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NO_x analyser interefence from alkenes

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Nitrogen oxides (NO and NO_2, collectively NO_x) are critical intermediates in atmospheric chemistry. NO_x abundance controls the levels of the primary atmospheric oxidants OH, NO_3 and O_3, and regulates the ozone production which results from the degradation of volatile organic compounds. NO_x are also atmospheric pollutants in their own right, and NO_2 is commonly included in air quality objectives and regulations. In addition to their role in controlling ozone formation, NO_x levels affect the production of other pollutants such as the lachrymator PAN, and the nitrate component of secondary aerosol particles. Consequently, accurate measurement of nitrogen oxides in the atmosphere is of major importance for understanding our atmosphere.

The most widely employed approach for the measurement of NO_x is chemiluminescent detection of NO_2* from the NO + O_3 reaction, combined with NO_2 reduction by either a heated catalyst or photoconvertor. The reaction between alkenes and ozone is also chemiluminescent; therefore alkenes may contribute to the measured NO_x signal, depending upon the instrumental background subtraction cycle employed. This interference has been noted previously, and indeed the effect has been used to measure both alkenes and ozone in the atmosphere.

Here we report the results of a systematic investigation of the response of a selection of NO_x analysers, ranging from systems used for routine air quality monitoring to atmospheric research instrumentation, to a series of alkenes ranging from ethene to the biogenic monoterpenes, as a function of conditions (co-reactants, humidity). Experiments were performed in the European Photoreactor (EUPHORE) to ensure common calibration, a common sample for the monitors, and to unequivocally confirm the alkene (via FTIR) and NO_2 (via DOAS) levels present. The instrument responses ranged from negligible levels up to 10 % depending upon the alkene present and conditions used. Such interferences may be of substantial importance for the interpretation of ambient NO_x data, particularly for high-VOC, low-NO_x environments such as remote forests.