14.1 HOURLY CONCENTRATIONS OF AMMONIA DURING THE WINTER IN MANCHESTER, UK, RELATED TO TRAFFIC AND BACKGROUND SOURCES

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SUMMARY

Concentrations of atmospheric ammonia have been measured using a high resolution Aerodyne Quantum Cascade Tunable Diode Laser Absorption Spectrometer from a rooftop laboratory centrally located in a large urban conurbation, Manchester, UK, overlooking a heavily trafficked street canyon. Continuous mean hourly concentrations measured over one month in winter 2004, are compared and related to background and local anthropogenic sources including traffic emissions. Mean concentrations were 2.3 ppb, (median 1.8 ppb, range 0.4 – 10.6 ppb). The highest ammonia concentrations were observed when the wind was from the southwest and during low wind conditions. Potential sources in the southwest have been identified, but require further investigation. Ammonia concentrations were related to concentrations of NO_x and CO, suggesting that traffic is a major urban source of ammonia. The contribution by traffic was also indicated by a diurnal cycle with peaks corresponding to those in traffic rates, although other urban sources could be as significant. Comparison with unpublished ammonia data from 1997 shows an increase in the slope of the relationship between ammonia and both NO_x and CO by approximately 40% since that time. In the same period, the proportion of petrol-engine cars fitted with catalytic converters has approximately doubled, thus supporting previous findings that link higher traffic emissions of ammonia to these vehicles.

1. INTRODUCTION

Enhanced ammonia concentrations in the atmosphere due to human activities have been identified as a cause of damage to sensitive ecosystems through eutrophication and acidification (e.g. Krupa, 2003). As the most important basic compound in the atmosphere, it also constitutes a major precursor gas for secondary aerosol formation through reactions with sulphuric and nitric acids (Erisman & Schaap, 2004). This has implications both for human health and for radiation forcing.

The main source of ammonia is agriculture, which contributes 85% of the emissions in the UK. Urban sources were, until recently, generally considered to be minor, and were mostly related to humans (through breath, sweat and smoking), pets, household products, certain industries and a small release from motor vehicles (Sutton *et al.*, 2000). Recent studies, however, have revealed higher ammonia emissions from petrol-engine motor vehicles than previously, due to the widespread introduction of three-way catalytic converters. From measurements in a roadway tunnel, Fraser & Cass (1998) concluded that the contribution of motor vehicle emissions had risen from 2% to 15% of the total ammonia emission in the Los Angeles area since the introduction of catalysts. Perrino *et al.* (2002) found a close link between ammonia and CO emissions in a series of experiments conducted in Rome. These results indicated that petrol-engine vehicles constitute a major source of urban ammonia.

This paper reports the use of a high resolution Aerodyne Quantum Cascade Tunable Diode Laser Absorption Spectrometer (TDLAS) to measure ammonia from a rooftop location in central Manchester, UK, in the winter of 2004. The data is compared with nearby measurements of NO_x and CO and analysed to examine the hypothesis that traffic is a major source of ammonia in Manchester.

2. METHODS

The TDLAS was deployed in a rooftop laboratory in the UMIST main building in central Manchester and sampled air from the outside (approximately 25 metres above street level) through a 13 metre length of Restek Silcosteel® tube. NH_3 concentrations were recorded at a rate of 1 Hz over the period 26/01/04 to 23/02/04 and integrated to hourly data for comparison with trace gas data.

Hourly concentrations of NO_x, CO and NO_2 were retrieved from the UK Automated Urban Network (AUN) monitor at Manchester Piccadilly for the same period. This site is in central Manchester, 600m from the UMIST main building, and is at ground level in an open space with busy traffic on one side and a busy bus station on another. It is classed as an 'Urban Centre' site. Meteorological information was recorded from the highest point of the UMIST Main Building with an automatic weather station and included wind speed and direction provided by an ultrasonic anemometer (Gill Solent, Model Windmaster).

3. RESULTS AND DISCUSSION

The TDLAS recorded mean NH_3 concentrations of 2.3 ppb for the whole period. In order to distinguish between urban and background ammonia, a number of data clusters were identified.

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It was noted that NH_3 concentrations were generally high compared to NO_x when the wind direction was from the south-southwest, particularly within the range 200° – 220°. During these periods (defined as 180° – 240°, but excluding the anti-cyclonic period of 9th – 16th February – see below) a background of 1.3 ppb is suggested. This may be explained by the presence of significant agricultural, industrial and domestic ammonia sources within this wind sector, although more local sources have been identified and cannot be ruled out.

Higher concentrations (in excess of 4 ppb) were also observed during an anti-cyclonic period that lasted for 6 days from the evening of the 9th February. Within this period, higher NH_3 compared to NO_x were observed twice, when the wind speed increased slightly from the southwest. It is suggested that the extra southwesterly source is enhanced due to reduced dispersion and then gently advected towards the city.

By removing the anti-cyclonic and southwesterly datasets, the influence of identified advected ammonia is removed leaving a hypothetically 'urban only' dataset. NH_3 in this dataset is plotted against NO_x in Figure 1. NH_3 data for the periods of southwesterly winds (both anti-cyclonic and otherwise) are plotted against NO_x in Figure 2. It can be seen that the background NH_3 during the southwesterly periods is higher than in the urban only data, particularly during the anti-cyclonic period. An approximate linear relationship between NH_3 and NO_x in all these data clusters supports the hypothesis that traffic is a major source of ammonia within the city, although the amount of scatter seen in Figures 1 and 2 indicate that other sources could be as significant. In a city centre location, these will largely be human sources and solvent use, and these possibilities are being investigated further.

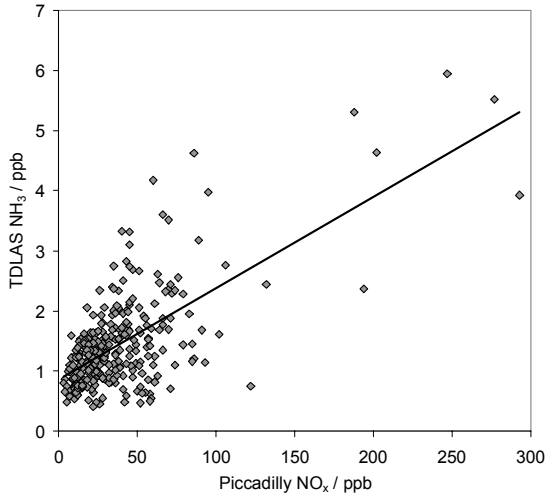

Figure 1: Scatter plot of NH_3 versus NO_x excluding southwesterly winds and anti-cyclonic period.

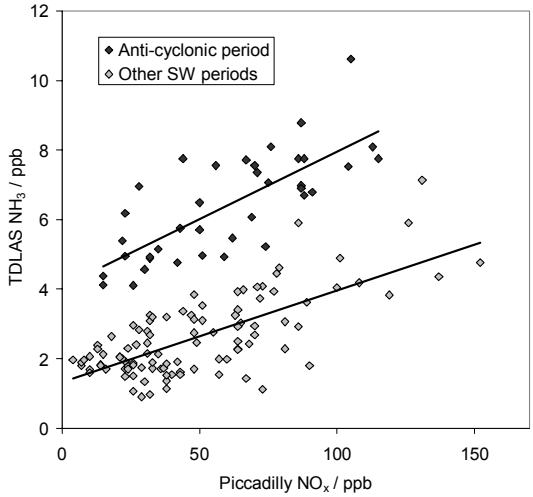

Figure 2: Scatter plot of NH_3 versus NO_x during southwesterly winds.

Figure 3 shows the diurnal cycle of the NH_3 concentrations for all datasets as well as the urban only NH_3 and NO_x data. Peaks in the NH_3 concentrations are seen roughly coinciding with peaks in traffic volume (the morning and evening rush hours), and with peaks in NO_x. This is further indication of a traffic source of NH_3, but again other sources are being considered.

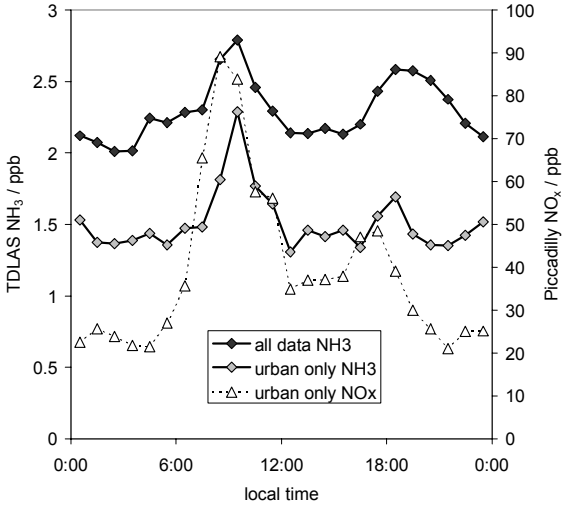

Figure 3: Diurnal averages of NH_3, 'urban only' NH_3 and 'urban only' NO_x.

Measurements of ammonia were made from the same location in 1997 using annular denuders, and compared with hourly NO_x and CO concentrations from the Piccadilly AUN monitor (previously unpublished data). Measurements were made continuously for six days from 8th – 14th December 1997. The linear relationships between NH_3 and NO_x, and between NH_3 and CO were found and compared to the same relationships in the 2004 data. It was noticed that in both relationships the intercepts had

not changed, but the slopes had increased by approximately 40%. This suggests a relative increase in the emission of ammonia from traffic sources unrelated to increases in traffic volume. Three-way catalytic converters became compulsory for new petrol-engine cars in the UK from 1993. By 1997, approximately 40% of cars in the UK were estimated to be so equipped, and it is estimated that this proportion had reached 88% by 2002. This supports previous findings (e.g. by Fraser & Cass, 1998) that increased NH_3 emission from traffic is related to the wider use of catalytic converters in petrol-engine vehicles.

4. CONCLUSIONS

Concentrations of ammonia have been measured using a tunable diode laser absorption spectrometer in a city centre rooftop location in cool and damp conditions in Manchester, UK. The mean of hourly concentrations measured over 27 days in January and February 2004 was 2.3 ppb. Ammonia concentrations were closely correlated to concentrations of NO_x measured at a nearby city centre location, suggesting a traffic source for ammonia, although the scatter suggests a significant contribution from other sources. The contribution of traffic is also indicated by a diurnal cycle, which exhibits peaks corresponding to peaks in urban traffic flow. The slope of the relationship between ammonia and both NO_x and CO has increased by approximately 40% since 1997, since when the proportion of petrol-engine cars in the UK fitted with catalytic converters has approximately doubled, further supporting previous findings that link higher traffic emissions of ammonia to these vehicles.

The results presented here show evidence of a significant contribution from local urban ammonia sources. Peaks in ammonia concentration were recorded when the wind was from the southwest and during low wind conditions. Potential sources in the southwest have been identified, but require further investigation.

Urban ammonia concentration trends may be changing rapidly in response to evolving vehicle technology. Further monitoring is required in order to quantify the changing urban contribution to atmospheric nitrogen budgets and secondary particle formation. The analysis discussed above indicates how meteorological conditions and a city's location relative to localised ammonia sources have a strong influence and must be taken into consideration in any monitoring programme.

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