Chapter

18 Nitrogen as a threat to European air quality

Lead authors: **Jana Moldanová, Peringe Grennfelt and Åsa Jonsson**

Contributing authors: **David Simpson, Till Spranger, Wenche Aas, John Munthe and Ari Rabl**

Executive summary

Nature of the problem

- Atmospheric emissions of nitrogen oxides and ammonia are contributing to a number of negative effects to human health and ecosystems. These effects include both effects of the primary emissions but more importantly through actions of secondary pollutants such as ground level ozone (O_3) and secondary particulate matter (PM).
- The main air pollution effects include effects of nitrogen dioxide to human health, effects from ground level ozone to human health and vegetation and effects from particulate ammonium and nitrate to human health. There is a difficulty of ascribing health effects to NO_2 per se at ambient levels rather than considering NO_2 as a surrogate for a traffic-derived air pollution mixture.

Approaches

- The chapter gives a brief review of our current understanding of the mechanisms and processes regarding N-containing air pollutants and their effects on human health, vegetation (effects of reactive nitrogen on ecosystems through eutrophication and acidification is treated in Dise *et al.*, 2011; Velthof *et al.*, 2011, Chapters 20 and 21, this volume) and materials. It presents historical development, current situation and outlines future perspectives of reactive nitrogen related air pollution and its effects in Europe in relation to national and EU legislation on emission limitation and air quality control.

Key findings/state of knowledge

- In the EU-27 countries, 60% of the population lives in areas where the annual EU limit value of NO_2 is exceeded. Air quality standards for nitrogen dioxide are exceeded mainly in urban areas. Concentrations have decreased since 1990, although the downward trends have been smaller or even disappeared after 2000.
- Episodic ozone concentrations have decreased over Europe since 1990 due to VOC and NO_x control. In the same time tropospheric background and continental background concentrations have increased. Present concentrations are still a threat to both human health and vegetation.
- Ammonium and nitrate comprise substantial fractions of PM_{10} and $PM_{2.5}$ (sometimes more than 1/3 and control of these compounds is important for meeting air quality standards).
- It is very likely that sensitive species are and will be negatively affected by emissions of ammonia almost everywhere in western, central and parts of southern Europe, at least in areas with intensive animal husbandry.

Major uncertainties/challenges

- There are large uncertainties with respect to further developments of continental-background ozone concentrations in the atmosphere due to uncertainties in future emissions of methane and nitrogen oxides.
- The role of particulate ammonium and particulate nitrate regarding human health effects is still under discussion. The long-term effects of NO_2 on human health found in epidemiological studies reflect rather effects of combustion or traffic related air pollution than effects of NO_2 per se, making it difficult to evaluate the health effects of NO_2 as such.

Recommendations

- The role of ammonia and nitrogen oxides regarding PM exposures needs to be further investigated, in particular with respect to their importance for health effects.
- The low success in controlling ammonia emissions needs to be further assessed, in particular in connection with the development of new agricultural policies.

The European Nitrogen Assessment, ed. Mark A. Sutton, Clare M. Howard, Jan Willem Erisman, Gilles Billen, Albert Bleeker, Peringe Grennfelt, Hans van Grinsven and Bruna Grizzetti. Published by Cambridge University Press.

Table 18.1 The role of N containing compounds and ozone in air pollution effects. The threats to ecosystems from N deposition are discussed in Grizzetti *et al.*, 2011 and Dise *et al.*, 2011 (Chapter 17 (threats to water)) and Chapter 20 (threats to biodiversity))

	Effects			
Compounds	**Human health**	**Ecosystems**	**Materials**	**Visibility**
Nitrogen dioxide	X		X	X
Ammonia		X	X	
Particles NH_4^+/NO_3^-	X		X	X
Ozone	X	X	X	
N deposition		X (acidification, eutrophication)		

18.1 Introduction

Air pollution is a major threat to human health and ecosystems in Europe. The EU Thematic Strategy on Air Pollution (TSAP) (CEC, 2005) estimated that air pollution in the year 2000 caused between 300 000 and 400 000 premature deaths, mainly due to particles but also with a significant contribution from ozone. Reactive nitrogen contributes significantly to formation of both these air pollutants. European ecosystems are also threatened from air pollution through deposition of N and S containing compounds and through direct effects on vegetation. In addition to the effects on human health and ecosystems there are also significant air pollution effects on materials an visibility.

The European Union has through several directives regulated emissions of air pollution. These regulations include directives on emission from combustion plants, motor vehicles, off-road machinery, industrial processes, etc., but also the emissions ceilings directive. Air quality is further regulated through air quality standards (EC, 2008a, b, c). In addition there is a protocol on national emissions ceilings under the Convention on Long-Range Transboundary Air Pollution (LRTAP Convention) regulating emissions of sulphur dioxide, nitrogen oxides, ammonia and volatile organic compounds. All these efforts have caused a decrease in emissions since 1990. Even if the emissions are going down and are expected to be further reduced over the next decade, air pollution will still be a significant threat to European population and ecosystems over the next decade.

Nitrogen oxides and ammonia emissions play an important role in these effects both directly through the action of the primary emissions but also indirectly through actions of secondary air pollutants and through their deposition to the ground (Table 18.1). In this chapter we will mainly assess the role of nitrogen in threats to human health, direct effects on vegetation (effects on acidification and eutrophication of ecosystems are treated in Dise *et al.*, 2011, Chapter 20 this volume) and effects on materials.

Combustion processes, e.g. road traffic and industry are large contributors to emissions of nitrogen oxides (NO_x), mainly in the form of nitric oxide, NO. As mentioned in Hertel *et al.*, 2011 (Chapter 9, this volume), NO is rapidly oxidised to nitrogen dioxide, NO_2, in the atmosphere. Nitrogen dioxide is a strong oxidant that absorbs visible light and hence may form a brownish red colour layer during high concentration episodes. Additionally, nitrogen dioxide is a toxic gas that can cause both long term and short term effects on health. As already mentioned in Hertel *et al.*, 2011 (Chapter 9, this volume), the threats of nitrogen oxides to air quality do not only concern NO and NO_2 themselves. Emission of NO_x also contributes to the formation of secondary pollutants, i.e. pollutants that are formed in the atmosphere, such as ozone (O_3) and secondary particulate matter (PM).

The exact formation pathways are covered in detail in Hertel *et al.*, 2011 (Chapter 9, this volume), and hence only briefly presented here. Ozone is formed photochemically in the presence of NO_2 and volatile organic compounds (VOC). However, ozone can also be destroyed by reaction with NO and therefore low ozone concentrations are often observed close to the NO_x sources while the high concentrations are observed further from the sources in urban background air. Ozone is one of the most important of the global air pollutants in terms of impacts to human health, croplands and natural plant communities, and may become more important in the future. Tropospheric ozone has also impacted on climate; according to IPCC (2007) the year 2005 radiative forcing caused by ozone formed from anthropogenic emissions was the third largest (0.35 W/m^2) after that of anthropogenic CO_2 and methane (1.66 and 0.45 W/m^2 respectively).

Particulate nitrate can be formed from oxidation of NO_2 to nitric acid (HNO_3) that can further react with ammonia to form ammonium nitrate or can be absorbed on existing particulate matter. Nitrate and ammonium are two of the major inorganic components in urban aerosol particles. In the atmosphere NH_3 reacts not only with HNO_3 but also with other acid gases such as H_2SO_4 and HCl, and aerosols, forming ammonium (NH_4^+) containing particles. Oxides of nitrogen can also contribute to formation of Secondary Organic Aerosol particles (SOA) in photochemical smog. Atmospheric particles have an adverse impact on both climate and health. The climate effect is both direct via absorbing terrestrial radiation and scattering solar radiation and indirect, e.g. by influencing clouds. Both effects lead to cooling of the climate (IPCC, 2007) and will be covered in more detail in Butterbach-Bahl *et al.*, 2011 (Chapter 19, this volume). The fact that particles scatter/absorb light also affects visibility in cities and scenic areas.

Particulate matter (PM) is the most important contributor to adverse health effects of air pollution (WHO, 2005a). Before assessing effects of reactive nitrogen through contribution to the PM-mass we will give a brief overview of PM properties, sources and sinks. Particles can be both natural and anthropogenic in origin. Soil erosion, sea spray, volcanic eruptions and oxidation of biogenic VOC are examples of natural sources, while e.g. biomass burning and fossil fuel combustion are anthropogenic sources. Particles are also addressed as being primary or secondary depending on how they arise in the atmosphere. If the particles are emitted directly from its source they are referred to as primary, whereas the term secondary is used for particles that are formed in the atmosphere via gas-to-particle conversion, often induced by chemical reactions. The formation of particulate nitrate is an example of a secondary particle formation process initiated by the oxidation of NO_2 to HNO_3. Particles are not only classified regarding their origin but also by size. The particle size range is divided into coarse particles, i.e. particles with a diameter of >2.5 μm, and fine particles < 2.5 μm. The fine fraction is further divided into accumulation mode (100 nm–2.5 μm), ultrafine mode (10–100 nm) and nucleation mode particles (< 10 nm). Regulation and guidelines are using the concept of PM_{10} and $PM_{2.5}$, which means particulate mass of particles with less than 10 μm or 2.5 μm in aerodynamic diameter, respectively. The reason for choosing 10 μm is that it includes the inhalable particles, i.e. those that are small enough to reach the thoracic region. $PM_{2.5}$ includes only fine particles, hence excluding the coarse particle fraction, as this fine fraction has a higher probability to penetrate deeper into the lungs, reaching the alveolar region. However, as air quality with respect to particles is assessed on mass based metrics, pollution by ultrafine particles (UFP) is to a large extent hidden (a particle with 2.5 μm diameter has ~16 000 times higher mass than a particle of same density and 100 nm diameter). The number of particles is a better metric if effects of ultrafine particles are considered. The size of the particles determines their transport and removal processes in the atmosphere. Deposition of very small particles (ultrafine or nucleation range) is driven by diffusion and these particles can also grow to larger size fraction by condensation and coagulation. Coarse particles are removed from the atmosphere at a rather fast rate by deposition which is mainly driven by settling/sedimentation. Growth of these particles by condensation or coagulation in terms of increase of their diameter is not very effective due to the large mass needed for any further growth. Fine particles in the accumulation mode (100 nm – 2.5 μm) have the lowest deposition velocity, as neither diffusion nor sedimentation are effective, grow slowly and hence tend to accumulate in the atmosphere. During a rain event particles are scavenged by rain droplets and removed through wet deposition. Lifetime of aerosol particles with respect to precipitation scavenging varies from days to minutes, depending on diameter of scavenged particles and type and intensity of precipitation. Particles in size- range 100 nm–1 μm, i.e. those in the accumulation mode, are scavenged with the least efficiency.

18.2 Effects of air pollutants associated to reactive nitrogen

18.2.1 International legislation

By the late 1970s, air pollution had become the main environmental problem faced by many countries in Europe and North America, harming people's health and damaging ecosystems, historic buildings and monuments. In 1979, the Member States of the UN Economic Commission for Europe adopted the Convention on Long-range Transboundary Air Pollution (UN/ECE, 1979) which was the first international environmental agreement to address this threat to human health and well-being. The Convention is of a rather general nature and specific reductions are given in eight Protocols to the Convention. Emissions of nitrogen species are treated by the Sofia Protocol from 1988 that entered into force in 1991 (UN/ECE, 1988) and the Gothenburg Protocol from 1999 (UN/ECE, 1999). The Gothenburg Protocol came into force in 2005 and set emission ceilings for European emission of NO_x which should be reduced by 41 % (VOC by 40%, NH_3 by 17%) by 2010 compared to the level of 1990 (see Jensen *et al.*, 2011, Section 3.3 of Chapter 3 this volume). Additionally, the EU introduced a National Emission Ceiling (NEC) Directive 2001/81/EC (EC, 2001a), concerning NO_x and other pollutants. Compared to the Gothenburg Protocol, this directive puts more pressure on some of the member states. The emission ceilings must be attained by 2010.

In the European Union several directives have set requirements and standards for NO_x emissions from all kinds of combustion sources: Directive 96/61/EC concerning integrated pollution prevention and control (IPPC) (EC 1996a), Directive 2000/76/EC on the incineration of waste (WID) (EC, 2000), Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from Large Combustion Plants (LCP) (EC, 2001b), Directive 97/68/EC regulating emissions of gases and particulate pollutants from non-road mobile machinery (EC, 1997a). The LCP Directive and the WID Directive were incorporated into a new EU Directive on industrial emissions concerning integrated pollution prevention and control 2008/1/EC (EC, 2008a) that replaced the old IPPC Directive 96/61/EC.

Motor vehicle emissions have originally been regulated by Directive 70/220/EEC (light-duty vehicles) (EEC, 1970) and 88/77/EC (heavy-duty vehicles) (EEC, 1988) and amendments to those directives. In 1992 Euro 1 (for light duty vehicles, petrol and diesel) and Euro I (for heavy duty vehicles) standards entered into force (91/441/EEC; 93/59/EEC) (EEC, 1991, 1993) and in 1996 the Euro 2 Euro II standards (94/12/EC; 96/69/EC) (EC, 1994, 1996b). These standards involved improved combustion and catalysts. The Auto-Oil Programme, which focused on the emissions of gases and particles, resulted in the Euro 3 and Euro 4 stages for light-duty vehicles (Directive 98/69/EC) (EC, 1998a) and in the Euro III and IV standards for heavy duty vehicles (Directive 99/96/EC now repealed) (EC, 1999a), as well as the fuel quality Directive 98/70/EC (EC, 1998b). Further reductions of emissions from light duty

vehicles were set in the Euro 5 stage that entered into force in 2009 (EC Regulations 715/2007 and 692/2008) (EC, 2007, 2008b) and which focused on emissions of particulate matter from diesel cars. Euro 6 is scheduled by the same regulations to enter into force in January 2014 and will mainly further reduce the emissions of NO_x from diesel cars. Directive 2005/55/EC (EC, 2005a) on Emission from Ignition Engines in Heavy-duty Vehicles (HDV Directive) replaced Directive 99/96/EC and set the Euro IV and V standards that were implemented by Directive 2005/78/EC (EC, 2005b). Euro IV entered into force October 2005 and Euro V October 2008. Euro VI stage was implemented by EC Regulation 595/2009 (EC, 2009) that replaced the HDV directive and scheduled Euro VI to enter into force in 2013.

Emissions from international maritime shipping contribute significantly to air pollution in Europe. Legislation is in force to control the emissions through Annex VI of the Marine Pollution Convention (MARPOL) that was adopted in 1997 by Marine Environmental Protection Committee (MEPC) of the International Maritime Organisation (IMO) and that came into force in May 2005 (IMO, 2006). Annex VI with its amendment from October 2008 put progressive limits on emissions of SO_2 and NO_x globally and contains provisions allowing establishment of Emission Control Areas (ECA) with more stringent reductions of emissions of SO_X, particulate matter, NO_x or all three pollutants (IMO, 2009). In Europe, Baltic Sea was established as SO_X ECA in 2005 and North Sea in 2006. In these areas also the most stringent controls for emissions of NO_x applies on ships constructed on or after 1 January 2016. Considering the long lifetime of ship engines, this legislation will impact the NO_x emissions only in the distant future. Further, the expected increase in the volume of ship movements will compensate for the environmental benefits of these measures and will lead to a continued growth in ship emissions.

Drivers for the aviation industry to reduce its emissions are the International Civil Aviation Organisation's (ICAO) aircraft engine emissions standards. In 1981, ICAO published its Annex 16, Volume II: Environmental Protection – Aircraft Emissions Standards; The Convention on International Civil Aviation. These standards covered the limits for emissions of HC, CO, and NO_x. The ICAO aircraft engine NO_x emissions standards have gradually been tightened. In 1993 ICAO reduced the permitted levels by 20% for newly certificated engines, with a production cut-off on 31 December 1999. In 1999 the ICAO further tightened the NO_x standard by about 16% for engines newly certified from 31 December 2003 and in October 2004, the 1999-standards for NO_x were further tightened by 12% for engines certified in 2008. It should be noted that the long lifetime of the aviation fleet causes a lag of NO_x emission reductions behind introduction of the ICAO standards.

Concerning air quality legislation, the LRTAP Convention and its Protocols were translated into a series of EC directives. In 1996, the Environment Council adopted a Framework Directive on Ambient Air (96/62/EC) (EC, 1996c) which addresses ambient air quality assessment and management. This framework directive includes a series of daughter directives, which set the numerical limit values for atmospheric pollutants. Two of them concern reactive nitrogen and its secondary products in air. The first daughter directive (1999/30/EC) (EC, 1999b) relates to limit values for among others oxides of nitrogen, nitrogen dioxide and particulate matter (PM_{10}) in ambient air and a date when they must be met. The third daughter directive (2002/3/EC) (EC, 2002) established target values and long term objectives for the concentration of ozone in air. Council Decision 97/101/EC and Commission Decision 2004/461/EC (EC 1997b, 2004) established a reciprocal exchange of information and data on ambient air pollution within the Member States and annual reporting on ambient air quality under the framework directive and its daughter directives.

The framework for environmental policy-making in the European Union for the period 2002–2012 was set out in the Sixth Environment Action Programme (EAP) of the European Community which was adopted by the European Parliament and the Council in 2002. The EAP includes Environment and Health as one of the four main target areas requiring greater effort and air pollution is one of the issues highlighted in this area. The Sixth EAP aims to achieve levels of air quality that do not result in unacceptable impacts and risks to human health, paying particular attention to sensitive populations. The Clean Air For Europe (CAFE) initiative of the European Commission provided the scientific background and set out the objectives and measures for this phase of European air quality policy. In its Thematic Strategy on Air Pollution (TSAP) (CEC, 2005), the European Commission has established health and environmental interim objectives for the year 2020 to guide the ambition level of further measures to reduce the impacts of air pollution in Europe. Acknowledging the preliminary nature of some of the input data that have been used for the CAFE analysis the approach in the TSAP is in terms of relative improvements compared to the situation as assessed with the same methodology for the year 2000. The health objectives of TSAP are a reduction of life years lost (YOLLs) from air pollution by particulate matter and a reduction of premature mortality cases from ozone (Table 18.2). Objectives of TSAP regarding effects on ecosystems are reductions of ecosystem areas where deposition of eutrophying and acidifying species exceeds critical loads of these areas (Table 18.2).

In order to incorporate the latest health and scientific developments, and objectives of the EAP, First, Second and Third daughter directives and the Council Decision 97/101/EC were replaced in 2008 by a single Air Quality Directive 2008/50/EC (EC, 2008c) that merges existing legislation for all groups of air pollutants and also contains a new regulation for $PM_{2.5}$, including a limit value, target value and an Exposure Concentration Obligation. The health-related concentration limits of the Air Quality Directive 2008/50/EC for primary and secondary air pollutants related to reactive nitrogen are presented in Table 18.3.

The vegetation-related concentration limits for primary and secondary air pollutants related to reactive nitrogen are presented in Table 18.4. The long-term objectives define the level to be attained eventually, save where it is not achievable through proportionate measures, with the aim of providing

Table 18.2 Environmental objectives of the Thematic Strategy expressed as percentage improvements relative to the situation in the year 2000 (from Amann *et al.*, 2008)

Indicator	Unit of the indicator	Percentage improvement in 2020 compared to the situation in 2000
Loss of life expectancy as a result of exposure to PM	YOLLs[a]	47%
Acute mortalities from exposure to ozone	Nr. of premature deaths	10%
Area of forest ecosystems where acid deposition exceeds the critical loads for acidification[b]	km^2	74%
Area of freshwater ecosystems where acid deposition exceeds the critical loads for acidification	km^2	39%
Ecosystems area where nitrogen deposition exceeds the critical loads for eutrophication[b]	km^2	43%
Area of forest ecosystems where ozone concentrations exceed the critical levels for ozone	km^2	15%

[a] Years Of Life Lost
[b] See glossary for 'Critical load'.

Table 18.3 Health-related limit- and target concentration values from EU-Directive 2008/50/EC. For $PM_{2.5}$ the exposure concentration limit value is also shown. This is determined as Average Exposure Indicator (AEI) which is a 3-year running annual mean $PM_{2.5}$ concentration averaged over the selected monitoring stations in agglomerations and larger urban areas set in urban background locations

	Limit/target values for the protection of human health			
Parameter	Averaging period	Target/limit value µg/m³	Permitted exceedances each year	Date when the limit/target value should be met
NO_2	1 hour	200	18	Limit value 1/1 2010
	1 year	40	—	Limit value 1/1 2010
PM_{10}	24 h	50	35	Limit value in force since 2005
	1 year	40	—	Limit value in force since 2005
$PM_{2.5}$	1 year	25	—	Target value 1/1 2010 Limit value 1/1 2015
	1 year	20	—	Limit value 1/1 2020
	1 year	20 (AEI)	—	Limit value 2015
Ozone	Maximum daily 8 hour mean	120	25 days per year averaged over 3 years.	Target value 1/1 2010

effective protection of both human health and the environment (see glossary for 'Critical level').

The European air quality legislation is built on the principle that EU Member States divide their territory into a number of air quality management zones and agglomerations. In these zones and agglomerations, the Member States should assess the air quality using measurements, modelling or other empirical techniques. Where air quality levels/ concentrations are elevated, the EU Member States have to prepare an air quality plan or programme to ensure compliance with the limit value before the date when the limit value formally enters into force. In addition, information on air quality should be disseminated to the public. The EU Member States submit annually their air quality data to AirBase, the European air quality information system, and report on air quality in the form of a predefined questionnaire (Decision 2004/461/EC) to the EU Commission. European Environmental Agency (EEA) on behalf of the EU Commission and supported by EEA's European Topic Centre on Air and Climate Change (ETC/ACC) maintain AirBase and produces technical papers for each reporting year with overviews and analyses of the submitted information concerning data quality and zone exceedances in the EU Member States.

On the UN-ECE level monitoring and evaluation of the international protocols negotiated within the LRTAP Convention is handled by EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) that was set-up by the first protocol to the LRTAP Convention in 1988. Main elements of EMEP are: collection of emission data, measurements of air and precipitation quality, modelling of atmospheric transport and deposition of air pollutions and from year 1999 also integrated assessment modelling.

Table 18.4 Critical level, target value and long-term objective from EU-Directive 2008/50/EC related to the protection of vegetation and ecosystems

Parameter	Averaging period	Value	Threshold type
NO_x	1 year	30 µg/m³	Critical level (in force)
	24 h	75 µg/m³	
Ozone	AOT40[a] from 1 h means during May–July averaged over 5 years	18 000 µg/m³*h	Target value (to be reached by 1/1 2010)
	AOT40[a], from 1 h means during May–July	6 000 µg/m³*h	Long-term objective (no defined attainment date)

[a] Accumulated exposure to ozone Over a Threshold of 40 ppb; see glossary for definition.

Table 18.5 Overview of nitrogen related health impacts

Pollutant	Health impacts and routes	Health impacts
NO_x	Inhalation - direct impacts of NO_2 - impacts via O_3 - impacts via PM	Asthma, respiratory disorder, inflammation of air ways, reduced lung functions, bronchitis, cancers
NH_3	Inhalation: - direct impacts (negligible) - impacts via PM Odour	See NO_x Small as odour contribution by NH_3 is modest
N_2O	Health impacts from global warming, often enhanced by eutrophication	Enhancement of vectors for infectious diseases (malaria) and frequency of infestations (HAB*, insects)

* Harmful Algal Bloom

18.2.2 Health effects

There are several routes by which nitrogen air-born pollutants can affect human health leading to a variety of impacts (Table 18.5; see also Townsend *et al.*, 2003).

In the sequel dose–response relations will be discussed for all listed impacts, except, due to lack of information, for the effects of odour and global warming.

Ammonia

Health effects of ammonia are indirect through contribution of NH_4^+ to particulate matter. Scientific findings of the CAFE programme pointed to the fact that ammonia emissions significantly contribute to the formation of secondary particulate matter in the atmosphere (~ 20% by mass). The main source of ammonia in the atmosphere is agriculture (cattle, pig and poultry farming and use of N-fertilisers).

Nitrogen dioxide (NO_2)

NO_2 is a toxic gas that has adverse health effects both in the long term (chronic) and short term (acute). Examples are: asthma, respiratory disorder, inflammation of the airways, reduced lung function, increased bronchitic symptoms and cancer. The major cause of these effects is oxidative stress, i.e. formation of radicals that are very reactive and destructive to cell tissues. This oxidative stress can be generated by gaseous compounds such as NO_2 and ozone or by increased production and release of oxygenated compounds in the body due to inflammation.

Epidemiological studies on the health effects of exposure to nitrogen dioxide have been extensively reviewed by the WHO (WHO, 2000, 2003, 2004, 2006). A 1 hour guideline of 200 µg/m³ and an annual mean of 40 µg/m³ were recommended in the second edition of 'Air quality guidelines for Europe' (WHO, 2000). These values have been adopted as limit values in the EU's air pollution directive 2008/50/EC that should be met by all Member States in 2010 (Table 18.3). Nitrogen dioxide is strongly related to PM, as both come from the same combustion sources, and it is converted to nitrates and contributes per se to fine particle mass. Several studies have noted a high correlation between nitrogen dioxide levels and suspended PM generated from the same combustion sources. At a given site, a high correlation exists between nitrogen dioxide and organic and elemental carbon, inorganic acids, $PM_{2.5}$ and ultrafine particles so that nitrogen dioxide may be considered a very good indicator of the complex gas–particle mixture that originates from vehicular traffic (Gauderman *et al.*, 2000; Seaton and Dennekamp, 2003) but it is very difficult to differentiate the effects of nitrogen dioxide from those of other pollutants in epidemiological studies (WHO, 2006). Factors such as temperature and humidity are also important when assessing the toxicity of a gaseous mixture (WHO, 2003). The spatial variability of NO_2 is greater that that of PM.

Short-term exposure studies have shown that daily average concentrations of nitrogen dioxide are significantly associated with increased overall, cardiovascular and respiratory mortality. The effect estimate for all-cause mortality derived from a well-conducted meta analysis is a 2.8% increase per 24 ppb NO_2 (24 h mean). Adjusting for the effect of PM reduces the effect estimate to 0.9%, and the lower confidence interval of the effect estimate includes zero (Stieb *et al.*, 2002). In the European multi-city studied (Samoli *et al.*, 2003), the effect of PM on daily mortality was greater in areas with high nitrogen dioxide levels. Hospital admission due to respiratory causes increased by 0.4%–0.5% per 10 µg/m³ 24 h average NO_2 (Bylin and Forsberg 2009). However, it is important to remember that not all people are affected the same. For instance, studies

indicate that children and people with asthma are more sensitive to NO_2 exposure.

Data from Europe suggested that long-term concentrations of nitrogen dioxide or nitrogen oxides ($NO + NO_2$) were associated with an increased risk of all-cause mortality (Filleul *et al.*, 2005; Hoek *et al.*, 2002; Nafstad *et al.*, 2004). However, none of the studies found evidence that nitrogen dioxide per se, but rather particulate pollution especially from traffic sources, seemed to be responsible for the observed associations. Other long-term effects of increased concentrations of NO_2 include association with childhood cancer and lung cancer in adults, association with decreased lung function in children and in adults and association with incidence of asthma in children (WHO, 2006, and references there in). None of these long-term exposure studies is able to attribute the effects to NO_2 concentrations per se.

Ozone

Ozone is a highly reactive gas that triggers oxidative stress when it enters the airways. Excessive ozone in the air can have a marked effect on human health. It can cause breathing problems, trigger asthma, reduce lung function and cause lung diseases. As to short-term exposures, recent epidemiological studies have strengthened the evidence that daily exposures to ozone increase mortality and respiratory morbidity rates. The risk of effects increases in proportion to the ozone level, with a significant increase in mortality observed above 50–70 $\mu g/m^3$ (measured as a 1 or 8 hour average) (WHO, 2008). In short-term studies ozone appears to have effects independent of other air pollutants such as particulate matter (PM). This notion that ozone may act independently is strengthened by controlled human studies and experimental animal studies showing the potential of ozone per se to cause adverse health effects, especially in vulnerable people. Controlled human studies on PM and ozone combined corroborate this view (WHO, 2008). The relative increase of risk of short-term mortality or hospital admission from increase in maximum ozone 1 h or 8 h average concentrations are shown in Table 18.6.

As to long-term exposures, new epidemiological evidence and experimental animal studies indicate effects of long-term exposure to ozone. A recent study of long-term air pollution exposure effects on mortality found that the long-term ozone exposure was associated with the risk of death from respiratory causes whereas $PM_{2.5}$ was associated with the risk of death from cardiovascular causes. The estimated increase in relative risk of death from respiratory causes that was associated with an increment in ozone concentration of 10 $\mu g/m^3$ was 2% (Jerrett *et al.*, 2009) (Table 18.6). With these long-term effects on respiratory-caused mortality O_3 would be one of the most important air pollutants associated with health in Europe and the currently implemented policies would not be sufficient to reduce the impacts significantly in the next decade (ECE, 2009).

The epidemiological studies pointed at existence of a threshold in the dose–response functions relating the short term ozone exposure to adverse health effects. The European APHEA2 study found a significant increase in risk of dying when ozone maximum daily 1 h average concentrations exceeded 50–60 $\mu g/m^3$ (Katsouyanni *et al.*, 2001). Study of Bell *et al.* (2006) from US cities found that the estimates of increased risk of mortality were statistically significant above daily average ozone concentration of 80 $\mu g/m^3$ and were stable for concentrations over 70 $\mu g/m^3$. WHO recommended a cut-off value of 70 $\mu g/m^3$ for integrated assessment modelling (WHO, 2008). In implementing the cut-off, no effects of ozone on health are calculated on days with a maximum daily 8 h average below 70 $\mu g/m^3$ and for days with ozone concentrations above 70 $\mu g/m^3$ as a maximum daily 8 h average, only the increment exceeding 70 $\mu g/m^3$ is used to calculate effects. Owing to the linearity of the concentration–response curve, the accumulated impact estimate is proportional to the sum of excess of maximum daily 8 h averages over the cut-off of 70 $\mu g/m^3$ calculated for all days in a year. This indicator of cumulative annual exposure is called SOMO35 (Sum Of Means Over 35 ppb, 35 ppb = 70 $\mu g/m^3$). For assessing ozone exposure in urban areas, urban background concentrations should be used and in line with most of the evidential health studies, it was regarded as sufficient to use one average ozone concentration per city. These recommendations were accepted by the 23rd session of the Working Group on Effects and used in the health impact assessment of CAFE (WHO, 2008). SOMO35 should not, however, be seen as a new, universal or lasting index. In particular, it reflects the evidence base as it was in 2004, i.e. that (a) effects from studies of long-term exposure were not well enough established to be quantified; and (b) there were substantial uncertainties about the slope of the concentration–response function at lower concentrations, say below 70 $\mu g/m^3$. The SOMO35 index should be reconsidered if and when that evidence base changes to an important degree.

Another uncertainty in use of SOMO35 for health impact assessment of CAFE is related to the grid size of EMEP model used for calculation of ozone concentrations. Ozone concentrations in urban areas are usually substantially lower than those in rural areas because of its reaction with primary emissions of nitric oxide, and it is not possible to capture this in a model with grid sizes measuring tens of kilometres. In addition, ozone formation is a non-linear process, and finer grid sizes in the model would presumably lead to a more accurate treatment of the ozone chemistry.

Particulate matter (PM)

Emissions of ammonia and contribute significantly to the formation of secondary particulate matter in the atmosphere. Oxides of nitrogen can be converted to nitrates which also contribute to fine particle mass. Reactive nitrogen thus contributes to particle mass and consequently also to the adverse health effects caused by the PM. Since current knowledge does not allow specific quantification of the health effects of individual PM components, it is appropriate that current risk assessment practices consider particles of different sizes, from different sources and with different composition, as equally hazardous to health (WHO, 2007).

As mentioned in the previous section, particles with a diameter less than 10 µm are inhalable. At which part of the

Table 18.6 Estimates of the relative increase of all-cause and cause-specific short-term mortality and respiratory hospital admissions and their confidence intervals (CI) attributable to an increase of 10 µg/m³ in daily, maximum 1 h or maximum 8 h average ozone (from WHO, 2008, their Table 2.1) and of relative increase of all-cause and cause-specific long-term mortality attributable to an increase of 10 µg/m³ in maximum 1 h average ozone concentrations (Jerrett *et al.*, 2009)

Meta-analysis /outcome/disease	Age group (years)	Percentage increase in risk per 10 µg/m³ ozone (95% CI)	Nr. of studies analysed
Short-term mortality Daily average (Bell *et al.*, 2007)			
All-cause mortality, all seasons	All ages	0.4 (0.3–0.9)	32
All-cause mortality, summer	All ages	0.7 (0.4–1.01.1)	10
Cardiovascular mortality, all seasons	All ages	0.5 (0.3–0.8)	18
Cardiovascular mortality, summer	All ages	1.2 (0.4–2.0)	4
Maximum 1 hr average (Ito *et al*, 2005)			
All-cause mortality	All ages	0.2 (0.1–0.3)	43
Maximum 1 h average (Levy *et al.*, 2005)			
All-cause mortality	All ages	0.2 (0.2–0.3)	46
Maximum 8 h average (WHO, 2005b)			
All-cause mortality	All ages	0.3 (0.1–0.4)	15
Respiratory mortality	All ages	0.0 (-0.4–0.5)	12
Cardiovascular mortality	All ages	0.4 (0.3–0.5)	13
Respiratory hospital admissions	0–14 15–64 ≥65	Not observed 0.1 (-0.9–1.2) 0.5 (-0.2–1.2)	3 5 5
Long-term mortality Maximum 1 h average, summer half-year (Jerrett *et al.*, 2009)			
All-cause mortality	≥30	Not observed	1
Respiratory	≥30	2.0 (0.7–3.4)	1
Cardiovascular	≥30	Not observed	1

respiratory tract the particles deposit mostly depends on their size. The upper airways (nasal and extrathoracic region) with high air velocities collect efficiently large particles in coarse mode and down to diameter of *c.* 1 µm by impaction process. Collection efficiency of bronchial region is low and only the smallest particles with diameter < 10 nm deposit efficiently in this region by diffusion process. Particles with diameter below 10 µm can reach the alveolar region but the collection efficiency there is the highest for ultrafine particles, i.e. those with diameter < 100 nm (Hinds, 1999).

Adverse health effects regarding particles are related both to respiratory and to cardiovascular systems. Examples of adverse health effects concerning the respiratory tract are inflammatory, exacerbation of existing airway disease and impairment of pulmonary defences (WHO, 2005). Cardiovascular effects may be variability in heart rate, arrhythmia and cardiac infarction (Bylin and Forsberg, 2009). The short term respiratory mortality due to particles is larger than the cardiovascular mortality on a percent basis, however, the total deaths from cardiovascular causes outnumber the respiratory (WHO, 2005).

Not all people are affected by air pollution to the same extent. Susceptibility is dependent on personal characteristics, i.e. age, health status, etc., and exposure characteristics. Which of these characteristics is most important is not yet fully clear. People with heart or lung problems, as well as the elderly, have been shown to be more sensitive to PM exposure. This fact is important to consider when future impacts of air pollution are predicted, e.g. for an ageing European population. Experimental studies have shown that people with asthma are more sensitive than people without problems with the respiratory system. It has been determined that increased particle concentrations cause increased occurrence of asthma-like conditions as well as increased respiratory hospital admissions (Bylin and Forsberg, 2009). During the last decade, human experiments regarding particle exposure have been performed. Results from these studies have shown that particle concentrations similar to real

world pollution situations can cause respiratory inflammation. However, in epidemiological studies it can be hard to differentiate between effects from PM and other co-emitted compounds. Exposure of particles together with other co-emitted gaseous pollutants may cause inflammatory effects at lower particle concentrations compared to particles alone (Bylin and Forsberg, 2009). Threshold levels for PM concentrations below which no adverse effects occur have not been identified, which makes it difficult to recommend limits.

There is some indication that particles of different size fractions may affect health in different ways. Coarse particles (diameter > 2.5 μm) may preferentially affect the airways and lungs, while fine particles (diameter > 0.1 μm) may preferentially affect the cardiovascular system. Ultrafine particles (UFP, diameter > 0.001 μm) may also migrate via the lung to other organs, including the liver, spleen, placenta and foetus, or via the nerve system to the brain. The health implications of these observations remain unknown since there are not yet enough epidemiological studies to be able to determine the exposure-response relationship for fine and ultrafine particles. This is why there are currently no guidelines for UFP exposure. Smaller particles have larger relative surface areas and therefore commonly induce more inflammation (Diociaiuti *et al.*, 2001; Pozzi *et al.*, 2003).

Health risks of PM in terms of increase of the diurnal average PM_{10} by 10 μg/m^3 are, according to an analysis done by the WHO (2000), an increase in relative risk of mortality by 0.6%–1.6%, an increase in occurrence of asthma related problems and medication usage by 3%–5% and increase of the number of daily hospital admission due to respiratory causes by 0.8%.

As the long-term exposure to PM results in a substantial reduction in life expectancy, the long term effects clearly have greater significance to public health than the short-term effects. $PM_{2.5}$ shows the strongest association with mortality indicating a 6% increase in the risk of deaths from all causes per 10 μg/m^3 increase in long-term $PM_{2.5}$ concentration. The estimated relative risk amounts to 12% for deaths from cardiovascular diseases and 14% for deaths from lung cancer per 10 μg/m^3 increase in $PM_{2.5}$ (Poppe *et al.*, 2002, 2004) (Table 18.7). Other effects related to long-term exposure include increases in lower respiratory symptoms and chronic obstructive pulmonary disease and reductions in lung function in children and adults. Studies on large populations show a strong effect of $PM_{2.5}$ on mortality, and have been unable to identify a threshold concentration below which ambient PM has no effect on health: a no-effect level. After a thorough review of recent scientific evidence, a WHO working group therefore concluded that, if there is a threshold for PM, it lies in the lower band of currently observed PM concentrations in the European Region.

The chemical composition of particles may also influence their health effects. The primary, carbon-centred, combustion-derived particles have been found to have considerable inflammatory potency (Armstrong *et al.*, 2004; Mudway *et al.*, 2004). One of the hypotheses considered for PM's mechanisms of action is the oxidative potential of the particles or specific components. PM from traffic sites seems to have high oxidative

Table 18.7 Estimates of increase of long-term mortalities attributable to an increase of the PM exposure by 10 μg/m^3 and their confidence intervals (CI) (Poppe *et al.*, 2002)

Long-term mortality	Age group (years)	Relative risk per 10 μg/m^3 (95% CI)
Mortality, cardiopulmonary	≥30	1.08 (1.02 – 1.14)
Mortality, lung cancer	≥30	1.13 (1.04 – 1.22)
Mortality, total (excluding violent death)	≥30	1.06 (1.02 – 1.10)

activity, and emissions from road traffic have been linked with a wide range of health effects, including effects on the cardiovascular and respiratory systems, and on atopic sensitisation to allergens in outdoor air. There is substantial epidemiological evidence of associations between health and sulphates that suggest that if sulphates are reduced (as part of the reduction of a mixture) then there will be real benefits to health. There is not much evidence for toxicity of airborne nitrates, which may be at least partly due to difficulties with measuring nitrates. Problem arises also with difficulty of epidemiological studies to distinguish effects of different pollutants in ambient air and of toxicological studies to describe effects across all sensitive groups in the population. The situation is very well summed up by this passage from a recent review paper by Reiss *et al.* (2007): '*For nitrate-containing PM, virtually no epidemiological data exist. Limited toxicological evidence does not support a causal association between particulate nitrate compounds and excess health risks. There are some possible indirect processes through which sulfate and nitrate in PM may affect health-related endpoints, including interactions with certain metal species and a linkage with production of secondary organic matter. There is insufficient evidence to include or exclude these processes as being potentially important to PM-associated health risk.*'

18.2.3 Effects on vegetation

Emissions of reactive nitrogen lead to increased atmospheric deposition into ecosystems. Various effects such as acidification and eutrophication of soils and waters, reduced biodiversity and formation of marine algal blooms are summarised in Butterbach-Bahl *et al.*, Durand *et al.*, Voß *et al.*, Grizzetti *et al.*, Dise *et al.* and Velthof *et al.*, 2011 (Chapters 6, 7, 8, 17, 20 and 21, this volume). These long-term effects are mostly associated with critical loads of nitrogen, 10–100 years deposition levels of total N_r that are set as upper thresholds below which negative effects do not occur in specific ecosystems. In this chapter only the direct effects of the primary and secondary gas-phase pollutants related to emissions of N_r to the air, i.e. NO, NO_2, NH_3 and ozone, will be assessed. These effects are associated with critical levels of individual air pollutants, i.e. short-term air concentration levels (1 h to 1 year means) 'fixed on the basis of scientific knowledge, above which direct adverse effects may occur' (EC, 2008c).

Legislation for the protection of natural vegetation against the direct effects from air pollution has developed together

with legislation for air pollution effects on human health. The vegetation-related concentration limits for primary and secondary air pollutants related to reactive nitrogen as set in Directive 2008/50/EC were presented in Table 18.4.

Ammonia, NH_3

Exposure to ammonia leads to a mixture of direct, indirect, primary and secondary effects on vegetation and ecosystems (Cape *et al.*, 2009; Sutton *et al.*, 2009). There are clear indications that the pathway of uptake of ammonia via leaf uptake from atmosphere, i.e. the direct effect of ammonia, is dominant (as opposed to the indirect effect which is via root system from the soil) (Sutton *et al.*, 2009). Ammonia acts as a macro-nutrient and at low exposure levels plants respond by increasing their biomass production. Growth stimulation is also considered as potentially adverse for (semi-) natural vegetation because plant growth is often limited by the supply of nutrient nitrogen, and so any increases in growth may lead to negative effects on community composition. The fertilisation effect can at higher exposure levels lead to secondary long-term adverse effects including increased susceptibility to abiotic (drought, frost) and biotic stresses. In addition, various primary toxic effects are known (Cape *et al.*, 2009; Sutton *et al.*, 2009). The critical levels have been revised in recent years on the basis of experimental data (Table 18.8). Annually averaged concentrations below 1 μg/m³ will protect (1) sensitive lichen communities and bryophytes and (2) ecosystems where sensitive lichens and bryophytes are an important part of the ecosystem integrity. Based on data from heathlands and forest ground flora, 3 μg/m³ (uncertainty estimate 2–4 μg/m³) are assumed to protect higher plants. The critical levels given in Table 18.8 apply for native and forest species. A monthly average critical level 23 μg/m³ was retained to deal with the possibility of high peak emissions during periods of manure application.

Oxides of nitrogen, NO_x

Oxides of nitrogen can have a fertiliser effect, but can also be toxic to plants, depending on concentrations. The critical levels for NO_x are based on the sum of the NO and NO_2 concentrations because there is insufficient knowledge to establish separate critical levels for the two pollutants, although some evidence indicates that at low concentrations typical of ambient conditions, NO is more phytotoxic than NO_2 (Mills, 2004). Since the type of response varies from a fertiliser effect to toxicity depending on concentration, all effects have been considered to be adverse. As for ammonia, the growth stimulation was also considered as potentially adverse for (semi-) natural vegetation owing to potential negative effects on community composition.

In the past, the critical level for nitrogen oxides referred only to NO_2. However, because of new evidence of the toxicity of nitric oxide (NO), the critical level now refers to NO_x, defined as the combined concentrations of NO and NO_2. The critical level value remains 30 μg/m³ (as NO_2 equivalent) as an annual mean and 75 μg/m³ as a 24 hour mean. As for ammonia, UN/ECE Working Group on Effects strongly recommended the use of the annual mean value, as this parameter is much more reliable than shorter-term averages, and the long-term effects of NO_x are thought to be more significant than the short-term effects (Mills, 2004).

Table 18.8 Critical levels (CL) of ammonia (Cape *et al.*, 2009)

Averaging period	Critical value μg/m³	Receptor
1 month	23	Provisional value for all plants
1 year	1	Lichen communities and bryophytes; ecosystems where these are a key part of ecosystem integrity
1 year	3 (2–4)	Higher plants (heath land, grassland and forest ground flora)

Ozone

Ozone damage to vegetation has been recognised and studied for many decades (Benton *et al.*, 2000; Matyssek and Innes, 1999; Skärby *et al.*, 1998). Today ozone is considered to be the most important gaseous pollutant causing effects on vegetation in Europe. It enters plants through leaf stomata and oxidises plant tissue, causing changes in biochemical and physiological processes and eventually death of the injured plant cells. Besides visible injuries on leafs and needles, ozone also causes premature leaf loss, reduced photosynthesis and reduced leaf, root, and total dry weights in sensitive plant species. This leads to significant decrease in productivity of some agricultural crops and to reduced forest production. In addition, many native plants in natural ecosystems are sensitive to ozone.

The developments in ecotoxicology led to development of critical levels for ozone effects on plants. Traditionally, these were related to ozone concentrations, using simple mean values for different time windows (day, month, etc.), as still is the case for other gaseous air pollutants (NO_x, SO_2, NH_3). In 1990s a new kind of critical level for ozone was elaborated, based on accumulated exposure over a concentration threshold, following the rationale that higher ozone concentrations are believed to be more damaging to plants. Example of such metrics is AOT40 used in Europe (Fuhrer *et al.*, 1997).

The LRTAP Convention's mapping manual (Mills, 2004) suggested two main metrics for use in performing regional scale risk assessments of ozone damage: the AOT40 index and the flux based AFstY approach (Accumulated stomatal Flux over thresholds of Y nmol/m²/s). The flux-based approach relates risk to the absorbed ozone dose rather than ambient ozone concentration, through the use of stomatal conductance algorithms. These flux-based metrics have been defined in detail in the revised UN-ECE Mapping Manual (Mills, 2004) and are strongly recommended rather than use of AOT40. Table 18.4 presents a summary of the limit and target values of the EU Directive 2008/50/EC related to effects on vegetation.

18.2.4 Effects on materials

Atmospheric pollution is an important factor in material deterioration including degradation of systems used for material protection and cultural heritage materials. Corrosion of materials was originally mostly associated with air pollution by sulphur dioxide (SO_2); however the more recent studies have shown that nitric acid (HNO_3), ozone and particulate matter contribute significantly to the negative effect of air pollution on materials. The lifetime of technological products is shortened because of air pollution. Buildings and other structures, as well as objects of cultural heritage, exposed to the atmosphere deteriorate more rapidly. The resulting physico-chemical and economic damage can be significant, not to mention the loss of unique parts of our cultural heritage and hazards due to decreased reliability of complicated technological devices. Also, as the result of weathering, especially that caused by acidifying pollutants, a significant part of the metals used in construction and manufactured products are released to the biosphere with a potential hazard to the environment.

Deterioration rates can be calculated using dose–response functions. The recommended functions have been derived from field research programmes undertaken as part of the UN-ECE ICP Materials Exposure Programmes. Two sets of dose–response functions have been derived. One was developed for SO_2-dominated situations taking into account the synergic effect of exposure to ozone and the effect of acid rainfall in combination with climatic parameters. The second was developed for multi-pollutant situations combining effects of gaseous SO_2, NO_x, O_3, HNO_3 and particulate matter together with acid rainfall in combination with climatic parameters. The impact of wet deposition of acidic species on sensitive materials is considered as an effect of the total load of H^+ deposition, and impact of deposition of the sea salt as an effect of the total load of Cl^- deposition. The dose–response functions use annual average concentrations of air pollutants and are available for limestone, sandstone, copper, bronze, zinc, steel and aluminium (ICP, 2010). The recommended unit of corrosion attack is the surface recession R (in µm) with the exception of aluminium, where the mass loss ML (in gm^{-2}) should be used instead. Table 18.9 summarises the available dose–response functions for materials and lists the dependencies of these functions. For zinc, bronze and limestone the multi-pollutant function should be used when levels of HNO_3 and/or particulate matter are expected to be high, as is the case with most European cities today with pollution dominated by traffic. Dose–response functions for paint coatings are also available, expressed as lifetime equations for the coatings.

Because atmospheric deterioration of materials is a cumulative, irreversible process, which proceeds even in the absence of pollutants, 'critical' values are not as easily defined as for some natural ecosystems. Some rate of deterioration must be defined which may be considered 'acceptable' based on technical and economic considerations. This approach provides the basis for mapping 'acceptable areas' for corrosion, and deriving areas where the acceptable pollution level/load is exceeded, in an analogous way to the maps produced for natural ecosystems. The term 'acceptable' is reserved for materials used in technical constructions, while 'tolerable' is used in connection with the degradation of cultural heritage. Based on maintenance intervals and tolerable corrosion attack before maintenance for cultural heritage objects, tolerable corrosion rates have been determined. These corrosion rates are 2.5 times higher than background corrosion values and values of tolerable corrosion for the first year exposure of some materials are listed in Table 18.9. Particles also contain soiling materials, and the tolerable PM_{10} level for soiling of three selected materials is 12–22 µg/m^3 based on reasonable cleaning intervals.

18.3 Historical trends in air pollution and their current effects on health, vegetation and materials

After an improvement of the air pollution situation in Europe at the beginning of nineties the trends in concentrations have been more or less stagnating for many air pollutants during the decade beginning at late 1990s. Overall exposure of Europe's population to pollutants with a health impact has not improved since the late 1990s; however, there have been some pollutant-specific exceptions. Figure 18.1 shows that increasing part of urban population is exposed to ozone and PM concentrations over the target values. Whilst exposure to high levels of NO_2 has steadily decreased, up to 30% of Europe's urban population may still be exposed to concentrations in excess of limit values. Thus, determined effort is still required if ambient air concentration and exposure targets are to be met. For ozone there was considerable variation between years. Usually, a maximum of 25% of the urban population was exposed to concentrations above limit values. In 2003 – a year with extremely high ozone concentrations – this fraction increased to approximately 60%. For PM_{10} the urban population potentially exposed to ambient air concentrations in excess of the EU limit value varied between 23% and 45% between 1997 and 2004. There was no discernible trend over the period (EEA, 2010).

Acidifying emissions in Europe have declined substantially since 1990. As sulphur emissions have fallen, nitrogen has become the predominant acidifying agent. Ozone concentrations have remained largely unchanged in recent years, even though emissions of precursor gases have been falling. Exposure of vegetation to ozone exceeds criteria for protection over very large areas of central and southern Europe.

Declining concentrations of acidifying air pollutants has resulted in decreased observed corrosion rates of materials at the ICP Materials sites, by about 50% on average in the period 1987–1997. The corrosion rate of carbon steel decreased further in 1997–2003 (Figure 18.2), though the rates for zinc and limestone increased slightly. Nitric acid and particulate matter currently contribute to corrosion, in addition to sulphur dioxide. Exceedances of tolerable levels of corrosion for cultural heritage materials were frequent. For 1990, it was estimated that air pollution caused € 1.8 billion of materials damage. Emission reductions envisaged under the Gothenburg Protocol are

Table 18.9 Functional dependencies of the dose–response functions for materials (UN/ECE ICP-materials, 2007). Situation (of air pollution) is SO_2-dominated (SO_2) or multi-pollutant (multi); dependencies of dose–response functions on concentrations of gaseous pollutants, wet deposition of acidity (H^+), chlorides (Cl^-), relative humidity (RH) and temperature (T) are based for annual mean values of these environmental variables

Material	Situation	SO_2	O_3	PM_{10}	HNO_3	H^+	Cl^-	RH	T	Tolerable corrosion
		µg/m³				*mg/m²/year*		*%*	*°C*	*µm/year*
Steel	SO_2	✓						✓	✓	20
	Multi	✓		✓		✓		✓	✓	
Zinc	SO_2	✓				✓		✓	✓	1.1
	Multi	✓			✓	✓		✓	✓	
Copper	SO_2	✓	✓			✓		✓	✓	0.8
Bronze	SO_2	✓				✓	✓	✓	✓	0.6
	multi	✓		✓		✓		✓	✓	
Aluminium	SO_2	✓					✓	✓	✓	0.22
Limestone	SO_2	✓				✓			✓	8
	multi	✓		✓	✓	✓		✓[a]		
Sandstone	SO_2	✓				✓			✓	7

[a] If RH < 60%, counts as RH = 0.

expected to improve materials damage across Europe by more than € 1 billion (UN/ECE ICP-materials, 2007).

18.3.1 Ammonia

Regional ammonia (NH_3) concentrations in Europe have been calculated with the EMEP MSC-West model; Figure 18.3 shows the yearly mean concentrations for the years 1990, 1995, 2000 and 2005. Note that with a grid size of 50 km × 50 km, the model cannot capture the large gradients in ammonia that exist at small spatial scales. The model overestimates low ammonia concentrations (for instance at the forest sites from the EU project NOFRETETE) and underestimates high concentrations (e.g. EMEP sites, which are situated in rural areas, often surrounded by agricultural activities). However, the model calculations did not show any systematic deviation for ammonia with respect to seasons. Comparing the calculated NH_3 concentration with the updated critical levels (1 µg/m³ for lichens and bryophytes and 3 µg/m³ for herbaceous plants; Cape *et al.*, 2009) reveals the actual risk of elevated NH_3 emissions on terrestrial ecosystems. Despite uncertainties, it is very likely that bryophytes and lichens are negatively affected almost everywhere in Western, Central and parts of Southern Europe, and herbaceous plants in areas with intensive animal husbandry (NW France, Flanders, Netherlands, Denmark, parts of Germany, Switzerland and Northern Italy). Not surprisingly, these are also the areas with highest nitrogen deposition rates and exceedances of critical loads, with additional adverse effects on sensitive ecosystems (see Dise *et al.*, 2011, Chapter 20 this volume).

The contribution of ammonium to the PM concentrations can be estimated from measurements of PM chemical composition. Putaud *et al.* (2004) reviewed composition of PM measured over the last decade at 24 sites situated in natural, rural, near-city, urban, and kerbside areas in Europe. Figure 18.4 shows the contribution of ammonium to $PM_{2.5}$, PM_{10} and coarse PM at the different types of locations. The figure indicates that contribution of ammonium to $PM_{2.5}$ in Europe is around 8%. The ammonium contribution to PM is by Amann *et al.* (2008) assumed proportional to the PM-related health effects calculated for the National Emission Ceilings analysis. Loss in statistical life expectancy attributable to the exposure of $PM_{2.5}$ is between 6 and 36 months in central Europe (Figure 18.51).

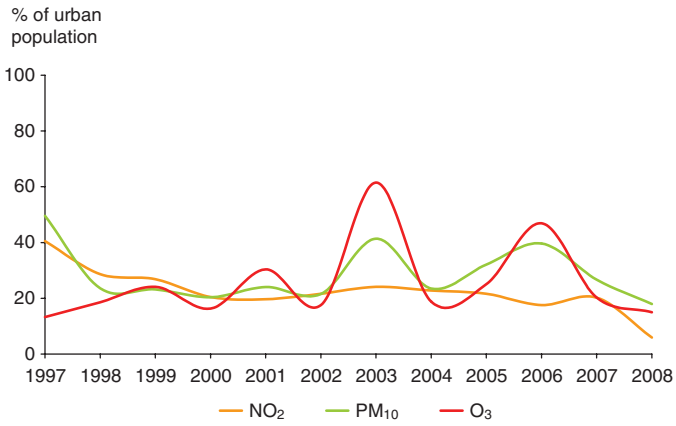

Figure 18.1 Percentage of the urban population in Europe (EEA member countries) potentially exposed to pollutant concentrations over selected limit/target values (only pollutants (partly) related to N_R) (NO_2: annual mean of 40 µg/m³ NO_2 not to be exceeded; PM_{10}: 24 h average of 50 µg/m³ not to be exceeded more than 35 times a calendar year; O_3: daily maximum of 8 h mean of 120 µg/m³ O_3 not to be exceeded more than 25 days per calendar year, averaged over three years) (EEA, 2010a).

18.3.2 Oxides of nitrogen

The concentrations of NO_2 are spatially very variable in the urban environment, depending on time of the day, season, reactivity and meteorological factors. The natural background annual mean of NO_2 is between 0.4–9.4 µg/m³, the urban annual mean is usually 20–90 µg/m³ (WHO, 2006) and for the rural background it is 15–30 µg/m³. Hence the WHO guideline, as well as the EU limit value concerning NO_2, is exceeded in many larger cities and, as emissions of NO_x are strongly traffic-related, there is a rising concern regarding NO_2 concentrations in growing cities with high traffic density. For instance in a megacity like Beijing the annual average NO_2 concentration in 2002 was 76 µg/m³ (Molina and Molina, 2004). In the EU-27

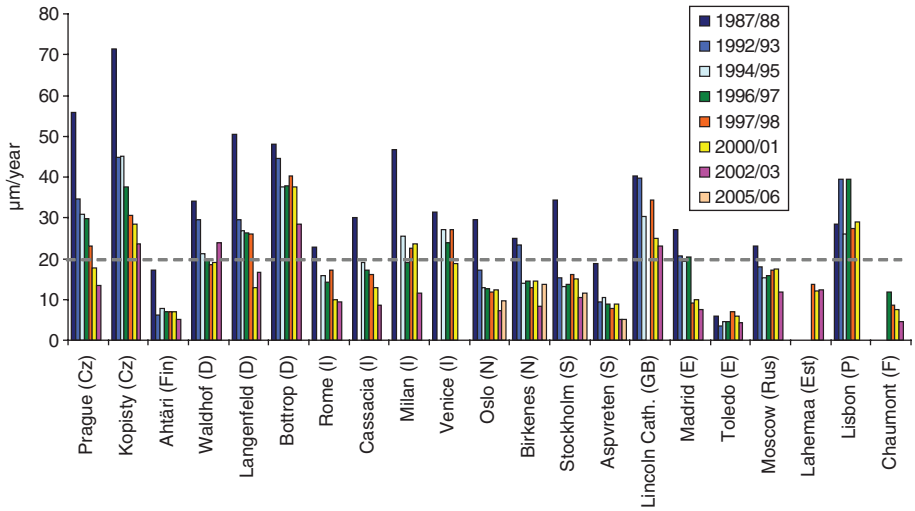

Figure 18.2 Carbon steel corrosion rates for sites in 21 European cities for years between 1987 and 2005 (see legend). The grey dashed line is the tolerable corrosion rate 20 µg/year (figure prepared from data in UN/ECE ICP-Materials, 2006, and 2007).

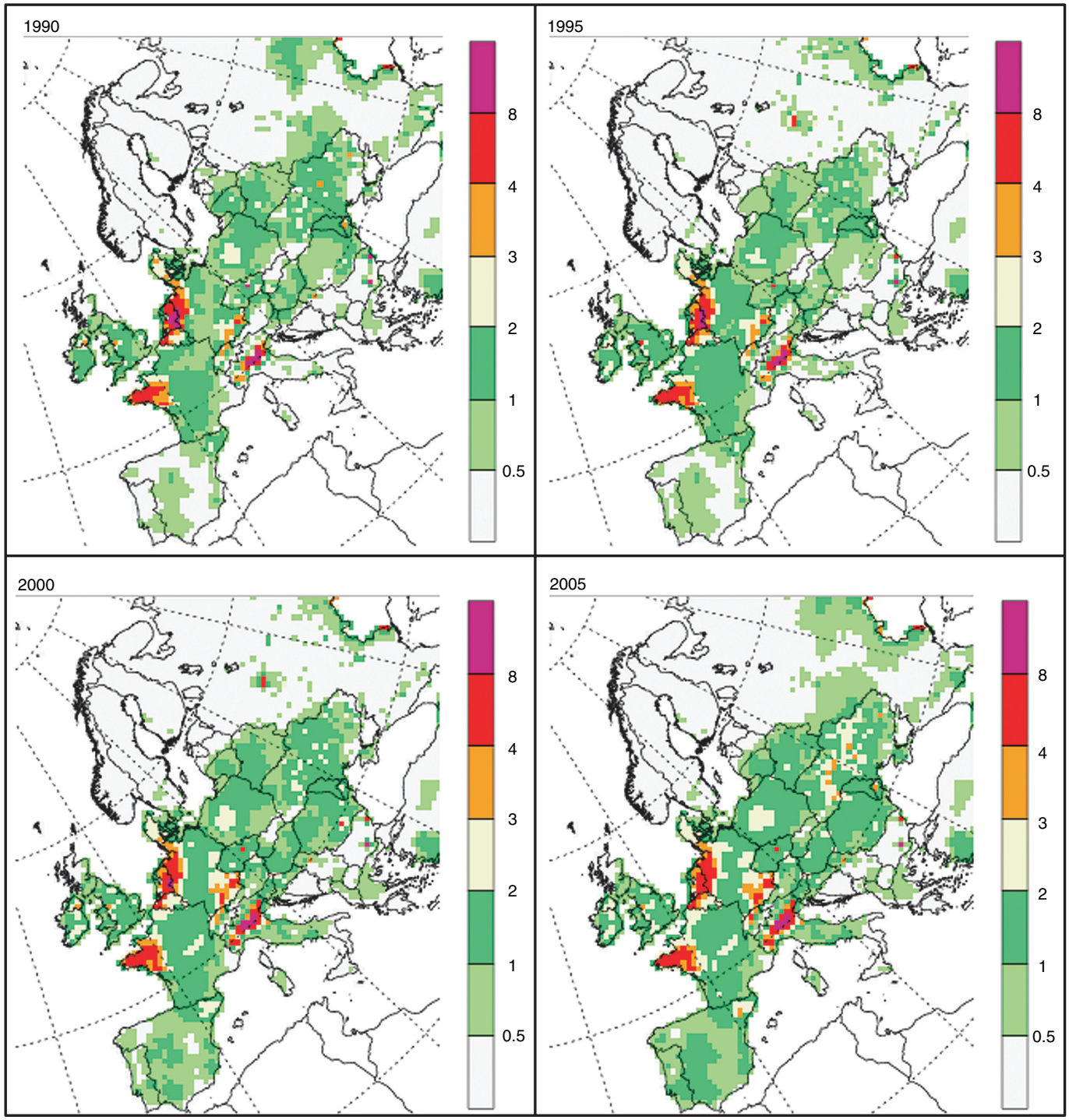

Figure 18.3 NH_3 concentrations (in µg/m³over Europe calculated with the EMEP model for the years 1990, 1995, 2000 and 2005 using a legend with limits of 1 µg/m³ for lichens and bryophytes (≥ darkgreen area) and of 3 µg/m³ for herbaceous plants (≥ dark orange area).

countries, 60% of the population lives in areas where the annual EU limit value of NO_2 is exceeded. The exceedance is primarily associated with the urban environment and its local traffic (Mol *et al.*, 2010). Urban pollution is assessed in detail in Svirejeva-Hopkins *et al.*, 2011 (Chapter 12 this volume). Also in suburban areas some Member States are still having problems with attaining the annual limit value as can be seen in Figure 18.5.

In Europe (the EEA32 countries) the NO_x emission have decreased by 18% in the period 1997–2006; traffic related emissions showed an even larger decrease of 28%. In line with this, the ambient NO_x concentrations showed decreasing trend throughout the region with decrease of about 22% at rural stations and 27% at urban/traffic stations between 1997 and 2007 (Figure 18.6). While the decrease in NO_2 concentrations at rural and urban stations was quite similar to the decrease in NO_x during this period, reduction in NO_2 concentrations at traffic stations was small (6%) (Figure 18.6; Mol *et al.*, 2009). This can be explained by two processes that are important only

very close to the sources. Firstly, at a constant oxidant level the NO_2/NO_x ratio increases with lowering NO_x concentration due to the NO titration. Secondly, there are clear indications that the fraction of directly emitted (primary) NO_2 in the total NO_x emission from road transport is increasing. The main reason is high proportion of the primary NO_2 in emissions from the growing fleet of diesel cars of Euro 3 and III standard and higher, equipped with oxidation catalysts or particle traps incorporating oxidation catalysts (Sjödin *et al.*, 2009).

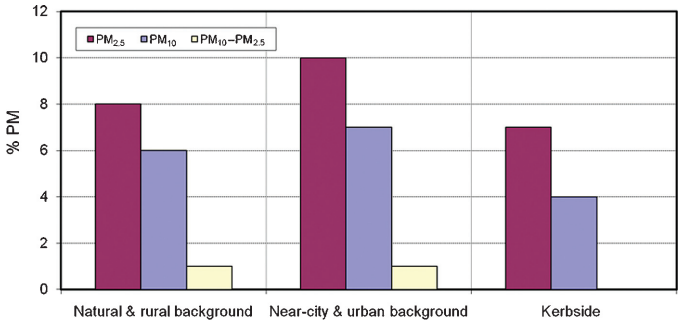

Figure 18.4 Contribution of ammonium to $PM_{2.5}$, PM_{10} and coarse PM (=PM_{10}–$PM_{2.5}$) at natural and rural background, near city and urban background, and kerbside measurement stations in Europe (24 in total). Data for years 1991–2001 were analysed after the data from Putaud *et al.* (2004).

18.3.3 Ozone

Rural O_3 concentrations had doubled from about 10–15 ppb in rural Europe at the end of the nineteenth century to 20–30 ppb in the 1980s. Volz and Kley (1988) were able to show that by analysing the more than 100 years old ozone data from around the turn of the nineteenth and twentieth centuries made at Montsouris by old-day measurement methodologies and comparing it with more modern techniques. Since the 1980s, rural O_3 concentrations have increased in many areas (Staehelin and Schnadt Poberaj, 2008) with quite different rates of change at different locations (The Royal Society, 2008).

The majority of ozone precursor emissions originate from anthropogenic sources. A recent review of the Gothenburg Protocol (TFIAM, CIAM, 2007) showed that the emissions of the O_3 precursors NO_x and NMVOC have declined substantially as a result of emissions controls. In 2005, NO_x and NMVOC emissions were 30% and 38% lower than 1990 levels for the European countries within the Protocol.

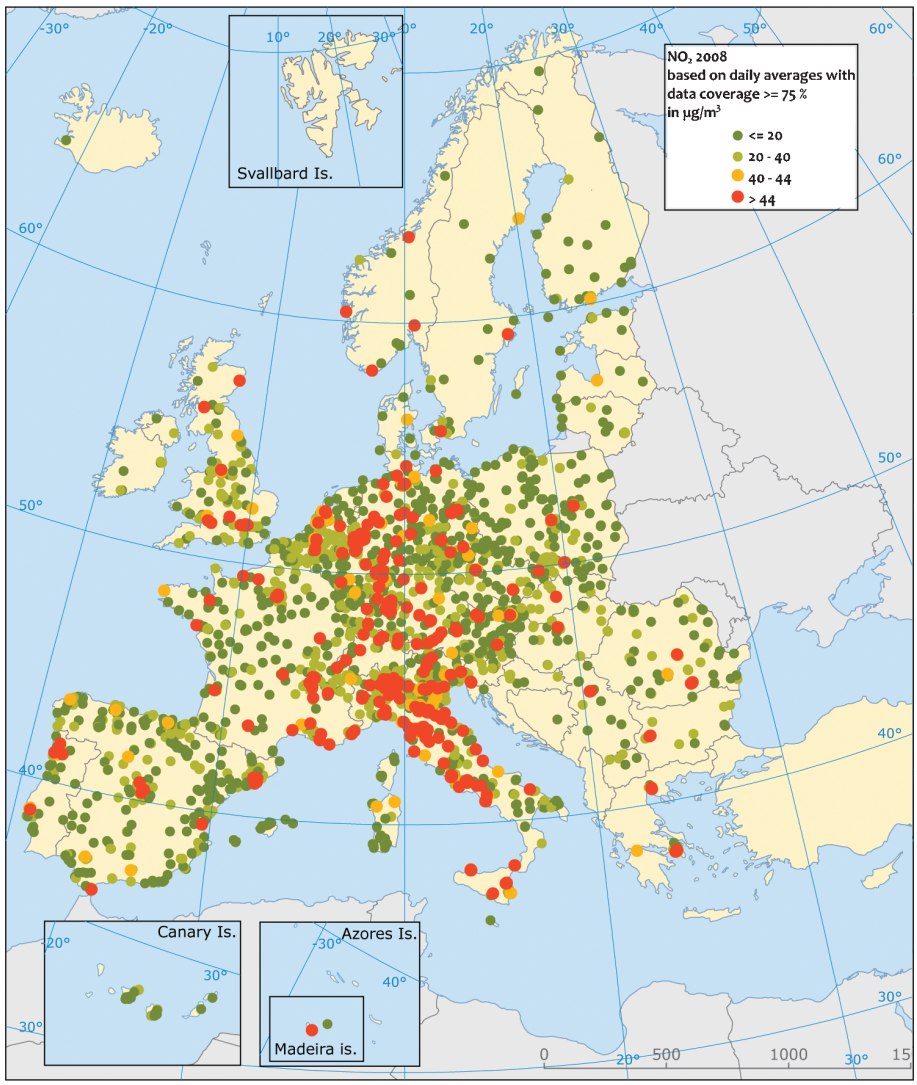

Figure 18.5 Annual mean concentration map of NO_2 (µg/m³) in 2008; the two highest concentration classes correspond to the limit value (40 µg/m³) and limit value plus margin of tolerance (44 µg/m³), respectively (Mol *et al.*, 2010).

The decrease in NO_x and NMVOC emissions in Europe has resulted in a reduction in the magnitude of short-term peak O_3 concentrations during episodes, with declines in daily peak concentrations of around 30 ppb. Reductions in peak O_3 concentrations have been observed widely in Europe, both in urban and rural areas. The temporal pattern of O_3 concentrations, however, reveals several additional changes during the period in which emissions of O_3 precursors over Europe have declined. In particular, the lower percentiles of the frequency distribution and even the mean concentration at many sites have been growing. These effects are illustrated in Figure 18.7a and Figure 18.7b, from Jenkin (2008). This figure shows the changes in O_3 concentrations at an urban site (Leeds) and a rural site (Lullington Heath) in the UK, and show similar trends to those observed at other sites across the UK, and more widely in Northern Europe (The Royal Society, 2008).

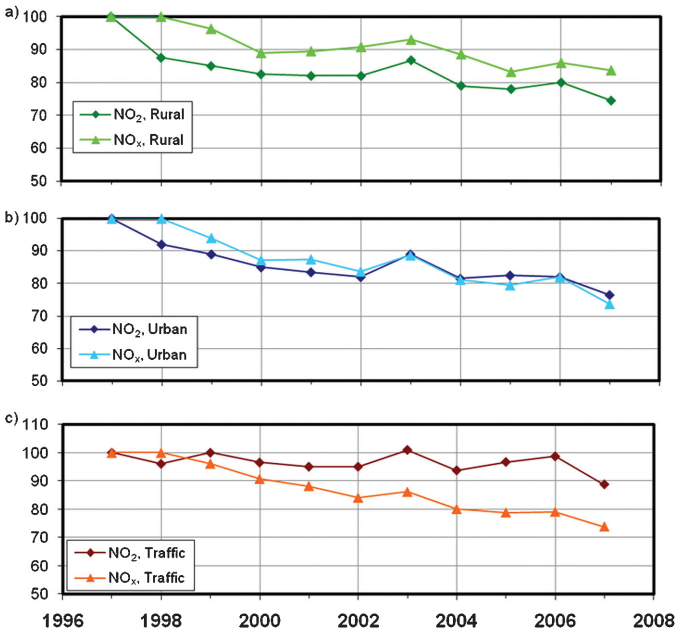

Figure 18.6 Relative changes in annual mean concentrations of NO_2 and NO_x to year 2007 for the three stations types of the AirBase network: rural (a), urban (b) and traffic (c) (data from Mol *et al.*, 2009).

Effects on health

The highest levels of exposure to ozone are estimated for southern Europe, with the highest levels found in northern Italy. The estimated population exposure indicates that large regions fail to meet environmental objectives and a notable fraction of the urban population, typically around 25%, is exposed to elevated ozone. Extreme conditions in 2003 pushed this to approximately 60%. Regional differences in exposure levels across Europe are shown in Table 18.10. These are expected to diminish in the next decade. Exposures in continental Europe are projected to fall by 20%–30% in southern France, Germany, northern Italy and Switzerland and to rise in the United Kingdom and Scandinavia (WHO, 2008). It can be expected that population exposure will increase regardless of currently planned precursor emission reductions, owing to increasing background levels and reduced ozone depletion in urban areas.

Current exposures to ozone in Europe are associated with premature mortality and morbidity. Effects include 21 000 premature deaths, 14 000 hospital admissions for respiratory disease and more than 100 million person-days of restricted activity per year in the EU 25 (WHO, 2008). These figures are underestimates, as they do not account for possible effects at levels below 70 µg/m^3.

The heat wave of summer 2003 gave an indication of the potential impact of a future warmer climate on air-pollution related health effects. Bell *et al.* (2007) investigated how climate

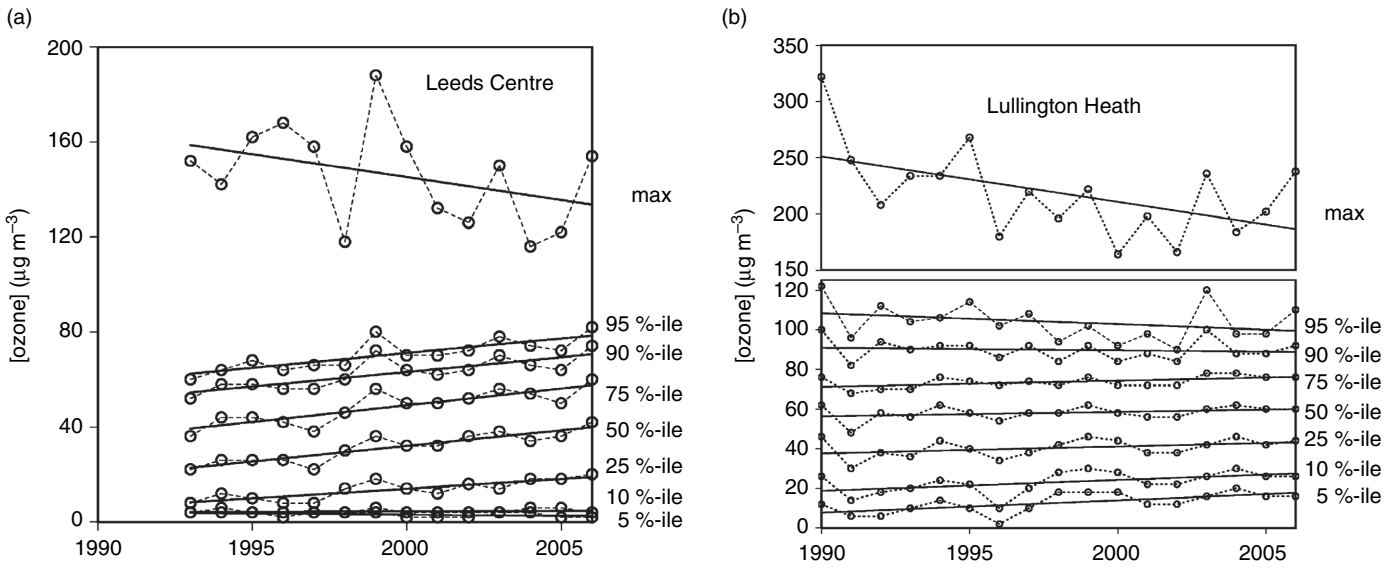

Figure 18.7 Changes in ground-level O_3 concentrations at (a) urban (Leeds centre) and (b) rural (Lullington Heath) sites in the UK, showing a decline in peak values and increases in the mean and lower percentiles of the distribution. Trend in hourly mean O_3 distributions based on data over the periods 1993–2006 and 1990–2006, respectively. The solid lines are linear regressions of data indicating the average trend over the period (Jenkin, 2008). With permission from Elsevier.

Table 18.10 Fractions of populations exposed to ozone levels exceeding the EU directive target value of 120 μg/m³ for more than 25 days a year, by region (WHO, 2008)

Region[a]	2002	2003
Northern Europe	0%	0%
Northwestern Europe	0–10%	40–50%
Central and eastern Europe	20–30%	80–90%
Southern Europe	60–70%	60–70%

[a] Northern Europe: Denmark, Estonia, Finland, Iceland, Latvia, Lithuania, Norway, Sweden; Northwestern Europe: Belgium, France (north of 45ºN), Ireland, Luxembourg, Netherlands, United Kingdom; Central and eastern Europe: Austria, Czech Republic, Germany, Hungary, Poland, Slovakia, Switzerland; Southern Europe: Cyprus, France (south of 45ºN), Greece, Italy, Malta, Portugal, Slovenia, Spain.

change could affect ambient ozone concentrations, using an hourly concentration model for 50 United States cities for 1990 and 2050. Future concentrations were based on the IPCC A2 scenario and the impact of altered climate on ozone was estimated. The maximum 1 h ozone levels were estimated to increase on average by almost 10 μg/m³ (maximum 19.2 μg/m³), the highest increases occurring in cities with current high pollution levels.

Effects on vegetation

Simpson *et al.* (2007) used the EMEP chemical transport model to map the different indicators of ozone damage across Europe for two illustrative vegetation types, wheat and beech forests. Figure 18.8a illustrates the AOT40 index for forests as calculated with the EMEP model for the year 2000, with Figure 18.8b showing the ratio of this AOT40 value to the recommended critical level (CL), 5000 ppb.h. Firstly, we can note that the spatial gradients of AOT40 are very large, with typically a factor 10 difference between AOT40 values in southern Europe and those in the Nordic countries. Exceedance of the 5000 ppb.h CL for AOT40 is widespread, with only a few areas (mainly in Northern Europe) experiencing lower values. Relative exceedances of the CL of more than a factor of 10 occur in southern Europe (Figure 18.8b).

Figure 18.8c,d present the corresponding results for AFst1.6, the relevant flux-based statistic for deciduous forests. The spatial pattern of AFst1.6 is rather different from that of AOT40. Whereas AOT40 clearly shows maxima in southern Europe, with much lower values in the Nordic countries, the spatial gradients in AFst1.6 are much smaller. Although the highest AFst1.6 values are still seen in parts of southern Europe, the difference between the Mediterranean and southern Sweden or Finland is typically less than a factor of two. Indeed, for the great majority of Europe, AFst1.6 values lie between 8 and 16 mmol/m². The suggested CL of 4 mmol/m² for AFst1.6 seems to be exceeded over essentially all of Europe.

As noted in the Royal Society's synthesis on ozone (The Royal Society, 2008), there is a substantial body of evidence from North America and Europe, supported by some work in Asia, Africa and Latin America, that elevated O_3 levels cause reductions in the yield of sensitive crop species (Mauzerall and Wang, 2001; Emberson *et al.*, 2003), and some estimates have been made of the economic impacts of crop loss due to ambient O_3 levels. The annual cost of arable crop production lost due to O_3 was estimated to be $2–4 billion in the USA in the 1980s, with an equivalent estimate for the EU of €6.7 billion (90% confidence interval €4.4–9.3 billion per year) in 2000 (Holland *et al.*, 2006). This is equivalent to 2% of arable agricultural production, but does not account for a range of other effects, including those on crop quality, visible injury, and susceptibility to pests and diseases. The greatest economic losses in Europe were predicted to be in Mediterranean countries, together with France and Germany, because the assessment used a concentration-based exposure index. Wheat, tomatoes, vegetables and potatoes were the crops with the greatest yield losses. Van Dingenen *et al.* (2009) recently provided the first global estimate of crop yield loss for four major commodities (wheat, rice, maize, soybean), of $14–26 billion in the year 2000. This is significantly higher than present day losses to crops projected to occur as a result of climate change.

The Royal Society (2008) report further noted that all of these estimates are primarily based on data from field chamber experiments which may under-estimate the real effects of O_3 in the field. For example, the decrease in soybean yield under open-air conditions in the Soy Free Air Concentration Enrichment (FACE) experiment, conducted in the USA, was greater than predicted by a synthesis of previous chamber studies (Morgan *et al.*, 2006). In one season, this was partly because O_3 exposure increased the impact of a major defoliating hail event. More field release experiments, in which O_3 is released over a crop which is not enclosed in chambers, are therefore needed to reduce the uncertainty in future estimates of loss in crop productivity. These need to be in a range of locations and to cover different cropping systems.

According to EEA (2007) large parts of the EEA 32 countries currently exceed exposure criteria for forests. More than half of the agricultural area exceeds criteria for crop protection, total crop yield losses reaching an estimated €3 billion per annum in 2000. Since 2000 the exposure of crops has not been reduced. Furthermore, in a number of areas ozone concentrations have actually increased in recent years as can be seen in Figure 18.9. Adverse meteorology and the changing balance of airborne pollutants lie behind this.

18.3.4 PM

Particles have been addressed as being one of the most important air pollutants regarding adverse human health impacts. The largest health impact estimates are for long term effects of $PM_{2.5}$. De Leeuw and Horalek (2009) estimated the number of premature deaths in EU-27 countries from $PM_{2.5}$ to be almost 500 000. The number of deaths that can be attributed to long-term PM_{10} exposure in the EU-25 countries is about 350 000– 370 000 premature (CEC, 2005; EEA, 2009a,b) (impacts from PM_{10} and $PM_{2.5}$ are not additive). Figure 18.10 shows the fraction of the European population that is exposed to a certain concentration range of PM_{10} (both annual mean and the 36th highest daily mean) and $PM_{2.5}$. WHO (2006) set an air quality guideline

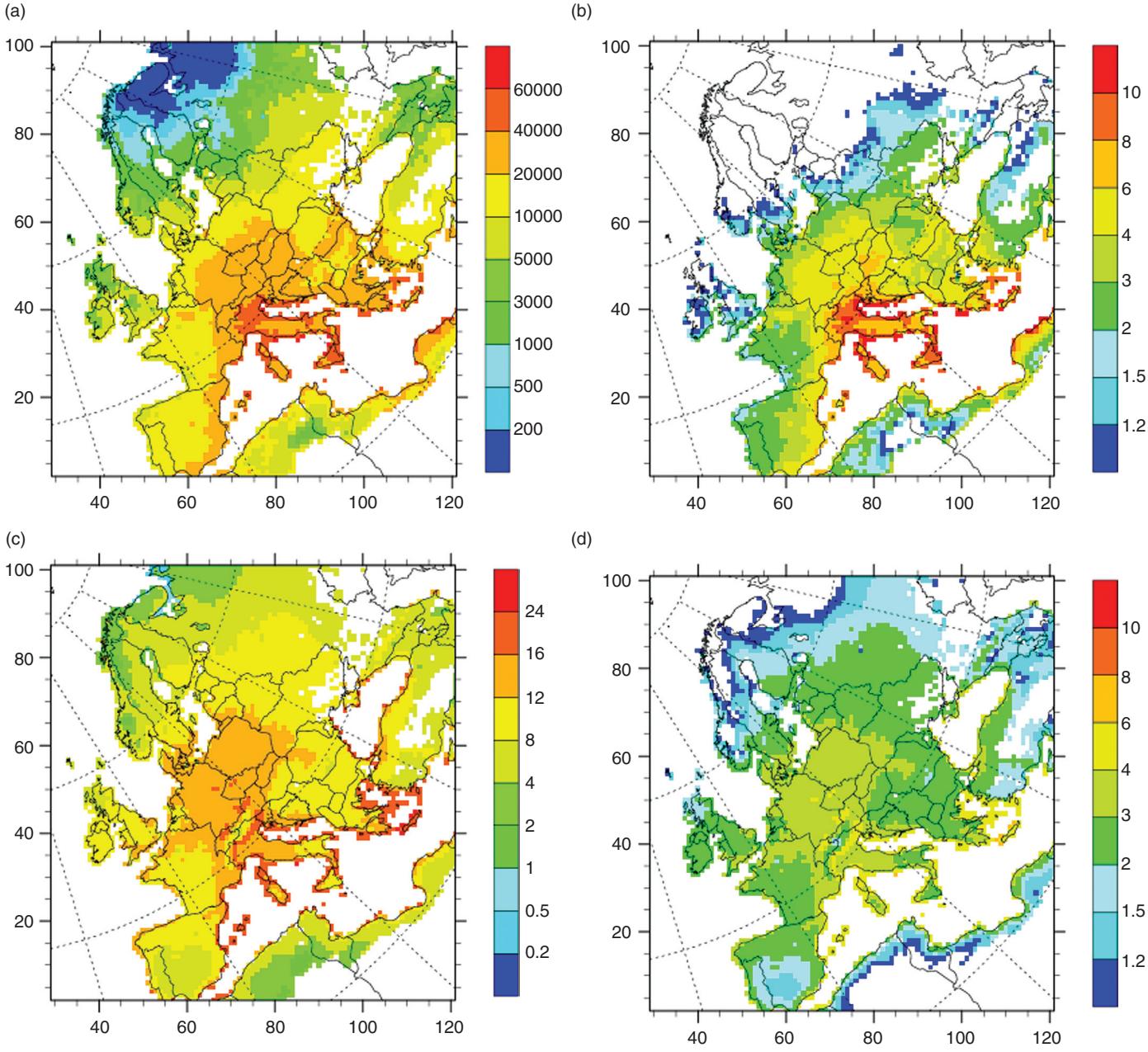

Figure 18.8 Calculated metrics for ozone damage to forests as calculated with the EMEP model for the year 2000: (a) AOT40 values (ppb.h), (b) ratio of calculated AOT40 to critical level of 5000 ppb.h, (c) AftY1.6 values (mmol/m^2), (d) ratio of AfstY1.6 to critical level of 4 mmol/m^2 (from Simpson *et al.*, 2007).

of 10 μg/m^3, the lowest level at which total, cardiopulmonary and lung cancer mortality have been shown to increase with confidence in response to $PM_{2.5}$. Only about 9% of the population is exposed to concentration below this guideline. Besides the guideline, the WHO has defined three interim targets, 15, 25 and 35 μg/m^3. The air quality guideline for PM_{10} is 20 μg/m^3 (WHO, 2000). About ¾ of the total European population is exposed to concentrations that are above this guideline for annual mean of PM_{10}.

Figure 18.11a shows the annual mean concentrations of PM_{10}. A statistical analysis of the monitoring data indicated that the daily PM_{10} limit value corresponds with an annual mean of 31 μg/m^3, although regional differences may occur (Mol *et al.*, 2010, and references there in), so both the exceedances of the annual limit value and of the short-term (daily) limit value can be derived from the figure. The map indicates that both limit values have been exceeded in many countries across Europe. Figure 18.11b shows the annual mean concentrations of $PM_{2.5}$ and enables a comparison with the $PM_{2.5}$ target value of 25 μg/m^3.

Data from the AirBase network show exceedance of PM_{10} limit values of both daily and annual means at all types of stations with increasing numbers from rural background to urban background to traffic stations. The extent of exceedance of the daily limit value is larger than of the limit value for annual mean. The daily limit value is frequently exceeded at urban background stations (about 28% of stations) and at traffic stations (more than 32% of stations) (Mol *et al.*, 2010). Regarding $PM_{2.5}$, the AirBase data show that at 6%, 14%, 5%

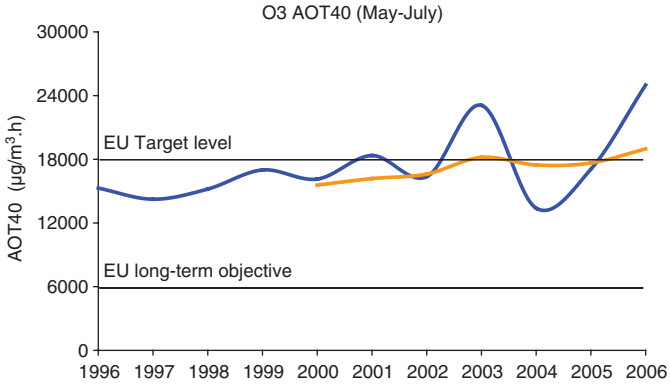

Figure 18.9 Annual variation in the ozone AOT40 value (May–July in µg/m³.h). Average values over all AirBase rural stations which reported data over at least six years in the period 1996–2006. The orange line corresponds to the 5 year averaged value (EEA, 2010b).

and 10% of the rural, (sub)urban background and traffic stations and industrial sites the $PM_{2.5}$ target value of 25 µg/m³ has been exceeded (Mol *et al.*, 2010).

There are regional and seasonal variabilities in PM_{10} and $PM_{2.5}$. In the Mediterranean region high concentrations of PM are often associated with inter-continental transport during the spring/summer (Saharan dust and Asian continental outflow) and it is therefore more common that PM concentrations are exceeded during spring and winter. For the rest of Europe, where PM is dominated by regional sources, winter time is the most common season for high PM concentrations which are a combination effect of higher emissions and less effective dispersion in wintertime.

The annual average PM concentrations in continental Europe are shown in Table 18.11 for different environments. Highest concentrations are often measured at the road side.

The Europe-wide tendencies in annual mean PM_{10} concentrations for the time period 1997–2007 are shown in Figure 18.12. The following observations can be made: PM_{10} concentrations in 2004 were approximately 25% lower than in 1997. However, an actual net tendency in PM_{10} concentrations from 1997 onwards cannot be discerned due to the large inter-year variations over the entire period. Variations in meteorological conditions between years can explain part of these variations. Urban and rural background concentrations trends follow each other closely. The rural background concentration provides the dominating contribution to total urban PM_{10}. PM_{10} concentrations at street level are on average approximately 8 µg/m³ higher than the average concentrations measured at 301 urban stations in 19 countries. Figure 18.S1 in supplement shows map with loss in statistical life expectancy attributable to the exposure to $PM_{2.3}$ which is highest in central Europe with statistical life expectancy loss between about 6 and 36 months.

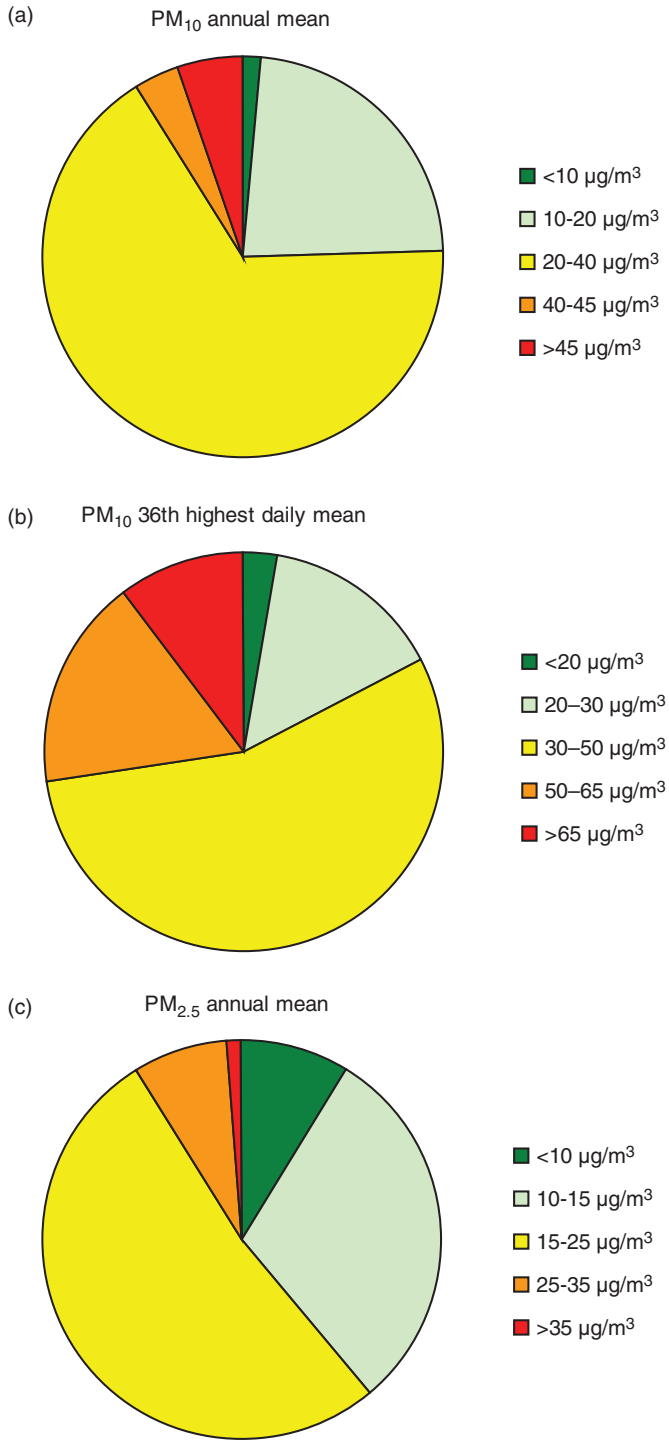

Figure 18.10 Exposure of European inhabitants in year 2005 to (a) PM_{10}, annual mean value; (b) PM_{10}, 36th highest daily mean value; (c) $PM_{2.5}$, annual mean value concentrations (sources: (a) and (b) EEA, 2009a; (c) de Leeuw and Morálek, 2009).

Chemical composition of particulate matter

Nitrate and ammonium contribute significantly to the particulate matter in Europe. From the EMEP measurements (rural stations, EMEP, 2008), NO_3^- and NH_4^+ contributed by between 6%–19% and 5%–9% respectively to the PM_{10}. This is in line with earlier assessments by Putaud *et al.* (2004). The relative quantity of nitrate tends to increase with increasing PM_{10} resulting in a higher relative contribution on exceedance days (daily average above 50 µg/m³) compared to annual averages. Putaud *et al.* (2004) found that on these days nitrate was a major component of PM_{10} and $PM_{2.5}$ together with organic matter. The more than proportional rise in nitrate levels as a function of PM_{10} appears to be valid for the whole of north-

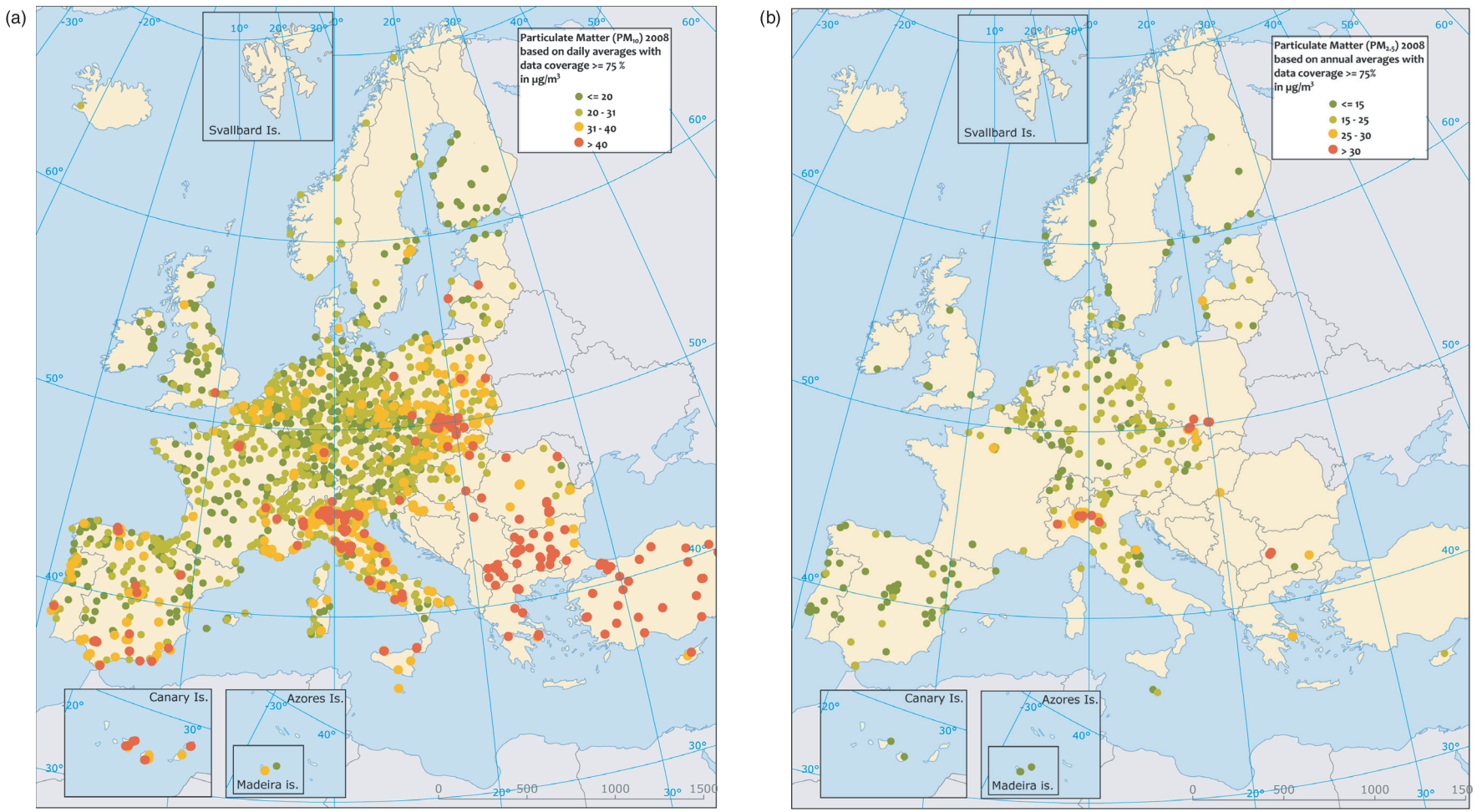

Figure 18.11 (a) Annual mean concentration map of PM_{10} (µg/m³); the two highest concentration classes corresponds to the annual limit value (40 µg/m³) and to a statistically derived level (31 µg/m³) corresponding to the short-term limit value). (b) Annual mean concentrations of $PM_{2.5}$ (from Mol *et al.*, 2010).

Table 18.11 Average PM_{10} and $PM_{2.5}$ levels in Europe for 2002 (WHO, 2006)

Type of PM value	µg/m³	Site
PM_{10} annual average	21.7	rural
	26.3	Urban background
	32	In street
PM_{10} daily average	38.1	rural
	43.2	Urban background
	51.8	In street
$PM_{2.5}$ annual average	11–13	Rural background
	15–20	Urban background
	20–30	In street

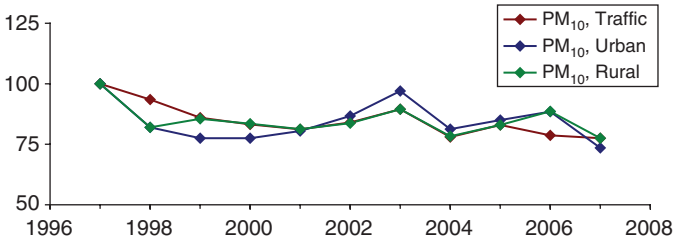

Figure 18.12 Inter-annual variation of PM_{10}, 1997–2007 annual means (from EEA, 2009a, b).

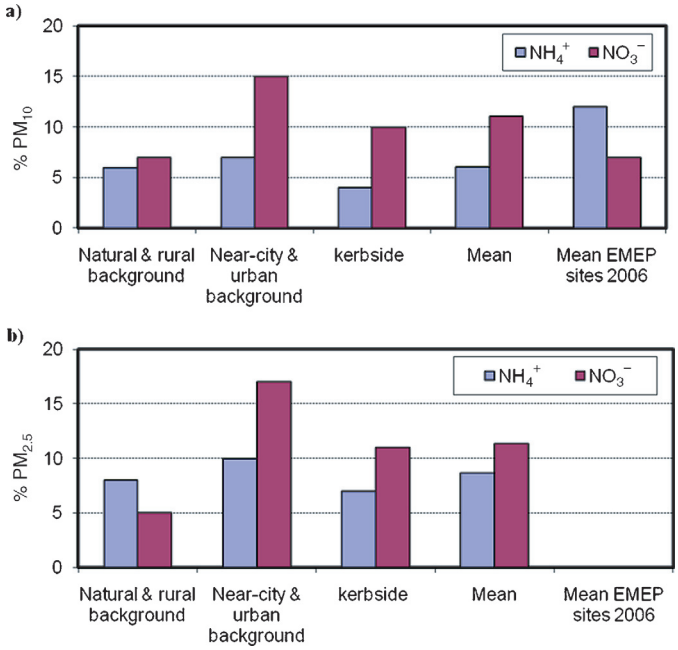

Figure 18.13 Mean contributions of NH_4^+ and NO_3^- ions to PM_{10} (a) and $PM_{2.5}$ (b) at 16 measurement sites evaluated by Putaud for time period 1991–2001 and in case of PM10 also at EMEP sites in 2006 (12 sites with NH_4^+ data and 25 sites with NO_3^- data, EMEP 2008).

western Europe. The reason for the extra high nitrate levels on exceedance days is that these days are often associated with very stagnant conditions. Ammonium nitrate, which has a more local character than sulphate, can build up fast, whereas the levels of pollutants from long range transport are not specifically enhanced.

There are no clear long-term trends in NO_3^- concentrations. NO_3^- concentrations do not follow general PM_{10} and $PM_{2.5}$ trends (Putaud *et al.*, 2004). The highest concentrations found in Europe are in the Po Valley, where there are large concentrations of NO_x as well as NH_3. Some of the smallest concentrations of NO_3^- are found in rural and natural backgrounds that may be due to lack of local sources of NO_x. However, the concentrations near cities are often higher than at kerbside sites, which may be due to the time needed to form NO_3^- from NO_x or due to low concentrations of NH_3 (Figure 18.13).

18.4 Future perspectives, national ceilings

18.4.1 Ammonia

In its Thematic Strategy on Air Pollution (TSAP), the European Commission outlined the strategic approach towards cleaner air in Europe (CEC, 2005) and established interim environmental objectives for the year 2020. Current emission ceilings for ammonia that should be met in 2010 were developed by 2006 (Klimont *et al.*, 2007). In order to meet new objectives for eutrophication, acidification and for particulate matter the following policies were suggested.

(1) A possible extension of the Integrated Prevention and Pollution Control (IPPC) Directive, to include installations for intensive cattle rearing and a possible revision of the current thresholds for installations for the intensive rearing of pigs and poultry.
(2) In the context of the current rural development regulation and the Commission proposals for rural development for 2007–2013, the Commission encourages the Member States to make full use of the measures related to farm modernisation, meeting standards and agro-environment to tackle ammonia emissions from agricultural sources.

The cost-effective emission ceilings for ammonium that would lead to achievement of the agreed interim objectives in 2020 and that are based on energy projections corresponding to the recent Climate and Energy Package of the European Commission and the national projections of agricultural activities were examined by Amann *et al.* (2008).

The 'Current policy' (CP) scenario was adopted as the starting point for the optimisation of additional emission-control measures to achieve the TSAP objectives. The 'Current policy' scenario considers implementation rates of already decided emission control legislation as currently laid down in national laws and implementation of the recent Commission proposals on the introduction of EURO-VI standards for heavy duty vehicles (EC, 2009) and on the revision of the Integrated Pollution Prevention and Control (IPPC) Directive for large stationary sources (EC, 2008a). To achieve the environmental objectives of the TSAP in 2020, further emission reduction measures on top of those considered in the 'Current policy' scenario would be needed to increase the reduction efforts for NH_3 emissions from 8% to 22%. Figure 18.14a shows the national emissions of NH_3 (Gg/y) in 2007, the national emissions ceilings for year

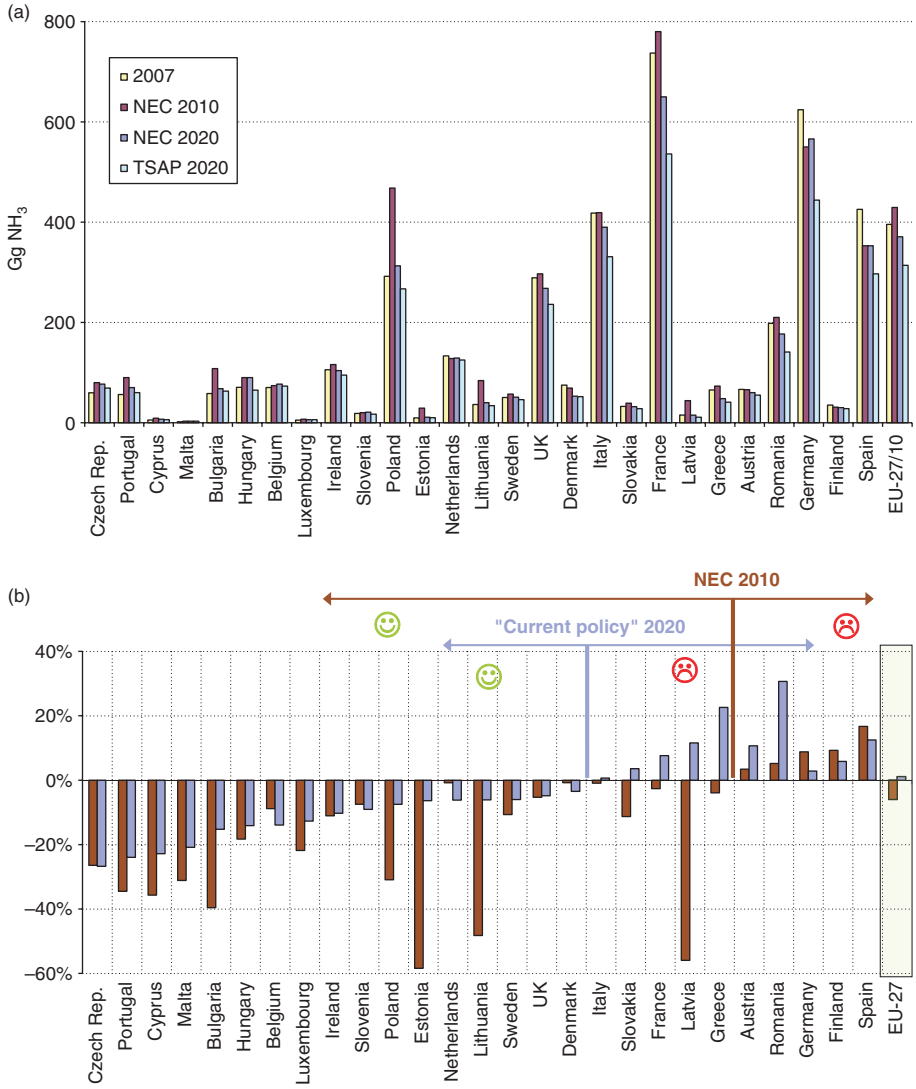

Figure 18.14 (a) National emissions of NH_3 (Gg/y) in 2007 (EMEP, 2010), the national emissions ceilings for year 2010 (NEC 2010) and the 'Current policy' scenario for 2020 for the 27 EU Member-States. The scenario with measures optimised to achieve the TSAP objectives in 2020 (TSAP 2020, the cost-effective scenario) is also shown. The EU-27 emission totals are divided by 10. (b) Distances of the year-2007 national NH_3 emissions from values for year 2007 on the straight-line emission trajectories from year 2000 to year 2010 (NEC 2010, brown) and to year 2020 ('Current policy' scenario, blue), respectively, expressed as difference in percent of the year-2007 value on the respective emission trajectory. The areas with green smiles indicate EU countries with NH_3 emissions that in 2007 were below the emission trajectory to NEC 2010 (afore the brown line) and to 'Current policy' 2020 (blue line), respectively. The total EU-27 NH_3 emissions in year 2007 were below the emission trajectory to NEC 2010 but above the emission trajectory to 'Current Policy' 2020. All emission scenarios come from Amann *et al.* (2008).

2010 and the 'Current policy scenario' for 2020, representing suggested NEC 2020, for the 27 EU Member States'. Distances of the year-2007 national NH_3 emissions from the emission trajectories going from the individual Member States emissions in 2000 to their respective NEC values are shown both for the NEC for 2010 and for the suggested NEC for 2020 in Figure 18.14b. It can be seen that only five Member States are above their emission trajectories to the 2010 NEC while more than a third are above their trajectories to the 2020 NEC. According to the national projections for 2010 published in the NEC directive status report for 2008 (EEA, 2009b) will only two Member States, Germany and Spain, miss their national ceilings.

18.4.2 Oxides of nitrogen

The decrease in NO_x emissions during the 1990s is partly due to the introduction of emission standards for road transport in Europe that included both light-duty vehicles (petrol and diesel) and heavy duty vehicles, but also regulations targeting other sectors have contributed. In May 2005 the *1999 Gothenburg Protocol* came into force regarding emission ceilings for (*inter alia*) NO_x. Compared to the level of 1990, Europe's emissions of NO_x should by 2010 be reduced by 41% (VOC 40%, NH_3 17%). Additionally, the EU introduced a national emission ceilings (NEC) Directive, 2001/81/EC, concerning NO_x and other pollutants. Compared to the Gothenburg Protocol, this directive puts more pressure on some of the member states than others. The emission ceilings must be attained by 2010.

While land-based NO_x emissions are expected to decrease in the coming decades, emissions from shipping are projected to increase. In 2000 the emissions from international maritime shipping in the seas surrounding the European Union (i.e. Baltic, North Sea, Northeast Atlantic, and Mediterranean Sea) amounted to approximately 30% of the land-based emissions in the EU-25. Legislation is in force to control emission of SO_2 and to some extent also NO_x from international shipping; however, Annex 6 of the MARPOL protocol regulates NO_x emissions only on newly installed engines after 2016. Considering the long lifetime of ship engines, this legislation will impact the NO_x emissions only in distant future. Further, the expected increase in the volume of ship movements will compensate for the environmental benefits of these measures and will lead to

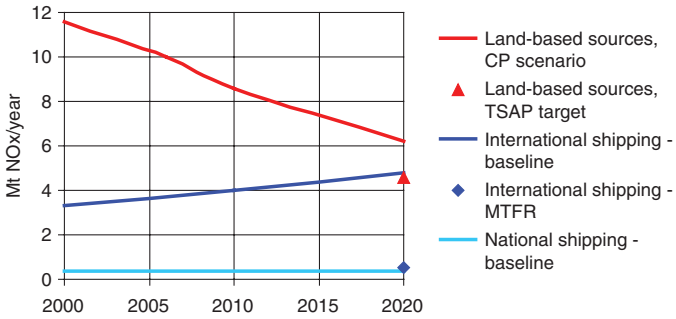

Figure 18.15 Emissions of nitrogen oxides from shipping (baseline scenario considering MARPOL Annex 6) compared with the emissions from land-based sources in the EU25 ('Current policy scenario'). Emissions at Maximal Technology-Feasible Reduction are shown for 2020 (after Cofala *et al.*, 2007).

a continued growth in ship emissions. By 2020 emissions from maritime activities would come close to the projected baseline emission levels from land-based sources and surpass the target levels established by the European Commission for land-based sources (Figure 18.15).

Airport studies confirm that aircraft continue to be a relatively small contributor to regional pollution although aircraft-related NO_x contributions could increase as air traffic increases and other non-aircraft emission sources become progressively cleaner.

The European Union have decided on a 10% substitution of traditional fuels in the road transport sector (petrol and conventional diesel) by alternative fuels before the year 2020 (Directive 2003/30/EC) in order to meet the challenges with increased transportation, decreased oil resources and enhanced greenhouse gas emissions. Impact of this directive on the NO_x emissions have not been fully investigated yet as the emission factors for many alternative fuels and their blends are not known. Up-coming Euro 5 and 6 standards (EC 715/2007, 1999/96/EC), embodying after-treatment technologies will be implemented 2010–2015 with the aim of further reductions of the NO_x emissions.

The usage of diesel is increasing in Europe and this may have implications on the NO/NO_2 ratio as diesel vehicles, especially when equipped with modern technology such as diesel particulate filters, emit more NO_2 compared to petrol vehicles. This effect should be pronounced only close to the source region. In some regions it is evident today that NO_2 is not decreasing at the same pace as NO_x. Combined measurement and modelling efforts have not been able, however, to prove that the potentially increasing share of NO_2 in NO_x emissions due to the emissions from diesel cars could alone explain this trend. Still, in future assessment strategies concerning vehicle emissions and NO_x this has to be taken into account. Additionally, it takes time to change the on-road fleet, hence, even though the latest vehicle technology means reduction in some pollutants, it may take time before that becomes a reality.

Projections of future NO_x emissions and their impact on future air pollution situation in Europe have been assessed by Amann *et al.* (2008) with GAINS model. The 'Current policy' scenario, i.e. scenario implementing all agreed legislation, projects a decrease of emissions of NO_x by about 48% in 2020 compared to the year 2000. This scenario approaches emission levels of the National Emission Ceilings. These emission ceilings must be attained by the EU member states in 2010. In Figure 18.16 is shown comparison of the NEC values for the Member States to the national emission values reported to EMEP for the year 2007. Comparison with target values of the TSAP is shown as well. Figure 18.16 indicates that almost half of the Member States were in 2007 above their emission trajectories leading from their year-2000 NO_x emissions to their NEC and large majority were above their respective trajectory to the planned NEC for 2020, in figure represented by the 'current policy' scenario for 2020 (scenarios from Amann *et al.*, 2008). The national projections for 2010 published in the NEC directive status report for 2008 (EEA, 2009b) give a similar picture of attainment of the 2010 NEC in the EU-27 Member States.

18.4.3 Ozone

Owing to the presence of stringent emission control legislation, ozone precursor emissions are expected to decline in the EU over the coming decade. VOC emissions are expected to decrease in EU15 by 33% in 2010 and 41% in 2020 compared to 2000. However, a lack of equivalent legislation will not prevent further increases in precursor emissions in other countries that are Parties to the Convention on LRTAP. This growth in emissions is expected to increase hemispheric ozone background concentrations. Furthermore, climate change could lead to higher biogenic emissions in the future (The Royal Society, 2008).

At the urban scale, projected O_3 precursor emissions controls (especially reductions in NO_x emissions) and changes in background O_3 concentrations will lead to changes in urban O_3 concentrations, with potentially large increases by the end of the century depending on the future scenario. As described earlier, the changes in urban O_3 concentrations result partly from reductions in the titration of urban O_3 by reaction with emitted NO, but are also influenced by changes in the background O_3 concentrations. This is because the reduction in the titration effect increases O_3 concentrations up to the background level (Jonson *et al.*, 2006).

Figure 18.17 shows projected exposure trends as expected changes in SOMO35 for 2020 compared to similar calculations with 2000 emissions. In some areas, such as parts of the Russian Federation and Scandinavia, SOMO35 levels are seen to increase in 2020 compared to 2000, although absolute levels are relatively low (around 2000 $\mu g/m^3 \cdot$days) in both cases. In those areas that had high levels of SOMO35 in 2000 (e.g. Italy and much of southern Europe), 2020 levels are seen to be significantly lower than 2000 levels, although this still leaves levels of around 4000–5000 $\mu g/m^3$ days in these areas (WHO, 2008).

Reduction in ozone exposure resulting from current policies, and thus in the health impact by 2020, is estimated to be small. Population ageing will increase susceptible groups and background risks in Europe in the foreseeable future.

18.4.4 PM

Projections for the future have been based on current legislation, i.e. 'business–as-usual', and emissions of $PM_{2.5}$ are

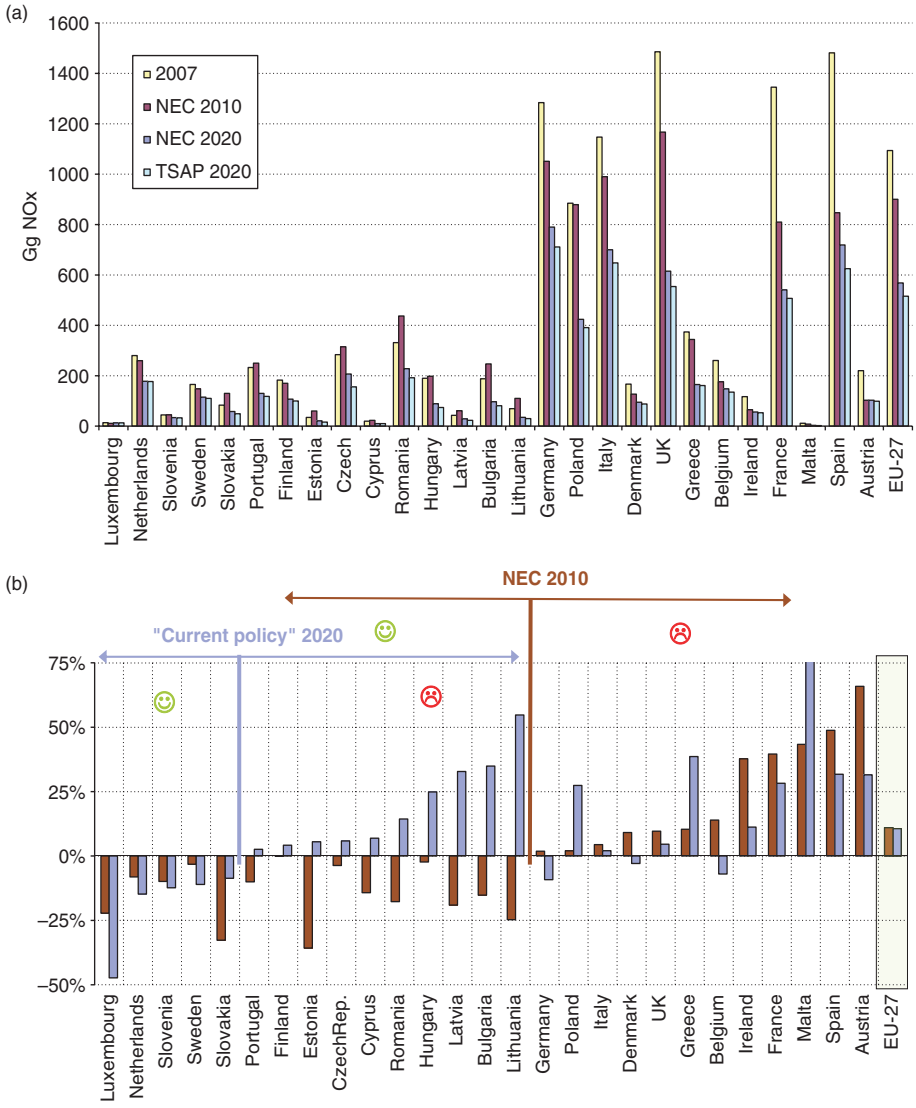

Figure 18.16 (a) National emissions of NO_x (Gg/year) in 2007 (EMEP, 2010), emissions ceilings for year 2010 (NEC 2010) and 'Current policy' scenario for 2020 (representing suggested NEC 2020) for the 27 EU Member States. The scenario with measures optimized to achieve the TSAP objectives in 2020 (TSAP 2020, the cost-effective scenario) is also shown. The EU-27 emission totals are divided by 10. (b) Distances of the year 2007 national NO_x emissions from values for year 2007 on the straight-line emission trajectories from year 2000 to year 2010 (NEC 2010, brown) and to year 2020 ('Current policy' 2020, blue), respectively, expressed as difference in percent of the year-2007 value on the respective emission trajectory. The areas with green smiles indicate EU countries with NO_x emissions that in 2007 were below the emission trajectory to NEC 2010 (before the brown line) and to 'Current policy' 2020 (blue line), respectively. The year 2007 NO_x emissions of Germany, Denmark and Belgium that are above the NEC 2010 trajectory fall below the emission trajectory for 'Current policy' 2020. All emission scenarios come from Amann *et al.* (2008).

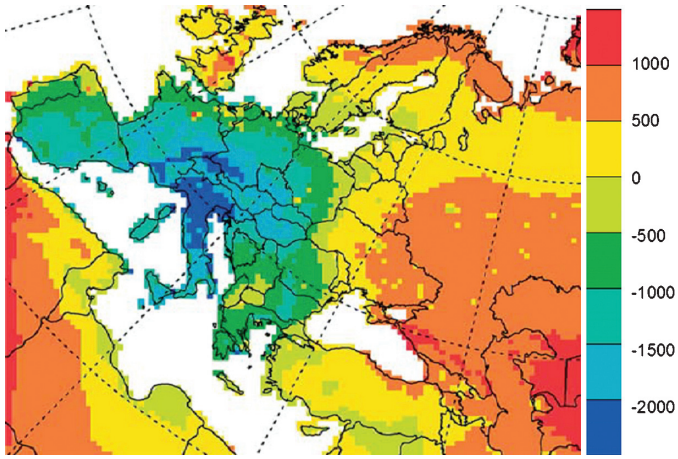

Figure 18.17 Calculated changes in SOMO35 values (μg/m³ × days) by 2020 compared with 2000 emissions (meteorology from 1997) (WHO, 2008).

projected to decrease by about 45% in 2020 compared to the year 2000. The main reason for this projected decline is expected to be improved vehicle technology, implemented in Euro standards 5 and 6. The PM_{10} is projected to decrease by 39% for the same time period which is mainly as a result of reductions in the transportation sector and power generation (CEC 2005). Subsequently, the projected life years lost due to $PM_{2.5}$ is decreased by around 32% and premature deaths by 21% (CEC 2005). However, $PM_{2.5}$ is still projected to account for 271 000 premature deaths in 2020. Table 18.12 summarises the estimated effects of air pollution on health. For 2020 it is projected that PM will cause less harm regarding both mortality and morbidity. Loss in statistical life expectancy attributable to the exposure to $PM_{2.5}$ in Europe projected for year 2020 in the current policy scenario is shown together with the year 2000 situation in Figure 18.S1 in the supplementry material. Taking the projected small reductions in ammonia comparing to SO_2 and NO_x, it can be expected that contribution of ammonia to the secondary (and total) PM will increase.

Table 18.12 Estimations of the effect of air pollution on health for the years 2000 (baseline) and 2020 (Current legislation in 2020 including Climate Policy) (Pye and Watkiss 2005).

Health end-point	Units (1000)	Pollutant	2000	2020
Acute mortality	Premature deaths	O_3	21,4	20,7
Respiratory hospital admissions	Cases	O_3	14	20
Minor Restricted Activity Days (MRADs)	Days	O_3	53,924	42,227
Respiratory medication use (Children)	Days	O_3	21,413	12,897
Respiratory medication use (Adults)	Days	O_3	8,837	8,136
Cough and lower respiratory symptoms (children)	Days	O_3	108,056	64,955
Chronic mortality[a]	Life years lost[a]	PM	3,001	1,900
Chronic mortality[a]	Premature deaths[a]	PM	288	208
Infant mortality	Premature deaths	PM	0.6	0.3
Chronic bronchitis	Cases	PM	135,7	98,4
Respiratory hospital admissions	Cases	PM	51,4	32,6
Cardiac hospital admissions	Cases	PM	31,7	20,1
Restricted activity days (RADs)	Days	PM	288,292	170,956
Respiratory medication use (children)	Days	PM	3,510	1,549
Respiratory medication use (adults)	Days	PM	22,990	16,055
Cough and lower respiratory symptoms (children)	Days	PM	160,349	68,819
Lower respiratory symptoms (adults with chronic symptoms)	Days	PM	236,498	159,724

[a] Note two alternative metrics are used for the presentation of chronic mortality from PM. Firstly in terms of years of life lost and secondly in terms of numbers of premature deaths. These are not additive.

18.5 Conclusions

As shown in this chapter, nitrogen air pollution is a serious threat to human health and ecosystems, both through direct effects from the emitted compounds but more seriously through the secondary compounds formed in the atmosphere. Legislation to improve air quality is in place which results in improving air quality, however, there are still large exceedances of air quality standards and critical levels in Europe. Even if present and proposed legislation is fully implemented, emissions of nitrogen oxides and ammonia will still pose a problem in Europe.

- Air quality standards for nitrogen dioxide are exceeded in many urban areas in Europe. The exceedance is primarily associated with the local traffic. The year-2007 NO_2 emissions of 12 out of 27 EU Member States were above the emission trajectory from year 2000 to the NEC for 2010.
- NEC for ammonia will be met in 2010 by most of the Member States; the 'Current policy' scenario, i.e. the scenario where all already agreed legislation has been implemented, is, however, above the emission level that would meet the TSAP objectives for 2020. It is very likely that sensitive species are and will be negatively affected by emissions of ammonia almost everywhere in Western, Central and parts of Southern Europe, at least in areas with intensive animal husbandry.
- There is still a need for better data on emissions and atmospheric concentrations, in particular for ammonia.
- Reduction in $PM_{2.5}$ mortality in 2020 for the 'Current policy' scenario gives lower than the TSAP goal for 2020, which is 47% reduction of the long-term exposure mortality taking year 2000 as a base. Considering the high contribution of N_r to $PM_{2.5}$, further reductions of N_r emissions could have a positive effect on reducing PM-related health effects and would contribute to meet the TSAP goal. Further, deposition of N_r in Europe also leads to exceedances of critical loads for nutrition nitrogen in large parts of Europe, both under the current situation and under the 'Current policy' scenario in 2020.
- The new findings on long-term exposure effects of ozone on mortality with the relative risk increase per additional 10 μg/m^3 ozone adding on the relative risk increase per 10 μg/m^3 $PM_{2.5}$ would make it difficult to meet the TSAP target of 47% reduction in mortality. As only small decreases are projected for ozone concentrations, the mortality from ozone would remain high in the 'Current policy' scenario in 2020.
- The uncertainties of the health impacts of nitrogen species (NO_2, NH_4^+, NO_3^-, HNO_3 and others) are very large and further epidemiological and toxicological research is needed to obtain more reliable exposure–response functions. In particular, the damage cost of NH_3 emissions is extremely uncertain.

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Supplementary materials

Supplementary materials (as referenced in the chapter) are available online through both Cambridge University Press: www.cambridge.org/ena and the Nitrogen in Europe website: www.nine-esf.org/ena.

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