# Fate of Deca-brominated diphenyl ether (BDE-209) adsorbed on model atmospheric particles: analytical development and heterogeneous reaction with ozone

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## Introduction.

Polybrominated diphenyl ethers (PBDEs) are a class of compounds widely used as flame retardant additives. Three major formulations of PBDEs are commercially produced: penta-BDE, octa-BDE and deca-BDE. Among all PBDEs, BDE-209 is the most widely produced. Prohibited in Europe, the lowest molecular weight congeners seem to have a toxic effect on the environment and health, by analogy with other POPs like dioxins. In the atmosphere, due to their low vapor pressure and their high molecular weight, PBDEs are mostly adsorbed on solid particles and subject to long-range transport (Gouin et al.2002, Gouin et al.2003, Ter Schure et al. 2004, Wania et al. 2003). Under solar irradiation or under the presence of different atmospheric oxidants (OH, $O_3$…), they may be degraded, generating potentially more toxic compounds (Ahn et al.1987, Sellström et al. 1998, Tysklind et al. 2001, Olsman et al. 2002, Söderström et al. 2003, Bezares-Cruz et al. 2004, Eriksson et al. 2004, Watanabe et al. 1987).

## Materials and Methods.

This study deals with the heterogeneous reactivity of ozone with BDE-209 adsorbed on silica particles. The reaction set-up developed for this study is presented in Figure 1 (Perraudin et al. 2006). Oxidation reactions were performed using a quasi-static ozone reactor. Ozone was generated using a low pressure mercury lamp. Particles were extracted by pressurized fluid extraction (ASE®) and BDE-209 was quantified with internal standards using gas chromatography coupled with an electron capture detector (GC-ECD).

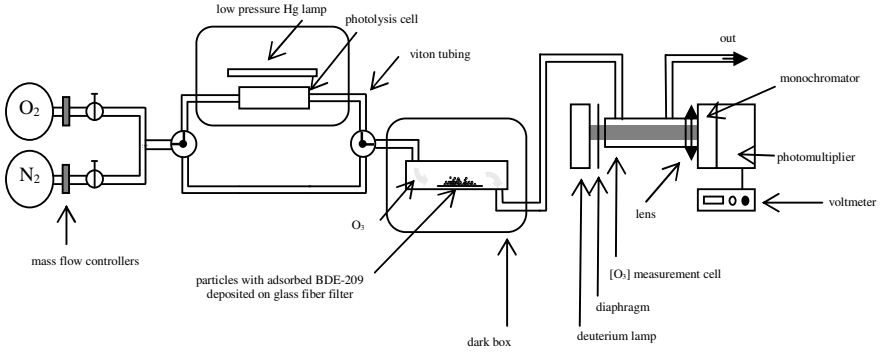


Fig 1. Scheme of the experimental set-up used for the study of ozone reaction with particulate BDE-209

## Results and Discussion.

Reaction rate constant was derived from BDE-209 concentration decay versus time of oxidant exposure (Figure 2) for ozone concentrations varying between $1 \times 10^{14}$ and $8 \times 10^{14}$ molecules $cm^{-3}$. The second order rate constant ($k^{II} = (2.6 \pm 0.2) \times 10^{-18}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) allows an evaluation of the particulate BDE-209 lifetime with respect to ozone concentration in the troposphere (25 ppb). No BDE-209 desorption was observed under our experimental conditions.

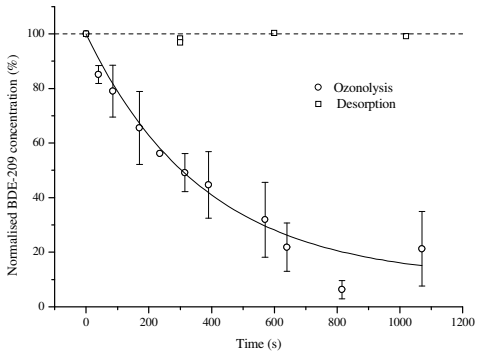


Fig 2. Variation of normalized concentration of BDE-209 adsorbed on silica particles versus time i) by desorption (□) or ii) by reaction with ozone (○) $[O_3] = 8 \times 10^{14}$ molecules $cm^{-3}$ – Error bars represent 1 standard deviation.

A mass spectrometer detector was used to tentatively characterize the oxidation products formed, which may be more toxic than the parent BDE-209.

## Conclusion.

The heterogeneous reactivity of BDE-209 adsorbed on silica particles has been studied. The preliminary results already allow to calculate a rate constant for the heterogeneous reaction with ozone in the absence of light at 22 °C and to detect some degradation products. For the first time, a calculated lifetime (7.2 days) has been determined. This study will be completed by the identification and the quantification of oxidation products of BDE-209 ozonation in order to propose a complete degradation mechanism.

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