ACTRIS TNA Activity Report

Training on NH3 measurement by wet chemistry techniques, NH3measurementTR

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- Introduction and motivation

Soils are a major source of primary and secondary greenhouse gases. Within the EU project ÉCLAIRE we are investigating soil gas exchange processes amongst other topics. We are currently designing a methodological approach to measure gas flux exchanges between biosphere and atmosphere within a laboratorial incubation experiment at BOKU, Austria. Additional to CO_2, CH_4, N_2O and NO_X gas measurements, we want to include an NH_3 measurement instrument (AiRRmonia) to our laboratorial incubation system. This methodological approach will be used to differentiate between soil and litter primary and secondary greenhouse gas emissions of samples originating from nine different sites across Europe.

- Scientific objectives

A one week training at CEH Auchencorth was provided on handling the AiRRmonia instrument correctly. Very helpful recommendations were given to optimize our laboratory incubation system for the experimental set-up at BOKU University.

- Reason for choosing station

Based on the infrastructure and long lasting expertise at Auchencorth regarding NH_3 measurements as well as AiRRmonia experiences, we decided to colaborate with CEH Auchencorth.

- Method and experimental set-up

The AiRRmonia measuring principle is based on wet chemistry techniques. Its analyzer contains a membrane sampler for quantitative sampling of the gas-phase of ammonia. After diffusion through the membrane, the ammonia is absorbed in a sampling solution, and the sample solution pumped continuously through a conductivity detector.
The AiRRmonia system has the potential to detect 0,1 µg/m³ to 100 µg/m³ (preliminary results).
The measurement period can be adjusted with a highest sampling resolution of 1 minute. [1]
Figure 1 shows the scheme of the AiRRmonia instrument and the different flow directions of the solutions. $NaHSO_4$ at concentrations of 50 ppb and 500 ppb, respectively, are used to calibrate the system.

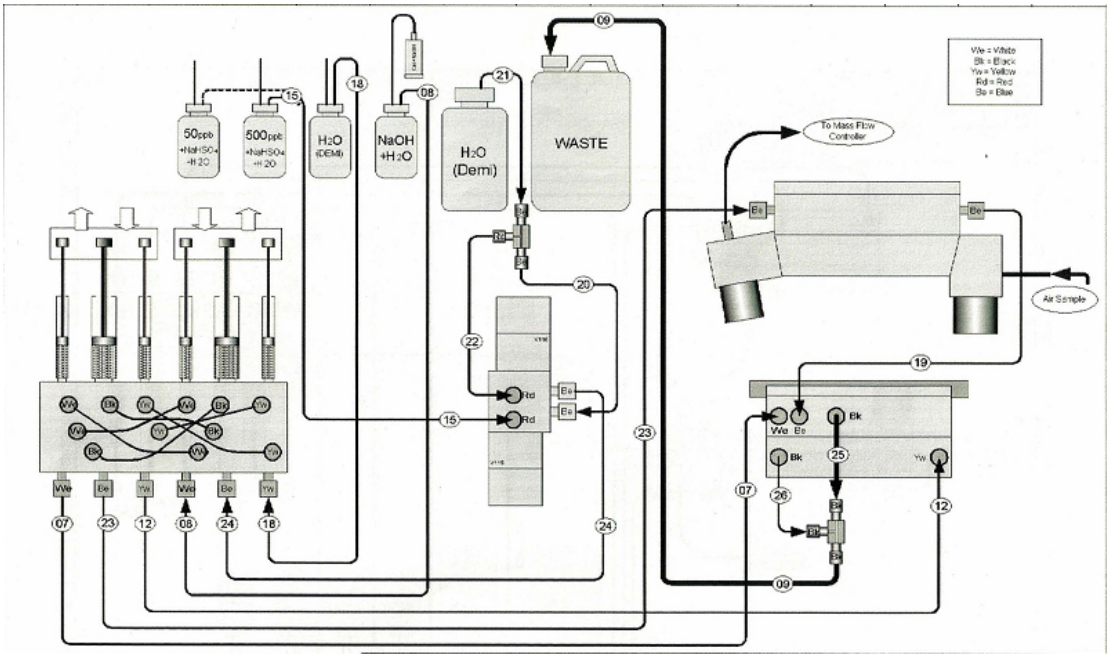

Fig. 1: Scheme of the AiRRmonia instrument describing direction and location of the different flows. Three of the six syringes pump the solutions out of the containers while the other three pump the solutions into the sample and detector block, respectively. [1]

The channel system is positioned on a Teflon membrane, which is permeable for gasses. On the opposite side of the membrane flows an absorption solution in counter-flow direction. The sampling channel is dimensioned in such a way that all the ammonia will pass the membrane and forms ammonium in the absorption solution. A three-channel syringe pump is used to displace the solutions with a fixed flow rate. All flows entering the detector block are led through a de-bubbling chamber first. In the detector block a hydroxide solution is mixed with the sample revealing gaseous ammonia again. Then the sampling solution is led along a Teflon membrane again. The gaseous ammonia is able to penetrate the membrane. This is the ammonia selective step in the process, since apart from small volatile amines, no known airborne compounds will be gaseous at this stage. A purified water flow at the opposite side of the membrane dissolves the ammonia that penetrated the membrane. A conductivity cell monitors the initial conductivity. The resulting content of ammonium and hydroxide after the membrane exchange is measured with a second conductivity cell. The conductivity difference is a measure for the original ammonia content in the sampled air. Figure 2 shows the measure principle of the AiRRmonia graphically. The conductivity is corrected for temperature drifts. The calibration curve has a second order shape due to the ammonium/ammonia dissociation equilibrium.

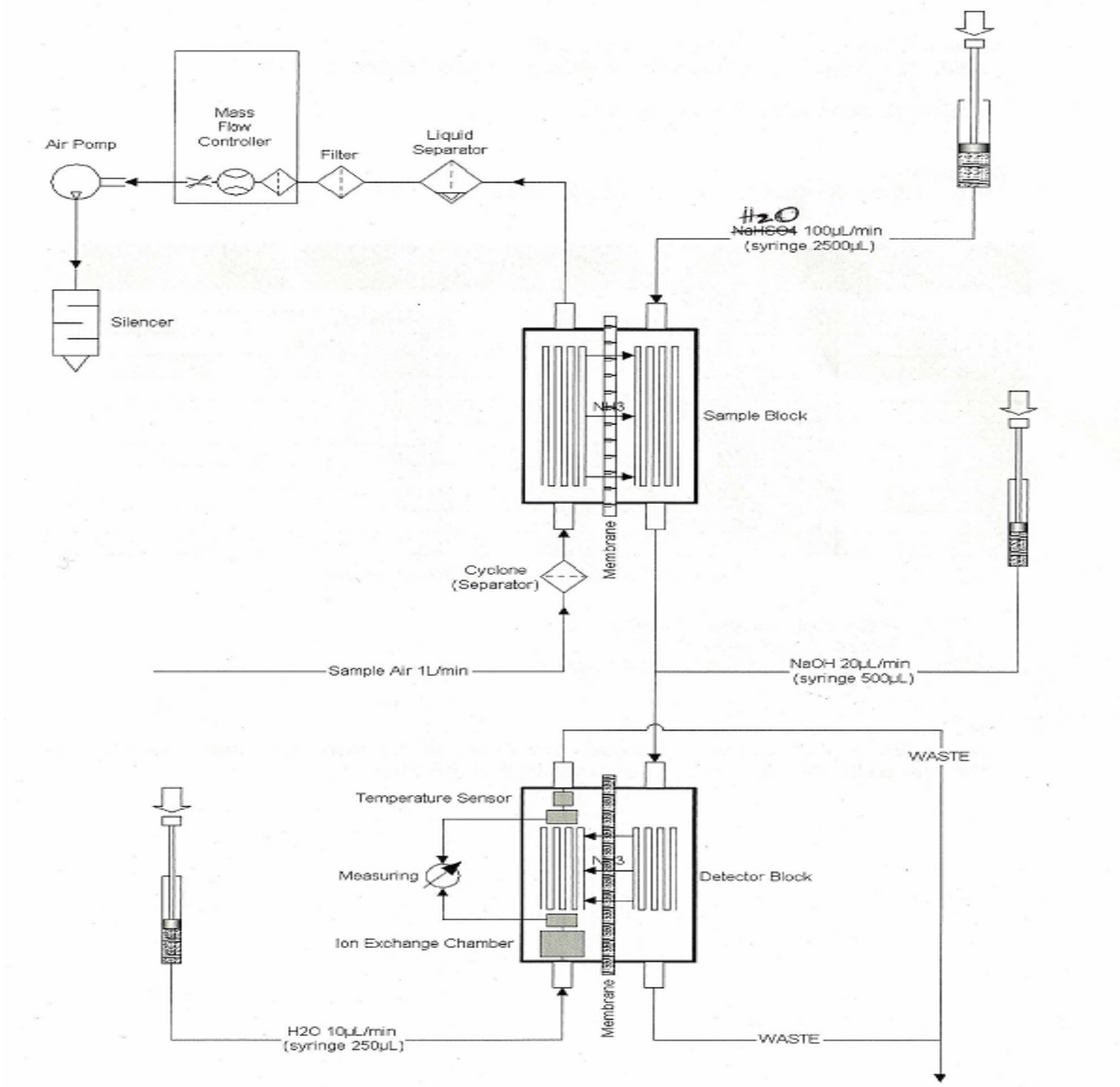

Fig. 2: Measure principle of the AiRRmonia Instrument. The Air sample gets mixed with a water flow in counter-flow direction within the sample block where ammonia turns after passing the membrane into ammonium. After reacting with a sodium hydroxide solution, ammonium turns into ammonia, passes again a membrane and a demineralized water flow within the detector block, where the conductivity differences between demineralized water and the ammonium solution are measured.

- Preliminary results and conclusions

The one week of NH_3 measurement training provided useful information about how to measure NH_3 with the AiRRmonia instrument as well as improved knowledge of handling NH_3 measurements in general. The training involved handling of the instrument from switched off mode to final measurements including all preparation and cleaning steps in between.

Once the instrument was switched off, reinitializing included replacement of syringes and parts of syringes, respectively, if necessary as well as removal of air bubbles. To replace the membranes of the detector, the sample block had to be disassembled and cleaned with demineralized water. A column containing resin for water purifying purposes needs to be maintained occasionally by adding quartz wool on both sides to avoid blockages. The instrument must be calibrated manually all four days and reaction solutions need to be refilled all 6 days. Values are calibrated against 0, 50 and 500 ppb NaHSO4 solution which must be prepared in advance. Data analysis are operated with a labview Airrmonia software programme written by Chris Flechard (INRA, France) and modified by CEH Edinburgh. The response time of the instrument takes about 40 minutes without heating of the tubes. Heating of tubes decreases the response time.

- Outcome and future studies

The AiRRmonia training provided familiarity with the instrument as well as a good knowledge of handling NH_3 measurements in general. Heating of tubes proofed to be necessary regardless of the instrument type used. Future studies with two other instruments will provide our final decision of choosing the most appropriate instrument to be included to our laboratorial incubation system at BOKU University.

- References

[1] MECHATRONICS AiRRmonia manual