Airborne Aldehydes as Altitude-Distributed Source of Particulate Matter in the Troposphere

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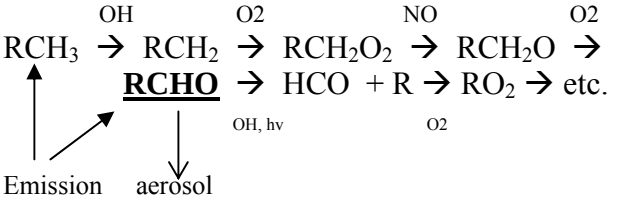
Aldehydes emitted into the atmosphere from natural and anthropogenic sources, as well as aldehydes formed as secondary pollutants in the atmospheric photooxidation of various hydrocarbons, are precursors of particulate matter. Our previous studies proved that even the simplest aliphatic and aromatic aldehydes form aerosol particles of nanometer size under photolysis (Dultseva et al., 2008). Surface sources of aldehydes have been assessed by researchers but the vertical (altitudinal) distribution of aldehydes in the troposphere remains unknown though the local concentration of aerosol-forming species is a very important characteristic to evaluate the rates and mechanisms of atmospheric photonucleation. In the present study we describe our approach to process the data on aldehyde concentrations at different altitudes to reveal the contributions from ground-based sources and chemical transformations of hydrocarbons in the troposphere.

Airborne measurements of aldehyde concentrations were carried out over the southern part of West Siberia in summer and autumn 2012, and in winter-spring 2013. Air samples were collected with an aircraft-mounted sampling device at the altitudes of 500 to 7000 m. Aldehyde concentrations were measured by means of HPLC using the procedure based on the reaction with 2,4-dinitrophenylhydrazine. Measurements revealed episodes with unexpectedly high [H_2CO] at some altitudes up to 7000 m, with nonmonotonic dependence on altitude, while aromatic aldehydes were not detected at altitudes above 2000 m. Keeping in mind the fact that benzaldehyde can be considered as a marker of anthropogenic air pollution, and our previous results on urban air pollution indicating that benzaldehyde in cities with high traffic usually accounts for *ca.* 10 % of formalehyde concentration, we used the relations between measured [H_2CO] and [C_6H_5CHO] as the basis to distinguish between anthropogenic and natural formaldehyde sources.

Formaldehyde at the altitude of 7000 m was thus related to natural sources. To reveal whether natural sources may account for high (> 0.3 mg/m^3) formaldehyde concentrations, we carried out modelling of the chemical mechanism of hydrocarbon photooxidation at the level of elementary stages, leading to gas-to-particle conversion under tropospheric conditions. We chose isoprene as a model compound emitted by vegetation and compiled the scheme of its transformations in the atmosphere according to Carter (2007), with focus on aldehydes formed at some stages as intermediate products. Rate constants for elementary stages were taken from the NIST Database when available, and the values for unknown rate constants were chosen on the basis of known ones for similar stages with other hydrocarbon species. This approach, together with the simulation of nucleation according to Smolukhowski's algorithm, allowed us to assess the biogenic contribution into formaldehyde concentration in middle troposphere. The general scheme of transformations can be represented as



This general scheme involves specific stages for the cases of R = alkenyl (hydrocarbon radical with double bonds) and R = alkyl. Hydrocarbons present in industrial emissions and those emitted by the vegetation can be clearly distinguished from each other in the samples collected in winter when only the contribution from coniferous trees is to be taken into account, while foliaceous trees, bushes and herbs do not emit organic compounds into the atmosphere. Aldehydes also exhibit a clear distinction of natural origin from the industrial sources. This evaluation allowed us to state that the origin of substituted aromatic aldehydes in the atmosphere is commonly biogenic, while benzaldehyde is an industry-related pollutant. Aliphatic aldehydes, including formaldehyde, originate both from vegetation and from industry; these contributions can be quantified through a comparison between summer and winter samples. Our results suggest that in summer about 80 % of airborne formaldehyde in the troposphere at an altitude of 5000 m and above has the biogenic origin, and among this amount, more than a half is formed as the secondary pollutant in alkene and alkane photooxidation, while the fraction of industry-related contribution reaches more than 90 % in winter but accounts for notmore than 20 % in summer. This feature may be significant for any region with climatic conditions close to those existing in the southern part of West Siberia.

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