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Interactive comment on "NO$_x$ cycle and tropospheric ozone isotope anomaly: an experimental investigation" *by* G. Michalski et al.

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Michalski et al. present a new set of experimental data on the isotopic coupling between NOx and Ox. While I have no major comment of the technical part of the manuscript, I have a major concern about the atmospheric extrapolation made by the authors. In abstract and more detailed in section 3.6, authors claim that isotope equilibrium between NOx and Ox will take hours to days to be established based on their model prediction. They also claim that because the model results are based only on isotopologue rate constants, the model can be used to predict the isotopic composition of NOx in the atmosphere. Both of these statements are excessive and incorrect.

For instance, they state : 1- Since the experimentally validated model results are based

only on isotopologue rate constants (independent of mixing ratios) the model can be used to predict the expected oxygen isotope composition of NOx in the atmosphere.

With this assertion, the authors seem to suggest that their model can predict atmospheric isotope equilibrium, which is wrong. The isotopic equilibrium values predicted (cap 17 46‰ and d18O = 115‰ are valid only for a system that includes only Ox and NOx interaction. Not taking into account the treatment of the HOx/RO2 and their interaction with NOx prevents the model to predict any atmospheric observations, thus the conclusion that their model can predict atmospheric isotopic composition is an overstatement.

2- In urban to rural conditions (1–10 ppbv) equilibrium is reached within a few hours, but in pristine environments it may take from days to over a week for NOx to reach isotope equilibrium.

This state is again wrong. As recognized by the authors few lines below, these time estimations are valid again for a model that includes only the NOx and Ox families setting O3 concentrations ca. 1000 times lower than atmospheric concentrations. In the atmosphere, with O3 concentration in range of tens of ppb, the Leigthon cycle (NO+O3; NO2 + hv, O2+O) will accelerate proportionally. Indeed, the limiting step in the Leigthon cycle at noon is the NO + O3 reaction (see attached document) and thus the kinetic is controlled by this reaction (same in their system as their JNO2 = 4 10(-3) s-1 is same order of magnitude than ground observations 10(-2) s-1). Therefore it can reasonably be argued that the time to reach isotope equilibrium in the atmosphere is as fast as the Leighton cycle goes, i.e. just few minutes in most cases, and definitely much faster than authors' model prediction.

It is also important to note that in the troposphere, the isotopic exchanges between NOx and O is always negligible as the chemistry (NO/NO2 interconversion) is orders of magnitude faster than these isotope exchange reactions (mainly due to the fact that O atom concentration is negligible in the troposphere and completely controlled by the

O_2+O exchange reaction). Only in the stratosphere and above the exchange reactions start to compete with the chemistry (Lyons, 2001, Zahn et al., 2006).

This can be demonstrated using the kinetic database and typical atmospheric concentrations. The kinetic rates (kNO+O3, and JNO2) have to be compared with their respective exchange rate reactions.

At 298 °C, kNO+O3 = 1.8 E-14 cm3 molecule-1 s-1 (IUPAC kinetic rates), JNO2= 1E-2 s-1 (from TUV model), kex(NO+O) = 4 E-11 cm3 molecule-1 s-1, kex(NO2+O) = 2E-11 cm3 molecule-1 s-1 , using O3 = 30 ppb (all cases), NO = 3 ppb (urban) 5 ppt (remote), NO2 = 50 ppb (urban) 50 ppt (remote), O atoms are assumed to be in photo steady state (1E+5 molecule cm-3 (urban), 1E+2 molecule cm-3 (remote)), we can calculate

NO+O3: (d(NO)/dt)kin = kNO+O3 [NO] [O3] = 1E+7 molecules/s (urban), 1.6E+6 molecule/s (remote)

NO + O exchange: (d(NO)/dt)ex = kNO+O [NO] [O] = 5E+5 molecules/s (urban), 8E+2 molecule/s (remote)

JNO2: (d(NO2)/dt)kin = JNO2 [NO2] = 1E+10 molecules/s (urban), 1E+8 molecule/s (remote)

and NO2 + O exchange (d(NO2)/dt)ex = kNO2+O [NO2] [O] = 4E+6 molecules/s (urban), 4E+0 molecule/s (remote)

In all cases, the chemistry overwhelms by orders of magnitude the isotope exchange, and thus the latter reaction has negligible impact on the isotope composition of tropospheric NOx thus demonstrating that isotopic equilibrium will be in phase with Leigthon photochemical equilibrium.

Detail of calculation can be found in the excel attached.

Reference Lyons, J. R. (2001), Mass-independent fractionation of oxygen-containing radicals in the atmosphere, Geophys Res Lett, 28(17), 3231-3234.

Zahn, A., P. Franz, C. Bechtel, J.-U. Grooß, and T. Röckmann (2006), Modelling the budget of middle atmospheric water vapour isotopes, Atmos Chem Phys, 6, 2073-2090.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C2837/2013/acpd-13-C2837-2013-supplement.zip

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 9443, 2013.