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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The role of volatile organic compounds in the polluted urban atmosphere of Bristol, UK" *by* A. C. Rivett et al.

A. C. Rivett et al.

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The authors would like to thank the referee for his valuable comments. The points raised are answered below. Referee's comments are shown in bold.

"... the paper would be more complete if it listed or referenced the numerical value of rate constants used in computing daytime OH concentrations."

A list of rate constants used in calculating daytime and night-time radical concentrations is now included in Appendix 1.

"It might also be good to explicitly state the assumption of the model used to derive Eq. 1, which I take to be a well-mixed, "box" model."

It is assumed that there is a large input of VOC into the atmosphere at time t = 0, i.e. the morning rush hour. Thereafter it is assumed that there is no further input, and the

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VOC concentration decays due to constant dispersion, reaction with OH and reaction with NO_3. A derivation of Equation 1 is now provided in Appendix 2.

"Also, it would be interesting to see the value for Kdispersion computed for alkenes..."

The average value for Kdispersion has now been included in the paper, as has an average value for the transport lifetime (1/kdisp) of the VOCs.

"1) The halocarbon spikes made me wonder if they were caused by changing wind directions or changing emissions in time."

Measured halocarbon concentrations in Bristol appear to be affected by both weather conditions and emissions. The most likely source of the large CFC peaks, for example, has been identified as fugitive emissions from the illegal dumping of old refrigeration equipment. The distinctive geography of Bristol – the city sits in a basin, surrounded by hills – means that emissions from local industrial and landfill sources are trapped during still, calm weather periods. This phenomenon accounts for many of the halocarbon spikes. A thorough analysis of the halocarbon time series is given in 'In-situ gas-chromatographic measurements of halocarbons in an urban environment', Rivett et al., 2003, Atmospheric Environment, 37, 2221–2235. Clearly there is much still to be learnt about the sources and behaviour of halocarbons in urban conurbations and work continues at Bristol on this topic.

"2) The authors argue that Cl radicals produced by halocarbon degradation may change the oxidizing capacity of the troposphere, but they do not consider the potential impact Cl radicals may have on the validity of the equations they use in estimating OH radicals. Presumably, the contribution is small. But if so, why do we care about halocarbons changing the oxidation capacity in urban atmospheres?"

The contribution is indeed probably small, especially in Bristol. However, given the

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paucity of measurements of chlorinated species in urban areas, attempting to quantify chlorine radical levels is almost impossible. Hence, there may be an impact, but of what magnitude it is extremely hard to say. In other areas of the world, where chlorinated species may be more prevalent (e.g. a study in Taiwan by Wang et al., Env. Sci. Tech. 34, 2243–2248, 2000), due to lack of emission controls or higher usage, elevated chlorine radical concentrations may have a measurable impact on tropospheric chemistry. Biogenically produced halogen radicals, particularly iodine, have been shown to have a significant effect on chemical cycles in coastal areas (Hebestreit et al., Nature 397, 572–573, 1999). This could also be the case in towns and cities which are close to the sea, such as Bristol.

"3) I wondered if a dispersion model coupled to an area wide emission model or traffic model would do any better than a box model? This is a important question because a lot of effort has been put into complex models. Maybe, it is not necessary."

We have not looked at this but will be looking at the dispersion numbers with a view to coupling them with an emission model. What is clear is that feeding the numbers derived from alkene analysis into the alkane decays, where data are available, does provide a consistent dataset.

4) Can the authors speculate, using their equations, as to how global warming would effect OH and ozone levels in urban areas?"

Work by one of the authors (A.C. Rivett, 'VOCs: Their sources, behaviour and impact in urban environments', Ph.D. Thesis, University of Bristol, 2002) using a simple zero-dimensional chemistry model to explore the effect of global warming and climate change on urban air quality has produced some interesting results. Emissions of VOCs and levels of water vapour in the troposphere are predicted to increase over the next century (3rd IPCC Report, 2001). Whilst increased VOC concentrations will increase ozone in NO_x-rich environments, it is generally thought that increased water vapour

levels will reduce global ozone concentrations (Collins et al., 2000, Quarterly Journal of the Royal Meteorological Society, 126, p.1925). However, in urban conurbations this does not appear to be the case. In NO$_x$-rich areas, increased water vapour significantly drives up ozone concentrations –
Increased water vapour initially enhances ozone destruction, leading to enhanced OH:
O_3+hv $\rightarrow O_2 + O(^1D)$ and then $O(^1D) + H_2O \rightarrow 2OH$
Enhanced OH produces more peroxy radicals (HO$_2$ and RO$_2$):
through the VOC oxidation cycle
More peroxy radicals mean more conversion of NO to NO$_2$:
$NO + HO_2OH + NO_2$ and $NO + RO_2 \rightarrow RO + NO_2$
The excess NO$_2$ is then photolysed to produce more ozone.
The implications of this for the health of city populations are worrying to say the least.

"5) Because hydrocarbons have different lifetimes, calculations with them in effect are sampling different effective box sizes. Thus, I wondered if there were any trends in the results that varied with hydrocarbon decay rates."

This is a good question, we have not obtained sufficient data at this stage to conclude anything but at a first glance, the alkane data is certainly consistent with the alkene data. What would be nice is to have a long range of lifetimes, i.e. species with k's ranging from $1 \times 10^{-10} - 1 \times 10^{-13}$ cm^3 molecule^{-1}, we have this range but there are big gaps in the dataset.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 769, 2003.

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