

Interactive comment on “Validation of an experimental setup to study atmospheric heterogeneous ozonolysis of semi-volatile organic compounds” by M. Pflieger et al.

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REPLY TO SHORT COMMENT

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19173, 2008.

It is true that we used off-line analysis technique. However, off-line measurements are not necessarily less accurate than on-line analysis. Moreover, the aim of this work was to develop an *alternative* device to provide first heterogeneous results for semi-volatile organic compounds that presumably exhibit slow reactivity towards the atmospheric oxidants such as ozone and OH. Therefore, the aim was not the development of a highly sophisticated analytical device but rather to focus on an experimental procedure which is adapted to study slow reactivity of semi-VOC. More precisely, the experimental pro-

cedure was specifically developed to study the heterogeneous reactivity of pesticides because it is currently not well-known. Naphthalene was chosen as a test compound because it has been widely studied in the past. Moreover, it is one of the most volatile SVOC (vapour pressure of 37 Pa at 25°C (Lei et al., 2002)). Therefore, this compound was an ideal candidate to test the possible experimental volatilization artefacts. Finally, naphthalene represents a good reference because it is both a PAH and a pesticide. The text has been accordingly modified.

We agree that the requirement of solvent for particle deposition may modify the particles' properties. Nevertheless, the surface characterization was not possible. Although some studies use a gas-solid equilibrium to simulate the adsorption of organics on aerosols' surface, a much larger number of works still use a liquid-solid equilibrium. Thus, it is important to highlight that this alternative experimental approach is based on the gas-solid equilibrium. The text has been modified in order to clarify that this procedure was already developed before. Accordingly, we have added in the introduction section the following references which used a gas-solid equilibrium for the adsorption of SVOC: Pöschl et al., 2001; Kwamena et al., 2004; Kwamena et al., 2007; Gloaguen et al., 2006. The following references have already been mentioned in the text: Pöschl et al., 2001; Kwamena et al., 2004; Kwamena et al., 2006; Kwamena et al., 2007 and Kahan et al., 2006, but some of them were omitted in the reference list. These references are now included in the reference list. The studies of Mmerekı and al. 2003a, 2003b and 2004 concerned the air-*aqueous* interface which is not the scope of our paper.

The pseudo-first order kinetics of adsorbed PAH towards OH and O₃ has been verified in most (maybe all) previous studies focused on this subject. Thus, we have checked it only with few experiments. The obtained results are showed in the Figure 2. This Figure, entitled 'Verification of pseudo-first order kinetics of O₃ (at fixed concentrations : 0.7 and 3 ppm) towards naphthalene (NAP) adsorbed on silica particles', is available on the following link: [Full Screen / Esc](http://www.univ-</p></div><div data-bbox=)

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provence.fr/gsite/document.php?pagendx=6832&project=lcp-ira. (Reply to ACPD).

Furthermore, one of the goals of the paper was to determine the influence of the nature of the particles on the kinetics. We only performed four experiments on XAD-4 particles because this support is not atmospherically relevant.

Discussion on the obtained results was added in the section 4.1 considering the influence of the substrate, as well.

In the previous version of the manuscript, the only fitted parameter was K_{O_3} while k_{max}^I remained fixed at the k_{obs}^I value obtained at the highest studied ozone concentration. The Langmuir-Hinshelwood fit has been improved by fitting both parameters: K_{O_3} and k_{max}^I giving better coefficient regression ($R^2 = 0.99$ and 0.94 for silica and XAD-4 particles, respectively). These changes have been included in the text and figures. In addition, we agree that our experimental data do not allow one to distinguish between the Langmuir-Rideal and the Langmuir-Hinshelwood mechanisms. To do so, it would be necessary to inject ozone concentrations of at least an order of magnitude higher than what was done. However, our device does not allow working at higher ozone level than 40 ppm. Moreover, giving a clear picture of the mechanism was not the scope of the paper. The experimental procedure was developed to study the heterogeneous kinetics of slowly reactive semi-volatile organic compounds in order to estimate their atmospheric lifetimes. Accordingly, it is not necessary to distinguish the mechanisms since there is not a significant difference between the two naphthalene's lifetimes calculated using both mechanisms under atmospherically relevant ozone concentrations. The discussion section has been accordingly modified.

Finally, the innovative part is that this alternative approach permits to elucidate the heterogeneous kinetics of semi-VOCs which presumably exhibit slow reactivity (such as pesticides) towards atmospheric oxidants (ozone, OH, etc.). These measurements are currently in progress in our laboratory, and the obtained results will be published elsewhere.

ACPD

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