

Rainfall chemistry, nitrogen deposition and ammonia concentrations in Hohenheim - Results from the practical “Air Pollution and Air Pollution Control (M3202-430)”

Zorica Kauf, Jürgen Franzaring, Andreas Fangmeier & students from the AirPo Module

1. Introduction

“Air Pollution and Air Pollution Control (M3202-430)” is an elective module in the third semester of the Master Study Programme “Environmental Protection and Agricultural Food Production” and a semi-elective module in the Master Study Programme “Environmental Sciences - Soil, Water, and Biodiversity”. The objective of this module is to provide information about air pollutants, their sources, emissions, atmospheric transport and their chemistry and deposition. Also the environmental impact of these pollutants, relevant air quality guidelines and the air quality legislation are addressed in the lectures. The module includes a laboratory course on selected air pollutants in which students have an opportunity to gain practical knowledge on measuring air pollution concentrations by means of passive samplers, rainfall samples and by compiling air pollution indices from air pollution databases. The laboratory course should also provide practical experience in determining interrelations between measured values and their theoretical explanation. The data presented here are the results from students’ practicals of the last four years (2005-2008).

With time, the importance of certain air pollutant changes. Sulphur dioxide and soot from the use of fossil fuels in heat and power production were the most important compounds in the 1970s and 1980s. By introducing cleaner fuels, higher stacks and flue gas cleaning technology this problem was partly solved. Today, the main air pollution problems remaining in the industrialised world are related to nitrogen oxides and ammonia, volatile organic compounds (VOCs) and photochemical oxidants connected with growing traffic loads, new hazardous compounds from the industry, and intensive agriculture as an important source of ammonia (FENGER, 2009). Man made changes in the sulphur and nitrogen cycles were recognized as an environmental problem causing acidification and eutrophication of natural ecosystems and successful efforts were made to decrease emissions of responsible pollutants. Acidification is caused by deposition of sulphur and nitrogen (both in reduced and oxidized form), and nitrogen is responsible for eutrophication (BOUWMAN et al., 2002).

The Convention on Long-range Transboundary Air Pollution (LRTAP), signed in Geneva in 1979, had a large influence on reducing emissions contributing to transboundary air pollution. Since then eight protocols were adapted, with Germany being a Party in all of them. While the first protocols dealt with the single pollutants and problems of sulphur, nitrogen oxides, volatile organic compounds, heavy metals

and persistent organic pollutants (POPs) emissions the multipollutant protocol is seen as an integrative approach to reduce air pollution. The 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Groundlevel Ozone is an innovative multi-effect, multi-pollutant protocol that aims to simultaneously address the three effects it describes through controlling the pollutants causing them. It entered into force in 2005 and seeks to control and reduce emissions of sulphur, NO_x , ammonia and VOCs from anthropogenic sources. As mentioned, it is the first Protocol under the Convention to tackle more than one pollutant, and the first to address ammonia. It also sets national emission ceilings (NECs) for 2010 for the four pollutants.

In the period from 1990 to 2005 Germany reduced emissions of NH_3 by 16 %, NMVOC (non-methane volatile organic compounds) by 65 %, NO_x by 49.6% and in the case of SO_x by 89.5 %. As many other countries and as UNECE region in general Germany had no difficulties in reaching the Gothenburg Protocol target for SO_x , but for NO_x and NH_3 the reductions in emissions were not yet satisfactory (UNECE, 2006). As shown in Figures 1 and 2, in Germany both emission and deposition of sulphur were strongly reduced between 1990 and 2000. For the rest of the presented period, however, no trend was observed. Emissions of oxidized nitrogen also show a slight decrease, but the trend is not present in deposition due to the transboundary movement of pollutants. Emissions of ammonia and deposition of reduced nitrogen do thus not show observable trends over time and feature a strong spatial variability. An overview on the results from the deposition monitoring network in Baden-Württemberg is given in HUG et al. (2005).

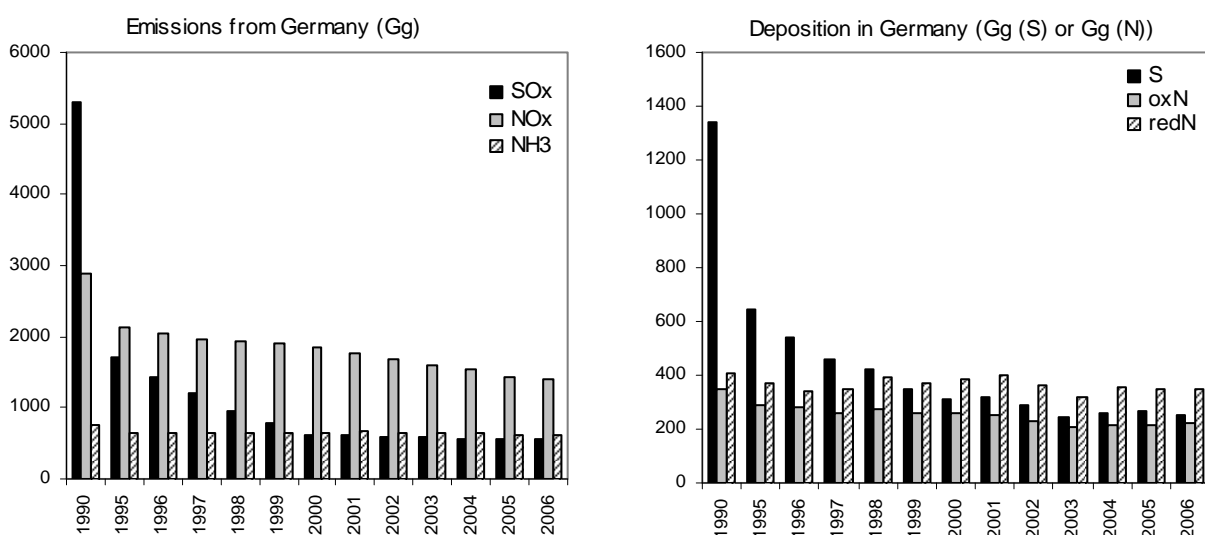


Figure 1: Emission (left) and deposition (right) of SO_x , NO_x and NH_3 in Germany between 1990 and 2006 after EMEP (2008).

The pH value of rainfall is the result of anions and cations present in it. With the decrease in sulphur deposition increases in rainfall pH were observed. However in some cases the increase in rainfall pH value is not only correlated with the deposition of sulphur, but also with the deposition of reduced nitrogen (Fig. 2).

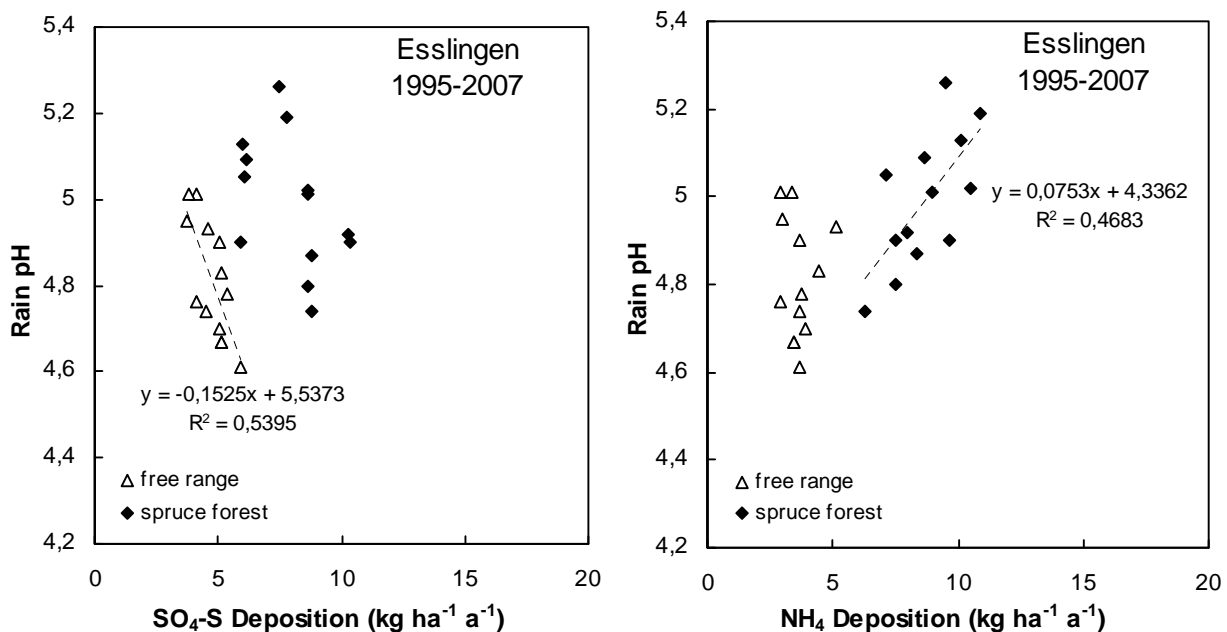


Figure 2: Relationship between sulphur (left) and ammonium (right) deposition and rain pH measured at the Esslingen forest monitoring site. While the sulphur deposition and rain pH are negatively correlated in free range samples, pH shows a slightly positive relationship to ammonium deposition in the closed spruce stand. Data taken from FVA available under <http://www.fva-bw.de/monitoring/index9.html>.

Even though ammonium has the tendency to increase pH in rainwater, after deposition it becomes an acidifying pollutant in ecosystems due to the nitrification and biological uptake by plant roots and the release of H⁺ ions to the soil. Higher deposition of air pollutants in forests shows their importance in removing anthropogenic sulphur and nitrogen from the atmosphere (VAN BREEMEN et al., 1982).

In order to determine the general state of the environment and the potential influences of a pollutant on ecosystems many abiotic and biotic parameters should be studied. The response of an ecosystem to a certain pollutant is site specific and depends on many factors. For example, response to nitrogen deposition depends on the successional stage, ecosystem types, their N demand or retention capacity, land-use history, soil quality, topography, climate, and the rate, timing, and type of N deposition (MATSON et al., 2002). In order to determine effects of a pollutant much information regarding the quantification of emissions and deposition, the understanding of physicochemical and biological processes for estimating critical

loads, and the assessment of the effectiveness and costs of emission abatement measures is needed (BULL et al., 1998).

2. Materials and methods

During the laboratory course, three different kinds of samples were analysed: wet only and bulk precipitation samples as well as passive samplers for ammonia analyses. Bulk and wet-only samples were collected at a site close to the institut's greenhouse (on the premises of the University of Hohenheim). The bulk sample vessel consisted of a PE bottle (surface 103.9 cm²) which was held by a metal basket at a reference height of 1.5 m. The wet-only sampler (Eigenbrodt GmbH NSA 181, surface 490.9 cm²) was situated 10 m away, at a slightly lower position.

Both wet-only and bulk precipitation samples were available from 25.2.2005 to 30.7.2007 and were gathered at the same dates with intervals between days to up to four weeks. Further on, only bulk samples were used due to the failure of the wet-only sampler, with the last analysed sample being taken on 17.10.2008. Rainfall volume was determined by a graduated plastic cylinder and samples were stored in labelled PE- bottles. A database was prepared with information on the sample (either wet-only or bulk), collection date and the volume of rainfall. Samples were kept at -20 °C in a refrigerator until analysis. In order to compare the amount of rainfall in the bulk or wet-only samples rainfall data from the DWD station Stuttgart/Echterdingen were retrieved from the internet (www.dwd.de).

Radiello® passive samplers (Sigma-Aldrich, Radiello-ready-to-use code 123-7) were used to determine ammonia (NH₃) concentrations in the air. Samplers were exposed in weekly intervals at five different locations: three positions at a sewage sludge treatment plant (Plieningen, Körschtal), close to a cow dung heap (as a reference for a highly polluted site) and at a "clean site" that was not directly influenced by ammonia emissions (reference). Sampling was done during six weeks between 15.9.2008 and 27.10.2008. The three positions at the sewage sludge treatment plant were: 20 meters away from the inlet (Sewage 1), 70 meters away from the inlet and close to the sludge activation basin (Sewage 2), 120 meters away from the inlet and close to the outlet (Sewage 3). Data from the DWD station Stuttgart/Echterdingen was also used to determine possible influence of meteorological conditions on ammonia emissions.

In order to analyse changes in the precipitation chemistry and to compare differences between wet-only and bulk samples pH, electronic conductivity (EC), ammonium and nitrate concentrations were determined. Rainfall volume in the bulk and wet-only samples was expressed in L m⁻² so that data could be compared to the rainfall amounts determined at the Stuttgart/Echterdingen meteorological station. The pH measurements were performed with a WTW pH meter at room temperature and the EC measurements were performed with an EC meter (WTW Weilheim).

From 25.2.2005 to 13.8.2007 both ammonium and nitrate concentrations were measured using simple colorimetric test kits. To determine ammonium concentrations

a VISOCOLOR® ECO Ammonium 15 and for nitrate a VISOCOLOR® ECO Nitrate kit (both MACHEREY & NAGEL) were used. With the given methods ammonium could be determined in the concentration classes between 0.5 and 15 mg L⁻¹ NH₄⁺ and nitrate measurements could be resolved in the range from 0 to 120 mg L⁻¹ NO₃⁻.

In the samples from 13.8.2007 to 17.10.2008 only ammonium measurements took place using a photometric method (FSM 2006). The same method was used when analysing the passive samplers for ammonium. To analyse the samplers, 10 ml of deionised water was added to the cartridges and stirred for 15 seconds. This step was not necessary for bulk samples because they were already liquid solutions containing the ammonium ions. The rest of the analysis was the same for both kinds of samples: 0.4 ml of phenol, 0.4 ml of cyanoferrate, 5 ml of a buffer solution and 1 ml of oxidizing solution were added respectively into 1 ml of the sample solution. The ammonium ion reacts with phenol and sodium hypochlorite under pentacyanonitrosylferrate catalysis, to the blue colourant indophenol. The ammonium ion was hence quantified at a wavelength of 635 nm by visible spectrometry as indophenol. The spectrophotometer (Beckman DU 640, Fullerton, California, USA) was calibrated by the use of empty cuvettes and standard samples containing known amounts of ammonium.

Nitrogen deposition can be calculated as the concentration of nitrogen ions (NO₃⁻ or NH₄⁺) multiplied by the precipitation amount and may then be expressed as pure nitrogen deposition in kg N per hectare. Calculation was done separately for every sample but due to the fact that many data were missing no attempt was made to estimate the annual deposition.

3. Results and discussion

3.1 Collection efficiency of samplers - Precipitation amounts

Precipitation amounts showed different patterns within the years (Fig. 3). This can partly be attributed to different and inconsistent sampling intervals. The longest sampling interval was between 13.8.2007 and 12.11.2007, and it resulted in a high discrepancy between precipitation amount gathered with bulk sampler and data obtained for Stuttgart/Echterdingen meteorological station. Another period of large differences among precipitation amounts can be observed in summer 2006. These inconsistencies are related to storm events that occurred between 6.6. and 2.8. The biggest difference in precipitation amounts between Stuttgart/Echterdingen and both bulk and wet-only samples from Hohenheim occurred between 7.7.2006 and 2.8.2006. It can be presumed that it represents real differences in precipitation amounts due to the local character of storms that happened in that time frame. The same can be presumed for preceding samples representing the time period between 28.6. and 7.7.2006. For storms that occurred between 6.6.2006 and 28.6.2006 (three samples) no such difference can be observed due to small precipitation amounts, or uniform rainfall distribution. Samples that were gathered on 28.8.2006 show the

biggest difference between bulk and wet-only samples and very small difference between Stuttgart/Echterdingen and wet-only samples. No satisfactory explanation can be given for these differences.

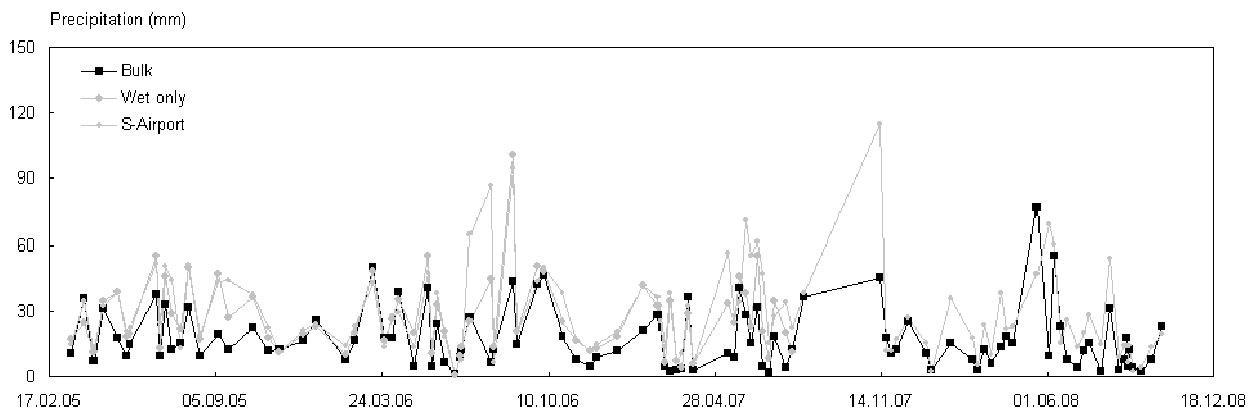


Figure 3: Time series of precipitation amounts determined with bulk (black dots) and wet-only (gray dots) samples in Hohenheim. Additional information on the precipitation amounts from the nearest meteorological station (light gray dots), Stuttgart/Echterdingen, is included.

Wet-only samples were not available after June 2007 due to a failure of the sampling device. No significant differences between wet-only and Stuttgart/Echterdingen precipitation amounts were observed, but bulk precipitation amounts significantly differed from the other two. Bulk sampler, in general, scored the lowest precipitation amounts. This can be explained by smaller catchment surface (103.9 cm^2), losses due to evaporation, especially during long sampling intervals with high temperatures, and difference in samplers positions. In the future, other sampling devices should be used, which are in line with the sampler specifications made in VDI (2008).

When examining the relationship between precipitation amounts and the difference in precipitation amounts measured with bulk and wet-only samplers (Fig. 4) it can be observed that with increase in precipitation amounts measured with wet-only sampler the difference between the two samplers increases as well, in the point when wet-only sampler measured 100.8 L m^{-2} , bulk sampler measured 57.5 L m^{-2} less. The lower efficiency of the bulk samplers can have profound effect when estimating deposition, resulting in its underestimation.

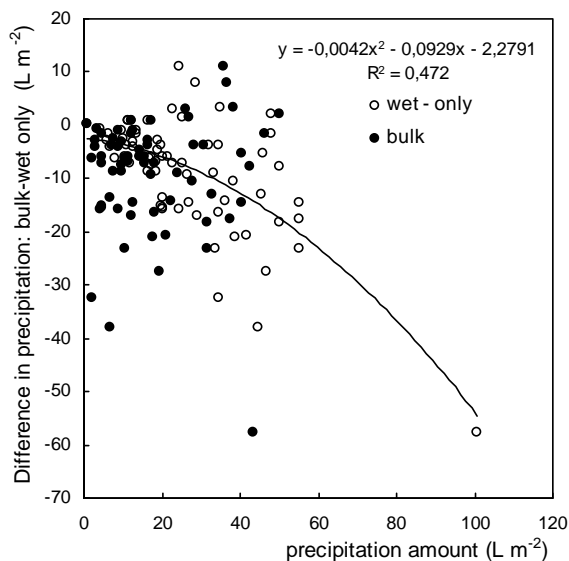


Figure 4: Relationship between precipitation amounts and difference in precipitation amounts between bulk and wet-only samplers

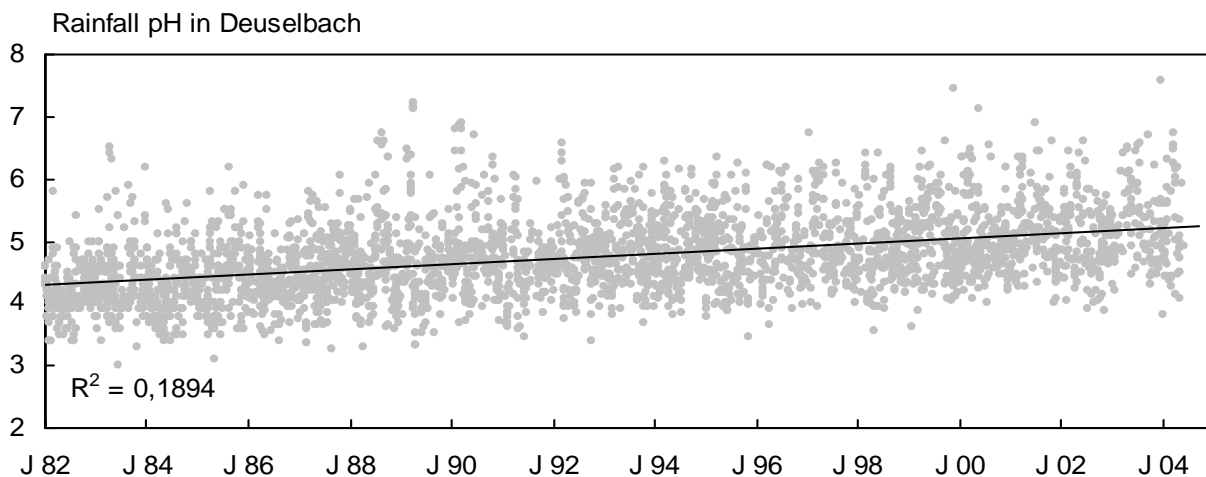
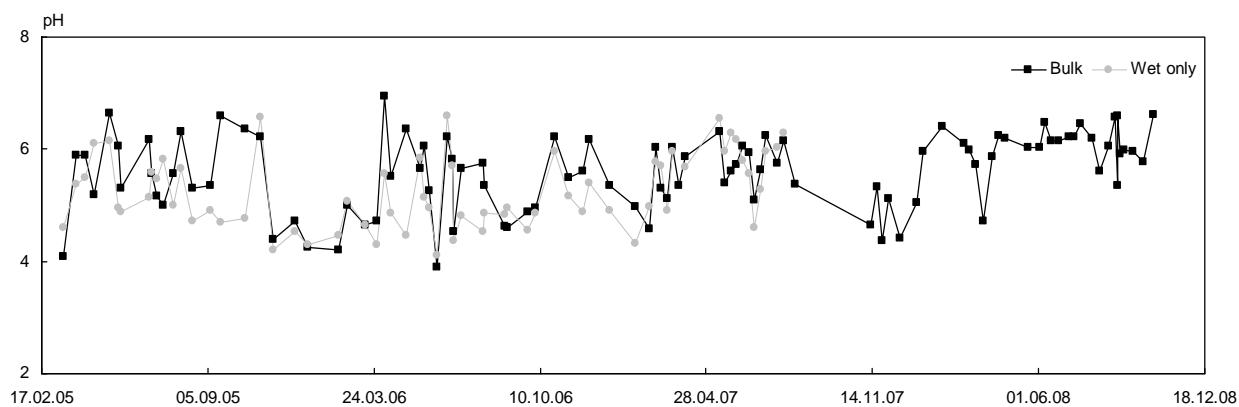


Figure 5: Time series of rainfall pH determined in bulk (black dots) and wet-only (grey dots) samples in Hohenheim (above) and pH values recorded between 1982 and 2004 in Deuselbach (SW-Germany, data after Umweltbundesamt, below). Note: Wet-only samples in Hohenheim were not available after June 2007 due to a failure of the sampling device.

3.2 Rainfall chemistry and N deposition

Results of pH measurements (Fig. 5) performed in Hohenheim show neither an observable trend over time nor a pronounced seasonal pattern (despite the somewhat lower winter values). In the year 2008 a period of elevated values was noted, but due to the short time span presented, this can not be interpreted as a general trend. In contrast, long national time series (Umweltbundesamt) of rainfall pH indicate a steady decrease in acidity in the past 20 years.

In most cases pH values of bulk samples were higher (often by over one unit) than those of wet-only ones (Fig. 6), indicating the presence of alkaline dry deposition, which partially neutralizes rainfall pH. Even though dry (particulate) deposition affects the pH values of bulk samples a significant correlation ($P=0.00015$) between pH values in bulk and wet-only samples can still be observed. Like pH, electric conductivity (EC) was also larger in bulk than in wet-only samples suggesting that dry deposition of particles indeed had a marked contribution to the ion concentrations in bulk rainfall (Fig. 7). Only five times in the studied period the EC was larger in wet – only samples (Fig. 8), but reasons for this were not clear.

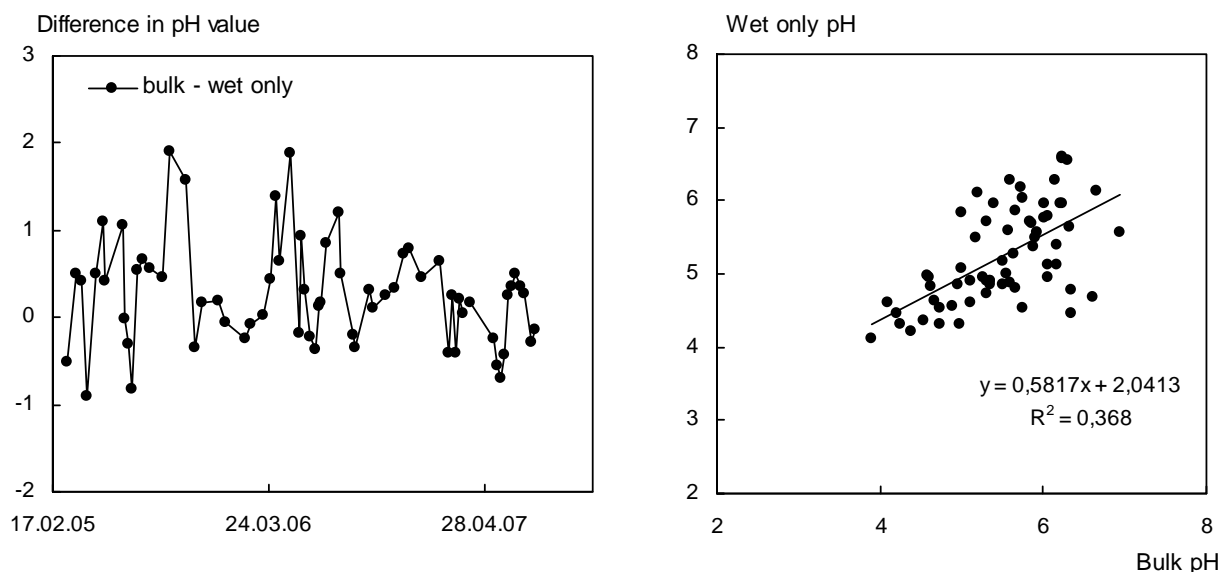
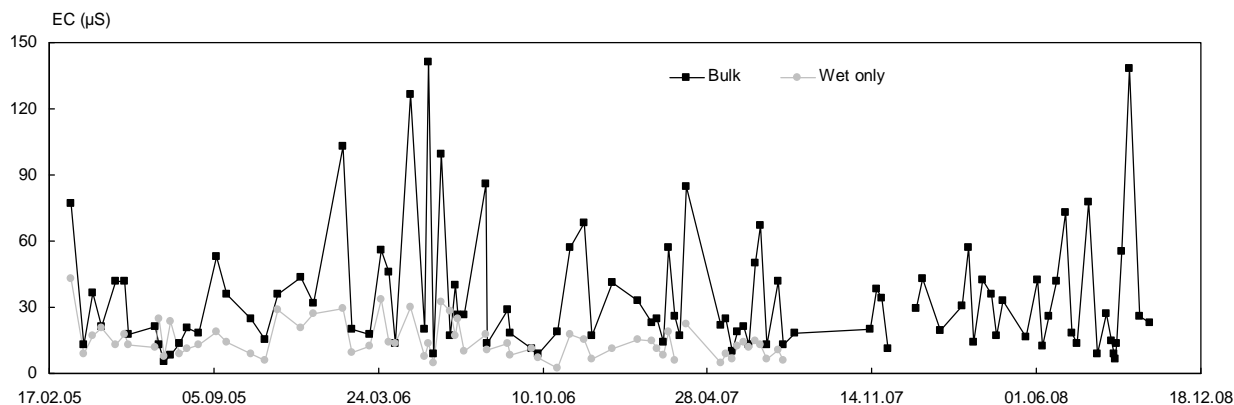


Figure 6: Differences in acidity between bulk and wet-only precipitation (left) and relationship between pH of bulk and wet-only precipitation samples collected in Hohenheim (right).

Furthermore, the variation of EC in either the bulk or wet-only samples differed markedly. While the standard deviation was $27.58 \mu\text{S cm}^{-1}$ in the bulk samples it was only $8.14 \mu\text{S cm}^{-1}$ in the wet-only samples. In two time periods, from 4.1.2006 to 24.03.2006 and from 25.6.2008 to 22.9.2008, EC of the bulk samples had the largest variations. Despite the large difference in values and variability, a non-linear relationship between EC in wet-only and bulk samples still exists (Figure 8). No changes over time were observed in the electric conductivity in the Hohenheim time series whereas long term records, e.g. from Deuselbach (SW-Germany) feature a downward trend in the past 20 years indicating the success of clean air policies in Western European countries.



Rainfall EC in Deuselbach

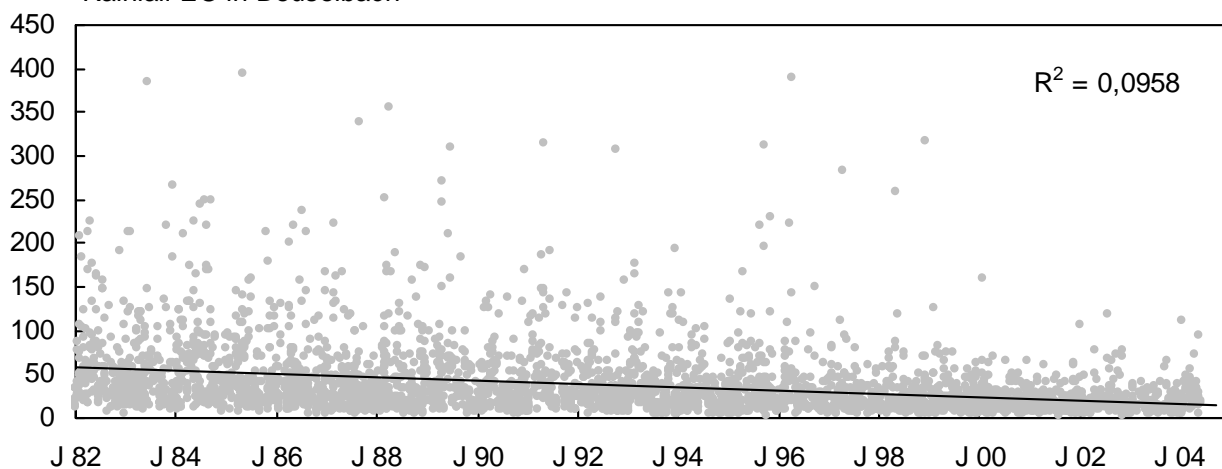


Figure 7: Time series of rainfall electronic conductivity ($\mu\text{S cm}^{-1}$) determined in bulk (black dots) and wet-only (grey dots) samples in Hohenheim (above) and EC values recorded between 1982 and 2004 in Deuselbach (SW-Germany, data after Umweltbundesamt, below). Note: Wet-only samples were not available after June 2007 due to a failure of the sampling device.

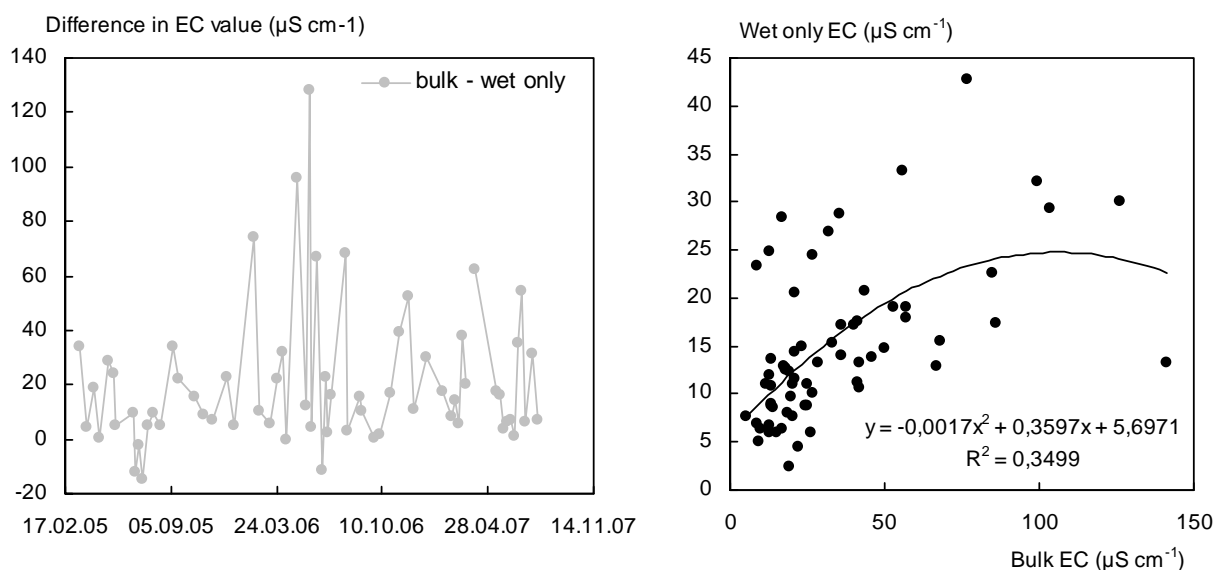


Figure 8: Differences in EC between bulk and wet-only precipitation (left) and relationship between EC in bulk and wet-only precipitation samples collected in Hohenheim (right).

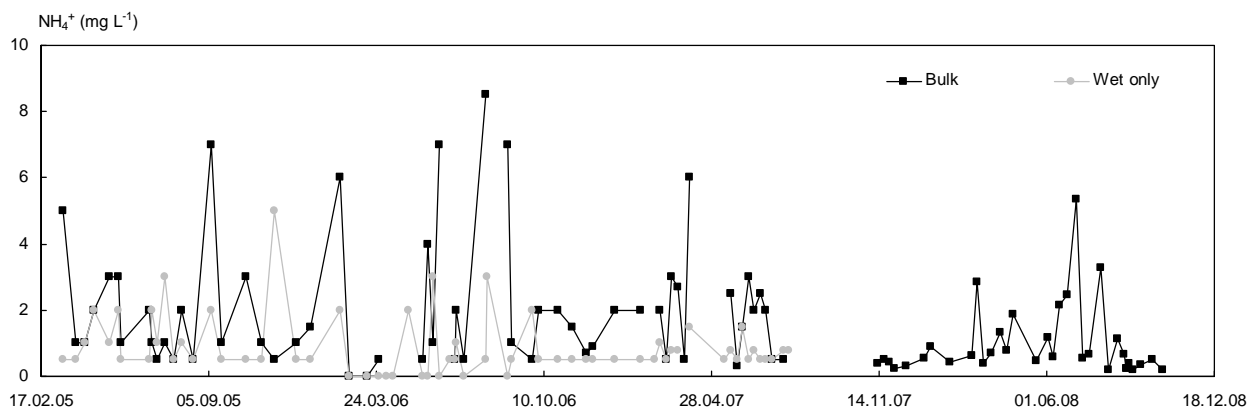


Figure 9: Time series of ammonium concentrations determined in bulk (black dots) and wet-only (grey dots) samples in Hohenheim. Note: Wet-only samples were not available after June 2007 due to a failure of the sampling device.

Ammonium concentrations also showed higher values (Fig. 9) and larger variation in the bulk as compared to the wet-only samples. In some of the samples no ammonium could be detected, which can be attributed to the insensitivity of the method (VISOCOLOR® ECO Ammonium 15), which can not determine NH_4^+ -concentrations below a value of 0.5 mg L^{-1} . In contrast to pH and EC, no correlation was observed between the concentrations of ammonium in bulk and wet-only samples (Fig. 10). However, part of the difference in EC between bulk and wet-only samples can be attributed to their differences in ammonium concentration (Fig. 11). Ammonium is therefore regarded as a considerable component of the particles included in the bulk samples, but it has no observable importance in wet-only samples. It can thus be concluded that ammonium is mainly dry deposited, both in the form of NH_4^+ containing particles and as gaseous NH_3 .

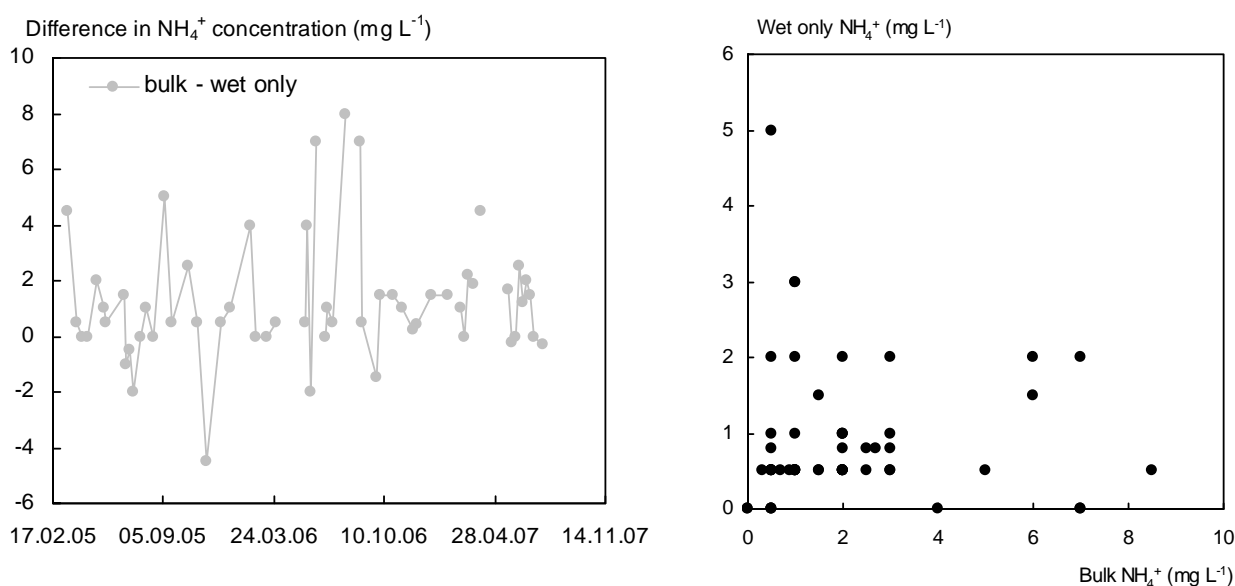


Figure 10: Differences in ammonium concentrations between bulk and wet-only precipitation (left) and relationship between ammonium concentrations in bulk and wet-only precipitation samples collected in Hohenheim (right).

It should be mentioned that ammonium is highly susceptible to chemical transformations resulting in decreases of concentration depending on time intervals, light and temperature (BUIJSMAN et al., 1988; RIDDER et al. 1985). However, decreases in ammonium concentrations were also determined in wet-only samples (MADSEN, 1982; SISTERTON 1985). Due to the fact that, in our case, bulk samples were not light protected, sampling intervals were inconsistent and a high variability in temperatures occurred it is highly likely that different losses of ammonium over time occurred.

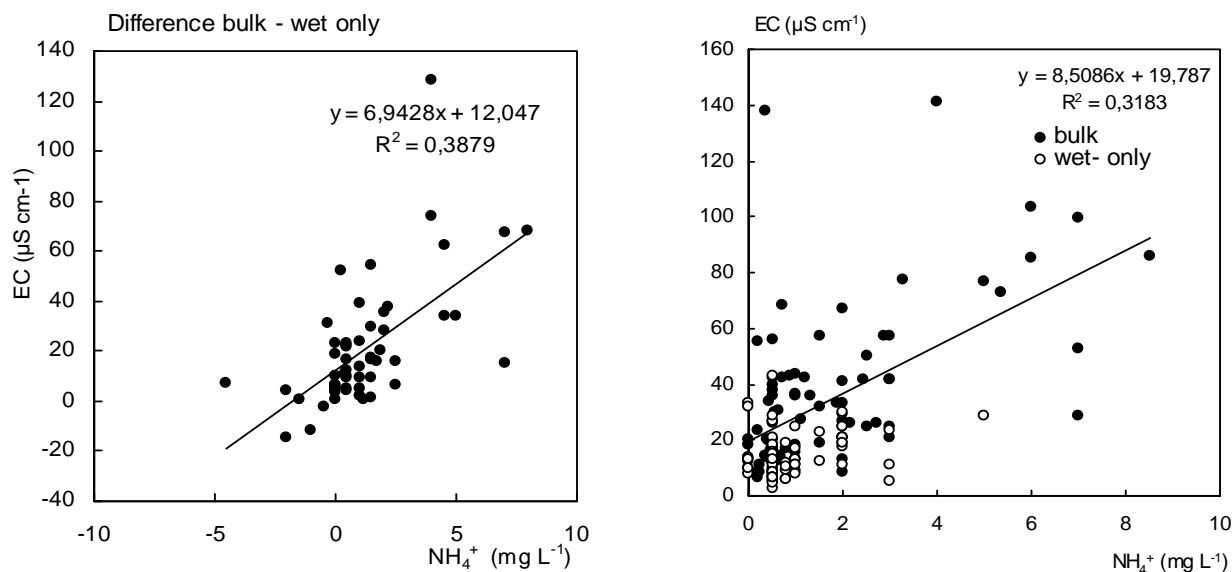


Figure 11: Relationship between the differences in ammonium concentrations between bulk and wet-only samples and the differences in EC between bulk and wet only samples (left) and the relationship between ammonium concentrations and the EC of wet-only (\circ) and bulk precipitation samples (\bullet) collected in Hohenheim (right).

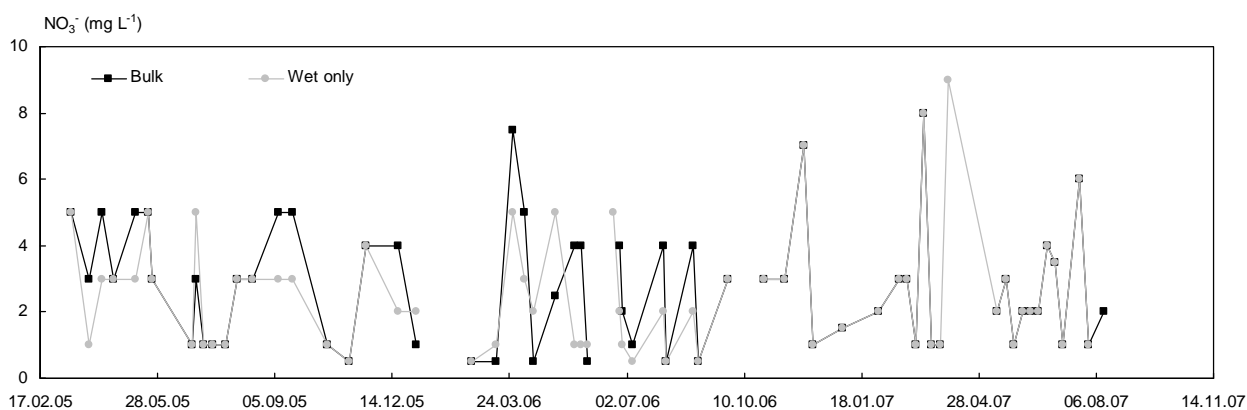


Figure 12: Time series of nitrate concentrations determined in bulk (black dots) and wet-only (grey dots) samples in Hohenheim.

Nitrate concentrations showed smaller differences between bulk and wet-only samples than the other measured variables (Fig. 12). In fact from 1.9.2006 to 30.7.2007, they were the same in both kinds of samples (Fig. 13). Small differences

in values resulted in a pronounced correlation between bulk and wet-only samples (Fig. 13). These results indicate mainly wet deposition of nitrate at the given site.

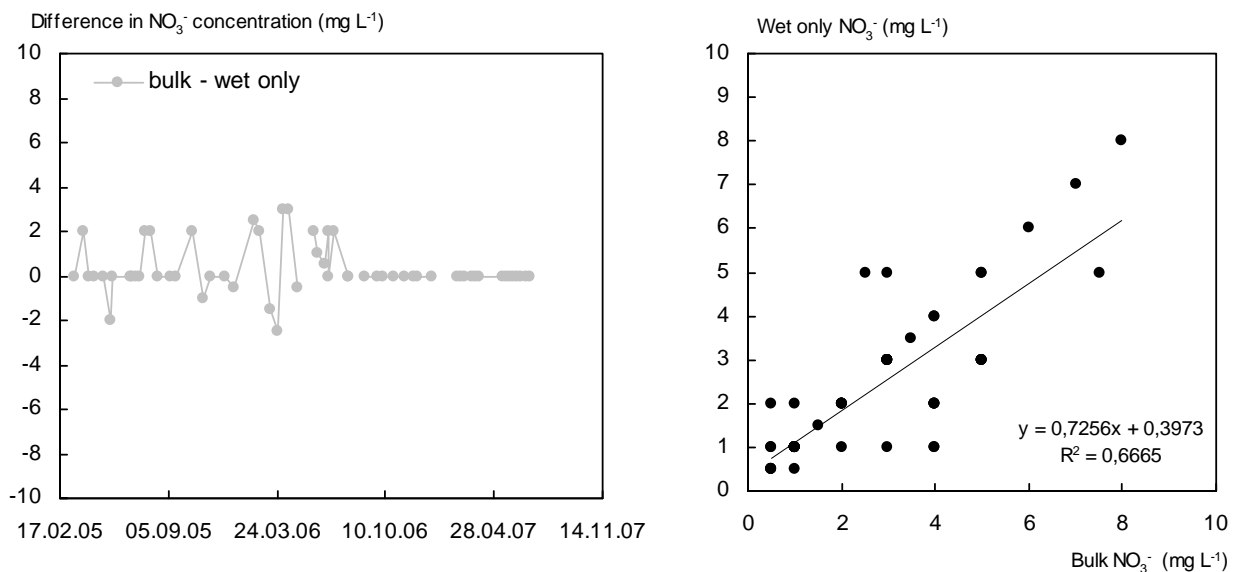


Figure 13: Differences in nitrate concentrations between bulk and wet-only precipitation (left) and relationship between nitrate concentrations in bulk and wet-only precipitation samples collected in Hohenheim (right).

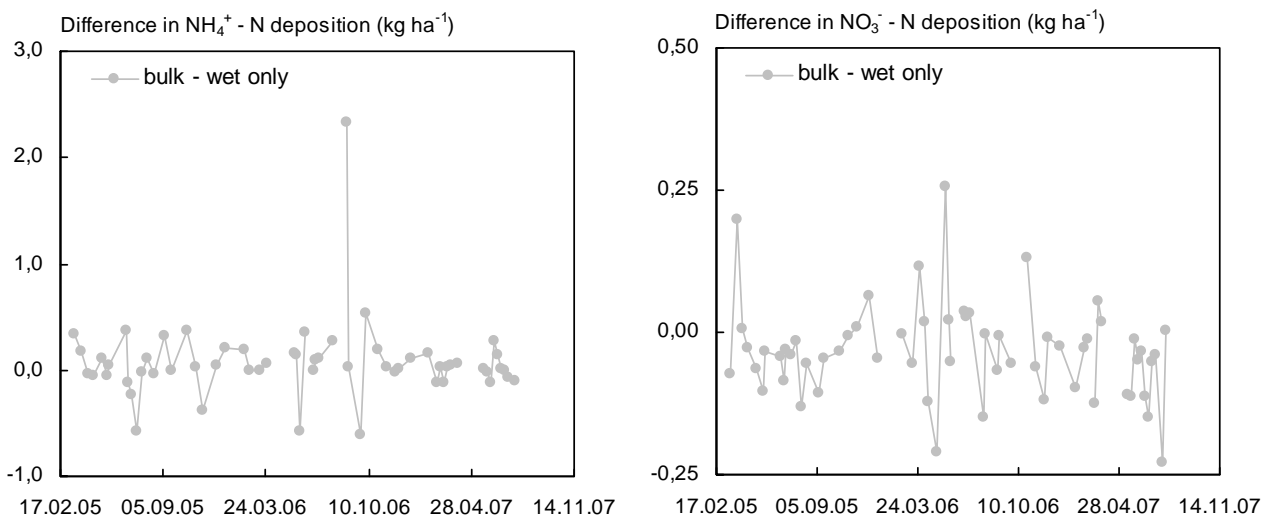


Figure 14: Differences in ammonium deposition, expressed as pure nitrogen per hectare, between bulk and wet-only samples (left) and differences in nitrate deposition, expressed as pure nitrogen per hectare, between bulk and wet-only samples (right).

Overall, the deposition data are not well suited for the determination of the annual nitrogen deposition. Due to the low efficiency of bulk samplers in collecting precipitation amounts and probable inconsistent losses of ammonium, nitrogen deposition would be underestimated. With bulk deposition including both wet and dry deposition it is expected to be higher than the wet-only deposition. This presumption is confirmed by several studies (BAYRAKTAR et al. 2005; LEE et al.

1992: STAELENS et al. 2005), but in our case wet-only deposition was often higher than bulk deposition for both ammonium and nitrate (Fig. 14).

3.3 Determination of NH_3 by passive samplers

When analysing ammonia concentrations (Fig. 15) large differences were noticed between the positions “sewage 1” (close to the inlet of sewage waters) and the two others positions on the premises of the Körschtal sewage treatment plant (Sewage 2 and Sewage 3). These data confirm that ammonia has a short atmospheric lifetime and that concentrations increase more than linear when approaching the source of the emission. Due to the fact that the location “sewage 1” is 20 m away from the inlet it can be presumed that the average ammonia concentration at the inlet is substantially higher. Concentrations measured at positions “sewage 2” and “sewage 3” are lower and show less variation than that measured at the reference site at the University of Hohenheim, so it can be followed that no substantial ammonia amounts are emitted close to the sludge activation basin (sewage 2) and outlet (sewage 3).

Overall, highest ammonia concentrations were measured close to the dung heap, suggesting that ammonia emissions from sewage treatment plants are substantially lower than emissions from livestock excrements. The smaller variability of the ammonia concentrations within the positions at the sewage sludge treatment plant over time (variability coefficient = 18 % for Sewage 1, 32 % for Sewage 2 and 25 % for Sewage 3) suggest that emissions in a given time period were mostly controlled by sludge treatment processes. However, we do not have further information on the operation of the facility and the amounts of ammonium present in the waste water.

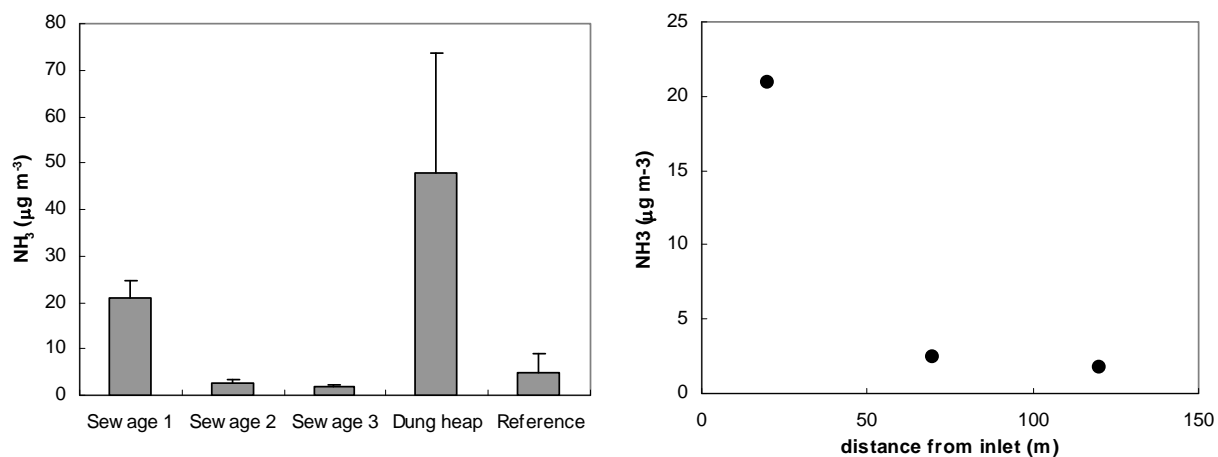


Figure 15: Average (\pm standard deviations) ammonia concentrations (left) and the relationship between distance from the sewage inlet and the average ammonia concentration for three positions at the sewage sludge treatment plant (right).

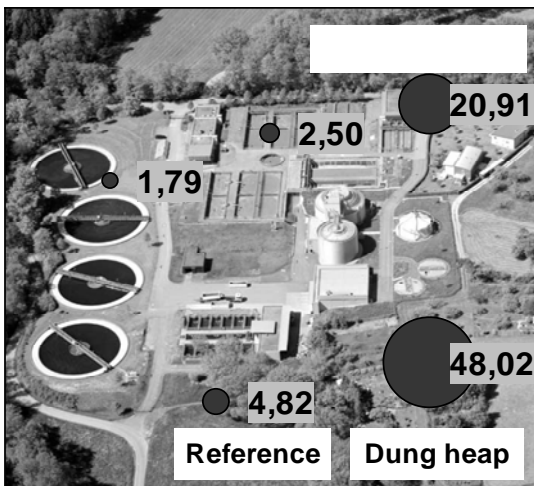


Figure 16: Bubble graph of mean ammonia concentrations across six series between 15.09. 27.10.2008 determined at 3 locations on the premises of the Körschtal sewage treatment plant and 2 locations („Reference“ and „Dung heap“) chosen at the University of Hohenheim about 1 km away from the sewage treatment plant.

Relationships between meteorological conditions and ammonia concentrations were found only for one position within the sewage sludge treatment plant. Ammonia concentrations at the position close to the sludge activation basin (Sewage 2) showed a weak ($R^2 = 0.42$) relationship with relative humidity (Fig. 17). At the same time, ammonia concentrations close to the dung heap were the highest and showed the biggest variation. It may be suggested that variation was mainly due to the addition of new material, but we do not have information on when animal excrements were added to the heap. Nevertheless, a slight dependence of emissions from the dung heap on meteorological conditions was seen in the data. On the one hand a slight relationship between air pressure and ammonia concentration ($R^2 = 0.37$) was present due to the large surface exposed and the decrease in ammonia concentrations with increases in precipitation ($R^2 = 0.67$) may be attributed to the leaching of ammonium. When discussing the relationship between meteorological data and concentrations of ammonia in the air it should be taken into account that measurements were taken over a relatively short time period (6 weeks) and that most of meteorological conditions, except the amount of precipitation, did not fluctuate much. Concentration of ammonia at a specific site is not only dependant on exposure to nearby emission sources, but also on the overall composition of the atmosphere. Without information on concentrations of other compounds at the locations it is thus impossible to explain why the concentrations of ammonia at positions “sewage 2” and “sewage 3” were lower than at the reference site.

4. Summary and outlook

Within the practical, students were able to use various, rather simple methods to measure selected air pollutants at different locations. Bulk and wet-only samplers were used to collect rainfall samples over three consecutive years but sampling intervals differed between a few days and two weeks so that part of the collected rainfall was lost due to evaporation at longer sampling intervals. In the future, this shortcoming should be overcome by a higher sampling frequency, if the availability of technical personnel permits. Laboratory methods were applied to identify pH, EC,

ammonium and nitrate concentrations in the rainfall samples. Over the time of the investigation, these parameters did not change much. Still, slight seasonal changes were detected within a year, e. g. lower pH values in the winter time, but due to sampling losses we could not calculate annual N deposition loads. The observed differences in ammonium concentrations, pH and EC detected between wet-only and bulk samplers were conclusive and demonstrated that part of the deposition in Hohenheim stems from dry particulate and gaseous deposition.

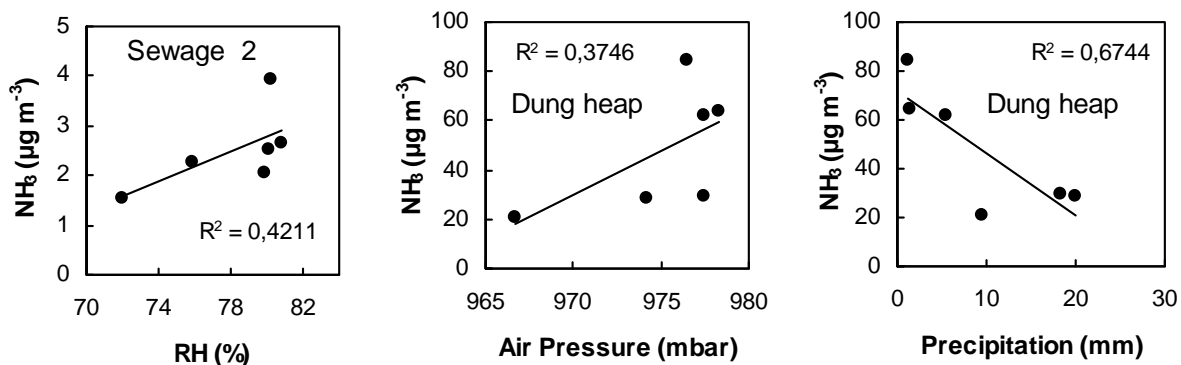


Figure 17: Relationship between relative humidity and ammonia concentrations at the position “sewage 2” (left), relationship between air pressure and ammonia concentrations at the dung heap (centre), and negative relationship between precipitation amounts and ammonia concentrations near the dung heap (right).

In a second part of the practical, a pilot study was performed determining ammonia (NH_3) concentrations with passive samplers. Samplers were operated at five locations, three at a nearby sewage sludge treatment facility, one at a dung heap and one reference site. Six weekly sampling intervals were chosen to address temporal variability and climatic effects on the emissions. Highest ammonia concentrations were determined at the dung heap but concentrations were also enhanced at the inlet of the sewage treatment facility. The method proved well practicable and reliable to measure mean ammonia concentrations and to determine spatio-temporal emission patterns. We therefore intend to use the method in future students’ practicals.

Acknowledgements

We appreciate financial support from the funds stemming from the student fees, which enabled us to pay for consumables and passive samplers for the ammonia analyses. Furthermore, student research assistant Mr. Felix Frey, also funded by these resources, is thanked for assisting with the passive sampler pilot study. Dr. Damsohn from the University of Hohenheim’s Institute for Landscape and Plant Ecology is thanked for assisting with the collection of wet-only and bulk precipitation samples. The main author of this paper ZK was funded as a student research assistant by the Institute.

References

- BAYRAKTAR, H., TURALIOGLU, F. S. (2005): Composition of wet and bulk deposition in Erzurum, Turkey. *Chemosphere* 59: 1537–1546.
- BOUWMAN, A. F., VAN VUUREN, D. P., DERWENT, R. G. & POSCH, M. (2002): A global analysis of acidification and eutrophication of terrestrial ecosystems. *Water, Air, and Soil Pollution* 141: 349–382.
- BUIJSMAN, E. & ERISMAN, J. W. (1988): Wet Deposition of Ammonium in Europe. *Journal of Atmospheric Chemistry* 6: 265-280.
- BULL, K. R. & SUTTON, A. (1998): Critical loads and the relevance of ammonia to an effects-based nitrogen protocol. *Atmospheric Environment* 32: 565-572.
- EMEP (2008): Transboundary air pollution by main pollutants (S, N, O₃) and PM, Germany. www.emep.int/publ/reports/2008/Country_Reports/report_DE.pdf.
- FENGER, J. (2009): Air pollution in the last 50 years. From local to global. *Atmospheric Environment* 43: 13–22.
- FSM (2006): Radiello Manual. Centro di Richerche Ambientale Padova. Fondazione Salvatore Maugeri IRCSS. Supelco – Sigma-Aldrich Edition, 56 pp.
- HUG, R., HEPP, R., VON WILPERT, K. (2005): 18 Jahre Depositionsmessnetz der Forstlichen Versuchs- und Forschungsanstalt Baden-Württemberg. *Berichte Freiburger Forstliche Forschung* 59, 95 pp.
- LEE, D. S. AND LONGHURST, J. W. S. (1992): A comparison between wet and bulk deposition at an urban site in the U.K. *Water, Air, and Soil Pollution* 64: 635-648.
- MADSEN, B. C. (1982): An evaluation of sampling interval length on the chemical composition of wet-only deposition. *Atmospheric Environment* 16: 2515-2519.
- MATSON, P., LOHSE K. A. & HALL, S. J. (2002): The Globalization of Nitrogen Deposition: Consequences for Terrestrial Ecosystems. *Ambio* 31: 113-119.
- RIDDER, T. B., BUIHAND, T. A., REIJNDERS, H. F. R., HART, M. J., SLANINA, J. (1985): Effects of storage on the composition of main components in rainwater samples. *Atmospheric Environment* 19: 759-762.
- SISTERSON, D. L., WURFEL, B. W., LESHT, B. M. (1985): Chemical differences between event and weekly precipitation samples in northeastern Illinois. *Atmospheric Environment* 19: 1453-1469.
- STAELENSA, J., DE SCHRIJVER, A., VAN AVERMAET, P., GENOUW, G., VERHOEST, N. (2005): A comparison of bulk and wet-only deposition at two adjacent sites in Melle (Belgium). *Atmospheric Environment* 39: 7–15.
- UNECE (2006): Convention on Long-range Transboundary Air Pollution, Strategies and Policies for Air Pollution Abatement, Review 2006.
- VAN BREEMEN, N., BURROUGH, P. A., VELTHORST, E. J., VAN DOBBEN, H. F., DE WIT T., RIDDER, T. B., REIJNDERS, H. F. R. (1982): Soil acidification from atmospheric ammonium sulphate in forest canopy throughfall. *Nature* 299: 548-550.

VDI (2008): VDI 4320 (Blatt 1). Messung atmosphärischer Depositionen. Probennahme mit Bulk- und Wet-Only-Sammlern. Grundlagen. VDI/DIN Handbuch Reinhaltung der Luft. Band 4: Analysen- und Messverfahren I, 11 S. transportation routes and port of Vancouver in western Canada. Environmental Biosafety Research 5: 67-75.

Address of authors:

Universität Hohenheim

Institut für Landschafts- und Pflanzenökologie -320 B-
Ökologiezentrum 2

August-von-Hartmann-Str. 3, 70599 Stuttgart

Tel. +49 (0)711 459-22329, Fax +49 (0)711 459-23044

E-mail: franzari@uni-hohenheim.de