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Impact of near-surface atmospheric composition on ozone formation in Russia

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One of the consequences of the human impact on the atmosphere is increasing in tropospheric ozone concentration, with the highest ozone level being observed in industrially developed and highly populated regions of the world. In these regions, main anthropogenic sources of carbon monoxide (CO), methane (CH4) and volatile organic compounds (VOCs) are concentrated. The oxidation of these compounds, when interacting with hydroxyl and nitrogen oxides at rather high temperature and sunlight, leads to ozone formation. CO and CH4 are slowly oxidized in the atmosphere and cause an increase in global and regional background ozone. However, the oxidation of some VOCs occurs during daylight hours and is accompanied by an increase in ozone concentration near VOCs sources, particularly in urban and industrial areas. The contribution of biogenic VOCs to ozone generation is estimated to be from 40 to 70% of the total contribution of all chemical ozone precursors in the troposphere [1], with isoprene playing the main role in ozone formation [2]. The impact of aromatic hydrocarbons to ozone formation is reported to be about 40% of the total ozone generation from the oxidation of anthropogenic VOCs [3]. In this study, the results of VOCs measurements (isoprene, benzene, toluene, phenol, styrene, xylene and propilbenzene) by proton mass spectrometry in different regions of Russia along the Trans-Siberian railway from Moscow to Vladivostok from TROICA-12 campaign on a mobile laboratory in summer 2008 are analyzed. It is shown that the TROICA-12 measurements were carried out mostly in moderately polluted ($2 \leq NO_x < 20$ ppb) environment ($\sim$78% of measurements) with the remaining part of the measurements divided between weakly polluted ($NO_x \leq 2$ ppb) and highly polluted ($NO_x > 20$ ppb) conditions ($\sim$20 and 2% of measurements, correspondingly). The lower troposphere chemical regime in the campaign is found to be mainly NO_x sensitive, both in rural and urban environments, with typical morning NMHC/NO_x ratios being well above 20. Hence, ozone production rates are expected to be controlled by regional NO_x emissions and their complex interplay with both natural and anthropogenic sources of VOCs. The quantitative contribution of aromatic VOCs to ozone formation in urban areas and in Russian regions along the railway is estimated. The greatest impact of aromatic VOCs to ozone formation (up to 7.5 ppb of O_3) is obtained in the large cities along the Trans-Siberian Railway, with the highest concentrations of aromatic VOCs (1-1.7 ppb) and nitrogen oxides (> 20 ppb) being observed. The results show a significant contribution of anthropogenic emissions of VOCs to the photochemical ozone generation (30-50%) in the large cities along the Trans-Siberian railway in hot and dry weather conditions against natural isoprene emissions determining the regional balance of ground-level ozone in summer.
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