Measurements of toxic nitramines and nitrosamines in particles formed during the photochemical degradation of amine emissions from CO_2 capture plants

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The development of CO_2 capture technology is an essential part of the global efforts to reduce the concentration of atmospheric CO_2. However, amine emissions to the atmosphere from CO_2 capture plants employing amine-based technology may have a major impact on the environment and human health. Photo-oxidation of amines can lead to the formation of potentially carcinogenic nitrosamines and nitramines in both the gas phase and the particle phase. The Atmospheric Chemistry of Amines (ACA) project was set up to investigate the gas phase photochemical degradation of amines under ambient conditions, and to characterize and quantify the resultant aerosol formation (Nielsen, 2011).

A series of photo-oxidation experiments were carried out under different atmospherically relevant conditions at the European Photoreactor (EUPHORE) in Valencia, Spain. During the measurement campaign we investigated the atmospheric photo-oxidation of two amines relevant to CO_2 capture, *tert*-butylamine and aminomethyl propanol (AMP).

We studied the composition of the aerosol formed using a range of analytical techniques. Firstly, we used a highly sensitive analytical method capable of separating several hundred trace level organic nitrogen (ON) compounds in ambient air (Farren, 2015), based on comprehensive two-dimensional gas chromatography (GC×GC) coupled to nitrogen chemiluminescence detection (NCD). GC×GC provides increased separation power, and offers better peak resolution and sensitivity compared to one dimensional GC. The nitrogen-specific detector offers high sensitivity and selectivity toward ON and ease of calibration due to the equimolar response of nitrogen-containing compounds. Our measurements allowed us to determine the amount of nitramine formed from amine degradation in the gas phase and partitioning to the particle phase. As shown in Figure 1, the AMP nitramine ($C_4H_{10}N_2O_3$) and the *tert*-butyl nitramine ($C_4H_{10}N_2O_2$) were the most abundant ON compounds found in the secondary organic aerosol (Fig. 1).

Secondly, we used two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOF-MS) in combination with GC×GC-NCD to characterise the aerosol composition in more detail. Several oxidised compounds were found to be present in the aerosol, including oxazolidones formed from condensation reactions between AMP and various small molecules such as aldehydes and ketones. Thirdly, nitrate salts of both *tert*-butylamine and AMP were identified using ion chromatography.

We also intend to discuss potential nitramine and nitrosamine formation as a result of the photo-oxidation of a series of amines to be studied at the European Photoreactor in the upcoming months.

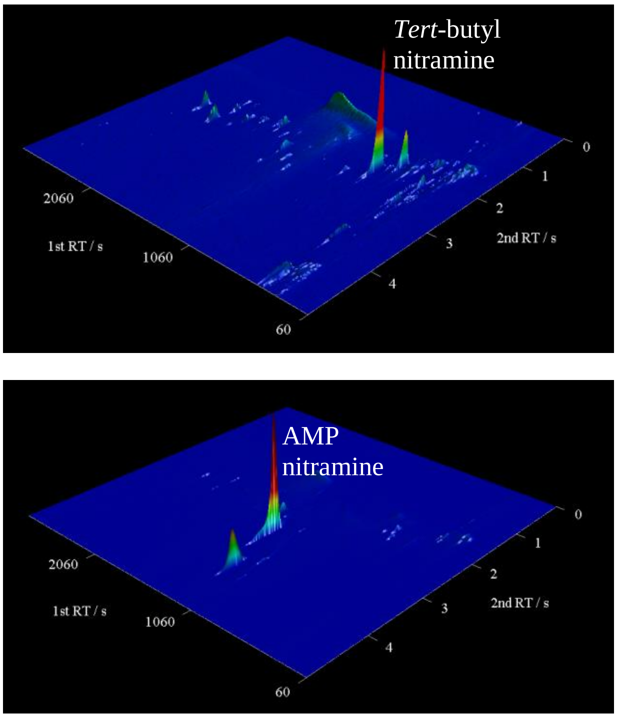

Figure 1. GC×GC-NCD chromatograms of aerosol samples from the photo-oxidation of *tert*-butylamine and aminomethyl propanol.

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Nielsen, C. et al. (2011) *Atmospheric Degradation of Amines*, Norwegian Institute for Air Research.

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