



What makes urban atmospheric chemistry different and special?

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ABSTRACT

There has been a tendency in the atmospheric chemistry community to regard urban atmospheric chemistry as no different to global processes and to differentiate only in terms of the emissions density in models. Such an approach may be suitable for assessing the impact of urban emissions upon regional and global processes but is unsuited to generating a clear understanding of processes within the urban atmosphere itself. The urban atmosphere differentiates itself from the global atmosphere in terms of its density of emissions and relatively short timescales for chemical reaction processes, a consequence of which is that the key processes in the urban atmosphere are often different from those in the regional and remote atmosphere. This lecture will give relevant examples.

One of the key aspects of both urban and rural/remote atmospheres is the oxidation of primary pollutants and the formation of secondary species. Such processes may differ markedly between urban and non-urban environments as there are major differences in the behaviour of key oxidants such as ozone, hydroxyl and NO_3 radical. In the remote atmosphere the key production process for hydroxyl is through the photolysis of ozone to form excited state oxygen atoms which react with water vapour to form OH. In the urban atmosphere, concentrations of ozone are typically depressed relative to the rural atmosphere and hence this source of OH is less favourable. There are likely to be much higher concentrations of both nitrous acid and formaldehyde in the urban atmosphere whose photolysis is probably the major source of OH. Additionally, there is far more possibility for nocturnal formation of OH in the urban atmosphere from reactions of Criegee intermediates resulting from the oxidation of alkenes. As a consequence, it has been shown that winter to summer ratios of hydroxyl radical concentrations are much higher in the urban atmosphere than is typical of rural atmospheres in northern mid-latitudes. In rural atmospheres, most NO_x is present as nitrogen dioxide with modest concentrations of NO arising from photolysis. Direct emissions of NO in the urban atmosphere can suppress ozone concentrations to the point where nocturnal ozone can be unmeasurable. Generally, concentrations of ozone are considerably lower in the urban atmosphere than in surrounding rural areas. The co-existence of nitrogen dioxide and ozone at night in rural areas is conducive to the formation of the NO_3 radical, whereas in urban areas it is often the case that nitrogen dioxide and nitric oxide (an NO_3 sink) are abundant close to the surface where ozone is highly depleted. Consequently, formation of NO_3 is likely to occur at a greater altitude where NO_2 -rich air from the surface meets ozone-rich air from above. These are but a few examples of the many differences prevailing between urban and non-urban atmospheres which argue for a more specialised treatment of urban atmospheric chemistry than is typically applied at present.