ENVIRONMENTAL MONITORING OF REACTIVE NITROGEN WITH SPECIAL REFERENCE TO USING PLANT BIOINDICATORS

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ABSTRACT

Nationwide chemo-physical measurements of ammonia are being performed online in the Netherlands alone, while regional passive sampler networks have been set up recently in the UK, Switzerland and Germany. Despite their use in identifying regional background concentrations of ammonia, concentration and deposition measurements as well as dispersion models do not fully explain for the so-called ammonia gap. Complementing such approaches, the determination of empirical critical loads and various effects-based bioindication systems have been set up in the UN-ECE region to address the impact of nitrogen deposition in forests and semi-natural vegetation. These approaches are paralleled by regional and local studies, which demand eutrophication indicators to be applied in decision making and EIA studies. The presentation will focus on various bioindicators to study the impact of reduced nitrogen. Ecological indicator values for nitrogen (Ellenberg values) are well suited for the study of long-term eutrophication impacts and may be linked directly to nature conservation issues and NATURA2000 reporting. Other plant ecological approaches relate to the study of foliar nitrogen contents in different plant species and may serve to identify critical plant nitrogen levels. Passive biomonitoring using mosses and conifer needles may be used for the integrated assessment of mid-term effects of regional and national nitrogen deposition loads, while source-oriented active biomonitoring may be used in local impact assessment of short-term effects. In conclusion, effects-based approaches may serve to better understand the dynamics and fate of nitrogen deposition and may offer ways to environmental policy evaluation and planning.

INTRODUCTION

While nitrogen cycles were more or less closed in ancient farming, the food demand of the growing world population caused the production of cheap fertilisers and livestock feed leading to the de-coupling of the food production from the availability of local resources and the agricultural area in many regions. In Germany the use of nitrogen has increased from 25 kg ha^{-1} per year in the early 1950s to 130 kg ha^{-1} in the late 1980s and since then levelled off to about 100 kg ha^{-1} per year [1]. However, the high anthropogenic input of nitrogen has not been restricted to agricultural land alone. High deposition loads of gaseous and particle-bound reduced nitrogen (NH_3 and NH_4^+, together termed NH_x) from intensive livestock farming and oxidised nitrogen (NO_y) from fossil fuel combustion have both lead to nitrogen saturation even in many of those remote semi-natural ecosystems, which previously thrived under extremely poor conditions. Latter types of ecosystems, e.g. heath, moorlands, dune or chalk grasslands and pine forests, have generally become rare throughout Europe despite strong efforts in sustainable management of these ecosystems. Apart from losses in oligotrophic, i.e. nutrient poor habitats and associated species, changes in the N-cycle in various land use systems and in remote regions have caused profound environmental cascade effects such as eutrophication, acidification, ruderalisation, loss of ecological functions (biological buffering, delivery of clean water) and even adverse impacts on the world climate through the release of N_2O. Moreover, reduced nitrogen is an important precursor of secondary aerosols and thus has direct relevance to health issues as well.

Anthropogenic changes of the N-cycle, the associated effects and solution options to the problem were recently addressed on the 1998 “confere-N-s“, the “N2001“ and the 2002 “UN-ECE Empirical N-Critical Loads conference” [2-4]. While the emission of oxidised N-species has decreased significantly in Western and Eastern Europe throughout the 1990´s due to clean air initiatives and technological progress, concentrations and deposition of reduced N remain high in many parts of Europe. Even in the Netherlands, which have significantly reduced animal numbers and introduced various national and regional political measures to cut back nitrogen emissions, strong reductions in NH_x concentrations were absent and satisfying explanations to the so-called “ammonia gap” could not yet be given. Uncertainties in the fate of nitrogen and approaches to an integrated assessment of the nitrogen policies have been addressed by [5]. Despite the anticipated future mitigation, scenarios based on economic and demographic growth reveal that “hot spots” of high N-deposition loads in Europe will still be present in the year 2040, but greatest environmental problems will then occur in subtropical SE-Asia [6, 7].

In Europe a political framework for the reduction of N-deposition has been established within the UN-ECE “multipollutant protocol“ and the EU “NEC-guideline”. By the year 2010 deposition of oxidised and reduced nitrogen will have to be brought back to “ecologically tolerable loads”. To fulfil these agreements, ammonia emissions will have to be reduced throughout Europe, taking the 1990 national loads as a reference. While oxidised N is routinely monitored at many sites throughout Europe, no EU wide monitoring networks exist, by which the temporal development of concentrations of reduced N could be thoroughly assessed. There is thus great demand for “policy evaluation studies“, which would afford the operation of such networks and the critical use of model approaches [8, 9]. At the same time more knowledge will have to be generated in coming years on the direct and indirect effects of gaseous and particle associated reduced N on sensitive receptors including both, ecosystems and the human respiratory system, in order to further specify the concepts of critical levels and loads.

In this paper, we will present approaches in environmental monitoring of reduced nitrogen, which can be used in national and regional reporting initiatives. These methods and ecological indicators are both cost-effective and suitable to follow whether agricultural intensification stays within sustainable limits. Furthermore, guidance will be given to establish monitoring and research programmes at the local level, where information is needed on the environmental impact of nitrogen emitting sources.

ENVIRONMENTAL MONITORING OF REDUCED NITROGEN

a) Technical approaches to measure gaseous ammonia at high and low concentrations have been summarised in [10]. Only in the Netherlands, ambient levels of ammonia are routinely monitored online using the denuder technology. Examples from three sites of the Dutch RIVM-LML network and typical concentrations for ambient ammonia are given in Figure 1.

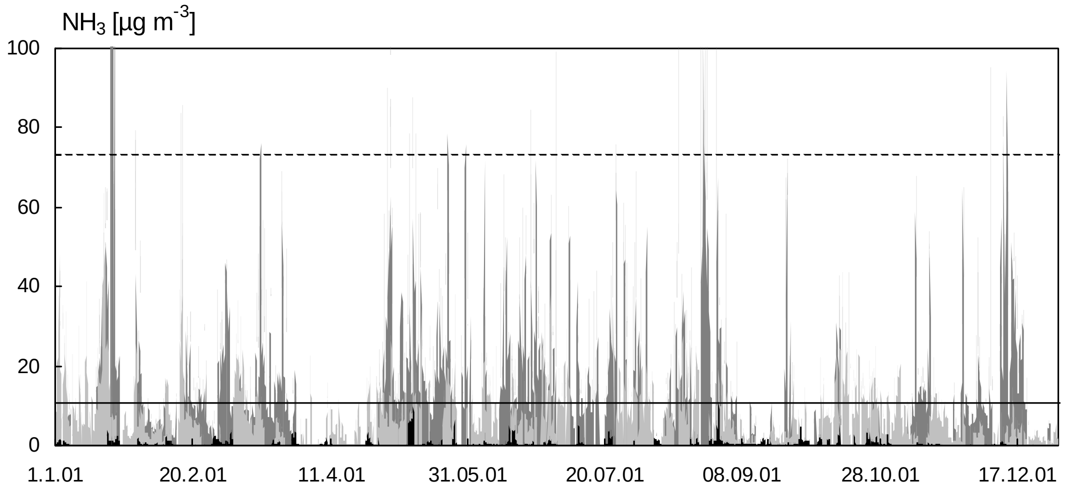

Figure 1. Hourly values of the ammonia concentrations at three locations in the Netherlands in the year 2001: a coastal site (De Zilk, black), a site close to the Dutch-German border representing moderate agricultural activities (Eibergen, light grey) and a site from the Brabant region with a high livestock density (Vreedepeel, dark grey). Original monthly data of the three sites downloaded from the Dutch LML-air pollution network (www.rivm.nl). Solid and broken lines in the diagram represent the annual means of 8 and 75 µg m^{-3}, which have been defined as thresholds for N-sensitive ecosystems and crops respectively by the UN-ECE and the German Federal State North-Rhine Westphalia [11]. The average ammonia concentrations in 2001 were 0.9, 8.6 and 19.1 µg m^{-3} in de Zilk, Eibergen and Vreedepeel respectively.

Ammonia monitoring may also be performed using passive samplers and an inter-comparison of various sampler types has confirmed the general suitability of most of such devices [12]. However, the rather cost-effective method does not have high temporal resolution; usually diffusive sampling is done over two to four weeks. A national ammonia monitoring programme using this methodology exists in the UK alone [13], while regional and local programmes have recently been performed in various European countries [14-17]. Figure 2 gives an impression of average concentrations of ammonia measured with diffusive samplers in the lee of livestock farms. These concentrations are much lower than ambient levels of ammonia close to fields with recent slurry application or to industrial ammonia spills. However, levels close to animal stables are distinctly higher than ammonia concentrations near major roads or tunnels [19]. For emission factors of different NH_3 emitting sources, gas-to-particle conversion, atmospheric transport, transmission and deposition of reduced nitrogen refer to [20].

b) Bioindication approaches to the effects-based monitoring of reduced nitrogen make use of plant responses at individual and community levels. Ambient concentrations of ammonia as described above will not have direct phytotoxic effects, but exposure of plants to levels above 1 mg m^{-3} NH_3 has repeatedly been reported to cause visible foliar injury. Lower concentrations of ammonia and the wet and dry particulate deposition of NH_x will normally not cause acute effects in plants, but the accumulation of nitrogen will have a fertilising effect, leading to higher plant tissue N concentrations and growth in the mid term as well as to pronounced floristic changes within vegetations on the long term. Both responses can be used to indicate the effects of reduced nitrogen in local source-oriented and regional to international monitoring programmes. However, the decision which of the identified responses represents an adverse effect on ecosystem stability, biodiversity or health is difficult to date. The evaluation of effects may vary with the environmental state before pollution was present and the conservation aims, e.g. tolerable loads of nitrogen deposition vary with EUNIS classification [4].

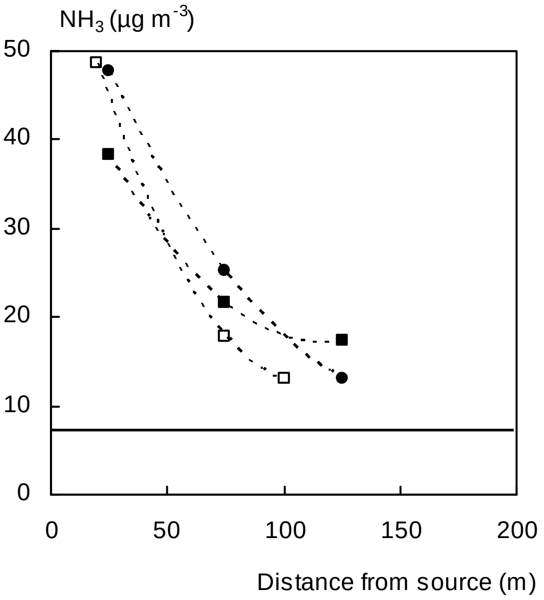

Figure 2. Mean ammonia concentrations determined with passive samplers downwind a pig stable emitting 4.5 Mg NH_3 a^{-1}(■), a pig stable emitting 5 Mg NH_3 a^{-1} (□) and a broiler stable emitting 5.3 Mg NH_3 a^{-1} (●). Data from a Dutch study performed in May 2000 after [18]. Solid line indicates the critical level of ammonia of 8 µg m^{-3}, which has been defined by the UN-ECE as the annual mean to avoid adverse effects on N-sensitive plant species.

Botanical monitoring of higher and lower (lichens and mosses) plant species and community composition is a suitable method to indicate eutrophication as well as acidification effects, which both are the result of long-lasting deposition of reduced nitrogen. Floristic changes may be identified through changes in species composition over time and the invasion of fast growing nitrophytes (N demanding species). Botanical monitoring programmes like the British *Countryside Survey* or the German *Floristische Kartierung* have high spatial resolution and are a wealthy basis for national biodiversity action plans (BAP) through the identification of indicator species for environmental change, including the effects of nitrogen deposition [21-23]. A widely used approach is the use of ecological indicator values which have been derived for over 2500 European plant species by [24]. While *Ellenberg indicator values* were restricted to Central Europe in the early days, their general validity has meanwhile been proven in North Western Europe and Scandinavia. Ellenberg N values have recently been used within the UN-ECE Intensive Monitoring Programme of Forest Ecosystems for the first time and it could be shown that they corresponded reasonably well to the long term N-deposition at the several hundred ICP Forest sites [25]. Moreover, mean Ellenberg N indicator values from vegetation relevés could be related to the mean N concentrations in conifer needles from the investigated stands, confirming their general accuracy. The compatibility of N indicator values and *foliar nitrogen concentrations* is also demonstrated in Figure 3. It must be noted, however, that significant changes of mean N indicator values within plant communities may only be observed in situations with a long-lasting nitrogen deposition and steep deposition gradients, e.g. in the lee of poultry farms [27, 28]. If in such regions eutrophication is observed and found to pose a problem, it may take decennia and costly nature management for the ecosystem to recover. So, methods for the well-timed identification of adverse effects would be appreciated.

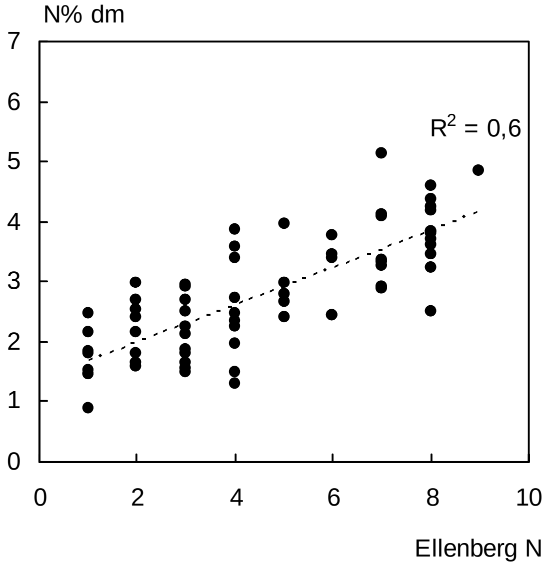

Figure 3. Relationship between foliar N concentrations and Ellenberg N values in 60 plant species collected in Central England. Data for N-indicators after [24] and data for N-contents of plant species collected in the field after [26].

In case of construction and excessive use of nitrogen emitting sources and technologies, field ecologists should be consulted especially in those regions with a high floristic diversity and nutrient restricted ecosystems, e.g. moor- and heathlands. Prior to affecting those ecosystems with low critical loads by economic and agricultural activities botanical monitoring should be made in order to identify indicator species and to document the a priori state of the ecosystem as a reference. Environmental impact assessment of anthropogenic activities releasing nitrogen can then be assisted by long term botanical monitoring and the investigation of nitrogen indicator values. Latter should be derived also for plant species outside Europe, e.g. SE-Asia, where eutrophication by reduced and oxidised nitrogen will become a problem in the near future.

Other bioindicator methods relate to the identification of nitrogen in individual plants from the local vegetation (**passive biomonitoring**) or in receptor plants exposed in the vicinity of a point, line or area source (**active biomonitoring**). Examples for passive biomonitoring along pollution gradients in the lee of livestock farms are presented in Figure 4. Nitrogen concentrations in the plants decreased with increasing distance from the pollution source and were also related to ammonia concentrations. In contrast to plants used for the active biomonitoring, the exact time of exposure of passive biomonitors to environmental pollution is not known, so that satisfactory dose-response relationships can not be derived. At the same time nitrogen concentrations above which adverse effects manifest themselves are unknown. Upon supply of nutrient nitrogen plants will produce more biomass and indeed, *growth* may be used as an indicator of plant exposure to reduced nitrogen. In many regions with high deposition loads growth and thus competition of grasses is well-known to have increased due to the increased nutrient availability and plant growth also proved to be increased by traffic emissions [30]. To utilise these findings for the development of active biomonitors, plants will have to be pre-grown and exposed under highly standardised conditions, e.g. after the VDI standardised rye grass culture method [31]. Complete nitrogen balances taking into account initial and final plant biomass and total nitrogen contents may give an indication on how much gaseous and particulate nitrogen was accumulated over defined time periods by a receptor plant. Preliminary work by [32, 33] suggests the feasibility of such methods, but future developments regarding the growth medium (soil substrate and non nitrogen nutrient supply) must be optimised in future research.

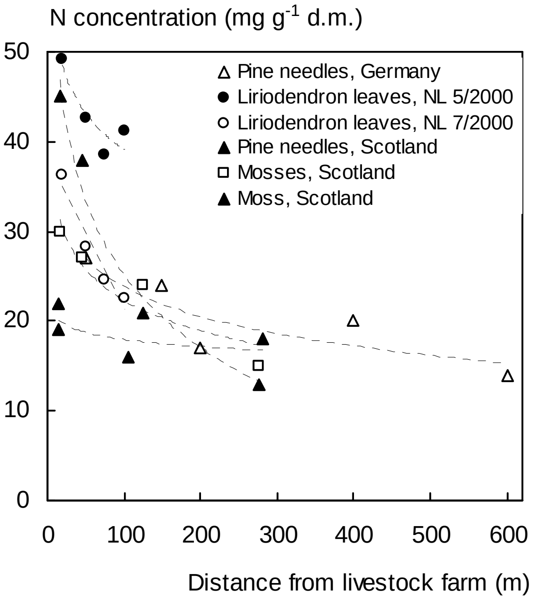

Figure 4. Results from gradient studies with passive biomonitors in the lee of NH_x-emitting animal stables. Response parameter is the nitrogen concentration of various plant species. Data from [18, 27-29]. The stables in the cited studies emitted about 5 Mg a^{-1} of ammonia.

Other physiological parameters to be included in bioindication studies are nutrient ratios and imbalances, which may result from the luxurious nitrogen supply of plants close to emission sources. Protein contents, the patterns of and the presence of characteristic free amino acids may also prove useful parameters in bioindicator studies on the effects of NH_x-emissions on plants. Especially, the amino acid arginin seems to be a suited indicator for reduced nitrogen on nearby an ecosystem which has been shown close to Finnish and Scottish animal farms [34, 35].

CONCLUSION AND OUTLOOK

International cooperative programmes, e.g. the UN-ECE ICP Forests and ICP Vegetation, have long-lasting expertise in using plant biomonitors for air pollutants and the use of accumulation indicators, e.g. mosses for heavy metals, has proven the efficiency of European clean air policies. However, air pollution from nutrient nitrogen has not been reduced significantly in past years despite the introduction of political measures (Gothenburg Protocol, EU NEC and IPPC guidelines, national nitrogen reduction programmes). Because of the high costs for technical monitoring devices and the inadequacy of model approaches at local scales the use of plant bioindicators may prove useful to assess adverse impacts of nitrogen deposition in the field. Coherent and integrated monitoring schemes using plant ecological approaches to assess local eutrophication may be applied in environmental reporting within the relevant political frameworks (NATURA2000 reporting, biodiversity and global change). The EU operates and supports various programmes (e.g. LIFE) and has launched new initiatives (e.g. the EU Environment and Health Strategy), in which biomonitoring of air pollutants with plants may play an important role.

REFERENCES

[1] Statistisches Bundesamt (2003): Produzierendes Gewerbe - Düngemittelversorgung. Fachserie 4 / Reihe 8.2, 23 S., Wiesbaden.

[2] Erisman, J.W., Brydges, T.G., Bull, K., Cowling, E., Grennfelt, P., Nordberg, L., Satake, T., Schneider, T., Smeulders, S., van der Hoek, K.W., Wisniewski, J.R., Wisniewski, J. (1998): Nitrogen, the Confer-N-s, First International Conference 1998. Summary Statement. Environ. Pollution 102 S1: 3-14.

[3] Galloway, J., Cowling, E. (2001): N2001 - The Second International Nitrogen Conference. Optimizing nitrogen management in food and energy production and environmental protection. Bolger Conference Center, Potomac, Maryland, USA. October 14-18, 2001, Conference Proceedings, 119 p.

[4] SAEFL (2003): Empirical critical loads for nitrogen. Expert Workshop held under the Convention on Long-range Transboundary Air Pollution (LRTAP) covering the region of the UNECE, Berne, 11-13 November 2002, Swiss Agency for the Environment, Forests and Landscape, SAEFL, Bern.

[5] Kroeze, C., Aerts, R., van Breemen, N., van Dam, D., van der Hoek, K., Hofschreuder, P., Hoosbeek, M., de Klein, J., Kros, H., van Oene, H., Oenema, O., Tietema, A., van der Veeren, R., de Vries, W. (2003): Uncertainties in the fate of nitrogen I: An overview of sources of uncertainty illustrated with a Dutch case study. Nutrient Cycling in Agroecosystems 66: 43-69.

[6] Busch, G., Lammel, G., Beese, F.O., Feichter, J., Dentener, F.J., Roelofs, G.J. (2001): Forest Ecosystems and the changing patterns of nitrogen input and acid deposition today and in the future based on a scenario. ESPR-Environ. Sci. & Pollut. Res. 8: 95-102.

[7] Bouwman, A.F., van Vuuren, D.P., Derwent, R.G., Posch, M. (2003): A global analysis of acidification and eutrophication of terrestrial ecosystems. Water, Air and Soil Pollution 141: 349-382.

[8] Erisman, J.W., Otjes, R., Hensen, A., Jongejan, P., van den Bulk, P., Khlystov, A., Möls, Slanina, S. (2001): Instrument development and application in studies and monitoring of ambient ammonia. Atmospheric Environment 35: 1913-1922.

[9] Sutton, M.A., Asman, W.A., Ellermann, T., van Jaarsveld, J.A., Acker, K., Aneja, V., Duyzer, J., Horvath, L., Paramonov, S., Mitosinkova, M., Tang, M., Achermann, B., Gauger, T., Bartniki, J., Neftel, A., Erisman, J.W. (2003): Establishing the link between ammonia emission control and measurements of reduced nitrogen concentration and deposition. Environmental Monitoring and Assessment 82: 149-185.

[10] KTBL (2001): Messmethoden für Ammoniak-Emissionen aus der Tierhaltung. KTBL Scrift 401, 137 pp., Kuratorium für Technik und Bauwesen in der Landwirtschaft, Darmstadt.

[11] MURL & MWMT (1999): Durchführung der Technischen Anleitung zur Reinhaltung der Luft. Gem. RdErl. d. Ministers für Umwelt, Raumordnung und Landwirtschaft - V B 1- 8001.7.25.1- (V Nr. 08/86) u. d. Ministers für Wirtschaft, Mittelstand und

Technologie 133-81-3.7 (19/86) v.14.10.1986 (SMBl. NRW 7130), in Fassung vom 10.06.1999.

[12] Kirchner, M., Braeutigam, S., Ferm, M., Haas, M., Hangartner, M., Hofschreuder, P., Kasper-Giebl, A., Römmelt, H., Striedner, J., Terzer, W., Thöni, L., Zimmerling, R. (1999): Field intercomparison of diffusive samplers for measuring ammonia. Journal of Environmental Monitoring 1: 259-265.

[13] DEFRA (2002): Ammonia in the UK. Department for Environment, Food and Rural Affairs, 89 pp, London.

[14] Thöni, L., Seitler, E., Blatter, A., Neftel, A. (2003): A passive sampling method to determine ammonia in ambient air. Journal of Environmental Monitoring 5: 96-99.

[15] Kirchner, M., Braeutigam, S. (2000): Erfassung von Ammoniak mit Passivsammlern. Schlussbericht zum EU-Interreg-II-Projekt im Auftrag des StMLU in Zusammenarbeit mit dem Amt der Salzburger Landesregierung. Materialien 152, 97 p., Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, München.

[16] Dämmgen, U. (2000): Versauernde und eutrophierende Luftverschmutzung in Nordost-Brandenburg. Landbauforschung Völkenrode Sonderheft 213: 1-152.

[17] Erisman, J.W., van der Eerden, L. (1999): Stikstofonderzoeksprogramma STOP. De stikstofproblematiek op lokale en regionale schaal nader onderzocht. VROM en LNV, Den Haag, 100 pp.

[18] Van Dijk, C.J., Franzaring, J., van Alfen, A.J. (2001): Invloed van ammoniak op boomkwekerijgewassen en fruitbomen. Nota 57, 28 p., Plant Research International, Wageningen.

[19] Kirchner, M., Braeutigam, S., Feicht, E., Löflund, M. (2002): Ammonia emissions from vehicles and the effects on ambient air concentrations. Fresenius Environmental Bulletin 11: 454-458.

[20] Asman, W.A.H., Sutton, M.A., Schjørring, J.K. (1998b): Ammonia: emission, atmospheric transport and deposition. New Phytologist 139: 27-48.

[21] Bunce, R.G.H., Smart, S.M., van de Poll, H.M., Watkins, J.W., Scott, W.A. (1999):. Measuring Change in British Vegetation. Ecofact Book Series No. 2. Monks Woods, CEH Centre for Ecology and Hydrology, 141 pp.

[22] Preston, C.D., Telfer, M.G., Carey, P.D. et al. (2002): The changing flora of the UK. DEFRA, UK Department for Environment, Food and Rural Affairs, 19 pp.

[23] Bundesamt für Naturschutz (1999): Ursachen des Artenrückgangs von Wildpflanzen und Möglichkeiten zur Erhaltung der Artenvielfalt. Schriftenreihe für Vegetationskunde 29, 444 pp., Bonn-Bad Godesberg.

[24] Ellenberg, H., Weber, E.H., Düll, R., Wirth, V., Werner, W., Paulissen, D. (1991): Zeigerwerte von Pflanzen in Mitteleuropa. Scripta Geobotanica 18, 3. Auflage, 248 pp.

[25] UN-ECE and EC (2003): Intensive Monitoring of Forest Ecosystems in Europe Technical Report 2003, Geneva and Brussels. FIMCI-Technical Report, 161 pp.

[26] UCPE, Unit of Comparative Plant Ecology, download of database on plant nutrient contents in March 2002 from http://www.shef.ac.uk/uni/academic/N-Q/nuocpe/ucpe/).

[27] Pitcairn, C.E.R., Leith, D., Sheppard, L.J., Sutton, M.A., Fowler, D., Munro, R.C.., Tang, S., Wilson, D. (1998): The relationship between nitrogen deposition, species composition and foliar nitrogen concentrations in woodland flora in the vicinity of livestock farms. Environ. Poll. 102 Suppl. 1: 41-48.

[28] Pitcairn, C.E.R., Skiba, U.M., Sutton, M.A., Fowler, D., Munro, R., Kennedy, V. (2002): Defining the spatial impacts of poultry farm ammonia emissions on species

composition of adjacent woodland ground flora using Ellenberg Nitrogen Index, nitrous oxide and nitric oxide emissions and foliar nitrogen as marker variables. Environ. Poll. 119: 9-21.

[29] Kaupenjohann, M., Döhler, H., Bauer, M. (1989): Effects of N-immissions on nutrient status and vitality of *Pinus sylvestris* near a hen-house. Plant and Soil 113: 279-282.

[30] Angold, P.G. (1997): The impact of a road upon adjacent heathland vegetation: effects on plant species composition. Journal of Applied Ecology 34: 409-417.

[31] VDI (2003): Biological measuring techniques for the determination and evaluation of effects of air pollutants on plants (bioindication). Method of standardised grass exposure. VDI 3957 Part 2, ICS 13.040.01, Verein Deutscher Ingenieure, Kommission Reinhaltung der Luft im VDI und DIN, Düsseldorf.

[32] Sutton, M., Pitcairn, C., Leith, I., van Dijk, N., Sheppard, L., Tang, T., Smart, S., Mitchell, R., Fowle, D. (2003): Bioindicator methods for monitoring of nitrogen impacts on statutory nature conservation sites. Presentation on the Workshop "Understanding the impacts of air pollution on the SSSI series" in the framwework of the Air Pollution and Ecosystem Change Symposium held on 28/29 October 2003 at Caernarforn (Wales). Download (02/2004): http://www.jncc.gov.uk/habitats/air_poll/caernarfon/sutton.pdf.

[33] Böhme, F., Russow, R., Neue, H.U. (2002): Airborne nitrogen input at four locations in the German state of Saxony-Anhalt - Measurements using the N-15-based ITNI-system. Isotopes in Environmental & Health Studies 38:95-102.

[34] Pietilä, M., Lähdesmaki, P., Pietiläinen, P., Ferm, A., Hytönen, J., Pätilä, A. (1991): High nitrogen deposition causes changes in amino acid concentrations and protein spectra in needles of Scots Pine (Pinus sylvestris). Environmental Pollution 72: 103-115.

[35] Pitcairn, C.E.R., Fowler, D., Leith, I.D., Sheppard, L.J., Sutton, M.A., Kennedy, V., Okello, E. (2003): Bioindicators of enhanced nitrogen deposition. Environmental Pollution 126: 353-361.