

David Simpson, Jerzy Bartnicki, Jukka-Pekka Jalkanen,  
Hans-Christen Hansson, Ole Hertel, Joakim Langner, and Sara C. Pryor

## Abstract

This chapter addresses sources and trends of atmospheric pollutants and deposition in relation to the Baltic Sea region. Air pollution is shown to have important effects, including significant contributions to nitrogen loading of the Baltic Sea area, ecosystem impacts due to acidifying and eutrophying pollutants and ozone, and human health impacts. Compounds such as sulphate and ozone also have climate impacts. Emission changes have been very significant over the past 100 years, although very different for land- and sea-based sources. Land-based emissions generally peaked around 1980–1990 and have since reduced due to emissions control measures. Emissions from shipping have been steadily increasing for decades, but recent measures have reduced sulphur and particulate emissions. Future developments depend strongly on policy developments. Changes in concentration and deposition of the acidifying components generally follow emission changes within the European area. Mean ozone levels roughly doubled during the twentieth century across the northern hemisphere, but peak levels have reduced in many regions in the past 20 years. The main changes in air pollution in the Baltic Sea region are due to changes in emissions rather than to climate change.

## 15.1 Introduction

In relation to the Baltic Sea region, this chapter attempts to answer the overriding questions: What are the main atmospheric pollutants and where do they originate? How has

deposition changed over time and how good are the estimates? How will climate change affect future trends?

The main pollutants addressed in this chapter are the acidifying compounds (sulphur and nitrogen oxides, as well as ammonia/ammonium) and ozone. Historically, much of the international activity concerning air pollution in Europe stemmed from the recognition that increasing emissions and deposition of sulphur in Europe after the Second World War led to the acidification of freshwaters and sensitive soils in northern Europe and parts of the Baltic Sea region (Odén 1968). Following a coordinated research effort by the Organisation for Economic Co-operation and Development (OECD 1977), transboundary fluxes of acidifying pollutants were proven to be significant sources of acid deposition across Europe (Eliassen 1978; Tørseth et al. 2012, and references therein). The Convention on Long-range Transboundary Air Pollution (CLRTAP) was established in 1979. The network of monitoring sites, and the modelling framework, established for the OECD project was later continued under the European Monitoring and Evaluation Programme (EMEP), which was established to provide scientific support

---

D. Simpson (✉) · J. Bartnicki  
Research Department, Norwegian Meteorological Institute,  
Oslo, Norway  
e-mail: david.simpson@chalmers.se

J.-P. Jalkanen  
Atmospheric Composition Research, Finnish Meteorological  
Institute, Helsinki, Finland

H.-C. Hansson  
Department of Applied Environmental Science, Stockholm  
University, Stockholm, Sweden

O. Hertel  
Department of Environmental Science, Aarhus University,  
Roskilde, Denmark

J. Langner  
Research Department, Swedish Meteorological and Hydrological  
Institute, Norrköping, Sweden

S.C. Pryor  
Department of Earth and Atmospheric Sciences, Cornell  
University, Ithaca, NY 14853, USA

to the CLRTAP contracting parties. Sulphur deposition has decreased significantly since the beginning of the 1980s due to the successful implementation of emission reductions in Europe under the protocols of CLRTAP (Mylona 1996; Vestreng et al. 2007).

Emissions and deposition of reactive nitrogen (Nr) species, such as nitrogen dioxide (NO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), ammonia (NH<sub>3</sub>) and ammonium (NH<sub>4</sub><sup>+</sup>), have proven harder to reduce. Indeed, deposition of Nr species is now 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; 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 onto 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).

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 Nr compounds is extremely complex, and observations can typically address only a small part of this chain. The following sections make use of both measurements and modelling results, discussing in turn emissions, concentrations and deposition. The ecosystem effects of air pollution are largely outside the scope of this chapter (but see Sutton et al. 2011 for a comprehensive discussion). This chapter concludes with a short discussion on the human health effects of air pollutants—probably the main driver of EU policy with regard to air quality.

## 15.2 Emissions

### 15.2.1 Land-Based Sources

Land-based emissions of the main acidifying compounds can be grouped into sulphur compounds and Nr species, where the predominant Nr groups are NH<sub>3</sub> and NO<sub>x</sub> (=NO + NO<sub>2</sub>) but also include other inorganic and organic nitrogen compounds (Hertel et al. 2012). Anthropogenic sulphur emissions decreased by more than 80 % from 1980 to 2004 in the HELCOM countries and by more than 70 % over the same period for the whole of Europe (Table 15.1; Vestreng et al. 2007). Between 1980 and 1990, the relative reduction in emissions was about the same in the whole of Europe as in the HELCOM countries, while after 1990, the reduction was greater in the HELCOM countries. Energy production from fossil fuel combustion has been the most important source of sulphur emissions. The reduction in emissions has mainly been achieved through a combination of reduced sulphur content of fuels, switching fuels and flue-gas desulphurisation in coal-fired power plants. The downturn in the economy in eastern Europe after 1989 was also an important factor.

Table 15.2 presents national NO<sub>x</sub> emission trends for the HELCOM countries and for Europe as a whole, and gives an overview of the emissions in the EMEP inventory between 1980 and 2005. The relative share of emissions from road transport is also shown. 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 ([www.gains.iiasa.ac.at/gains](http://www.gains.iiasa.ac.at/gains)) developed at the International Institute for Applied Systems Analysis

**Table 15.1** Trends in sulphur emission (kt SO<sub>2</sub> year<sup>-1</sup>) for the HELCOM Contracting Parties and for Europe as a whole, 1980–2004

Country	1980	1985	1990	1995	2000	2004
Denmark	450	333	176	133	27	23
Estonia	287	254	274	117	96	90
Finland	584	382	259	95	74	83
Germany	7514	7732	5289	1708	630	559
Latvia	96	97	97	47	10	4
Lithuania	311	304	263	92	43	40
Poland	4100	4300	3278	2381	1507	1286
Russian Federation	7323	6350	6113	3101	2263	1858
Sweden	491	266	117	79	52	47
Total Europe	55,340	48,448	42,896	26,282	18,263	15,162

Vestreng et al. (2007)

**Table 15.2** Trends in nitrogen oxide emissions (kt NO<sub>x</sub> as NO<sub>2</sub> year<sup>-1</sup>) for the HELCOM Contracting Parties and for Europe as a whole, 1980–2005

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 Federation	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 Europe	23,944 (36)	24,550 (36)	25,256 (38)	20,507 (41)	17,809 (42)	17,059 (39)

Percentage contribution from road transport in brackets. Vestreng et al. (2009)

(IIASA) and for a few countries from EDGAR emission data ([www.mnp.nl/edgar](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. The emissions and their uncertainties are discussed further by Vestreng et al. (2009).

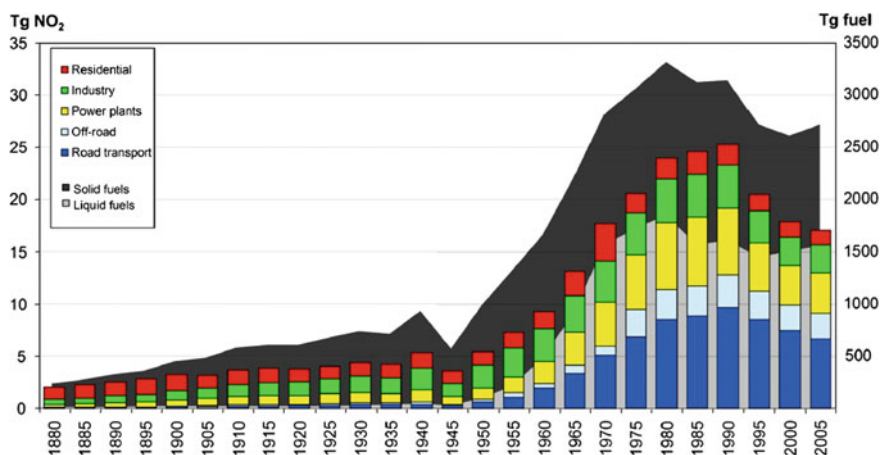
As also noted by Vestreng et al. (2009), a trend study by Konovalov et al. (2008) applying inversion techniques with satellite measurements between 1996 and 2004, broadly confirmed that the NO<sub>x</sub> emission trends in Europe have been decreasing, and further indicated that the quality of the EMEP inventory has increased over the past few years. This study also suggested that the greatest uncertainties in emission inventories probably concern southern and eastern Europe.

Long-term trends in emissions 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, for example, to inefficiency or lack of control

measures. Figure 15.1 shows the development of fuel use and NO<sub>x</sub> 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 significantly. Fuel use peaks around 1980 and emissions peak 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 technologies, particularly with respect to road vehicles.

To illustrate the uncertainty associated with such inventories, Vestreng et al. (2009) compared estimates of long-term NO<sub>x</sub> emission changes with three other major inventory efforts. In recent years, all studies gave 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 were also similar, although this may reflect a lack of alternative data rather than inherent accuracy. However, between 1950 and 1990, significant differences were seen in western Europe and more so in eastern Europe. Lack of information on emission factors for older vehicles and combustion appliances is a major limitation in

**Fig. 15.1** Sector trends in European NO<sub>x</sub> emissions (million t year<sup>-1</sup>, as NO<sub>2</sub>) and European solid and liquid fossil fuel consumption (million t year<sup>-1</sup>) since 1880. Vestreng et al. (2009)



**Table 15.3** Annual emissions of carbon monoxide (CO), non-methane volatile organic compounds (NMVOC), nitrogen oxides (NO<sub>x</sub>), sulphur oxides (SO<sub>x</sub>), fine particulate matter (less than 2.5 µm in diameter; PM<sub>2.5</sub>) and coarse particulate matter (between 2.5 and 10 µm in diameter; PM<sub>C</sub>) from Baltic Sea shipping as reported to EMEP

Year	CO (kt) (C)	NMVOC (kt)	NO <sub>x</sub> (kt) (as NO <sub>2</sub> )	SO <sub>x</sub> (kt) (as SO <sub>2</sub> )	PM <sub>2.5</sub> (kt)	PM <sub>C</sub> (kt)
1980	29.0	8.0	1157	456	na	na
1985	29.0	8.0	1157	456	na	na
1990	24.2	8.2	775	336	na	na
1995	27.4	9.2	881	382	na	na
2000	31.1	10.5	907	376	21.9	1.20
2005	35.2	11.8	996	426	24.8	1.40
2009	38.8	13.1	1074	244	16.6	0.92

EMEP CEIP ([www.ceip.at/ceip/](http://www.ceip.at/ceip/)). na: no data available

estimating such emissions. (Emission trends for sulphur are usually simpler to make than for Nr compounds, since uncontrolled emissions depend in a fairly straightforward way on the sulphur content of fuel, which is reasonably well documented.)

Ammonia emissions are dominated by agricultural sources, and in Central to northern Europe, these contribute 85–98 % of atmospheric emissions ([www.emep.int](http://www.emep.int)). In the HELCOM countries, Denmark, Poland and Germany achieved considerable emission reductions over the period 1985–2010, while Sweden and Norway achieved marginal reductions only. The reasons for this difference are partly structural changes and increased efficiency in agricultural production methods as seen in Denmark (Skjøth et al. 2008) but also political restructuring affecting industry and energy production in eastern Europe as seen in Poland (Reis et al. 2009). One cause of uncertainty in the quantification of NH<sub>3</sub> emissions is the incomplete data sets—for example due to the lack of data on natural emissions (e.g. Reis et al. 2009) and limited access to high-quality emission factors. Uncertainty associated with the national totals may be down to 5–10 % in the most data-rich regions such as Denmark (Geels et al. 2012a), but the lack of data and poor emission factors may cause uncertainties of up to a factor of ten in data-poor regions (e.g. Nowak et al. 2012). Another cause of uncertainty is the use of fixed emission factors in the calculation of national emission inventories for NH<sub>3</sub>, a practise that is used despite the fact that the emission process depends on meteorology. This point is addressed in Sect. 15.2.3.

## 15.2.2 Shipping

The Baltic Sea is a very busy shipping route with over 2000 vessels sailing at any given time. Until recently, emissions from shipping were based on national statistics only, with assumed activity statistics and emission factors. However, in the past few years, ship emission estimates have become

more consistent through the inclusion of real ship activity data offered by the Automatic Identification System (AIS).

### 15.2.2.1 Historical Perspective

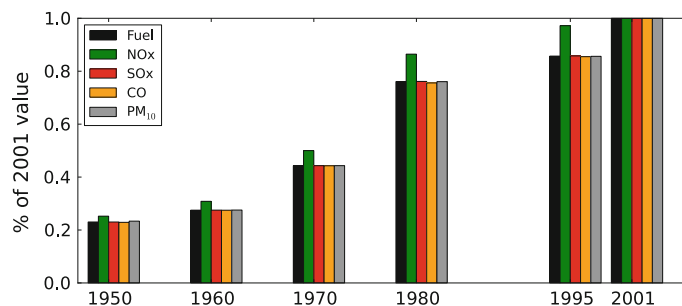
Compared to estimates of current ship emissions in the Baltic Sea (see Sect. 15.2.2.2), the accuracy of past and future emission estimates is much lower. Nevertheless, it is important to evaluate general trends in emissions over time in the Baltic Sea (see Table 15.3).

The reported shipping emissions of carbon monoxide (CO) and non-methane volatile organic compounds (NMVOC) in 2009 are higher than in 1980 (by 34 and 64 %, respectively), whereas NO<sub>x</sub> and sulphur oxide (SO<sub>x</sub>) emissions in 2009 are lower than in 1980 (7 and 46 %, respectively). Annual emissions of both particulate matter (PM) components are more than 20 % lower in 2009 than in 2000.

For all pollutants, annual emissions in 1985 are the same as in 1980. There is a clear increasing tendency for emissions of CO, NMVOC and NO<sub>x</sub> in the period 1990–2009. Emissions of SO<sub>x</sub> also show increasing trends until 2005 and then a significant drop between 2005 and 2009. Some of the differences between the consecutive values (e.g. 1985–1990) in Table 15.3 are hard to understand and suggest problems in the reporting of the inventories.

Estimates of ship emissions in the Baltic Sea before 1980 are difficult to make. However, historical data concerning global ship emissions are available based either on energy statistics (e.g. Endresen et al. 2003) or international shipping statistics (e.g. Corbett and Koehler 2003). Eyring et al. (2005b) used an activity-based approach to calculate total fuel consumption and global annual ship emissions back to 1950. Based on these data, Fig. 15.2 shows the relative global annual ship emissions of NO<sub>x</sub>, CO, sulphur dioxide (SO<sub>2</sub>) and PM, expressed as a fraction of the 2001 values. Emissions of all these pollutants rose significantly between 1960 and 1980, due to a rapid increase in the merchant fleet: the number of ships doubled in the period 1960–1980. Furthermore, the tanker business reached its peak in 1973–1975, and the

**Fig. 15.2** Development of global shipping fuel consumption and emissions, relative to 2001. Based on Eyring et al. (2005b)



container vessel class was introduced (Eyring et al. 2005b). Assuming that ship traffic on the Baltic Sea developed in a similar manner to the global trends, these data would indicate that annual ship emissions on the Baltic Sea in 1950 were at least 60 % lower than ship emissions in 2000, for all pollutants considered. It should be noted, however, that applying global inventories to the Baltic Sea leads to an underestimate of ship emissions, mainly due to a lack of accounting for ‘short-sea’ traffic (i.e. the movement of cargo and passengers on routes in enclosed sea areas or near coastlines without crossing an ocean) (Jalkanen et al. 2009).

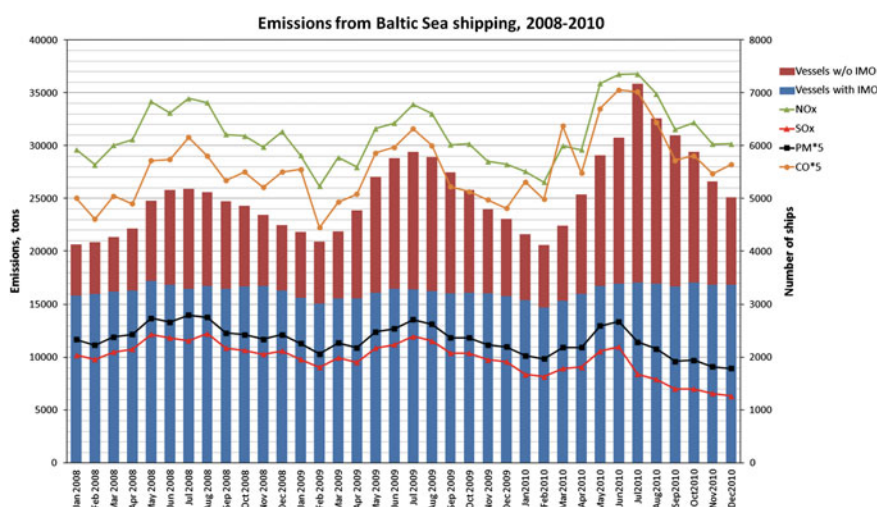
### 15.2.2.2 Recent Developments

Emission estimates for shipping have become more consistent in the past few years with the inclusion of real ship activity data offered by AIS. This device automatically reports the identity, location and speed of any vessel. The use of AIS data in ship emission modelling was demonstrated in the Baltic Sea area, as part of the so-called Ship Traffic Emissions Assessment Model (STEAM, STEAM2, Jalkanen et al. 2009, 2012). The amount of data provided by AIS is immense, for example the vessel movement data for the Baltic Sea over five years (2006–2010) comprises over 1100 million position

reports. Using AIS data also removes the need to use average speeds or estimated travel distance between ports. AIS became obligatory for all large ships in 2005, which is the earliest year when such emission studies are possible.

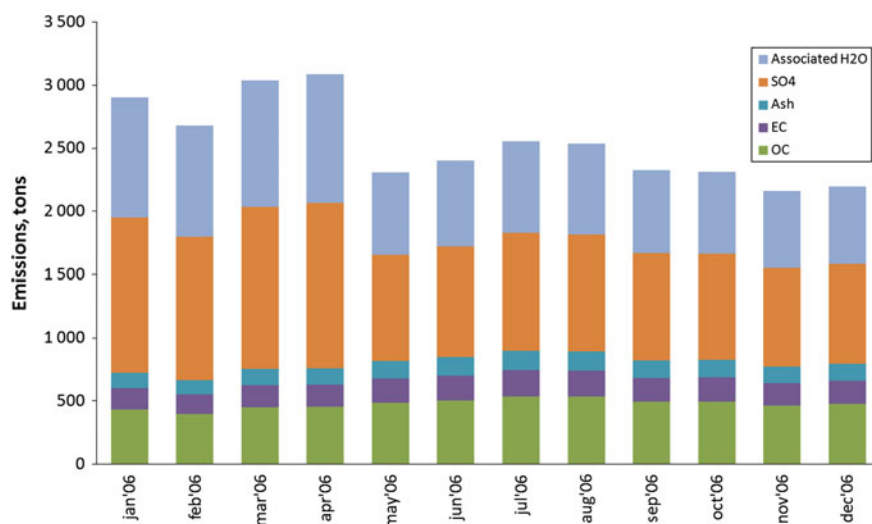
Significant uncertainties remain, especially on the sulphur content of ship fuel for which compliance with the SO<sub>x</sub> Emission Control Area (SECA) requirements of the International Maritime Organisation is assumed (IMO 1998). A recent study indicates, however, that this assumption is in reasonable 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 using 0.1 % fuel inside EU port areas. This helps to mitigate the harmful emissions of PM from ships in areas that are close to human populations (e.g. ports).

Emissions from Baltic Sea shipping usually peak during summer months, because of increased passenger traffic at this time. During these months, there is a significant number of small craft (Fig. 15.3). Commercial marine traffic also peaks during summer months, but this effect is less pronounced than for small craft.



**Fig. 15.3** 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 an

IMO registry number). Lines represent pollutant emissions each month. Note that, emissions of particulates (PM) and carbon monoxide (CO) have been multiplied by five. STEAM2 model (Jalkanen et al. 2012)



**Fig. 15.4** Emissions of particulate matter from Baltic Sea shipping through 2006. The reduction in emissions from May 2006 was due to the required reduction in the sulphur content of marine fuels in the SO<sub>x</sub> Emission Control Area (SECA). The pre-SECA sulphur content of

2.4 % was reduced to 1.5 %, but the emissions of PM components unrelated to fuel sulphur remain unaffected. STEAM2 model (Jalkanen et al. 2012)

In May 2006, the Baltic Sea became the first SECA and the North Sea/English Channel followed in November 2007. The sulphur content of marine fuels was reduced to 1.5 % from a global average of 2.4 %, reducing both gaseous and particulate sulphur emissions from shipping (Fig. 15.4). A further reduction in fuel sulphur from 1.5 to 1.0 % and the requirements of the EU sulphur directive in port areas decreased the SO<sub>2</sub> emissions by 20 % during 2010 (compared to an uncontrolled emission level). Particulate matter emissions from ships are not entirely associated with sulphur emissions, but nonetheless a decrease of 9 % was observed in PM emissions as a result of sulphur reductions in 2006 (Fig. 15.4).

Emissions of sulphate aerosols and associated water were also reduced by the fuel sulphur requirements, whereas the emissions of elemental carbon, organic carbon and ash increased because these components are not dependent on fuel sulphur content of marine fuels and reflect the increased amount of fuel used by Baltic Sea shipping. Sulphate aerosol emissions from ships in 2010 were almost half (47 %) those in 2009.

Emissions from the shipping sector are also affected by economic factors. The global recession of the late 2000s reduced emissions from Baltic Sea shipping by 0.5–5 % depending on the pollutant. Passenger traffic was relatively unaffected by the recession, whereas traffic by bulk, vehicle and container cargo carriers declined. However, by 2010, emission levels had already recovered relative to those before 2008.

The EMEP ship emission inventories for NO<sub>x</sub> and SO<sub>x</sub> (309 and 190 kt in 2006) show reasonable agreement with STEAM inventories (336 and 144 kt in 2006), but the PM and CO emissions are significantly larger in STEAM than

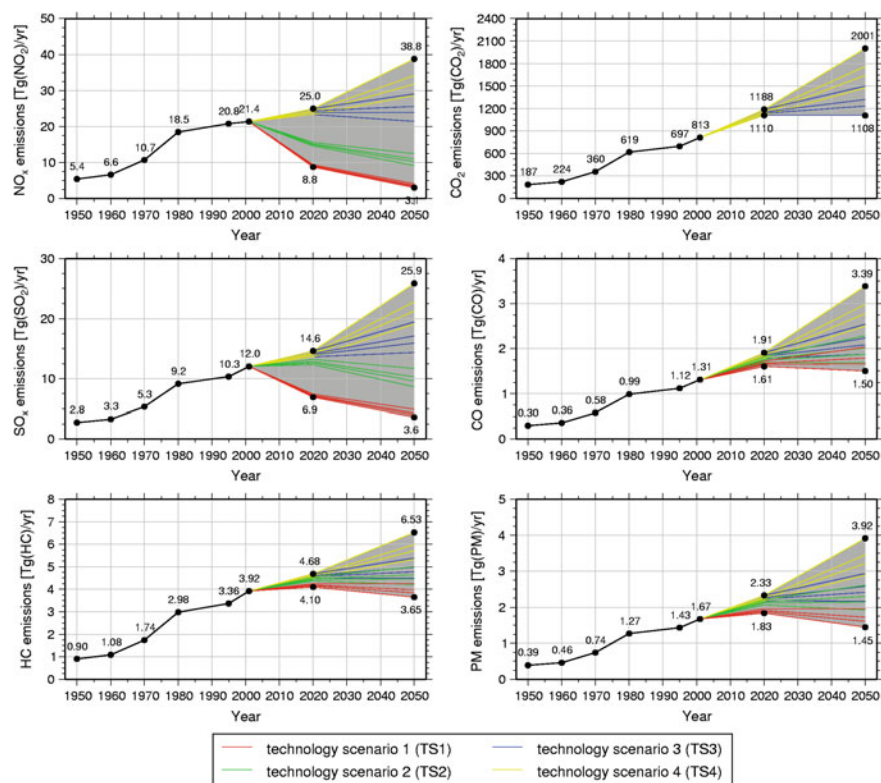
EMEP. The methods used in the construction of these two emission inventories are very different but both include uncertainties arising from the fuel sulphur content. In addition, EMEP inventories are not based on real vessel movements and do not include the contribution from ships in port areas. The use of AIS improves geographical accuracy thus enabling local-scale studies in port areas.

At least two factors affect the reported emission trends for Baltic Sea shipping: the increase in ship traffic, which contributes to the increased number of vessels in the area, and the strong increase in small vessels with AIS equipment. AIS is voluntary for small vessels, whereas it is required for large ships. The popularity of AIS in small vessels may explain some of the increase in reported emissions, especially for CO, in the Baltic Sea area. Over the long term, this will help improve the quality of emission projections because less small vessel traffic will fall outside vessel tracking and emission calculations. However, no centralised database exists for the technical specifications of small vessels which are required for emission studies. To date, default specifications of tugboats are used for small vessels, which may overestimate their contribution.

### 15.2.2.3 Future Projections

Estimates of future shipping emissions vary widely. Although there is some variation in forecasts of ship movements, the main cause of variation in emission projections relates to the wide range of technologies that could be used to reduce pollutant emissions. Figure 15.5 illustrates the range in one such study (Eyring et al. 2005a) where projections started in 2002. As noted by Eyring et al. (2010),

**Fig. 15.5** Possible range of future emissions of nitrogen oxides ( $\text{NO}_x$ ), carbon dioxide ( $\text{CO}_2$ ), sulphur oxides ( $\text{SO}_x$ ), carbon monoxide (CO), hydrocarbons (HC) and particulate matter (PM) according to four technology scenarios (TS1-4) and four ship traffic demand scenarios (giving four lines per technology scenario). Eyring et al. (2005a; which also provides details of the scenarios), figure redrawn by V. Eyring



even this wide range in projected emissions could not include the unexpectedly high growth rates in shipping traffic between 2002 and 2007.

The Baltic Sea nations have finalised an application to the IMO for an  $\text{NO}_x$  emission control area (NECA), but this has not yet been submitted to the IMO because of a lack of political consensus in the Baltic Sea countries. The decision taken by the IMO Marine Environmental Protection Committee (66th session, 2014) allows a date for NECA establishment beyond the previously agreed 2016. Declaration of the Baltic Sea as a NECA would make  $\text{NO}_x$  reduction techniques mandatory for all vessels built after the starting date defined by the countries applying the NECA status. Designation of the Baltic Sea as a NECA should cut  $\text{NO}_x$  emissions from ships by 60 %, but as the stricter emission standards will apply only to newly built ships, the gradual phase-out of existing more polluting vessels means that the full effects will not be seen until 30 years after the effective date (Acid News 2012).

### 15.2.3 Land and Sea Emissions—Impact of Climate Change

The wider impact of climate change on combustion emissions (e.g.  $\text{NO}_x$ ,  $\text{SO}_x$ ) involves complex policy and technology decisions and is beyond the scope of this chapter. In

contrast, emissions of  $\text{NH}_3$  are highly dependent on climatic variables, especially temperature (e.g. Hertel et al. 2012, and references therein). An important new understanding is that the projected rise in temperature may be enough to induce significant increases in  $\text{NH}_3$  emissions owing to increased evaporation; Skjøth and Geels (2013) and Sutton et al. (2013) suggested possible increases of 20–50 % over the next century. Model studies to assess the potential impact of this important climate effect on nitrogen deposition and the exceedance of critical loads have begun, but as noted by Sutton et al. (2013), they will require a new paradigm of emission and deposition calculations.

A rise in temperature is also commonly assumed to cause an increase in biogenic VOC emissions and hence results in higher  $\text{O}_3$  and PM levels (e.g. Langner et al. 2012b; Doherty et al. 2013; Hedegaard et al. 2013). However, some studies indicate that increased levels of atmospheric  $\text{CO}_2$  may reduce some biogenic VOC emissions (e.g. Young et al. 2009); the net impact of climate change on such emissions is still unknown.

A potentially important impact of climate change on shipping emissions concerns the Arctic. The observed decline in Arctic sea ice is likely to result in a significant increase in shipping activities. According to Corbett et al. (2010),  $\text{NO}_x$  emissions from Arctic shipping could increase by a factor of 1.7 (by 2030) and 3.8 (by 2050), relative to 2004. If new shipping routes are introduced (such as the

Northern Sea Route and Northwest Passage), these increases will be even higher. The impacts of these changes are discussed in Sect. 15.4.

### 15.3 Observed Concentrations and Deposition

Concentrations of many pollutants over the Baltic Sea region have changed significantly over the past century, mainly due to changes in emissions, either within Europe or globally. However, systematic measurements (with a few exceptions) did not really begin until the 1970s and later. Many of the sulphur- and nitrogen-related pollutants have their greatest environmental impact after they are deposited, while concentrations of aerosol species in particular are of concern due to their health impacts (Sect. 15.6). Ozone is a toxic gas affecting human health and vegetation.

#### 15.3.1 Sulphur and Nitrogen

Tørseth et al. (2012) used data from a selection of long-term monitoring sites within the EMEP network to analyse trends in sulphur, Nr compounds and O<sub>3</sub> across Europe. Although they reported concentration information for many compounds, this section focuses on a few key findings plus some complementary studies. Sulphur compounds have been measured for the longest period within EMEP. Figure 15.6 illustrates both the network development and trends in total SO<sub>4</sub><sup>2-</sup> (including sea-salt sulphate) from 1974 to 2009.

There is a clear reduction in total SO<sub>4</sub><sup>2-</sup> concentration across the entire region. Tørseth et al. (2012) also presented (more limited) data on non-sea-salt (nss) SO<sub>4</sub><sup>2-</sup> and SO<sub>2</sub>. The EMEP monitoring results for SO<sub>4</sub><sup>2-</sup> in air and precipitation from 1980 to 2009 reflect the emission reductions achieved throughout Europe, whereas the observed reductions in SO<sub>2</sub> are even greater than implied by emission reductions. This apparent nonlinearity is probably due to a combination of factors, including changes in the oxidation capacity of the atmosphere, changes in cloud water pH, changes in surface deposition and changes in emission height (Lovblad et al. 2004; Fowler et al. 2007, 2009).

Earlier assessments (Bartnicki and Lovblad 2004; Lovblad et al. 2004) also found the widespread reduction in observed concentrations of SO<sub>2</sub> and nss-sulphate in air in the Baltic Sea countries in the period 1980–2000 to be in line with sulphur emission reductions. The reduction in concentrations of SO<sub>2</sub> observed in the Baltic Sea region were in the range 85–90 % for stations in Denmark, Finland, Sweden and Germany, while the reductions were smaller at 50–80 % for stations in Belarus, Estonia, Latvia, Lithuania and Poland (Lovblad et al. 2004). The nss-sulphate concentrations in air and precipitation have

also decreased substantially, but the decrease has not been as large as the decrease in SO<sub>2</sub>. Vuorenmaa (2004) found significant decreasing trends in SO<sub>4</sub><sup>2-</sup> in precipitation all over Finland in the period 1986–2000.

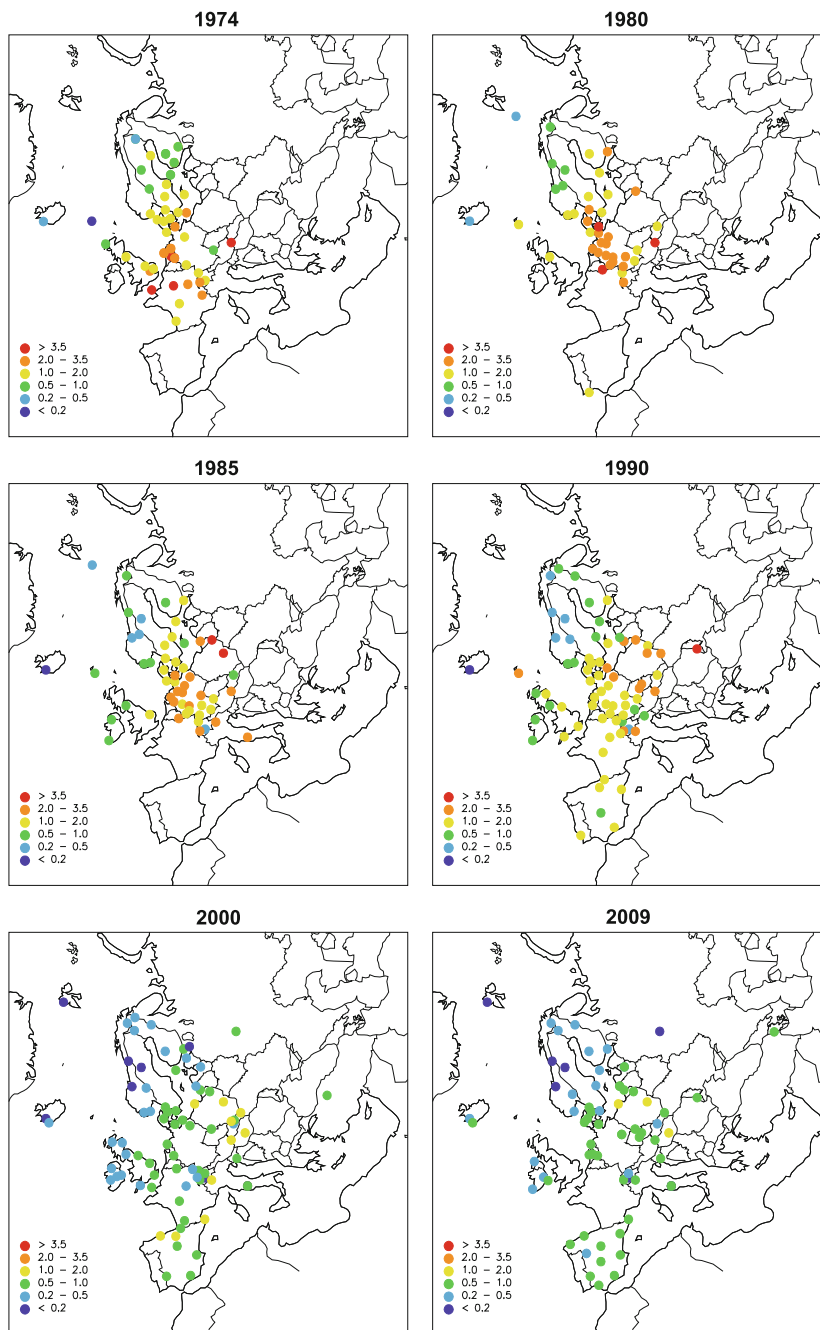
Tørseth et al. (2012) compared the observed trends in sulphur (from 1980) and Nr (from 1990) to 2009. The analysis for the Nr compounds was especially limited because of the lack of complete and consistent data across all years, but the results illustrate the significant changes in air quality that have taken place in this period. As shown in Fig. 15.7 and discussed in more detail by Tørseth et al. (2012), the trends in SO<sub>x</sub>, NO<sub>x</sub> and NH<sub>3</sub> emissions are generally reflected in the measurements, with the exceptions of SO<sub>4</sub><sup>2-</sup> (discussed above) and NO<sub>3</sub><sup>-</sup>. Colette et al. (2011) also found robust trends in NO<sub>2</sub> over the past ten years, with the majority of monitoring stations in Europe showing reductions of about 50–60 % over this period.

The concentrations of total airborne NO<sub>3</sub><sup>-</sup> decreased on average by only 8 %. These differences in trends can partly be explained by a shift in equilibrium towards more particulate ammonium nitrate relative to HNO<sub>3</sub> caused by a reduction in SO<sub>2</sub> emissions (Fagerli and Aas 2008). A more rapid oxidation of NO<sub>x</sub> may also have contributed (Monks et al. 2009). The total reduction in observed concentrations of NO<sub>x</sub> from 1980 to 2009 is larger than from 1990 to 2009. A similar trend is not seen in the emission data, but the discrepancy may partly be explained by significant changes in the number and location of sites when comparing the 1980s with more recent years (Tørseth et al. 2012).

Tørseth et al. (2012) reported that the total European NH<sub>3</sub> emissions decreased by 29 % from 1990 to 2009, although with large regional differences. A majority of the EMEP sites show a decreasing trend both in air and precipitation, on average 24–25 %. It should be noted that some EMEP sites are, due to their location in rural districts, partly affected by local NH<sub>3</sub> emissions (Tørseth et al. 2012). Pihl Karlsson et al. (2011) also 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. Their analysis of the time series 1996/97–2007/08 showed that SO<sub>2</sub> and NO<sub>2</sub> air concentrations have decreased substantially, whereas there was no trend for NH<sub>3</sub>. This study found reductions in SO<sub>4</sub><sup>2-</sup> deposition for the majority of monitoring sites across Sweden and other Nordic countries and that the reductions were of the same order of magnitude as the European emission reductions. Soil water SO<sub>4</sub><sup>2-</sup> concentrations decreased at most, but not all, monitoring sites across Sweden in parallel with the SO<sub>4</sub><sup>2-</sup> deposition reductions. The soil water acidification indicators—pH, acid neutralising capacity (ANC) and inorganic aluminium concentrations—indicated acidification recovery at some sites, but there were also many sites with no significant change. Despite the substantial decrease



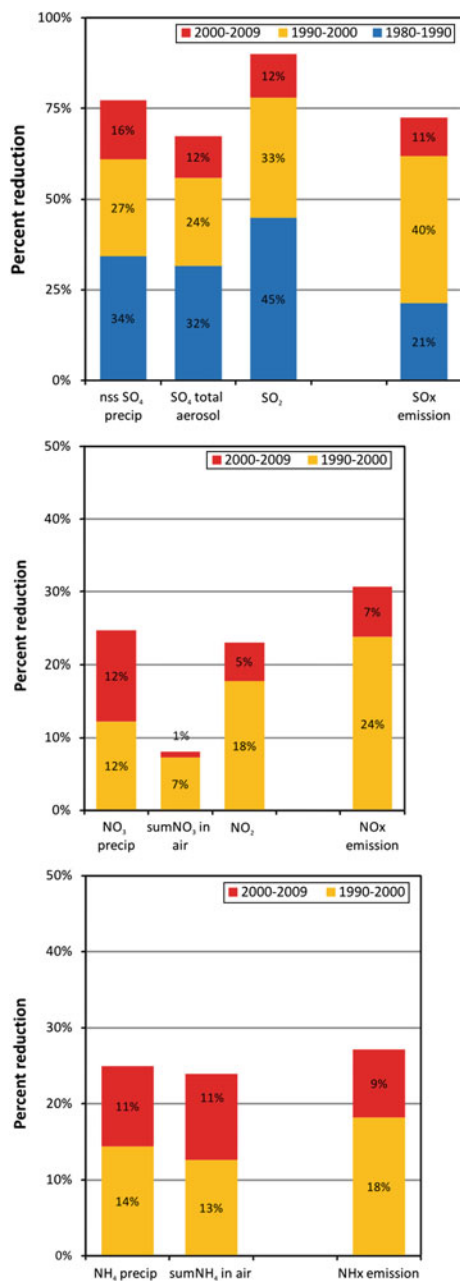
**Fig. 15.6** Annual mean concentrations of sulphate ( $\text{SO}_4^{2-}$ ) in aerosols across Europe from 1974 to 2009, as estimated from the EMEP network for selected stations. Unit:  $\mu\text{g S m}^{-3}$ , Tørseth et al. (2012)



in  $\text{NO}_2$  air concentrations, no statistically significant decrease in the bulk deposition of inorganic nitrogen could be demonstrated. (They were not able to include dry nitrogen deposition in the trend analyses, however.) Elevated  $\text{NO}_3^-$  concentrations in the soil water occurred intermittently, but also after massive felling caused by severe storm events, particularly at some sites in southern Sweden. This indicated that nitrogen stocks in the forest soils of southern Sweden are increasing and may be approaching saturation.

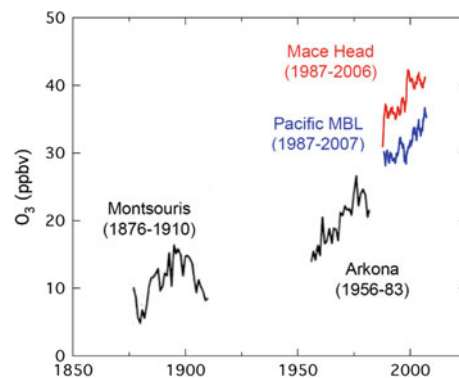
### 15.3.2 Ozone

There has been a significant increase in  $\text{O}_3$  since the start of the twentieth century (Fig. 15.8), which is largely attributed to changes in anthropogenic emissions of  $\text{NO}_x$  and other precursors (Monks et al. 2009; Parrish et al. 2009, 2012). Annual trends appear to have flattened out in Europe since about 2000. The reasons for this are not fully understood, but reductions in European emissions are certainly affecting



**Fig. 15.7** Observed reduction in sulphur and nitrogen compounds relative to emission reductions in Europe for ten-year periods from 1980 (sulphur) and 1990 (nitrogen). Sulphur reductions are calculated using data from the 14 sites that measured all three compounds since 1980; although data from 14 sites were also used for nitrogen, it is not necessarily the same site used for all compounds, Tørseth et al. (2012)

O<sub>3</sub> trends. In general, mean O<sub>3</sub> levels in Europe are increasing in wintertime because of the reduction in NO<sub>x</sub> emissions (the NO<sub>x</sub>-titration effect, important in winter, in which NO<sub>x</sub> acts as a sink rather than a source of O<sub>3</sub>). In summer, the European emission reductions help to reduce O<sub>3</sub>, although these are sometimes counteracted by increasing hemispheric background levels (e.g. Jenkin 2008).

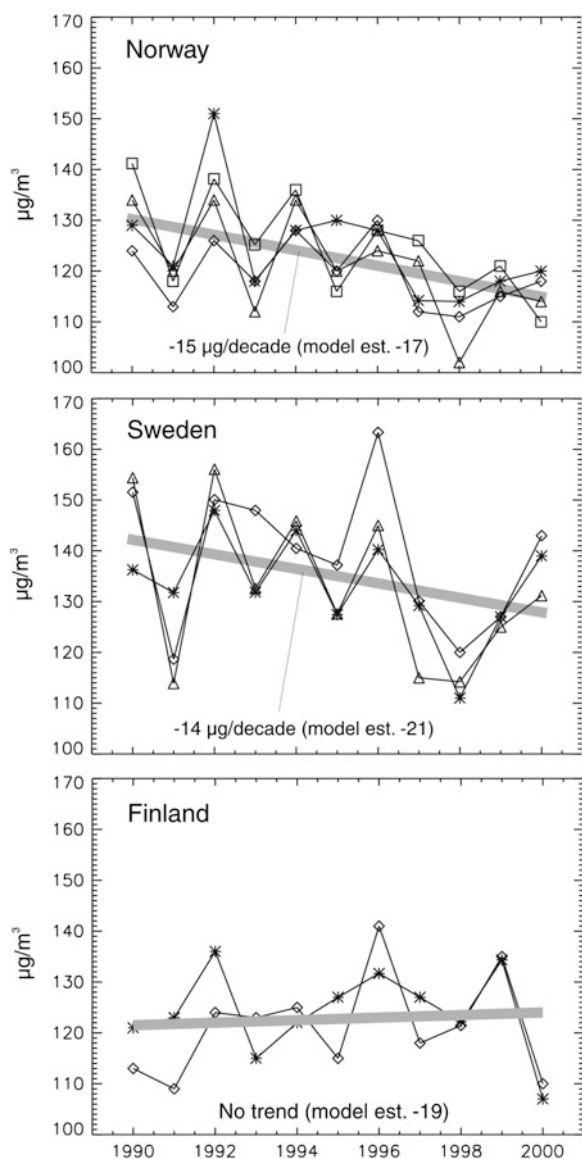


**Fig. 15.8** Comparison of the 12-month running mean ozone (O<sub>3</sub>) concentrations from three northern European sites and the Pacific marine boundary layer (MBL), Parrish et al. (2009)

Colette et al. (2011) presented trends in O<sub>3</sub> (as well as NO<sub>2</sub> and PM<sub>10</sub>) over the past ten years. They found that (as expected) the trends in O<sub>3</sub> reflect trends in NO<sub>2</sub>. On average, O<sub>3</sub> increases of 0.37, 0.27 and 0.05 μg m<sup>-3</sup> year<sup>-1</sup> were found at urban, semi-urban and rural sites, respectively. For daily means, the trends were positive at about 31 % of stations, whereas for daily peaks, only 18.5 % of stations showed positive trends. This difference between mean and peak O<sub>3</sub> trends is reasonably well understood (e.g. Jonson et al. 2006; Vautard et al. 2006; Jenkin 2008; Wilson et al. 2012); in short, mean O<sub>3</sub> is increasing, while peaks in O<sub>3</sub> are being reduced. Figure 15.9 illustrates the decline in peak O<sub>3</sub> concentrations at some Nordic sites.

## 15.4 Modelled Concentrations and Deposition

The number of model studies specifically addressing sulphur deposition to the Baltic Sea region is limited. Many studies cover the region but do not report estimates specifically for the Baltic Sea or for the surrounding catchment. Hongisto et al. (2003) reported estimates for 1993–1998 for the Baltic Sea and some of the surrounding land areas, and in the work of EMEP, model estimates of sulphur deposition to the Baltic Sea and individual surrounding countries are available for different years starting from 1985. Based on the EMEP model results, total deposition of nss-sulphur to both the Baltic Sea and the countries bordering the Baltic Sea decreased by about 80 % between 1985 and 2009 to a level of about 7700 t S year<sup>-1</sup> for the region as a whole region and about 1300 t S year<sup>-1</sup> for the Baltic Sea itself in 2009 (Table 15.4). The EMEP estimate for the Baltic Sea is comparable to that by Hongisto (2003) for 1993–1998 of about 1500 t S year<sup>-1</sup>.



**Fig. 15.9** Hourly observed ozone ( $\text{O}_3$ ) 99th percentile concentrations for 1990–2000 at sites in the southern parts of Norway, Sweden and Finland. The shaded grey line indicates the regression of the average of the 99th percentiles. The trend estimated by this regression is given together with the estimated trend in modelled 99th percentiles (MATCH model), Solberg et al. (2005)

Several modelling studies have specifically addressed the deposition of Nr to the Baltic Sea and surrounding areas (de Leeuw et al. 2001, 2003; Hertel et al. 2002; Schlunzen and Meyer 2007; Bartnicki and Fagerli 2008; Langner et al. 2009; Bartnicki et al. 2011; Geels et al. 2012b). As illustrated in Figs. 15.10 and 15.11, wet deposition of nitrogen is greater than dry deposition of nitrogen, and oxidised nitrogen deposition is greater than reduced Nr deposition. All studies show that modelled dry deposition of both the oxidised and reduced forms of nitrogen exhibits strong south–north gradients across the Baltic Sea region, declining by

well over an order of magnitude from Denmark to the northern part of Sweden (Langner et al. 2009). Indirect estimates of the atmosphere as an ‘external’ source of nitrogen to the Kattegat undertaken within the MEAD project suggest that the atmosphere may account for a substantial fraction ( $\sim 40\%$ ) of the total flux (the sum of land runoff, upwelling flux and atmospheric deposition) during the summer months, dropping to less than 20% for the year as a whole (Spokes et al. 2006). The estimates are in broad agreement with data for the Baltic proper (Elmgren and Larsson 2001; Rolff et al. 2008; Langner et al. 2009) but the wet, and particularly the dry, deposition fluxes are comparatively poorly constrained. Deposition to ice in the northern Baltic Sea 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 deposition originating from emissions on land has 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.  $\text{NO}_x$  deposition has a weaker gradient, reflecting a longer residence time in the atmosphere ( $\text{NO}$  and  $\text{NO}_2$  do not deposit efficiently, but are transformed to  $\text{HNO}_3$  which is efficiently dry deposited or forms  $\text{NO}_3^-$  aerosols). Furthermore, slower deposition processes for aerosols over water surfaces are assumed in all models.

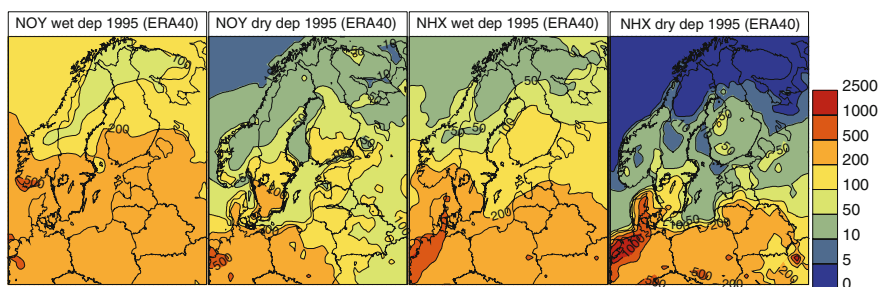
Some studies have assessed the contribution of different countries to Nr deposition in the Baltic Sea region. For example, Geels et al. (2012b) using the DEHM model, estimated that the nine countries bordering the Baltic Sea contributed about 50% of the Nr deposited in both 2007 and a projected 2020 scenario, with Germany the largest single contributor (Fig. 15.12). Bartnicki et al. (2011), using the EMEP MSC-W model (Simpson et al. 2012), found greater contributions from some countries, with five contributing about 55% of total Nr deposition, and emissions from international shipping on the Baltic Sea contributing 4–5% (Fig. 15.13). They also found Germany to be the single largest contributor (almost a factor of two greater than Poland at 12%), but that even the UK made a significant contribution (7%). As to source types, Hertel et al. (2002) estimated that around 40% of the nitrogen deposited to the North Sea originated from agricultural activities and that around 60% was from combustion sources.

Table 15.5 compares nitrogen deposition estimates from a number of studies using several chemical transport models (CTMs). For current years, the CTMs gave similar estimates: 230–260 kt N for 1995 or near 200 kt N for 2006/2007. To estimate changes in nutrient loads to the Baltic Sea over a longer period (1850–2006), Ruoho-Airola et al. (2012)

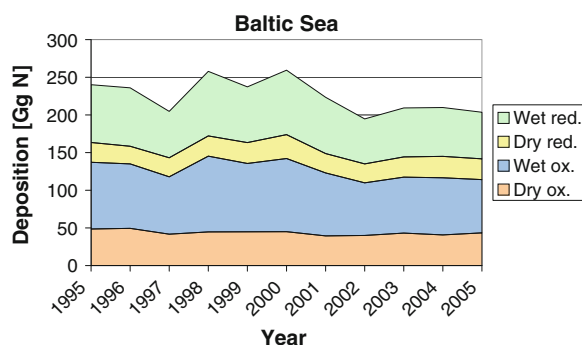
**Table 15.4** Sulphur deposition trends for the HELCOM Contracting Parties and Baltic Sea ( $\text{t S year}^{-1}$ )

Country	1985 EMEP (1994)	1990 EMEP (1994)	1995 EMEP (1998)	1993–1998 Hongisto (2003)	2009 EMEP (2011)
Denmark	716	547	320		183
Estonia	530	430	311		133
Finland	2262	1659	968		431
Germany	17,080	12,428	5440		1966
Latvia	850	600	439		211
Lithuania	1160	890	565		276
Poland	12,517	11,456	5948		2524
Sweden	2737	2205	1359		641
Baltic Sea	5853	4218	2572	1526	1334
Total	43,705	34,433	17,922		7699

Note that, EMEP model versions and inventories have changed over the course of the reports cited, so the data are not fully consistent



**Fig. 15.10** Simulated wet and dry deposition of oxidised ( $\text{NO}_x$ ) and reduced ( $\text{NH}_x$ ) nitrogen in 1995 from the MATCH-ERA40 model. Units:  $\text{mg N m}^{-2} \text{ year}^{-1}$  (Langner et al. 2009)



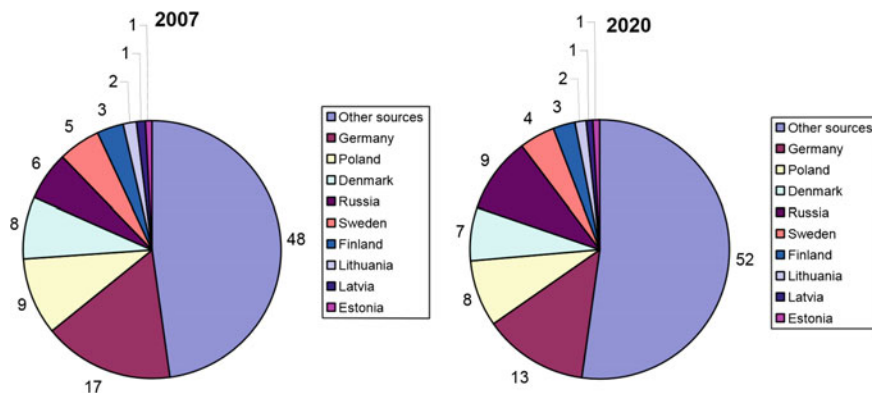
**Fig. 15.11** Time series of annual nitrogen deposition to the Baltic Sea for 1995–2005 as calculated by the EMEP MSC-W model. Adapted from Bartnicki and Fagerli (2008)

combined time series of deposition data, published historical monitoring data and deposition estimates, and recent emission estimates. Figure 15.14 presents their estimates of annual deposition, with changes in oxidised Nr similar to the changes in emissions of Fig. 15.1.

### 15.4.1 ‘Climate’ Meteorology, Impacts of Climate Change

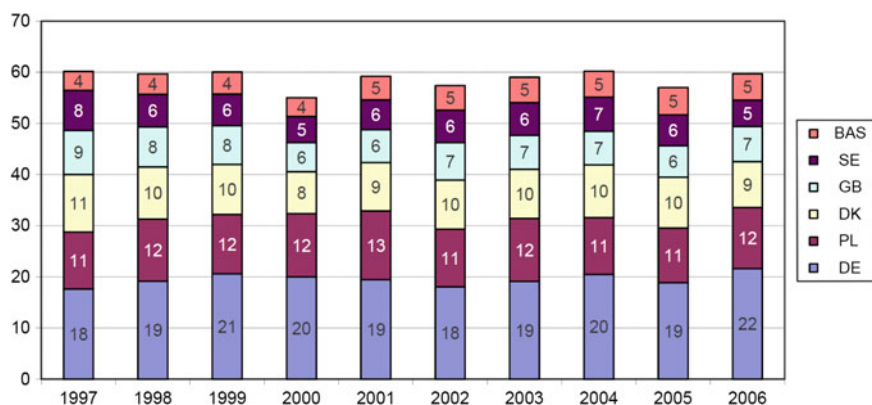
Modelling historical and future changes in concentration and deposition shares many common features. In both cases, the models must be driven by ‘estimates’ of meteorology rather than by observed meteorological fields. Hindcasting recent decades is easier than forecasting the future, although the lack of satellite data and other observations in earlier years makes such data less reliable than current numerical weather prediction 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 (i.e. general circulation models; GCMs) are available, but for estimating changes over the Baltic Sea region, it is better to run finer resolution models that are forced by GCMs and more capable of capturing the effects of local topography and land cover. An important



**Fig. 15.12** Nitrogen deposition to the Baltic Sea as calculated using the DEHM model, subdivided according to the contribution from the nine bordering countries and other sources (i.e. remaining emissions in

the model domain). The contributions are given as percentages for the present-day scenario and a projection for 2020, Geels et al. (2012b)



**Fig. 15.13** Major contributions to the annual deposition of nitrogen to the Baltic Sea basin for 1997–2006. Contributions are shown as a percentage of total deposition. International ship traffic on the Baltic

Sea (BAS), Sweden (SE), UK (GB), Denmark (DK), Poland (PL) and Germany (DE), Bartnicki et al. (2011)

data set in this respect is that generated by the Rossby Centre regional climate model, RCA3 (Samuelsson et al. 2011).

Estimates of future concentrations and deposition depend on forecasts of both emissions and meteorology. Many studies have shown that meteorological/climate factors are generally less important than emission changes for concentrations and deposition (Hole and Engardt 2008; Langner et al. 2012a, b; Doherty et al. 2013; Engardt and Langner 2013; Hedegaard et al. 2013). Such simulations suggest that specification of future emissions is almost certainly the major factor when attempting to project future deposition amounts. Figure 15.15 (from Langner et al. 2012a) presents a clear illustration of this for  $O_3$  (see also Engardt et al. 2009), comparing daily maximum values calculated by the MATCH model for scenarios that examine the relative impact of changes in climate, European emissions and increasing hemispheric background levels of  $O_3$ . Emission

changes are clearly of most importance in these model runs, although the background  $O_3$  level is also significant. Wild et al. (2012) highlighted the large uncertainties in assumptions concerning changes in background  $O_3$  levels.

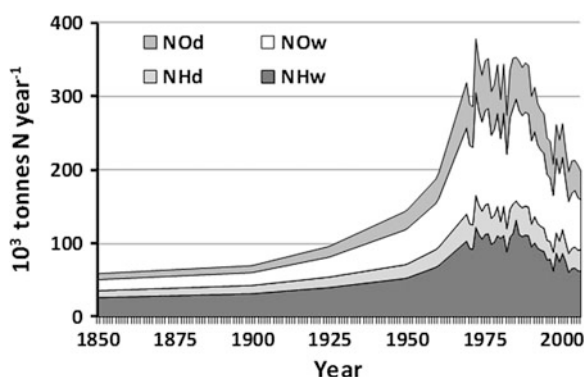
The MATCH model has been run for both historical and future scenarios in a number of studies. Andersson et al. (2007) used ERA40 to run MATCH for 1958–2001. Hole and Engardt (2008) used 30-year periods of meteorological data produced by RCA3, with forcing by the ECHAM4/OPYC3 GCM (Roeckner et al. 1999).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

**Table 15.5** Comparison of model estimates of total, dry and wet deposition of nitrogen ( $\text{kt N yr}^{-1}$ ) to the Baltic Sea

Year	Model	Dry	Wet	Total	Comments
1995	HILATAR			255	(a)
	EMEP rv2.5 EMEP			244	(a, b)
	rv3.1 MATCH-			230	(c)
	ERA40			260	(a)
1996–2000	EMEP			300	(a, b)
	MATCH-ERA40			271	(a)
2006	EMEP rv3.1			199	(c)
2007	DEHM			203	(d)
<i>Historical</i>					
1961–1990	MATCH-RCA3	41	207	248	(a), year 2000 emissions
<i>Projections</i>					
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

Extended from Langner et al. (2009)

Notes (a) Langner et al. (2009); (b) EMEP model rv2.5 from ca. 2005–2006; (c) EMEP model rv3.1 from 2008, data from Bartnicki et al. (2011); (d) Geels et al. (2012b)



**Fig. 15.14** Estimated annual integrals of inorganic nitrogen deposition to the Baltic Sea, 1850–2006. The graphic shows dry and wet deposition of oxidised nitrogen ( $\text{NO}_d$  and  $\text{NO}_w$ ) and dry and wet deposition of reduced nitrogen ( $\text{NH}_d$  and  $\text{NH}_w$ ), Ruoho-Airola et al. (2012)

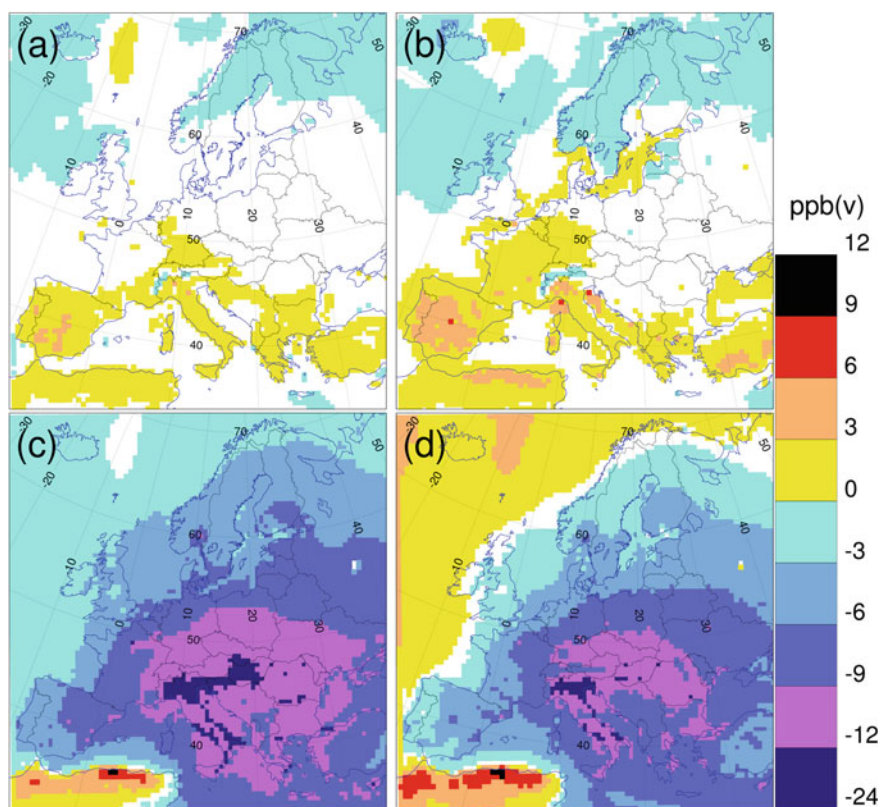
(2009) investigated the results of these MATCH model runs for the Baltic Sea region in particular.

In a study to examine the potential effect of historical and possible future climate change (not emissions) and variability on atmospheric deposition of nitrogen 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 Sea region (of 4–5 %), but generally increased deposition of oxidised nitrogen over the Baltic Sea. This tendency is of smaller magnitude than current interannual variability (Hongisto 2011).

For Europe, Geels et al. (2012b) used an inventory based on a combination of the EU Thematic Strategy on Air Pollution and scenarios for the 27 EU countries made by IIASA as part of the work towards a revised EU directive on national emission ceilings (NEC-II). For the remaining European countries and the western Asian countries, the projected emissions were based on 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 IMO, and the same projections were used for the North Sea and Baltic Sea. For the nine countries bordering the Baltic Sea, nitrogen emissions were projected to decline by about 50 % between 2007 and 2020 (although for Russia the projected decrease was just 11 %).

Another potential impact of climate change is increased emissions from shipping due to reduced sea ice in the Arctic. Tuovinen et al. (2013) assessed the changes in nitrogen deposition and the phytotoxic ozone dose (POD) arising from both climate change alone, and from potential changes in ship emissions, including a possible new Northeastern Passage route (Corbett et al. 2010). The emissions changes resulted in significant changes in POD and nitrogen deposition, mainly along the Norwegian coastline. POD values increased in some areas by more than 10 %, but decreased close to sources; such nonlinearity is expected and common in  $\text{O}_3$  scenarios, but highlights the need for high spatial resolution in such model simulations.

**Fig. 15.15** Projected change in summer (April–September) daily maximum surface ozone ( $O_3$ ) concentration for 2040–2059 relative to 1990–2009 **a** and **b** changes due to change in climate only; RCA3 downscaling of ECHAM5 and HadCM3, respectively. **c** ECHAM5 downscaling and change in European  $O_3$  precursor emissions. **d** Increasing boundary case; change due to combined change in climate, change in  $O_3$  precursor emissions and an increasing hemispheric background of  $O_3$  level of  $0.1 \text{ ppb(v) year}^{-1}$ . Non-significant changes at the 95 % confidence level are masked *white*, Langner et al. (2012a)



## 15.5 Uncertainty of Estimates

Table 15.5 presented a comparison of nitrogen deposition estimates from a number of studies using CTMs. As was apparent, for any given year, the different CTMs seemed to give similar estimates. Much of the similarity may be ascribed to the use of similar emissions data and that much of the deposition is driven by precipitation events that are not that sensitive to model formulation. Consistency of emissions data, or deposition estimates, is not always guaranteed, however. For example, Winiwarter et al. (2011) found large discrepancies between the emissions and deposition over Europe as estimated by Schulze et al. (2010) and those from the EMEP inventory and EMEP model estimates. Model calculations clearly need to be thoroughly evaluated against observations.

### 15.5.1 Wet Deposition

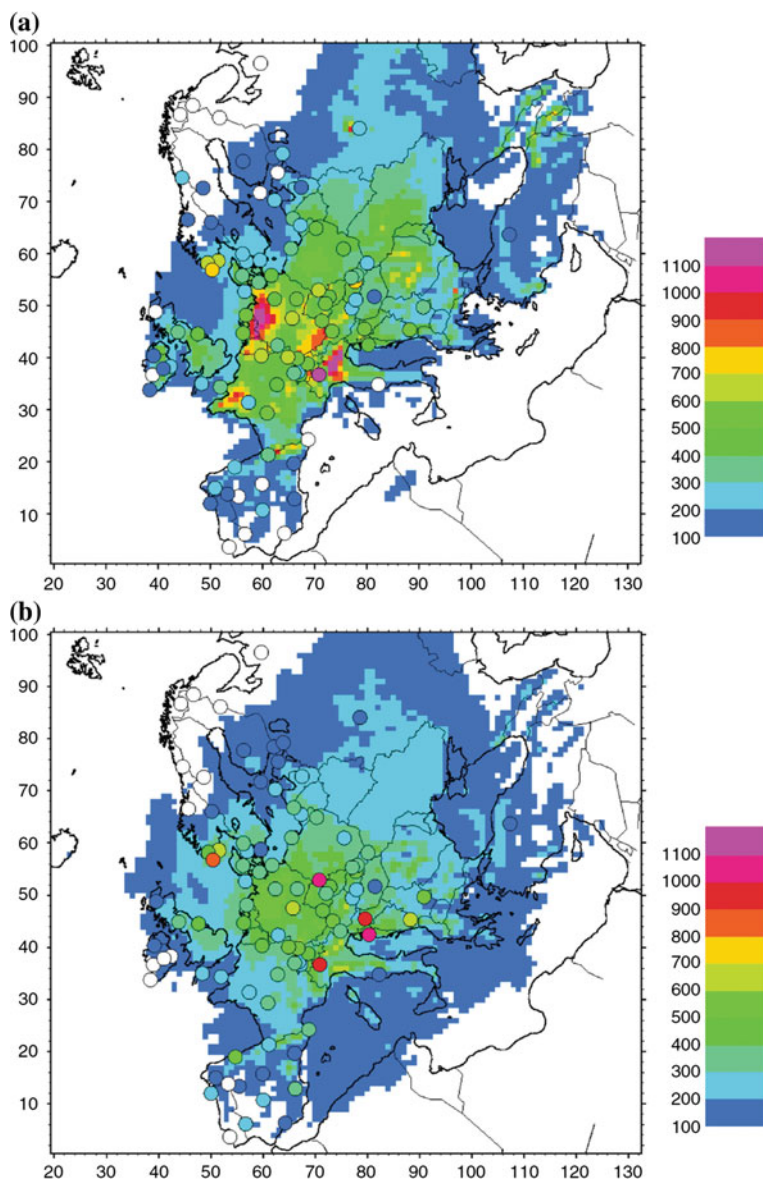
Comparison of model results for wet deposition or concentrations in precipitation is in many ways more difficult than comparing gas concentrations. The most important issue concerning the wet removal of species in CTM models is probably the meteorological input; model performance for wet deposition fluxes or concentrations in precipitation is

strongly limited by the quality of the numerical weather prediction 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 nonlinear 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).

Large differences between models were found in the global models participating in the COSAM study, in which the wet deposition efficiency varied by a factor of four (Roelofs et al. 2001). A similar spread was also found for global models by Dentener et al. (2006) and Textor et al. (2006).

At the European scale, the EMEP MSC-W model (Simpson et al. 2012) has been subject to extensive evaluation against observed wet deposition estimates. Standard scatter plots showing model performance against observed concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are available in the annual EMEP status reports (e.g. Fagerli and Hjellbrekke 2008; Berge and Hjellbrekke 2010). The EMEP MSC-W model results have also been compared to observed wet deposition for nitrogen from the ICP Forests monitoring network (Simpson et al. 2006). Differences in mean values between modelled and observed (ICP Forests)  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and

**Fig. 15.16** Comparison of modelled and observed annual means of reduced nitrogen **a** and oxidised nitrogen **b** in wet deposition ( $\text{mg N m}^{-2} \text{ year}^{-1}$ ). Data are for 2001. 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, Simpson et al. (2011). The model used is the EMEP MSC-W model (Simpson et al. 2012)



$\text{NH}_4^+$  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  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in precipitation were on average very similar (differences of 0–14 %), and the correlation between modelled and observed data was high for this type of comparison ( $R^2 = 0.4\text{--}0.8$  for most components and years).

Figure 15.16 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  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentration in precipitation. For reduced nitrogen, Fig. 15.16a 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 estimated wet deposition have only a limited number of measurement sites (e.g. the Netherlands, Belgium), and so it is difficult to evaluate model performance here. The EMEP model has a tendency to underestimate wet deposition in Nordic sites.

For oxidised nitrogen (Fig. 15.16b), five sites stand out as having 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 (by a factor of two for the Norwegian site). However, there is good agreement between model results and measurements at almost all other sites, which provides confidence that the modelled wet deposition budget is within the uncertainty of the measured value.



## 15.5.2 Dry Deposition

Although wet deposition represents an important fraction of the nitrogen deposition over the Baltic Sea region, Figs. 15.10 and 15.11 show that dry deposition is also important. Many of the physical/chemical processes controlling dry deposition of Nr compounds were discussed by, for example, Flechard et al. (2011), Hertel et al. (2012) and Fowler et al. (2009). Deposition processes over land and sea involve different processes and challenges.

### 15.5.2.1 Land

Efforts to estimate aerosol particle dry deposition to terrestrial ecosystems face many of the same challenges as efforts to estimate deposition to water surfaces (see Sect. 15.5.2.2), but vertical velocities over terrestrial surfaces are typically greater (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, only limited direct measurements are available and are principally focused on size-resolved, rather than chemically resolved, fluxes (Pryor et al. 2008a; Fowler et al. 2009). Furthermore, 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 may dominate the chemical flux. Those recent studies have tended to indicate a very strong influence of vegetation canopy morphology and aerosol properties on deposition velocities, 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, such as the 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, for example, artefacts 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 (NEU) project (Sutton et al. 2007) 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. This study suggested that  $\text{NH}_3$  is the single highest atmospheric Nr dry input in many parts of Europe. At

suburban sites of the NEU network,  $\text{HNO}_3$  and particulate  $\text{NO}_3^-$  and  $\text{NH}_4^+$  also contributed significant fractions of the total dry deposition. There were however substantial differences between models, with annual deposition rates varying as much as twofold between models at given monitoring sites. This highlights the variability in model parameterisations, stemming from the variability in measured deposition rates and canopy resistances. For  $\text{NH}_3$ , the stomatal compensation point and the external leaf surface (or non-stomatal) resistance were the largest sources of divergence between models.

The importance of bidirectional fluxes was also discussed by Geels et al. (2012b). They noted that although several parameterisations of bidirectional fluxes over land exist for  $\text{NH}_3$ , they have so far mainly been used in field-scale  $\text{NH}_3$  exchange models (Massad et al. 2010). Geels et al. (2012b) also noted that bidirectional 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 deposition over the sea (Sorensen et al. 2003).

Model estimates of aerosol deposition velocity ( $V_d$ ) differ greatly among the various modelling approaches and parameterisations (see Ruijgrok et al. 1997 for a review), but it is in the size range 0.1–1.0  $\mu\text{m}$  that variability and uncertainty are greatest. Whereas mechanistic models predict very low deposition velocities for fine aerosols, typically of the order of 0.1  $\text{mm s}^{-1}$ , field measurements suggest that  $V_d$  is 1–3 orders of magnitude higher (Zhang et al. 2001; Gallagher et al. 2002). Nevertheless, such field measurements are also subject to great uncertainty (Rannik et al. 2003; Pryor et al. 2008a, b). This is especially relevant for Nr in the aerosol phase, as  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are mostly (>90 %) present as sub-micron particles.

### 15.5.2.2 Sea

The difficulty in making in-site direct aerosol particle dry deposition observations over water derives principally from the following: (i) the bidirectionality 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 parameterised model of the dry deposition rate to determine the deposition flux (e.g. Matsumoto et al. 2009; Buck et al. 2010; Uematsu et al. 2010). Such studies and recent numerical modelling have suggested

a key role for atmospheric transport and deposition of aerosol particles in nutrient supply (Krishnamurthy et al. 2010), as well as toxin transport (Paytan et al. 2009) to aquatic ecosystems. Also, 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 (Uno et al. 2007; Tian et al. 2008). 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 for deposition rates (Slinn and Slinn 1980; Giorgi 1986; Hummelshøj et al. 1992; Pryor et al. 1999) 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 0.1–1.0  $\mu\text{m}$  (Pryor and Barthelme 2000), however, in a wave tunnel experiment deposition velocities for magnesium oxide particles in the diameter range 0.1–1.0  $\mu\text{m}$  showed an enhancement of  $\leq 30\%$  (Larsen et al. 1995).

## 15.6 Human Health Effects of Air Pollution

In a major review of the health effects of fine particulate air pollution, Pope and Dockery (2006) stated that ‘Despite important gaps in scientific knowledge and continued reasons for some scepticism, a comprehensive evaluation of the research findings provides persuasive evidence that exposure

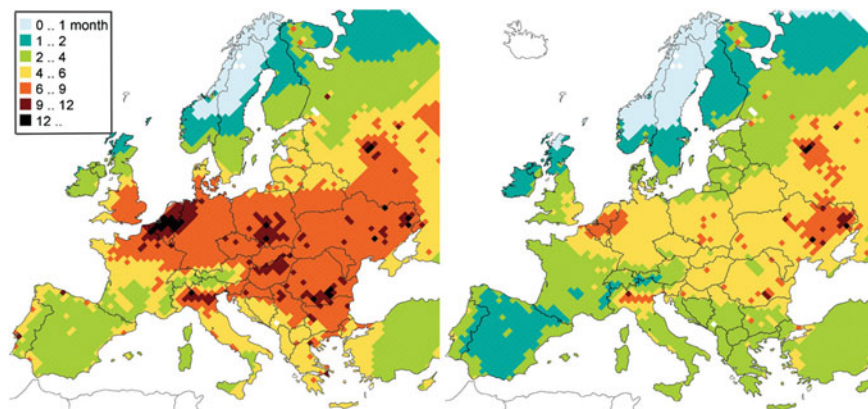
to fine particulate air pollution has adverse effects on cardiopulmonary health’. In their extensive review, Pope and Dockery (2006) concluded ‘There has also been emerging evidence of PM-related cardiovascular health effects and growing knowledge regarding interconnected general pathophysiological pathways that link PM exposure with cardiopulmonary morbidity and mortality’. They pointed to substantial progress in research providing several interesting observations and viable hypotheses for how the human body reacts to inhaled particles. Most investigations to establish the relative importance of different air pollution components for health effects indicate particle mass to be of major importance. However, additive or synergistic effects of co-occurring pollutants may also be important (Pope and Dockery 2006).

Estimates of current and future health impacts of air pollution were presented by Amann et al. (2011) using the GAINS model. The GAINS methodology is based on using pollutant concentration data from GAINS itself or EMEP, linked to population maps across Europe. For different emission scenarios, GAINS quantifies premature mortality that can be attributed to long-term exposure to  $\text{PM}_{2.5}$ . The link to health effects follows the outcomes of the American Cancer Society cohort study and its re-analysis (Pope et al. 2002, 2009).

For the health impact assessment of policy scenarios, GAINS calculates the loss in statistical life expectancy as the total amount of life years lost (YOLL) for the entire population over 30 years. Health impacts for people younger than 30 years, and in particular impacts on infant mortality, are presently not considered in GAINS.

Figure 15.17 shows the impact of PM across Europe for 2005 and a 2020 scenario. The GAINS model estimates that the average loss in statistical life expectancy that can be attributed to exposure to fine particulate matter ( $\text{PM}_{2.5}$ ) could decline from 7.4 months (2005) to 4.4 months (2020)

**Fig. 15.17** Loss in statistical life expectancy attributable to exposure to fine particulate matter ( $\text{PM}_{2.5}$ ) from human activities. *Left* 2005; *right* baseline projection for 2020, Amann et al. (2011)



in the EU-27 and to 6.1 months in non-EU countries. Particularly, high threats to human health occur in industrial areas, where air pollution is estimated to shorten life expectancy by more than a year (Amann et al. 2011).

## 15.7 Conclusion

This chapter has documented the changes in atmospheric chemical components over the Baltic Sea region, using a mixture of measurements, emissions estimates and modeling. The focus was on the period from around 1900 to 2050, since this period has received the most attention in the literature. The majority of the information concerns sulphur and Nr compounds, as well as O<sub>3</sub>, since these pollutants have significant ecosystem and health impacts.

Emissions of sulphur and nitrogen species, and of other ozone precursors such as hydrocarbons, have changed significantly over the last 100 years, although very differently for land- and sea-based sources. Land-based emissions generally peaked around 1980–1990 and have since been reduced as a result of emissions control measures. Emissions from shipping have been steadily increasing for decades, but recent measures have reduced sulphur and particulate emissions. Future developments depend strongly on policy developments.

In general, the main driver of changes in atmospheric concentration and deposition with time is found to be changes in emissions rather than impacts of meteorological changes. The dramatic increase in emissions after the 1940s, in Europe and North America, resulted in substantial changes in Nr and sulphur deposition and in O<sub>3</sub> levels. Reductions in emissions in Europe starting around the 1980s have resulted in significant reductions in sulphur and oxidised Nr compounds in the European atmosphere. Emissions of reduced Nr compounds have not declined to the same extent, and indeed in some areas, NH<sub>3</sub> emissions are increasing.

For the future development of air pollution in Europe, some climate-induced changes are potentially important, however. For example, potential increased shipping activity and new shipping routes within the Arctic may lead to increased nitrogen deposition in environmentally sensitive areas and even to increased phytotoxic ozone uptake. A new understanding is also that higher temperatures may increase NH<sub>3</sub> emissions from evaporative sources over land by very substantial amounts (e.g. 20–50 %), a process that is not yet included in NH<sub>3</sub> emission inventories. In summary, while it seems likely that air pollution impacts from sulphur and oxidised nitrogen will be substantially reduced in future

compared to recent years, the situation for ozone and reduced nitrogen is still unclear, and very dependent on future emission control measures, both at regional and (for ozone) hemispheric scale.

**Open Access** This chapter is distributed under the terms of the Creative Commons Attribution Noncommercial License, which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

## References

- Acid News (2012) NO<sub>x</sub> controls for the Baltic on the horizon, Acid News 2012 No.2
- Amann M, Bertok I, Borcken-Kleefeld J, Cofala J, Heyes C, Hoeglund-Isaksson L, Klimont Z, Nguyen B, Posch M, Rafaj P, Sandler R, Schoepp W, Wagner F, Winiwarter W (2011) Cost-effective control of air quality and greenhouse gases in Europe: Modeling and policy applications. *Environ Modell Softw* 26:1489-1501
- Andersson C, Langner J, Bergstrom R (2007) Interannual variation and trends in air pollution over Europe due to climate variability during 1958-2001 simulated with a regional CTM coupled to the ERA40 reanalysis. *Tellus* 59:77-98
- Barrie L (1992) Scavenging ratios: black magic or a useful scientific tool? In: Schwartz S, Slinn W (eds) Proceedings of the 5th international symposium on precipitation scavenging and atmosphere-surface exchange processes, 1:403-420
- Bartnicki J, Fagerli H (2008) Airborne load of nitrogen to European seas. *Ecol Chem Eng S* 15:297-313
- Bartnicki J, Lovblad G (eds) (2004) EMEP Assessment Part II National Contributions, EMEP/CCC Report, The Norwegian Meteorological Institute, Oslo, Norway
- Bartnicki J, Semeena VS, Fagerli H (2011) Atmospheric deposition of nitrogen to the Baltic Sea in the period 1995-2006. *Atmos Chem Phys* 11:10057-10069
- Berg N, Mellqvist J, Jalkanen J-P, Balzani J (2011) Ship emissions of SO<sub>2</sub> and NO<sub>2</sub>: DOAS measurements from airborne platforms. *Atmos Measurement Tech Disc* 4:6273-6313
- Berge H, Hjelbrekke A-G (2010) Acidifying and eutrophying components: validation and combined maps, Supplementary material to EMEP status report 1/2010, The Norwegian Meteorological Institute, Oslo
- Buck CS, Landing WM, Resing JA, Measures CI (2010) The solubility and deposition of aerosol Fe and other trace elements in the North Atlantic Ocean: Observations from the A16N CLIVAR/CO(2) repeat hydrography section. *Mar Chem* 120:57-70
- Colette A, Granier C, Hodnebrog Ø, Jakobs H, Maurizi A, Nyiri A, Bessagnet B, D'Angiola A, D'Isidoro M, Gauss M, Meleux F, Memmesheimer M, Mieville A, Rouil L, Russo F, Solberg S, Stordal F, Tampieri F (2011) Air quality trends in Europe over the past decade: a first multi-model assessment. *Atmos Chem Phys* 11:11657-11678
- Corbett J, Koehler H (2003) Updated emissions from ocean shipping, *J Geophys Res* 108. doi: [10.1029/2003JD003751](https://doi.org/10.1029/2003JD003751)
- Corbett JJ, Lack DA, Winebrake JJ, Harder S, Silberman JA, Gold M (2010), Arctic shipping emission inventories and future scenarios. *Atmos Chem Phys* 10:9689-9704
- de Leeuw G, Cohen L, Frohn L, Geernaert G, Hertel O, Jensen B, Jickells T, Klein L, Kunz G, Lund S, Moerman M, Muller F,

- Pedersen B, von Salzen K, Schlunzen K, Schulz M, Skj oth C, Sorensen L, Spokes L, Tamm S, Vignati E (2001) Atmospheric input of nitrogen into the North Sea: ANICE project overview. *Cont Shelf Res* 21:2073-2094
- de Leeuw G, Skj oth C, Hertel O, Jickells T, Spokes L, Vignati E, Frohn L, Frydendall J, Schulz M, Tamm S, Sorensen L, Kunz G (2003) Deposition of nitrogen into the North Sea. *Atmos Environ* 37: S145-S165
- Dentener F, Drevet J, Lamarque JF et al (2006) Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation. *Global Biogeochem Cy* 20. doi:10.1029/2005GB002672
- Doherty RM, Wild O, Shindell DT, Zeng G, MacKenzie IA, Collins WJ, Fiore AM, Stevensen DS, Dentener FJ, Schultz MG, Hess P, Derwent RG, Keating TJ, (2013) Impacts of climate change on surface ozone and intercontinental ozone pollution: A multi-model study. *J Geophys Res* 118:3744-3763
- Draaijers G, Erisman J (1993) Atmospheric sulfur deposition to forest stands – throughfall estimates compared to estimates from inference. *Atmos Environ* 27:43-55
- Eliassen A (1978) The OECD study of long-range transport of air pollutants: long-range transport modelling. *Atmos Environ* 12: 479-487
- Elmgren R, Larsson U (2001) Nitrogen and the Baltic Sea: managing nitrogen deposition in relation to phosphorus. *The Scientific World Journal* 1:371-377
- EMEP (1994) Transboundary acidifying pollution in Europe. Calculated fields and budgets. EMEP MSC-W Report Report 1/1994. The Norwegian Meteorological Institute, Oslo
- EMEP (1998) Transboundary acidifying pollution in Europe. Calculated fields and budgets. EMEP MSC-W Report Report 1/1998. The Norwegian Meteorological Institute, Oslo
- EMEP (2011) MSC-W: Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe in 2009. EMEP Status Report 1/2011. Norwegian Meteorological Institute, Oslo
- Endresen  , S rg rd E, Sundet J, Dals ren S, Isaksen I, Berglen T, Gravir G (2003) Emission from international sea transport and environmental impact. *J Geophys Res* 108:4560. doi: 10.1029/2002JD002898
- Engardt M, Langner J (2013) Simulations of future sulphur and nitrogen deposition over Europe using meteorological data from three regional climate projections. *Tellus B* 65:20348. dx.doi.org/10.3402/tellusb.v65i0.20348
- Engardt M, Bergstrom R, Andersson C (2009) Climate and emission changes contributing to changes in near-surface ozone in Europe over the coming decades: results from model studies. *Ambio* 38:452-458
- Erisman J, Vermeulen A, Hensen A, Flechard C, D mmgen U, Fowler D, Sutton M, Gr nhage L, Tuovinen J (2005) Monitoring and modelling of biosphere/atmosphere exchange of gases and aerosols in Europe. *Environ Poll* 133:403-413
- Eyring V, Kohler H, Lauer A, Lemper B (2005a) Emissions from international shipping: 2. Impact of future technologies on scenarios until 2050. *J Geophys Res* 110:D17306. doi: 10.1029/2004JD005620
- Eyring V, Kohler HW, van Aardenne J, Lauer A (2005b) Emissions from international shipping: 1. The last 50 years. *J Geophys Res* 110:D17305. doi: 10.1029/2004JD005619
- Eyring V, Isaksen ISA, Berntsen T, Collins WJ, Corbett JJ, Endresen O, Grainger RG, Moldanova J, Schlager H, Stevenson DS (2010) Transport impacts on atmosphere and climate: Shipping. *Atmos Environ* 44:4735-4771
- Fagerli H, Aas W (2008) Trends of nitrogen in air and precipitation: Model results and observations at EMEP sites in Europe, 1980-2003. *Environ Poll* 154:448-461
- Fagerli H, Hjellbrekke A (2008) Acidification and Eutrophication, In: *Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe in 2006*, EMEP Status Report 1/2008:41, The Norwegian Meteorological Institute, Oslo p 41-56
- Flechard CR, Nemitz E, Smith RI, Fowler D, Vermeulen AT, Bleeker A, Erisman JW, Simpson D, Zhang L, Tang YS, Sutton MA (2011) Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network. *Atmos Chem Phys* 11:2703-2728
- Fowler D, Smith R, Muller J, Cape J, Sutton M, Erisman J, Fagerli H (2007) Long term trends in sulphur and nitrogen deposition in Europe and the cause of non-linearities. *Water Air Soil Pollut Focus* 7:41-47
- Fowler D, Pilegaard K, Sutton M et al (2009) Atmospheric composition change: Ecosystems-Atmosphere interactions. *Atmos Environ* 43:5193-5267
- Gallagher MW, Nemitz E, Dorsey JR, Fowler D, Sutton MA, Flynn M, Duyzer J (2002) Measurements and parameterizations of small aerosol deposition velocities to grassland, arable crops, and forest: Influence of surface roughness length on deposition. *J Geophys Res* 107(D12). doi: 10.1029/2001JD000817
- Geels C, Andersen HV, Ambelas Skj oth C, Christensen JH, Ellermann T, L fstr m P, Gyldenk rne S, Brandt J, Hansen KM, Frohn LM, Hertel O (2012a) Improved modelling of atmospheric ammonia over Denmark using the coupled modelling system DAMOS. *Biogeosciences* 9:2625-2647
- Geels C, Hansen KM, Christensen JH, Ambelas Skj oth C, Ellermann T, Hedegaard GB, Hertel O, Frohn LM, Gross A, Brandt J (2012b) Projected change in atmospheric nitrogen deposition to the Baltic Sea towards 2020. *Atmos Chem Phys* 12:2615-2629
- Giorgi F (1986) A particle dry-deposition parameterization scheme for use in tracer transport models. *J Geophys Res* 91:9794-9806
- Granskog M, Kaartokallio H (2004) An estimation of the potential fluxes of nitrogen, phosphorus, cadmium and lead from sea ice and snow in the northern Baltic Sea. *Water Air Soil Pollut* 154:331-347
- Hedegaard GB, Christensen JH, Brandt J (2013) The relative importance of impacts from climate change vs. emissions change on air pollution levels in the 21st century. *Atmos Chem Phys* 13:35619-3585
- Hertel O, Ambelas Skj oth C, Frohn LM, Vignati E, Frydendall J, de Leeuw G, Schwarz U, Reis S (2002) Assessment of the atmospheric nitrogen and sulphur inputs into the North Sea using a Lagrangian model. *Phys Chem Earth Pt A/B/C* 27:1507-1515
- Hertel O, Skj oth CA, Lofstrom P, Geels C, Frohn LM, Ellermann T, Madsen PV (2006) Modelling nitrogen deposition on a local scale - A review of the current state of the art. *Env Chem* 3:317-337
- Hertel O, Skj oth CA, Reis S, Bleeker A, Harrison RM, Cape JN, Fowler D, Skiba U., Simpson D, Jickells T, Kulmala M, Gyldenk rne S, S rensen LL, Erisman JW, Sutton MA (2012) Governing processes for reactive nitrogen compounds in the European atmosphere. *Biogeosciences* 9:4921-4954
- Hole L, Engardt M (2008) Climate change impact on atmospheric nitrogen deposition in northwestern Europe: A model study. *Ambio* 37:9-17
- Hongisto M (2003) Hilatar, a limited area simulation model of acid contaminants – Part I: model description and verification. *Atmos Environ* 37:1535-1547

- Hongisto M (2011) Variability of the marine boundary layer parameters over Baltic Sea sub-basins and their impact on nitrogen deposition. *Oceanologia* 53:391-413
- Hongisto M, Sofiev M, Joffe S (2003) Hilatar, a limited area simulation model of acid contaminants - Part II: long-term simulation results. *Atmos Environ* 37:1549-1560
- Hummelshøj P, Jensen N, Larsen S (1992) Particle dry deposition to a sea surface. In: Schwartz S, Slinn W (eds), *Precipitation Scavenging and Atmosphere-Surface Exchange*, Proceedings of the 5th International Conference on Precipitation Scavenging and Atmosphere-Surface Exchange Processes, p 829-840
- IMO (1998) Regulations for the prevention of air pollution from ships and NOx technical code. Annex VI of the MARPOL convention 73/78, International Maritime Organization, London
- Jalkanen JP, Brink A, Kalli J, Pettersson H, Kukkonen J, Stipa T (2009) A modelling system for the exhaust emissions of marine traffic and its application in the Baltic Sea area. *Atmos Chem Phys* 9:9209-9223
- Jalkanen J-P, Johansson L, Kukkonen J, Brink A, Kalli J, Stipa T (2012) Extension of an assessment model of ship traffic exhaust emissions for particulate matter and carbon monoxide. *Atmos Chem Phys* 12:2641-2659
- Jenkin ME (2008) Trends in ozone concentration distributions in the UK since 1990: Local, regional and global influences. *Atmos Environ* 42:5434-5445
- Jonson J, Simpson D, Fagerli H, Solberg S (2006) Can we explain the trends in European ozone levels? *Atmos Chem Phys* 6:51-66
- Kononov IB, Beekmann M, Burrows JP, Richter A (2008) Satellite measurement based estimates of decadal changes in European nitrogen oxides emissions. *Atmos Chem Phys* 8:2623-2641
- Kowalski A (2001) Deliquescence induces eddy covariance and estimable dry deposition errors. *Atmos Environ* 35:4843-4851
- Krishnamurthy A, Moore JK, Mahowald N, Luo C, Zender CS (2010) Impacts of atmospheric nutrient inputs on marine biogeochemistry. *J Geophys Res* 115(G1) doi:10.1029/2009JG001115
- Langner J, Andersson C, Engardt M (2009) Atmospheric input of nitrogen to the Baltic Sea basin: present situation, variability due to meteorology and impact of climate change. *Boreal Environ Res* 14:226-237
- Langner J, Engardt M, Andersson C (2012a) European summer surface ozone 1990-2100. *Atmos Chem Phys* 12:10097-10105
- Langner J, Engardt M, Baklanov A, Christensen JH, Gauss M, Geels C, Hedegaard GB, Nuterman R, Simpson D, Soares J, Sofiev M, Wind P, Zakey A (2012b) A multi-model study of impacts of climate change on surface ozone in Europe. *Atmos Chem Phys* 12:10423-10440
- Larsen S, Edson J, Hummelshøj P, Jensen N, De Leeuw G, Mestayer P (1995) Dry deposition of particles to ocean surfaces. *Ophelia* 42:193-204
- Lovblad G, Tarrason L, Torseth K, Dutchak S (eds) (2004) EMEP Assessment Part I, European Perspective. Norwegian Meteorological Institute, Oslo, Norway
- Massad R-S, Nemitz E, Sutton MA (2010) Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere. *Atmos Chem Phys* 10:10359-10386
- Matsumoto K, Minami H, Uyama Y, Uematsu M (2009) Size partitioning of particulate inorganic nitrogen species between the fine and coarse mode ranges and its implication to their deposition on the surface ocean. *Atmos Environ* 43:4259-4265
- Monks P, Granier C, Fuzzi S et al (2009) Atmospheric composition change - global and regional air quality. *Atmos Environ* 43:5268-5350
- Mylona S (1996) Sulphur dioxide emissions in Europe 1880-1991 and their effect on sulphur concentrations and depositions. *Tellus B* 48:662-689
- Nakićenović N (2000) Greenhouse gas emissions scenarios. *Technol Forecast Soc* 65:149-166
- Nemitz E, Jimenez JL, Huffman JA, Ulbrich IM, Canagaratna MR, Worsnop DR, Guenther AB (2008) An eddy-covariance system for the measurement of surface/atmosphere exchange fluxes of submicron aerosol chemical species - First application above an urban area. *Aerosol Sci Tech* 42:636-657
- Nowak JB, Neuman JA, Bahreini R, Middlebrook AM, Holloway JS, McKeen SA, Parrish DD, Ryerson TB, Trainer M (2012) Ammonia sources in the California South Coast Air Basin and their impact on ammonium nitrate formation. *Geophys Res Lett* 39:L07 804. doi: 10.1029/2012GL051197
- Odén S (1968) The acidification of air and precipitation and its consequences on the natural environment. Swedish National Science Research Council. *Ecol Comm Bull* 1:1-68
- OECD (1977) The OECD Programme on Long Range Transport of Air Pollutants: Measurements and Findings. Organisation for Economic Co-operation and Development, Paris, France
- Parrish DD, Millet DB, Goldstein AH (2009) Increasing ozone in marine boundary layer inflow at the west coasts of North America and Europe. *Atmos Chem Phys* 9:1303-1323
- Parrish DD, Law KS, Staehelin J, Derwent R, Cooper OR, Tanimoto H, Volz-Thomas A, Gilje S, Scheel H-E, Steinbacher M, Chan E (2012) Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes. *Atmos Chem Phys* 12:11485-11504
- Paytan A, Mackey KRM, Chen Y, Lima ID, Doney SC, Mahowald N, Labiosa R, Post AF (2009) Toxicity of atmospheric aerosols on marine phytoplankton. *P Natl Acad Sci USA* 106:4601-4605
- Petroff A, Zhang L, Pryor SC, Belot Y (2009) An extended dry deposition model for aerosols onto broadleaf canopies. *J Aerosol Sci* 40:218-240
- Pihl Karlsson GP, Akselsson C, Hellsten S, Karlsson PE (2011) Reduced European emissions of S and N - Effects on air concentrations, deposition and soil water chemistry in Swedish forests. *Environ Pollut* 159:3571-3582
- Pope CA, Dockery DW (2006) Health effects of fine particulate air pollution: Lines that connect. *J Air Waste Manag Assoc* 56:709-742
- Pope C, Burnett R, Thun M, Calle E, Krewski D, Ito K, Thurston G (2002) Lung cancer, cardiopulmonary mortality and long-term exposure to fine particulate air pollution. *J Am Med Assoc* 287:1132-1141
- Pope C, Ezzati M, Dockery D (2009) Fine-particulate air pollution and life expectancy in the United States. *New Engl J Med* 360:376-386
- Pryor S, Barthelmie R (2000) Particle dry deposition to water surfaces: Processes and consequences. *Mar Pollut Bull* 41:220-231
- Pryor S, Binkowski F (2004) An analysis of the time scales associated with aerosol processes during dry deposition. *Aerosol Sci Tech* 38:1091-1098
- Pryor S, Barthelmie R, Geernaert L, Ellermann T, Perry K (1999) Speciated particle dry deposition to the sea surface: results from ASEPS '97. *Atmos Environ* 33:2045-2058
- Pryor S, Gallagher M, Sievering H, Larsen SE, Barthelmie RJ, Birsan F, Nemitz E, Rinne J, Kulmala, M, Groenholm T, Taipale R, Vesala T (2008a) A review of measurement and modelling results of particle atmosphere-surface exchange. *Tellus* 60:42-75
- Pryor S, Larsen SE, Sorensen LL, Barthelmie RJ (2008b) Particle fluxes above forests: Observations, methodological considerations and method comparisons. *Environ Pollut* 152:667-678
- Pryor S, Barthelmie RJ, Spaulding AM, Larsen SE, Petroff A (2009) Size-resolved fluxes of sub-100-nm particles over forests. *J Geophys Res* 114:D18212. doi: 10.1029/2009JD012248
- Rannik U, Aalto P, Keronen P, Vesala T, Kulmala M (2003) Interpretation of aerosol particle fluxes over pine forest: Dry deposition and random errors. *J Geophys Res* 108-4544

- Reis S, Pinder RW, Zhang M, Lijie G, Sutton MA (2009) Reactive nitrogen in atmospheric emission inventories. *Atmos Chem Phys* 9:7657-7677
- Roeckner E, Bengtsson L, Feichter J, Lelieveld J, Rodhe H (1999) Transient climate change simulations with a coupled atmosphere-ocean GCM including the tropospheric sulfur cycle. *J Clim* 12:3004-3032
- Roelofs G, Kasibhatla P, Barrie L, Bergmann D, Bridgeman C, Chin M, Christensen J, Easter R, Feichter J, Jeuken A, Kjellstrom E, Koch D, Land C, Lohmann U, Rasch P (2001) Analysis of regional budgets of sulfur species modeled for the COSAM exercise. *Tellus B* 53:673-694
- Rolff C, Elmgren R, Voss M (2008) Deposition of nitrogen and phosphorus on the Baltic Sea: seasonal patterns and nitrogen isotope composition. *Biogeosciences* 5:1657-1667
- Ruijgrok W, Tieben H, Eisinga P (1997) The dry deposition of particles to forest canopy: A comparison of model and experimental results. *Atmos Environ* 31:399-415
- Ruoho-Airola T, Eilola K, Savchuk OP, Parviainen M, Tarvainen V (2012) Atmospheric nutrient input to the Baltic Sea from 1850 to 2006: A reconstruction from modeling results and historical data. *AMBIO* 41:549-557
- Samuelsson P, Jones CG, Willen U, Ullerstig A, Gollvik S, Hansson U, Jansson C, Kjellstrom E, Nikulin G, Wyser K (2011) The Rossby Centre Regional Climate model RCA3: model description and performance. *Tellus A* 63:4-23
- Schlunzen KH, Meyer EMI (2007) Impacts of meteorological situations and chemical reactions on daily dry deposition of nitrogen into the southern North Sea. *Atmos Environ* 41:289-302
- Schulze ED, Ciais P, Luysaert S et al (2010) The European carbon balance. Part 4: integration of carbon and other trace-gas fluxes. *Global Change Biol* 16:1451-1469
- Seitzinger S, Kroeze C, Bouwman A, Caraco N, Dentener F, Styles R (2002) Global patterns of dissolved inorganic and particulate nitrogen inputs to coastal systems: Recent conditions and future projections. *Estuaries* 25:640-655
- Simpson D, Fagerli H, Hellsten S, Knulst J, Westling O (2006) Comparison of modelled and monitored deposition fluxes of sulphur and nitrogen to ICP-forest sites in Europe. *Biogeosciences* 3:337-355
- Simpson D, Aas W, Bartnicki J, Berge H, Bleeker A, Cuvelier K, Dentener F, Dore T, Erisman JW, Fagerli H, Flechard C, Hertel O, van Jaarsveld H, Jenkin M, Schaap M, Semeena VS, Thunis P, Vautard R, Vieno M (2011) Atmospheric transport and deposition of nitrogen in Europe. In: Sutton MA, Howard CM, Erisman JW, Billen G, Bleeker A, Grennfelt P, van Grinsven H, Grizzetti B (eds) *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives*. Cambridge University Press, p 298-316
- Simpson D, Benedictow A, Berge H, Bergström R, Emberson LD, Fagerli H, Flechard CR, Hayman GD, Gauss M, Jonson JE, Jenkin ME, Nyiri A, Richter C, Semeena VS, Tsyro S, Tuovinen J-P, Valdebenito A, Wind P (2012) The EMEP MSC-W chemical transport model – technical description. *Atmos Chem Phys* 12:7825-7865
- Skjøth CA, Geels C (2013) The effect of climate and climate change on ammonia emissions in Europe. *Atmos Chem Phys* 13:117-128
- Skjøth CA, Gyldenkerne S, Ellermann T, Hertel O, Mikkelsen MH (2008) Footprints on ammonia concentrations from environmental regulations. *J Air Waste Manag Assoc* 58:1158-1165
- Slinn S, Slinn W (1980) Predictions for particle deposition on natural waters. *Atmos Environ* 14:1013-1016
- Solberg S, Bergstrom R, Langner J, Laurila T, Lindskog A (2005) Changes in Nordic surface ozone episodes due to European emission reductions in the 1990s. *Atmos Environ* 39:179-192
- Sorensen L, Hertel O, Skjøth C, Lund M, Pedersen B (2003) Fluxes of ammonia in the coastal marine boundary layer. *Atmos Environ* 37: S167-S177
- Spokes L, Jickells T, Weston K et al (2006) MEAD: An interdisciplinary study of the marine effects of atmospheric deposition in the Kattegat. *Environ Pollut* 140:453-462
- Sutton M, Nemitz E, Erisman J et al (2007) Challenges in quantifying biosphere – atmosphere exchange of nitrogen species. *Environ Pollut* 150:125-139
- Sutton M, Howard C, Erisman J, Billen G, Bleeker A, Grennfelt P, van Grinsven H, Grizzetti B (eds) (2011) *The European Nitrogen Assessment. Sources, Effects and Policy Perspectives*. Cambridge University Press
- Sutton M, Reis S, Riddick SN et al (2013), Towards a climate-dependent paradigm of ammonia emission and deposition. *Phil Trans Roy Soc B* 368:20130166
- Textor C, Schulz M, Guibert S, Kinne S, Balkanski Y, Bauer S, Bernsten T, Berglen T, Boucher O, Chin M, Dentener F, Diehl T, Easter R, Feichter H, Fillmore D, Ghan S, Ginoux P, Gong S, Kristjansson JE, Krol M, Lauer A, Lamarque JF, Liu X, Montanaro V, Myhre G, Penner J, Pitari G, Reddy S, Seland Ø, Stier P, Takemura T, Tie X (2006) Analysis and quantification of the diversities of aerosol life cycles within Aero-Com. *Atmos Chem Phys* 6:1777-1813
- Thomas RM, Trebs I, Otjes R, Jongejan PAC, Ten Brink H, Phillips G, Kortner M, Meixner FX, Nemitz E (2009) An automated analyzer to measure surface-atmosphere exchange fluxes of water soluble inorganic aerosol compounds and reactive trace gases. *Environ Sci Technol* 43:1412-1418
- Tian Z, Ollivier P, Veron A, Church TM (2008) Atmospheric Fe deposition modes at Bermuda and the adjacent Sargasso sea. *Geochim Geophys Geosys* 9:Q08007. doi: [10.1029/2007GC001868](https://doi.org/10.1029/2007GC001868)
- Tørseth K, Aas W, Breivik K, Fjæraa AM, Fiebig M, Hjellbrekke AG, Lund Myhre C, Solberg S, Yttri KE (2012) Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009. *Atmos Chem Phys* 12:5447-5481
- Tuovinen J-P, Hakola H, Karlsson PE, Simpson D (2013) Air pollution risks to Northern European forests in a changing climate. *Dev Environm Sci* 13:77-99
- Uematsu M, Hattori H, Nakamura T, Narita Y, Jung J, Matsumoto K, Nakaguchi Y, Kumar MD (2010) Atmospheric transport and deposition of anthropogenic substances from the Asia to the East China Sea. *Mar Chem* 120:108-115
- Uno I, Uematsu M, Hara Y, He YJ, Ohara T, Mori A, Kamaya T, Murano K, Sadanaga Y, Bandow H (2007) Numerical study of the atmospheric input of anthropogenic total nitrate to the marginal seas in the western North Pacific region. *Geophys Res Lett* 34. doi: [10.1029/2007GL030338](https://doi.org/10.1029/2007GL030338)
- Uppala S, Kallberg P, Simmons A et al (2005) The ERA-40 re-analysis. *Q J Roy Meteorol Soc* 131:2961-3012
- van Aardenne JA, Dentener FJ, Olivier JGJ, Goldewijk CGMK, Lelieveld J (2001) A 1 degrees x 1 degrees resolution data set of historical anthropogenic trace gas emissions for the period 1890-1990. *Global Biogeochem Cy* 15:909-928
- van Vuuren DP, Den Elzen MGJ, Lucas PL, Eickhout B, Strengers BJ, van Ruijven B, Wonink S, van Houdt R (2007) Stabilizing greenhouse gas concentrations at low levels: an assessment of reduction strategies and costs. *Climatic Change* 81:119-159
- Vautard R, Szopa S, Beekmann M, Menut L, Hauglustaine DA, Rouil L, Roemer M (2006) Are decadal anthropogenic emission reductions in Europe consistent with surface ozone observations? *Geophys Res Lett* 33:L13810. doi:[10.1029/2006GL026080](https://doi.org/10.1029/2006GL026080)

- Vestreng V, Myhre G, Fagerli H, Reis S, Tarrasón L (2007) Twenty-five years of continuous sulphur dioxide emission reduction in Europe. *Atmos Chem Phys* 7:3663–3681
- Vestreng V, Ntziachristos L, Semb A, Reis S, Isaksen ISA, Tarrasón L (2009) Evolution of NO<sub>x</sub> emissions in Europe with focus on road transport control measures. *Atmos Chem Phys* 9:1503–1520
- Vuorenmaa J (2004) Long-term changes of acidifying deposition in Finland (1973–2000). *Environ Pollut* 128:351–362
- Wild O, Fiore AM, Shindell DT, Doherty RM, Collins WJ, Dentener FJ, Schultz MG, Gong S, MacKenzie IA, Zeng G, Hess P, Duncan BN, Bergmann DJ, Szopa S, Jonson JE, Keating TJ, Zuber A (2012) Modelling future changes in surface ozone: a parameterized approach. *Atmos Chem Phys* 12:2037–2054
- Wilson RC, Fleming ZL, Monks PS, Clain G, Henne S, Konovalov IB, Szopa S, Menut L (2012) Have primary emission reduction measures reduced ozone across Europe? An analysis of European rural background ozone trends 1996–2005. *Atmos Chem Phys* 12:437–454
- Winiwarter W, Obersteiner M, Smith KA, Sutton MA (2011) The European nitrogen cycle: commentary on Schulze et al. *Global Change Biol* 16:1451–1469. *Global Change Biol* 17: 2754–2757
- Young PJ, Arneth A, Schurgers G, Zeng G, Pyle JA, 2009 The CO<sub>2</sub> inhibition of terrestrial isoprene emission significantly affects future ozone projections. *Atmos Chem Phys* 9:2793–2803
- Zhang L, Gong S, Padro J, Barrie L (2001) A size-segregated particle dry deposition scheme for an atmospheric aerosol module. *Atmos Environ* 35:549–560