Kinetic multi-layer model of surface and bulk chemistry in the lung lining fluid (KM-SUB-LLF): An investigation into reactions occurring within the respiratory tract

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Atmospheric oxidants can cause damage to biosurfaces such as the lung epithelium unless they are effectively scavenged. High levels of O_3 have been shown to lead to an elevated mortality rate, especially of people already suffering from pulmonary diseases (Stedman, 2004). The inhalation of particulate matters is also known to cause serious respiratory and cardiovascular problems and leads to an increased mortality rates (e.g. Pope et al. 1995). Several studies have shown that semiquinones and transition metal ions contained in particulate matter can trigger the formation of H_2O_2 followed by generation of extremely reactive OH radical via Fenton reactions within the lung lining fluid (e.g., Charrier *et al.* 2014).

The kinetic multi-layer model of surface and bulk chemistry in the lung lining fluid (KM-SUB-LLF) is developed for description of chemical reactions and mass transport in the lung lining fluid. The model structure and formulations are based on the kinetic multi-layer model for aerosol surface and bulk chemistry (KM-SUB) (Shiraiwa *et al.* 2010). The model treats the following processes explicitly: gas-phase diffusion, adsorption and desorption from the surface, bulk-phase diffusion and chemical reactions at the surface and in the bulk. The LLF is split into many layers: a sorption layer, a surfactant layer, a near surface bulk layer and several bulk layers allowing for concentration gradients to be resolved.

The model was used to investigate reactions occurring in the respiratory tract including reactions between two oxidants (ozone and the hydroxyl radical) and antioxidants (ascorbate, uric acid, glutathione and α-tocopherol) as well as surfactant lipids and proteins. Reactions leading to the formation and destruction of H_2O_2 in the presence of semiquinones (phenanthrenequinone (PQN), 1,4-naphthoquinone (1,4-NQN), 1,2-naphthoquinone (1,2-NQN)), copper and iron were also included within KM-SUB-LLF. A schematic of these reactions is shown in Figure 1.

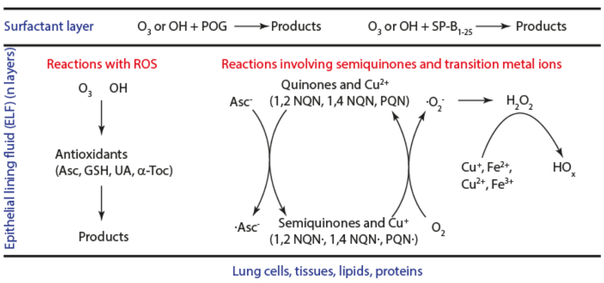

Figure 1: A schematic of KM-SUB-LLF

Three different regions of the respiratory tract were considered within the model; the nasal cavity with a LLF thickness of 10 µm, the bronchides with a LLF thickness of 500 nm and the alveoli with a LLF thickness of 50 nm. Initial results using KM-SUB-LLF suggest that at a constant O_3 concentration the O_3 will rapidly saturate the LLF at all LLF thicknesses whereas the antioxidants and surfactant species are effective scavengers of OH. Chemical half-lives of the antioxidants, surfactant species and gas phase species were estimated. The half-lives of O_3 and OH were short, ~ 10^{-6} seconds and ~ 0.1 seconds in the bronchides, respectively, suggesting that both OH and O_3 will be significantly depleted within the respiratory tract. The pH dependence of the products of reactions between O_3 and antioxidants was also investigated and KM-SUB-LLF predicted that a harmful ascorbate ozonide product would increase by three orders of magnitude from 1.4×10^{11} cm^{-3} at pH 7.4 to 1.1×10^{14} cm^{-3} at pH 4 after 1 hour, although a uric acid ozonide product would decrease by three orders of magnitude.

KM-SUB-LLF successfully reproduces measurements by Charrier et al. (2014) for the production of H_2O_2 in the presence of PQN, 1,2-NQN, 1,4-NQN and copper and for the destruction of H_2O_2 in the presence of iron. At typical concentrations of semiquinones, iron and copper within the LLF it can be estimated that H_2O_2 concentrations would equilibrate to ~ 10^{13} – 10^{14} cm^{-3}. However, OH concentrations would be low (< 1000 cm^{-3}) due to reactions with antioxidants and surfactant species within the LLF.

Charrier *et al.* (2014) *Environ. Sci. Technol.*. **48**, 7010-7017

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