 10 ppmv and the measuring time is less than 1 s at each mass. For more details, see IONICON Analytik GmbH product description, http://www.ptrms.com.

Also it is note that advantages of PTR-MS are real-time measurements, real-time quantification, low fragmentation, easy to operate, no sample preparation is necessary, relatively compact and robust instrumental technique. These advances made that PTR-MS has been deployed on a range of atmospheric-measurement moving platforms including research and operational aircraft platforms, see [13],[14].

The TROICA-12 expedition took place July 21 – August 4, 2008 on the route Moscow – Vladivostok – Moscow. The PTR-MS Compact detector was established on the head train carriage; the train on all part of this route moved by using electricity power engines. More detailed description about TROICA expeditions can be found in [15].

3. The analysis of TROICA experimental data

3.1 Spatial distribution of isoprene along the Trans-Siberian Railway
The spatial distributions of isoprene concentrations along the Trans-Siberian Railway for expeditions TROICA-12 East and West were drawn by using of ARC Info GIS system, (figure 1a and b). The MCD12Q1 v5.1, IGBP (2007) vegetation map of broadleaf, needleleaf and mixed forest with 500 m resolution was used as background layer on figure 1a and b. The high concentrations of isoprene along the route were corresponding to biogenic emissions at noon. The comparison of different vegetation maps was previously discussed in [16].

3.2 Diurnal variation of isoprene, MVK + MACR and MVK + MACR-to-isoprene

The diurnal variation of isoprene concentrations (figure 2a, 2c) and MVK+MACR (figure 2b, 2d) have been constructed and investigated. The total numbers of isoprene measurements are equal to 24,247 and 24,241 for TROICA-12 East and West expeditions, respectively. The local time (LT) was calculated from the longitude of the measurement point. As you can be seen from the figure 2, the MVK+MACR diurnal variation of isoprene oxidation products are well defined such as diurnal variation of isoprene. At the same time the some heterogeneity in the isoprene concentration diurnal
distribution at the TROICA-12 West expedition is observed. Probably the reason of this effect was explained that our measures were done at days in which it was differences at locations downwind of the isoprene emissions from a particular vegetation types and differences in the sunlight and temperature conditions. Note that the night isoprene growth was not observed.

![Figure 2](image)

**Figure 2.** The diurnal variations of sum MVK+MACR and isoprene along the Trans-Siberian Railway, calculated by TROICA-12 East (a, b), and West (c, d) expeditions data, July 2008. The 10 sec values are shown as a background.

To analyze the proper operation of the chemical blocks of CTM models it can be of interest to investigate the MVK+MACR-to-isoprene ratio. A diurnal variation of the ratio it is not revealed, see (figure 3a, 3c). The high noise in ratio distribution, with abnormally high values up to ~ 30–35 both in daytime and at night, was observed such as in [17]. For details of figure 3a, 3c, it was built ratio which is equal to 10 min average values of (MVK + MACR) to average isoprene. This average ratio is shown in figure 4. Apparently from the figure, the diurnal variation is not visible to average values also. However, large night values of the average ratio, is disappear (figure 4a, 4b).
Figure 3. The diurnal variations of (MVK+MACR)-to-isoprene ratio (3a and 3c) and linear regressions (3b and 3d) along the Trans-Siberian Railway, according to TROICA-12 East and West expeditions. The regression line in 3b and 3d were marked as dashed lines.

Figure 4. The average diurnal variations of (MVK+MACR)-to-isoprene ratio. The enlarged version of the figure 3a and 3c in the range of 0.8–2.0. The shaded area is corresponded of daytime values.

The linear regression of MVK+MACR to isoprene have been defined, (figure 3b, 3d) for TROICA-12 East and West expeditions respectively. The correlation coefficients (R), slopes (B) and standard deviations (SD) were calculated for a pair of MVK+MACR and isoprene. The linear regressions are characterized by a high degree of correlations (R = 0.68 and 0.79), and affinity slopes to 1 (B = 0.93 and 1.04) for TROICA-12 East and West, accordingly. The 10 sec distributions were
uniform and do not disintegrate into separate areas corresponding to night and day chemical reactions (figure 3b, 3d). Such divergence between the theory and experiment is the first weak alarm signal.

3.3 Dependence MVK+MACR-to-isoprene ratio of NOx

The correlation (R), slope (B), a standard deviation (SD) and quantity of measurements (N) for pair MVK+MACR and isoprene according NOx atmosphere pollution have been calculated and presented in table 1.

| NOx, ppbv | K_{MVK+MACR/ISOP} (TROICA-12 East/West) | R     | B     | SD    | N      |
|-----------|----------------------------------------|-------|-------|-------|--------|
| < 2.5     | 0.1031/0.7749                          | 0.7586/0.9946 | 0.2229/0.2041 | 1674/8839 |
| 2.5 – 5.0 | 0.7344/0.7748                          | 0.8639/0.9812 | 0.4331/0.3877 | 9984/11450 |
| 5.0 – 10.0| 0.6218/0.7235                          | 1.0084/1.1926 | 0.5832/0.4366 | 9111/2620  |
| 10.0 – 50.0| 0.6003/0.8375                         | 0.8975/1.3316 | 0.4560/0.5973 | 3177/1114  |
| > 50.0    | 0.6648/0.8613                          | 1.0189/1.3307 | 0.3399/0.4957 | 128/107   |

As it can be seen from table 1, the calculated slopes (B) weakly depends on the NOx pollution of the atmosphere. Let’s note that in the TROICA-12 East expedition it was dominated by long-range transportation from the central and the north-eastern industrial region of China, thus the maximum numbers of measurements was mainly recorded (in 79.2% cases) in the range of pollution with NOx ~ 2.5 – 10.0 ppb. In the TROICA-12 West expedition the air masses coming mainly (in 36.6% cases) from the clean areas with contamination less than NOx < 2.5 ppb. In the both expeditions the correlation coefficients (R) are significant and are in range of ~ 0.60 – 0.86, except for of the isoprene oxidation in the background conditions with NOx < 2.5 ppb in the expedition TROICA-12 East (R = 0.1031, within 6.95% cases of total measurements). This case with R = 0.1031 requires the separate consideration. The low correlation is determined by the fact that in this particular situation it is dominated by twilight – night isoprene oxidation in the time interval 21–24 h (0.875–1.0) with depressed reaction on OH and O3. Thus, it is possible to conclude that in the twilight conditions the vegetation for some time to continue to emits isoprene from leaves, while its secondary isoprene oxidation products are already depressed. The significant dependence of MVK+MACR-to-isoprene ratio from the NOx concentration is not detected.

9. Conclusions

This work is devoted to the study of the spatial and temporal distribution of isoprene and its oxidation products. The measurements of isoprene, methyl vinyl ketone and methacrolein were carried out using by the mobile observatory, placed on the railcar chassis. The vast area of deciduous and mixed forests in Far East, which crosses Trans-Siberian Railway, was selected as the object. According to TROICA-12 expedition data the isoprene growth at night was not observed. The isoprene and MVK+MACR concentrations are satisfy to a linear regress; the slopes (B) are close to the ~ 1 (0.93 and 1.04 for TROICA-12 East and West, accordingly). The correlation coefficients (R) are significant and equal to 0.68 and 0.79 for for TROICA-12 East and West with a number of measurements more than 24,000. The noise of the initial 10 sec measured values of MVK+MACR-to-isoprene ratio is significant. The high ratios (ratio > 5) are observed not only at night but also during the day. At night, the high values somewhat larger than in the daytime. However, based on the initial measurements for isoprene and MVK+MACR is not possible to identify this phenomenon as a PTR-MS noise. Let’s note that in other publications it was marked ratio noise only at night. The average
MVK+MACR-to-isoprene ratio does not have a pronounced diurnal variation. The pair of MVK+MACR and isoprene has a high degree of correlation (R~0.60–0.86) and weakly dependent on NOx, except in one case in which the twilight emission of isoprene was dominated. It has also been paid attention that at twilight the isoprene oxidation reaction at period of 21:00–22:00 LT leads to reduction slope, which lay below 1:1 line.

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