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**PROCESS OF AMMONIA EXCHANGE
BETWEEN SURFACE / ATMOSPHERE :**

APPROACH ABOUT ITS MODELLISATION

May-June 1993

ABSTRACT

For ammonia measurements of air concentration and fluxes between the atmosphere and the surface, using the ammonia analyzer (2 diffusion denuders), a temperature correction of 5% / °c over the data is required (at present, just available for $12 < T < 26$ °c).

In order to complete the lack of data about NH_3 concentration, and to estimate annual fluxes over specific ecosystems, monitoring of air concentration was realized at Bush, Scotland. The two techniques used (diffusion denuders, diffusion filters) show a low level in atmospheric ammonia during the months of May-June 1993. In addition, no specific variation of its concentration over the day is significant.

Measurements of the exchange of gaseous ammonia between the atmosphere and a natural unfertilized vegetation were made at Great Dun Fell, England, using the micrometeorological techniques and diffusion denuders in gradient. NH_3 was generally found to deposit rapidly with near zero surface resistance (R_c) (except sometimes for very low air concentration in ammonia). In addition, when periods of low level of atmospheric concentration in ammonia were recorded, emission and deposition both occurred, bringing to the fore the hypothesis of an ammonia concentration equilibrium into the leaf, even for natural vegetation, only for low level in air concentration.

ACKNOWLEDGEMENTS

I would like first to thank Dr David Fowler, for giving me the opportunity to do my training period at I.T.E., in Air Pollution sector.

Then, thanks to Mark Sutton to welcome me as an assistant, taking time to explain me how to manage these experiments, taking time to spend good moments too (picnics in the sunshine...).

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INTRODUCTION

Ammonia, recognized as an important atmospheric pollutant, comes mainly from agricultural sources (fertilizer and animal waste). The scale of its emission results is one of the main cause of NH_3 deposition over ecosystems, alongside NO_x . In addition, oxidation of NH_3 to nitrates in some soils contributes to their acidification.

Of course, for agricultural crops, such inputs may be small compared to fertilizer. However, over natural unfertilized ecosystem, with no other nitrogen added, this may represent a considerable shift in the nitrogen balance, leading to biological changes associated with eutrophication.

In order to improve understanding about the process of NH_x circulation and then to model it (emission, transport, deposition, reaction...), air concentration and fluxes data are required. Which was the subject of this study : monitoring of air concentration in ammonia near Edinburgh, and fluxes measurements over a natural unfertilized ecosystem.

GENERAL BACKGROUND ON ATMOSPHERIC AMMONIA

1- Definition and properties of Ammonia

As a background to understanding the behaviour of NH₃ in the environment, a brief introduction to its physical and chemical properties seems to be useful.

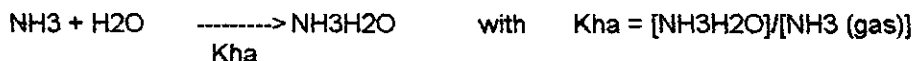
Ammonia (NH₃) is an alkaline and colourless gas, detected by its pungent odour (when [NH₃] >50 ppmv, NRC, 1979).

As NH₃ is a base, it neutralizes acids in the atmosphere (It is the only major gaseous base present) (e.g. Allen et al, 1989) :



In addition, it is a reactive gas, soluble in water, readily adsorbed on to dry surfaces (NRL, 1979) and ionizing to NH₄⁺ (Ammonium). The solubility of Ammonia is particularly important in its environmental circulation.

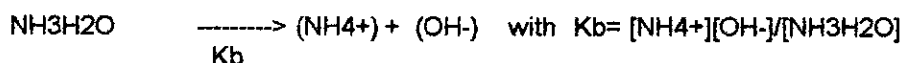
According to the HENRY equilibrium :



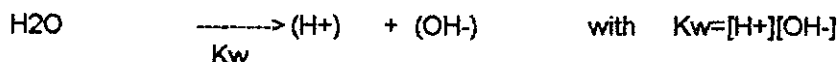
where Kha, which is the dimensionless HENRY constant, is temperature dependant, with solubility decreasing with increasing temperature.

However, the ionization in solution to form NH₄⁺ makes the total NH_x solubility much larger than given solely by Kha.

And :



Such NH₃ acts as a base, hence the effect of this upon pH may be quantified by relating to the ionizing of water :



where Kb and Kw are increasing with increasing temperature.

The solubility of NH₄⁺ is extremely sensitive to pH and an increased quantity of NH₃ gas will give a rise to an increased pH. The effect of temperature are smaller than that due to pH, though still considerable. HALES and DREWES (1979) and NRC (1979) have provided relationships accounting for the temperature dependance (when Kha=Kw/Kb) :

$$[\text{NH}_3 (\text{gas})] = 10^{\frac{(1.60352 - 4207.62/T)}{[\text{NH}_4^+]/[\text{H}^+]}}$$

In environmental conditions, other species will be present such as the products of dissolved gases (CO₂, SO₂, HNO₃, HCl...), and such as ions from the soils (Humic acids, Ca²⁺...). This all have effects on pH and correspondingly modify NH_x solubility. Some examples of reaction are given :

In the soil : NH₃ $\xrightarrow{\text{Oxidation}}$ (NO₃⁻) (Nitrates) which leads to the acidification of the ecosystem.

In the air : NH₃ $\xrightarrow{\text{with SO}_2}$ NO_x

In addition, the waterbalance of a surface affects total quantities dissolved. As a consequence, these factors are expected to be important in the exchanges of NH₃ between the ground and the atmosphere and between phases in the atmosphere itself.

2- Sources of Atmospheric Ammonia

As sea should rather be acting as a sink for NH_x (Ayers and Gras, 1983), major sources of NH_x appear to be continental (by way of combustion, volatilization or losses).

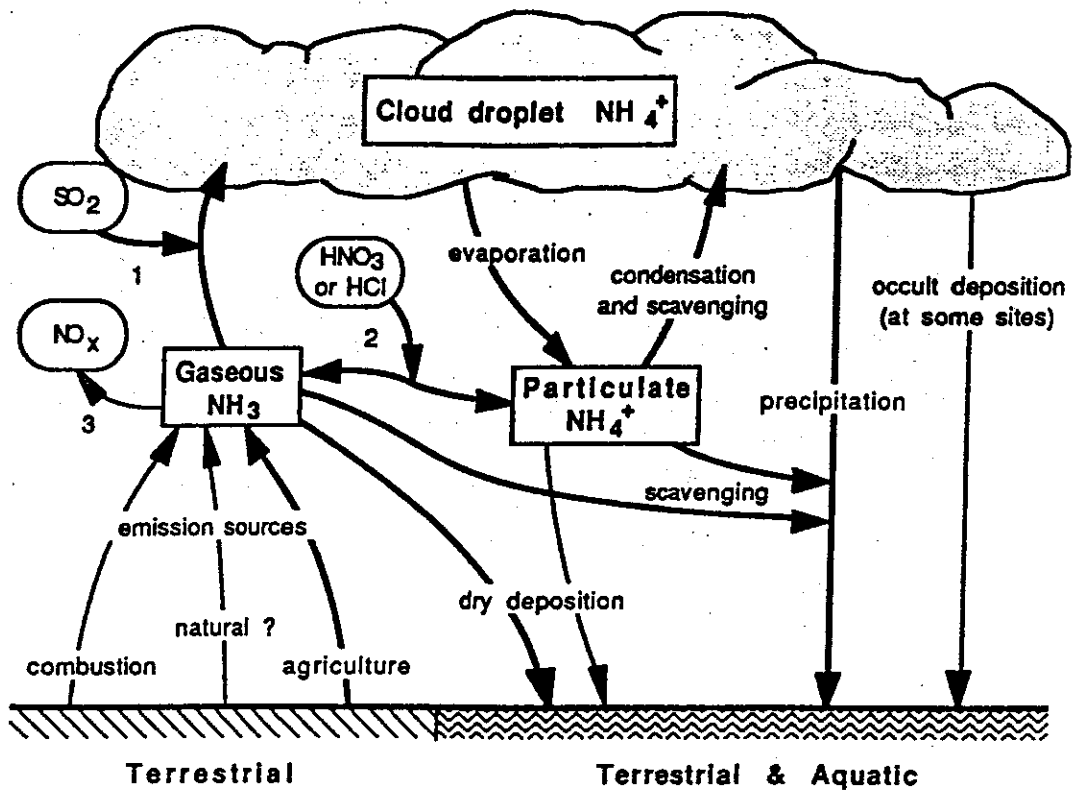
- > The combustion of coal is a source of ammonia.
- > The emission of NH₃ from soil is another one.
- > And, at last, there are the losses of NH₃ from fertilizers and animal waster.

In alkaline soil, neutral mineral fertilizer promotes losses. The hydrolysis of fertilizer ((NH₄)₂SO₄ or NH₄NO₃) in the soil liberates NH₃, which raises the pH locally, reducing the solubility and thus favouring emission (Vlek and Crasswell, 1981).

Concerning the mainure and subsequent decomposition of dead plants and animals, which may then volatilize into atmosphere, they may return to earth later, either by direct uptake as NH₃ or NH₄⁺ (dry deposition), or as NH₄⁺ dissolved in precipitation (wet deposition).

All of these losses bring us differences in results, which arise from stocking density, animal species, sward fertilization and grazing management.

The following scheme is a simplified scheme of the surface/atmosphere circulation of NH_3 :



Simplified scheme of the surface/atmosphere circulation of NH_x . Major fluxes are shown by bold lines. The three reactions noted are: 1) SO_2 oxidation to SO_4^{2-} and neutralization by NH_3 to give ammonium sulphate (e.g. $(\text{NH}_4)_2\text{SO}_4$); 2) Equilibria of the gases NH_3 , HCl and HNO_3 to form particulate NH_4NO_3 and NH_4Cl ; 3) Oxidation of NH_3 by OH^* to form NO_x .

3- Some of the different measures realized

At present, there are three main approaches to measure NH_3 concentration in the air :

→ Diffusion denuders

The air sample is drawn by a pump through a tube which has been coated initially with an acid solution for collection of ammonia. The solution is then analyzed to determine the NH_3 concentration.

→ Filter packs

The aerosol particles are collected on a PTFE (polytetrafluoroethane) filter and NH_3 is collected subsequently on reactive acid impregnated filters.

→ Diffusion tubes

The principle of a diffusion tube is to provide a diffusion path, of known length and cross-sectional area, between the atmosphere and a sink for the gas of interest.

Through all these methods, it is possible first to measure the air concentration in ammonia.

Then, the emission has to be estimated. Emission is the gaseous loss from a surface or at a defined atmosphere above this (at the most : 1 meter). Agricultural sources represent the bulk of the emission, mainly animal wastes compared to fertilizer (Buijsman et al, 1987). Combustion sources and natural soils are insignificant and ignored (their exclusion may be supported).

The general method of this approach is to estimate individual emission factors for the different source types, and then to sum occurrences of these sources over the region of study. Another approach use reference heights of the order of hundreds of meter. Then the effects of different lands are integrated, which enable to estimate a net flux to the atmosphere.

Then, the deposition has to be measured. As NH_x is present in the atmosphere as NH_3 gas, NH_4^+ in cloud and precipitation, NH_4^+ particles, different removal mechanisms apply for each of these. It has been suggested that NH_3 gas may be oxidized in the atmosphere (e.g. McConnell, 1973 ; Levine et al., 1980), however this reaction is slow, and accounts for only a small fraction of the loss from the atmosphere (Soderlund and Svensson, 1976). The bulk of the removal is therefore by deposition back to earth.

The estimation of NH_x dry deposition is made by analysing washings of artificial or real leaves, by using precipitation events to do the washing (large quantities of NH_x are adsorbed on leaf surfaces, which are later washed off by rain). Thus the dry deposition is estimated as the difference between the wet deposition and throughfall fluxes. Although throughfall measurements have been the most popular technique, some disadvantages appear : some errors may due to canopy exchange of the ions studied, and this method assumes no emission from the soil beneath (so it is not possible to use the results to predict deposition at other sites). Thus, because of canopy exchange processes, the use of throughfall studies to estimate deposition fluxes should be treated with caution.

Dealing with the dry deposition of NH_4^+ , it is useful to know how the airborne particles deposit. It has been intensively studied and reviewed (Nicholson, 1988 ; Chamberlain and Little, 1981 ;...). These particles are transported by atmospheric turbulence close to the surface, where they deposit, by way of either sedimentation or impaction (large particles), or Brownian diffusion (small particles). Now, atmospheric NH_4^+ is both too small for sedimentation or impaction to be important, yet too large for efficient diffusion. hence, this particles are expected to deposit slowly, and the bulk of dry deposition is due to NH_3 deposition rather than NH_4^+ .

The rate of dry deposition of NH_3 is often expressed as a deposition velocity (V_d), which is considered to be independant of air concentration, and is referenced at a particular height (z) above the depositing surface :

$$V_d \{z\} = \text{Deposition flux} / \text{concentration} \{z\}$$

The controlled environment studies show us a foliar absorption of NH_3 . The plant enrichment is proportionnal to air concentration, and a clear relationship has been established between uptake and stomatal opening (comparison with the flux of CO_2 in light and dark periods). Hence appeared the idea of an NH_3 "Compensation point" (noted X_{cp}), which is increasing with increasing temperature. In addition, Nitrogen status is affecting the size of X_{cp} , and there is no X_{cp} for unfertilized plant species. So, when the ammonia concentration in the air is above this level, then deposition occurs. On the contrary, when the air concentration is below, NH_3 emission occurs. And at this level, nothing happens. For example, for a constant air concentration, emission varies with time and is greatest following anthesis and during leaf senescence. X_{cp} confirms the greater emission during senescence (Morgan and Parton, 1989).

4- Short introduction to the micrometeorological field measurements

As the NH_x gradient is dominated by NH₃ exchange, it is used to calculate a reasonably valid flux. This one is measured in the free air above the surface and adequated with exchange at the surface (which must be not disturbed, while the net exchange is measured). But one practical measurement restriction exists : an uniform land surface of several hundred metres upwind is required. In addition, as samples cover a large area, variation in exchange over the site are averaged out.

Thus, the method is assuming a constant flux layer :

$$F_x = \overline{W' X'}$$

, where W' is the fluctuation about vertical windspeed
and X' the fluctuation about concentration

or :

$$F_x = K_x (\Delta X / \Delta Z)$$

, where K_x is the turbulent diffusion coefficient of
trace of gas or particulate exchange and
 $(\Delta X / \Delta Z)$ is the gradient of height

The estimation of K_x is given by the aerodynamic gradient method :

$$K_x = [k(z-d)u^* / \phi_h]$$

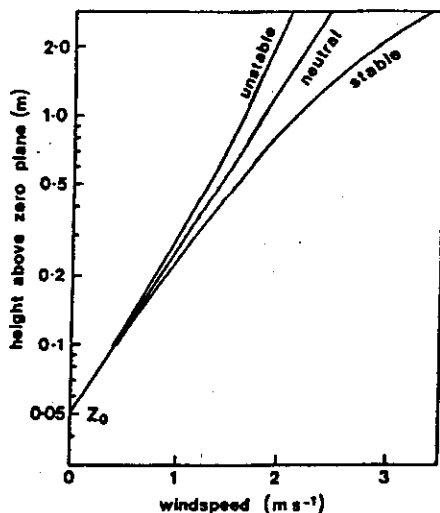
, where k is the von Karman's constant of
proportionality of mixing length to height above zero
plane $(z-d)$ in neutral conditions, u^* is the eddy
velocity, and ϕ_h is the empirically estimated heat
gradient correction factor for non-neutrality.

which may then be substituted into the flux equation :

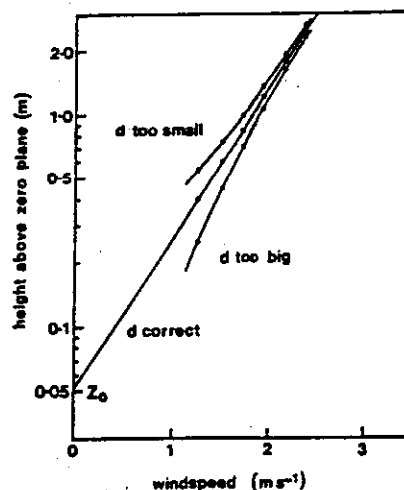
$$F_x = u^* X^*$$

, where $X^* = [K_x / u^*] (\Delta X / \Delta Z)$, if u^* is different to zero.

Although the flux may be calculated using the formulae above, since the gradients with height are non linear, some log-linear approach exist : the first one integrating ϕ as a constant, the second one integrating ϕ as a function of height in stable or unstable conditions. The practical considerations (windspeed profiles) show us the conditions (unstable, neutral or stable) and the effect of the estimate of zero plane displacement on the logarithmic wind profile in neutral conditions :



Effect of non-neutrality on windspeed profiles.



Effect of the estimate of zero plane displacement

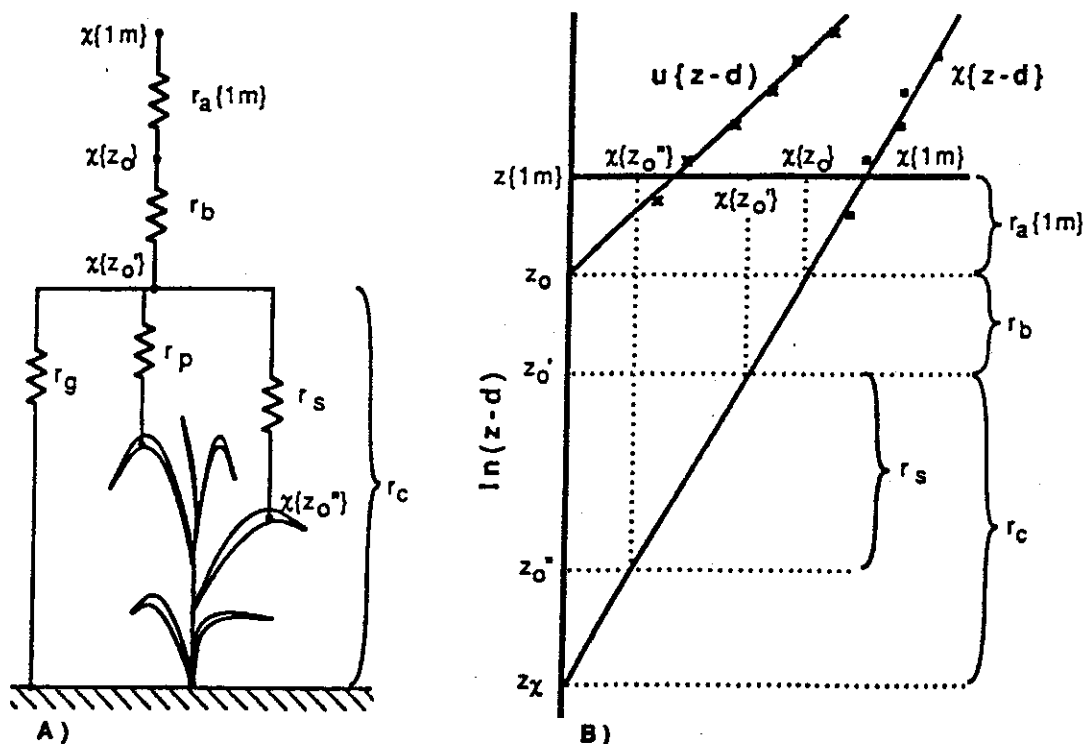
In addition, the resistance analysis allow to identify the controlling factors in exchange. Following the constant flux layer methods of estimating surface exchange, each resistance to transfer of the trace compound between two levels can be defined :

$$r\{z_1, z_2\} = (X\{z_1\} - X\{z_2\}) / F_x \quad \text{where } z_1 \text{ and } z_2 \text{ are two heights above the surface.}$$

In measurements of the dry deposition of trace gases, the absorbing surface is often assumed to have a zero air concentration, and the flux therefore viewed as being dependent on the atmospheric concentration (Fowler and Unsworth, 1979). In this case, if z_2 is considered to be the notional height of the absorbing surface, where concentration is zero, and a zero plane displacement is accounted for, a total resistance from a defined height to the surface ($r\{z-d\}$) may be defined (Sutton, 1990) :

$$r\{z-d\} = X\{z-d\} / F_x = 1 / V_d\{z-d\}$$

Thus the inverse of r is the deposition velocity V_d .



Resistance analogy of trace gas transfer between the atmosphere and vegetation.

A) For a gas of concentration χ the component resistances to transfer are given as: r_a , atmospheric resistance; r_b , laminar boundary-layer resistance, r_c , surface or canopy resistance. r_c may be considered as several parallel resistances: r_g , resistance to soil uptake; r_p , resistance to leaf surface uptake by pollutant reaction; r_s , resistance to uptake through stomata. The notional surface concentrations at z_0' and z_0'' are given for different points between resistances.

B) The resistances may be viewed as accounting for the transfer between notional heights above the surface. For this hypothetical example, deposition would be recorded with a value of r_c which is greater than r_s . For further details of this analysis see text.

For example, the approach of the surface resistance (R_c) is made to understand its behaviour and then to model the exchange. In dewfall conditions, the stomatal uptake is increasing (R_c diminishes), so wet leaf surfaces will be an efficient sink of SO_2 .

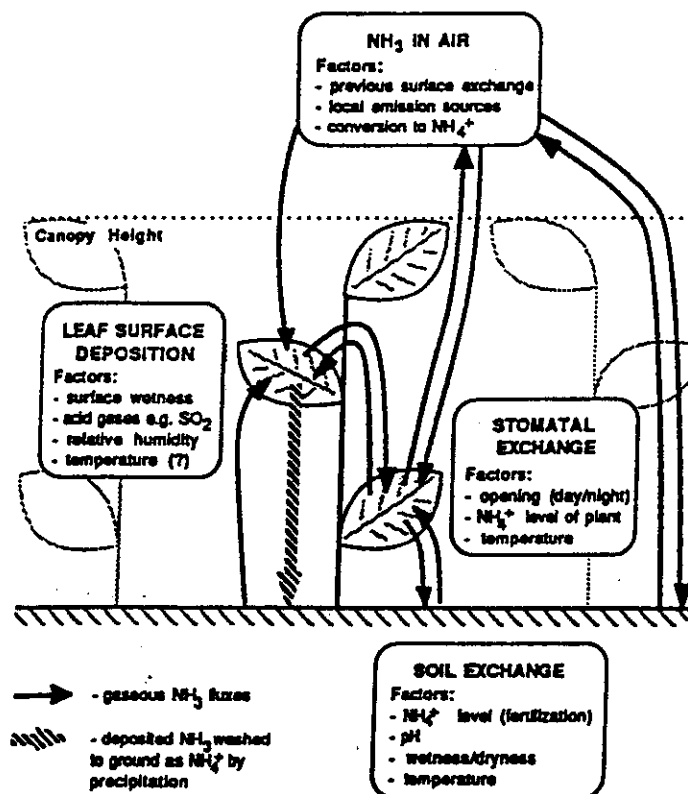
Thus, the different stages in the micrometeorological studies are :

- The field sampling,
- Windspeed measurement (using sensitive cup anemometers),
- Temperature and Humidity measurement (the best one is a system of ventilated psychometers to provide both of them),
- Ammonia measurement.

5- Surface exchange results : over natural or fertilized sites.

M. Sutton, 1990, studied NH_3 exchanges between air and natural or fertilized soils. The main difference between the natural unfertilized sites and the fertilized agricultural sites was that of the nitrogen fertilization received by the latter, although none of the measurements were made immediately following fertilizer applications.

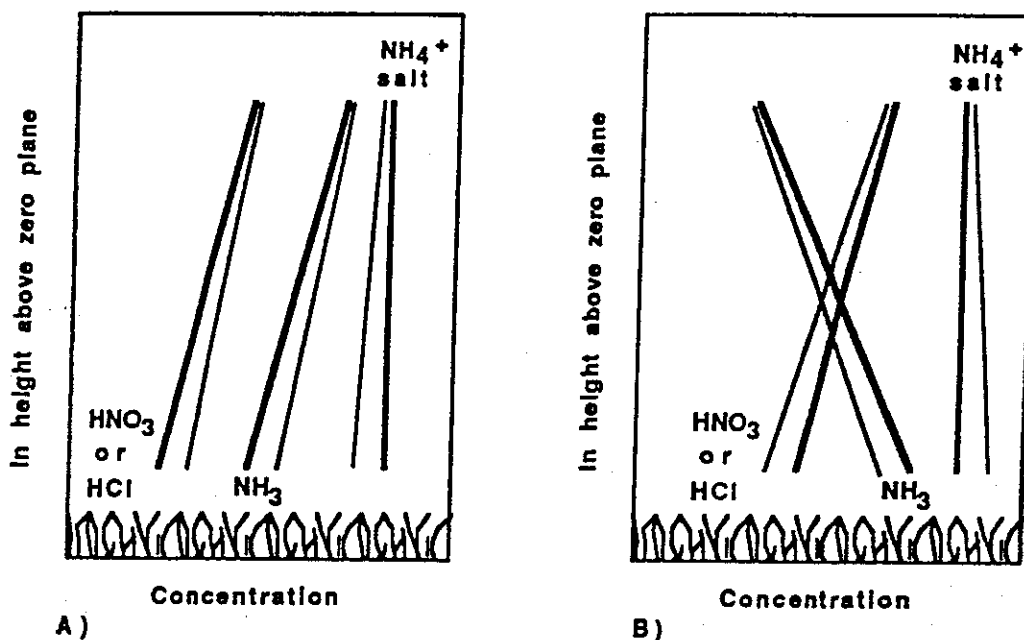
The different pathways, exchanges sites and factors for such systems are summarized in the following figure :



Proposed NH_3 cycles in a soil/vegetation/atmosphere system. Individual fluxes are denoted by arrows. Boxes denote surface exchange sites and NH_3 atmospheric concentration, for which factors controlling each are noted.

In the one hand, over natural and unfertilized ecosystems (grasslands, moorlands, and forests are included), measurements are not realized near to major livestock installations. There, at all the sites, rapid NH_3 deposition was recorded. It depend on both the atmospheric concentration of ammonia and the turbulent condition prevailing during the experiments, which is due to an atmospheric resistance (R_a) higher than canopy resistance (R_c). At this sites, R_c is generally approximating to zero. Only on a calcareous grassland surface, a higher R_c was found and, as a consequence, another result : one could understand it, because the deposition is normally to water associated with the leaf surfaces, and the high soil pH would limit NH_3 solubility, and hence deposition. Another way of examining processes at the surface, analogous to R_c , is $X\{Z_0\}$, which is the mean concentration of ammonia in the atmosphere at an apparent height above the zero plane of the mean point of exchange of entrained properties with a surface, accounting for R_a and R_b . In cases of deposition it represents the maximum possible mean concentration at the surface of the canopy elements ($X\{Z_0\}$ is approximating to zero too). Moreover, according to the aerodynamic gradient method assuming that gaseous NH_3 is conserved as it deposits, the comparison between the air concentration in ammonia and $X\{Z_0\}$ show us when either deposition or emission occurs.

The following scheme shows us the possible effects of gas particle conversion on observed gradients of NH_3 and NH_4^+ over an extensive homogeneous surface :



Possible effects of gas-particle conversion on observed gradients of NH_3 and NH_4^+ over an extensive homogeneous surface. Bold lines represent profiles where fluxes are conserved. Light lines show profile modification where fluxes are not conserved. A) NH_3 deposition, B) NH_3 emission from the ground surface. For both cases it is assumed that surface exchange of NH_4^+ is negligible in comparison to the gas exchange.

The effects of temperature and wetness/dryness have been observed about promotion a small value of R_c and $X\{Z_o\}$. Warm dry condition are favouring the development of a surface resistance. It is clear though that even in the dry runs in warm condition the values of R_c are still smaller than might be expected by stomatal transfer alone (given that the minimal R_{st} for this surfaces is 50sm^{-1})(Jarvis 1981). Additionally, if transfer was through stomata a greater R_c would be expected at night, this was'nt seen anywhere. Nevertheless, the small values of R_c even in dry condition imply that the deposition must be to the leaf surfaces, as these are the roughness elements to which the resistance analogy (R_a , R_b) models transfer. So if R_c is low ($<10\text{sm}^{-1}$), vegetation is an efficient sink of the NH_3 . On the contrary, a high R_c is expected either when (NH_4^+) deposition was unusually rapid, or when the NH_3 level in the air is low, or at last in very cold condition.

On the other hand, over fertilized agricultural ecosystems, the results of the ammonia exchange measurements separate clearly between the winter and summer-time campaigns, with ammonia deposition occurring throughout the former, and a bi-directional exchange, with emission predominating in the latter. During the winter (wet vegetation, melting snow), small surface resistances were observed (in agreement with the results for natural and unfertilized surfaces). Thus deposition was recorded during this period. When large values of R_c occurred, deposition is independant of the air concentration, and R_c is the most suitable interpretation of the excess. The interpretation of the surface exchange process for the summer (dry and warm conditions) also differs to that for the winter and natural surface. Here it is clear that since emission may occur, the assumption of a concentration independent rate of exchange (V_d) and zero surface concentration fails. Some form of crop or soil compensation point concentration (X_{cp}) must exist to drive the emission. In this case, the resulting flux depends on the X_{cp} , the concentration in the air, and the resistances to transfer between them. Different sources of the NH_3 emission exist :

---> Stomatal emission : The atmospheric transfer accounts for by R_a and R_b , and exchange elements are the leaves. The intercellular solution in the plant tissue might have a concentration of (NH_4^+) controlled by the plant metabolism, which has an equilibrium atmospheric NH_3 concentration.

---> Other possibility for emission is a compensation point, where free (NH_4^+) in the soil solution has an equilibrium atmospheric NH_3 concentration, which is higher than air concentration.

---> At the base of the canopy, senescing vegetation and leaves near ground level are other possible sources.

The tendency to net emission or deposition would thus depend, on the one hand, on the balance of sources and sinks within the soil/canopy system and, on the other hand, on the presence of surface water on the vegetation. The latter appeared to be the main factor controlling the switch between emission and deposition.

6- Interests in Ammonia Measures

On the one hand, there is the ecological interest in Ammonia . Man has increasingly disrupted the natural levels (industrial fixation of NH₃ for fertilizers, the ensuing intensive agriculture, production of nitrogen by the increased use of legumes ; releasing NH₃ by the burning of fossil fuels). As a consequence, there are different effects of NH_x on the environment, specially about its deposition, which are :

---> *increasing nitrogen inputs*

A recent interest has been concerned with the effects on natural (unfertilized) ecosystem. The eutrophication of heathlands is a major issue. Deposition of atmospheric NH₃ is blamed for a decline in ericaceous communities and their replacement by grasslands communities (it favours the growth of taller rough grasses)(Schneider and Bresser, 1987). Moreover, increased deposition NH_x may exacerbate the poor health of forests : over 50% of forests in the Netherlands are recorded as being less than vital (Van Breeman and Van Dijk, 1988). In addition, the increased nitrogen supply can result in unbalances of the other nutrients (K, Mg, Ca, P...).

---> *causing soil acidification*



This reaction explains the decline of poorly buffered water pools in the Netherlands. Thus most have now vanished, being replaced by acid tolerant, nitrophilous plants.

---> *leading to toxic effects on organism*, by way of infiltration and run off from agricultural residues, increasing level of (NO₃⁻) in river water.

In addition, one recent interest is in ammonia as a pollutant. Thus NH₃ and SO₂ pollution from industry and combustion encourage the formation of high levels of (NH₄)₂SO₄ which is being present as particles reduced visibility (fog,...)(Soderlund, 1977).

On the other hand, there is the recent agricultural interest in ammonia, which is aimed to know exactly what affects the degree of ammonia release. Allison (1955), reviewing the literature, suggested that several environmental conditions would affect this degree :

---> A high pH soil will be more liable to volatilization.

---> Losses from wet soils are likely to be small unless.

---> It is a drying alkali soil with much NH_x near the soil.

---> Losses will be greater at higher temperature.

---> Soils of low cation exchange capacity will suffer greater losses.

---> Losses may occur from decomposing nitrogenous material, even if the soil is acid since the NH₃ produced will raise the pH locally.

THE AMMONIA ANALYZER : brief presentation.

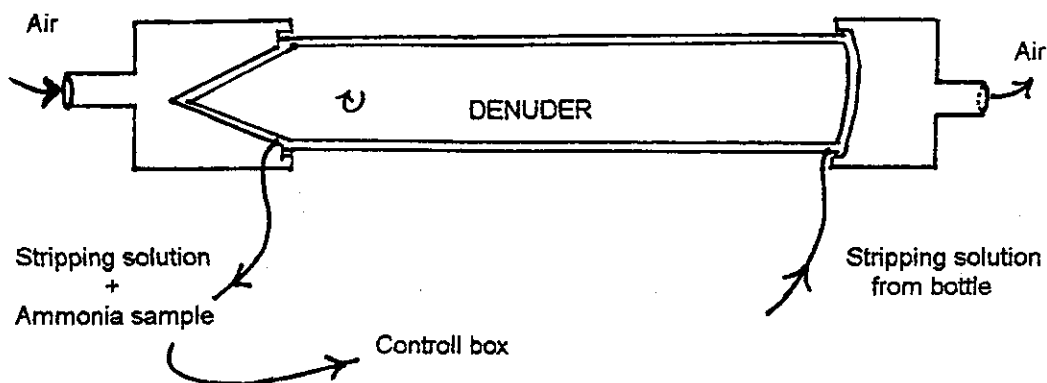
This ammonia analyzer is one of the only two in the world, the second one is from Netherland.

The mean principle of this machine is the measurement of the conductivity, which occurred by NH_3 in water. Thus, the system is based on a succession of chemical reactions, which leads at last to the ammonia transformation in ammonium into a deionized water solution.

The machine is made up of four boxes :

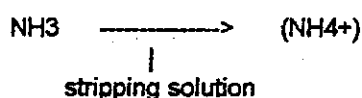
- Two Denuders boxes,
- A controll box,
- An air pump box.

Into the Denuder box occurs the NH_3 molecule selection from the air (see the following scheme) :



Each denuder is made of two glass tubes, one inserted in the other, with a very small space of 1.5 mm between them : the annulus, in which the stripping solution is streaming. The denuder has to rotate thanks to a belt system, causing a liquid film to coat the surface of the annulus. As the air is sucked laminar through the tubes, it leads to the catch of atmospheric ammonia in the liquid phase. Because of their slow diffusion velocity, aerosols (NH_4^+ for example) can't be absorbed.

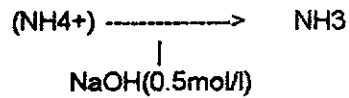
By way of the reaction :



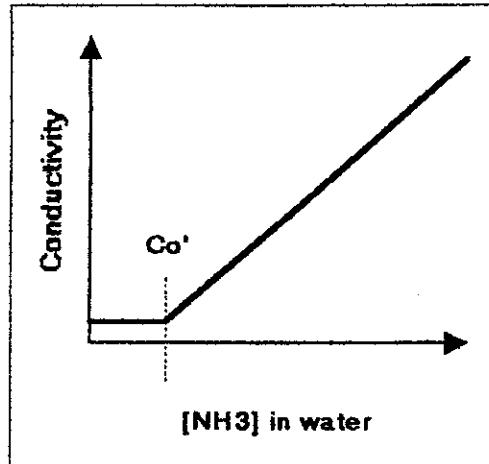
The stripping solution (deionized water, NaHSO_4 , Formaldehyde) is an acid solution, which allows the ammonia ionization in ammonium.

Into the control box, conductivity measurements are made and data are recorded by a logger. Adding alkaline solution, (NH₄⁺) gives back ammonia.

Thus :



However, the conductivity is not proportional to the NH₃ concentration in water, when small concentrations are recorded (shown by the following graph) :

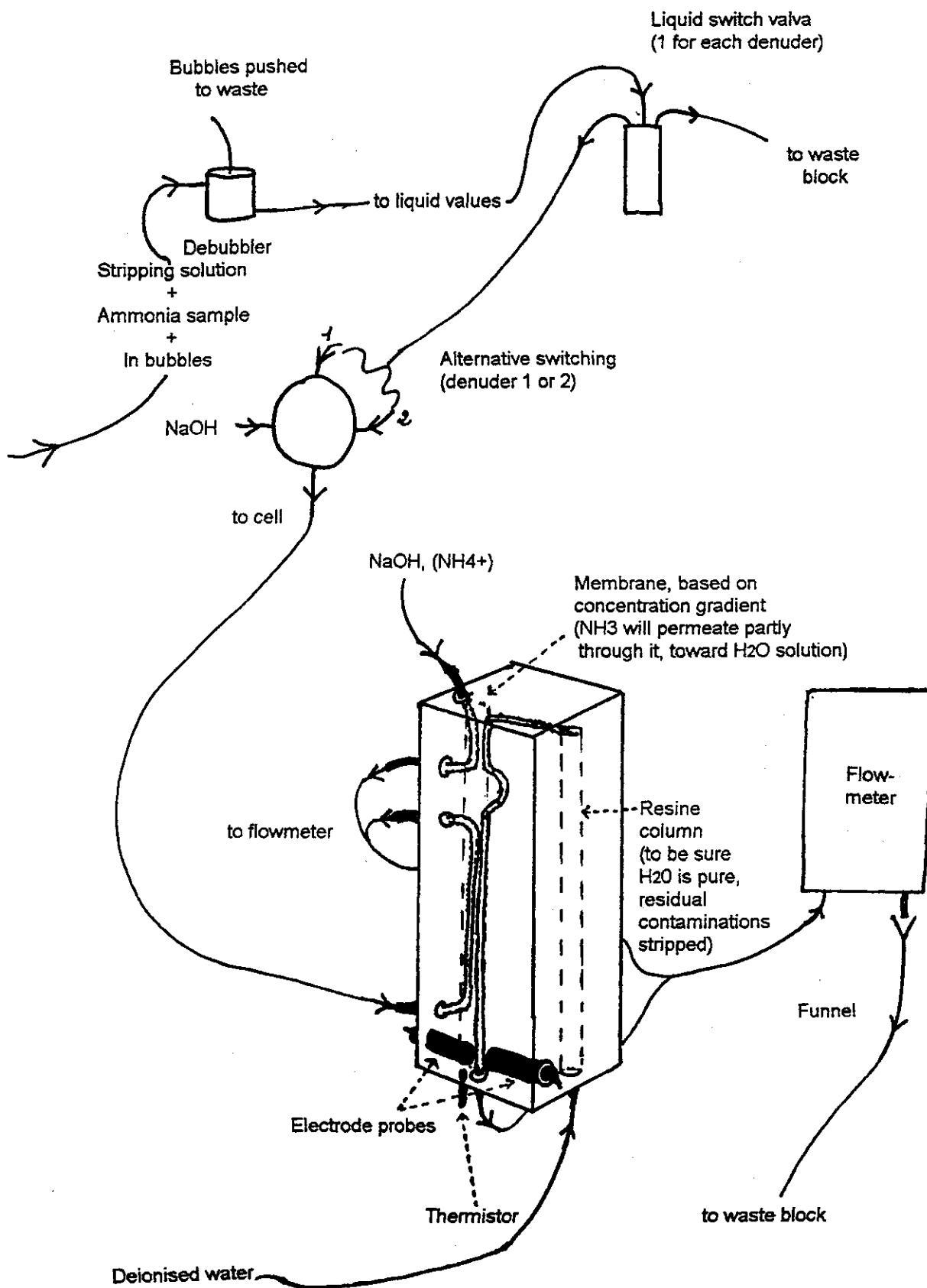


Thus, before measurement, instead of being taken by pure deionized water, the sample of NH₃ will be taken by a deionized water solution, which is enriched in ammonium ions (thanks to a NaOH + (NH₄⁺) solution), in order to increase the water conductivity on the threshold (Co') of linear form.

At last, the NH₃ sample into this solution gives back (NH₄⁺) (for pure H₂O, pH=7), which as an ion conducts electricity. Conductivity measurements are made by a resistance (mV), and temperature measurements are realized too. Thus, of course, to conductivity data corresponds NH₃ concentration data.

Two reagent pumps into the control box allow liquids to circulate.

Control box plan



The calibration of the machine is realized using stripping solution (0ppb of (NH₄⁺)), a 50ppb standard solution of (NH₄⁺) and a 500ppb other one. After, these settings are used to calculate the air concentration in ammonia.

Data are recorded every four minutes for each denuder, and the logger, which could contain 56000 values, which represents 38 days, is usually downloaded at the most every 10 days. The data logger can be linked to a computer, which thanks to the programm AMANDA (AMmonia ANalyzer DATA processing) and a correction temperature programm (see first part of my experiments) allows to download the data (conductivity, temperature and flowrate).

The last box, the air pump box, allows to switch the air pump on/off, following the wanted experiments :

Thus, three abilities to use the machine are itemized :

Air pump off, to obtain a zero. Conductivity measurements are done without any atmospheric NH₃ sample. Most of the time, in order to check the zero and the real values of data. Sometimes, in order to do some temperature tests on zero (using stripping solution) or on 50ppb concentration level of (NH₄⁺) (using 50ppb standard solution). The latter (temperature tests) have been realized at Bush Estates, near Edinburgh, during three days (18-19-20/5/93).

Air pump on-Denuders on cosampling. Either to check if both denuders agree, or to make measurements of air concentration in ammonia (experiment realized at Bush Estates, for a month-15/5/93 to 15/6/93).

Air pump on-Denuders on gradient. Specially to make gradient measurements, in order to see when deposition or emission occur (experiment realized during three weeks (21/4/93 til 7/5/93), at Great Dun Fell, in the north of England).

A chart recorder, which is linked to the conductivity measurement into the control box, allows to see at each moment how the ammonia analyzer is working. In addition, it is used to check a zero, to check the calibration, or to measure ammonia concentration using the method of low injection analysis (Experiment realized at Bush Estates, during one day, 8/06/93, on diffusion filters).

AMMONIA MEASUREMENTS : METHODS

By looking both at the temperature and ammonia concentration graphs over time, a relation can be found. This means that the level of NH_3 in the air is temperature dependent : an increasing temperature leads to an increasing concentration of ammonia in the air. Thus in order to reduce the part of temperature effect and to make then possible the analysis of the other main factor behaviour, it has to be corrected. The first experiment was aimed to determine which temperature correction was needed (Bush Estates, 18-19-20/5/1993). The temperature tests have been made, leaving the air pump off, either thanks to the real atmosphere temperature, or thanks to artificial increasing temperature. In the latter, a heating belt was used to cause a greatest temperature amplitude, and thus to obtain a better result in choice of the efficient program in temperature correction.

Information on air concentration is useful both for modelling deposition inputs using the inferential technique and for assessing the results of a long range transport models (Sutton et al., 1993). These approaches are necessary because actual measurements of fluxes such as by micrometeorological methods, are extremely labour intensive, and allows measurements at only a few sites for limited periods. In order to model long term dry deposition, the simplest way is to couple monitored air concentration to representative deposition velocities. This approach is often termed the inferential technique, and may vary from a simple constant value of V_d , to calculation of time series of V_d from information on R_a , R_b and R_c (e.g. Hicks et al, 1985). It may be used to estimate deposition to specific sites or applied with mapped concentration fields to estimate regional dry deposition patterns. Long range transport models for NH_3 consider the entire atmospheric cycle of NH_3 , including emission, diffusion, reaction and deposition, so that the mass consistent budget is maintained. The main aim of these models is to describe the regional, country to country, transport and deposition of pollutants. Thus, in order to reduce the lack of air concentration information, the second experiment was to measure daily air concentration in ammonia at Bush Estates for a month (15/05-15/06/1993), using the previous temperature correction. Denuders boxes were leaving on the floor, and the air was sucked through both denuder via the same polyethylene tube at the height of 1.32m.

The third experiment was to measure air concentration from two sites near Bush Estates, using the method of the flow injection analysis (NH_3 samples in diffusion filters)(8/06/1993). In this study, cylindrical tubes were used, these being orientated vertically, with the lower end open to the atmosphere and the upper end closed off by an inert cap covering an acidified matrix. The latter acts as an efficient adsorbent of NH_3 . Then, given that the molecular diffusivity of NH_3 and the dimensions of the tube are known, and the total amount of NH_3 captured in a given period is found by chemical analysis, the mean air concentration may be found. The method for this is described now : the data logger wasn't used, only the chart recorder. The principle of this method is easy : six concentration standard solutions of (NH_4^+) (0,50,100,200,400, and 800ppb) are measured by the conductivity meter into the control box, one after the other, which give us a spike of calibration on the paper. Then, for the ten samples of each sites and for ten samples of witness tubes, which have never been opened, diffusion filters are rinsed using 1ml of deionized water during at least 25 minutes. Then, the solution conductivity is measured. The heights of the calibration spikes, following the concentration of the standard solutions, give a polynomial curve, which equation is given by the logiciel GRAPHIS. So, it becomes possible to calculate a concentration estimation for each sample spike height and a mean concentration for both sites. At last, subtracted by the mean concentration of the witness

tubes, a real mean concentration (in $\mu\text{g m}^{-3}$) is found for both site. Its variation is given, using a Student test : two-sample t-Test assuming unequal variances (the non-equality of the variances hadn't to be determined, it was acknowledged). Thus some approximate air concentration were found.

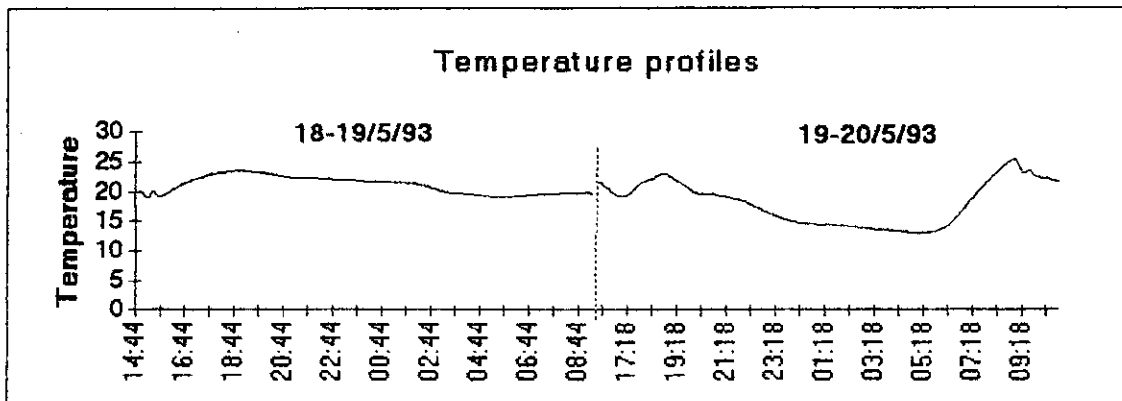
The fourth one, the labour intensive one, was NH_3 fluxes measurements at Great Dun Fell, north of England, during three weeks (21/04 until 7/05/93). We were there working in a van, collecting data from NH_3 analyzer, SO_2 mast, Thermister mast, Anemometer mast and R_n (net rediation flux) recorder. Speaking of the NH_3 analyzer, denuders were on gradient, one above the other one (respective heights : 0.3 and 2.3m). The data analysis was realized using the meteorological method, after using previous temperature correction for ammonia data. These experiment took place in order to improve the former analysis made in the same site 5 years ago, using a filter pack mast. In addition, Great Dun Fell is well known for experiments in clouds. But, in cloud, it is not possible to measure fluxes. That is why, when cloud cover occured, then the NH_3 concentration in the air was recorded.

First experiment :

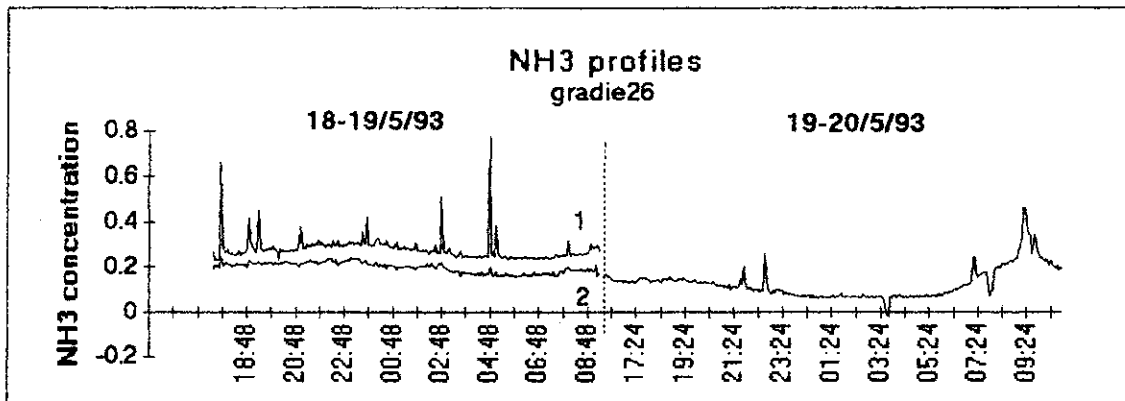
TEMPERATURE TESTS ON "ZERO", USING 0ppb AND 50ppb (NH₄⁺) SOLUTIONS

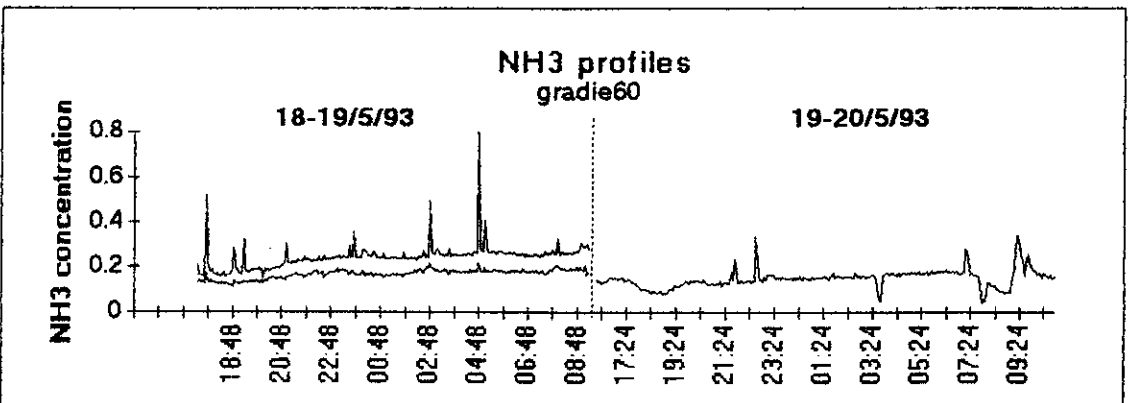
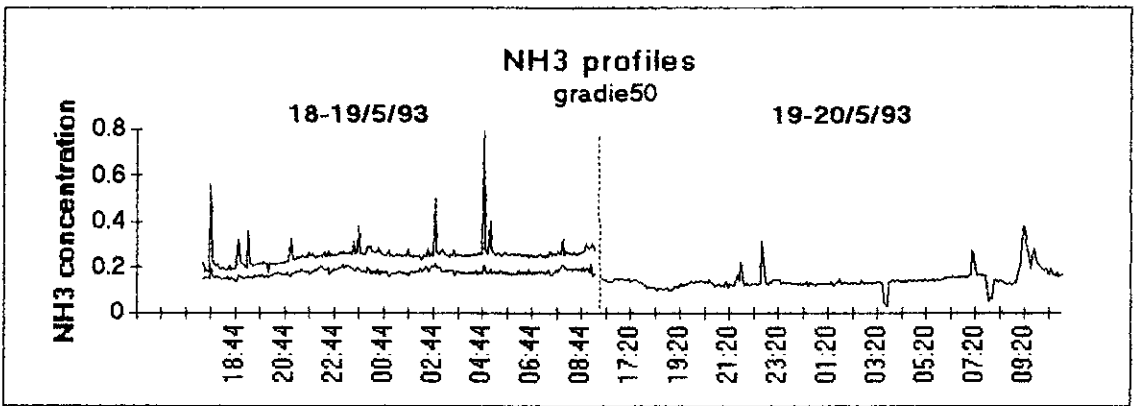
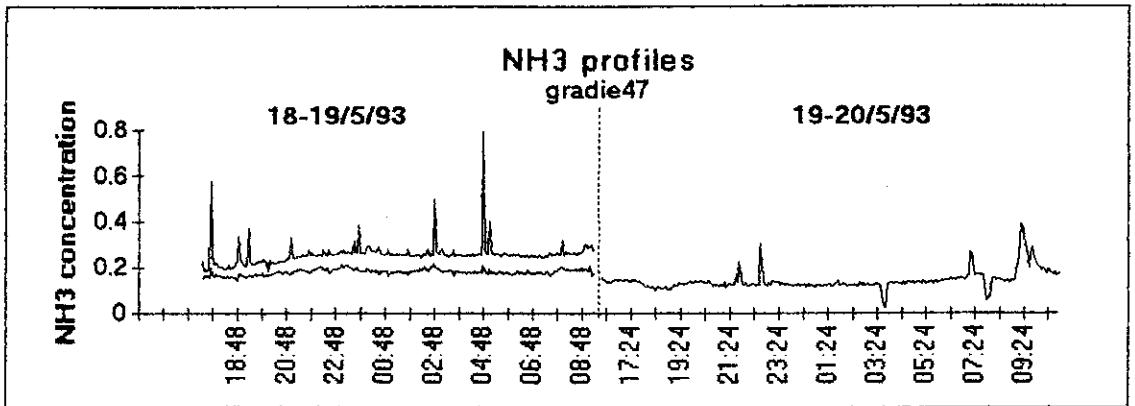
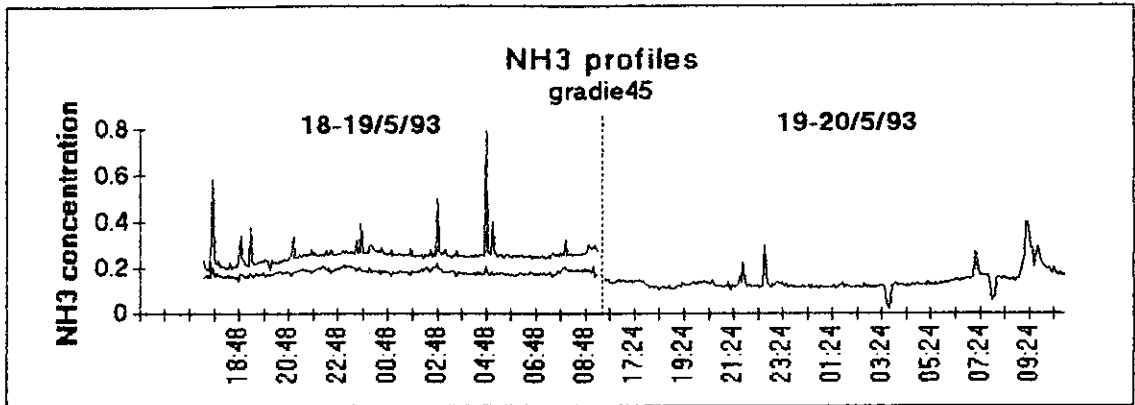
All the temperature correction programmes are called GRADIE. Several programmes were used in this experiment : GRADIE26, GRADIE45, GRADIE47, GRADIE50 and then GRADIE60. For example, using a GRADIE26, it means that the temperature correction will be of 2.6% per degree Celsius.

On the one hand, temperature tests on 0ppb solution of (NH₄⁺) were realized during three days, 18-19-20/5/93, at Bush Estates. The following graphs show the differences in ammonia concentration profiles, using each GRADIE, compared to temperature profiles :



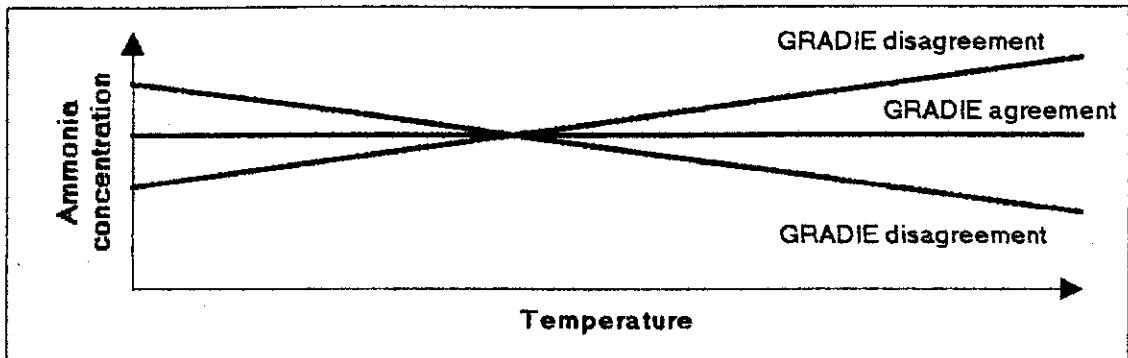
For ammonia concentration profiles, 1 and 2 mean respectively denuder 1 and 2 (18-19/5/93 : a light difference was recorded between them, but they varied in the same way- 19-20/5/93 : only denuder 2 is used, denuder 1 was wrong)



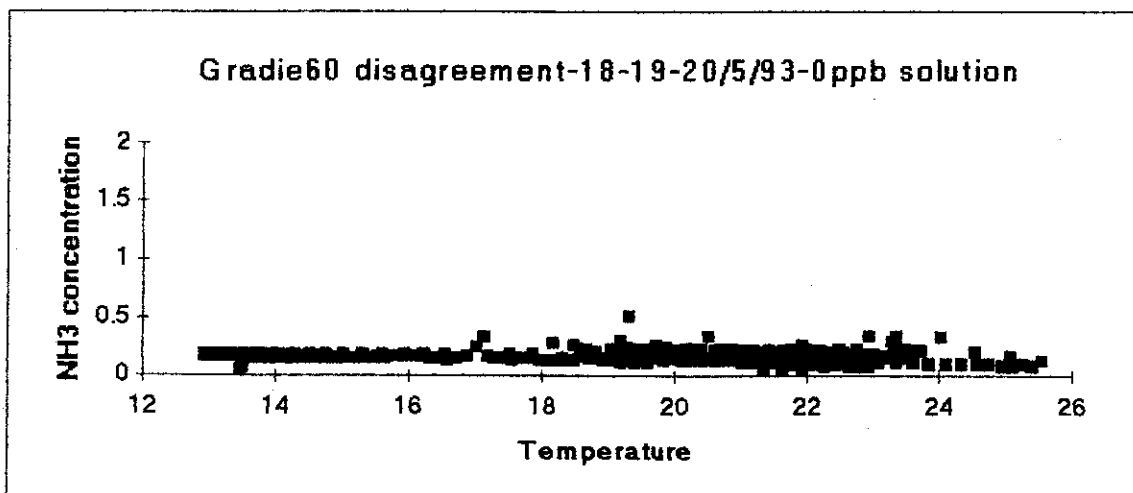
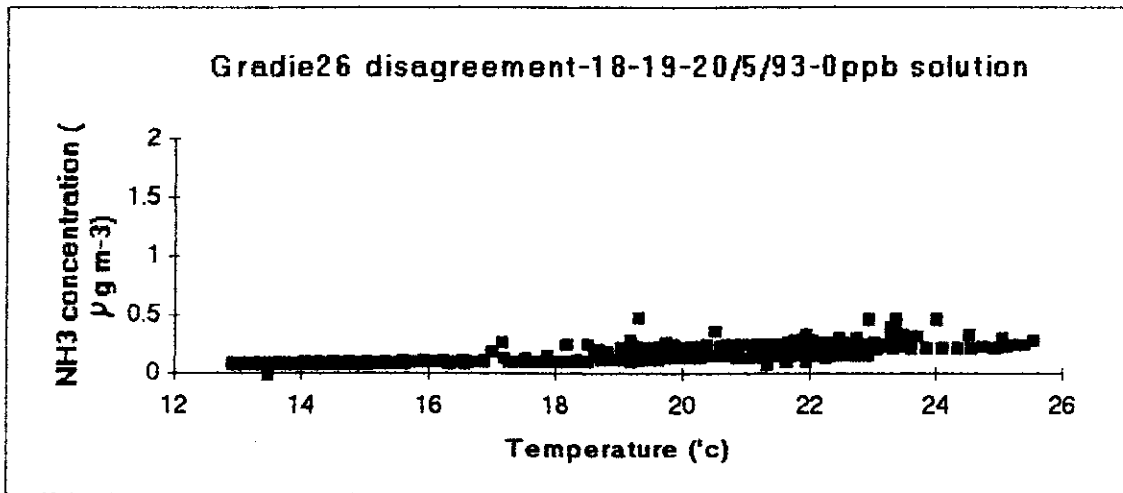


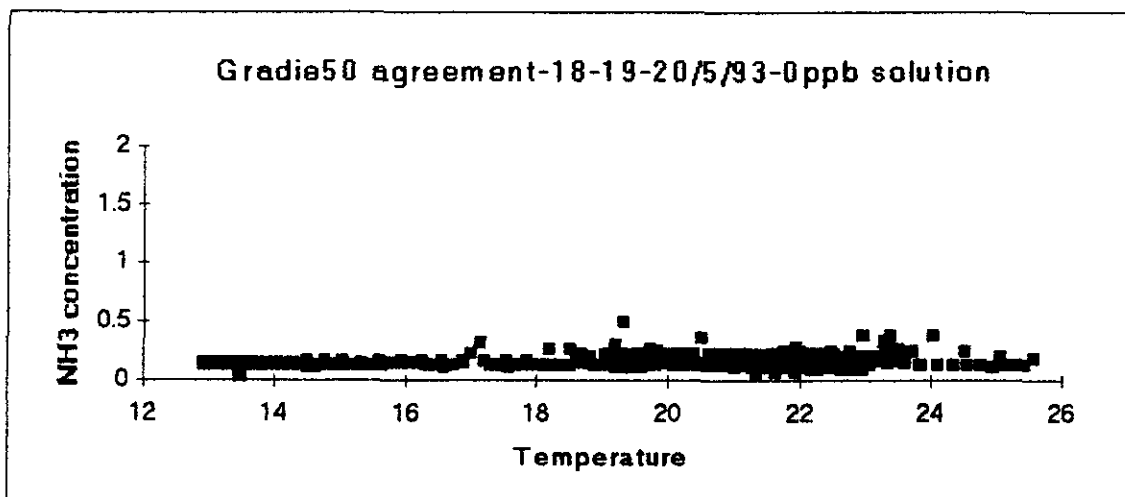
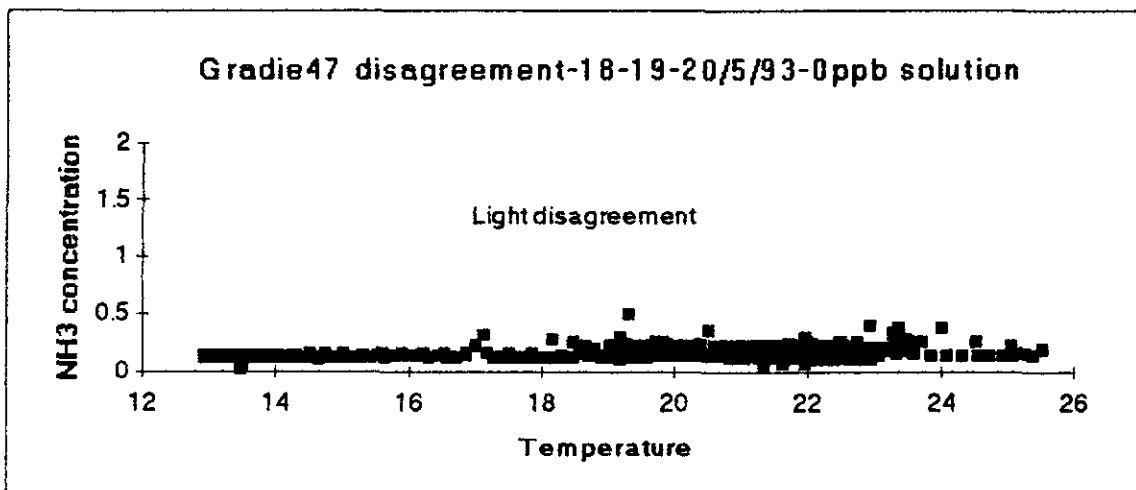
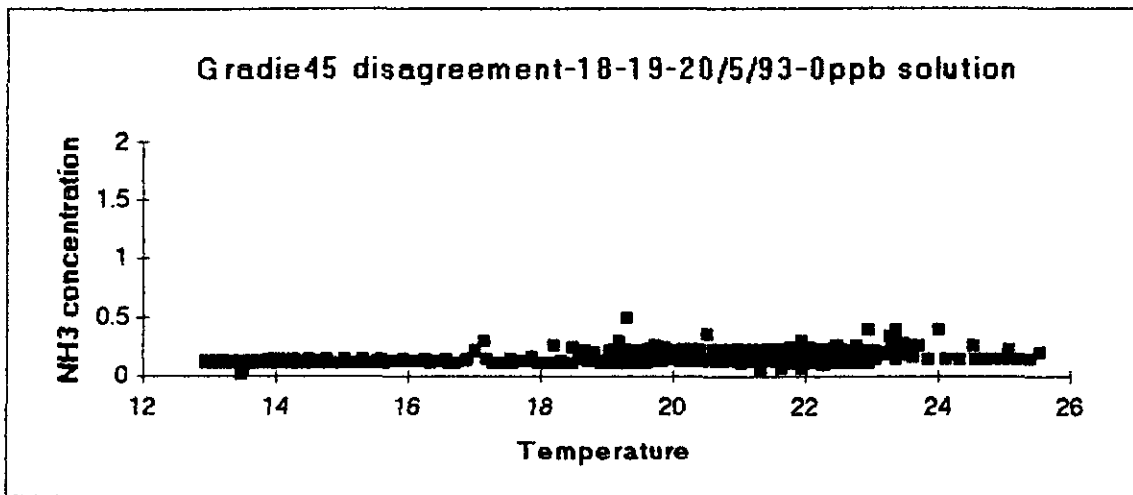
Watching the graphs, it appears that GRADIE47 and GRADIE50 look the best ones, compared to the other (they have the most linear aspect). But it has to be confirmed.

The general method used to check which is the most efficient GRADIE is to see the ammonia concentration evolution with temperature for each GRADIE :



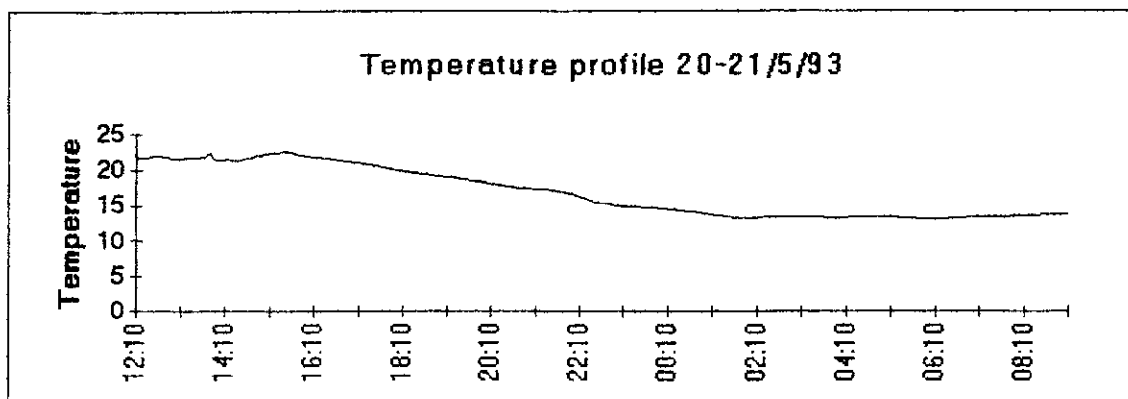
Thus the following graphs show us which is the efficient GRADIE to correct the temperature effect :



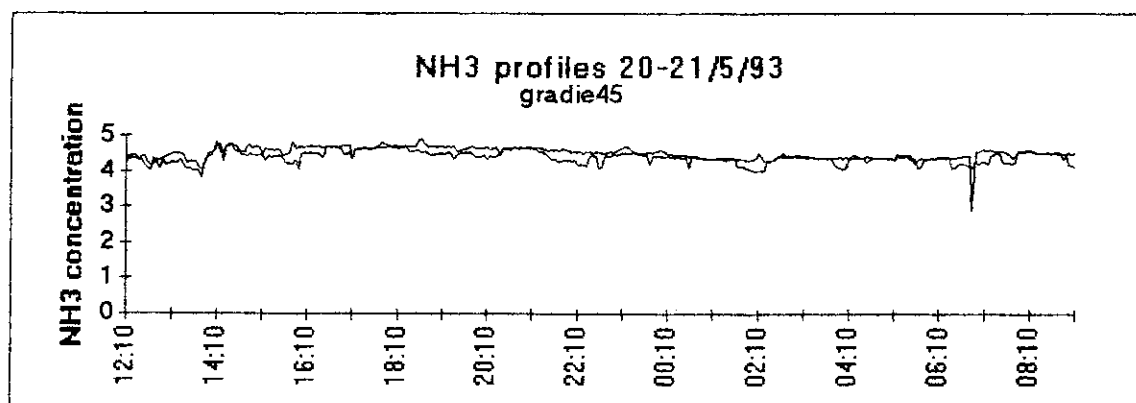
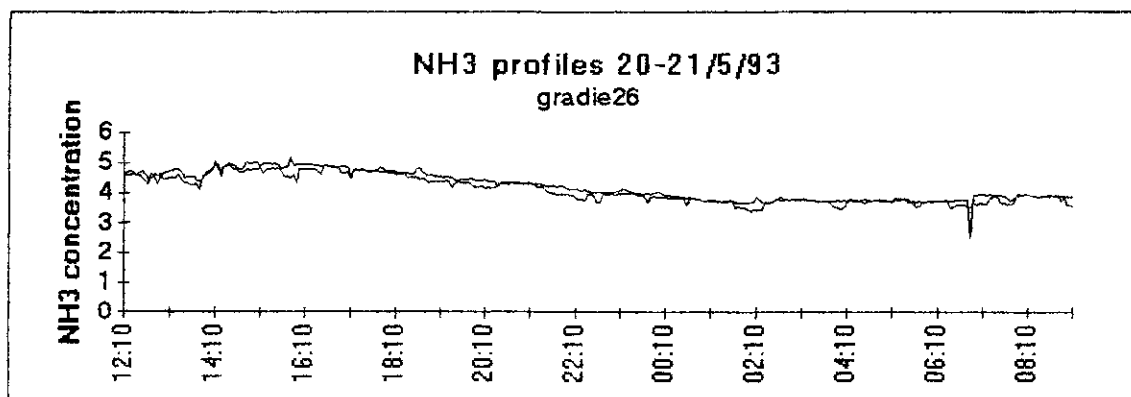


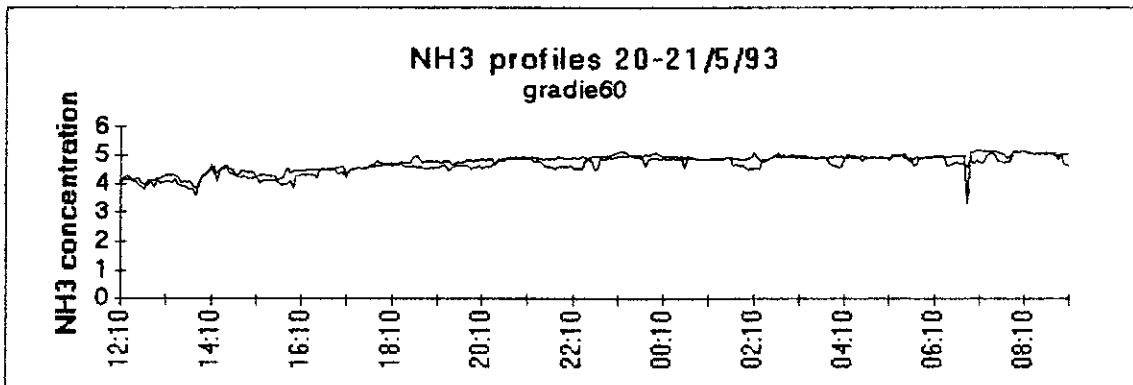
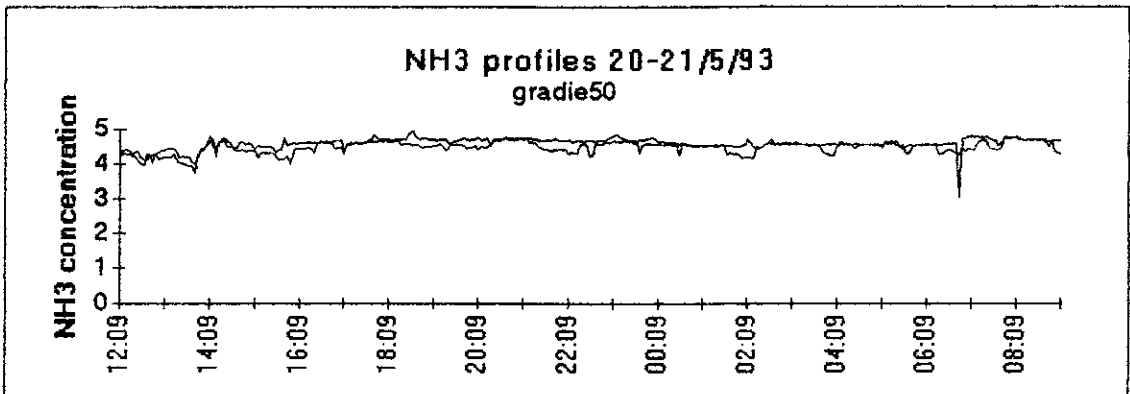
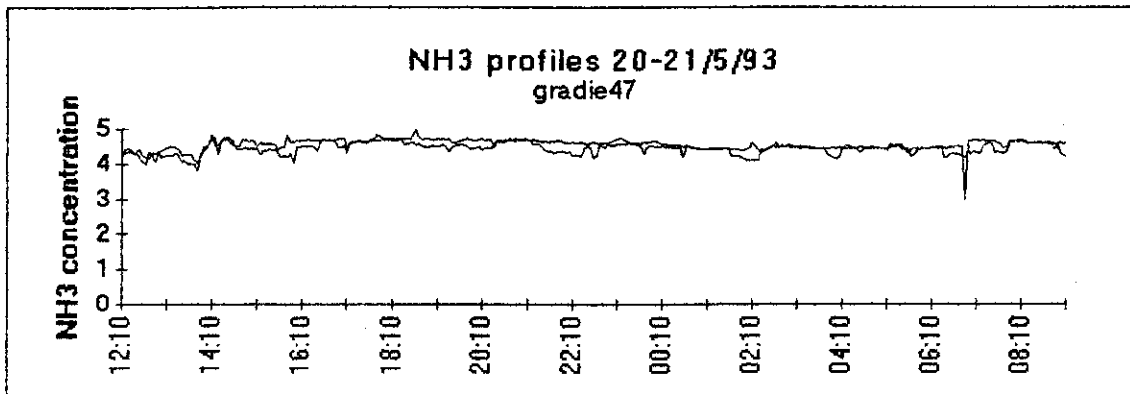
So, through this test, GRADIE50 is clearly defined to be the most efficient temperature correction on 0ppb solution. Thus, when very low ammonia concentration are recorded, GRADIE50 has to be used. However, the ammonia concentration in the air is not constant, and could increase quickly. That is why another serie of tests was realized on 50ppb solution, to check if the GRADIE50 is suited to high levels of atmospheric ammonia.

So, on the other hand, temperature tests on 50ppb solution of (NH₄⁺) were realized two days long, 20-21/5/93, at Bush Estates. The following graphs show the differences in ammonia concentration profiles, using each GRADIE, compared to temperature profile :

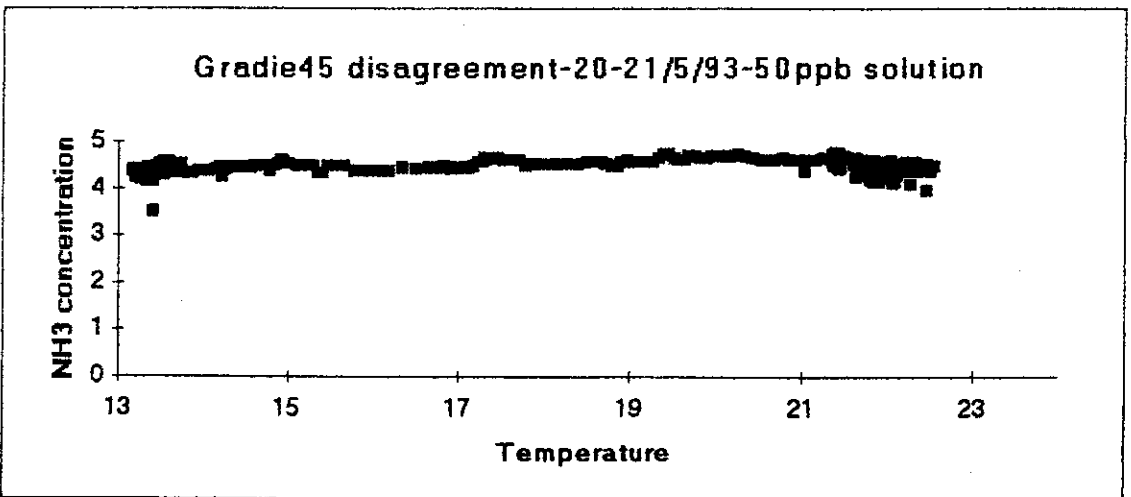
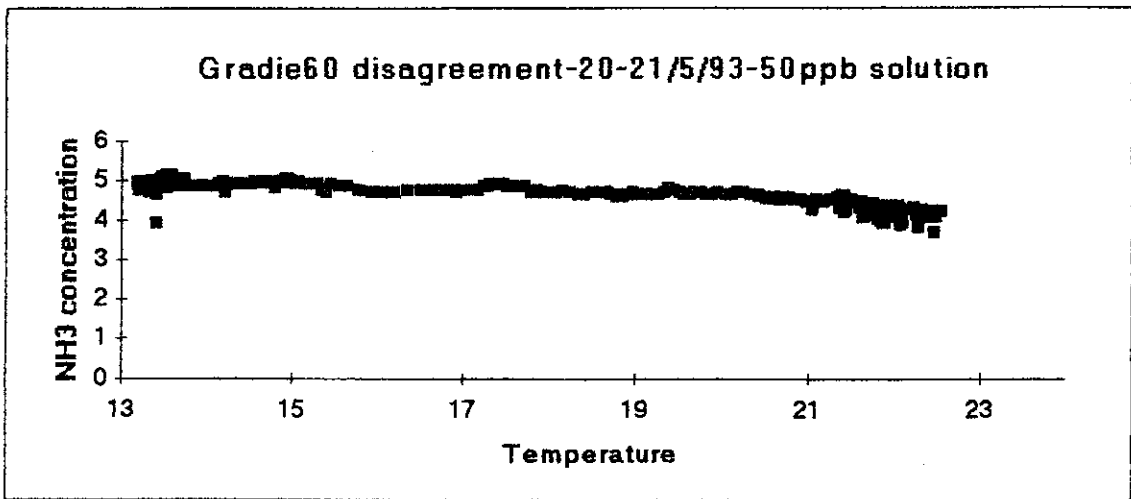
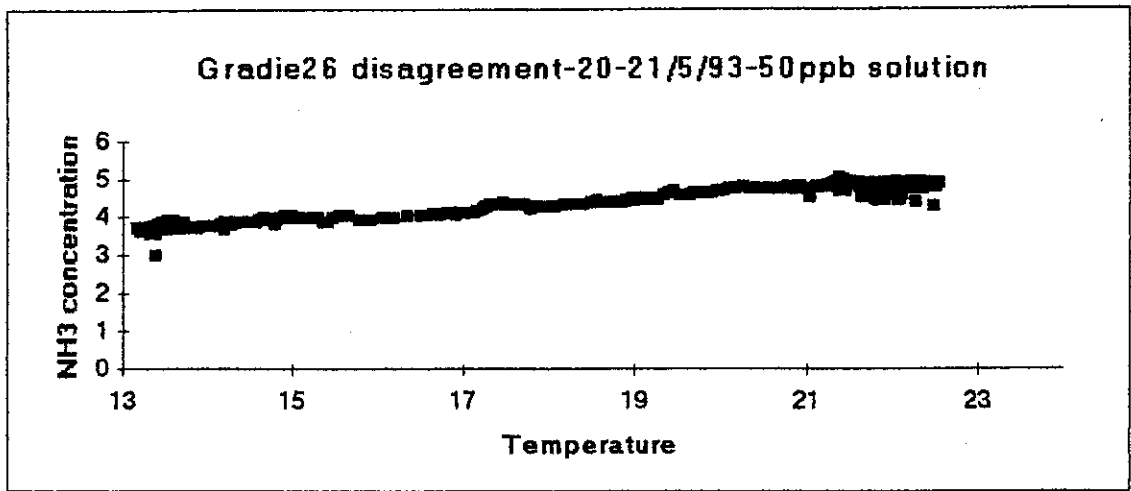


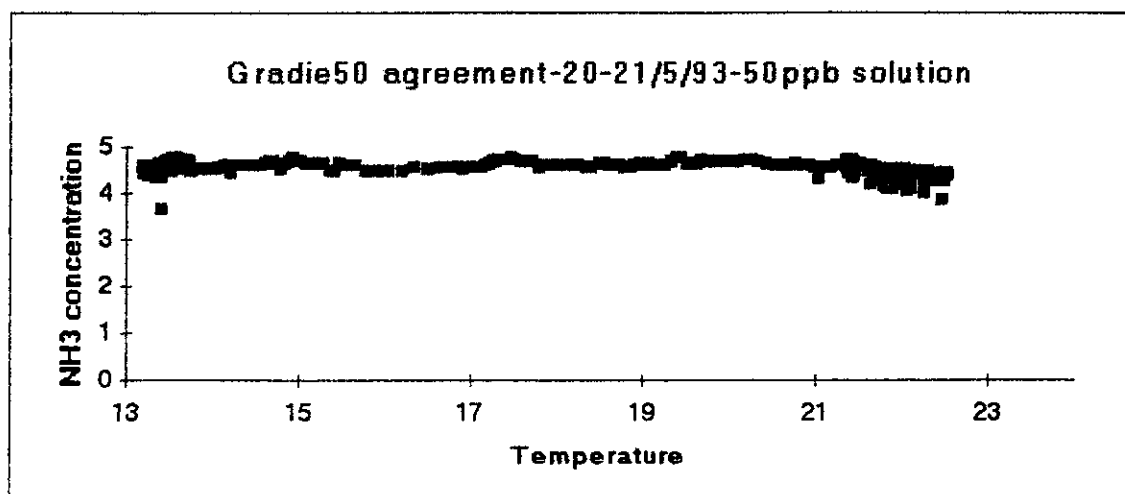
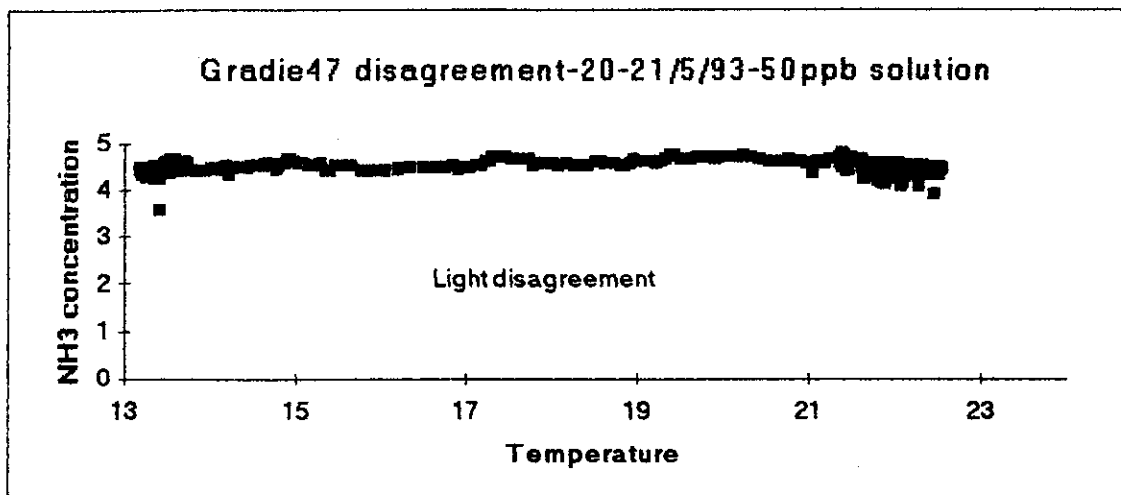
There, the agreement between both denuder is rather good.





The analysis of ammonia concentration profiles show a preference to GRADIE47 and GRADIE50 ; so it looks like to be the same as the first series of tests on Oppb solution, which is an encouragement. A confirmation is now expected (see next page) :





So, through this second test, GRADIE50 is clearly defined to be the most efficient temperature correction on 50ppb solution. Thus, GRADIE50 has to be used either when the ammonia concentration in the air are very low or when they are quite high. Otherwise, if the respective efficient GRADIEs were different, it would have been difficult to correct the temperature effect following the air concentration in ammonia. One solution was envisaged : to enrich the stripping solution in ammonium (until 10 or 20ppb, to determine) in order to increase the level of the zero, changing the machine calibration. Thus, if the GRADIE would have been the same on both 10 or 20ppb and 50ppb solutions (the concentration difference is lower, so a better agreement would have been expected), it would have been O.K.!

However, this experiment allows to agree with the use of pure stripping solution as the basis of ammonia concentration measurements. So, following the result of this experiment, GRADIE50 has been used to correct temperature effect on the one hand on air concentration monitoring data and on the other hand on ammonia fluxes data.

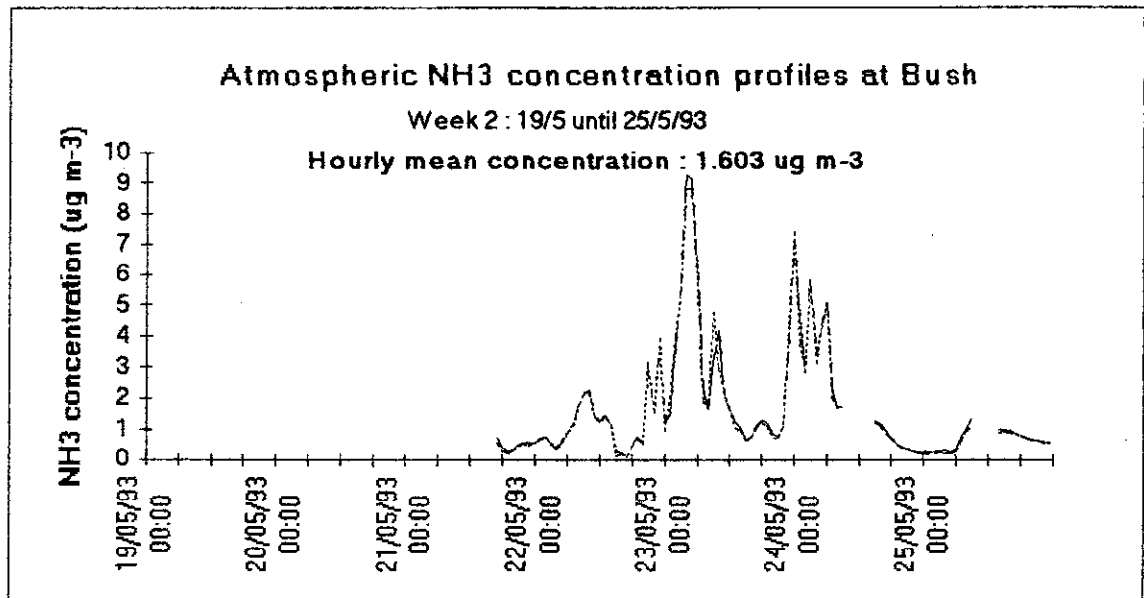
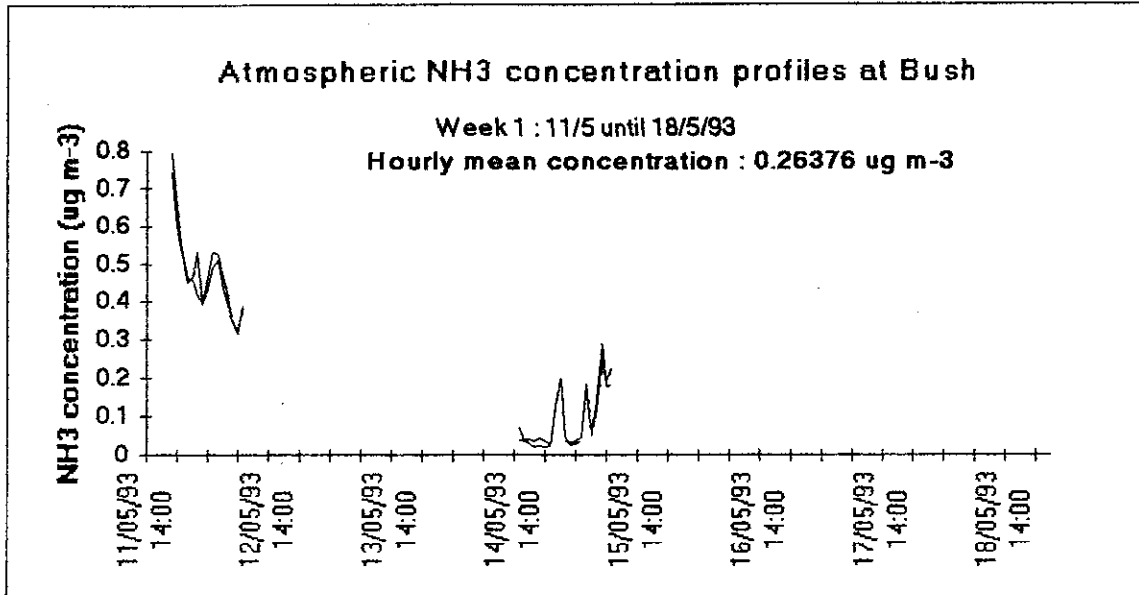
In addition, this experiment was realized with median temperature (12 to 26 °c). So, it has to be checked for lower and higher temperature. Of course, GRADIE50 is hoped to be the good temperature correction program, to make the analysis easier. On the contrary, if GRADIE50 won't suit to these temperature, it will make the work harder, and a temperature correction program for every temperature level will have to be found (for instance : GRADIE45 if $0 < T (^{\circ}c) < 12$, then GRADIE50 if $12 < T (^{\circ}c) < 26$, ...). But it would be the subject of another experiment.

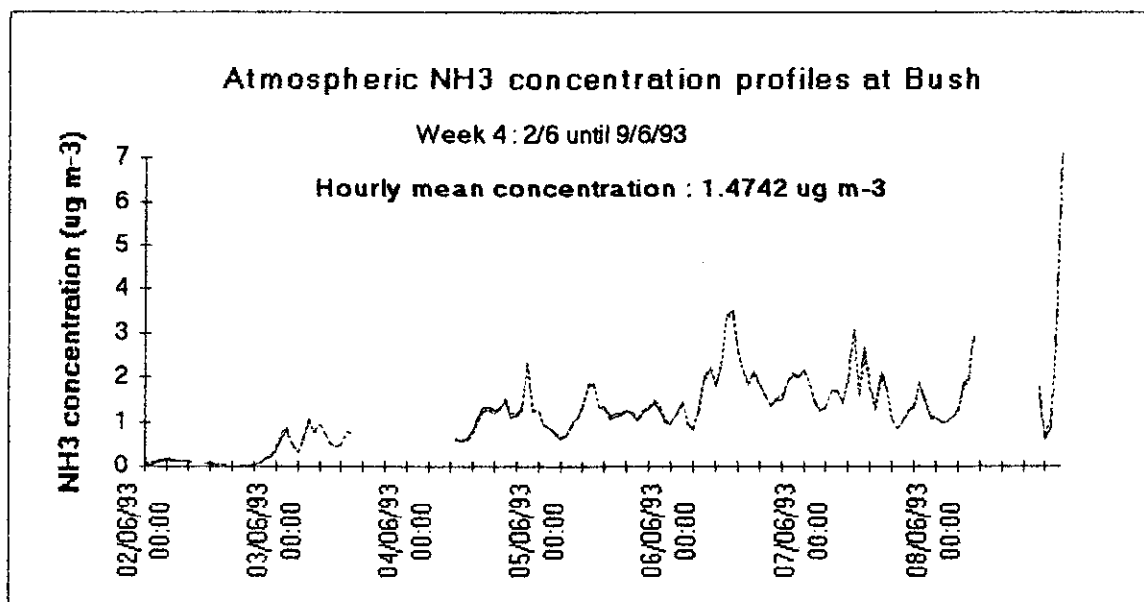
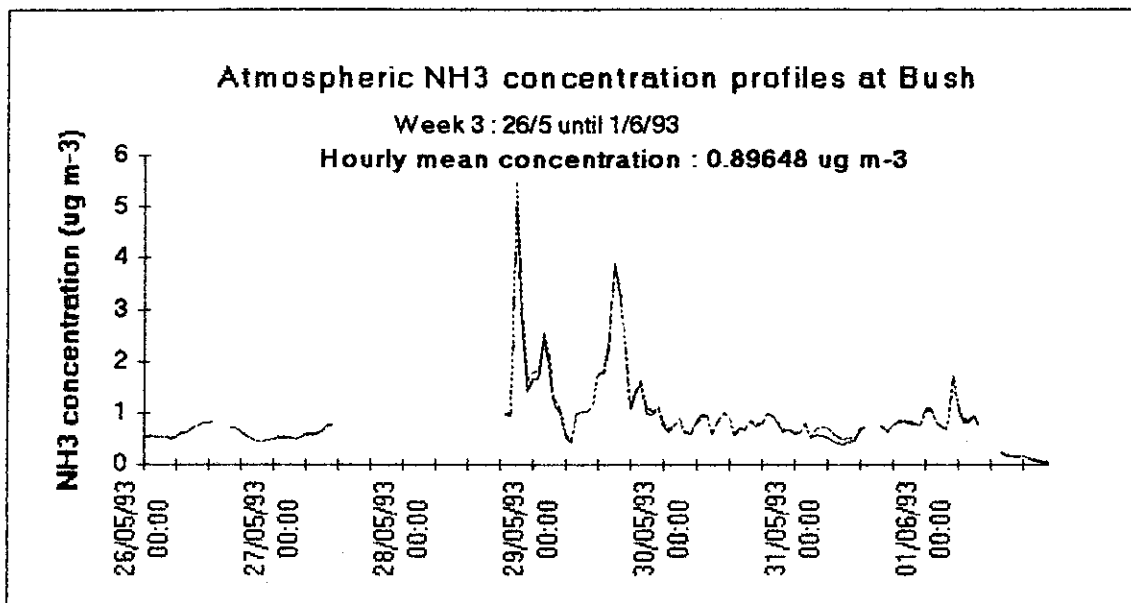
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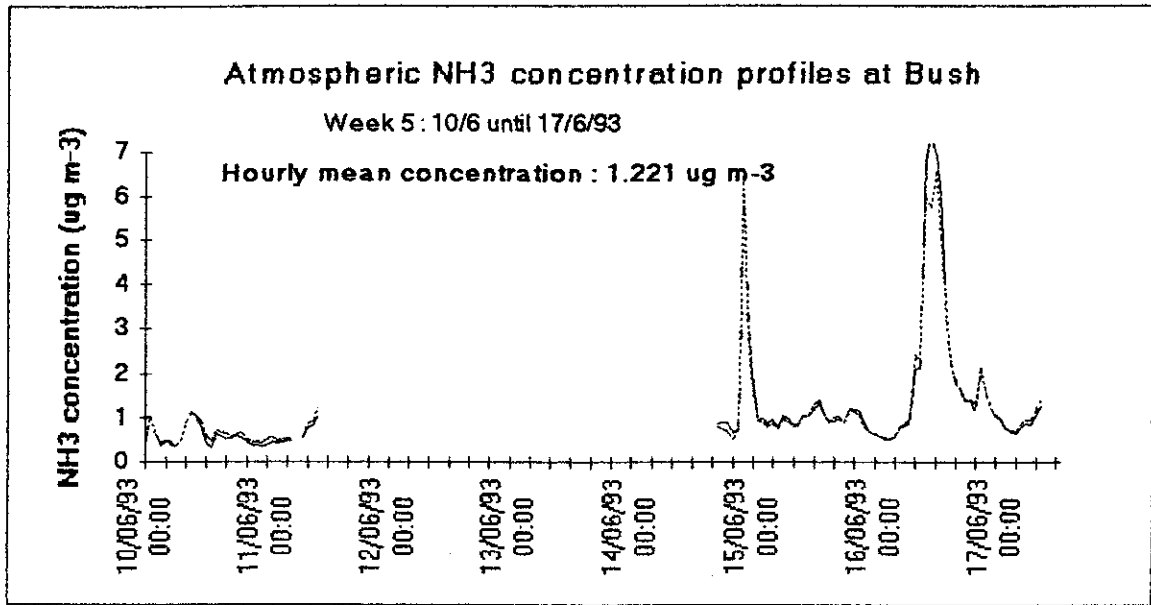
Second experiment :

MONITORING OF ATMOSPHERIC AMMONIA CONCENTRATION

The results of this experiment, using GRADIE50 as temperature correction program, are given in the following hourly graphs :

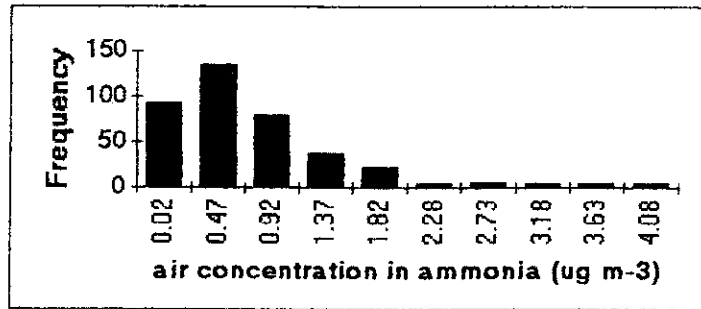




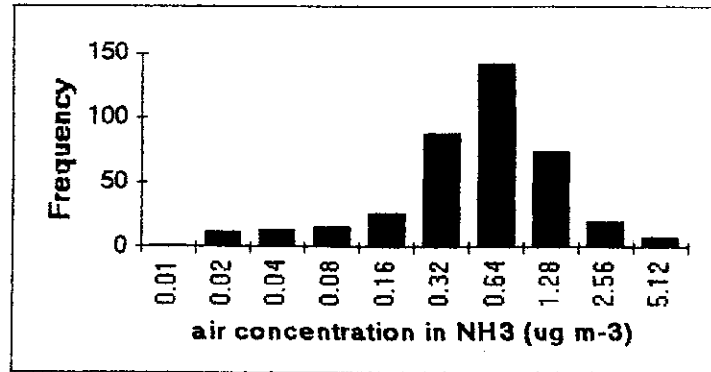


During this period, the mean ammonia concentration in the air was 1.092 ug m⁻³.

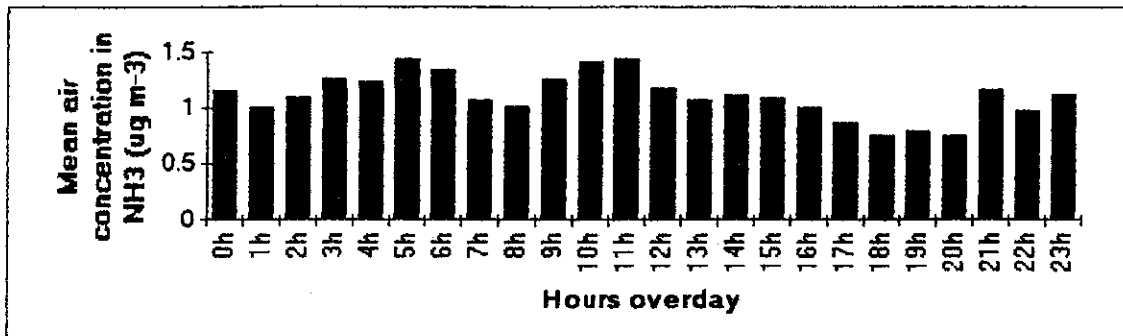
To show if the air concentration in ammonia is different in several parts of the day, a statistical test was realized (over the data for the first four weeks). First, the following histogram, which shows the distribution of air concentration during the four weeks, allows us to consider the air concentration as a normal population :



Given the fact that negative concentrations are not expected, a logarithmic axis scale might suit better :



Then, the hourly mean ammonia concentrations are calculated and shown in the following graph :



Apparently, some periods in the day differ from the other, following this graph evolution. First, a peak is observed at 5h-6h. During the night, the atmospheric stability is usually lower, so less mixing occurs. Given that this site is located to a big farm, in no wind conditions, higher concentrations in ammonia were recorded, coming from the farm (it must correspond to a farm activity). Then, early in the morning, at 7h-8h, the stability height is increasing, leading to an increasing mixing (kind of ammonia concentration dilution in the air). Moreover, at that time occurs the dew, causing two mechanisms : quick deposition of the atmospheric ammonia (wet surfaces), leading to a decreasing air concentration in ammonia, and emission from the canopy (farm fields), due to the compensation point (Xcp). All this factors explain the low level in air concentration in ammonia recorded during this period. Then, at 10h-11h-12h, high levels in ammonia concentration are noted, due to emission from the farm fields. The emission is greatest in warm and low humidity surface condition. In addition, some reactions occur during the night time : $\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3$, which is an aerosol. During the day time, the reaction gives back ammonia gas, explaining the increasing concentrations found (similar reaction occurs with chlorine). Last year, a similar analysis was realized at Bush during the period of the first until the sixteenth of September 1992, and high concentrations levels were found about 11h too (but for this test, less data for midday were recorded and no program of temperature correction was used, suspecting temperature effect as the main factor). Then, at 18h-19-20h, low levels in air concentration may due to the dew again, as well as at 21h the high levels may due to a lower atmospheric stability and a farm activity.

So, two hypothesis are
 H_0 : the hourly mean concentrations are equal
 H_1 : the hourly mean concentrations are different

Assuming the equality of the variances, an Anova test-Simple Factor was used : if $F_{obs} > F_{critical}$, so H_0 is rejected, with an Alpha risk of 5%. On the contrary, if $F_{obs} < F_{critical}$, H_1 is rejected with the same risk Alpha of 5%.

Now, let us have a look to the Anova test-Simple Factor results :

ANOVA						
Source of Variation	SS	df	MS	F	P-value	Fcrit
Between Groups	15.28823	23	0.664706	0.444449	0.988781	1.55806
Within Groups	562.3354	376	1.495573			
Total	577.6236	399				

This table shows clearly that F_{obs} is inferior to $F_{critical}$ ($0.444 < 1.558$).

Thus, the hypothesis H1 is rejected with an Alpha risk of 5% and for this four weeks period, between 11/5/93 and 8/6/93, the hourly mean concentration in ammonia were equal overday (the effects of stability height, farm activity, dew and emission were non-significant during that period).

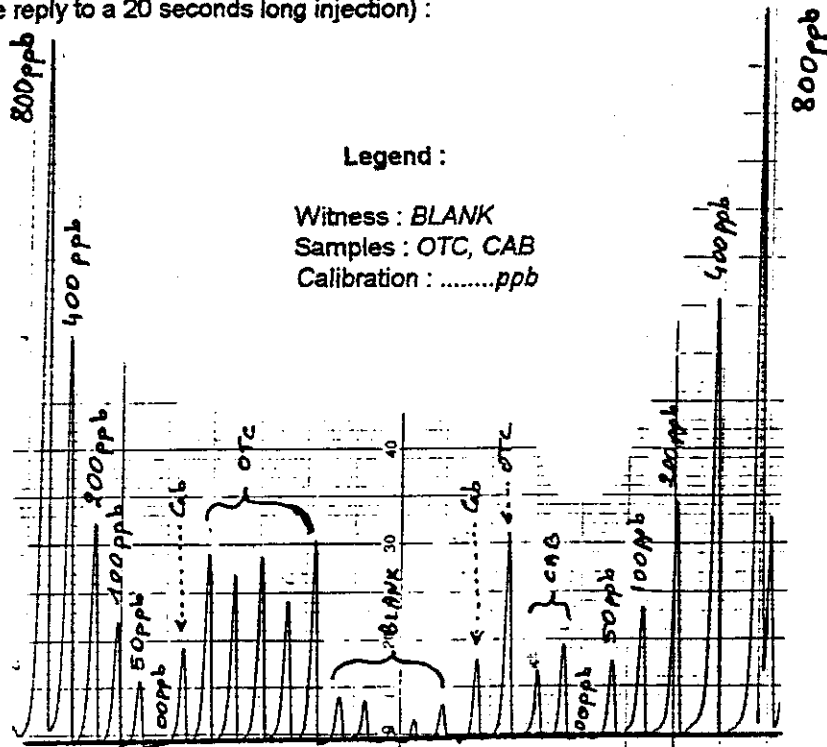
Nevertheless, many differences appeared over time and especially over days, following above all the windspeed, the wind direction, the SO₂ concentration and the humidity rate. So all these data, which aren't available at that time, are required to analyse the air concentration. Most of the time, at Bush, peaks in ammonia air concentration were expected when the atmosphere was dry, when the windspeed was low, when the wind direction was West/South-West (it is due to a local source of ammonia, a big farm is located in this direction) and the air concentration in SO₂ was low.

Third experiment :

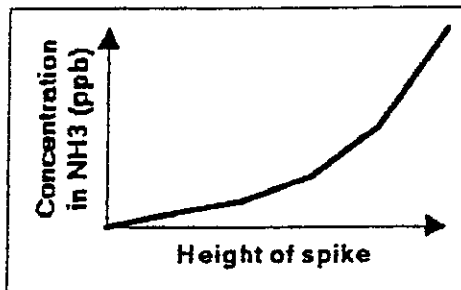
THE FLOW INJECTION ANALYSIS

The method of the diffusion tubes is a simple method to provide estimates of background air concentration in ammonia, needing a low input monitoring. The conductivity measurements were made using the controll box of the NH₃ analyzer.

As for example, one part of the results on the chart recorder are given below (each spike is the reply to a 20 seconds long injection) :



Because of a blockage in one of the tubes, three different calibrations were made. Each of them is following the graph, shown below :



For each calibration, an equation is found :

$$\text{concentration (ppb)} = 0.18581 + 34.46716 \times \text{height of spike (Hs)} + 1.23716 \text{ Hs}^2 \quad (\text{calibrat. 1})$$

$$\text{concentration (ppb)} = -19.6573 + 36.0089 \text{ Hs} + 1.58833 \text{ Hs}^2 \quad (\text{calibrat. 2})$$

$$\text{concentration (ppb)} = -5.2375 + 37.7573 \text{ Hs} + 1.341 \text{ Hs}^2 \quad (\text{calibrat. 3})$$

The tubes were exposed during about 28.25 days, from the fourth of May 11:00 until the first of June 15:00. Knowing the air deposition volume over time, which is 0.1 l/hour, the total air volume, which deposited during this period, may be calculated :

$$0.1 \times 28.25 \times 24 = 67.8 \text{ litres of air}$$

Thus :

$$(C_{se} - C_w) / 67.8 = C_s$$

where C_{se} is the mean concentration of the exposed solution in ppb,
 C_w is the mean concentration of the witness solution in ppb,
and C_s is the concentration in the site in $\mu\text{g m}^{-3}$.

Brief return : $\text{ppb} / \text{l} = \text{ng g}^{-1} / \text{l} = \text{ng ml}^{-1} / \text{l}$

but each filter was rinsed with 1 ml of deionized water

$$\text{so : } (\text{ng ml}^{-1} / \text{l}) \times 1 \text{ ml} = \text{ng} / \text{l} = \mu\text{g m}^{-3}$$

The following tables show the main results of the Student test :

t-Test: Two-Sample Assuming Unequal Variances		
	<i>cab</i>	<i>blank</i>
Mean	63.038	30.097
Variance	309.493	182.266
Observations	10	10
t obs	4.697	
S E d	0.098	
P(T<=t) one-tail	0.000121083	
t Critical one-tail	1.746	
95% C L	0.170	

Thus, the air concentration in ammonia for Cab site (cabine site) can be calculated :

$$(63.038 - 30.097) / 67.8 = 0.485 \mu\text{g m}^{-3}$$

However, this result must be corrected, because of the difference in the molecule mass between (NH_4^+) ($M_1 = 18 \text{ g mol}^{-1}$), measured in this experiment, and NH_3 ($M_2 = 17 \text{ g mol}^{-1}$), which concentration in the air is expected.

Thus :

$$0.485 \times (17 / 18) = 0.4587 \mu\text{g m}^{-3}$$

So, the Standard Error (S E d), which is the mean concentration, found above, divided by "t obs", given by the test, is $0.098 \mu\text{g m}^{-3}$.

At last, with 95% confidence limits of air concentration, which is (S E d x "t Critical"), a minimum significant concentration of $0.170 \mu\text{g m}^{-3}$ is recorded.

t-Test: Two-Sample Assuming Unequal Variances		
	<i>OTC</i>	<i>blank</i>
Mean	140.178	30.097
Variance	683.770	182.266
Observations	9	10
t obs	11.342	
S E d	0.135	
P(T<=t) one-tail	1.03631E-07	
t Critical one-tail	1.796	
95% C L	0.243	

The mean ammonia concentration, which is found here, is 1.533 ug m-3 (after mass ratio correction). The other results are shown in the table.

As a conclusion, the different ammonia concentrations in the air were :

for Cab site : 0.459 ug m-3 \pm 0.1 (S E d)
 \pm 0.17 (95% C L)

for OTC site : 1.533 ug m-3 \pm 0.13 (S E d)
 \pm 0.24 (95% C L)

At present, the analysis of the previous results is not expected, because this experiment took place in a longer one, which is monitoring the air concentration in NH₃ during a year long. However, it is interesting to note that :

---> This results in air concentration agree with previous results made five years ago (Sutton, 1990). The baseline concentration of 0.8 ug m-3 in 1988 was present through much of the year, with a peak in early spring of 1.5-2 ug m-3 and early summer peak of up to 3 ug m-3.

---> The higher mean air concentration found for OTC site was expected, because it is located near a local source of ammonia (near a farm), on the contrary to Cab site.

---> A higher S E d was expected for OTC site too, because standards errors are seen to increase with air concentration, reflecting variability due to sampling, as well as fixed component due to the variability of BLANK filters (Sutton, 1990).

---> Nevertheless, it is possible that the values in this study may also overestimate air concentration, because of the laboratory contaminations.

Fourth experiment :

FLUXES MEASUREMENTS AT GREAT DUN FELL

To make ammonia fluxes measurements, a surface providing an adequate fetch over uniform terrain is required. Great Dun Fell site provided extensive fetches over uniform natural unfertilized vegetation (grass) and an undulating land surface, not ideal according to usual micrometeorological criteria. Nevertheless, it provided suitable conditions for flux measurement, demonstrated by the existence of good logarithmic wind profiles.

GRADIE50 was used to correct the temperature effect, following the first experiment result.

Only the periods of good fluxes measurements are shown in this part.

Graphs are given for flux measurement and environmental conditions, as following :

NH₃ air concentration (ug m⁻³), measured by the ammonia analyzer,

U* (m s⁻¹) : eddy velocity (m s⁻¹),

Flux NH₃ (ng m⁻² s⁻¹) : Flux of NH₃ to or away from the surface,

X NH₃ (ug m⁻³) : mean concentration of NH₃

at different heights : {1m} : in the atmosphere
{Z₀} : above the surface,

Vd{1m} (mm s⁻¹) : deposition velocity of NH₃ at 1m above the surface,

Rc (s m⁻¹) : surface or canopy resistance to deposition, which was calculated using first the Average method (hourly average values) and then the Median method (hourly median values),

L (m) : estimate of atmospheric stability above a surface,

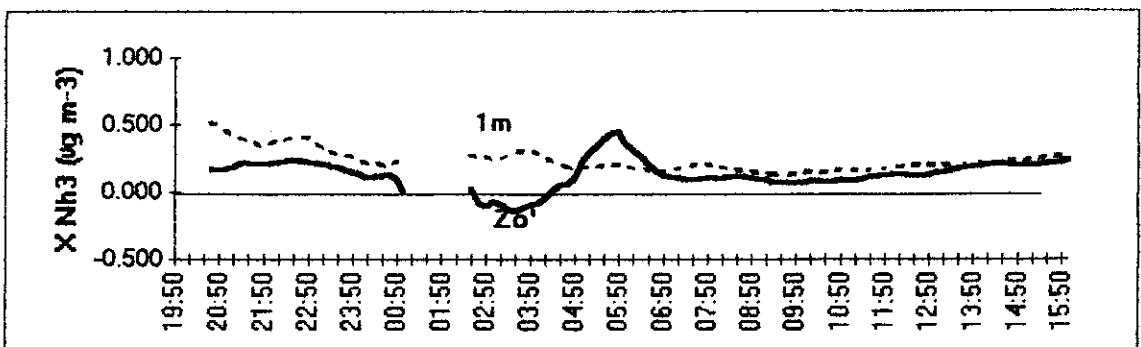
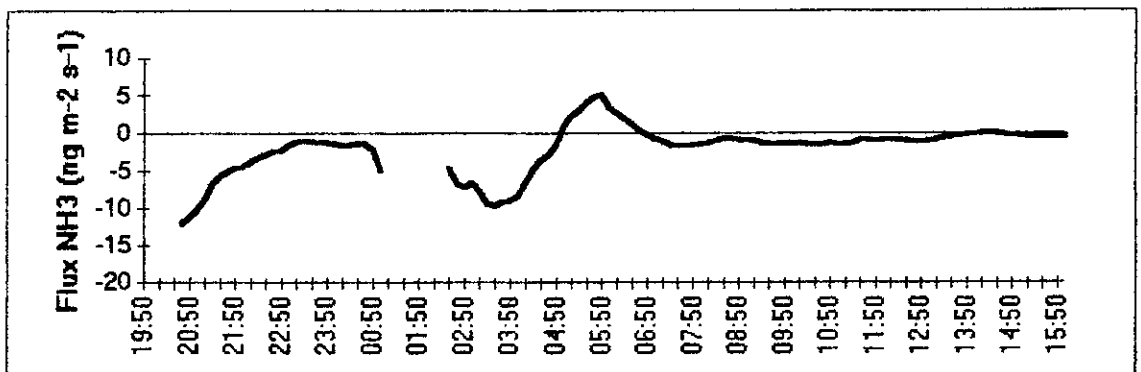
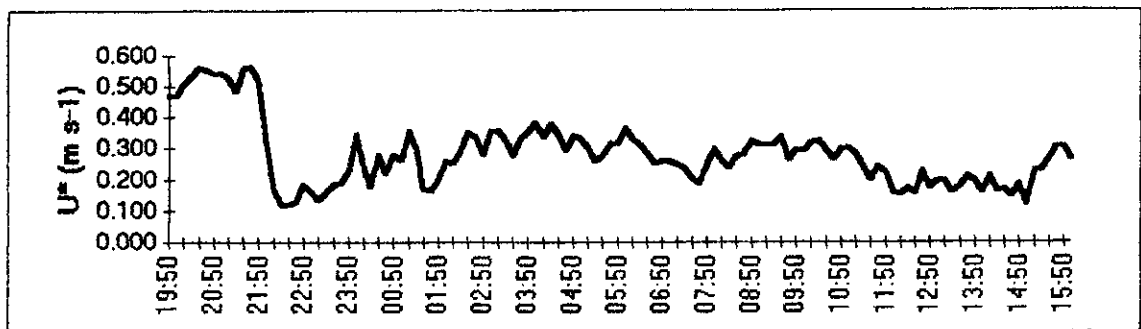
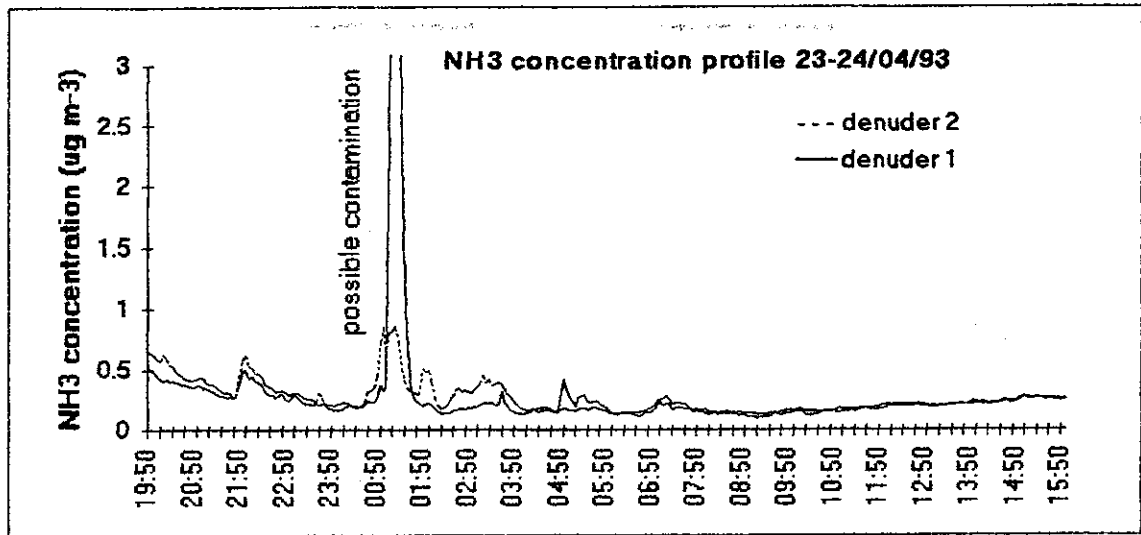
Heat fluxes (W m⁻²) : sensible and latent heat fluxes to or away from a ground surface,

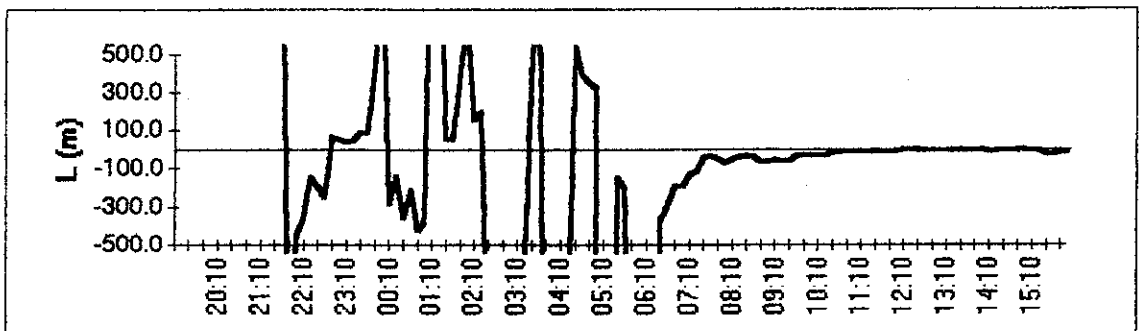
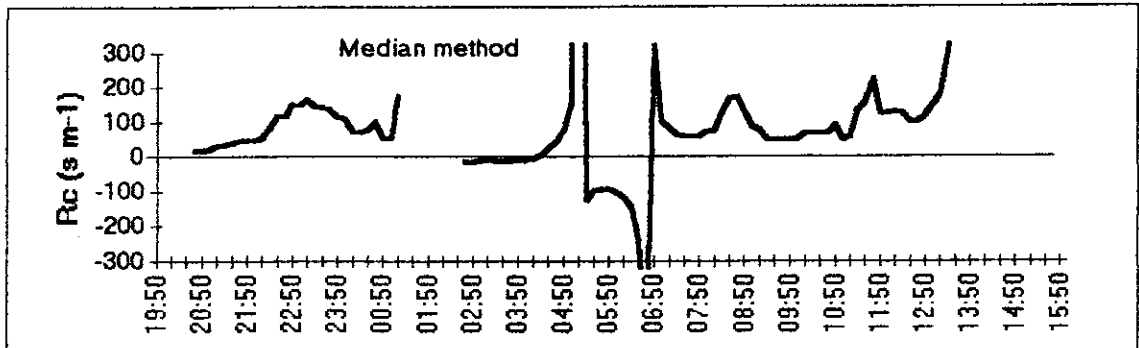
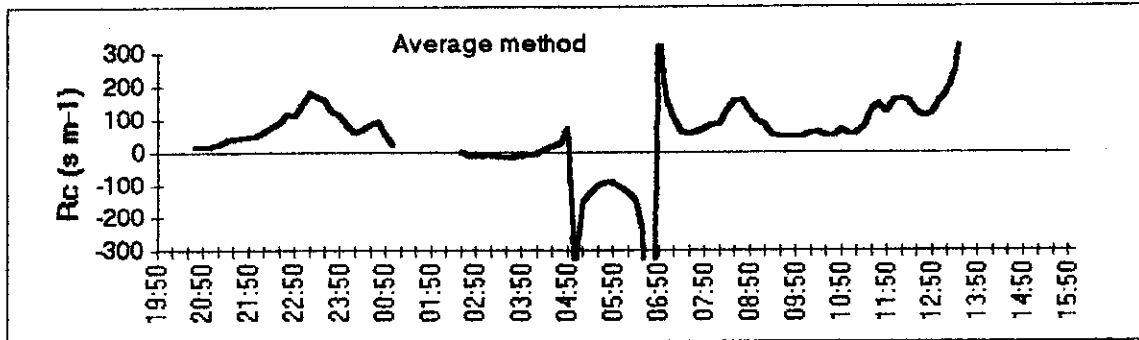
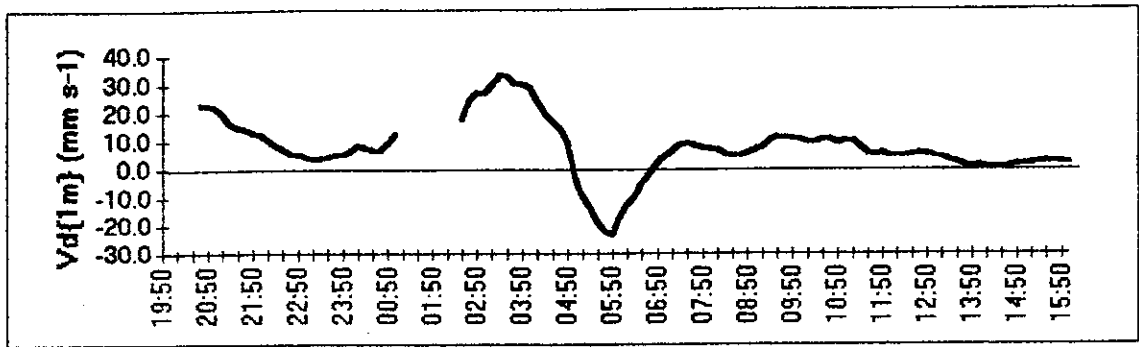
Temperature (°c) : at different heights : {1m} : in the atmosphere
{Z₀} : above the surface,

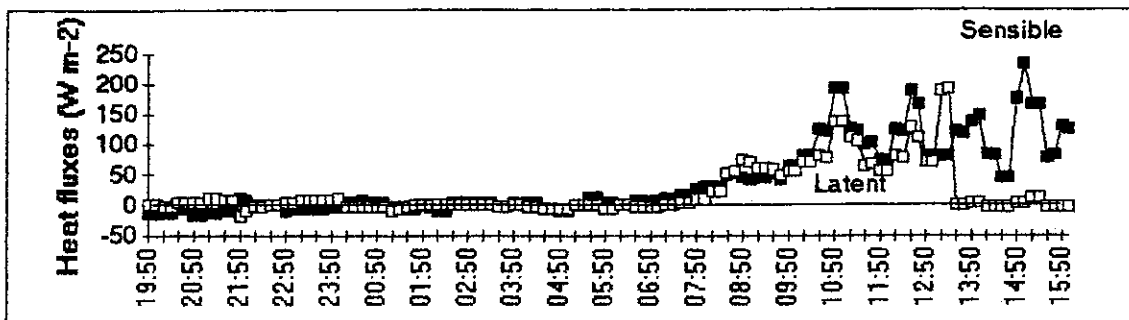
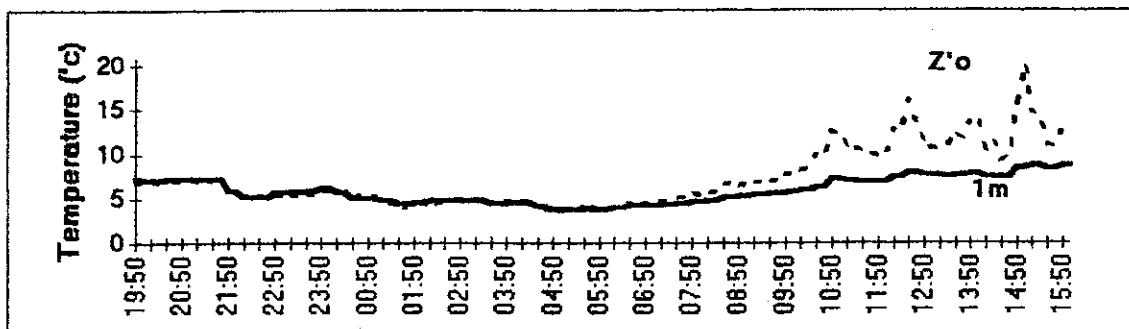
SO₂ (ug m⁻³) : air concentration in SO₂ (see Appendix 1).

C / λE ratio : part of latent Heat fluxes compared to sensible Heat fluxes (see Appendix 2)

**Course of ammonia exchange and environmental conditions over time at Great Dun Fell
23-24/04/93 :**







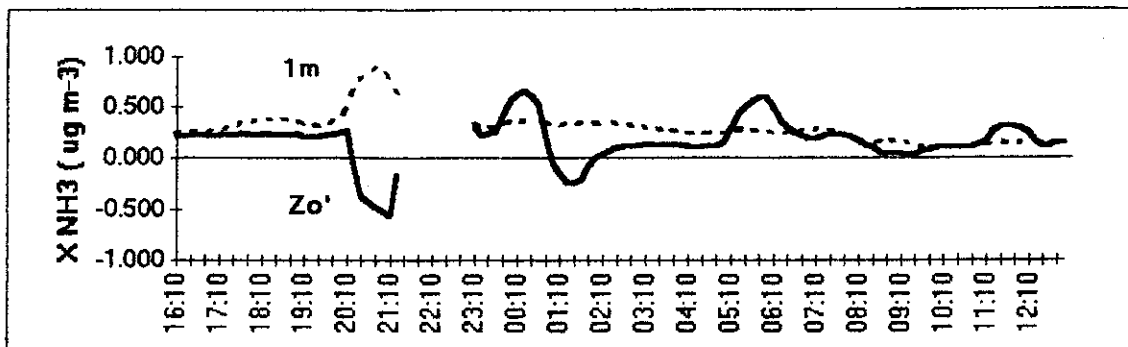
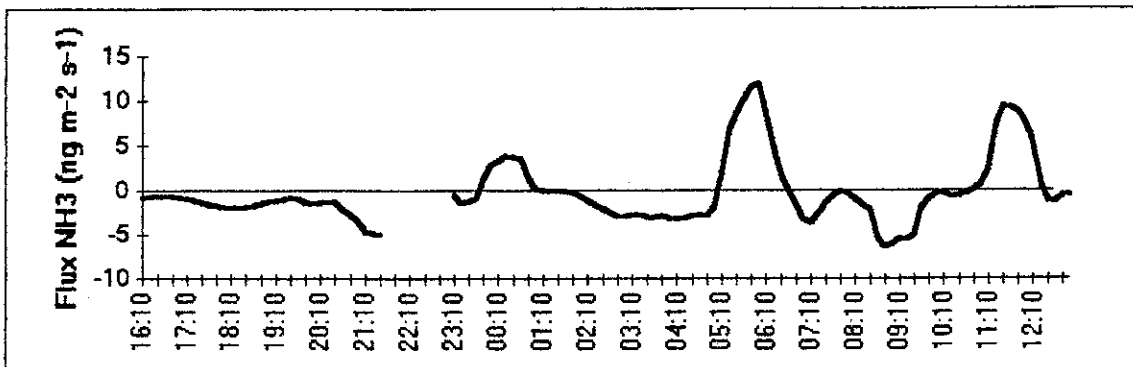
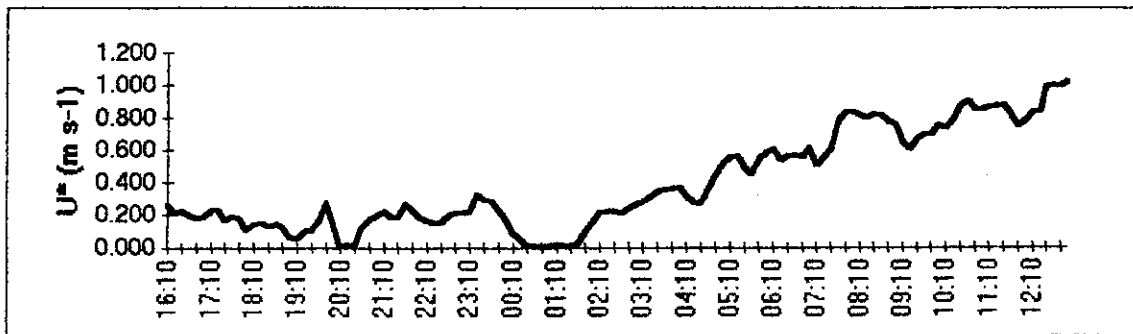
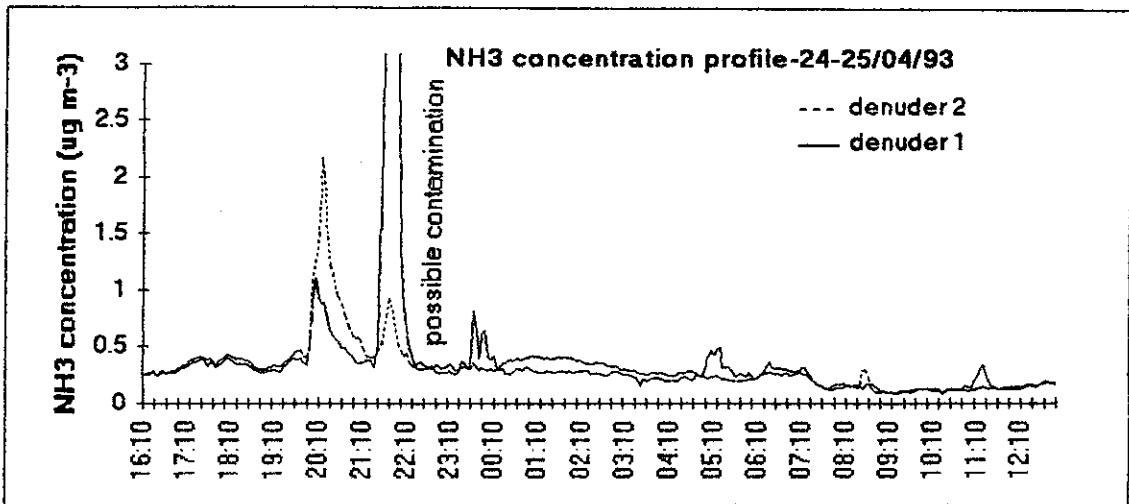
By definition, both the flux and $V_d\{1m\}$ are positively related to U^* . However, in addition so is $X\{1m\}$, which is treated as independent of U^* in this analysis. So the highest $V_d\{1m\}$ and lowest flux are recorded until 22h BST (British Summer Time), when the highest U^* was noted. A greater U^* steepens the surface gradient such that $X\{1m\}$ is less depleted by the surface. It is therefore possible that the cause of variation of the NH_3 levels is the changing temperature throughout the day (GRADIE50 was used to calculate the data, but its agreement has to be determined over lower temperature, $t < 12^\circ C$). There, an increasing temperature (still inferior to $12^\circ C$ until 12h BST) doesn't lead to a significant increasing ammonia concentration. It is nevertheless important to notice that the air concentration in ammonia is very low.

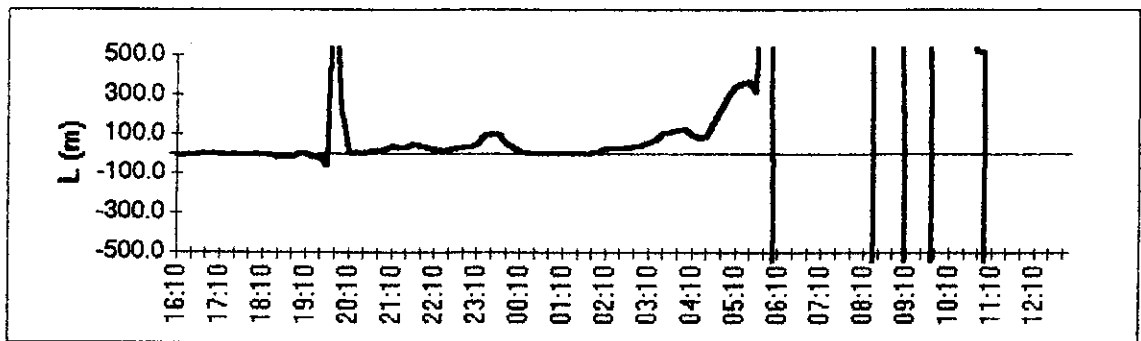
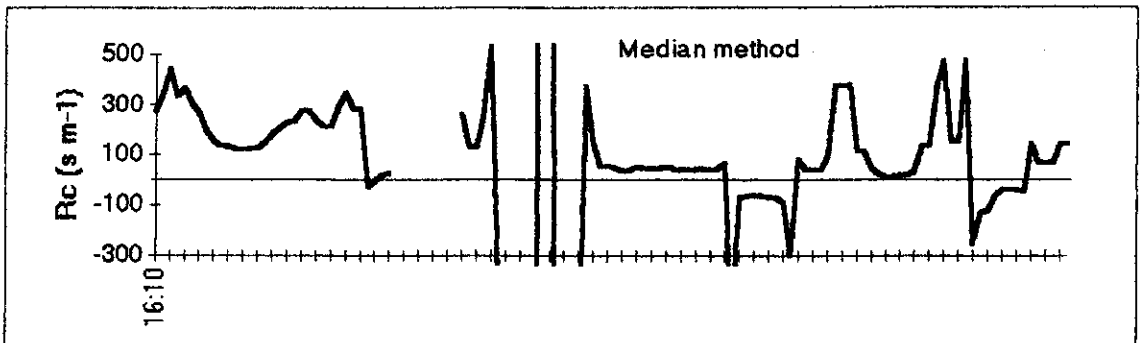
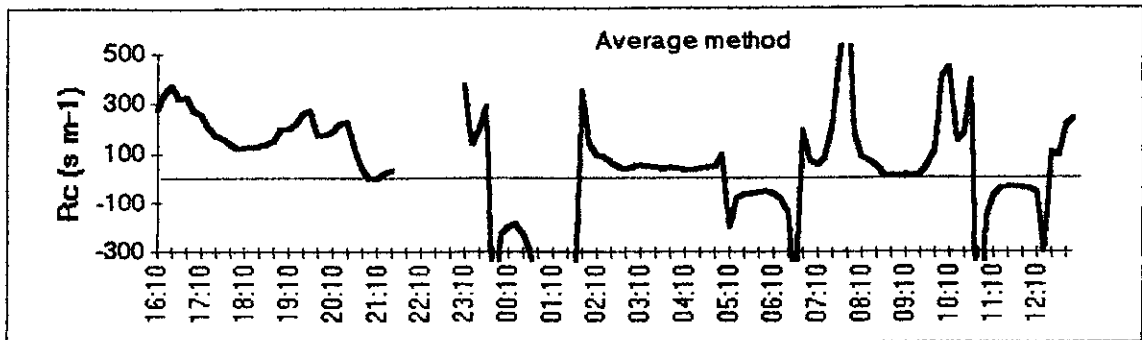
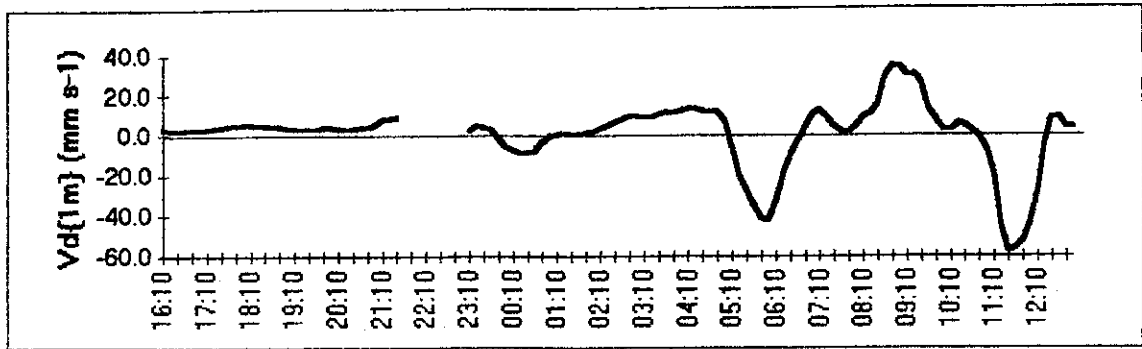
The value of R_c is generally quite small and positive, with NH_3 depositing to the surface at rates limited by turbulence (the sink for the NH_3 must be the surface roughness elements-leaf surface). However, two exception periods appeared :

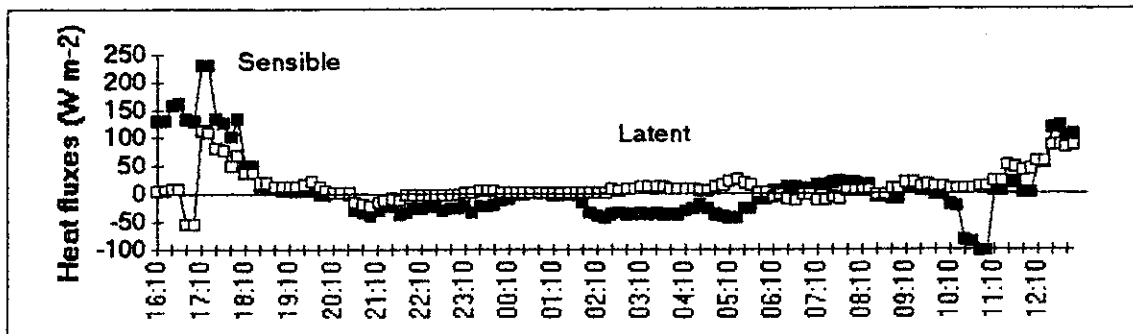
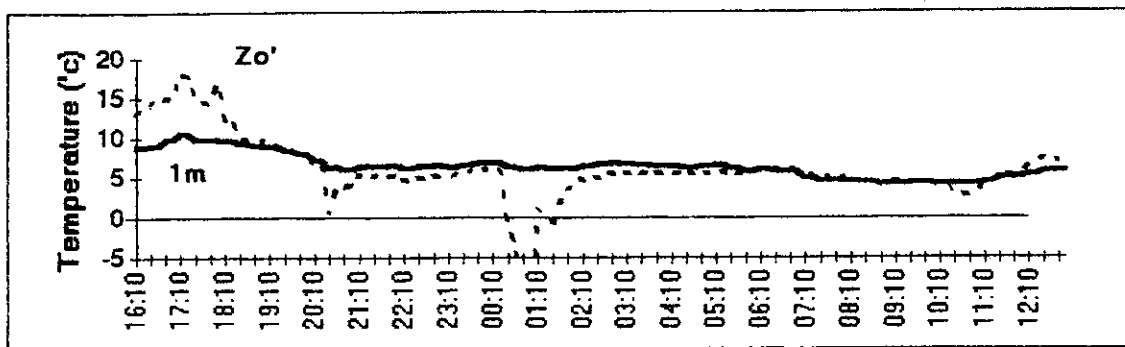
---> 5h to 6h50 (BST), where emission occurred, shown by the positive flux, by a higher $X\{Z_o\}$ compared to $X\{1m\}$, by V_d and R_c , which appeared negative. That was during a short period of big instability ($L = -16\ 000m$). The main hypothesis about this reaction, over unfertilized ecosystems, is that the canopy elements had received, as usual, NH_3 deposition, and suddenly the process changed, turning to brief emission, and then was back to deposition. This may relate to an equilibrium surface concentration into the leaf (but it has to be checked through other fluxes measurements).

---> 13h30 to 15h (BST), where a large R_c was noted. It may be due to the low level of NH_3 in the air. But, considering the excess resistance (R_c) as a concentration ($X\{Z_o\}$), all the values are positively close to zero, confirming that deposition occurred during that period. There, very dry conditions appeared (the sensible heat fluxes profile follows the surface temperature profile), leading to a sudden break in latent heat fluxes profile (the evaporation stopped).

**Course of ammonia exchange and environmental conditions over time at Great Dun Fell
24-25/04/93 :**



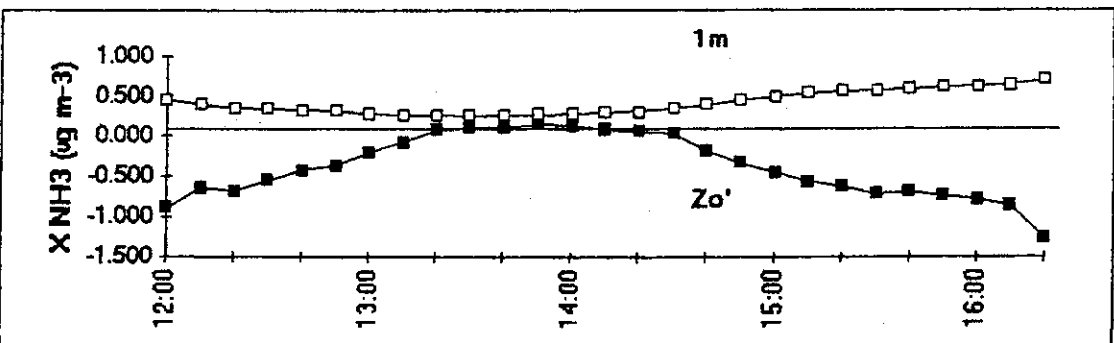
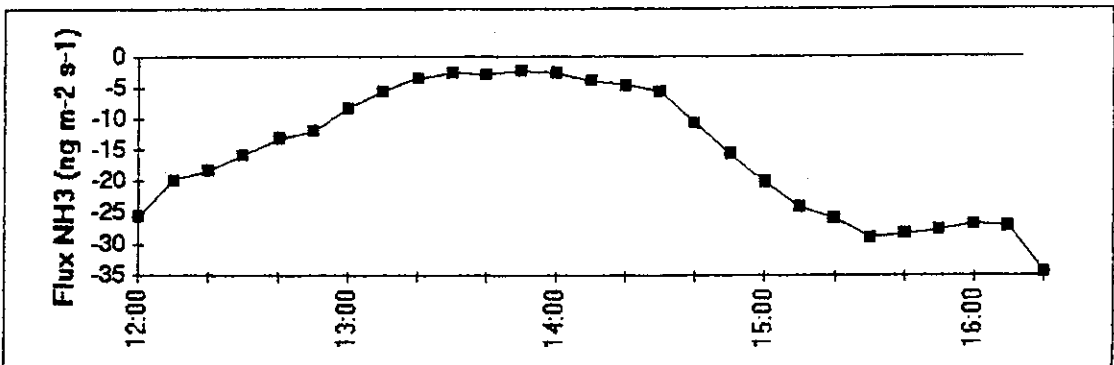
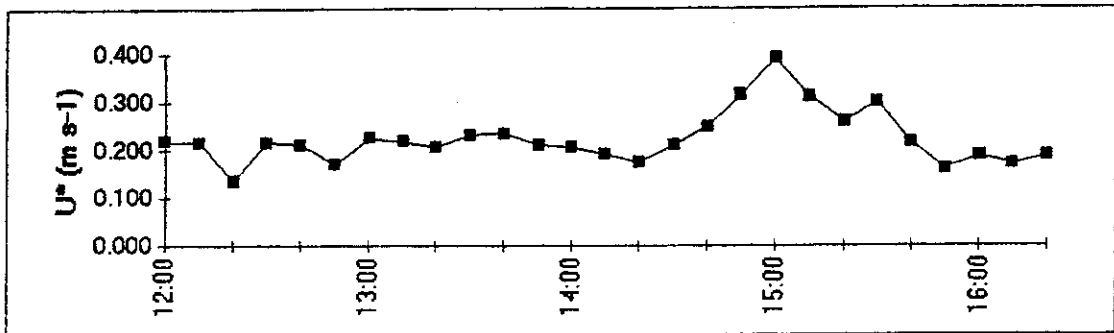
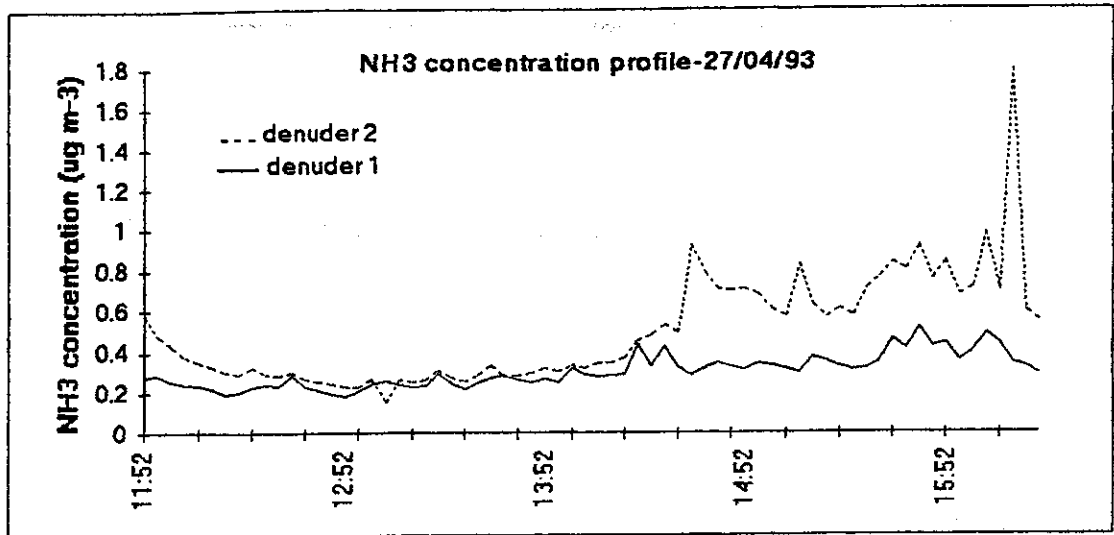


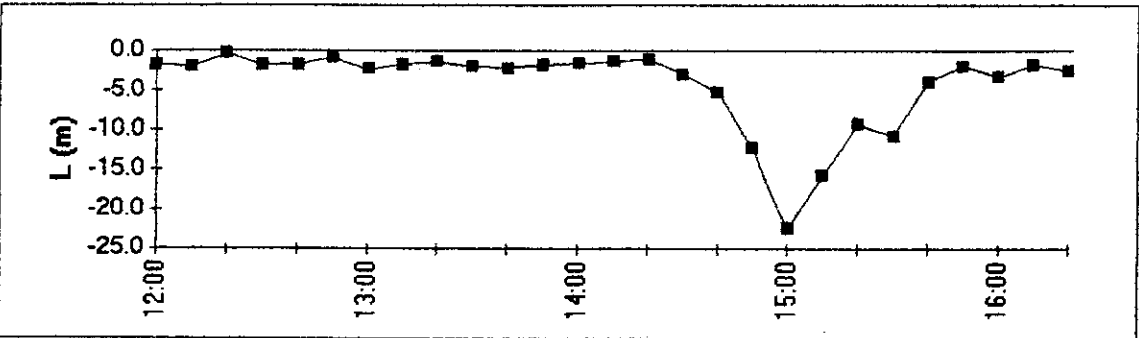
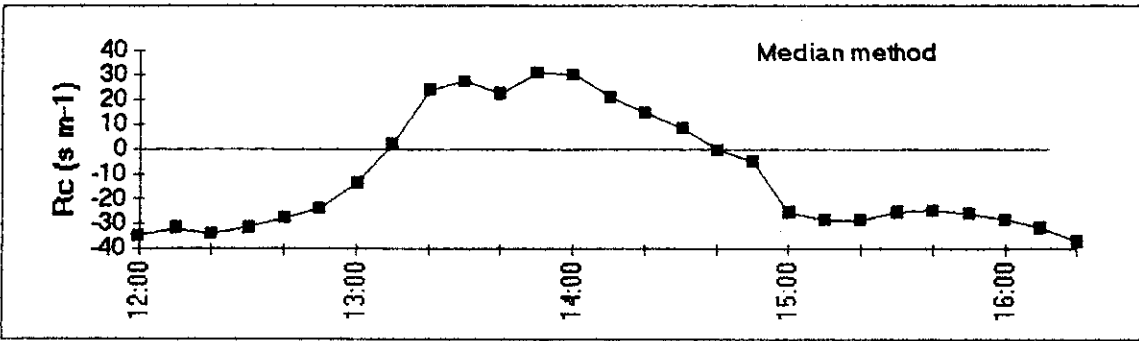
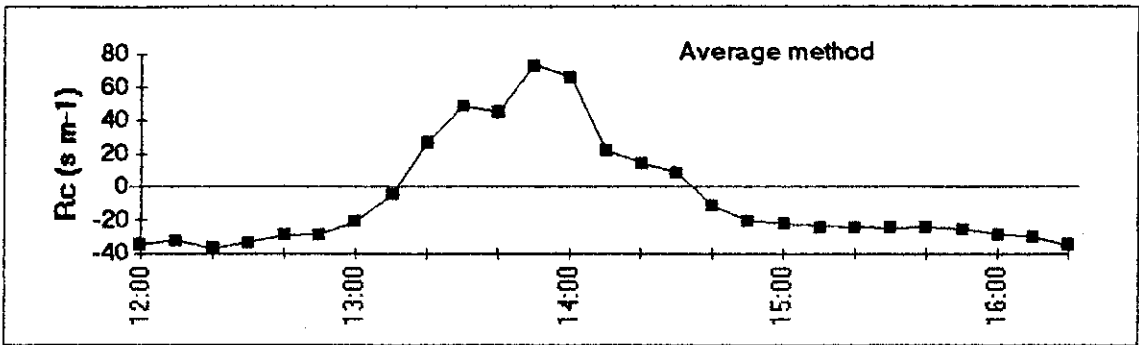
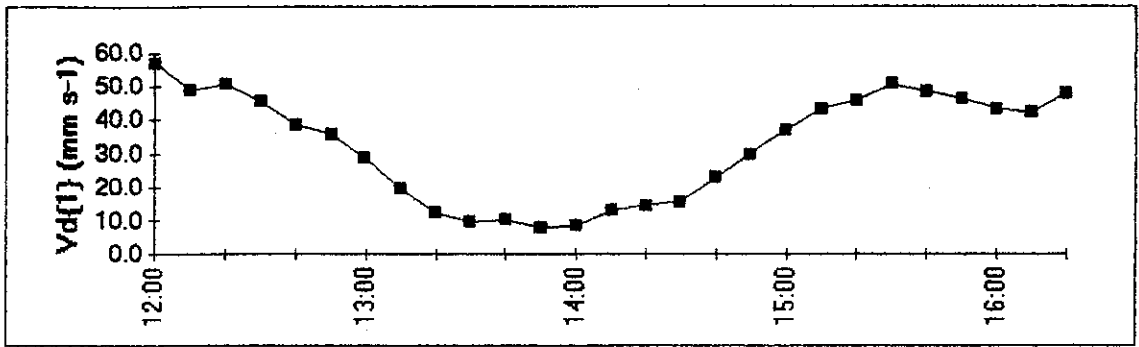


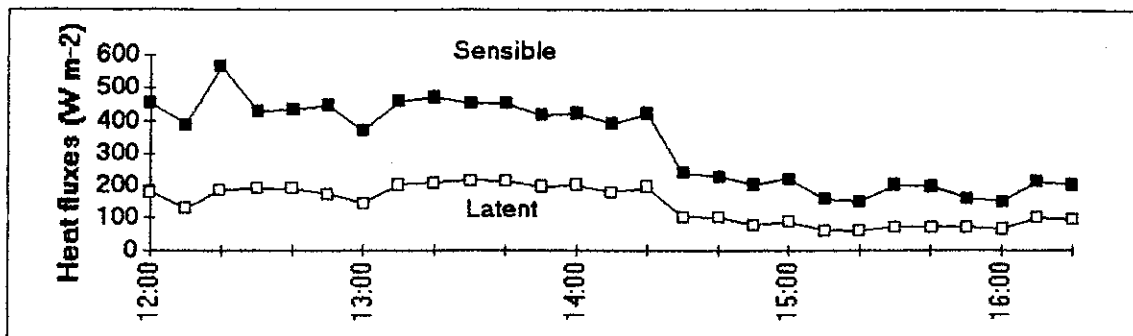
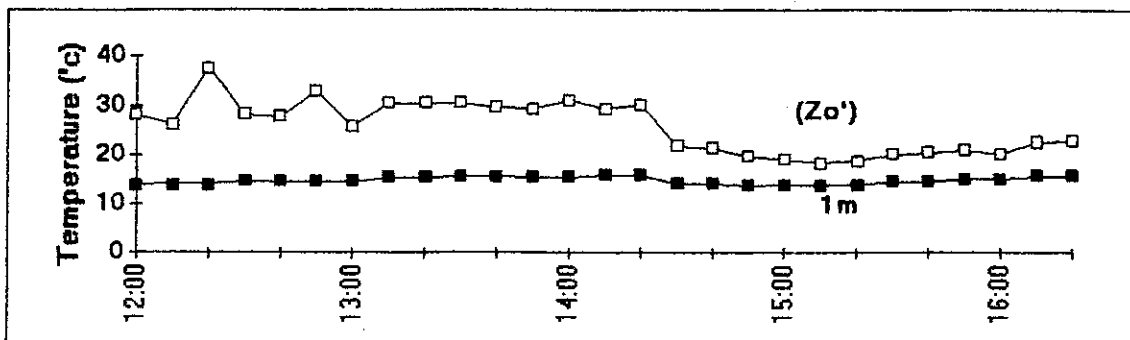
Here, very low air concentration were recorded too (mean atmospheric concentration : 0.29 ug m-3) over this period. U^* was very low until 4h (BST), then it was increasing constantly to reach high levels at 12h (BST) (which could explain the high amplitude noted on $V_d\{1m\}$ in the late period). Most of the time, deposition occurred, with low values of R_c . Two periods of frost appeared, each time corresponding to $U^* = 0$. From 16:10 until 19:10 (BST), a larger $T\{Z_o'\}$, superior to $T\{1m\}$ (the weather was sunny), was recorded, which renders unstable conditions and deposition due to the convection.

Apparently, one emission period occurred, interestingly exactly at the same time than the previous day, between 5:10 and 6:10 (BST). There, too, a sudden peak of unstable conditions was recorded ($L = -5500m$). The apparent emission, noted at 00:30 (BST) might due to $U^* = 0$ (not a real emission), and the other one (11:00 until 12:30 (BST)) can not be interpreted because of clouds down over the site. It was noticed heavy rain conditions too, which might started at 7:30 (BST), watching the first graph about NH_3 concentration profile : NH_3 in rain deposits very quickly so that concentration in the air becomes smaller, and a sudden decreasing air concentration was recorded. The sensible heat fluxes profile seems to agree about that time : although clear sky at night occurred, no or not much sun shine appeared after 7:00 (BST).

**Course of ammonia exchange and environmental conditions over time at Great Dun Fell
27/04/03:**



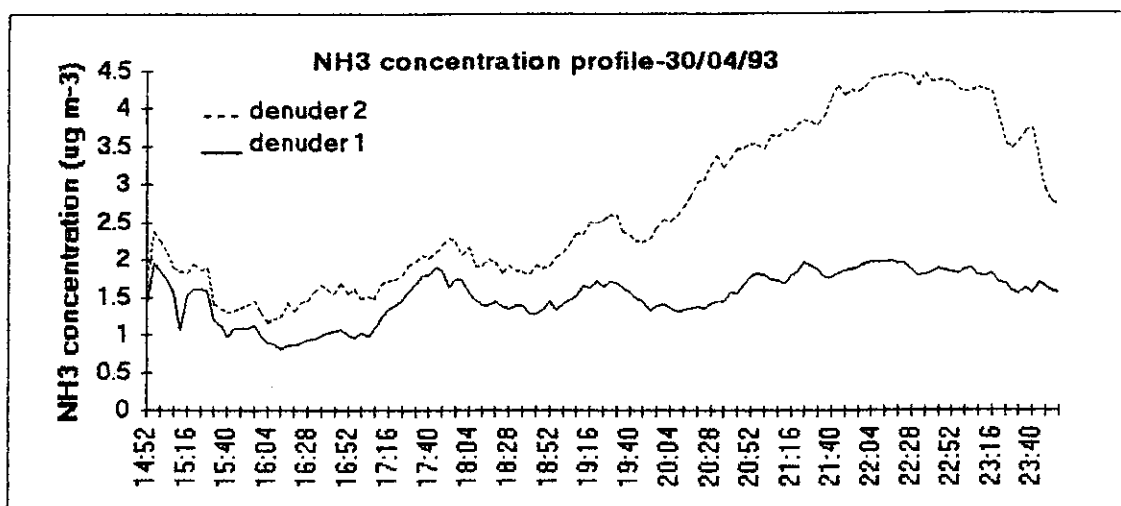


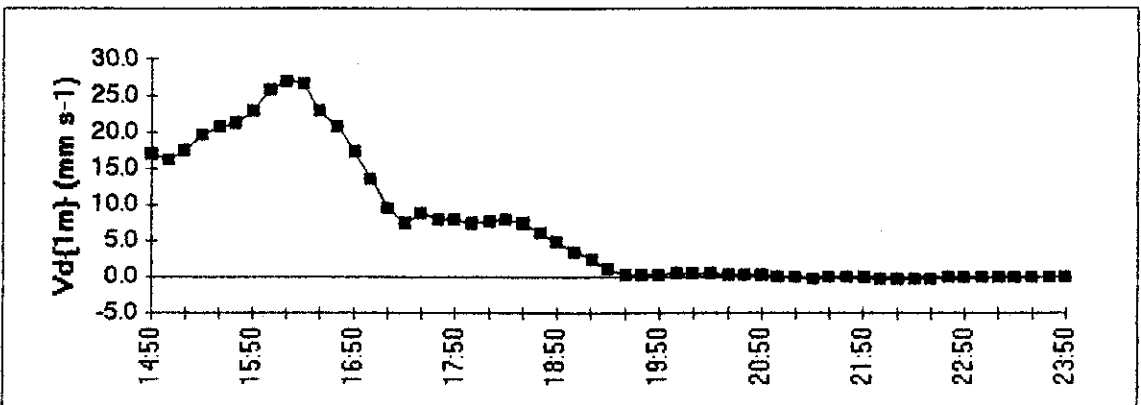
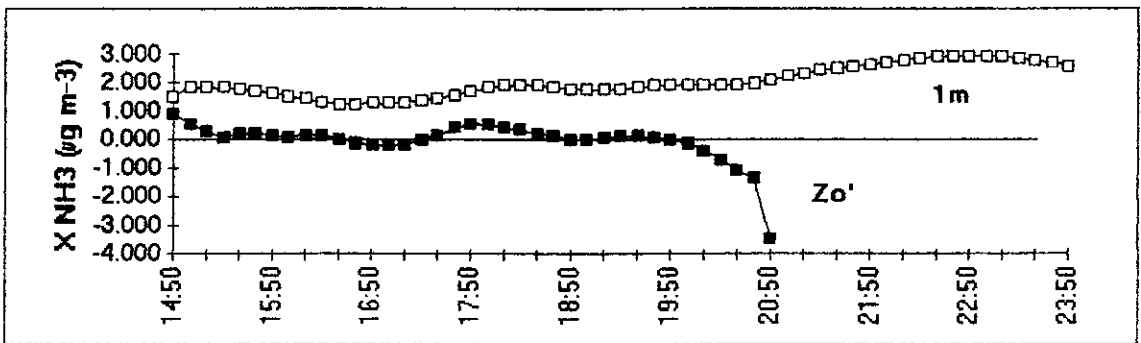
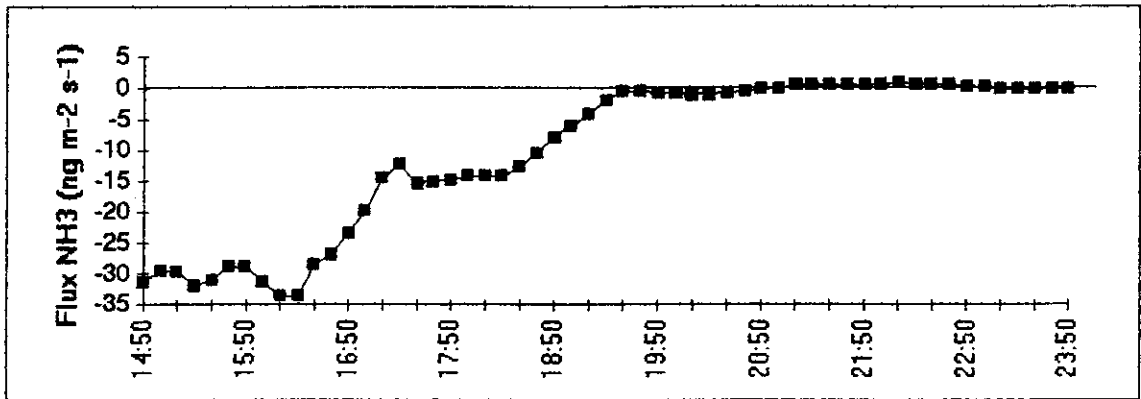
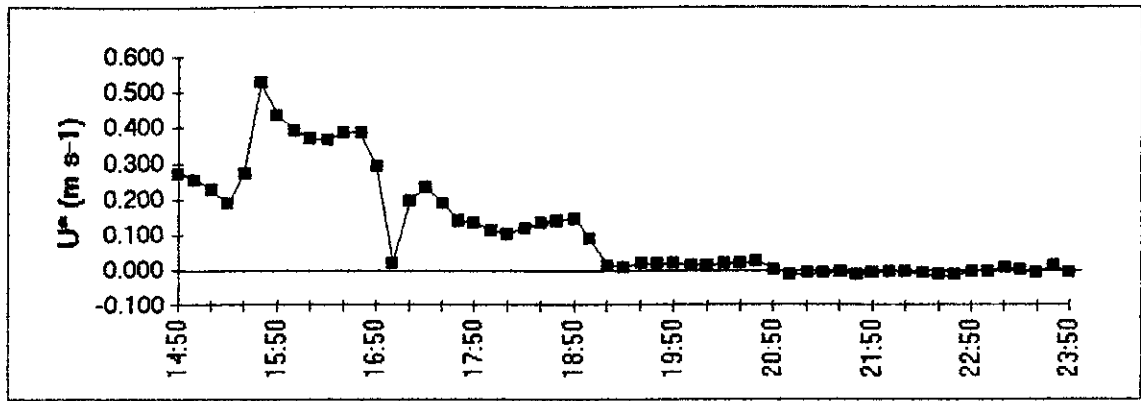


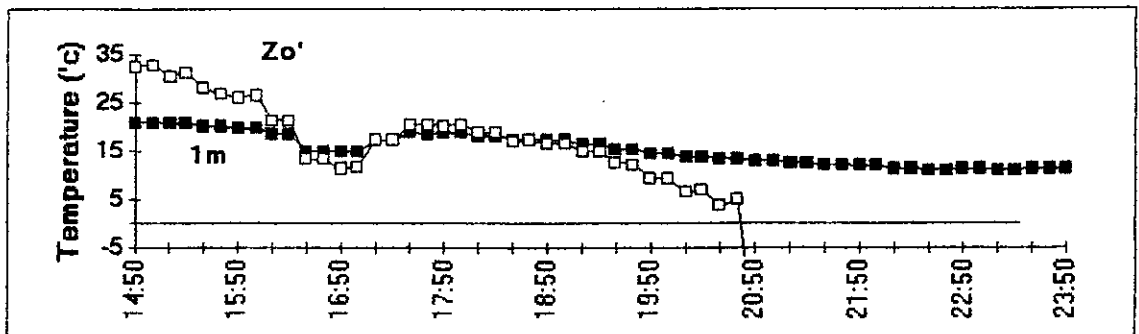
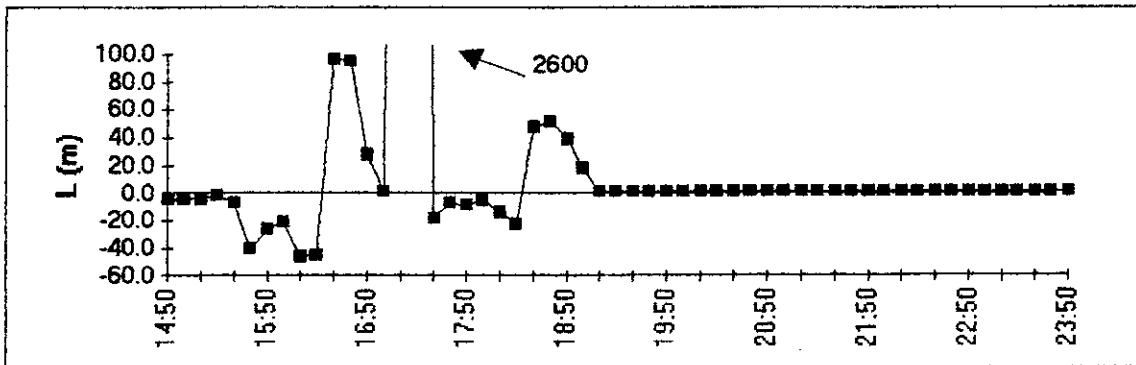
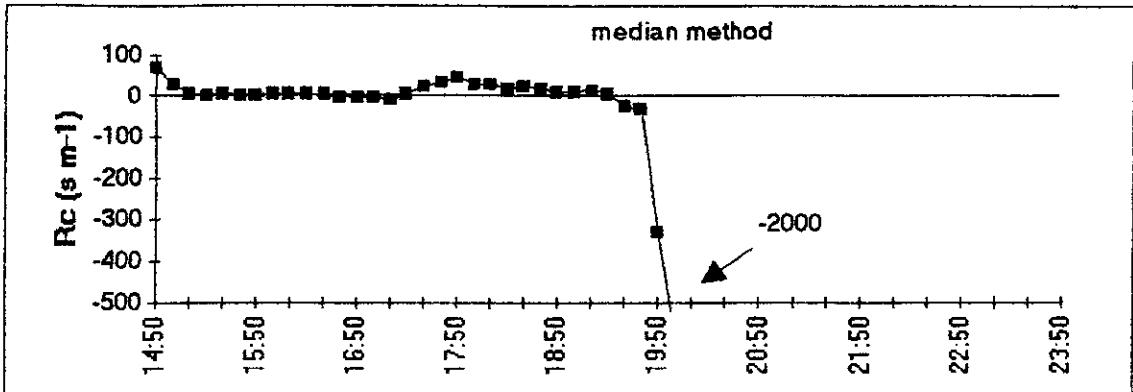
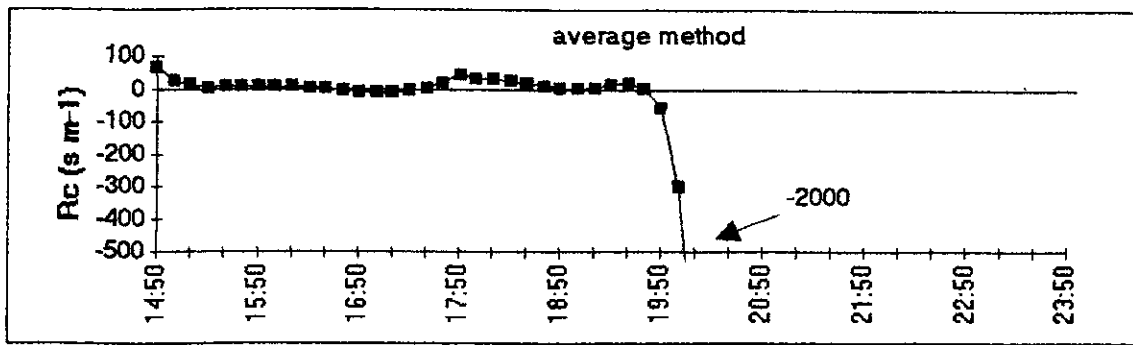
This short period took place in low windspeed condition and high temperature as well as high heat fluxes were recorded. Rc profile shows a good period of deposition, where fast deposition occurred between 12:00 and 13:00 (BST) and between 14:30 and 16:20 (BST). However, the estimated concentration above the surface ($X(Z_0')$) seems to be too negative, during this period, to be true. A co-sampling test was realized just after this period and revealed first a real disagreement between both denuder, that is why all these results must be treated with caution.

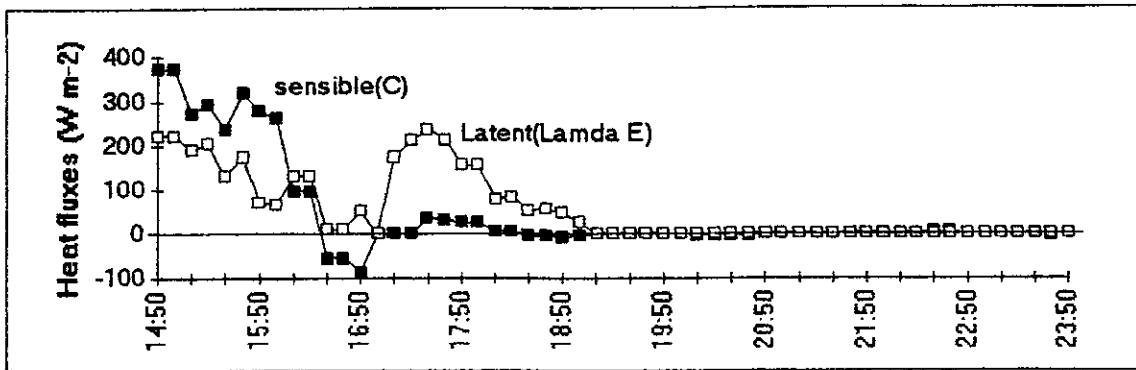
Constant light unstable conditions and temperature profile show that if NH_3 deposition was real, it was due to convection.

Course of ammonia exchange and environmental conditions over time at Great Dun Fell 30/04/93 :







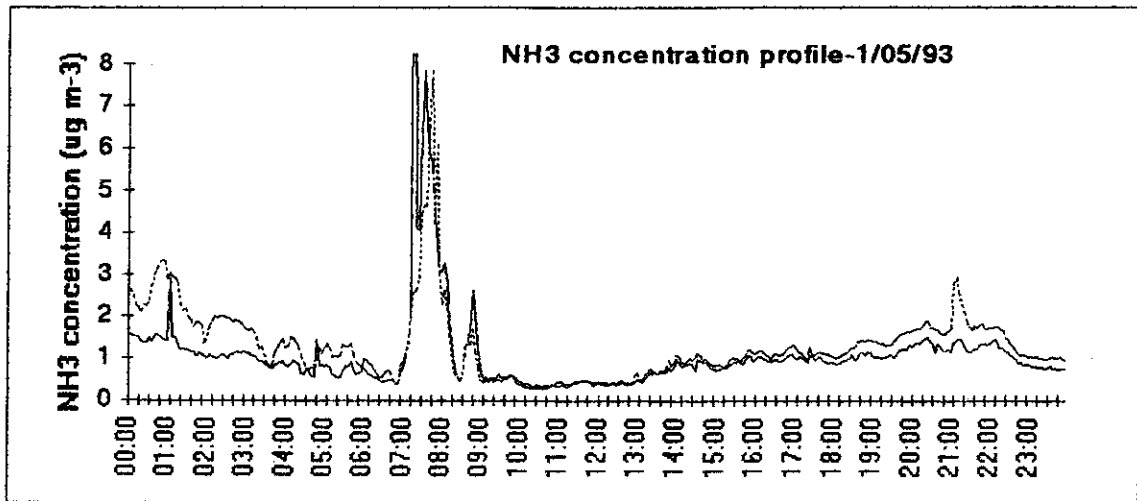


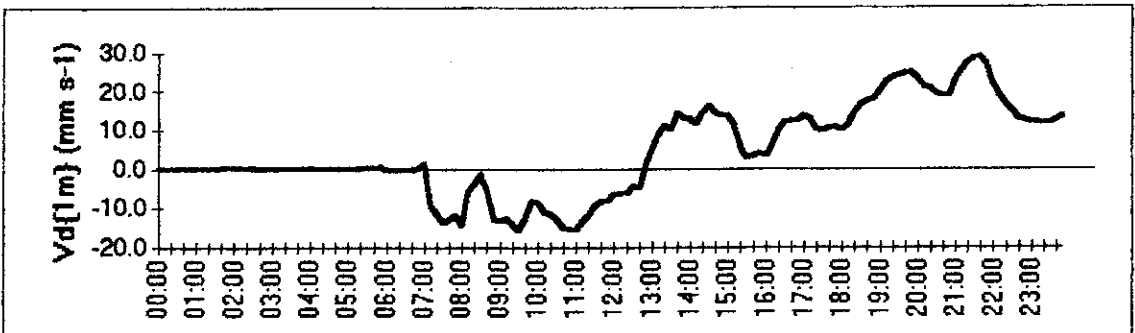
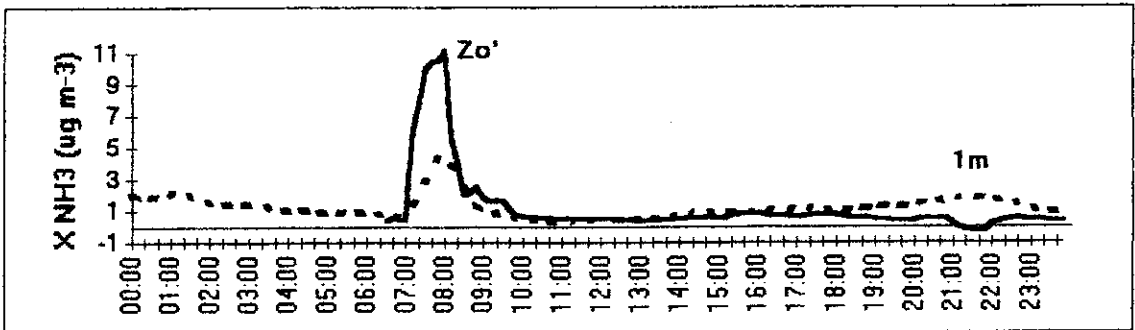
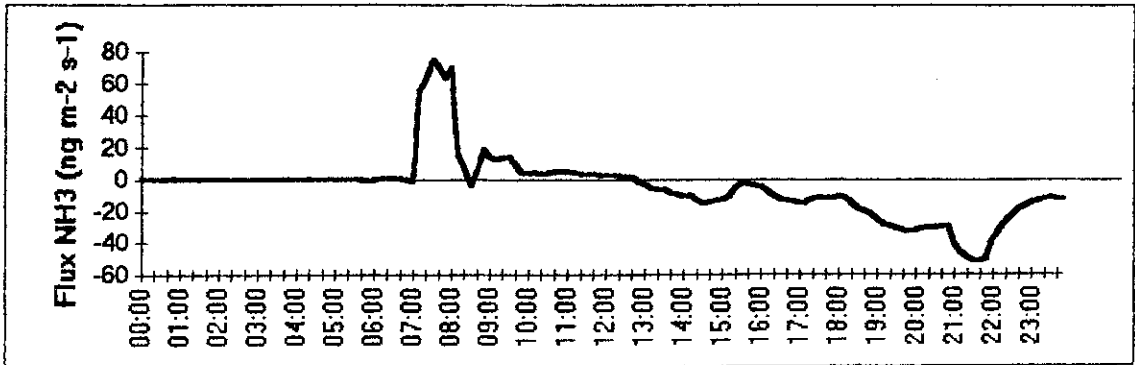
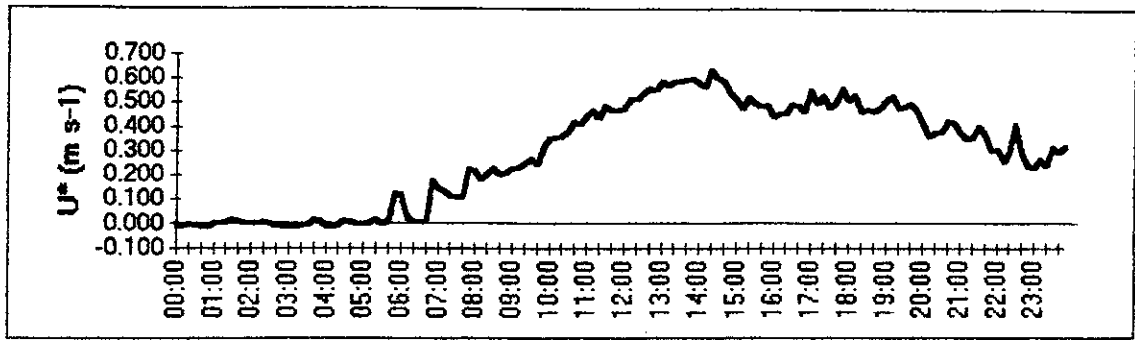
The estimate of both R_c and $X\{Z_o\}$ are still approximate to values about zero. Consequently, given the higher air concentrations in NH_3 during these measurements (mean concentration = $2.019 \mu g m^{-3}$), the fluxes were larger, ranging to $-33.57 ng m^{-2} s^{-1}$ (until 18:30 (BST), the mean value was $-23.29 ng m^{-2} s^{-1}$). This is despite the relatively small windspeeds (very low U^* were recorded), which restricted $V_d\{1m\}$ to a maximum of $27 m s^{-1}$. So deposition occurred most of the time. Until 16:30 (BST), deposition was due to convection ($T\{Z_o\} > T\{1m\}$). Temperature and heat fluxes profiles show dry conditions, which suggest that the NH_3 was efficiently bound to the leaf surfaces even when the surfaces appeared dry.

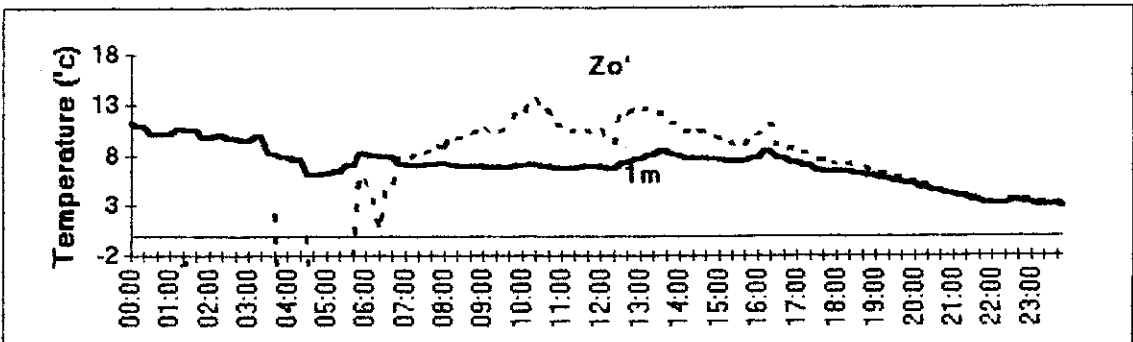
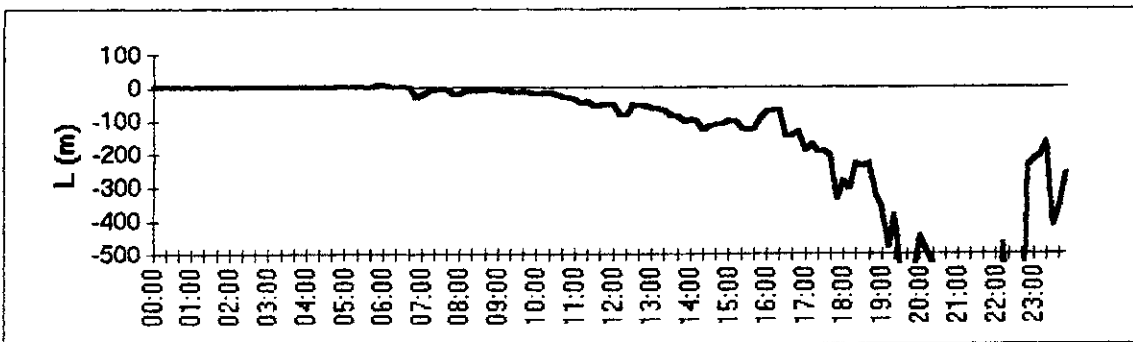
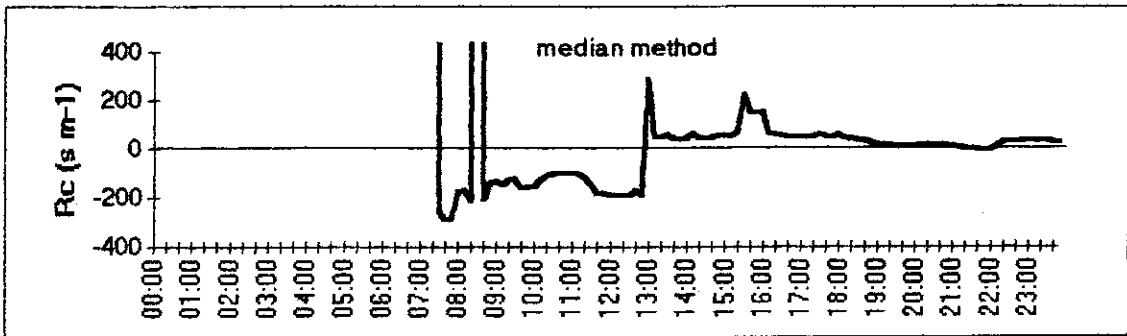
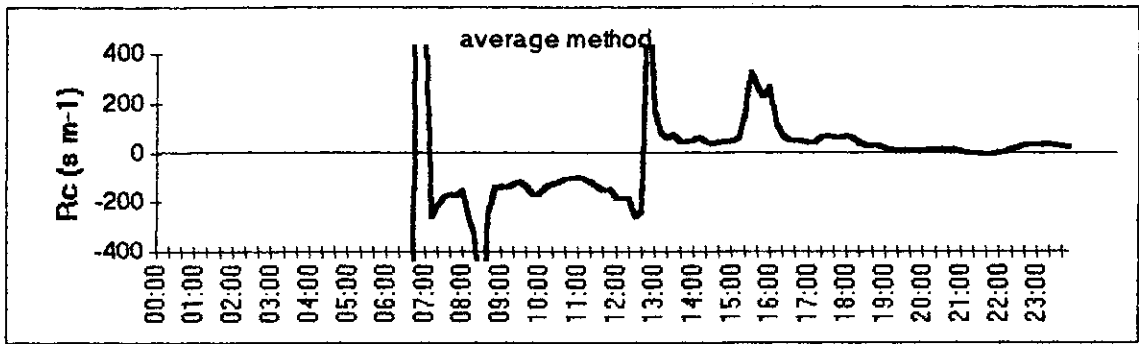
Then, the decreasing fluxes, noted between 16:30 and 17:10 (BST), is due to $T\{Z_o\}$, which became inferior to $T\{1m\}$, leading to the air stratification and thus less mixing. Moreover, during that period, the evaporation became very low as well as the air concentration in ammonia, which became lightly lower: a rain period took place (maybe a stormy rain, because of the evaporation peak, which followed, even in dark sky conditions).

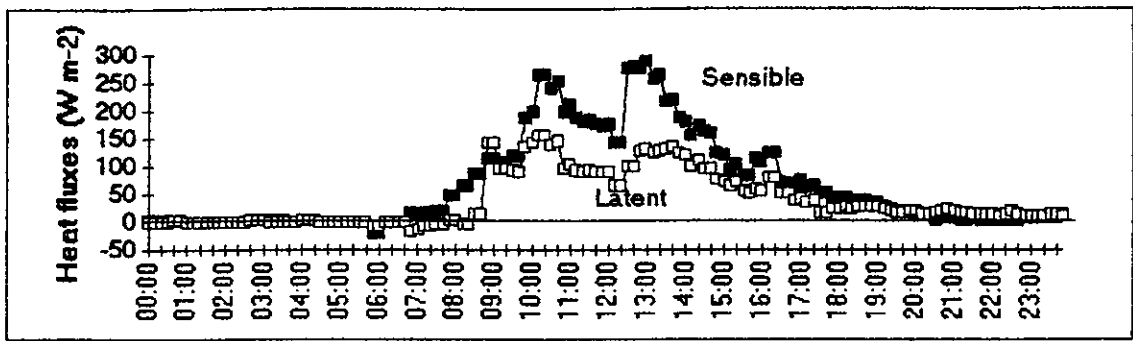
In addition, after 20:00 (BST), due to U^* close to zero, $X\{Z_o\}$ became too negative, which can not be possible, the expected deposition would have been too fast.

Course of ammonia exchange and environmental conditions over time at Great Dun Fell 1/05/93:







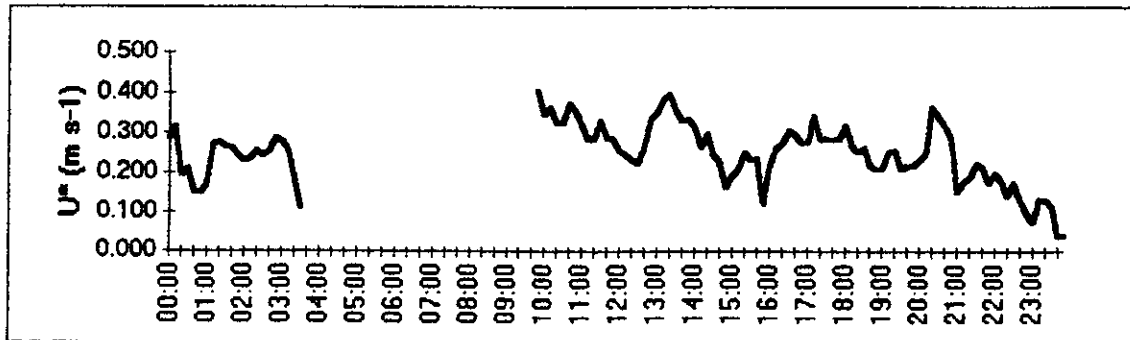
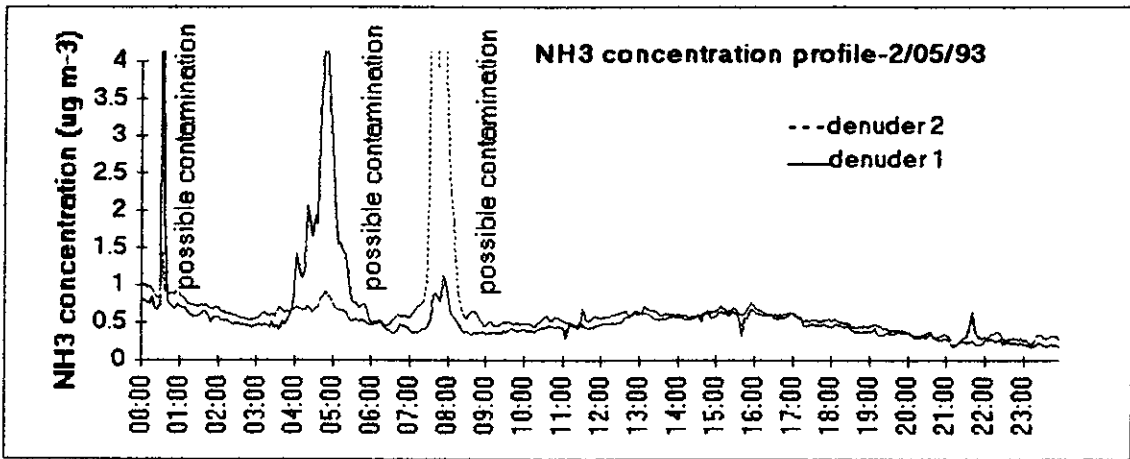


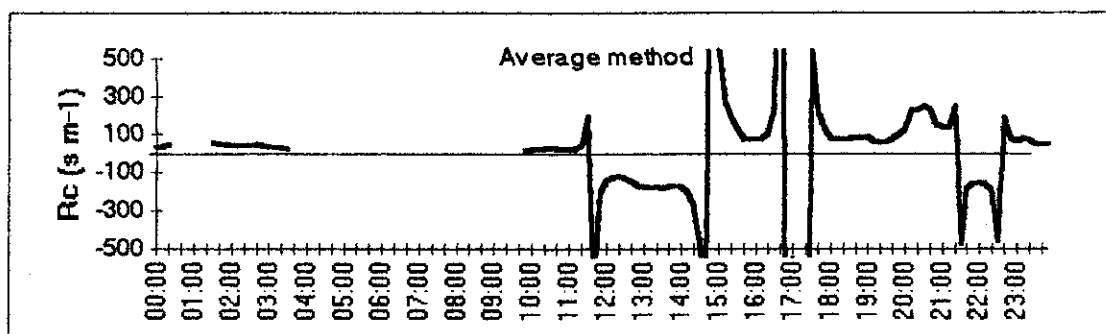
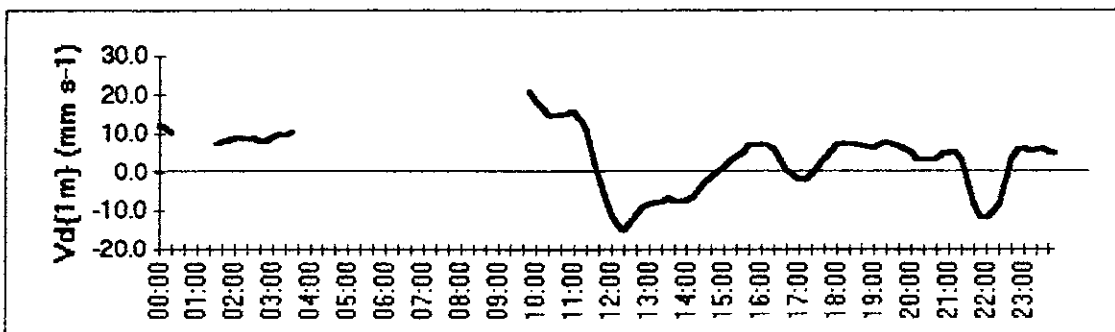
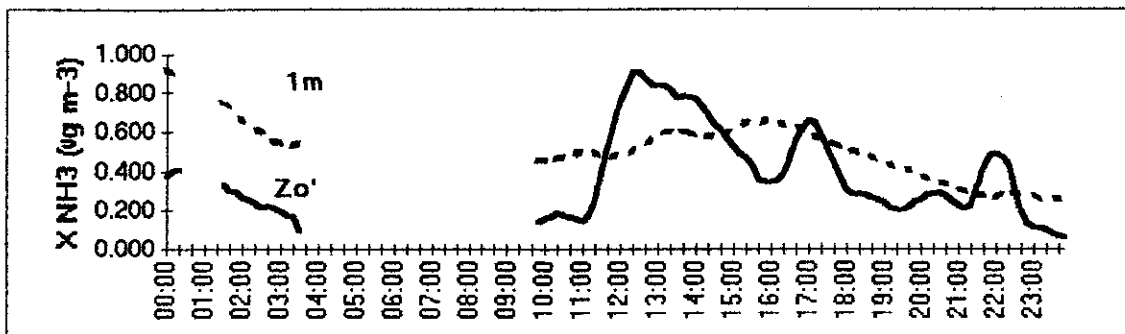
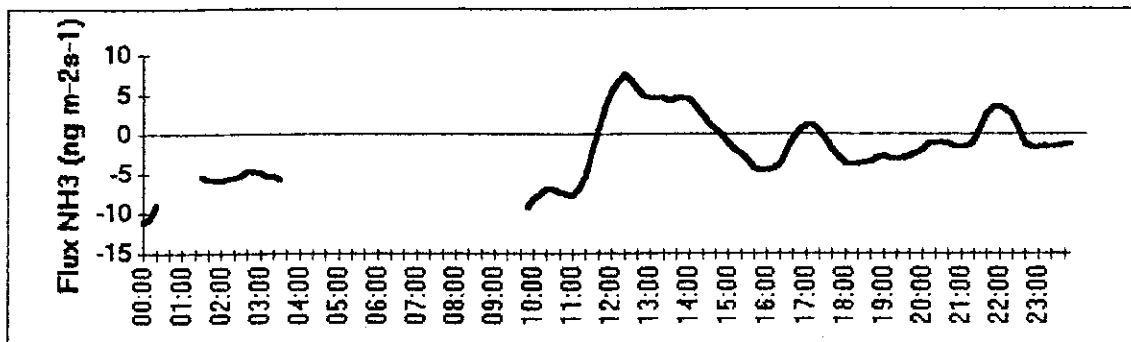
U^* was close to zero until 7:00 (BST), which did not enable to calculate fluxes and estimate concentration at Z_o' during this period. In addition, a frost period occurred during the night until 5:40 (BST). In spite of low air concentration in ammonia (mean air concentration : $1.209 \mu\text{g m}^{-3}$), not many very high R_c values were found.

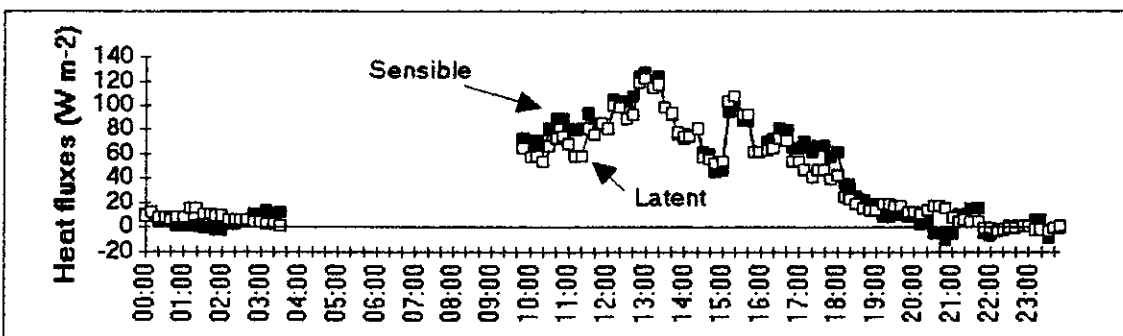
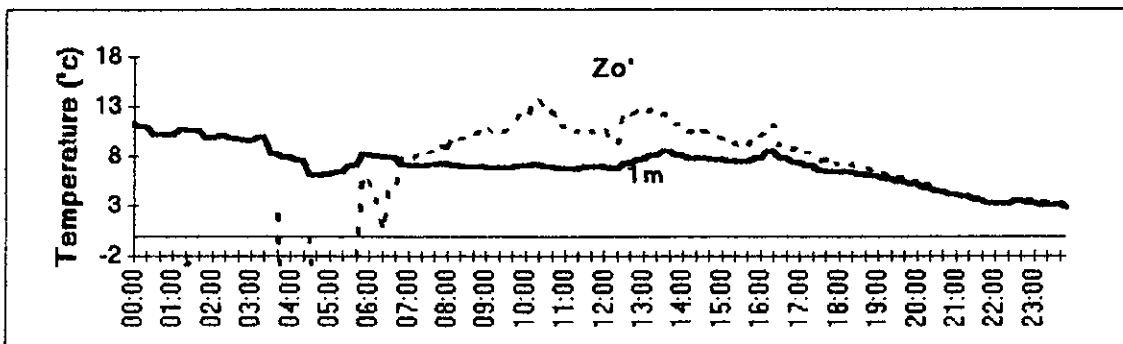
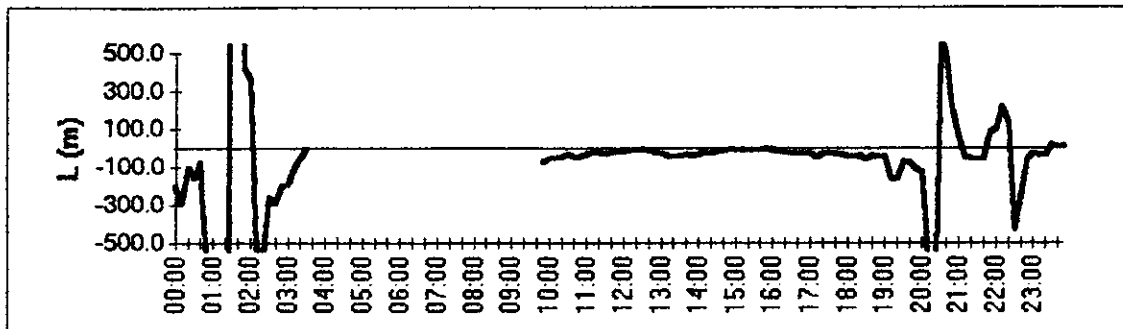
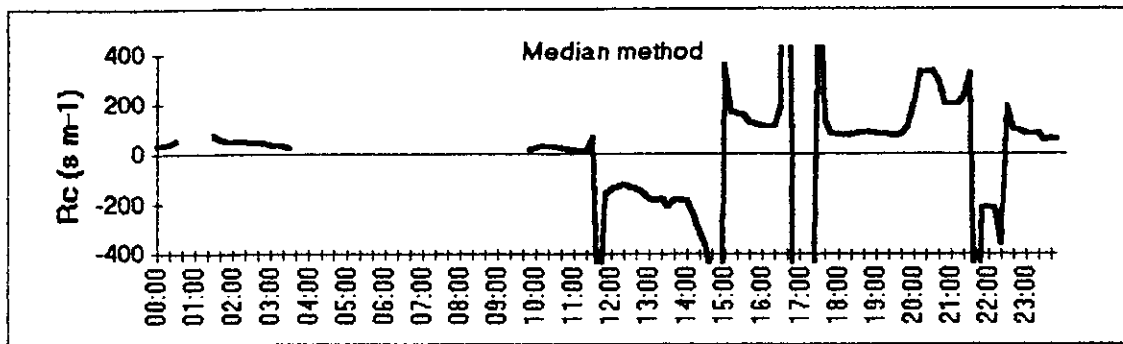
Thus, during the first part of the day (7:00 til 12:30 BST), emission occurred. It might be due either to a local source (sheep ?) or to a similar process than these observed the 24th and the 25th of April. There, L is low and show light unstable conditions. But dry conditions were recorded, corresponding to a sudden peak in evaporation (see latent heat fluxes profile).

During the last part of the day, deposition occurred, due to convection mechanism ($T\{Z_o\} > T\{1m\}$). Just a short period of rapid ammonia deposition was noted about 21:30 (BST), due to higher instability and dewfall.

Course of ammonia exchange and environmental conditions over time Great Dun Fell 2/05/93 :

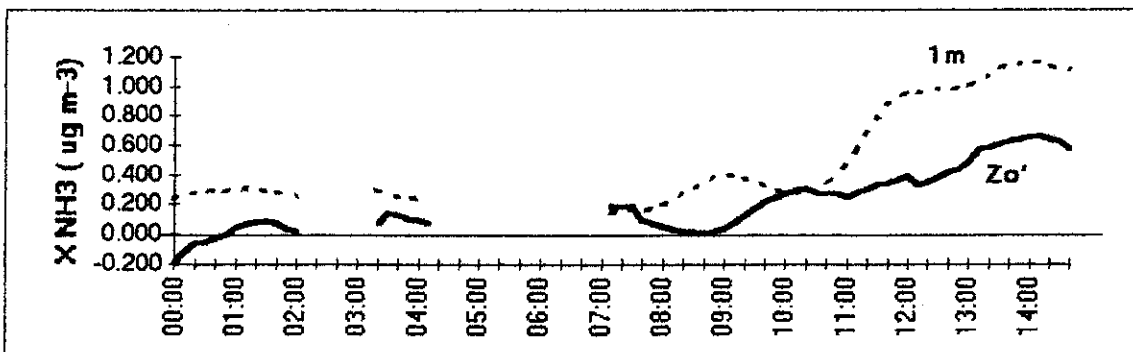
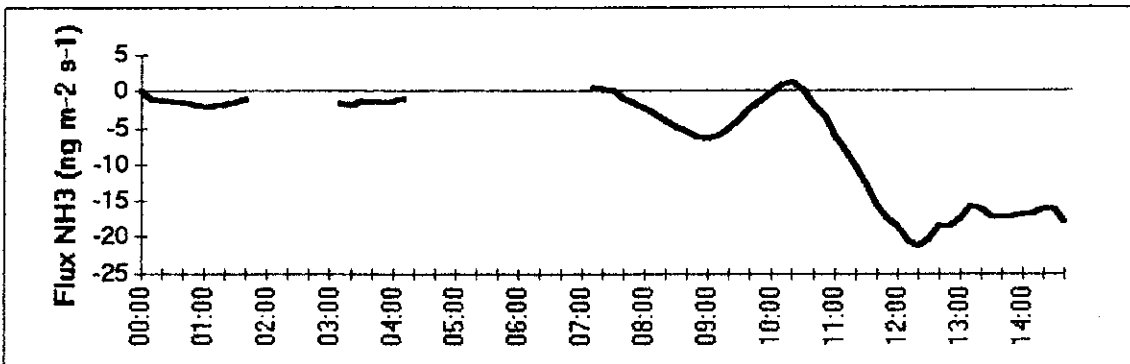
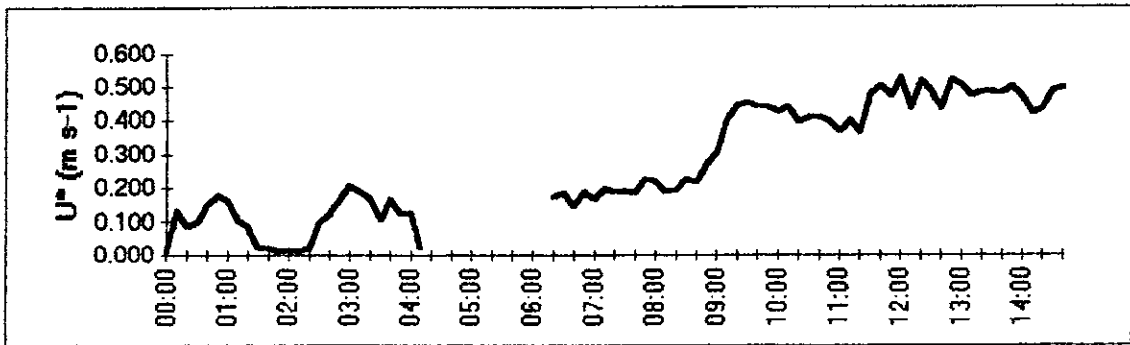
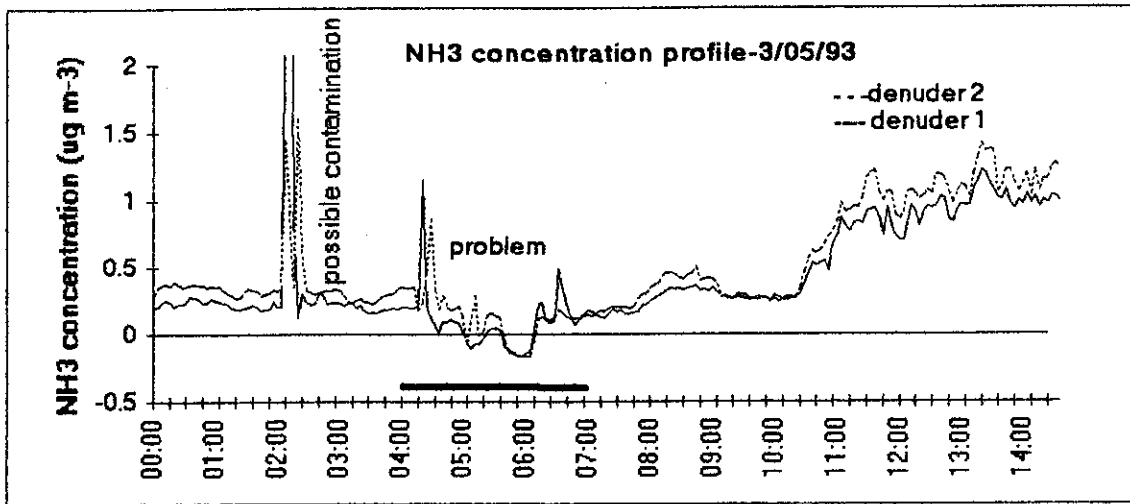


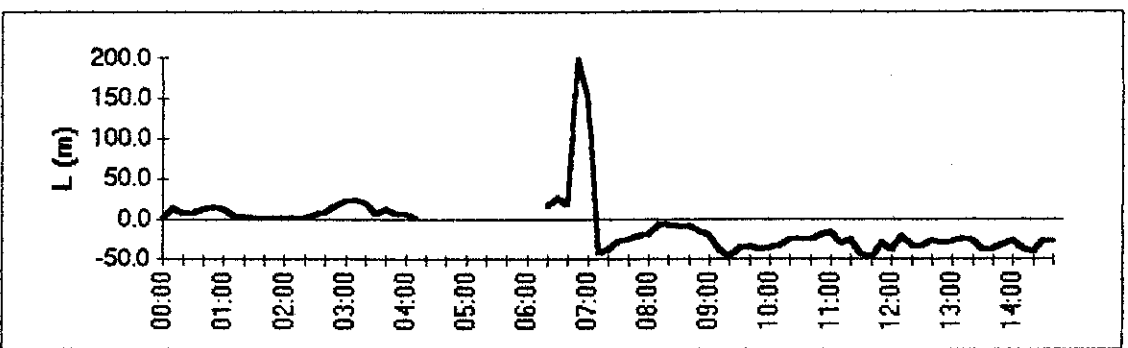
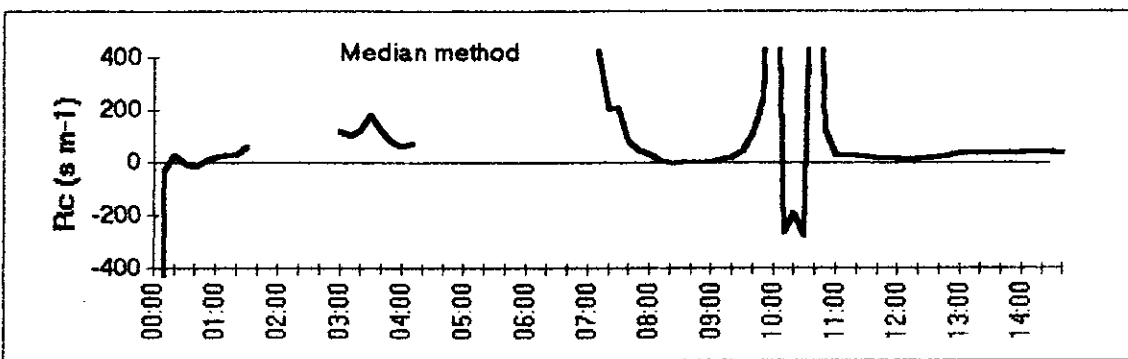
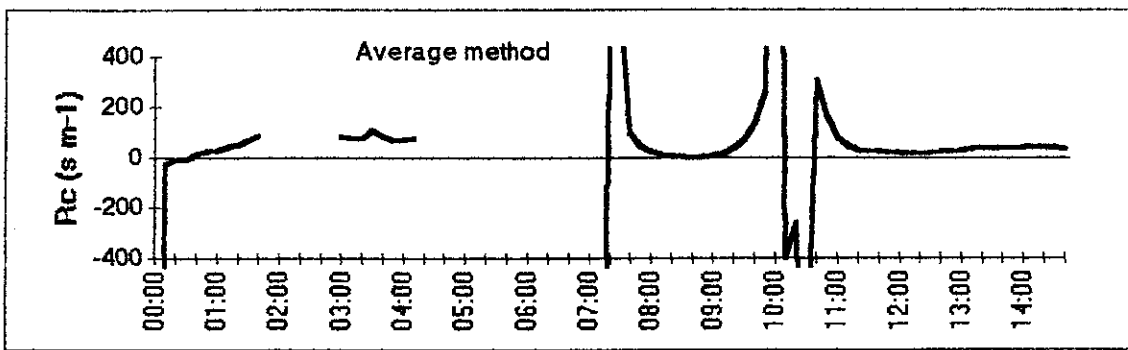
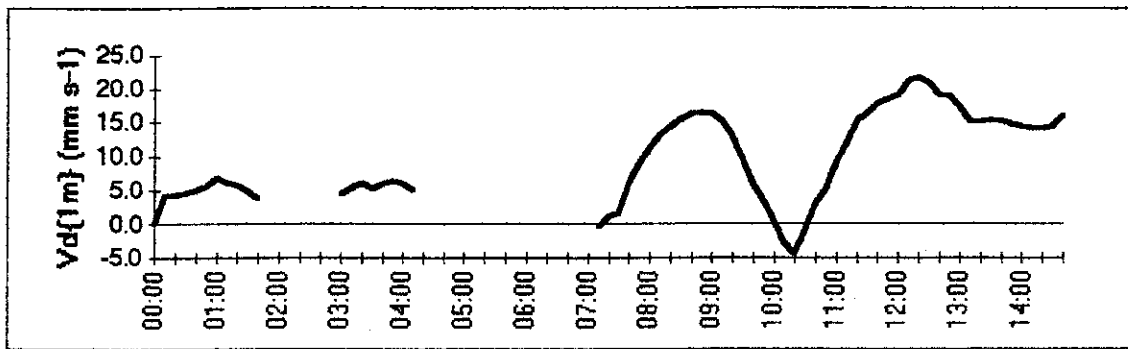


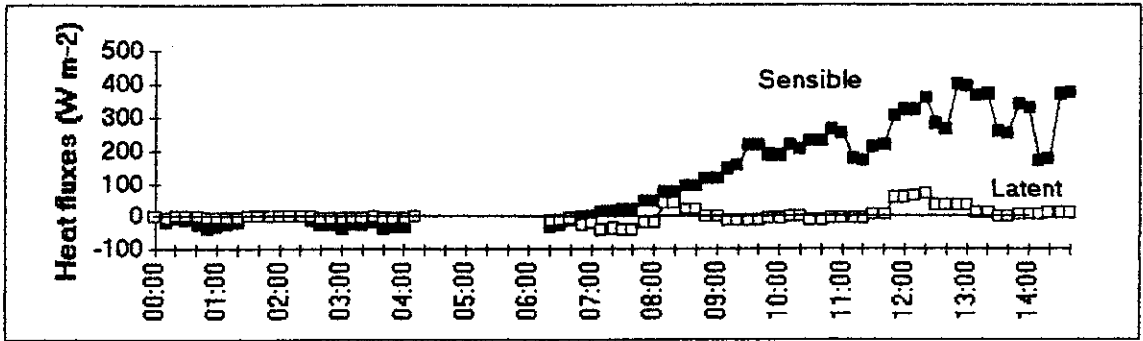
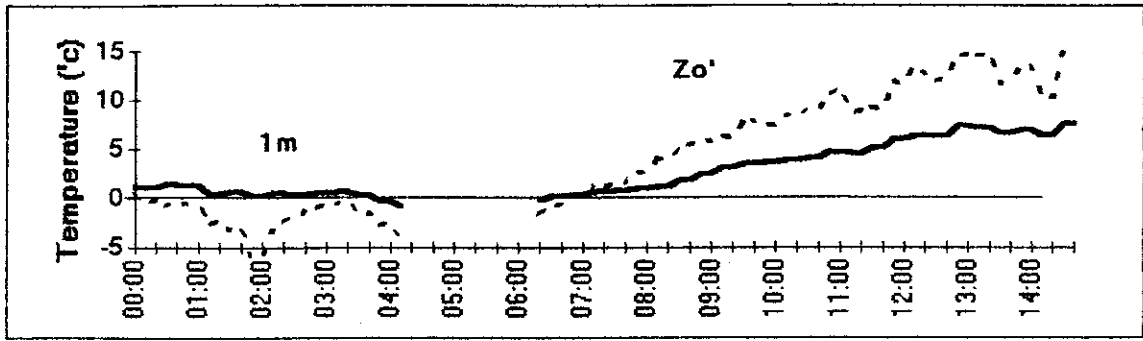


Still low air concentration in ammonia were recorded there (mean concentration : 0.499 $\mu\text{g m}^{-3}$). R_c values are lightly higher, due to colder temperature conditions. Both, emission and deposition occurred, with a very low U^* , which seems to confirm the trend to an equilibrium surface concentration into the leaf (regulating deposition/emission mechanism), when low air concentration in ammonia appear. Light unstable conditions were seen (L was low and $T\{Z_o\} > T\{1m\}$), and thus fluxes were due to convection.

**Course of ammonia exchange and environmental conditions over time at Great Dun Fell
3/05/93 :**



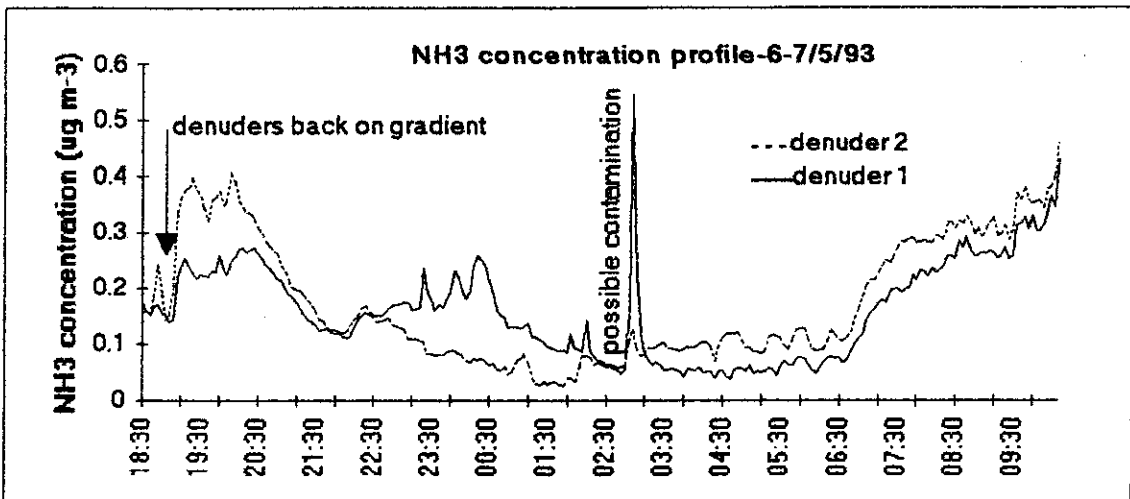


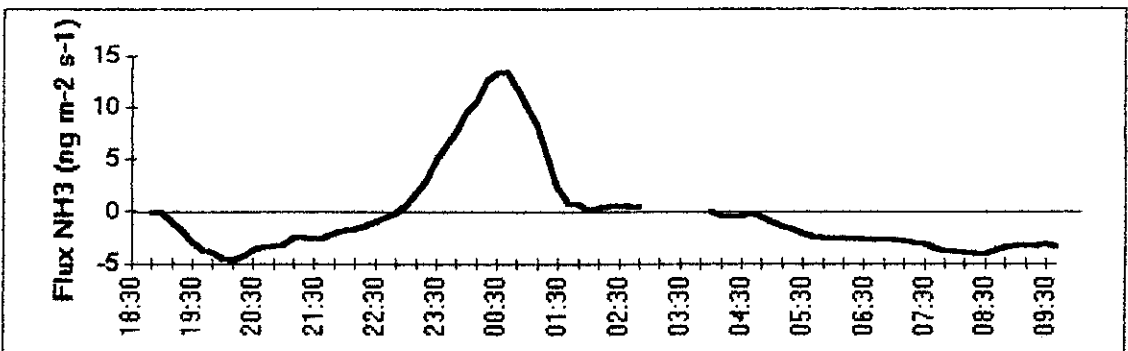
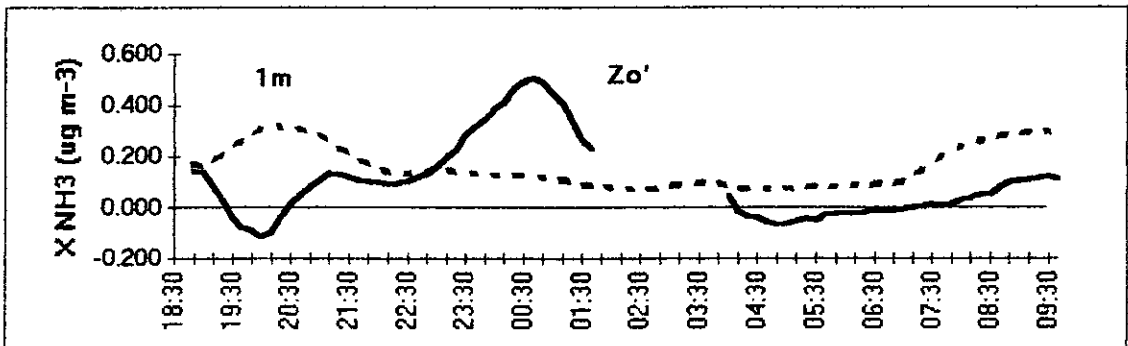
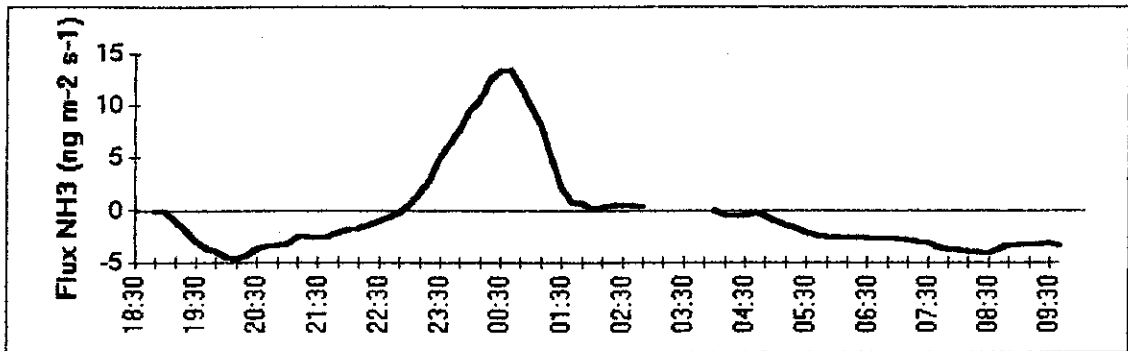
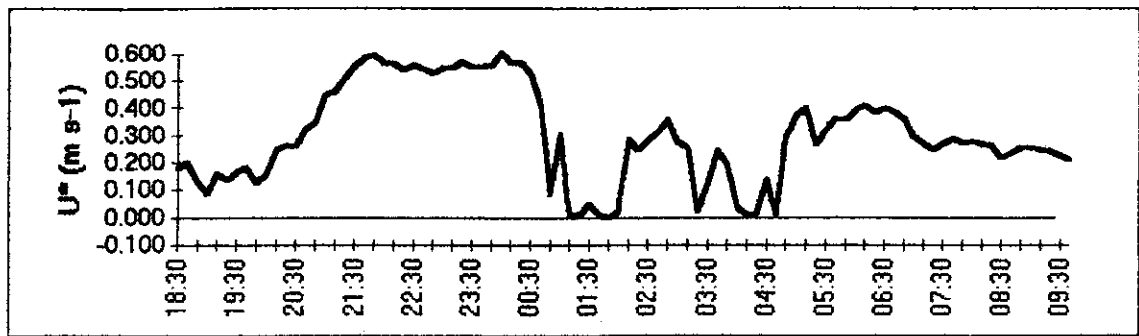


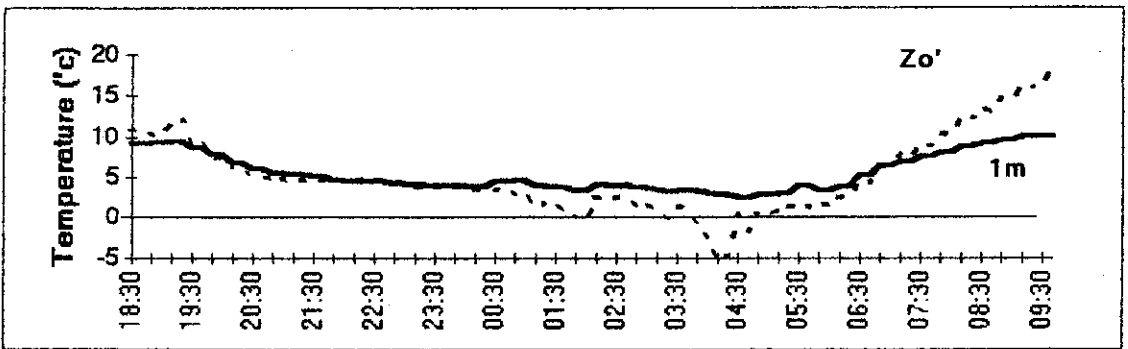
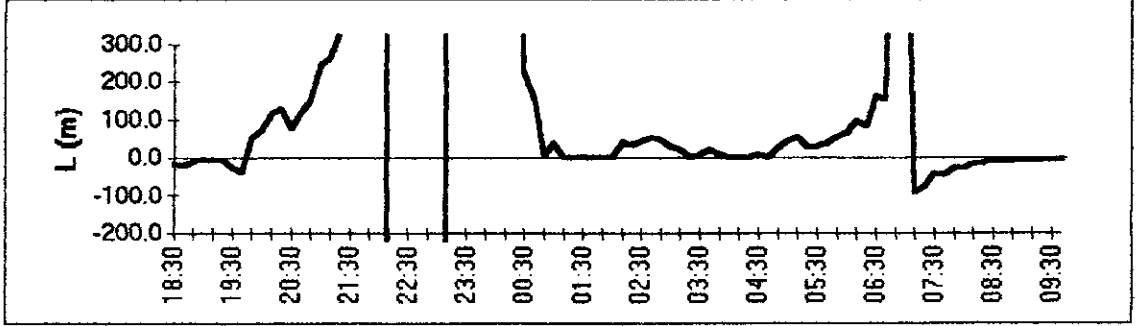
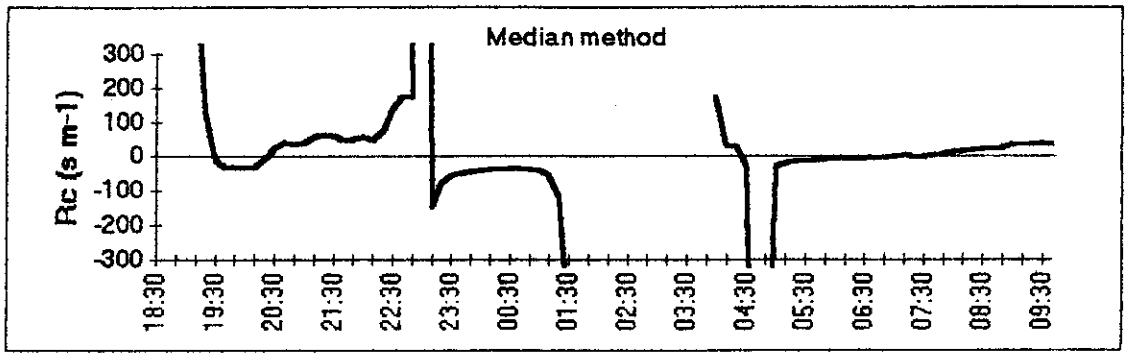
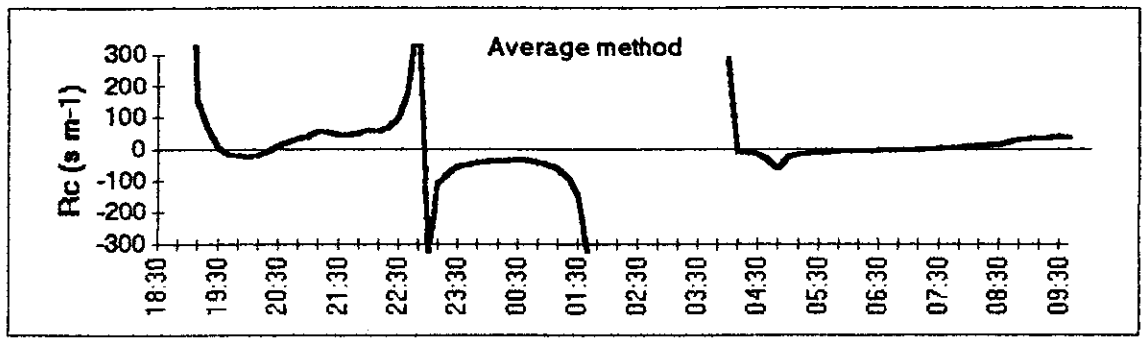
Very low U^* were recorded during the first part of the day (until 4:00 (BST)) as well as a great period of frost, which led to low values of NH_3 flux (mean flux : $-1.459 \text{ ng m}^{-2} \text{ s}^{-1}$) and deposition velocity (mean V_d : 4.6 mm s^{-1}). Then, following the increasing eddy velocity, flux and V_d were increasing. A big frost period occurred too, so that the rapid deposition observed at 00:00 must be not real. The evaporation, which was increasing at 8:00 (BST) then decreasing at 9:00 (BST), shows wet conditions.

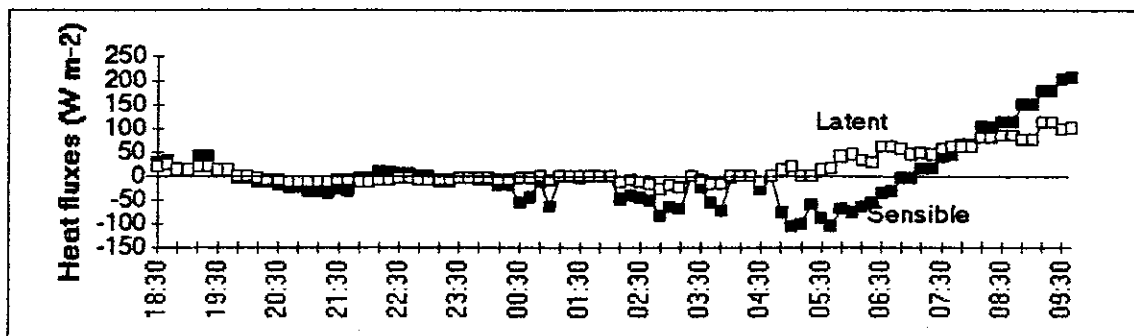
The low canopy resistance allows to say that the sink for the NH_3 was the surface roughness elements. However, during this deposition period, two short periods of emission occurred in the morning, when the air concentration in ammonia was still low.

Course of ammonia exchange and environmental conditions over time at Great Dun Fell 6-7/05/93 :









There, very low air concentrations in ammonia were recorded (mean value : 0.159 ug m⁻³).

Dealing with deposition, the values of R_c are very small, which shows, that deposition fluxes were limited by turbulence. However, rapid deposition periods occurred between 19:30 and 20:30 (BST) and between 4:00 and 6:00 (BST), during the dewfall period. The increasing deposition fluxes until 20:30 are due to the long period of stability ($L > 0$). After that period, between 00:30 and 7:00 (BST), another long period of stability occurred, as well as two short periods of frost.

At 22:30 (BST), fluxes were decreasing toward emission mechanism. The height of the emission peak is doubled due to U^* peak. During the emission period, sudden unstable conditions occurred. The sky was clear, with no evaporation from the canopy (stomata are closed at night).

At last, in the morning, a quick heating of the atmosphere was noticed, so that unstable conditions occurred again, leading to deposition due to convection.

DISCUSSION ABOUT GREAT DUN FELL RESULTS

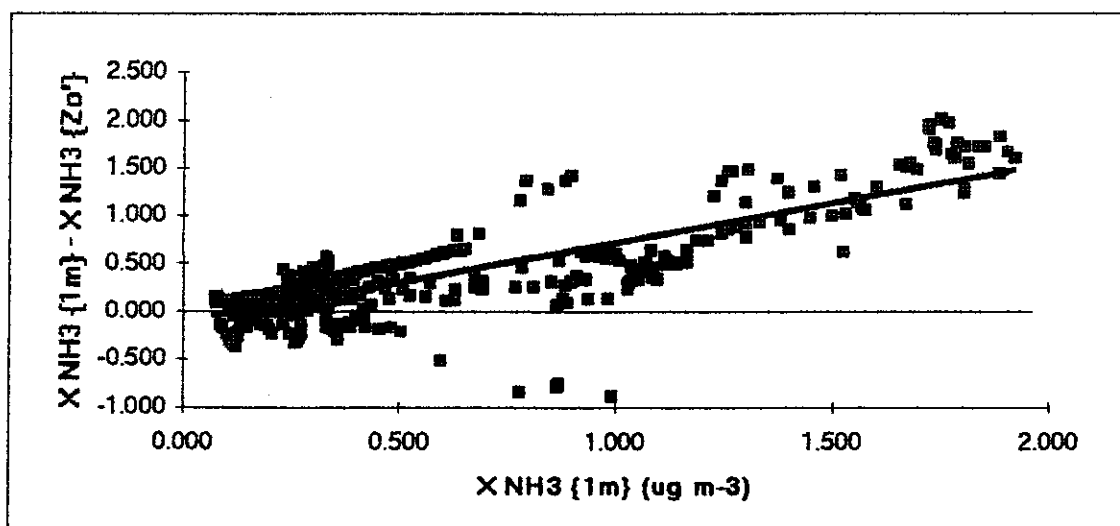
Over a natural and unfertilized ecosystem, the results here present a clear picture of rapid ammonia deposition (R_c was small even in dry conditions, so that deposition must be to the leaf surfaces) throughout the different period of fluxes measurements (according to the previous experiments).

In addition, with the present environmental conditions, short periods of ammonia emission were almost daily recorded, which was unusual over natural vegetation. Sutton, 1990, noticed that a none of his selection of sites was there any good evidence of ammonia emission (over the range of temperate conditions investigated) during the years of 1988-1989. But he used the filter pack system to measure air concentrations in ammonia. Given that this system measures atmospheric concentration every only two hours (compared to the ammonia analyzer every four minutes), one can understand the differences in precision between these two systems. Indeed, that is why in 1988 most of the time no emission was recorded, or when it was, it was considered as insignificant (compared to deposition mechanism).

$X\{Z_0\}$ represents the concentration in the air at the surface, which is presumably maintained by equilibrium with the surface. In this case, the deposition process would be dependent on air concentration, so that when air concentrations were above $X\{Z_0\}$, deposition would occur, and when they were below $X\{Z_0\}$, emission would occur.

Small values of $X\{Z_0\}$ are present, which is often more consistent than the values of R_c . At Great Dun Fell, for the month of March 1988, a mean $X\{Z_0\}$ of 0.09 ug m^{-3} was found in wet conditions. In 1993, in the experiment, mean $X\{Z_0\}$ was not clearly defined, because of the very low level of air concentration in ammonia, leading to an estimation of $X\{Z_0\}$ sometimes below zero.

The graph below shows when both deposition and emission occurred, following the air concentration in ammonia, using $[X\{1m\} - X\{Z_0\}]$ as the estimator of the exchange mechanisms. When deposition occurred, it is positive. When emission occurred, it is negative. The method using the flux measurement as estimator is given in Appendix 3.

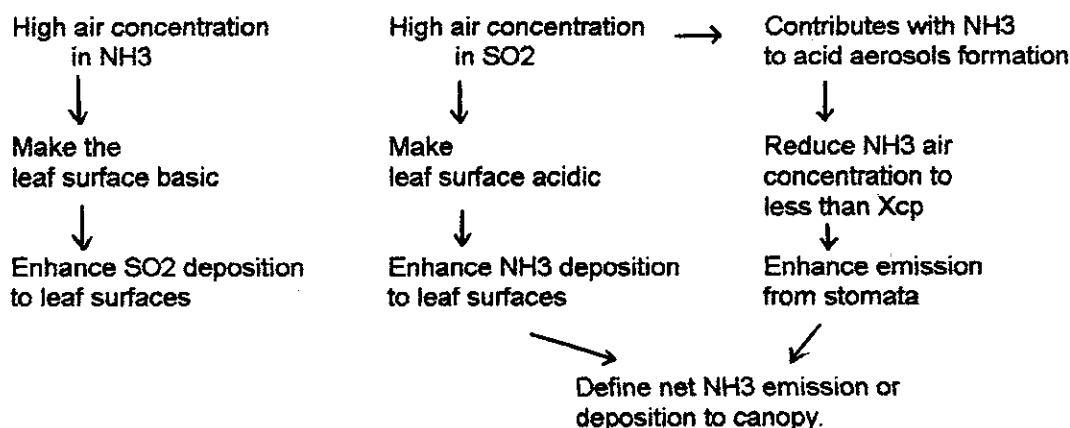


It confirms that emission periods are minority compared to deposition periods, even when low air concentrations in ammonia were recorded. To check the stomatal effect (the stomata resistance is higher at night, because the stomata are closed), graphs were made in order to divide night and day times (Appendix 4). A real difference appeared (excepted for the last period 6-7/5/93), showing an efficient effect of stomata status on emission process. But, however, more data are required, especially for the night time, and it has to be confirmed over other site and over different environmental conditions.

So, now, appears the idea of X_{cp} , the compensation point, even for unfertilized natural areas, only when low air concentration in ammonia are recorded. Its value was between 0.1 and 0.5 $\mu\text{g m}^{-3}$ during the experiment at Great Dun Fell site.

Thus, the X_{cp} found over this natural area could be treated as an usual compensation point over fertilized ecosystems.

A recent experiment about a possibility of an interaction between the deposition of NH_3 and SO_2 , over fertilized field (Sutton et al, 1993) shows the following effects :



To a large air concentration in SO_2 was associated a low air concentration in NH_3 (and conversely). From a large air concentration in SO_2 it might be anticipated that NH_3 (essential component of plant metabolism) would deposit rapidly.

However, at Great Dun Fell, where the air concentration in NH_3 was usually low, emission of NH_3 occurred sometimes both when high levels or low levels of SO_2 were recorded. So emission occurred, either following the mechanism of aerosols formation, when high SO_2 concentrations appeared, or reacting to a natural air concentration poor in nitrogen ($X_{1m} < X_{cp}$), when low SO_2 concentration occurred.

Thus, since no real anti-correlation between air concentration in SO_2 and NH_3 (especially the second week, where both were low) was observed, it is difficult to keep SO_2 factor as a determinant factor of fluxes direction at Great Dun Fell site in late April-early May 1993. Of course, it has to be deepened in some fluxes measurements over other unfertilized areas.

As noted by Sutton (1990), another point of interest is the effect of wetness/dryness and temperature, which promotes a small value of R_c and X_{zo} . They trend to occur together in the environment, with an increase in solar radiation causing both heating and drying.

For the first time, the use of an efficient temperature correction program (5% / °C) allows to deal with uniform data over temperature, which give a better view of the real exchange processes (and a better estimation of their dimensions) between the surface and the atmosphere.

In addition, the ammonia analyzer seems to allow a better approach in modelling of NH_3 exchanges between the atmosphere and the surface. It allows to make more often precise measurements, even if it needs power installation (restriction about the site, where the experiments have to take place) and much checkwork too (at present, it is as precise in measurements of air concentration in ammonia as sensitive to any trouble). Moreover, measurements can not be made during frost periods, because the ammonia analyzer stops in that case. So, if data will be required during frost period, it won't suit (although, at present, they are not studied as data of basic importance, except for R_c).

Some areas requires still further study. The more important ones deal with :

----> Canopy resistance, R_c (either for unfertilized surfaces in very dry conditions, or in frozen conditions).

----> The relative size of soil and plant compensation points for fertilized agricultural and unfertilized natural ecosystems.

----> The importance of surface wetness/dryness and temperature in controlling the bi-directional exchange.

----> The concentration of NH_3 in the atmosphere.

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APPENDICES

Contents

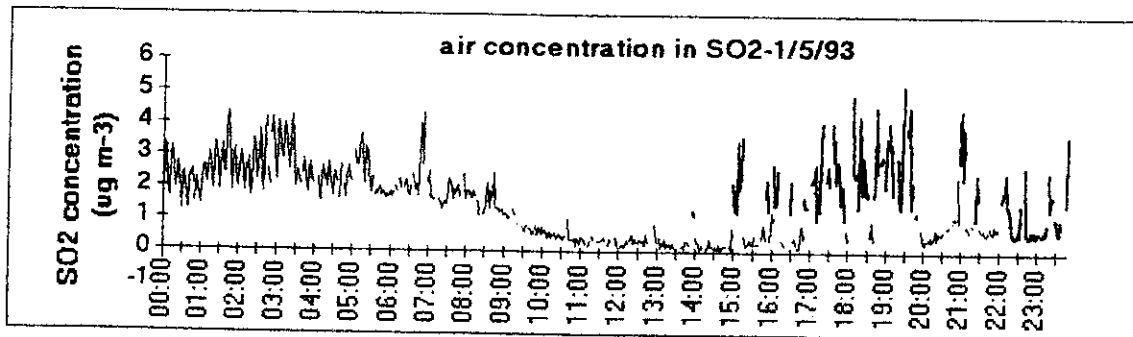
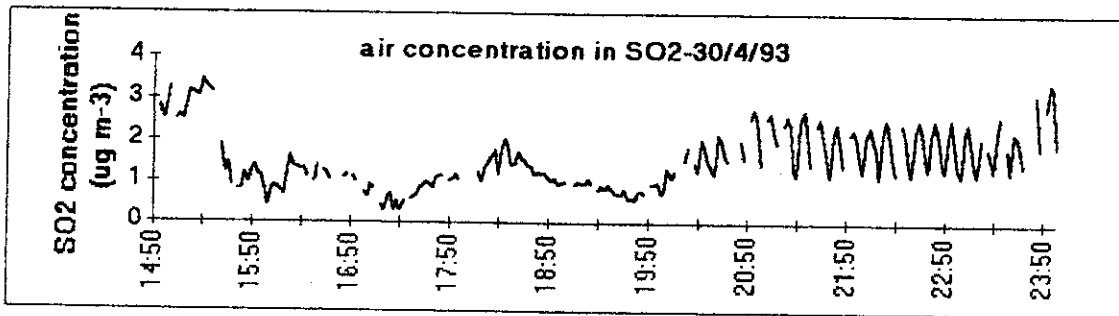
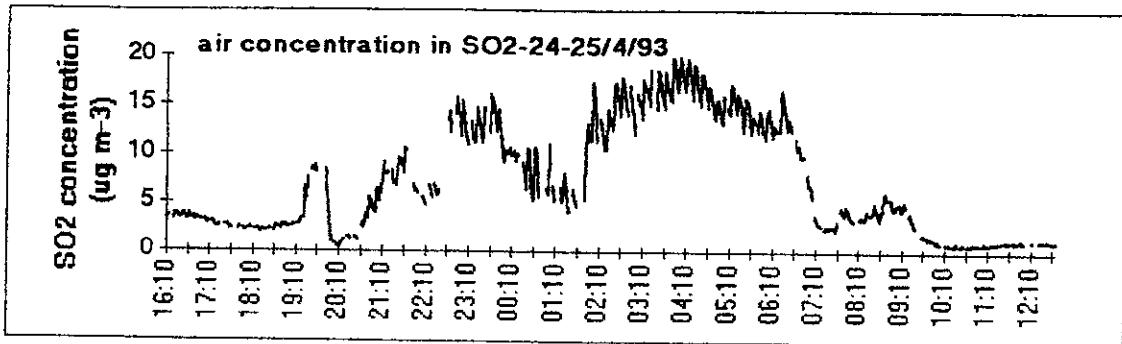
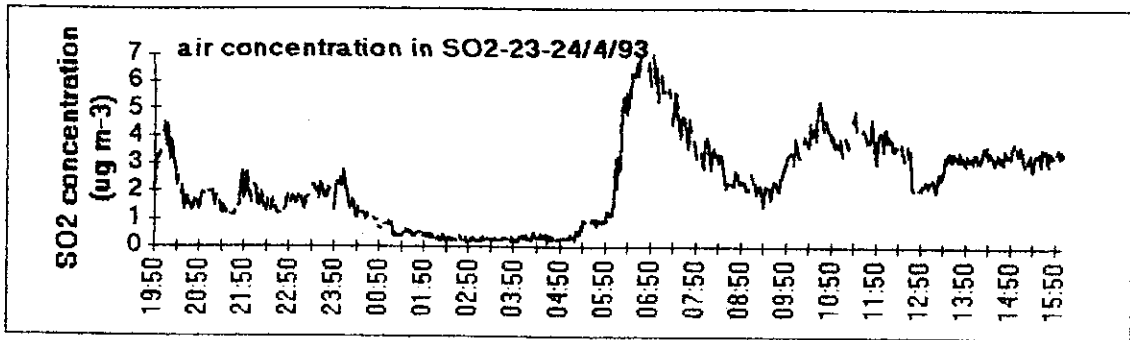
Appendix 1 : Air concentration in SO₂ during the periods of fluxes measurements at Great Dun Fell - 21/4-7/5/93.

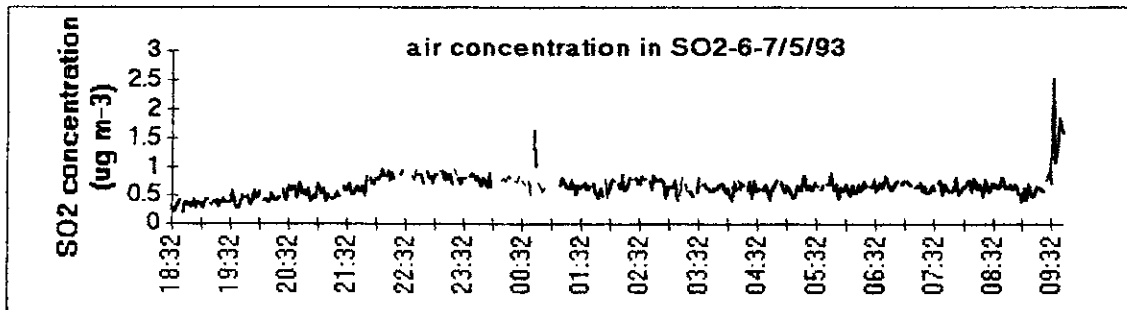
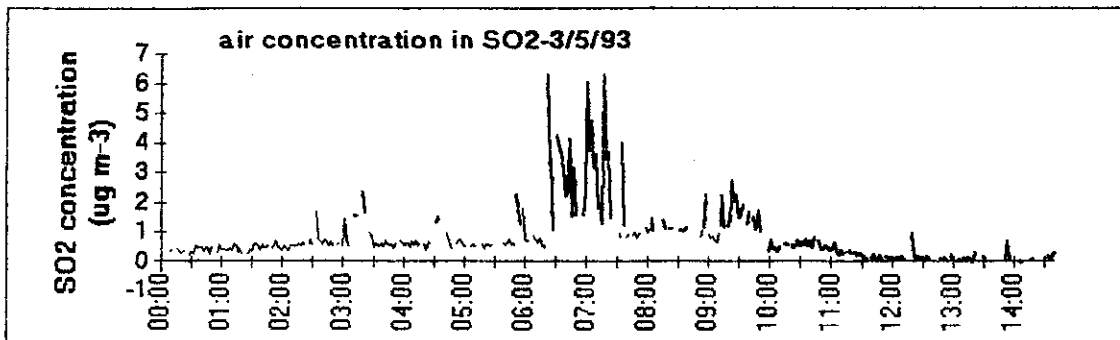
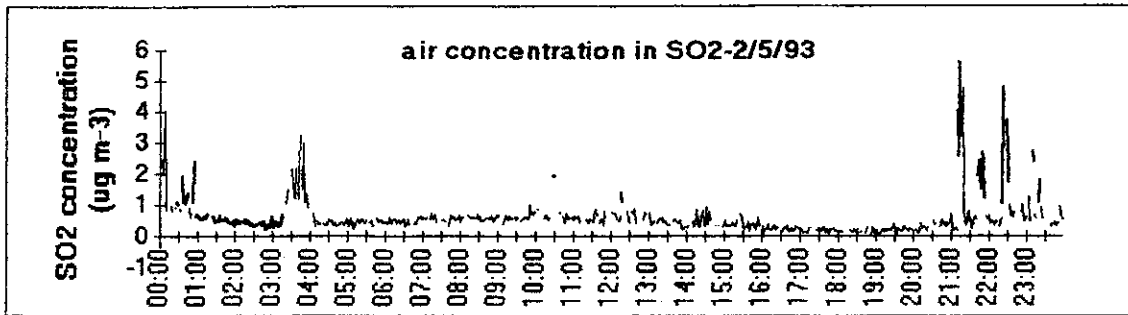
Appendix 2 : Profiles of [C / E], part of latent Heat fluxes compared to sensible Heat fluxes at Great Dun Fell, during the periods of fluxes measurements - 21/4-7/5/93.

Appendix 3 : Graph about the use of Flux NH₃ measurements at Great Dun Fell to estimate the exchange mechanisms, following the air concentration in ammonia.

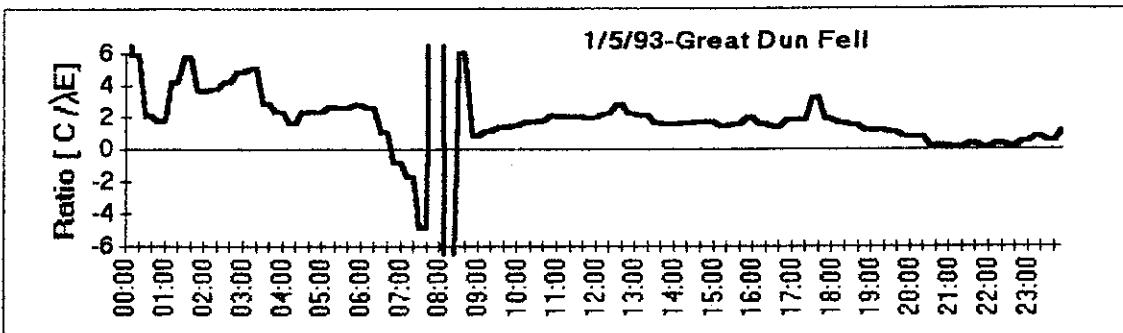
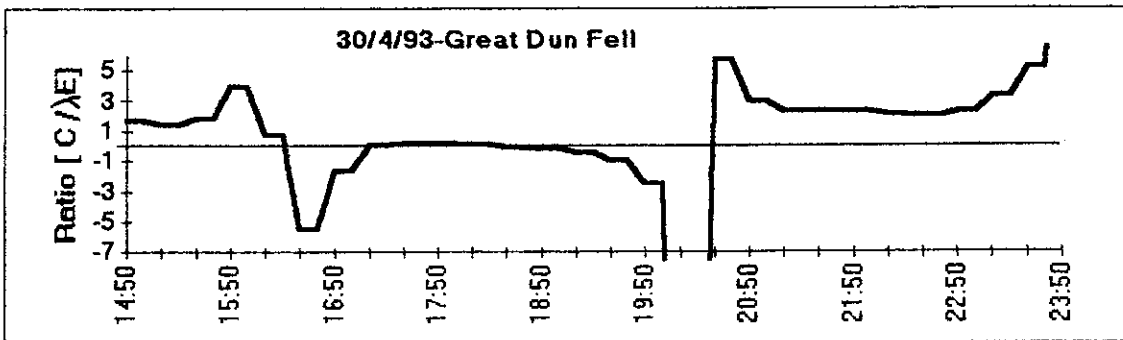
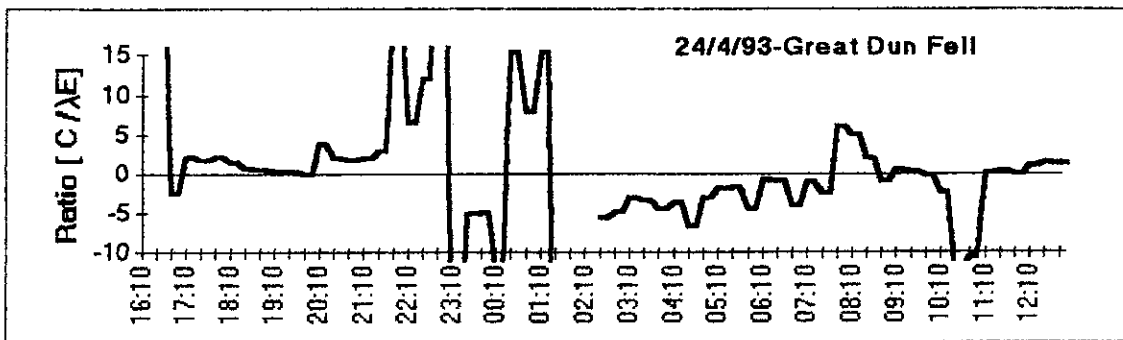
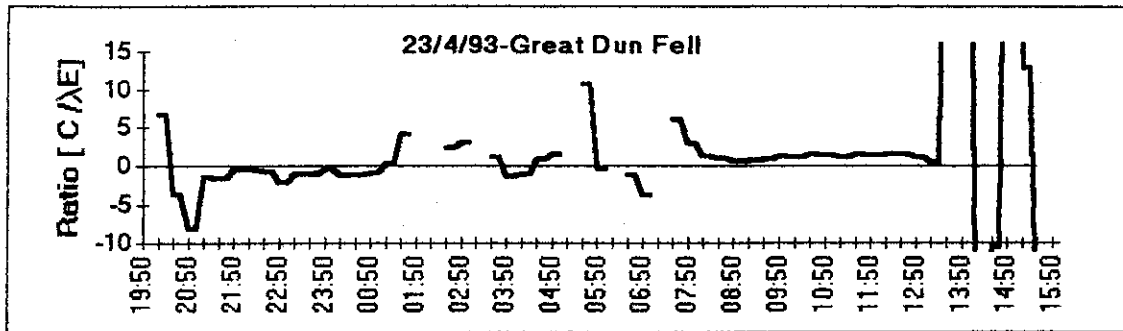
Appendix 4 : Graphs about exchange mechanisms, following the air concentration in ammonia, using $[X\{1m\} - X\{Z_0\}]$ as an estimator (day time-night time).

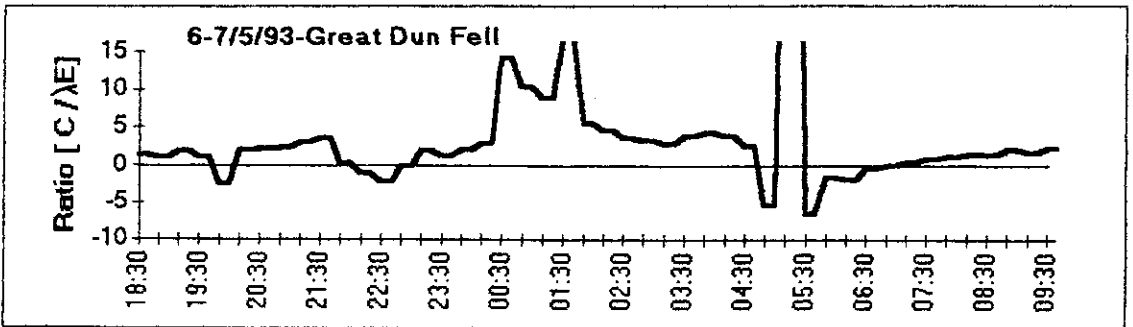
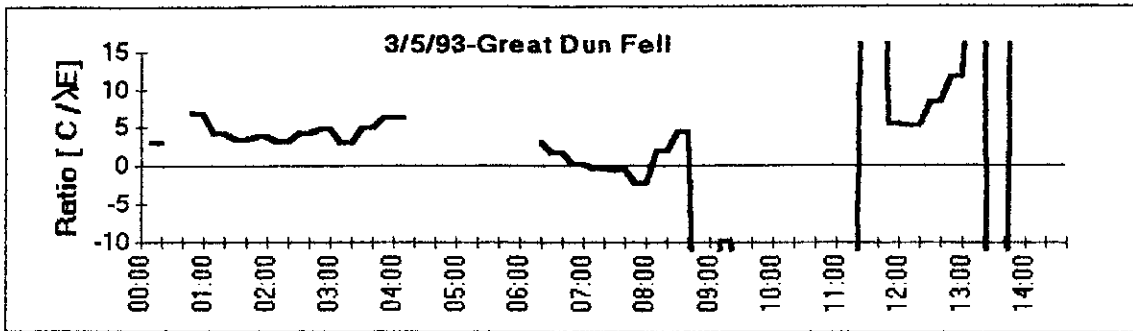
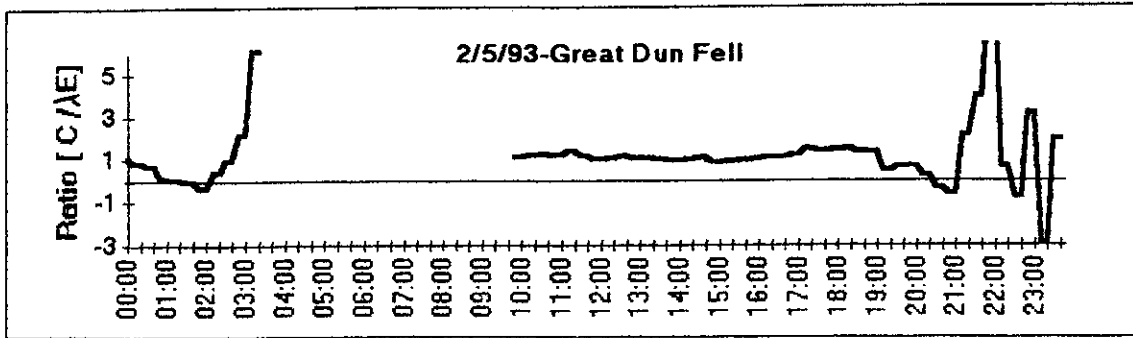
Appendix 1: Air concentration in SO₂ at Great Dun Fell- Avril-May/1993



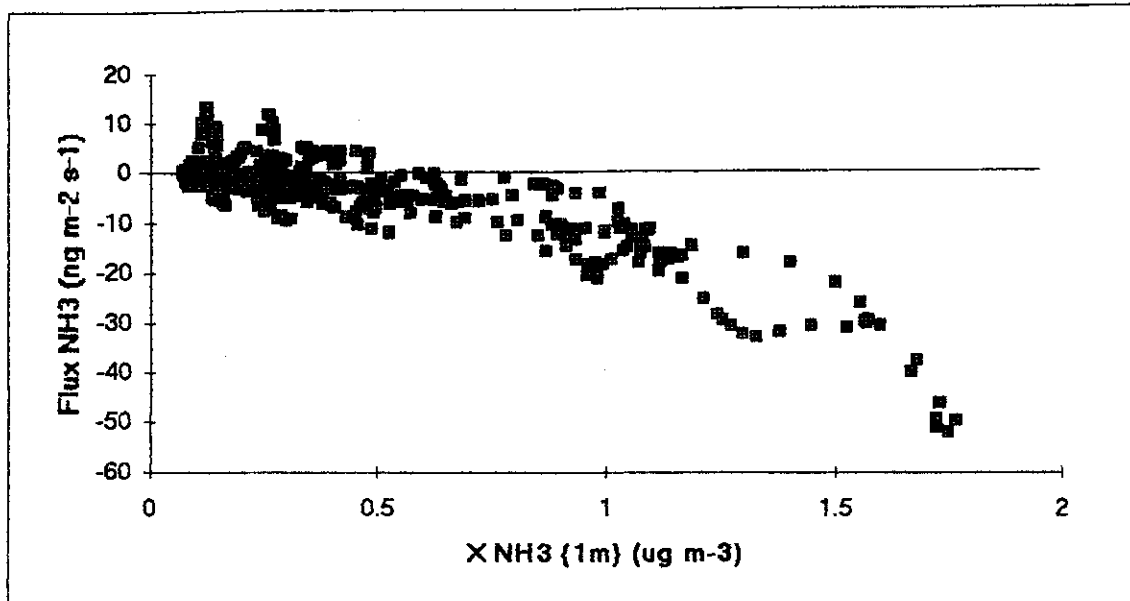


Appendix 2: Part of latent Heat fluxes compared to sensible Heat fluxes over the periods of fluxes measurements- April-May 1993.





Appendix 3 : Use of Flux NH₃ to estimate the exchange mechanisms, following the air concentration in ammonia.



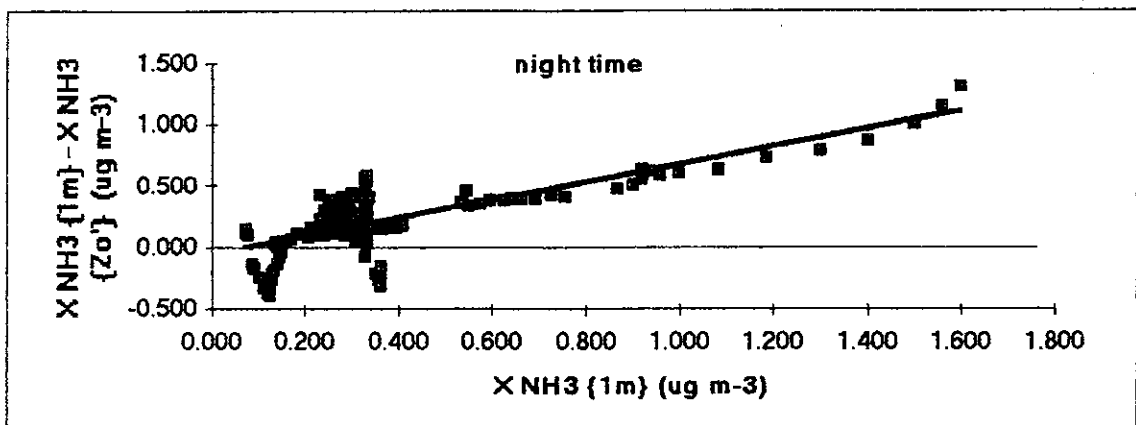
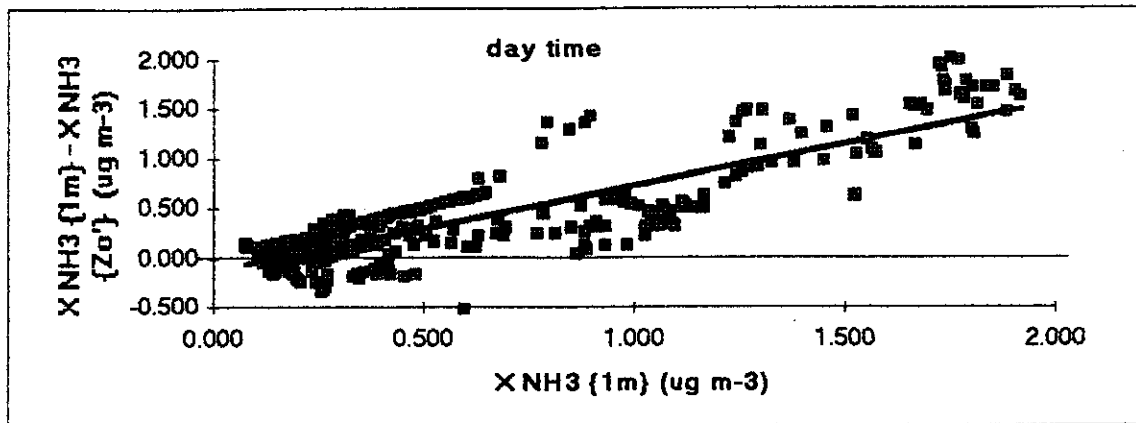
No significant differences with $[X\{1m\} - X\{Z_0\}]$ estimator are observed, except for a higher scattering for the points, which was expected, due to the higher values of Flux NH₃ (compared to the values of concentration).

A similar result is found :

---> deposition occurred most of the time, even for low level in air concentration.

---> X_{cp} might be between 0.1 and 0.5 ug m⁻³.

Appendix 4 : Use of $[X\{1m\} - X\{Z_0\}]$ as an estimator of exchange mechanisms, following the air concentration in ammonia. Day time-Night time.



During the day time, both emission and deposition mechanisms occurred, with a greater frequency for deposition periods.

During the night time, deposition periods occurred. For the only emission period, which occurred during the last night, it is more suspicious. It might due either to an emission from soil, to an emission from only the leaves surfaces, or at last to an error in measurements. In addition, more data are required for the period of night time (it was assumed that the night time was between 22:00 and 5:00 (BST) during the period of fluxes measurements).