Chapter 3

(a, ii) Atmospheric chemistry

Note on draft

This is the first draft of a sub-chapter concerning atmospheric chemistry relevant tp the Baltic Sea environment. The text covers current status, changes associated with past (100-200 yr) and future emissions and climate, and a discussion of uncertainties. Some caveats are:

- This is a very first draft, needs discussion among co-authors as well as external reviewers.
- The chapter is very focussed on nitrogen deposition, since this is a clear environmental problem. Other pollutants should be brought in more though.
- It is, however, difficult to include many pollutants in a short chapter.
- So far very focussed on models. Needs more information from measurements, although these are probably very limited.
- Need more on longer-term trends, past and future.
- Acronyms have to be introduced properly. So far intended for people 'in the know'., Spell check, etc., will be done for more final versions

3.1 Introduction

This chapter attempts to answer the overriding questions: what are the main atmospheric chemical changes over the Baltic Sea region? What are their inputs

to the Baltic region, now and in the previous 100-200 years? How well can we quantify this? In order to answer these questions we will address firstly the emissions of pollutants and their precursors, then present an overview of atmospheric concentrations, and finally we will discuss deposition estimates and uncertainties.

Reactive nitrogen (Nr) species are of particular concern for the Baltic sea and surrounding semi-natural ecosystems as here the atmospheric supply of nitrogen can form an appreciable part of the total nitrogen load. Indeed, Bartnicki et al. (2011) calculated that about one quarter to one third of Nr input to the Baltic Sea originates from airborne nitrogen deposited directly to the sea surface. In addition, part of the nitrogen deposition into the Baltic Sea drainage basin reaches the sea via runoff from land (Seitzinger et al. 2002).

Of course, measurements are essential for understanding the state of the atmosphere. However, the chain of processes linking emissions, atmospheric dispersion, chemical transformation and loss from the atmosphere of polluting compounds Nr compounds is extremely complex. Observations can typically address only a small portion of this chain. In particular, observations of atmospheric deposition are severely restricted in spatial extent and type. This sub-chapter will therefore have a strong modelling focus. The driving force for most changes is though emissions, so we discuss this first.

3.2 Emissions

3.2.1 Land-based sources

Table 3.1 presents national NOx emission trends for the HELCOM Contracting Parties and EU, and gives an overview of the emissions in the EMEP inventory between 1980 and 2005, adapted from (Vestreng et al. 2009). The relative share of emissions from road transport is also listed. It should be noted that official EMEP emissions had to be supplemented by data from other sources for many countries. These data sources included data from the GAINS model (http://gains.iiasa.ac.at/gains) developed at IIASA, and for a few countries EDGAR emission data (http://www.mnp.nl/edgar). The coverage of officially reported emissions is about 40% in the 1980s, increasing to nearly 60% after 1990. The level of confidence is considered to be higher for the reported and reviewed emission data, due to country specific insight and the detailed input to the calculations. These emissions and their uncertainties are discussed further in Vestreng et al. (2009).

Table 3.1: Nitrogen oxides trends for the HELCOM Contracting Parties, and total Europe (EUR), 1980–2005 (Unit: GgNO2. Percentage contribution from road transport in brackets. From Vestreng et al. 2009.

Country	1980	1985	1990	1995	2000	2005
Denmark	273 (26)	291 (32)	274 (38)	264 (37)	207 (39)	186 (37)
Estonia	67 (43)	74 (41)	74 (41)	38 (42)	35 (38)	32 (34)
Finland	295 (36)	275 (44)	299 (53)	258 (51)	235 (45)	177 (32)
Germany	3334 (35)	3276 (38)	2861 (47)	2170 (53)	1817 (55)	1443 (45)
Latvia	61 (43)	67 (41)	67 (30)	40 (37)	38 (42)	41 (43)
Lithuania	152 (36)	166 (34)	158 (34)	65 (36)	49 (51)	58 (58)
Poland	1229 (38)	1500 (26)	1581 (25)	1121 (28)	838 (27)	811 (28)
Russian Fedn.	3280 (37)	3600 (33)	3600 (31)	2563 (36)	2357 (40)	2795 (43)
Sweden	404 (44)	426 (41)	314 (55)	280 (54)	231 (49)	205 (41)
Total EUR	23944 (36)	24550 (36)	25256 (38)	20507 (41)	17809 (42)	17059 (39)

As also noted in Vestreng et al. (2009), a trend study by Konovalov et al. (2008) applying inversion techniques with GOME and SCIAMACY measurements between 1996 and 2004, broadly confirms that the NOx emission trends in Europe have been decreasing, and further indicates that the quality of the EMEP inventory has increased over the last few years. This study also suggested that the largest problems were probably in southern and Eastern Europe.

Long term emission trends are the result of two main factors: changes in fuel use, and changes in emission factors. Older technology tends to be associated with higher emissions, due to such factors as inefficiency or lack of control measures. Fig. 3.1 addresses the development of fuel use and NOx emissions from 1880 to 2005, as calculated by (Vestreng et al. 2009). Dramatic changes are seen after 1945, when liquid fuel use and road transport emissions increase signifcantly. Fuel use peaks around 1980, and emssions around 1990. The reduction in emissions in later years is stronger than the reduction in fossil-fuel use, and reflects the increasing use of improved emission control technoologies, particularly with respect to road vehicles.

In order to illustarte the uncertainties associated with such inventories, Fig. 3.2 compares the Vestreng et al. (2009) estimates of long term NOx emission changes with three other major inventory efforts. In recent years all studies give similar estimates for both Western and Eastern Europe. For the earliest years (around 1920) the Vestreng et al. (2009) and van Aardenne et al. (2001) values are also rather similar, although this may reflect a lack of alternative data rather than accuracy. In

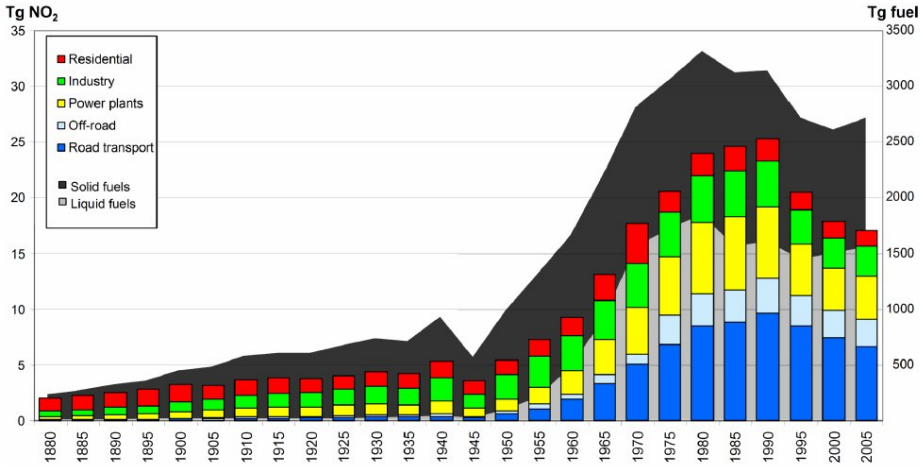


Figure 3.1: European solid and liquid fossil fuel consumption 1880âĂŞ 2005. Data from the GAINS model 1990–2005 (Tg fuel/year, right axis). Sector trends in European NO2 emissions 1880–2005 (Unit Tg NO2, left axis). From Vestreng et al. (2009)

the years between 1950 and 1990 though, some significant differences are seen in Western Europe, and more so in Eastern Europe. Lack of information on emission factors in older vehicles and combustion appliances is of course a major limitation in estimating such emissions. (Emission trends for sulphur are usually simpler to make, since uncontrolled emissions depend in a fairly straighforward way on the sulphur content of fuel, which is reasonably well documented.)

3.2.2 Shipping emissions

A summary of recent results, with an emphasis on what we do and don't know about shipping emissions, and how they are changing, would be great. Plus some key Figures. The whole chapter should aim at ca. 30 pages of Word document, so I guess that somewhere between 3-6 pages on this topic would do to start.

The Baltic Sea is a very busy shipping route with over 2000 vessels sailing at any given time. Until XXXX emissions were based upon national statitsics only, with assumed activity statistics and emission factors. However, in the last few years ship emission estimates have become more consistent with the inclusion of real ship activity data offered by the Automatic Identification System (AIS). This device automatically reports the identity, location and speed of any vessel without

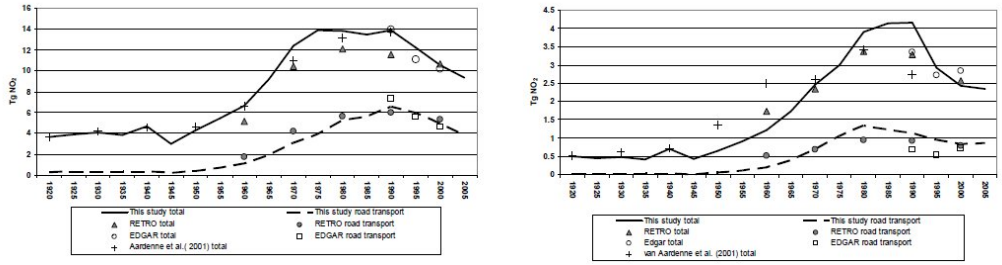


Figure 3.2: Development of NOx emissions in Europe, 1920–2005. Comparison between emissions of Vestreng et al. (2009) ('this work' in Fig.), van Aardenne et al. (2001), RETRO and EDGAR inventories for OECD Europe (left) and Eastern Europe (right); EDGAR domain definitions. From Vestreng et al. (2009)

human input. The use of AIS data in ship emission modeling was demonstrated in the Baltic Sea area (Jalkanen et al. 2009, 2011). Because AIS is based on GPS navigation it facilitates tracking of individual ships with a very high accuracy thus removing the most significant obstacle in ship emission studies: the lack of activity data. For example, the vessel movement data for the Baltic Sea during five years (2006-2010) consists of over 1100 million position reports. The use of AIS data removes the need to use average speeds or estimated travel distance between ports, but AIS became obligatory for all ships in 2005, which is the earliest year when such emission studies are possible. Effects of sea ice and marine currents are not usually considered in ship emission inventories, but the effect of waves to Baltic Sea ship emissions was estimated as 1-2% on the inventory level, but may be up to 50% on ship level (Jalkanen et al. 2009). Significant uncertainties also remain especially on the sulphur content of ship fuel for which compliance with the SOx Emission Control Area (SECA) requirements of the International Maritime Organization is assumed (REF?). Recent study indicates that this assumption is in reasonable agreement with experimental measurements (Berg et al. 2011). Currently the sulphur content of marine fuels is restricted to 1% (w/w) in SECA areas of the Baltic Sea, North Sea, English Channel and North America. In addition, the EU sulphur directive commits all vessels to use 0.1% fuel inside EU port areas. This helps to mitigate the harmful emissions of Particulate Matter (PM) from ships in areas which are close to human populations, because quite often large ports are close to major cities. Results Emissions from the Baltic Sea shipping usually peak during the summer months, because of increased passenger traffic. During these months there are a significant number of small craft, which

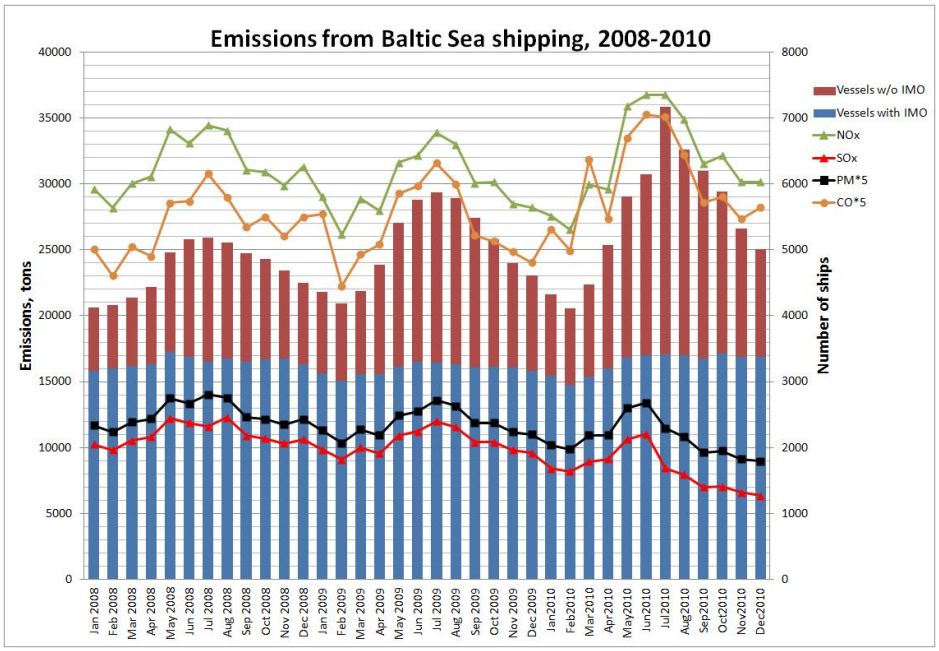


Figure 3.3: Emissions from Baltic Sea shipping in 2008-2010. Blue bars indicate the number of large vessels (with an IMO registry number) and red bars illustrate the number of small vessels (without IMO registry number). Lines represent the emissions of various pollutants each month in the units of tons (Green=NOx, Orange=CO, Black=Particulate Matter, Red=SOx). Note, that emissions of PM and CO have been multiplied by five.

can be seen in Fig. 3.3. Commercial marine traffic also reaches a maximum during summer months, but this effect is less pronounced than that of the small craft.

In April 2006 the Baltic Sea became the first SECA and North Sea/English Channel soon followed in Nov 2007. The sulphur content in marine fuels was reduced to 1.5% from global average of 2.4%, which turned the SOx emissions from shipping down (Fig. 3.4).Further reduction of fuel sulphur from 1.5% to 1.0% and the EU sulphur directive requirements in port areas decreased the SO2 emissions by 20% during 2010 when compared to the same time period without the sulphur reduction. However, particulate matter emissions from ships cannot be eradicated completely by eliminating sulphur from marine fuels because there are chemical components of PM which are not dependent on fuel sulphur. However, decrease of 9% was observed in PM emissions as a result of sulphur reductions of 2010 (Fig. 3.5).

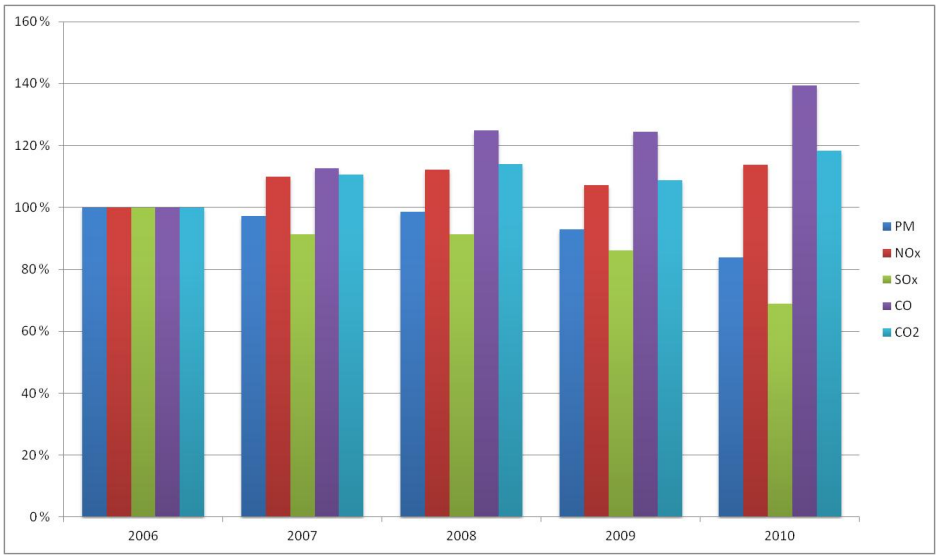


Figure 3.4: Emissions from Baltic Sea shipping during 2006-2010. Emissions of year 2006=100%.

Emissions of sulphate aerosols and associated water were reduced by this requirement whereas the emissions of elementary carbon, organic carbon and ash increased. Sulphate aerosol emissions from ships in 2010 were almost halved (-47%) when compared to SO4 emissions of 2009.

Emissions from shipping sector have been affected by the economic downturn and recent policy options. Global recession reduced emissions from Baltic Sea shipping by 0.5-5% depending on the pollutant, but emission levels of 2010 have already surpassed those before the 2008 recession. Passenger traffic was practically unaffected by the recession whereas bulk, vehicle and container cargo carriers suffered the most.

Emissions of CO2 were 18% larger in 2010 than during 2006, which correspond to linear annual growth of 3.5% in CO2 emissions if the temporary decrease of emission due to recession during 2008 were neglected. However, with detailed activity data it is possible to gain insight on the temporal variability of emissions without the need to use constant annual growth factor to estimate emissions of Baltic Sea shipping. This will improve the description of ship emissions in air quality models and may offer better compatibility with air quality observations.

Ship emission inventories of EMEP (European Monitoring and Evaluation Programme) for NOx and SOx (309 and 190 kt in 2006) are in good agreement

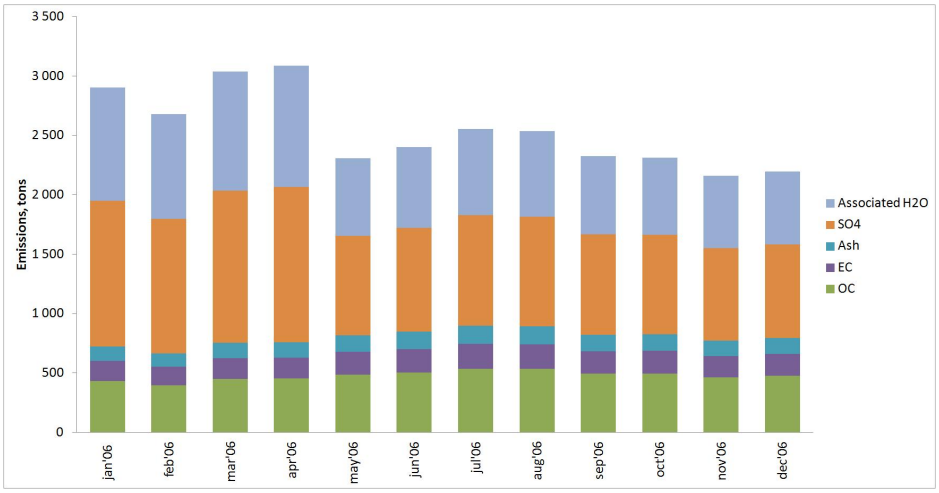


Figure 3.5: Emissions of Particulate Matter from Baltic Sea shipping. The reduction of Particulate Matter emissions from Baltic Sea shipping occurred as a result of tightened sulphur content requirements of SOx Emission Control Area. Pre-SECA sulphur content of 2.4% was lowered to 1.5%, but the emissions of PM components not related to fuel sulphur remained unaffected.

with STEAM inventories (336 and 144 kt in 2006), but PM and CO emissions are significantly larger in STEAM than in EMEP. The material and methods used in the construction of these two emission inventories are completely different but both suffer from uncertainties arising from fuel sulphur content. In addition, EMEP inventories are not based on real vessel movements and they do not include the contribution from ships in port areas. The use of AIS facilitates improved geographical accuracy thus enabling local scale studies in port areas.

There are at least two factors affecting the emission trends of the Baltic Sea shipping. First is the increase of ship traffic, which contributes to the increased number of vessels in the area. Second is the strong increase of small vessels with AIS equipment. AIS is voluntary for small vessels whereas it is required from large ships. The popularity of AIS in small vessels may explain some of the increase of emissions, especially CO, in the Baltic Sea area. In the long run this will help to improve the quality of predicted emissions because less small vessel traffic falls outside vessel tracking and emission calculations. However, no centralized data base exists for the technical specifications of small vessels which are required for the emission studies. Presently default specifications of tugboats are used for small vessels, which may overestimate their contribution.

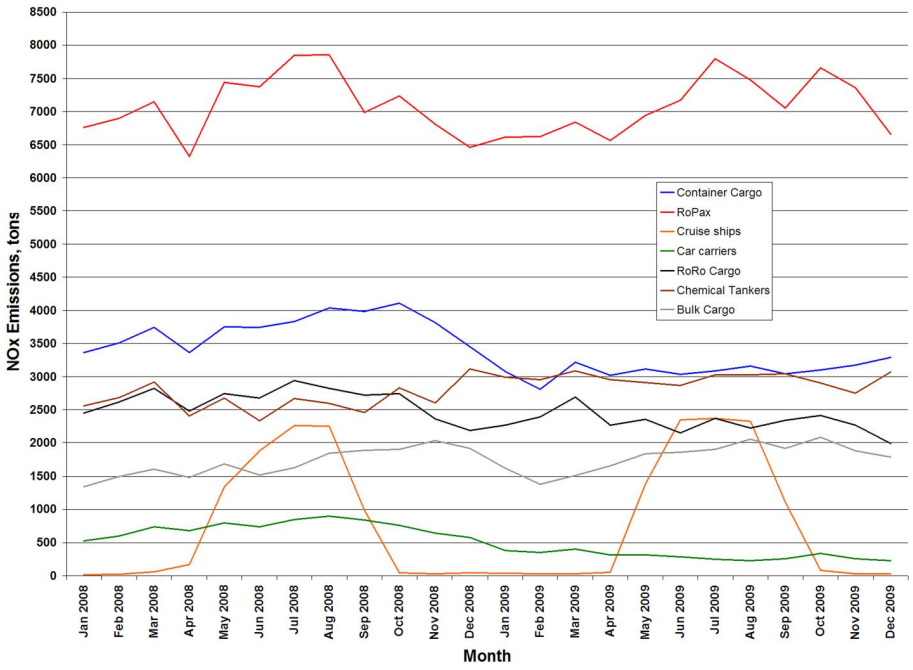


Figure 3.6: NOx emissions from selected ship types during 2008-2009 in the Baltic Sea area. The economic recession in Q4/2008-Q2/2009 had a variable impact on emissions of different ship types. Passenger traffic and oil tankers were largely unaffected by the recession whereas the emissions from RoRo, bulk cargo, container ships and vehicle carriers were decreased.

3.3 Concentrations

Concentrations of many pollutants over the Baltic region have changed significantly over the last century, mainly as a result of changes in emissions, either within Europe or globally. Many of the sulphur and nitrogen related pollutants have their biggest environmental impact once they are deposited, and deposition changes will be discussed in Sect.3.4, so these are only briefly discussed below. Ozone on the other hand has its impact through air concentrations, being a toxic gas with both health and vegetation impacts.

As shown in Fig. 3.7 there has been a significant increase in ozone since the start of the 21st century, which is largely attributed to changes in anthropogenic emissions of NOx and other precurors (Parrish et al. 2009, Monks et al. 2009). The annual trends appear to have flattened out in Europe since about the year 2000. The reasons for this are not fully understood, but reductions in European emissions are certainly affecting ozone trends. In general ozone in Europe is found to be increasing in wintertime because of the reduction in NOx emissions (the NOx-titration effect, important in winter, in which NOx acts as a sink rather than source of ozone), as discussed in eg Jonson et al. (2006). In summer, the European emission reductions act to help reduce ozone, although these are sometimes counter-acted by increasing hemispheric background levels (*ibid.*). Peak ozone levels are being reduced though, as illustrated in Fig. 3.8 for some Nordic measurement sites.

Pihl Karlsson et al. (2011) investigated changes over about a decade in sulphur and nitrogen air concentrations, deposition and soil water concentrations in forest ecosystems in Sweden as well as in other Nordic countries. The analysis of the time series 1996/97–2007/08 showed that SO2 and NO2 air concentrations have decreased substantially, whereas there was no trend for NH3.

3.4 Deposition

A number of model studies have addressed specifically deposition of Nr to the Baltic sea and surrounding areas (Bartnicki and Fagerli 2008, Bartnicki et al. 2011, Geels et al. 2011, Hertel et al. 2002, Langner et al. 2009, de Leeuw et al. 2001, 2003, Schlunzen and Meyer 2007). As seen in Figs.3.9 and 3.10, wet deposition dominates over the dry deposition of nitrogen, and oxidised nitrogen deposition is greater than reduced Nr deposition. All studies show that modelled dry deposition of both the oxidized and reduced N forms exhibit strong south-north

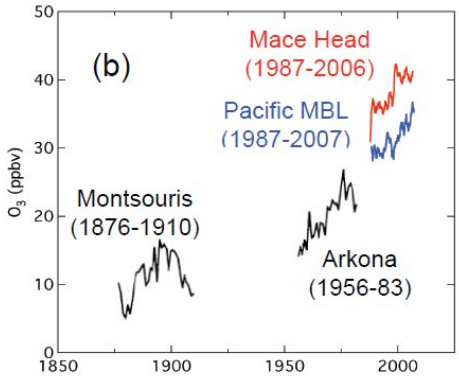


Figure 3.7: Comparison of the 12-month running mean O3 concentrations from three northen European sites: Mace Head, Arkona, and Paris, and the marine Pacific boundary layer (MBL). Figure from Parrish et al. (2009).

gradients across the Baltic Sea region; declining by well over an order of magnitude from Denmark to the northern portion of Sweden (Langner et al. 2009). Indirect estimates of the atmosphere as an 'external' source of N to the Kattegat undertaken within the MEAD project suggests that it may be a substantial fraction (i.e. $\sim$40%) of the total flux (the sum of land run-off, upwelling flux and atmospheric deposition) during the summer months, dropping to less than 20% for the whole year (Spokes et al. 2006). These estimates are in broad accord with information for the Baltic Sea proper (Elmgren and Larsson 2001, Langner et al. 2009, Rolff et al. 2008), but the wet and particularly, the dry deposition, fluxes are comparatively poorly constrained. Deposition to ice in the northern Baltic comprises 6% of the annual nutrient supply and up to 40% of the annual cadmium and lead flux into the Bothnian Bay, implying that sea ice may play a key role in determining the timing and magnitude of chemical fluxes to the water column (Granskog and Kaartokallio 2004).

In general, nitrogen depositions originating from emissions on land have a strong gradient towards the sea. Ammonia is efficiently dry deposited close to the source areas and most of the reduced nitrogen that reaches the open sea comes in the form of ammonium particles which are efficiently wet deposited. NOx depositions have a somewhat weaker gradient, reflecting a longer residence time

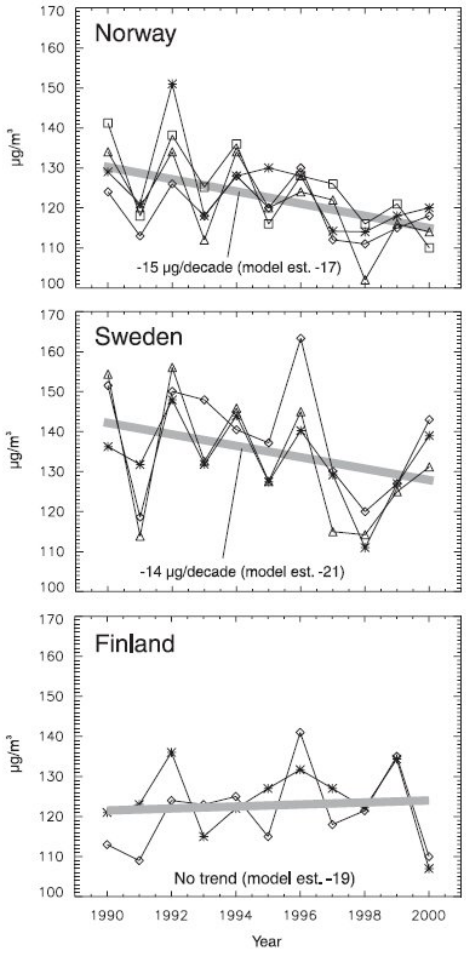


Figure 3.8: 99-percentiles of hourly observed ozone concentrations in the years 1990–2000 for sites in the southern parts of Norway, Sweden and Finland, respectively. The shaded grey line indicates the regression of the average of these 99th percentiles. The trend estimated by this regression is given in the diagrams together with the estimated trend in modelled 99-percentiles (MATCH model). From Solberg et al. (2005).

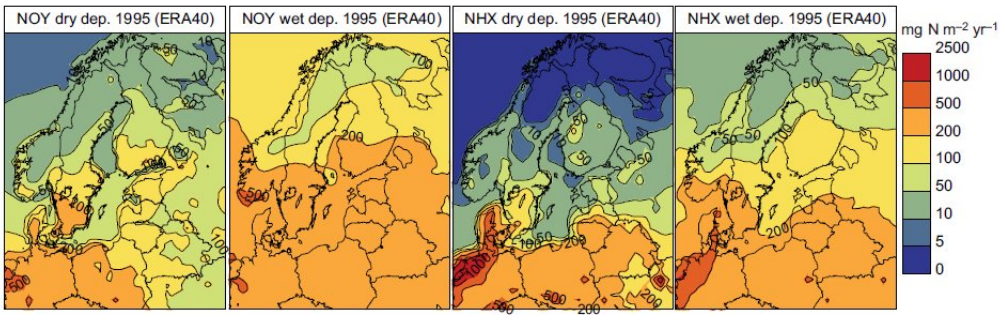


Figure 3.9: Simulated dry and wet depositions of NOy and NHx in 1995 from the MATCH-ERA40 model (Langner et al. 2009).

in the atmosphere (NO and NO_2 do not deposit efficiently, but are transformed to HNO_3 which is efficiently dry deposited or forms nitrate aerosols.) Furthermore, slower deposition processes of aerosols over water surfaces are assumed in all models.

Some studies have also assessed the contribution of different countries to Nr deposition in the Baltic region. For example, Geels et al. 2011, using the DEHM model, estimated that the nine countries bordering the Baltic sea contribute about 50% of the Nr deposition in both 2007 and a projected 2020 scenario, with Germany being the largest single contributor (Fig. 3.11). Bartnicki et al. (2011), using the EMEP model (Simpson et al. 2012), found somewhat greater contributions from some countries, with five countries contributing about 55% of total Nr deposition, and emissions from international shipping on the Baltic contributing 4–5% (Fig. 3.12). They also found Germany to be the biggest single contributor (with 20%, almost a factor of two over Poland, 12%), but that even the United Kingdom made a significant contribution (7%).

As to source types, Hertel et al. (2002) estimated around 40% of the nitrogen depositions over the North Sea to originate from agriculture activities and around 60% from emissions from combustion sources.

Table 3.2 presents a comparison of N-deposition estimates from a number of studies using several CTMs. The historical and forecast estimates will be discussed shortly, but for current years the different CTMs seem to give rather similar estimates, eg between 230-260 Gg(N)/yr for 1995, or near 200 for 2006-2007.

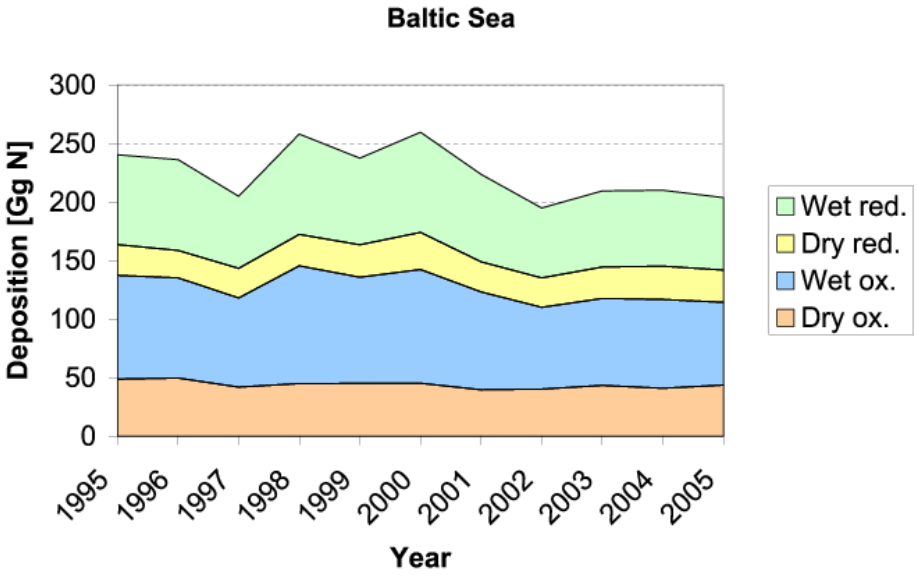


Figure 3.10: Time series of annual tropospheric laods (Gg N/yr) of nitrogen to the Baltic sea in the period 1995-2005. Oxidised and reduced dry and wet deposition are shown, as calculated by the EMEP MSC-W model. Adapted from Bartnicki and Fagerli (2008).

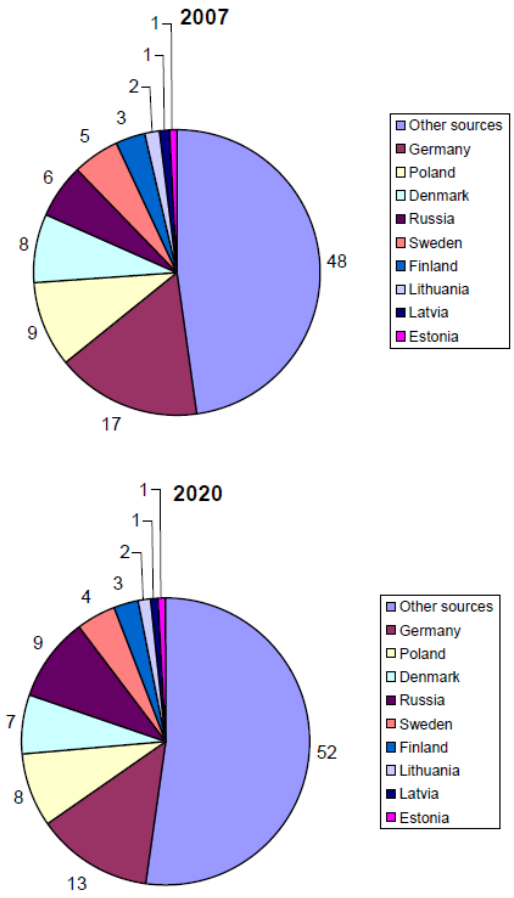


Figure 3.11: The nitrogen deposition to the Baltic Sea as calculated using the DEHM model, divided into the contribution from the nine bordering countries and other sources (i.e. from the remaining emissions in the model domain). The contributions are given in percent (%) for both the present day scenario and the projections for 2020. Each contributing country has the came colour in the two pies. Adapted from Geels et al. 2011

Table 3.2: Comparison of model estimates of total, dry and wet deposition of nitrogen to the Baltic sea. Unit: Gg N/yr. Extended from Langner et al. (2009). NEED TO check/make it clear which runs have emission changes!

Year	Model	Dry	Wet	Total	Comments
1995					
	HILATAR			255	(a)
	EMEP rv2.5			244	(a,b)
	EMEP rv3.1			230	(c)
	MATCH-ERA40			260	(a)
1996-2000					
	EMEP			300	(a,b)
	MATCH-ERA40			271	(a)
2006	EMEP rv3.1			199	(c)
2007	DEHM			203	(d)
Historical :					
1961-1990	MATCH-RCA3	41	207	248	(a), year 2000 emissions(?)
Projections:					
2020	DEHM			165	(d), Projected emissions
2021-2050	MATCH-ERA40	42	206	248	(a), year 2000 emissions(?)
2071-2100	MATCH-ERA40	44	218	262	(a), year 2000 emissions(?)

Notes: (a) As given in Langner et al. (2009); (b) EMEP model rv2.5 (check) from ca. 2005-2006; (c) EMEP model rv3.1 from 2008, data from Bartnicki et al. (2011); (d) As given in Geels et al. (2011)

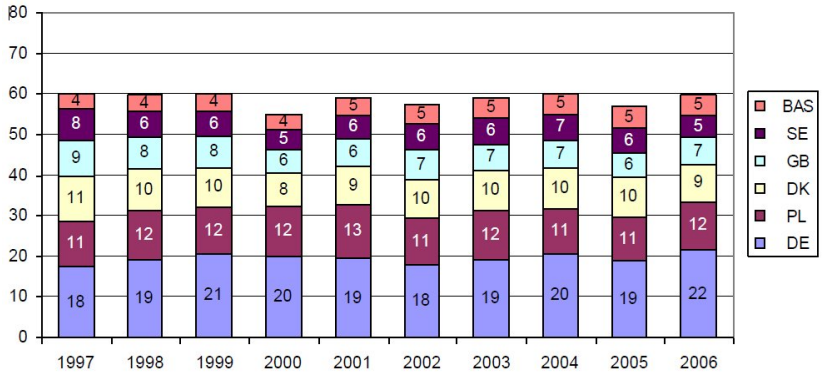


Figure 3.12: Time series of main contributions to annual deposition of nitrogen into the Baltic Sea basin in the period 1997âĂŞ2006. Contributions are in % of: (a) oxidised, (b) reduced and (c) total deposition. Source codes: DE – Germany, DK – Denmark, FI – Finland, FR – France, GB – United Kingdom, PL – Poland, RU – Russia, SE – Sweden, BAS – international ship traffic on the Baltic Sea, NOS – international ship traffic on the North Sea

3.4.1 Historical and Future deposition estimates

This section needs much more work! Observations - what do we have? Any sediment data we can use? Other?

Modelling of historical and future changes in concentrations and depositions shares many common features. In either case, the models must be driven by 'estimates' of possible meteorology rather than evaluated meteorological fields. Of course, hindcasting recent decades is somewhat easier than forecasting the future, although the lack of satellite and other observations in earlier years makes such data less reliable than current NWP systems can deliver.

The most valuable historical data set for CTMs is 'ERA40', a set of meteorological data going back to 1957, that has been produced from global meteorological reanalysis by the European Centre for Medium-range Weather Forecasts (ECMWF) (Uppala et al. 2005).

For future meteorology, many global climate models (GCMs) are available, but for estimates of changes over the Baltic region it is desirable to run finer-resolution models, which are forced by GCMs, but are far better at capturing the effects of local topography and landcover. An important set of data here are those produced by the Rossby Centre regional climate model, RCA3 (Samuelsson et al. 2011).

Estimates of future deposition depend of course on forecasts of both emissions and meteorology. We will show later that meteorological factors are relatively less important than emission changes for such simulations, with the conclusion that specification of future emissions is almost certainly the biggest source of uncertainty when attempting to preduct future deposition amounts.

The MATCH model has been run for both historical and future scenarios in a number of studies. Andersson et al. (2007) used ERA40 to run MATCH for the 1958–2001 period. Hole and Engardt (2008) used 30-year periods of meteorological data produced by RCA3, with forcing by the ECHAM4/OPYC3 GCM (Roeckner et al. 1999). These simulations were for the SRES A2 scenario (Nakićenović et al. 2000) in "transient" mode from 1961 to 2100 with gradually changing climate forcing, i.e. changing atmospheric aerosol and greenhouse gas concentrations. MATCH was applied to data from three different time windows (1961–1990, 2021–2050 and 2071–2100) representing past and future climates. The two setups are denoted MATCH-ERA40 and MATCH-RCA3, respectively, and Langner et al. (2009) investiated the results of these MATCH model runs for the Baltic region in particular.

In a study to examine the potential effect of historical and possible future

climate change (not emissions) and variability on atmospheric deposition of N to the Baltic Sea based on the MATCH model under the assumption of constant emissions, Langner et al. (2009) found modest projected increases when averaged over the entire Baltic region (of 4-5%), but generally increased deposition of the oxidized form of N over the Baltic Sea. This tendency is thus of smaller magnitude than current interannual variability (Hongisto 2011).

For Europe, Geels et al. (2011) used an inventory based upon a combination of the EU thematic strategy for clean air in Europe and scenarios for the 27 EU countries made by IIASA (Amann et al., 2008) as part of the analysis towards a new directive on national emission ceilings (NEC-II). For the remaining European countries and the western Asian countries the projected emissions were based on the estimates provided in the EU Clean Air For Europe (CAFE) programme. For the rest of the Northern Hemisphere, 2020 emissions were based on the RCP 3-PD projections (van Vuuren et al. 2007). Ship emissions from the area around Denmark were assumed to follow new regulations adopted by the International Maritime Organisation (IMO) and the same projections are used for the North Sea and the Baltic Sea. For the nine countries bordering the Baltic Sea, N-emissions were projected to decline by ca. 50% between 2007 and 2020 (although for Russia the projected decrease was just 11%).

Something on published observational trends. Most studies lack focus on Baltic region though, and do not go back many decades. Here's a starter:

The Pihl Karlsson et al. (2011) study (cf Sect. 3.3) found reductions in SO4-deposition for the majority of monitoring sites across Sweden from 1996/97–2007/08, as well as for the other Nordic countries, and the reductions were in the same order of magnitude as the European emission reductions. Soil water SO4-concentrations decreased at most, but not all, monitoring sites across Sweden in parallel with the SO4- deposition reductions. The soil water acidification indicators pH, ANC and inorganic Al-concentrations indicated acidification recovery on some of the sites but there were also many sites with no significant change. Despite the substantial decrease in NO2 air concentrations, no statistically significant decreases in the bulk deposition of inorganic nitrogen deposition could be demonstrated. (They were not able to include the dry nitrogen deposition in the trend analyses, however). Elevated NO3-concentrations in the soil water occurred at irregular occasions, but also after massive fellings caused by severe storm events, at some sites particularly in southern Sweden. This indicated that nitrogen stocks in the forest soils in southern Sweden are increasing and may be approaching saturation.

3.4.2 Uncertainty of estimates

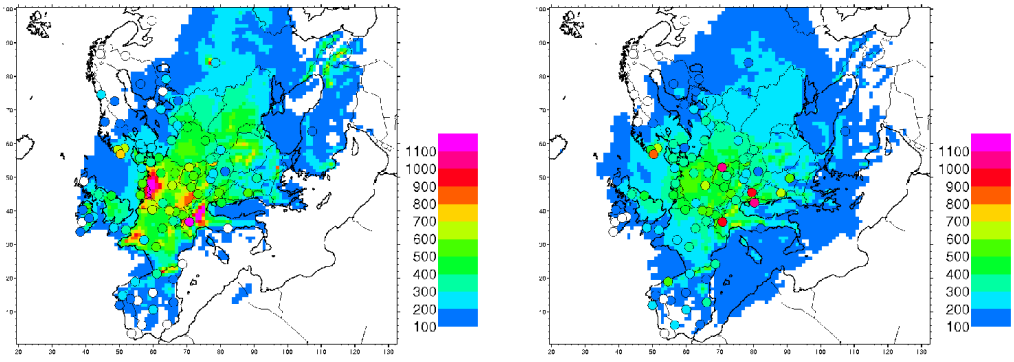
In Table 3.2 we presented a comparison of N-deposition estimates from a number of studies using several CTMs. As already noted, for any given year the different CTMs seem to give rather similar estimates. Much of the similarity may be ascribed to the use of similar emissions data, and the fact that much of the deposition is driven by precipitation events that are not so sensitive to model formulation. Such model calculations need to be thoroughly evaluated against observations. We discuss the evaluation of wet and dry deposition processes (and their uncertainties) below.

Wet Deposition

Comparison of model results for wet deposition or concentrations in precipitation is in many ways trickier than comparing gas concentrations. As noted in van Loon et al. (2004), the most important issue concerning the wet removal of species in CTM models is probably the meteorological input; model performance for wet deposition fluxes or concentrations in precipitation is strongly limited by the quality of the NWP models providing meteorological data. For example, models generally have problems with sub-grid precipitation, simulating precipitation more often, but in lower amounts, than reality. As precipitation scavenging is a complex and non-linear process (e.g. Barrie 1992), such issues will cause errors in modelled wet deposition that are difficult to evaluate. There are also many uncertainties inherent in the deposition monitoring methods themselves (Draaijers and Erisman 1993, Erisman et al. 2005).

In an early intercomparison of six different CTMs used in Europe, van Loon et al. (2004) found very poor model performance for the wet-deposited components, despite fair to good performance for airborne components. A clear result of this study was that no model achieved good correlation coefficients (the best was just r=0.35) for wet-components, and bias and RMSE values could be very substantial (up to 60–70% for wet-deposition fluxes) relative to observed values. These results were much worse than equivalent results for concentrations in air. The models used in this study have been improved to some extent since this intercomparison, but it seems likely that a study using today's models would still show discrepancies of up to 50%.

The relatively poor agreement between modelled and observed wet deposition fluxes is not a specific feature of this inter-comparison or these models. Large differences between models were also found in the global models participating in



(b) Wet deposition of oxidised nitrogen

(b) Wet deposition of reduced nitrogen

Figure 3.13: Comparison of modelled and observed annual means of wet deposition of (a) NHx and (b) NO_3^- (HNO_3 and aerosol nitrate). Data are for 2001 in the EMEP model with observations. The bullets depict observations with the same colour bar as the modelled field. Measured annual means are calculated by using the measured precipitation amount and the nitrate and ammonium concentration in precipitation.

the COSAM study, in which the wet deposition efficiency ranged over a factor of 4 (Roelofs et al. 2001). A similar spread was also found for global models by Dentener et al. (2006), Textor et al. (2006).

The EMEP model (Simpson et al. 2012) seems to have been subject to most evaluation against observed wet-deposition estimates. Standard scatter plots showing the performance of the model against observed concentrations of NO_3^- and NH_4^+ can be found in the yearly EMEP status reports, e.g. Fagerli and Hjellbrekke (2008), Berge and Hjellbrekke (2010). The model has also been compared to observed wet depositions for nitrogen from the ICP-forest network (Simpson et al. 2006). Differences in mean values between modelled and observed (ICP-forest) SO_4^{2-}, NO_3^- and NH_4^+ total and wet deposition were within 20% in 1997 and 30% in 2000, with the EMEP model showing slightly lower values than the observations (Simpson et al. 2006). Modelled and observed concentrations of SO_4^{2-}, NO_3^- and NH_4^+ in precipitation were very similar on average (differences of 0-14%), and the correlation between modelled and observed data rather high for this type of comparison (between r^2=0.4 – 0.8 for most components and years).

Figure 3.13 compares measured wet deposition of oxidised and reduced nitrogen against results from the EMEP model. In these plots the measured deposition

is calculated using the measured precipitation amount and the nitrate and ammonium concentration in precipitation. For reduced nitrogen, Fig. 3.13(a) reveals good agreement between modelled and measured values, across almost all of Europe. The high modelled values near northern Italy are reflected in the measurements. Unfortunately, other regions with high predicted wet-deposition have only a limited number of measurement sites (e.g. Netherlands, Belgium), and so it is difficult to evaluate model performance here. The EMEP model has a tendency to under-predict wet deposition in Nordic sites.

For oxidised nitrogen (Fig. 3.13(b)), four sites stand out with much higher measured wet deposition than modelled. The reason for this seems to be that the observed precipitation at the sites far exceeds the modelled precipitation (e.g. by a factor of two for the Norwegian site). However, there is a very good agreement between model results and measurements at almost all other sites, which gives some confidence that the modelled budget of wet-deposition is within the uncertainty of the measured value.

Dry Deposition

Although wet deposition represents an important fraction of N-deposition over the Baltic region, dry deposition is also important as seen in Figs.3.9 and 3.10. Many of the physical/chemical processes controlling dry-deposition of Nr compounds have been discussed in for example Hertel et al. (2010, ENA REF to be added) or Fowler et al. (2009). Deposition processes over land and sea involve somewhat different processes and challenges, we discuss both separately.

Land

Efforts to estimate aerosol particle dry deposition to terrestrial ecosystems are faced by many of the same challenges to those faced over water surfaces (discussed below), but vertical velocities over terrestrial surfaces are typically larger (reducing the uncertainty associated with direct micrometeorological techniques), and platforms suitable for deployment of flux instrumentation are more readily available (and do not exhibit motion as would be experienced on a ship). Nevertheless, still only limited direct measurements are available and are principally focussed on size-resolved, rather than chemically-resolved, fluxes (Fowler et al. 2009, Pryor et al. 2008a). Further, there has recently been a greater focus on the aerosol particle diameters that dominate aerosol number concentrations (i.e. sub-micron) (e.g. Pryor et al. 2009) rather than aerosol particles in sizes that

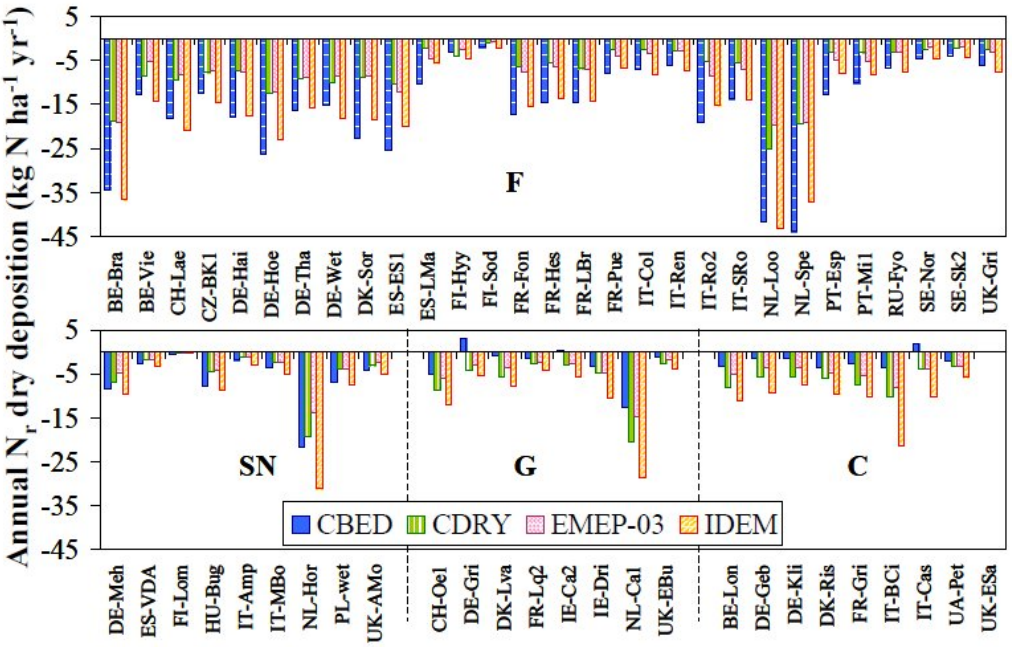


Figure 3.14: Modelled annual Nr dry deposition to NEU monitoring sites. Data are calculated as the sum of NH3, HNO3, aerosol NH+4 and NO-3 fluxes from DELTA measurements, plus NO2 dry deposition from modelled (EMEP 50 km) or measured NO2 concentrations. Deposition estimates are to: (F) forests, (SN) semi-natural ecosystens, (G) grasslands, and (C) crops. From Flechard et al. 2011

may dominate the chemical flux. Those recent studies have tended to indicate a very strong influence of deposition velocities on canopy morphology and aerosol properties, and thus they explain – at least to some degree – the large variability in measurement data sets of particle number fluxes to vegetated surfaces taken under superficially similar atmospheric conditions (Petroff et al. 2009). Recent instrumentation innovations (e.g. Time-of-flight Mass Spectrometer (TOF-MS) and Aerosol Mass Spectrometers (AMS)) that are capable of measuring the size and chemically resolved aerosols with high time resolution has facilitated initial direct flux measurements (e.g. Nemitz et al. 2008, Thomas et al. 2009) over terrestrial surfaces. However, there remain comparatively large uncertainties on aerosol particle fluxes, and the technical challenges (e.g. artifacts associated with hygroscopicity or other non-stationarity in the aerosol size distribution (Kowalski 2001, Pryor and Binkowski 2004) exceed those associated with atmosphere-surface exchange of gases (Pryor et al. 2008a).

Recent studies within the EU NitroEurope (Sutton et al. 2007) project also illustrate the level of uncertainty in dry-deposition estimates. Flechard et al. (2011) conducted inferential modelling with deposition codes from three European dry deposition models at selected sites across Europe. The deposition modules are from the UK-CBED model (Smith et al. 2000), the Dutch IDEM model (Bleeker et al. 2004) and the code from an older version of the EMEP MSC-W model (Simpson et al. 2001, 2003). This study suggested that NH_3 is the single highest atmospheric N_r dry input in many parts of Europe. At sub-urban sites of the NEU network, HNO_3 and particulate NO_3^- and NH_4^+ also contributed significant fractions of total dry deposition. As illustrated in Fig. 3.14, there were however substantial discrepancies between models, with annual deposition rates varying as much as two-fold between models at given monitoring sites. This highlights the variability in model parametrisations, stemming from the variability in measured deposition rates and canopy resistances.

For NH_3, the stomatal compensation point and the external leaf-surface (or non-stomatal) resistance are the largest sources of divergence between models. The effective annual mean deposition velocity (V_d) predicted by the CBED model is negative for the cropland and grassland sites, as a result of a non-zero compensation point for these land-use classes, but otherwise the lowest V_d for NH_3 is always that predicted by the EMEP scheme. The discrepancies can be ascribed to different parameterisations for the non-stomatal resistances.

The importance of bi-directional fluxes was also discussed by Geels et al. (2011). They noted that although several parameterizations of bi-directional fluxes over land exist for NH3, they have so far mainly been used in field-scale NH3

exchange models (Massad et al. 2010). Geels et al. (2011) also noted that bi-directional fluxes have been observed over marine surfaces Hertel et al. (2006) and the inclusion of such fluxes in a CTM can lead to a redistribution of the deposition in the coastal areas and hence in the gradients of nitrogen depositions over the sea Sorensen et al. (2003).

Model estimates of aerosol V_d differ greatly among the various modelling approaches and parameterisations (see Ruijgrok et al. 1997, for a review), but it is in the size range 0.1-1.0μm that the variability and uncertainty are greatest. Whereas mechanistic models predict very low deposition velocities for fine aerosols, typically of the order of 0.1 mm s-1, field measurements suggest that V_d is 1-3 orders of magnitude higher (Gallagher et al. 2002, Zhang et al. 2001). Still, such field measurements are also subject to great uncertainty (Pryor et al. 2008a,b, Rannik et al. 2003). This is especially relevant for reactive nitrogen in the aerosol phase, as NH_4^+ and NO_3^- are mostly (>90%) present as sub-micron particles.

Sea

The difficulty in making in-site direct aerosol particle dry deposition observations over water derives principally from: (i) the bi-directionality of the flux (i.e. the surface acts as both a source and sink for particles), (ii) challenges in making direct size and composition resolved measurements with sufficient time resolution to allow application of micrometeorological techniques and (iii) the typically low turbulence intensity (which both suppresses vertical transport and can challenge flux detection) (Pryor et al. 2008a). For this reason, the overwhelming majority of studies focused on aerosol particle atmosphere-surface exchange (including those focused on nutrient supply) continue to take time-averaged measurements of aerosol particle size and composition and apply a parameterized model of the dry deposition rate to determine the deposition flux (eg Buck et al. 2010, Matsumoto et al. 2009, Uematsu et al. 2010). Such studies and recent numerical modeling have suggested a key role of atmospheric transport and deposition of aerosol particles in nutrient supply (Krishnamurthy et al. 2010), but also toxin transport (Paytan et al. 2009) to aquatic ecosystems, and further that in some environments and for some key micro and macro-nutrients dry deposition of aerosols to water surfaces may dominate over the wet deposition flux (Tian et al. 2008, Uno et al. 2007). However, aerosol deposition velocities used in such studies are poorly constrained and flux estimates derived thus exhibit large uncertainties, in part because aerosol particle dry deposition velocities exhibit multiple functional dependencies beyond the direct dependence on aerosol particle diameter. For similar reasons

many postulated functional dependencies remain essentially unverified. For example, it has been proposed that transfer across a thin laminar layer close to the surface is a major limiting factor of deposition rates (Giorgi 1986, Hummelshøj et al. 1992, Pryor et al. 1999, Slinn and Slinn 1980) and that the observed increase in particle dry deposition with wind speed may be linked to disruption of that layer by bubble burst activity. Indeed, one model study showed that bubble burst activity almost doubled the deposition velocity of aerosol particles in the diameter range of 0.1 to 1 μm (Pryor and Barthelmie 2000), however, in a wave tunnel experiment deposition velocities for magnesium oxide particles in the diameter range 0.1 to 1 μm showed an enhancement of $\leq 30\%$ (Larsen et al. 1995).

3.4.3 Climate impacts?

The main climate impacts are probably C-sequistration issues associated with N-deposition changes and ozone-effects, and (probably more important for this region) aerosols. However, another chapter will deal with aerosols, so no action planned in this chapter on that. (Need to discuss with aerosol lead author).

3.4.4 Conclusions

Here we summarise and try to present a concise answer to the starting question.

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