Testing and improvement of passive diffusion tubes for the determination of atmospheric ammonia (NH_3)

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Abstract

Ammonia concentrations were measured with Radiello® diffusion tube passive samplers around a pig farm situated on the Swabian Alb plateau. Ten sites were selected along the prevailing wind direction with a maximum distance of ~830 meters and in the near vicinity of the pig farm. Ammonia concentrations decreased according to a logarithmic function from the emitting origin to the sample sites with increasing distance. Wind direction data was collected on-site to interpret gradient variations. The aim of this study is to test the method to measure ammonia in the atmosphere using Radiello® diffusion tube passive samplers and to identify potential improvements.

Keywords: Ammonia; Emissions; Diffusion tubes; Concentration gradient

Introduction

Ammonia emissions originating from agriculture, especially from livestock farming have raised an intensive political discussion in the last years. Ammonia (NH_3) and its conversion product ammonium (NH_4) present one of the most important air pollutants which have adverse effects on ecosystems. According to Stroh and Djeradj (2007) ammonia emissions in Germany were about 765000 t in 1990 and decreased to 624000 t in 1999. Agriculture is with around 95% the main driver for ammonia emissions. Pig farming accounts for 22% of the ammonia emissions from agriculture (Figure 1).

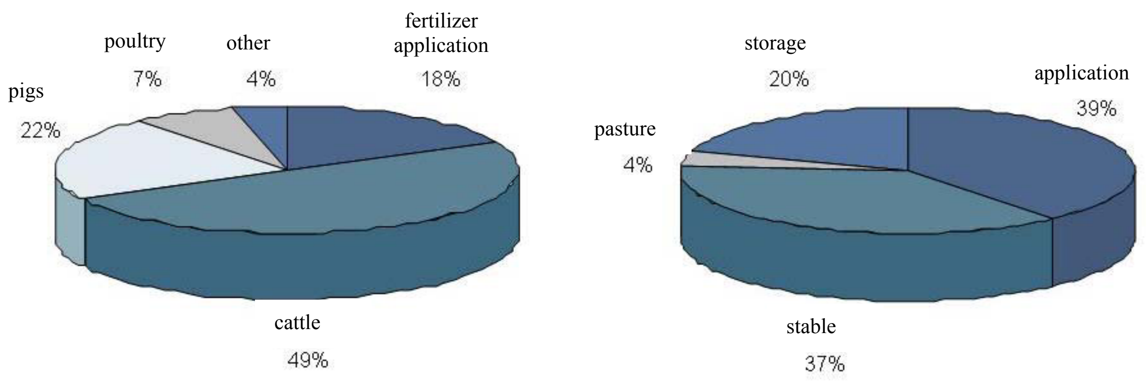


Figure 1: NH_3 emissions from agriculture (left) and livestock farming (right)

source: Stroh & Djeradj (2007)

Mode of action

The retention time of ammonia in the atmosphere is relatively short and so the transport of atmospheric NH_3 is restricted to short distances and it is therefore usually deposited in the near vicinity of the emitter. Most of the ammonia rapidly reacts with water and other compounds in the atmosphere to form the dissolved ion or ammonium salt (NH_4). Ammonia and ammonium deposition may cause serious problems to ecosystems in many different ways.

They cause acidification and eutophication in terrestrial and aquatic ecosystems, leading to forest decline and changes in ecosystem composition, -structure, -function (Dämmgen and Erisman, 2005) and nutrient dynamics. Ammonia emissions may also cause direct damage to vegetation which grows next to large livestock farms (Stroh and Djeradj 2007). At the same time, ammonia is having an increasing contribution to the formation of particulate matter, with its associated human health risks (Sutton et al., 2009). According to Stroh and Djeradj (2007) 80% of natural and near-natural ecosystems in Germany were prone to acidification in 1990. It is estimated that NH_3 will be the largest single contributor to each of acidification, eutrophication and secondary particulate matter in Europe by 2020, which is particularly a reflection of the success of European policies to reduce SO_2 and NO_x emissions (Sutton et al., 2009). Therefore reducing ammonia emissions and the associated environmental impacts remain major challenges for the future.

Legal background

The current critical levels (CLE) for NH_3, defined as "the concentration in the atmosphere above which direct adverse effects on receptors, such as plants, ecosystems or materials, may occur according to present knowledge" (Posthumus, 1988) for different averaging times are currently as follows: for 1 hour 3300 µg NH_3 /m³, for 1 day 270 µg NH_3 /m³, for 1 month 23 µg NH_3 /m³ and for 1 year 8 µg NH_3/m³.

According to these CLEs, an average atmospheric ammonia concentration of 8 µg NH_3/m³ over the whole year will have no adverse effects on receptors. However, new information exists that CLEs will have to be reduced to levels as low as 3µg/m³ (Sutton et al., 2009). In order to reduce the environmental impacts of ammonia emissions, several measures and regulations were introduced on a national and international level: the National Emission Ceilings (NEC) of the EU deals with the national maximum amount for ammonia emissions. The goal of this regulation is to halve the area where critical loads, which are defined as "a quantitative estimate of deposition of one or more pollutants below which significant harmful effects on specific elements of the environment do not occur according to present knowledge" (Posthumus, 1988) are exceeded. Therefore NH_3 emissions in Germany should be reduced to 550000 t. The federal ambient pollution control act (Bundes-Immissionsschutzgesetz BlmSchG) is responsible for the construction and operation of subjects/stables, which have to be officially approved due to their possible emissions. These targets are concretized in the so called "TA Luft". It determines minimum distances for newly built stables to the next residential area to avoid odour nuisance through NH_3.

These regulations indicate that there is a NH_3 problem in Germany, which is mainly due to livestock farming. The emitted NH_3 concentrations from livestock are important for the implementation of further actions/ conditions, like the above mentioned minimum distances to residential areas. To monitor ambient NH_3 concentrations, the Radiello® passive samplers could be an adequate option.

Related studies

As these Radiello® passive samplers have been developed only in the mid 1990s, the scientific usage is still limited but its usage is increasing in the last few years. Frati et al. (2007) worked with lichen biomonitoring of ammonia emissions around a pig farm and used the Radiello® passive samplers to measure the real NH_3 concentrations. According to Frati et al. (2007), the NH_3 concentrations were negatively correlated with the distance from the pig farm, according to a logarithmic function. The method seemed to be adequate for their project. In another study, Sommer et al. (2009) used passive diffusion samplers to validate a Danish model which monitors NH_3 transport, dispersion and deposition from and in the neighbourhood of a poultry farm. The passive diffusion samplers were used to provide long-term mean values of the NH_3 concentration in different directions and distances from the farm similar to our investigation concept. In this study there was also a clear tendency for decreasing concentrations with increasing distance from the farm.

Goal setting of this study

The aim of this study was to test a method to measure NH_3 emissions using Radiello® diffusion tubes around a pig farm and to identify method improvements if necessary.

Materials and methods

Investigation area

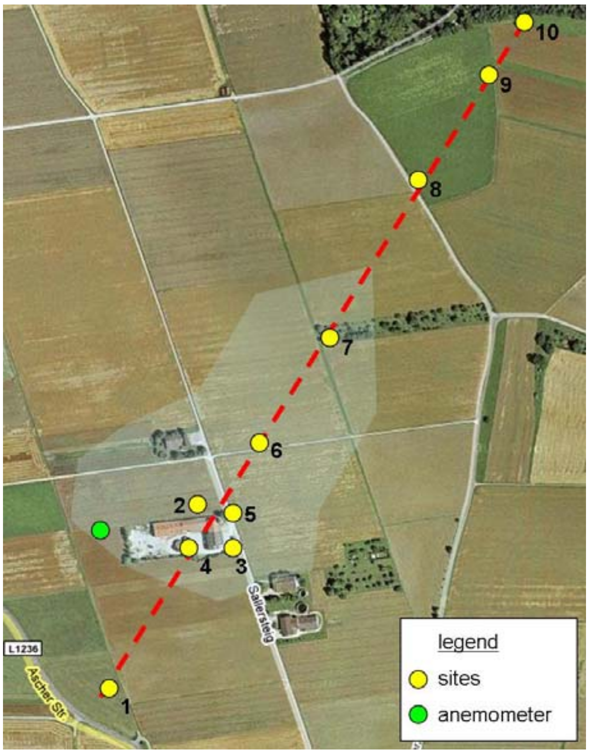
The pig farm around which ammonia emissions were measured is situated near the village “Blaustein-Wippingen” which is close to the city of Ulm on the Swabian Alb. Blaustein-Wippingen is located at an altitude of 646 m above sea level. The climate is moderately cool with an average yearly temperature of 7°C and an amount of precipitation of 965 mm per year. The main wind direction is south-west. The climate data is taken from the meteorological station “Laichingen” [2] which is 10-15 km away from the investigation area. The pig farm is situated in the north of Blaustein-Wippingen (Figure 2). During the time of the investigation, there were 1200 pigs in the stable. The stable has forced ventilation and is therefore categorised as a “warm stable”. It has both full and partly slatted floors, where the slurry (liquid manure) is stored.

Figure 2: Location of the pig farm

Experimental set up

In the vicinity of the pig farm, ten measurement sites were selected. On each site, a plastic box was fixed on a metal pole at a height of 1.2 meters. The plastic box is composed of several parts and it is open on two sides to ensure an undisturbed air flow. Each box contained two Radiello® diffusion tubes, which were exposed in each case over a time period of 14 days. The measurement sites one, six, seven, eight, nine and ten were located according to the main wind direction which is brightly highlighted in Figure 3, while the sites two, three, four and five were situated around the farm (Figure 3).

Site two is right beside a window of the pig stable and therefore seen as a major emission origin. Site four is located in a kind of courtyard, shielded by two farm buildings in the north and east of the site. Site three is located south-eastwards of the farm buildings and the emission origin. The difference in altitude between the sites is about 13 meters. While there is a slight and nearly constant increase in altitude from site one to seven, a significant decrease in altitude follows from site seven to ten, in front of a forest (Figure 4).



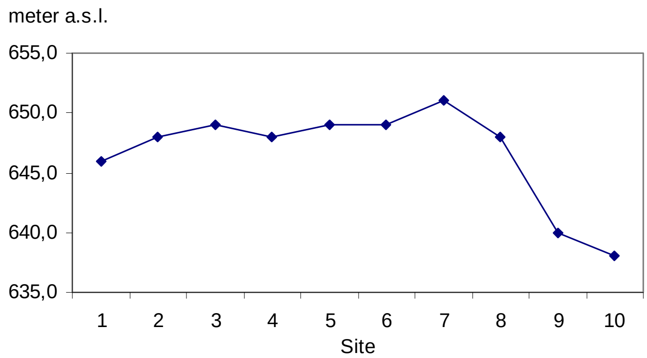


Figure 3: Location of the measurement sites

Figure 4: Altitude of the sites (cross country tread)

Altogether the measurements were carried out over a time period of 14 weeks, from 24.11.2007 to 29.02.2008, resulting in seven measurement series of two weeks each.

Ammonia measurements

Ammonia emissions were measured with Radiello® diffusion tubes, distributed by Sigma-Aldrich and developed by FSM (2006). Such a Radiello® diffusion tube consists of two compounds: a diffusive and an adsorbing body (Figure 5).

The diffusive body is a cylindrical tube with a diameter of 5.8 mm and a height of 60 mm. It is made of porous polypropylene which is permeable for gases. Inside the diffusion body, the

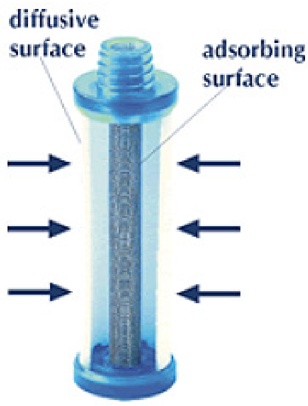


Figure 5: Radiello® diffudion tube

adsorbing body is located. It consists of a cartridge impregnated with phosphoric acid, where ammonia is chemically adsorbed as ammonium ion. Airborne ammonium salts dispersed as particulate matter do not cross the diffusive membrane of Radiello® diffusion tubes (FSM, 2006). The adsorbing body is stored air-tightly and inserted into the diffusion body just before the measurement starts. Due to the symmetry of these passive samplers, the ammonia can access the adsorbent material throughout the 360° surrounding diffusive body resulting in a relatively high uptake rate[1] and yielding exact results. Two diffusion tubes were exposed in parallel in each measuring station.

Wind measurement

In addition to the Radiello® diffusion tubes, a so called "Wölfle" anemometer, produced by Lambrecht (Germany), was also installed at a height of 2.5 meters. The location of the anemometer was west of the pig farm (Figure 3). This anemometer recorded mechanically the wind direction. The information was plotted on a strip of paper, which had to be changed every 30 days. Due to the mechanical method of recording, there were some periods of failure, where no data was plotted.

Measurement principle of Radiello® diffusion tubes

The ammonium ion is quantified by visible spectrometry as indophenol: at basic buffered pH the ammonium ion reacts with phenol and sodium hypochlorite, with pentacyanonitrosylferrate catalysis (in the following cyanoferrate), to form indophenol. The reaction product is intensely coloured blue, and its absorbance is being measured photometrically at 635 nm.

Calculation of concentrations

The concentration C in $\mu g \cdot m^{-3}$ is obtained according to the equation:

$$C = 0{,}944 * \frac{m}{235 * t} * 100000$$

m = mass of ammonium ion in µg found on the cartridge
t = exposure time in minutes
0.944 = is the numerical factor necessary to convert the ammonium ion into ammonia.

Analysis

After the adsorbing bodies of the Radiello® diffusion tubes were removed each of them was stored separately in a reclosable tube. The amount of the adsorbed ammonium was quantified by first adding 10 ml of deionised water to the tube and then stirring it for at least 15 seconds, to bring the adsorbed ammonium into solution. After that, 1 ml of the solution was pipetted into another tube along with 0.4 ml of phenol solution, consisting of 10 g of phenol in 100 ml of ethanol. Furthermore 0.4 ml of cyanoferrate solution were pipetted into the tube, consisting of 0.5 g sodium pentacyanonitrosylferrate dihydrate (Na2Fe(CN)5NO·2H2O) dissolved in 100 ml of water plus a few drops of 10% NaOH. Finally 5 ml of buffer solution, consisting of 1.1 g NaOH and 3.04 g of $NaHCO_3$ and 1

ml of oxidising solution, consisting of sodium hypochlorite with 1% of active chlorine in 0.2 M NaOH were added to the tubes.
After these components were added, the mixture was allowed to settle for at least one hour and then the absorbance of the solution was measured at 635 nm. Deionised water was used to zero the spectrophotometer.
NH_4^+ calibration curves were prepared every day when samples were analysed using ammonium chloride standards in the range from 0.5 to 50 mg/l to calibrate the photometer and to ensure the correctness of the absorption values measured by the photometer.

Results

As the adsorbing bodies of the Radiello® diffusion tubes were changed every 14 days, the results are consequently presented for the individual bi-weekly time series.
For the illustration of the results, a set of five figures is used. The first two graphs show the measured ammonia concentration at each of the ten sites, once within a topographical map, showing the exact position of the different sites and the measured ammonia concentrations and once in a simple bar chart.
The first graph in the second line shows the ammonia concentration as a function of the distance to the emitting pig stable.
The next graphs illustrate the NH_4^+ calibration curves produced for the corresponding analytical sample investigation of the particular time series.
The final graph shows the wind rose, indicating the mean daily wind direction values for all days in the particular time series.
The table illustrates the average climatic data like temperature, precipitation and wind speed, measured at the meteorological station in Gerstetten [3], 30 km away from Blaustein Wippingen.
The full set of five figures is presented in the following only for series one. For series two to seven, only three selected figures are presented.

Series 1 (24.11.2007 – 09.12.2007)

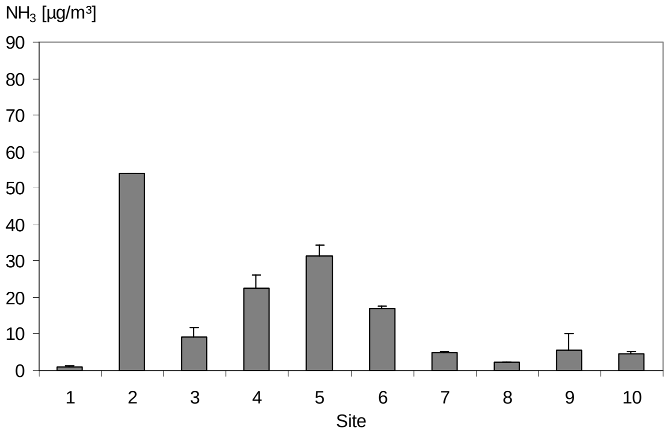


Figure 5: Mean ammonia concentrations measured in series 1
Error bars = standard deviation over two parallels

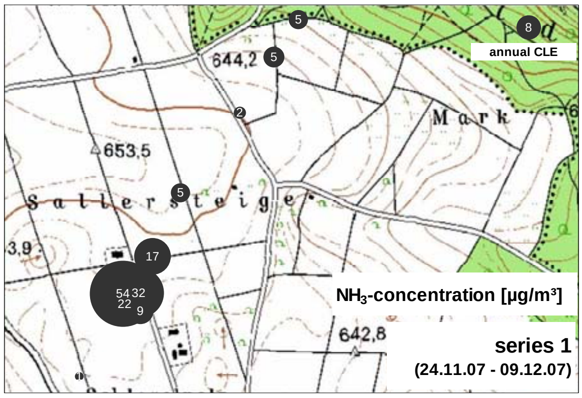


Figure 6: Site localisation and measured ammonia concentrations [µg/m³] in series 1

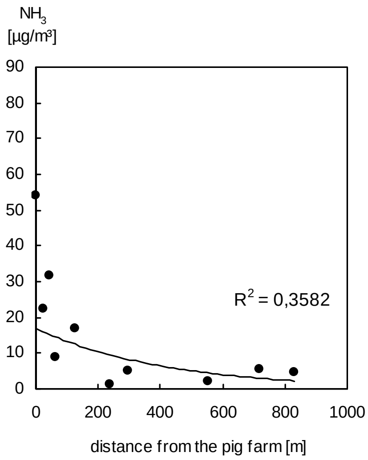


Figure 7: Ammonia concentrations as a function of distance from the pig farm series 1

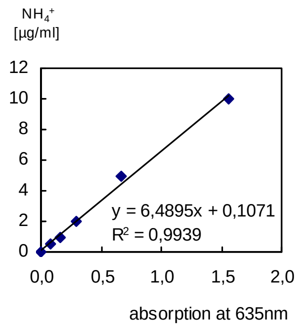


Figure 8: NH_4^+ Calibration curve series 1

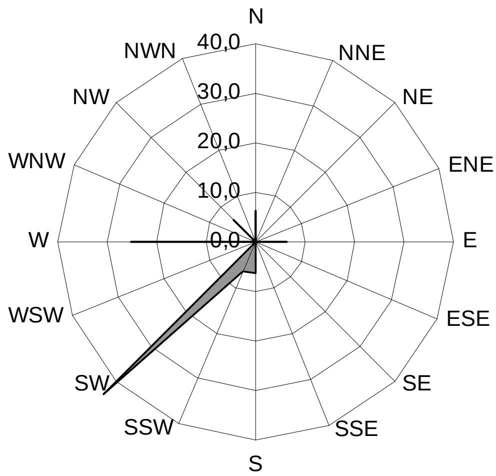


Figure 9: Mean daily wind direction values in series 1

temperature	2,9	°C
precipitation	3,2	mm
wind speed	4,4	m/s

Table 1: Average climate data from the meteorological station Gerstetten for series 1

As the dominant wind direction in series one was southwest (Figure 9), the measured ammonia concentrations at site one, which is located south west of the pig farm, were therefore very low, with 1 µg/m³. (Figure 5 & 6). The ammonia concentrations north east of the pig farm (following the predominant wind direction and the installed sites) decrease with increasing distance from the emitter (Figure 7). A congestion effect was observed at sites nine and ten, where the ammonia concentrations increase again (Figure 6). This is probably due to the fact that these sites are located in front of the forest, where the altitude decreases slightly so that the impact of the dominant southwest wind to clear away the ammonia is limited. The calibration curve of series one (Figure 8) results in an R^2 value of 0.9939, suggesting proper analytical work.

Series 2 (09.12.2007 – 23.12.2007)

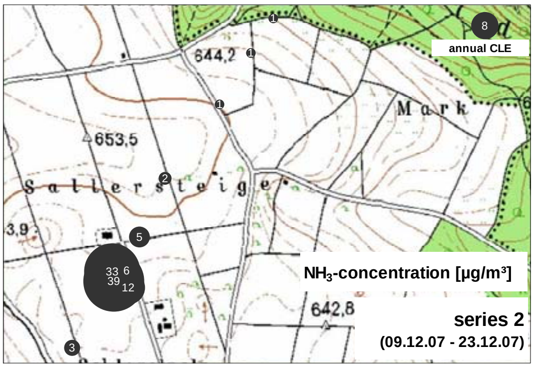


Figure 10: Site localisation and measured ammonia concentrations [µg/m³] in series 2

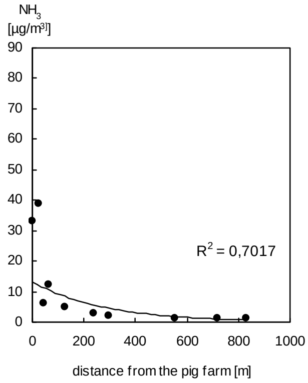


Figure 11: Ammonia concentrations as a function of distance from the pig farm series 2

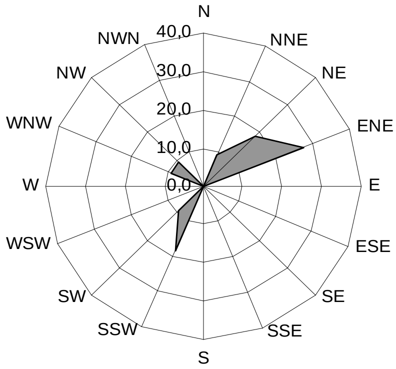


Figure 12: Mean daily wind direction values in series 2

There was no predominant wind direction in series two (Figure 12). Ammonia concentrations are in general rather low in this time series which is due to the fact that the changing wind directions drift away the emissions in more than one direction and therefore no real gradient was visible. The highest ammonia concentrations were found at site four, which is the site best sheltered from the wind through the farm buildings. It is interesting to note that there was a quick decrease of the concentrations with increasing distance from the emission origin (Figure 11).

Series 3 (23.12.2007 – 05.01.2008)

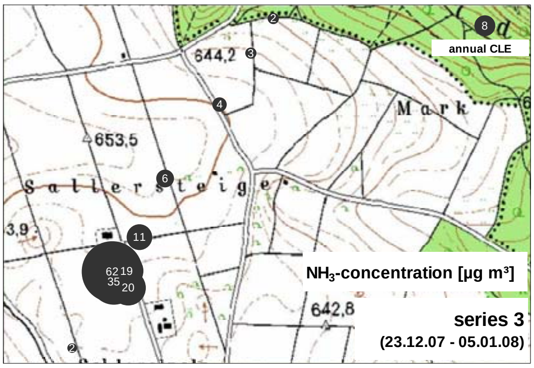


Figure 13: Site localisation and measured ammonia concentrations [µg/m³] in series 3

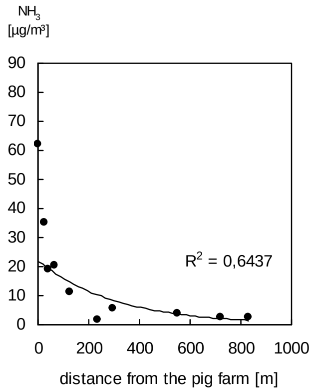


Figure 14: Ammonia concentrations as a function of distance from the pig farm series 3

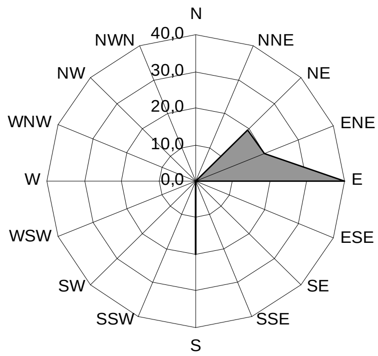


Figure 15: Mean daily wind direction values in series 3

Ammonia concentrations in series three were highest at the emitter representing the second highest throughout the whole investigation period (Figure 13). Due to mechanical problems within the anemometer, about two thirds of the wind direction data of series three were not available. The data in Figure 15 show wind directions mainly northeast to east which is maybe not representative for the whole series three. According to the higher ammonia concentrations northeast of the stable at site five, than southwest of the stable at site one, it is likely that the dominant wind direction of those days when the wind direction was not registered was somewhere between south and west.

Series 4   (05.01.2008 – 20.01.2008)

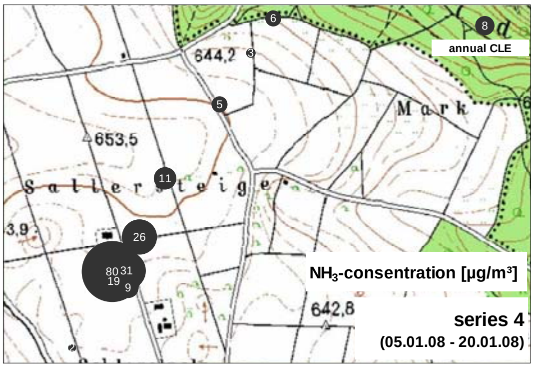


Figure 16: Site localisation and measured ammonia concentrations [µg/m³] in series 4

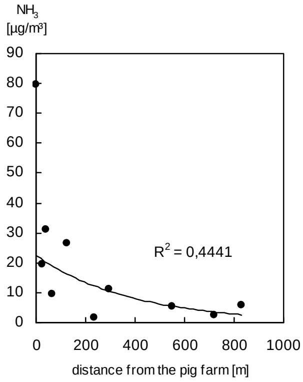


Figure 17: Ammonia concentrations as a function of distance from the pig farm series 4

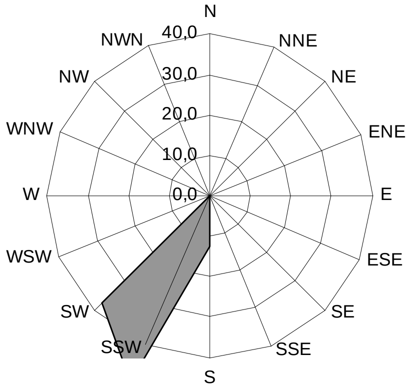


Figure 18: Mean daily wind direction values in series 4

The predominant wind direction in series four was southwest to south southwest (Figure 18). Ammonia concentrations in this investigation period were again highest directly beside the emitter with 80 µg/m³ and at site six with 26 µg/m³ each time the highest throughout the whole study (Figure 16). Ammonia concentrations again decrease with increasing distance from the pig farm until site nine (Figure 17). As the main wind direction was roughly southwest, like in series one, the reported congestion effect in front of the forest turned up again, where we found a slight concentration increase from site nine (3 µg/m³) to site ten (6 µg/m³).

Series 5   (20.01.2008 – 02.02.2008)

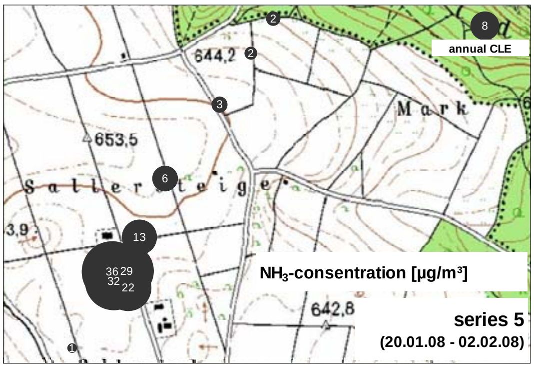


Figure 19: Site localisation and measured ammonia concentrations [µg/m³] in series 5

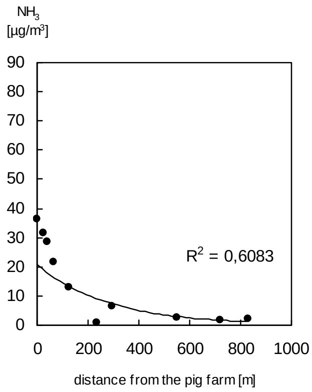


Figure 20: Ammonia concentrations as a function of distance from the pig farm series 5

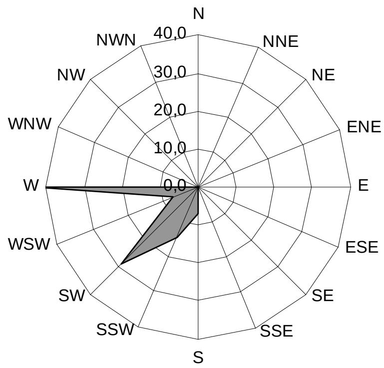


Figure 21: Mean daily wind direction values in series 5

As shown in Figure 21 the main wind directions in series five were from west as well as from southwest. In the time periods where there was dominantly west wind, most of the ammonia was cleared away directly along the stable wall at site two, where the concentrations are in general, with predominant southwest wind notably higher than the measured ones. The ammonia concentration was therefore hardly higher at site two (36 µg/m³) than at site four (32 µg/m³) and five (29 µg/m³), which were in this case better sheltered from the wind through the farm buildings than site two (Figure 19 & 20).

Series 6 (20.01.2008 – 16.02.2008)

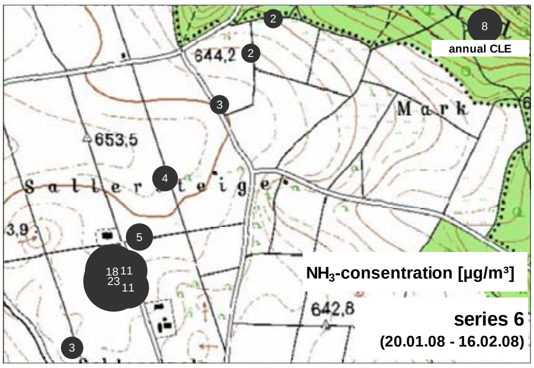


Figure 22: Site localisation and measured ammonia concentrations [µg/m³] in series 6

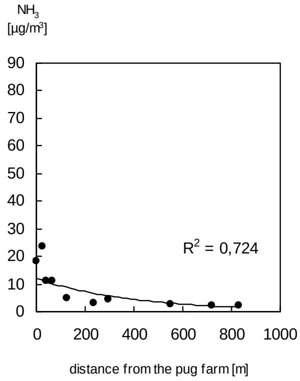


Figure 23: Ammonia concentrations as a function of distance from the pig farm series 6

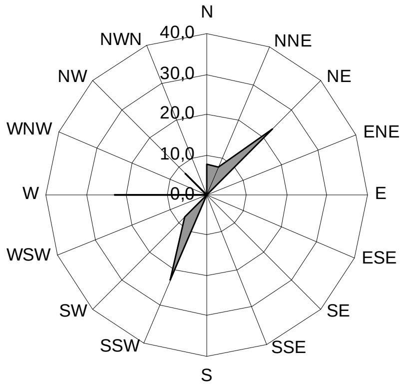


Figure 24: Mean daily wind direction values in series 6

According to Figure 24, the two main wind directions in series six were south southwest and northeast indicating a complete shift of wind directions throughout this series. Both wind directions appeared in comparable frequency with the result that the ammonia emissions were not drifted away through the wind in one main direction but in both directions. This is probably the reason why the measured ammonia concentrations were relatively low in series six similar to the situation in series two. Even samples from the sites which were located directly around the emitting farm showed the lowest ammonia concentrations throughout the whole study (Figure 22 to 23).

Series 7 (16.02.2008 – 29.02.2008)

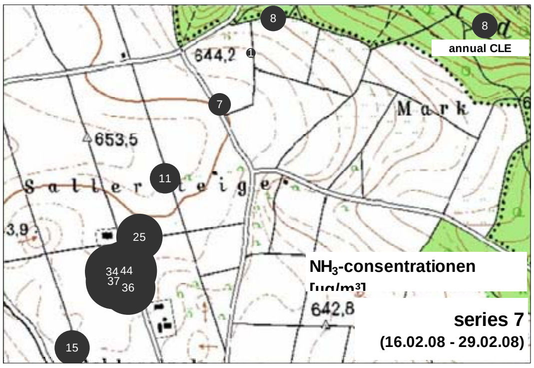


Figure 36: Site localisation and measured ammonia concentrations [µg/m³] in series 7

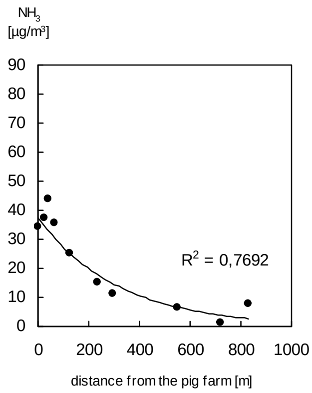


Figure 37: Ammonia concentrations as a function of distance from the pig farm series 7

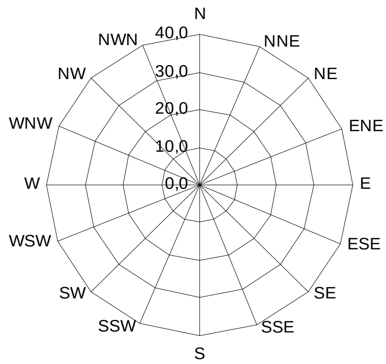


Figure 39: No data available for mean daily wind direction values in series 7

Due to mechanical problems, the anemometer failed again in series seven and therefore no wind direction data were available. Notable are the very high ammonia concentrations at sites one to six with relatively small differences among each others. Again the congestion effect in front of the forest was observed, which may be an indicator for at least partly southwesterly wind. On the other hand, the high ammonia concentrations at site one may indicate no southwest wind as main wind direction. The fact that manure was spread on several fields within the investigation area in the time period of series seven may better explain the high ammonia concentrations at most of the sites not being affected by the main wind direction. Figure 40 summarizes the ammonia concentrations per site for the results of all time series.

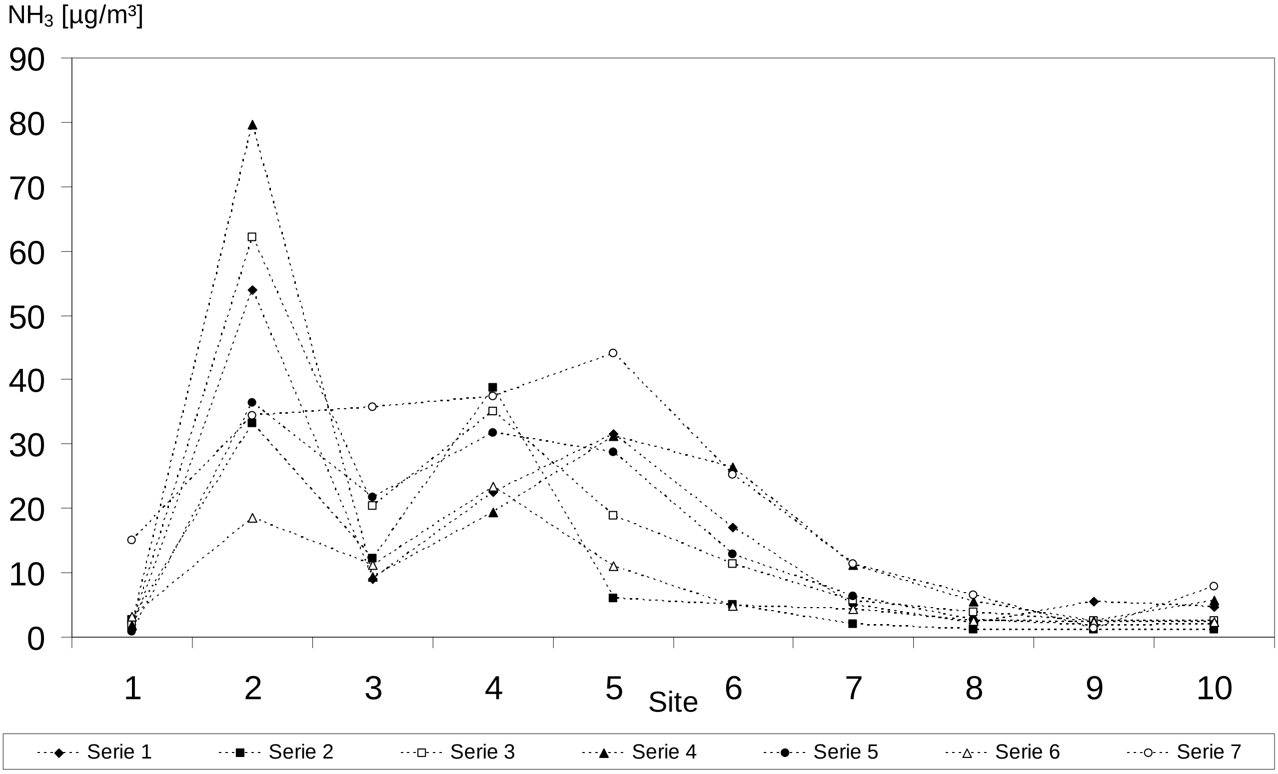


Figure 40: Ammonia concentrations measured per site for all time series

Site two shows the highest ammonia concentrations. However, the diagram of series seven is noticeably different from the other series. There is no low concentration at site three like in all other series without exception. Additionally, series seven has a peak at site five, not at site two and a notable higher concentration at site one than all other series.
This exceptional situation in series seven is probably due to the fact that in this time period slurry was sprayed on the fields so that the ammonia emissions from the manure exceeded those from the pig stable. This situation probably resulted in a distortion through additional, not expected ammonia emissions.

Discussion

Overall, the Radiello® diffusion tube passive samplers used in this study to monitor ammonia emissions worked well. The negative correlation of ammonia concentrations with the distance from the pig farm followed a logarithmic function and was visible in all time series with R^2 between 0.382 in series one and 0.769 in series seven. The emission origin was set to site two and the distances from all other sites to site two were taken as distances from the emitter, irrespectively of buildings or trees that may shield some sites from ammonia emissions. This fact might be one reason for the unprecise assessment of the distances of the sites from the emission origin.

The analysis of the samples worked well and handling of the method was easy. The calibration curves had R^2 values between 0.9896 in series four and 0.9992 in series two and three indicating correct detection of the NH_4^+ standard solutions and consequently also of the samples by the photometer.

The Radiello® diffusion tube method is adequate for ammonia monitoring with investigation periods between 1 hour and 14 days. It has the ability to provide reliable information on spatial patterns. Individual sites can thus be compared, allowing assessment of local horizontal gradients as demonstrated in this study. The disadvantage of this method is that it does not allow diurnal emission variations to be assessed if the investigation period is shorter than one day.

One problem that occurred during the investigation was that a few diffusion tubes fell down due to heavy wind and therefore showed different ammonia concentrations than the corresponding replication diffusion tubes. This was the case at site two in series seven where one of the two diffusion tubes was found in a field that was additionally freshly manured.

Due to the fact that the anemometer was not working all the time, some of the data got lost. The evaluation of the available wind data was very complex and time-consuming. More modern equipment (including a data logger) would have probably been more appropriate.

Acknowledgements

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