

Chapter 2

Progress in Monitoring and Modelling Estimates of Nitrogen Deposition at Local, Regional and Global Scales

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Abstract This chapter discusses the status and progress of activities around the world to measure and model dry and wet deposition of reactive nitrogen (N_r), i.e. the final removal processes from the atmosphere, at the local, regional and global scales. It gives an overview of present status and developments in networks and techniques for measuring deposition of N_r . We describe recent developments in the modelling of emissions and deposition, and finish by giving research and policy recommendations regarding N-deposition measurement and modelling, including the need for;

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- an increase in the number of regional-scale, long-term monitoring sites for the routine measurement/estimation of wet and particularly dry deposition worldwide;
- an increase in the number of N species routinely measured, especially dissolved organic N (DON), ammonia (NH_3) and nitrogen dioxide (NO_2);
- global and regional models to improve their estimation of dry deposition and their resolution, especially in situations with complex topography.

Keywords Atmospheric deposition • Emissions • Measurement • Modelling • Oxidized and reduced deposition • Wet and dry deposition

2.1 Introduction

Reactive nitrogen (N_r) compounds in the oxidized form (NO_y) and the reduced form (NH_x) play a central role in the chemistry of the atmosphere as well as in the functioning of marine, freshwater and terrestrial ecosystems. There is ample evidence that increasing human activities seriously disturb the natural nitrogen (N) cycle. Reactive nitrogen enters the environment through a number of processes related to fertilization, waste discharge and atmospheric emissions, transport and deposition.

Here we discuss progress pertinent to measurement and modelling of dry and wet deposition of N_r , i.e. the final removal processes from the atmosphere, at the local, regional and global scales. We cover (a) present status and developments in networks and techniques for measuring deposition of N_r , (b) recent developments in the modelling of emissions and deposition, and (c) research and policy recommendations regarding N-deposition.

2.2 Measurements

2.2.1 Introduction

The term dry deposition applies to all removal processes of gases and aerosols at the earth's surfaces; this process does not necessarily have to be 'dry', in fact the removal of gases like SO_2 is rather efficient to wetted surfaces or ocean water. The research of dry deposition processes has been stimulated by the acid rain problem in the USA, Europe and Asia. Many different techniques have been used to measure dry deposition fluxes such as gradient methods, eddy correlation techniques, chambers or the use of artificial surfaces. Whereas these measurements provided new insights into the processes playing a role for removal of air pollutants by dry deposition, they were by no means routine determinations, and required a large effort

in terms of equipment, labor and interpretation. The accuracy of the measurements was in the best case of the order of $\pm 30\%$. The validity of the measured fluxes for a larger region (the so called 'fetch') was in most cases rather limited. Aircraft measurements provided a new method for estimating dry deposition fluxes, mainly by means of eddy correlation techniques. However these measurements are generally very expensive, and the sampling period limited. The geographical coverage was obviously much better than the 'local' measurements mentioned previously and in addition showed the complex behavior of boundary layer dynamics and the resulting effect on dry deposition. Measurements are generally presented as dry deposition velocities [cm/s] or as surface resistances, which is approximately reciprocal of the dry deposition velocity.

Wet deposition refers to the removal of gases and aerosols by scavenging in clouds (uptake in cloud droplets/ice crystals, formation and sedimentation of rain) and precipitation scavenging (falling rain droplets and frozen hydrometeors interacting with particles and gases). Measurements of wet deposition are almost entirely made by collection and analysis of rain and snow samples. Whereas in the past frequently bulk samplers were utilized, which measured a substantial and largely unquantified amount of dry deposition, nowadays mostly wet-only samplers are employed, opening and closing the sampler at the beginning and end of rainfall events.

2.2.2 *Worldwide Networks of Wet Deposition*

Continuous large-scale measurements of wet deposition have been made since the 1970s. Since then, many international, national, and sub-national monitoring networks/programs have been operated and, in some cases, expanded, reduced and/or closed. The major long-term, large scale, regionally-representative monitoring networks that exist at this time include the Canadian Air and Precipitation Monitoring Network (CAPMoN) and related Canadian provincial networks, the Acid Deposition Monitoring Network in East Asia (EANET), the European Monitoring and Evaluation Program (EMEP), the International Global Atmospheric Chemistry (IGAC) Program's Deposition of Biogeochemically Important Trace Species Project (DEBITS) in Africa (IDAF), Asia (CAD and EANET) and South America (LBA), the United States National Atmospheric Deposition Program (NADP), and the World Meteorological Organization Global Atmosphere Watch Precipitation Chemistry Program (GAW). A number of other national and sub-national networks also operate in countries such as Russia, China, Korea, Taiwan, and India. These networks typically measure the concentrations of the following major anions and cations in precipitation: SO_4^{2-} , NO_3^- , Cl^- , H^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ and K^+ (and in some cases, organic acids and phosphorus) as well as precipitation amounts. Figure 2.1 shows the regional sites of the aforementioned major networks that reported data in 2005.

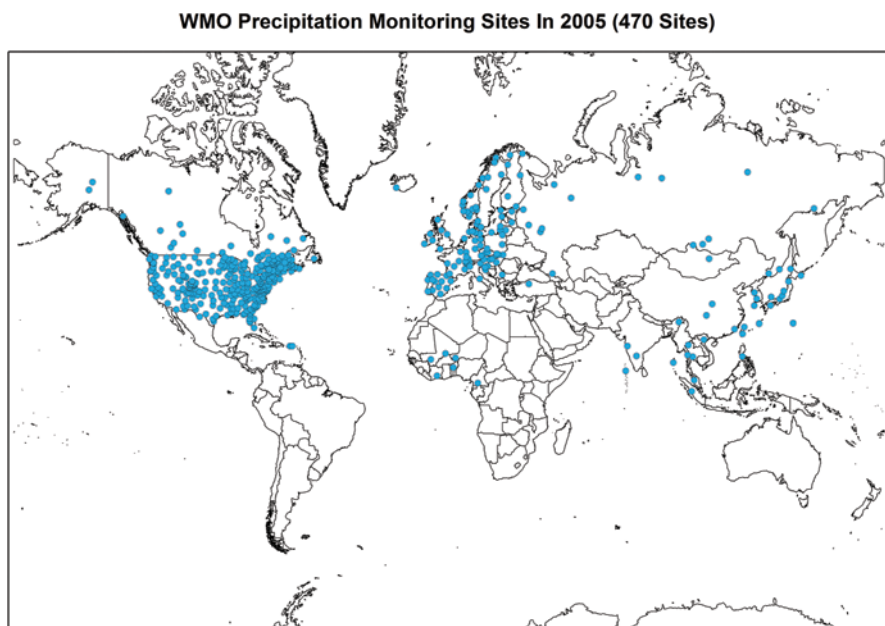


Fig. 2.1 Regional-scale wet deposition monitoring sites that reported data in 2005

The scientific objectives of wet deposition monitoring networks vary depending on the country and/or the specific scientific program, but most networks focus on the following: defining the spatial patterns of ion wet deposition, investigating the long term trends of ions in precipitation, evaluating chemical transport models, calculating critical loads, and investigating atmospheric processes. The World Meteorological Organization (WMO), through its Scientific Advisory Group for Precipitation Chemistry is currently preparing a scientific assessment of global deposition and, to that end, has integrated and synthesized data from most of the foregoing networks. An example of that effort, a preliminary global pattern of N-NO_3^- wet deposition in 2005, is shown in Fig. 2.2.

Over the last decade, the number of wet deposition monitoring sites has generally increased in Asia, Eastern Europe and the USA. Unfortunately, large areas of the world still have few if any measurements, namely, South America, Africa, Australia, Oceania, western/northern Canada, the oceans, and the polar regions.

The major problems with wet deposition measurements, beyond the paucity of measurement sites, are poor laboratory performance and inaccurate field measurements. The World Meteorological Organization is addressing these problems through the long-term operation of semi-annual laboratory inter-comparison studies and the publication of a manual for the proper measurement of wet deposition (WMO 2004). Nevertheless, these problems persist in many countries.

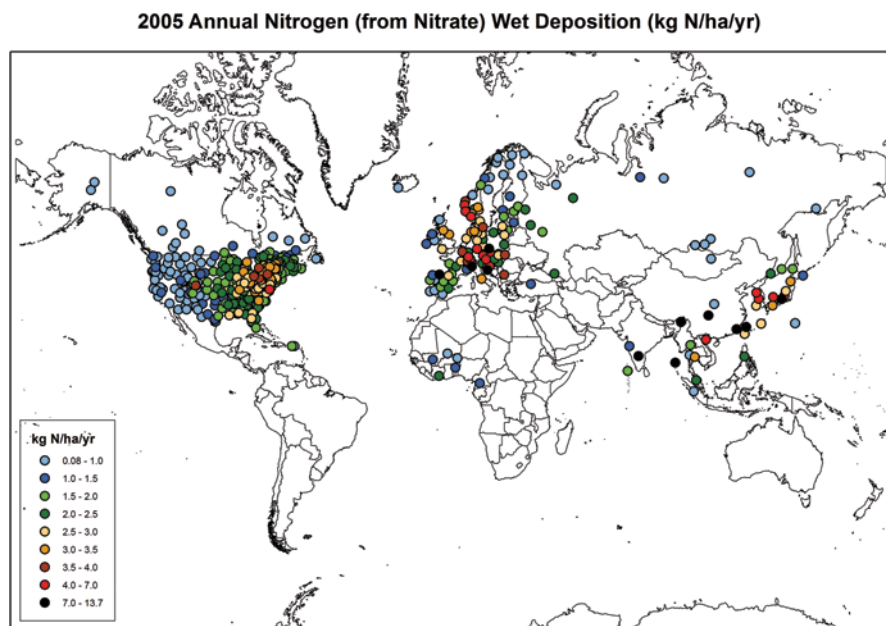


Fig. 2.2 Preliminary 3-year average annual deposition of wet deposition of NO_3^- as N (in $\text{kg N ha}^{-1} \text{ year}^{-1}$) for the period 2005. Some sites do not have all 3 years of data

2.2.3 Dry Deposition Measurement Networks

Dry deposition is not measured directly by large-scale monitoring networks because of the requirement for sophisticated instrumentation and methods. Instead, networks measure ambient gas and particle concentrations and model the associated dry deposition velocities. This method, which ultimately requires multiplying the ambient concentrations by the modelled dry deposition velocities, is called the *inferential technique*. Only two major networks currently make regionally-representative routine inferential estimates of dry deposition fluxes, namely, the United States Clean Air Status and Trends Network (CASTNET) and the Canadian Air and Precipitation Monitoring Network (CAPMoN). The former currently comprises 86 sites in the USA (www.epa.gov/castnet/docs/CASTNET_factsheet_2007.pdf) and the latter 15 sites in Canada (www.msc.ec.gc.ca/capmon/index_e.cfm). An inferential model is currently under development for Africa under the IDAF (IGAC/DEBITS/AFrica) project of the International Global Atmospheric Chemistry/Deposition of Biogeochemically Important Trace Species (IGAC/DEBITS) program (<http://medias.obs-mip.fr/idaf>).

Unfortunately, neither the US nor Canadian networks measure all of the major oxidized and N_r species needed to estimate the total atmospheric loading of N. Both

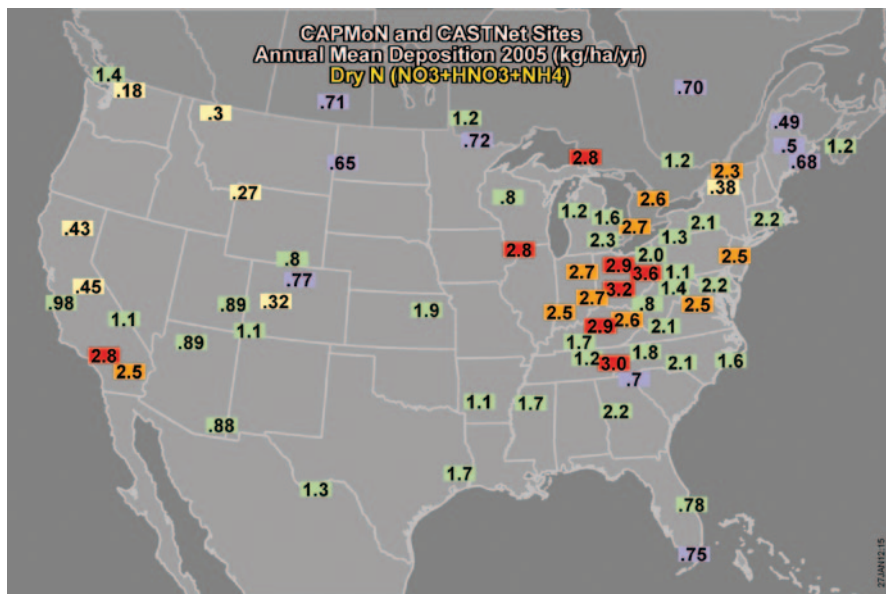


Fig. 2.3 Estimated 3-year-average dry deposition fluxes of nitrogen ($\text{N ha}^{-1}\text{year}^{-1}$) from particle- NO_3^- , particle- NH_4^+ , and gaseous HNO_3 based on data from the United States Clean Air Status and Trends Network and the Canadian Air and Precipitation Monitoring Network

networks measure particle- NO_3^- , particle- NH_4^+ , and gaseous HNO_3 , but not NO , NO_2 , PAN, NH_3 or organo-nitrates—some of which are important contributors to dry deposition. Thus, the dry deposition fluxes (and wet + dry deposition fluxes) of N estimated by these two networks are thought to be quite conservative.

An illustration of the CASTNET and CAPMoN dry deposition monitoring sites and their estimated 2005–2007 annual average dry deposition fluxes of N is shown in Fig. 2.3. As mentioned above, these estimates are based only on particle- NO_3^- , particle- NH_4^+ , and gaseous HNO_3 fluxes and are missing the other potentially-important nitrogen species, most notably NH_3 and NO_2 . From Fig. 2.3, one can see that dry deposition fluxes are higher in eastern North America than in western North America (with the exception of southern California), which is a reflection of the spatial distribution of NO_x emissions in North America.

Globally, the number of sites that provide inferential dry deposition estimates is insufficient, with few estimates in South America, Africa, Australia, Oceania, northern Canada, Asia, the oceans and the polar regions. Additionally, most ambient air monitoring networks do not measure all of the N compounds necessary to determine the total atmospheric loading of N. Even the two existing North American inferential dry deposition networks, CASTNET and CAPMoN, have known measurement uncertainties due to the volatilization of particle- NH_4NO_3 , and large uncertainties in the flux estimates due to differences in their respective inferential models. As a result, dry deposition monitoring on a global basis is inadequate.

There needs to be a commitment in the measurement community to developing routine network measurement systems that provide the data required to assess dry deposition on a regional and global basis.

In the appendix to this chapter we give a short overview of some of the networks, Table 2.1 lists some of the issues that were identified for these networks.

2.2.4 Use of Deposition Measurements

How are the network measurements being used? Using statistical techniques like Kriging or Optimal Interpolation, the measurements can be directly interpolated to larger geographical regions. The applicability of such methods depends on the presence of sufficient data that are at a short-enough-distance to be correlated with each other. They can be combined with meteorological modelling, for instance to derive dry deposition fluxes. They can be used as independent data sets to verify atmospheric models, as will be elaborated in Sect. 2.3 (this chapter), the measurements can be assimilated in models to achieve an optimized agreement between model and measurements space- a process known as data-assimilation. An overarching theme in all techniques is the representativeness of point measurements for larger scales.

2.3 Modelling

2.3.1 Models

There is a large range of models available to describe air pollution chemistry and transport. These models range from describing near-point source dispersion to global transport processes- the choice of model depends on the issue and the availability of input data.

Many processes are parameterized in models, and consequently the models can only provide a limited representation of reality. The models in use to describe N emissions, chemistry and transport, can be typically separated into plume models, useful at say farm-scale, Lagrangian and trajectory models tracking long range transport of pollution plumes, and Eulerian grid-point models. While plume models continue to be useful in a regulatory framework, today overwhelmingly Eulerian models are used to describe ozone and aerosol chemistry, and are also providing estimates of the deposition of N components. Global models are increasingly used for providing maps of reduced and oxidized N. Resolutions of global models are currently ranging from $1^\circ \times 1^\circ$ to $4^\circ \times 5^\circ$ lat-lon, and expected to improve to $0.5^\circ \times 0.5^\circ$ in the coming years. The global models obviously cannot cover many of the regional deposition details; nevertheless a recent comparison of Dentener et al. (2006) showed good comparison of 21 global models with measurements in North America and

Table 2.1 Issues associated with regional nitrogen deposition monitoring networks

North America: CASTNET/ NADP/CAPMoN	Europe (EMEP)	South Asia (CAD)	South East/East Asia (EANET)	Africa (DEBITS/IDAF)
<p><i>Wet deposition:</i> Incomplete closure of N budget; no DON</p> <p>Too few measurement sites in certain areas</p> <p><i>Dry deposition:</i> Not all gases being measured rou- tinely e.g. NH_3; NO_x; PAN and organo-nitrates are missing</p> <p>Too few measurement sites</p>	<p>Measurements performed on country basis, dif- ferences in measure- ment quality and sampling protocols?</p> <p>In some regions very few measurements (South- ern Europe)</p>	<p>Data quality: delay in analysis leading to underestimate of NH_4 and NO_3</p> <p>Lack of rural sites, and long term measurements</p> <p>Lack of quality controlled data</p>	<p>Currently focus on acid deposition rather than N deposition. DON is not measured. Insufficient sites in China</p> <p>Organic nitrogen species (e.g. PAN and organo-nitrates) are missing</p> <p>In some sites especially in China, dry N deposition data is missing</p> <p>Insufficient sites in rural and remote places. More sites needed in China</p> <p>Regional specific models need to estimate the rates of dry deposition</p>	<p>Eight stations covering con- tinental scale; representing major ecosystems</p> <p>Wet deposition budget incom- plete (no DON)</p> <p>Dry deposition complete NO_2 + HNO_3 + NH_3 + pNO_3^- + pNH_4^+</p> <p>Dry deposition of gases combining long-term passive samplers measurements and site-specific deposition veloc- ities: large uncertainty. Bulk measurements for particles</p> <p>All the African Sites are located in non perturbed rural regions</p> <p>Lack of urban sites to measure hot spots sources and associ- ated deposition (planned)</p>
<p>Siting criteria require placement of the sites away from large sources. Thus, the network will miss hot spots and estimates of deposition budgets based on interpolation of sparse sites will be biased low</p> <p>At some sites, violation of theoret- ical siting requirements for dry deposition monitoring, e.g., locating sites in complex terrain</p> <p>Lack of comparability between the US and Canadian inferential dry deposition estimates</p>	<p>Measurements for N budget incomplete</p>	<p>Difficulties estimating deposition of NO_x and NH_3 gases</p>		<p>Development of an inferential model for African ecosystems</p>
	<p>High ammonia specific for India</p>		<p>Nitrogen deposition in coastal areas should be emphasized especially in east China</p>	

Europe, reasonable performance in South East Asia, but larger problems in Africa, South Asia, and South America.

The spatial domain and resolution of regional models has been steadily improving. In the USA and Europe the typical resolution of continental models has decreased from 36 km to 12 km grid sizes. However, 12 km is still too coarse for critical load modelling in complex terrain (hills, valleys), where much of the critical load work in e.g. the USA is focused. Throughfall measurements suggest that there is a high degree of deposition variability within a grid in complex terrain that is important to critical loads (Weathers et al. 2006). These problems are associated with the inability of models to capture orographic effects on rainfall amounts, or effects of terrain and land cover type on dry deposition. Parameterizations for this subgrid variability would be helpful.

Also, even in flat terrain, dry deposition will depend on land cover type. It is essential that methods be developed to account for this variability rather than use a single number per grid. Efforts are being made to make dry deposition land-use specific within a grid.

A similar problem occurs in Europe, and probably also elsewhere, where patches of natural land are included in farmland. Current global and regional models should address this sub-grid phenomenon.

It is worth mentioning here, that models describing NO_x and NH_x chemistry and deposition, are almost always part of larger models describing photochemistry and aerosol dispersion processes in general, and not necessarily focusing on correctly describing deposition processes. Increasingly, models now combine their aerosol and photochemistry modules.

2.3.2 *Land Use Databases*

As mentioned above models use land cover databases to describe a number physical processes (e.g. albedo, surface roughness), but also the parameters needed to perform calculations of dry deposition. These databases are provided on a relatively detailed resolution by the USGS and the updated NLCD (National Land Cover Data base) in the USA, or CORINE (Coordination of information on the environment) in Europe. Examples of relatively high resolution global land cover database include the GLC2000 land cover database, MODIS land cover, and the IGBP. A recent comparison of 3 global land cover databases (Herold et al. 2008) shows large differences in these databases arising from the use of different remote sensing instruments, interpretation methods, and perhaps most importantly different classification methods, that may regionally differ. Especially among classes of mixed vegetation there are large differences. These uncertainties are propagated into atmospheric models, and often it is not clear what land-cover database is actually included in the various model results. Very recently, a global land-cover database from the MERIS (Envisat's Medium Resolution Imaging Spectrometer) at 300 m resolution has become available. The high spatial resolution should help to more unambiguously attribute

land-cover classes—with less need to define ‘mixed’ classes. A recurring theme in the land-cover and land-use databases is the adequacy of the chosen classification to accurately address the users need. We mention here that many atmospheric models work with often outdated landcover databases, possibly leading to large inconsistencies.

2.3.3 Emissions

Because photochemistry and aerosol physics are involved, description of N deposition, emissions for local, regional and global models requires inclusion of NO_x , VOC, NH_3 and SO_x emissions at a minimum. Except for power plant SO_2 and NO_x emissions, which can be measured at the stack, emissions are estimated using models and emission factors multiplied by activity indicators. Then these emissions must be geographically located, which introduces additional uncertainty. SO_x emissions are mostly from power plants, and industry. NO_x emissions involve many sectors, including on-road and off-road vehicles, area sources, and industrial and power plant stacks. NH_3 emissions are mostly from animal operations and fertilizer application (agriculture). Assessments of emission uncertainty for the USA suggest SO_x emissions are the most certain, due to the use of stack Continuous Emissions Monitors (CEMs). NO_x emissions have an intermediate level of uncertainty and NH_3 emissions are the least certain (Dennis et al. 2008). This ranking is corroborated by comparisons of the regional models in the USA against NADP wet deposition data. Similarly, in Europe country total emissions are relatively well known, and detailed spatial desegregation (gridding) is available for some countries. EMEP interprets national reports on emissions, and provides an expert based emission inventory on a 50 km scale. Elsewhere in the world inventories have been created on a project-basis (i.e. TRACE-P), but there are generally no officially endorsed gridded emission databases available. There are attempts to provide compilations of gridded datasets on global and regional scales by the IGAC endorsed GEIA (Global Emissions Inventory Activity; <http://www.geiacenter.org>). Consistent inventories of pollutant and greenhouse gas emissions are provided by the EDGAR team (edgar.jrc.ec.europa.eu/index.php). EDGAR4 will contain global high resolution 10 km by 10 km data for the major pollutant emissions.

Emission projections (e.g. the new projections in the context of the IPCC AR5 report) indicate that air pollution control strategies may lead to stabilization or even a decrease of NO_y depositions worldwide. Mitigation strategies addressing climate change may also lead to reduced NO_y deposition. Much less attention is given to NH_3 emissions, and most scenarios indicate further growth of NH_3 emissions.

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