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The measurement of ammonia in the National Air Quality Monitoring Network (LML): (1) instrumentation and network set-up

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1. introduction

Ammonia (NH_3) plays an important role in the total acid deposition in the Netherlands. On the average, its relative contribution to this deposition (SO_x+NO_x+NH_x) is estimated to be about 50% for the whole country. Immission and deposition levels are calculated with a transport model which takes into account emissions on a 5 x 5-km scale, meteorologics and NH_3-specific deposition parameters. To calibrate and validate such a model, measurements are, however, indispensable. The instrumentation and LML configuration used will be described.

2. instrumentation

The instrument used is the continuous-flow wet denuder manufactured by the Netherlands Energy Research Foundation (1). It is not primarily designed for use in an automatic network; the set-up is more-or-less experimental. Therefore it is only used in an interim network. An operational instrument has been developed in the meantime for use in the final network (see §4).

The principal of the continuous-flow wet denuder is as follows (see Figure 1). Air is sampled at a flowrate of about 30 l/min through a rotating annular denuder which contains an absorption solution (0.1M $NaHSO_4$). NH_3 in the air sampled is efficiently absorbed by the solution, which is continuously withdrawn from the denuder to the detector at a flowrate of ~1.5 ml/min. After adding a 0.5M NaOH solution, by which dissolved NH_4^+ is converted into gaseous ammonia, the solution passes through a semi-permeable membrane. The dissolved gaseous ammonia diffuses through the membrane and dissolves as NH_4^+ in demineralised water (with a certain NH_4^+ offset) on the other side.

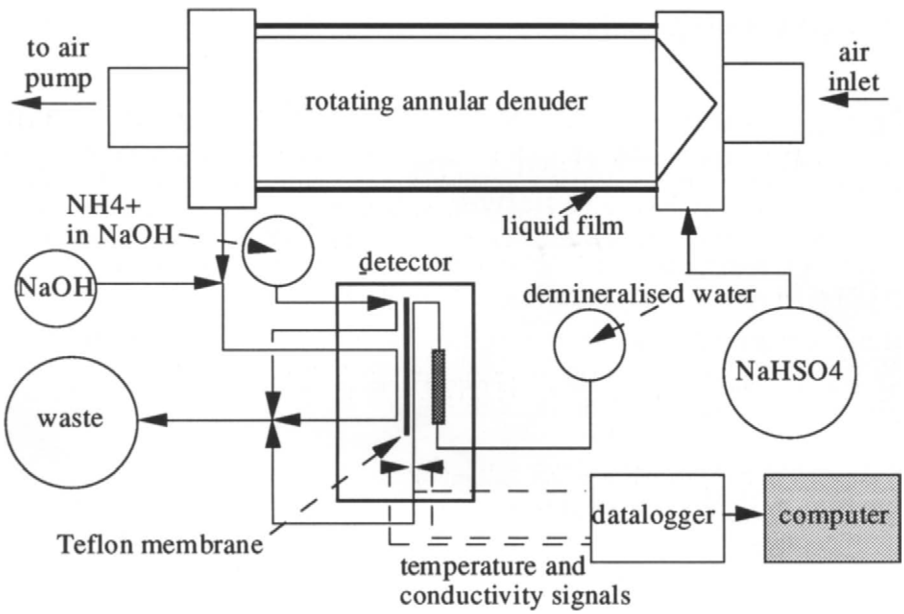

Figure 1. Schematic view of the continuous-flow wet denuder.

This NH_4^+ -containing solution then proceeds to a conductivity cell. The temperature-corrected conductivity is a direct measure for the NH_4^+ concentration. The NH_3 concentration in the sampled air is calculated from this value, gas and liquid flow, and calibration data. All data is stored in the datalogger of the instrument, which can be read out by a computer. Time resolution is 1 min.

During an extensive test - programme at RIVM (2,3) the instrument performed as follows:

detection limit (3s)	0.02	$\mu g/m^3$	(at zero air)
precision (1s)	< 2	%	
linear range	>500	$\mu g/m^3$	
drift	-0.3	% per day	
max. deviation	< 0.4	$\mu g/m^3$	(at zero air)
	< 4	%	(at 10 $\mu g/m^3$ NH_3)
	< 1.2	%	(a 100 $\mu g/m^3$ NH_3)

This performance meets the required specifications.

It should be noted that the above stated maximum deviation assumes an environmental temperature of the instrument in the range 15 - 25 ^oC. Therefore the measurement containers have to be temperature conditioned for use in the field.

3. network configuration

LML stations

The interim network consists of 8 stations located in areas with different levels of ammonia emission densities. For model validation purposes this is necessary. The emission - levels vary from < 1 ton NH_3/km^2 per year (background areas) to ~ 30 ton NH_3/km^2 per year (high emission areas). The network was set up in August 1992. Since then, the selected locations have changed slightly. From May 1994 the configuration has been as follows (see also Figure 2):

stations in background - areas:
LML 235 Huijbergen
LML 444 De Zilk
LML 538 Wieringerwerf

stations in areas with average emission density:
LML 633 Zegveld
LML 928 Witteveen

stations in areas with high emisssion density:
LML 131 Vredepeel
LML 722 Eibergen
LML 738 Wekerom

Figure 2. Ammonia measurement locations in the Netherlands (August 1994).

Because ammonia sticks to almost every surface, special attention is given to the inlet configuration, which consists of a polyethene funnel (with the opening faced downwards) connected to the instrument by polyethene tubing. Also, the instrument is installed at the top of the measurement container to keep the inlet length as short as possible. Sampling height is 3 m above ground level.

van - locations for representativeness measurements

For the distance to local emission sources, these locations are selected in the same way as the LML stations. This means at least 300 m from local ammonia sources in emission-and average areas, and about 1000 m in background areas. Because the expected gradient of ammonia levels in the emission areas is higher than in the background areas, the necessary number of van - locations is 8, 6 and 4 for emission, average and background areas, respectively.

logistics

Each LML - station is visited once a week. The measurement period is finished with a final calibration of detector-cel and flows. Data is stored in a portable computer for validation and storage in Bilthoven. Solutions, tubing etc. are replaced and after calibration, a new measurement period is started. These field - activities take about 3 to 4 hours, depending on the chance of malfunctioning of the instrument. Representativeness measurements are carried out frequently.

4. future developments

As previously stated, the instrument is not configured for use in an automatic network like LML. So, from the beginning of 1993 large efforts have been put in the development and extensive testing of an operational continuous-flow wet denuder in the cooperation of RIVM with ECN. The most important improvements with this instrument are the continuous control of important measurement parameters (flows, temperatures etc.) and essential functions, like rotation of the annular denuder. For this, an RS232 communication with local station processors (SPS) will become possible. These processors (which are part of the existing network) are connected with the central station at RIVM by a telephone line. Maintenance interval time for the instruments will be increased from 1 week to 1 month. These new ammonia monitors are expected to be completely implemented at the beginning of 1995.

4. references

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