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A NOVEL COMBINATION OF METHODS FOR AIR QUALITY MANAGEMENT SUPPORT WITH FOCUS ON PARTICULATE MATTER

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LIST OF ACRONYMS AND ABBREVIATIONS

µg.m^{-3}	Microgram(s) per cubic metre
°C	Degree Celsius
AEI	Average exposure indicator
AQG	Air Quality Guideline
AT	Austria
ATSDR	Agency for Toxic Substances and Disease Registry
BaP	Benzo[a]pyrene
BA	Bosnia and Herzegovina
BE	Belgium
BG	Bulgaria
BY	Belarus
BMI	Body Mass Index
CEIP	Centre on Emission Inventories and Projections
CLE	Current legislation emissions
CO	Carbon monoxide
CO_2	Carbon dioxide
CTM	Chemical transport model
CY	Cyprus
CZ	Czech Republic
DE	Germany
DK	Denmark
EAP	Environment Action Programme
EC	European Commission
ECMWF	European Centre for Medium-Range Weather Forecasts
EE	Estonia
EEA	European Environment Agency

EMEP	European Monitoring and Evaluation Programme
EPER	European Pollutant Emission Register
ES	Spain
ETC/ACM	European Topic Centre on Air Pollution and Climate Change Mitigation
EU	European Union
EU27	European Union with 27 member states, 2007 to 2013
EU28	European Union with 28 member states, including Croatia from 2013
Fe	Iron (chemical element)
FI	Finland
FR	France
GAINS	Greenhouse Gas and Air Pollution Interactions and Synergies
GB	United Kingdom
Gg	Gigagrams
GHG	Greenhouse gas
GR	Greece
HNO_3	Nitric acid
H_2SO_4	Sulphuric acid
HPA	Health Protection Agency, United Kingdom
HR	Croatia
HU	Hungary
IARC	International Agency for Research on Cancer
IE	Ireland
IIASA	International Institute for Applied Systems Analysis
INERIS	French National Institute for Industrial Environment and Risks
IT	Italy
IPCC	Intergovernmental Panel on Climate Change
IPCS	International Programme on Chemical Safety
JRC	Joint Research Centre

LAT	Lower assessment threshold
LRTAP	Long-range Transboundary Air Pollution
LT	Lithuania
LU	Luxembourg
LV	Latvia / Limit Value
MACC	Monitoring atmospheric composition and climate
MARS	Meteorological Archival and Retrieval System
MD	Republic of Moldova
MK	the former Yugoslav Republic of Macedonia
Mn	Manganese (chemical element)
MPE	Mean prediction error
MT	Malta
MSC-E	Meteorological Synthesizing Centre – East
MSC-W	Meteorological Synthesizing Centre - West
MWs/m^2	Megawatt-second per square meter
NEC	National Emission Ceilings
NERT	National Exposure Reduction Target
N	Nitrogen
NH_3	Ammonia
NH_4^+	Ammonium
$(NH_4)_2SO_4$	Ammonium sulphate
NH_4NO_3	Ammonium nitrate
NIOSH	National Institute for Occupational Safety and Health
NL	The Netherlands
NMVOC	Non-methane volatile organic compounds
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
NO_x	Nitrogen oxides

O_3	Ozone
•OH	Hydroxyl radical
PAH	Polycyclic Aromatic Hydrocarbons
PL	Poland
PM	Particulate matter
PM2.5	Particulate matter with particle diameter below 2.5 µm
PM10	Particulate matter with particle diameter below 10 µm
POP	Persistent organic pollutants
PPM	Primary particulate matter
PPM2.5	Primary particulate matter with particle diameter below 2.5 µm
PPMcoarse	Primary particulate matter with particle diameter between 2.5 and 10 µm
PT	Portugal
R^2	Coefficient of determination
RES	Renewable energy source
RMSE	Root Mean Square Error
RRMSE	Relative Root Mean Square Error
RO	Romania
SE	Sweden
±SE	± standard error
SI	Slovenia
SIA	Secondary inorganic aerosol
SK	Slovakia
SNAP	Standardized Nomenclature for Air Pollutants
SO_2	Sulphur dioxide
SO_4^{2-}	Sulphate
SOA	Secondary organic aerosol
SO_X	Sulphur oxides
SVOC	Semi-volatile organic compounds

TNO	Netherlands Organisation for Applied Scientific Research
TR	Turkey
TV	Target value
UAT	Upper assessment threshold
UFP	Ultrafine particles
UK	United Kingdom
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
UR	Unit risk
USEPA	United States Environmental Protection Agency
VOC	Volatile organic compounds
WHO	World Health Organization
WMO	World Meteorological Organization
W/m^2	Watt per square metre
YLL	Years of life lost

INTRODUCTION

Particulate matter (PM) is the general term used for a mixture of particles (solid and liquid) suspended in air, collectively known as aerosols. PM in the ambient air has many sources and is a complex heterogeneous mixture whose size and chemical composition change in time and space, depending on emission sources and atmospheric and weather conditions.

Particulate matter is either of natural origin, e.g., sea salt, naturally suspended dust, pollen, volcanic ash or from anthropogenic sources, mainly from fuel combustion in power generation, households for domestic heating and vehicles, as well as incineration, amongst others. In cities, vehicle exhaust, road dust re-suspension, and combustion of wood, coal, or other fuels for domestic heating are very important local sources.

Particulate matter may be directly emitted (e.g., from combustion) also called primary PM (PPM), or formed in the atmosphere via gas-to-particle conversion, often induced by chemical reactions of primary gaseous emissions, also called secondary PM. The most important precursor gases for secondary particles are sulphur dioxide (SO_2), nitrogen oxides (NO_X), ammonia (NH_3), and volatile organic compounds (VOC). The precursor gases SO_2, NO_X and NH_3 react in the atmosphere to form, respectively, sulphate ($\mathrm{SO_4^{2-}}$), nitrate ($\mathrm{NO_3^-}$), and ammonium ($\mathrm{NH_4^+}$) compounds that condense and form new particles in the air, called secondary inorganic aerosol (SIA). Certain VOCs are photo-oxidised to less volatile compounds, which form secondary organic aerosol (SOA). Both primary and secondary PM may have metals and persistent organic pollutants (POPs) in its composition.

When all of the previously mentioned main chemical components of the aerosol, including crustal material, sea salt, black carbon, dust, SIA and SOA are measured, they account for about 70% or more of the PM10 and PM2.5 mass. The rest of the PM mass is thought to be due to the presence of water or to the possible underestimation of the molecular mass ratio when estimating organic matter concentrations (Putaud et al, 2004).

Particles are not only classified according to their origin (primary/secondary) but also by size. PM2.5 refers to 'fine particles' which have an aerodynamic diameter of 2.5 μm or less. PM10 refers to the particles with a diameter of 10 μm or less. PM10 includes the 'coarse particles' fraction, i.e., particles with a diameter between 2.5 and 10 μm, in addition to the PM2.5 fraction. 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). Current regulation and guidelines use the concept of PM10 and PM2.5, i.e., particulate mass of particles with less than 10 μm or 2.5 μm in aerodynamic diameter, respectively. The reason for choosing a cut-off size of 10 μm is that it includes the inhalable particles, i.e., those that are small enough to reach the thoracic region. PM2.5 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 and entering the blood stream.

Particulate matter (PM) is the most important contributor to adverse health effects of air pollution (WHO, 2005). It is responsible for increased mortality and morbidity, primarily via cardiovascular and respiratory diseases (Schlesinger et al., 2006). In addition to effects on the human health, PM can also have adverse effects on climate change and ecosystems. Furthermore, PM contributes to soiling and can have a corrosive effect on materials and cultural heritage, depending on the PM composition. Finally, PM contributes to reduced visibility.

1.1 Effects of PM on human health

In terms of potential to harm human health, PM is one of the most important pollutants as it penetrates into sensitive regions of the respiratory and cardiovascular systems and can lead to health problems and premature mortality. Epidemiological studies attribute the most severe health effects from air pollution to PM. There is a large body of evidence on the health impacts of PM, as knowledge in this area has increased considerably over the last decades.

Health effects related to exposure to air pollution, including PM, are divided into short-term (due to exposure over a few hours or days and described as acute effects) and long-term (due to exposure over months or years and described as chronic effects). Health impacts are often quantified in relation to mortality and morbidity. Mortality reflects the reduction in life expectancy due to air pollution exposure. Morbidity relates to illness occurrence, ranging from minor effects such as coughing to serious conditions that may require hospitalisation.

The evidence base for the association between particulate matter observed at levels commonly present in Europe and short-term, as well as long-term, health effects has become much larger and broader. The latest study from the World Health Organization (WHO, 2013a) links long-term exposure to fine particles (PM2.5) with cardiovascular and respiratory premature deaths, as well as increased sickness, such as childhood respiratory diseases.

Not all people are affected by PM to the same extent. Susceptibility is dependent on personal characteristics like age, health status, etc., and exposure characteristics. The effects of PM are most pronounced among those with increased susceptibility such as infants, the elderly, and people with high body mass index (BMI) (Puett et al., 2009) or with chronic diseases such as diabetes (O’Neill et al., 2005) or asthma (Dales et al., 2009).

Health effects of PM are caused after their inhalation and penetration into the lungs and blood stream, leading to adverse effects in the respiratory, cardiovascular, immune, and neural systems. Ultrafine particles may penetrate into the brain through the nose (Breysse et al, 2013). Both chemical and physical interactions with lung tissues can induce irritation or damage. The smaller the particles, the deeper they penetrate into the lungs. PM's mortality effects are clearly associated with the PM2.5 fraction, which in Europe represents 40–80 % of the PM10 mass concentration in ambient air. However, the coarser 2.5–

10 µm fraction of PM10 also has health impacts and affects mortality (Meister et al., 2012; Tobías et al., 2011).

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 and < 2.5 µm) may preferentially affect the cardiovascular system. Ultrafine particles (UFP, diameter > 0.001 µm and < 0.1 µm) may also migrate via the lungs to other organs, like the liver, spleen, placenta and foetus, or even 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. Coarse particles (Brunekreef and Forsberg, 2005, Meister et al, 2012; Stafoggia et al., 2013) and ultrafine particles (Oberdörster, 2011; Strak et al., 2012; Breysse et al., 2013) have been associated with adverse health effects that can be different from those of the fine-particle fraction.

The chemical composition of particles plays also a significant role in the health effects attributed to PM (Rohr and Wyzga, 2012). 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 components within the particles. PM measured at traffic stations seems to have high oxidative activity, and emissions from traffic have been linked to a wide range of health effects, mostly with effects on the cardiovascular and respiratory systems and cancer incidence. It has also been associated with atopic sensitisation to allergens, poor birth outcomes, immunologic changes, decreased cognitive abilities (Currie et al., 2009; Hansen et al., 2008), and even development of autism (Volk et al., 2013).

There is also substantial epidemiological evidence of associations between health and sulphates that suggest that a reduction in exposure to sulphates (as part of the reduction of a mixture) has real health benefits. On the other hand, there is not much evidence for toxicity of airborne nitrates, which may be partly due to difficulties with measuring nitrates. A problem arises also with the 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 summed up in the 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 sulphate 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'. This conclusion is also supported by the latest WHO (2013a) review: "No new toxicological evidence has been presented to support a causal role for such inorganic secondary aerosols as ammonium, sulphates and nitrates.

However, epidemiological studies continue to report associations between sulphates or nitrates and human health“.

The World Health Organization (WHO) estimated that an increase of the daily mean PM10 concentration of 10 μg.m^{-3} leads to: 1) an increase in relative risk of mortality of 0.6%– 1.6%, 2) an increase in occurrence of asthma related problems and medication usage of 3%–5%, and 3) an increase of the number of daily hospital admission due to respiratory causes of 0.8% (WHO, 2000). As long-term exposure to PM results in a substantial reduction in life expectancy, the long-term effects have greater significance to public health than the short-term effects. PM2.5 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 annual mean PM2.5 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 PM2.5 (Pope et al., 2002, 2004). 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.

After a comprehensive review, Pope and Dockery (2006) concluded that “the literature provides compelling evidence that continued reductions in exposure to combustion-related fine particulate air pollution as indicated by PM2.5 will result in improvements in cardiopulmonary health”. In a 2009 study, Pope et al. concluded that “a decrease of 10 μg.m^{-3} in the concentration of fine particulate matter was associated with an estimated increase in mean (±SE) life expectance of 0.61 ± 0.20 year (P=0.004[1]).”

Based on the recent long-term studies showing associations between PM2.5 and mortality at levels well below the current annual WHO air quality guideline level for PM2.5 (10 μg.m^{-3}) corroborating earlier scientific evidence, it is suggested that there is no threshold below which no adverse health effects of exposure to PM would be anticipated (WHO, 2006a, 2006b, 2013a). Indeed, 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 current levels of PM exposure experienced by most urban and rural populations have therefore harmful effects on human health. The European Environmental Agency (EEA, 2015) estimates a total of about 4,8 million of years of life lost (YLL) and about 430 000 premature deaths due to exposure to PM2.5 in Europe in 2012. Mortality associated with air pollution is about 15–20 % higher in cities with high levels of pollution compared to relatively cleaner cities. In the European Union, average life expectancy is estimated to be 8.6 months lower due to exposure to PM2.5 resulting from human activities (WHO, 2014).

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[1] I.e. 99.6% confidence interval.

In summary, as threshold levels for PM concentrations below which no adverse effects occur have not been identified (i.e., a no-effect level), all reductions of PM concentrations in ambient air will have a positive health outcome. The current knowledge on the impacts of PM ambient air concentrations on human health provides therefore sufficient scientific arguments for actions to improve current concentration levels and reduce the burden of disease associated with PM concentrations in Europe. (WHO, 2013b).

1.2 Effects of PM on climate

Atmospheric particles are both an important air pollutant and a climate forcer. Suspended particulate matter (aerosols) and its chemical constituents influence the Earth's energy balance directly, through reflection and absorption of solar and infrared radiation in the atmosphere. In general, absorption of radiation leads to a positive forcing (increase in temperature), whereas reflection leads to a negative forcing (cooling of the atmosphere). One of the constituents of fine particulate matter, black carbon has a warming effect, while other constituents, for instance sulphates and nitrates, may cool the climate.

On the other hand, particles may also have indirect effects on the climate, as they play an important role in the formation, shape and duration of clouds, and influence the radiation properties of clouds and precipitation patterns. In addition, deposition of black carbon particles on snow and ice can contribute to raising temperatures locally, and an increased melting rate of the ice. The disappearance of snow or ice from the earth or sea surface will exacerbate global warming, as the property of reflecting sunlight (albedo) of the surface changes dramatically.

The complexity of particles characteristics and their uneven distribution and transformation in the atmosphere makes it very difficult to predict their direct and indirect role in the climate system. Current atmospheric models still lack a complete and detailed process description of the behaviour and effects of particles on the atmosphere, especially concerning aerosol-cloud interactions. Furthermore, and despite considerable advances since the IPCC's Third Assessment Report, the complex relations and feedback mechanisms between particles, climate and ecosystems (which also emit particles, depending on external conditions such as climate and atmospheric composition) are not fully understood nor fully described in the models (Solomon et al., 2007).

Particles mainly contribute to cooling the climate, even if some contribute to warming (such as black carbon and minerals containing specific copper and iron compounds). IPCC (Solomon et al, 2007) estimated the total direct effect of particles on climate to be -0.5 ±0.4 W/m^2, including both cooling effects and heating effects (the latter estimated to be 0.2 ±0.15 W/m^2 for black carbon). The total indirect effect of particles on climate forcing was estimated to be between -0.3 and -1.8 W/m^2. Ramanathan and Carmichael (2008) estimated considerably higher heating effects, due to black carbon particles. As indicated by UNEP/WMO (2011) and other studies some win-win strategies have been identified where reduction of greenhouse gas emissions like black carbon does not lead to increase of air pollution problems whereas the success of mitigation of climate change remains in the reduction of CO_2 emissions.

1.3 Other effects of PM

Fine particles (PM2.5) are the main cause of reduced visibility. When sunlight encounters fine particles in the air, the clarity and colour of what we see is reduced, resulting in visibility impairment in all directions over a large area. Secondary aerosols often grow in size as humidity in the air increases, further impairing visibility under humid conditions.

Particulate matter has also negative effects on the physical environment, e.g., infrastructure and buildings. PM deposition can stain and damage stone and other materials, including culturally important objects such as statues and monuments. Particularly deposition of acidic PM compounds can dirty buildings, structures, and e.g., vehicles, leading to increased maintenance costs and enhanced corrosion.

1.4 Sources and formation of PM

Various source sectors contribute to the primary anthropogenic PM. Commercial, institutional and household fuel combustion dominates the emissions of PPM in Europe, followed by transport and industry. In addition, the energy, agriculture, and waste sectors also contribute to the anthropogenic emissions of PM. There are also important natural sources of PPM; they are windblown dust, wildfires, sea salt spray, pollens and ashes from volcanos.

In addition to the natural and anthropogenic PPM emissions, PM concentrations are determined by contributions from secondary particles, divided into SIA and SOA, as previously mentioned. The formation of secondary PM depends on a variety of chemical and physical factors: 1) the concentrations of the main precursors; 2) the reactivity of the atmosphere which depends on the concentrations of highly reactive substances such as ozone (O_3) and the hydroxyl radical (•OH); and 3) on the meteorological conditions, like solar radiation (e.g., by influencing the formation of O_3), relative humidity and cloud cover.

In Europe, about one third of the PM10 concentration and half of the PM2.5 concentration in the regional background consist of SIA[2]. For example in 2010, SIA contributed to 35% of the PM10 mass in rural

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[2] Based upon the chemical speciation measurements of PM within the EMEP (European Monitoring and Evaluation Programme) station network. EMEP provides parties in the Long-range Transboundary Air Pollution (LRTAP) Convention with information on concentration and deposition rates of air pollutants transported across Europe and reaching rural background monitoring sites.

air in Europe, while Central Europe had the highest SIA contribution to rural background concentrations of PM10 in 2010 with around 50% (EMEP, 2012). SIA is composed by inorganic chemical substances such as ammonium (NH_4^+), nitrate (NO_3^-) and sulphate (SO_4^{2-}). These substances are the result of chemical reactions in the atmosphere involving the PM precursor gases: NH_3, NO_X and sulphur oxides (SO_X). The agriculture sector is by far the main emitter of NH_3 in Europe. The main emission sector of NO_X is transport, responsible for almost half of the total European emissions. Finally, the energy sector is the main emitter of SO_X, accounting for more than half of the total European emissions[3].

Sulphate forming reactions involve the gas phase conversion of SO_2 to sulphuric acid (H_2SO_4) and aqueous phase chemical reactions, which may occur in cloud and fog droplets or in liquid films on atmospheric particles. The rate of some of these reactions is enhanced by the presence of metals, e.g., iron (Fe) and manganese (Mn). The NO_2 portion of NO_x reacts in the gas phase with hydroxyl radicals and is oxidised to nitric acid (HNO_3) during the day. At night NO_x is mainly oxidized to HNO_3 by a sequence of reactions initiated by O_3. Both sulphuric and nitric acids thus formed react with NH_3 and form ammonium nitrate (NH_4NO_3) and ammonium sulphate $(NH_4)_2SO_4$. In addition, nitric acid may react with chemical substances in coarse particles and provide additional nitrate to the coarse particle fraction. Nitric acid behaves differently from sulphuric acid with respect to ammonia; sulphuric acid reacts irreversibly with ammonia, while nitric acid is in equilibrium with ammonia, therefore particulate ammonium nitrate can decompose back to gaseous ammonia and nitric acid. The gas-phase reaction of NO_2 with hydroxyl radicals is ten-times faster than the reaction with SO_2, therefore in winter more nitric acid is formed and much less sulphate is observed.

Organic substances contribute in average to about 30% of the PM2.5 concentrations and to about 20% of the PM10 concentrations in the European regional background[4]. Organic PM is composed of hundreds of individual chemical substances, some of which are semi-volatile, i.e., they may be both gaseous or condensed in the PM. Atmospheric reactions in the gas phase, fog and cloud droplets, as well as aqueous particulates, involve a variety of VOCs such as alkanes, olefins, aromatics, and organic compounds such as isoprene and terpenes released by vegetation, leading to the formation of organic end-products, including SOA. Volatile organic compounds react with hydroxyl radicals, O_3 and other substances in numerous interlinked chemical reactions to form a large suite of organic compounds. Atmospheric oxidation processes tend to reduce the vapour pressure of these species, increasing their condensation from gas to particulate matter and contributing to increase secondary PM. There is therefore a clear link between O_3 episodes and formation of organic PM.

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[3] Based on the EU emission inventory report 1990-2013 under the UNECE Convention on LRTAP (http://www.eea.europa.eu/data-and-maps/data/data-viewers/air-emissions-viewer-lrtap).

[4] Based upon the chemical speciation measurements of PM within the EMEP station network.

SOA is thus formed from VOCs and SVOCs emitted from anthropogenic sources (e.g., alkanes, aromatics and carbonyls) (Wei et al., 2008) and from biogenic sources (e.g., isoprene, terpenes and sesquiterpenes) (Guenther et al., 2000) and from anthropogenic sources. The main anthropogenic emission sector of VOC in Europe is industrial processes and product use[5].

Coarse particles are mainly of primary origin and are mostly mechanically generated (e.g., by abrasion). For example, soil dust, sea salt, and particles from abrasion of roads, tires and vehicles brakes are all primary particles mostly in the coarse fraction. Coarse particles are removed from the atmosphere by dry and wet deposition: concentrations of coarse particles are therefore higher near the sources.

In situ measurements and satellite observations have established the importance of intercontinental transport of PM from arid regions, forest fires, and anthropogenic sources. Studies have shown that due to atmospheric transport and chemistry processes, particle formation can take place at long distances from the sources of precursor gases. However, gaps remain in the knowledge and understanding of aerosol particle properties and direct aerosol and aerosol precursor emissions fluxes (pollution, dust, biomass-burning emissions) between continents (UNECE, 2010).

1.5 Current challenges associated with management of PM levels

The levels of particulate matter (PM) across Europe continue to cause significant negative impacts on human health and PM is considered the main air quality problem in Europe (EEA, 2013). About 33% of the EU urban population lives in areas where the EU air quality 24-hour limit value for PM10[6] was exceeded in 2011, while 88 % of the EU urban population was exposed to PM10 levels exceeding the WHO air quality guideline[7] in 2011 (Guerreiro et al., 2014). Furthermore, concentrations of PM2.5 measured at both urban and rural background stations tended to increase on average between 2006 and 2011. Several countries have registered increasing trends of PM2.5 annual mean concentrations in the period 2006-2011, indicating that the development is clearly not satisfactory across Europe (Guerreiro et al., 2014).

Further decrease in PM2.5 levels is needed in order to meet the targets set by the Directive (EU, 2008), particularly the National Exposure Reduction Targets (NERT) for PM2.5 for the period 2010-2020, based on urban background measurements.

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[5] Based on the EU emission inventory report 1990-2013 under the UNECE Convention on LRTAP.

[6] 50 $\mu g.m^{-3}$, not to be exceeded more than 35 days a year.

[7] 20 $\mu g.m^{-3}$ as an annual mean.

Air pollution and greenhouse gas (GHG) emissions often relate to the same sources, hence GHG reduction measures (e.g., on power generation and transport) can deliver substantial reductions also of air pollutants such as NO_2, SO_2, O_3 and PM and vice-versa. Measures to cut, e.g., black carbon will have double benefits, protecting both human health locally and the climate (Shindell et al, 2012). However, decarbonisation tends not always towards reducing emissions of PM, one of the air pollutants of highest concern. Large scale introduction of biomass to replace fossil fuel combustion as part of a climate change policy may lead to substantially higher emissions of PM and other carcinogenic substances such as Polycyclic Aromatic Hydrocarbons (PAHs), including BaP.

Implemented European policies have been little effective in reducing the environmental impacts from agricultural activities, while other activity sectors such as transport, energy and industry have achieved considerable reductions of their emissions to air. For example, the emission of ammonia from agriculture has only been reduced by about 7% over the last decade, despite its important impact on ecosystems, e.g., eutrophication and acidification leading to loss in biodiversity and ecosystem services, and its role in PM formation.

To reduce the negative effects of air pollution on human health or natural eco-systems, it is useful to model the impact of different mitigation measures and policies on the reduction of pollution levels and ultimately on the reduction of effects. This allows to determine an optimal regulation strategy, targeting activity sectors that may have been overlooked, before planning and implementing policy and regulatory measures.

THEORETICAL PART

2 Problem definition

As mentioned in the previous chapter, PM levels have not decreased enough in the last decade, exceedances of the PM standards occur over large areas, and considerable health effects are still associated with exposure to ambient air PM in Europe.

While significant emission reductions of PPM and PM precursors have been achieved by the industry and transport sectors, little has been achieved in the agricultural and household fuel combustion sectors (EEA, 2014b).

Although ammonium (NH_4^+, formed by the protonation of NH_3) constitutes only a small fraction of the PM mass, it plays a decisive role in the formation of SIA, determining the amounts of ammonium sulphate ($(NH_4)_2SO_4$)) and ammonium nitrate (NH_4NO_3) as PM constituents. The agricultural sector is responsible for more than 90% of the NH_3 emissions in Europe, and several studies point out the importance of agricultural NH_3 emissions to PM concentrations in different European regions, highlighting the need to investigate the potential of NH_3 emission reductions to reduce PM levels over Europe. Reducing NH_3 emissions is pointed as an effective way of reducing SIA concentration levels, thus PM concentration levels, including the number of PM10 daily limit exceedances (Erisman and Schaap, 2004; Putaud et al., 2010).

Emissions of primary PM2.5 and BaP from commercial, institutional and household combustion have been increasing, respectively, by 11 % and 24 % in the EU28 between 2003 and 2012 (EEA, 2014b). BaP is a better indicator for emissions from this sector, since it emits about 85% of total emissions of BaP in the EU28 in 2012 (EEA, 2014b). While concentrations of PM, NO_2 and O_3 and their health impacts are regularly estimated for the whole Europe, much less has been done regarding the estimation of BaP concentrations, exposure and health effects. It is therefore important to improve the estimation of current BaP concentrations over the whole Europe, and of its associated population exposure and health impacts, in order to discuss necessary mitigation measures targeting emissions of PAHs.

2.1 Part 1: Household combustion: contribution to BaP emissions and its impact on health

Particulate matter has been classified recently as carcinogenic (Loomis et al, 2013). PM is constituted by several chemical compounds that contribute to its carcinogenic and health effects. PAHs are considered among the most dangerous air pollutants due to their carcinogenic and mutagenic character. They possess high carcinogenic potential to animals and humans and are bio-accumulated in the food chain. The PAHs with highest carcinogenicity are attached to airborne particles.

Polycyclic aromatic hydrocarbons (PAHs) is a class of complex organic chemicals of increasing concern for their occurrence in the environment and effects. The term commonly refers to a large class of organic compounds, containing mainly carbon and hydrogen and are comprised of two or more fused aromatic rings (also called benzene rings). The smaller PAHs with 2 to 4 rings are volatile and are found in the gas phase to a higher degree than the 5- to 7-ring PAHs, which occur mainly or entirely as particles (PM2.5 and PM10) (Possanzini et al., 2004). PAHs with low vapour pressures emitted from combustion or other high temperature sources (e.g., Benzo(a)pyrene - BaP) are typically associated with particulate matter of small size (<1µm) (Sheu et al., 1997). Due to their low vapour pressure and large molecular weight, PAHs are believed to contribute to the fine particulate matter toxic potential (Dejmek et al., 2000; Binkova and Sram, 2004; Ohura et al., 2004; Hertz-Picciotto et al., 2007; Rubes et al., 2007; Soucy et al., 2007; Sram et al., 2011; 2013).

PAHs associated with particulate matter can be transported over long distances in the atmosphere (Bjørseth et al., 1979) resulting in a widespread distribution on the continental scale. Due to their toxic and ecotoxic characteristics PAHs pose a threat to humans and the environment, and the international community has therefore implemented policies to reduce their emissions. The Protocol to the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) on POPs[8] (UNECE, 1998) obliges the parties to report PAH emissions[9] and has as objective to control, reduce or eliminate discharges, emissions and losses of POPs, including PAHs.

BaP has five aromatic rings and is the most widely investigated PAH as a marker for the carcinogenic risk of PAHs in ambient air. Around 90% of BaP in ambient air is adsorbed onto aerosols and around 10% is in the gas phase. It has been classified as carcinogenic to humans (IARC, 2012). The European directive (EU, 2004) sets a target value for ambient air concentration of BaP, as a marker for the carcinogenic risk of PAHs in ambient air, in order to avoid, prevent or reduce harmful effects of PAHs on human health and the environment as a whole. The target value for BaP (measured in PM10) was set to 1 $ng.m^{-3}$ as an annual mean, to be met by 2013.

Guerreiro et al. (2014) identified the increase in BaP emissions from domestic combustion in Europe over the last years as a matter of concern, as it contributes to the increased exposure of the European population to BaP concentrations, especially in urban and suburban areas.

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[8] Persistent organic pollutants (POPs) are organic substances that: (i) possess toxic characteristics; (ii) are persistent; (iii) bioaccumulate; (iv) are prone to long-range transboundary atmospheric transport and deposition; and (v) are likely to cause significant adverse human health or environmental effects near to and distant from their sources.

[9] Annex III of the Protocol specified four indicator PAHs for emission inventories: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene.

2.1.1 *Health effects*

The carcinogenicity of PAH in humans seems to be beyond dispute (Adonis and Gil, 2000; Dejmek et al., 2000; Deng et al., 2006; Massolo et al., 2002; Pohjola et al., 2003; Strandell et al., 1994). In a series of monographs (see, for example, IARC, 1987), the International Agency for Research on Cancer has evaluated a number of PAH-containing materials or mixtures and occupational situations in which exposure to PAH occurs. In the latest review of human carcinogens, IARC (2012) concluded: “The strong and extensive experimental evidence for the carcinogenicity of BaP in many animal species, supported by the consistent and coherent mechanistic evidence from experimental and human studies provide biological plausibility to support the overall classification of BaP as a human carcinogen (Group 1).”

BaP is therefore a widely used indicator for carcinogenic PAHs, even if it may only explain about half of the PAH overall carcinogenic potency. In addition, WHO (2013a) has found new evidence linking PAH exposure to cardiovascular morbidity and mortality, although at present the effects of PAH exposure cannot be easily separated from those of particles.

PAHs can be absorbed through the respiratory tract, both through inhalation of tobacco smoke and ambient air, gastrointestinal tract (diet is the main route of exposure to PAHs in the general population), and skin. Most studies to date have not considered all routes of exposure (IARC, 2010; Reid et al., 2012). After absorption into the human body, PAHs may be altered into substances that can damage the genetic material cells and initiate the development of cancer, although individual PAHs have different capacities to damage cells thus.

There is strong evidence for the relationship between PAHs exposure and lung cancer (Boström et al., 2002). Other health effects include increased incidence of skin, bladder and urinary system cancers in humans, though there is less evidence for these than for lung cancers (Armstrong et al., 2003; Bosetti et al., 2007). Long-term exposure to PAHs has also been associated with gene mutation (Taioli et al., 2007), cell damaging and increased risks of cardiopulmonary mortality. Furthermore, several studies have shown that prenatal exposure to airborne PAHs adversely affects children’s cognitive development and behaviour (Perera et al., 2006, 2009, 2012, 2014; Edwards et al., 2010). BaP has also been reported to have other adverse health effects than cancer, including significant reproductive and developmental effects (ATSDR, 1995; Ramos et al., 1996; IPCS, 1998; NIOSH, 2002). Kim et al. (2013) has recently published a review of health effects of airborne PAHs.

It summarises the health effects of PAHs as follows:

- Short-term effects
    - Eye and skin irritation,
    - Nausea and vomiting,

    - Inflammation;
- Longterm effects
    - Skin, lung, bladder, and gastrointestinal cancers,
    - DNA, cataracts, kidney and liver damage,
    - Gene mutation, cell damaging, and cardiopulmonary mortality.

In ambient air a number of individual PAH can be found (see, for example, Brown et al, 2013; Garrido et al., 2014). The carcinogenic potency varies widely over the PAH. Although BaP is not the most abundant pollutant, its carcinogenic potency is amongst the highest (Boström et al., 2002; Collins et al., 1998; Amarillo et al., 2014).

BaP alone will underestimate the carcinogenic potential of ambient PAH mixtures since co-occurring substances are also carcinogenic. Holland et al. (2001) estimated that BaP makes a contribution to the overall carcinogenicity of reported PAH mixtures of between 5% and 41%. Given that the relative contributions of more potent PAHs, such as dibenzo[a, l]pyrene (Pufelete et al., 2004), in ambient air have not been adequately evaluated and there are only limited data on their presence and formation, it is possible that their relative contribution to the carcinogenic activity of a total PAH mixture is far greater than that of BaP. Thus, further work is required to investigate the potential role of high potency PAHs in air pollution related lung cancer (Okona-Mensah et al., 2005). Nevertheless, in view of its carcinogenic potency and its abundance in the PAH mixture, BaP is widely used as an indicator.

2.1.2 *Sources of BaP and development in emissions*

Depending on their formation mechanism, PAHs may be classified into pyrogenic (from incomplete combustion or pyrolysis of organic material at elevated temperatures), petrogenic (from the transformation of biogenic organic materials such as fossil fuels at moderate temperatures), diagenic (from the transformation of organic material in soils and sediments), and biogenic (synthesized by organisms) (Neff, 2002). The first two kinds are clearly predominant in the environment, with the most important sources being anthropogenic from incomplete combustion of organic fuels (residual oil, wood, coal, gasoline and diesel). Natural sources of PAHs, with much less incidence than anthropogenic ones, are forest fires and volcanic eruptions (Ravindra et al., 2008).

PAH and BaP emissions are reported by the countries under the UNECE Convention on LRTAP. Figure 1 shows the contribution (in %) of the main emission sectors to BaP emissions in the 20 countries of the EU28 that reported emissions in 2012. Household combustion is by far the most important sector, contributing to 82.4 % of the total BaP emissions, mainly from wood- and coal-burning. Other sources are solid fuels transformation, aluminium production, natural emissions, and road traffic.

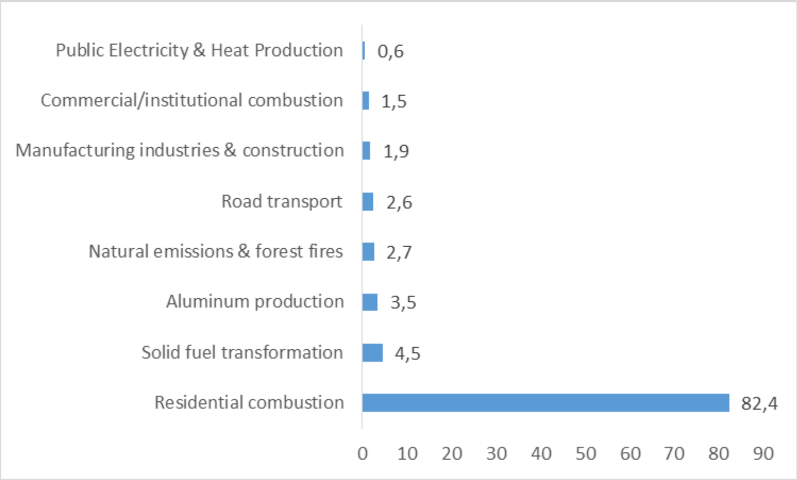

Figure 1: ***Officially reported emissions of BaP in 2012 (20 countries of EU28) by the main sectors and in % of total (source: EEA, 2014a).***

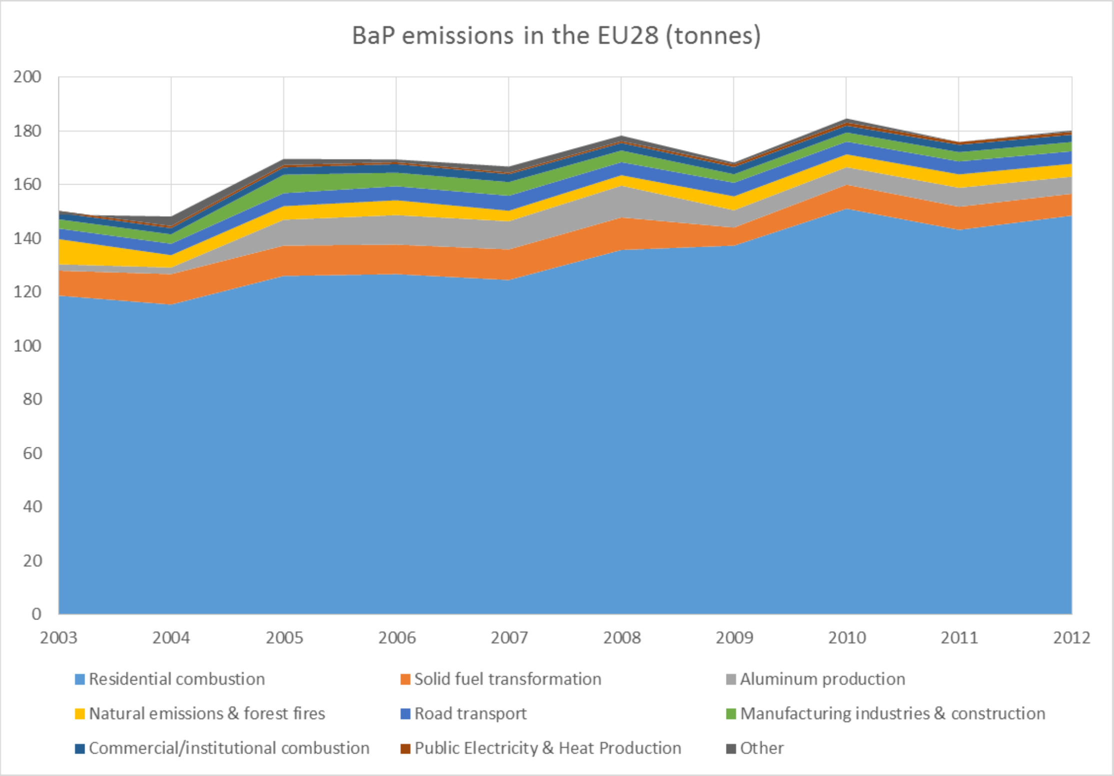

Figure 2: ***Development of BaP emissions in 21 countries in the EU28 from 2003 to 2012 in total and for the main emission sectors (source: EEA, 2014a).***

The development in the officially reported emissions of BaP from 2003 to 2012 is shown in Figure 2 for the same 20 countries and for Luxembourg, which reported emissions in a few years. The household combustion sector has been the dominating emission sector over the period and the BaP reported emissions for this sector have increased by 25 % between 2003 and 2012. This increase may be partially due to an increase in the use of biomass (e.g., wood) and solid fuels (e.g., coal) for domestic heating, due to either government incentives to increase the use of renewable fuels (i.e., biomass), or to increasing costs of other energy sources and in response to economic hardship (Saffari et al., 2013; Sarigiannis et al., 2015).

To corroborate these hypotheses, Figure 3 shows the increase in household combustion emissions of BaP, total PAHs and PM2.5, between 2003 and 2012, as a percentage of the total reported emissions in the EU28. In addition, Figure 4 shows the development in the solid fuel[10] and biomass[11] consumption in the residential sector as a percentage of the total fuel consumption in the sector (left) and in terajoules (right). It shows a clear increase (by 27%) in the use of biomass for domestic heating, while the consumption of solid fuels only had a small increase (12%).

Household combustion was responsible for, respectively, 49%, 64% and 82 % of the total anthropogenic emissions of PM2.5, total PAHs and BaP in 2012 and its importance has increased the last 10 years as shown in Figure 3. Thus, domestic heating is an important source of air pollutants harmful to human health and the environment.

The use of biomass, including wood, for domestic heating has clear climatic benefits due to the low net GHG emissions. The EU counts on biomass heating to play a very important role in meeting its “20-20-20” targets. Solid biomass for heating was the main renewable energy technology in 2012 in the EU28 accounting for 43 % of all renewable energy source (RES) share (EEA, 2014d). Its use is expected to increase further and remain the main RES in 2020. However, household combustion of biomass has important impacts on local and regional scale air quality, with relatively high PM emissions and PAHs emissions, including BaP, as shown above. It is therefore important to assess better the level and development of BaP concentrations in Europe, in order to quantify its impacts on human health. This will also support a better understanding and quantification of the impacts of climate policies promoting the use of biomass for domestic heating, leading to an increase in BaP emissions in populated areas.

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[10] Solid fuels include mainly coal and coal briquettes.

[11] Biomass includes wood/wood waste, charcoal and other primary solid biomass.

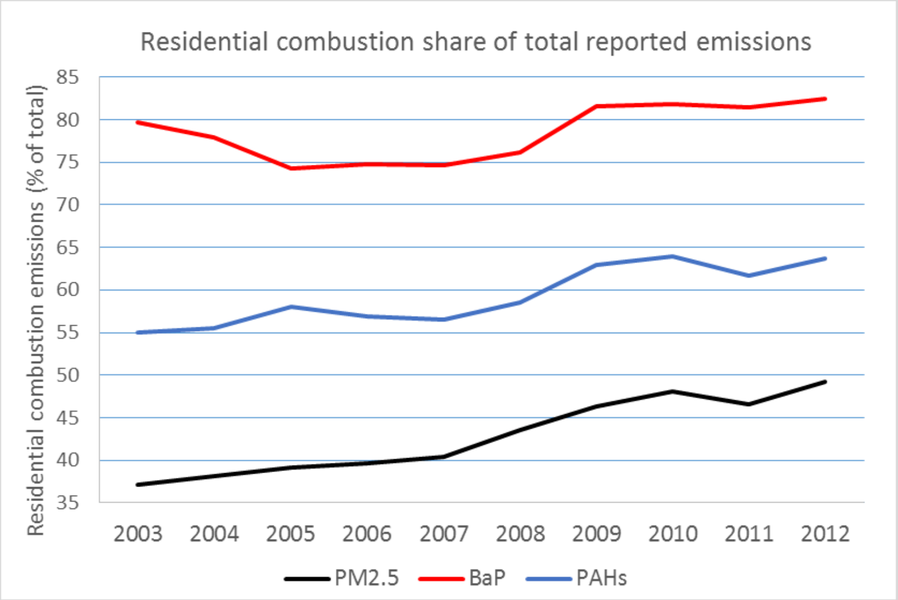

Figure 3: ***Development of the household combustion emissions share (in %) of total reported emissions of BaP, PAHs and PM2.5 in EU28 from 2003 to 2012 (source: EEA, 2014a).***

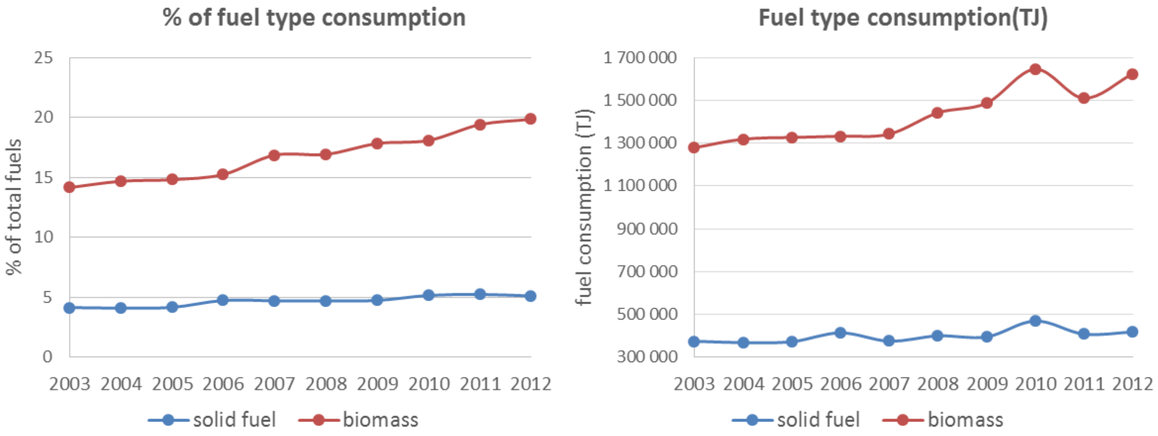

Figure 4: ***Development of the use of solid fuels and biomass in household combustion. Left: as a % of total fuels consumption in the sector; Right: as total emissions (source: EEA, 2014d).***

EMEP's analysis on emission and concentration trends in BaP goes back to 1990. EMEP (2013) concludes that the reduction of PAH pollution levels was more significant during the 1990s. In particular, BaP air concentrations in the EU countries dropped by 38% from 1990 to 2000. However, after 2000 the decreasing trend was almost levelled off and during the recent years BaP air concentrations in more than half of the EU countries tended to increase following the growth of their emissions (EMEP, 2013). Furthermore, EMEP (2014) concludes that for about 70% of the EMEP countries the contribution of transboundary transport to deposition of BaP over their territory exceeds the contribution of national emission sources.

2.2 Part 2: Agriculture: contribution of NH_3 emissions to secondary PM and reduction potential

2.2.1 *Contribution of agriculture to NH_3 emissions*

Agriculture is the main sector responsible for the NH_3 emissions, an important precursor of PM. In 2011, agriculture was responsible for 93% of the total NH_3 emissions in the EU27 (EEA, 2013a). These emissions are of main concern as they lead to both local and regional problems, such as health impacts due to PM exposure, and to two of the most important effects of air pollution on European ecosystems, i.e., acidification and especially eutrophication.

While continuous progress in emission reductions has been observed in other sectors, air pollutant emissions from agriculture has decreased very little over the last 10 years. Among the main air pollutants, NH_3 emissions declined the least (by only 7%) in the EU27 in the period 2002–2011, while other PM precursor emissions as NO_X decreased by 27%, NMVOC by 28%, and SO_2 by 50% in the same period. NH_3 emissions have actually increased by 0.4 % from 2010 to 2011, mainly due to emission increases in France and Germany (EEA, 2013a). Furthermore, three countries exceeded their NH_3 emission ceilings in 2011, as set in the NEC Directive (EU, 2001) which should have been reached in 2010: Germany by 2.4%, Spain by 7.8%, and Finland by 20% (EEA, 2013b; EEA, 2014a).

The most important sources of NH_3 emissions in the EU27 are livestock farming, especially cattle and swine, accounting for 54% of the total NH_3 emissions in the EU27 in 2011, followed by the application of synthetic nitrogen fertilizers, which contributed to 20% of the total NH_3 emissions. Poultry farming was responsible for 10% of the total NH_3 emissions in the EU27 in 2011.

2.2.2 *Importance of NH_3 emissions to PM formation*

Several studies highlight the importance of agricultural emissions to PM concentrations, and particularly of NH_3 emissions to PM2.5. For example, Deutsh et al. (2008) estimates that the Flemish agricultural emissions contribute to 12% of the PM2.5 levels in Flanders, and to 22% of the PM10 levels in Flanders. The high contribution of agricultural emissions to PM10 is predominantly due to high emissions of primary particles in the coarse fraction, while the high contribution of the agricultural emissions to the PM2.5 is due to the formation of ammonium nitrate and ammonium sulphate in the atmosphere. According to Deutsch et al. (2008) NH_3 emission abatement should be considered in order to reduce PM2.5 levels. Erisman et al. (2008) estimate that NH_3 emissions from agriculture in EU15 give a substantial contribution to PM formation in Europe (13%), as well as acidifying emissions (31%) and especially eutrophying emissions (45%) of ecosystems. It states further that much larger NH_3 emissions reductions than foreseen in current legislation should be aimed at, in order to meet targets on acidification, eutrophication and PM concentrations.

The sensitivity of secondary PM formation to NH_3 and other precursor gases emissions has been investigated in different studies. Erisman and Schaap (2004) has investigated the role of ammonia in particle formation and found that secondary PM can only be efficiently reduced if ammonia emissions are reduced in much the same way as SO_2 and NO_x emissions. They state that after the neutralisation of sulphate, nitrate may (partially) compensate for the decline in sulphate (due to SO_2 emission reductions), especially at low temperatures. The results of their modelling exercise using the LOTOS-EUROS model showed that, except for south-western France and Spain, where temperatures are generally high and relative humidity low, ammonia emission reductions are more effective for decreasing Secondary Inorganic Aerosol (SIA as the sum of sulphate, nitrate and ammonium) than SO_2 and NO_x emission reductions.

The EURODELTA II study (Thunis et al, 2008) showed that the relative effectiveness of different emission reductions (NO_x, SO_2, NMVOC[12] and NH_3) for PM2.5 concentration reduction may vary considerably within Europe. The effectiveness of NH_3 emission reductions in the UK is large compared with NH_3 reductions in other countries and much greater than the effectiveness of reduction of other precursor emissions. In the other countries the ammonia effectiveness is less than or similarly to NO_x or SO_2 emission reductions.

For a rural location in southern England, Derwent et al. (2009) examined the linearity of the formation of the secondary PM components by sensitivity studies to 30% reductions in SO_2, NO_x, NH_3, VOC, and CO emissions. The chemical environment revealed by these sensitivity studies appeared to be "ammonia-limited" and the PM mass concentrations appeared to be markedly non-linear with PM precursor emissions. The largest reduction in PM2.5 mass is modelled for a 30% reduction in NH_3 emissions; however, all precursor reductions except NH_3 result in a reduction in nitrate in coarse PM. The increase in coarse nitrate by reduced NH_3 emissions is described to the interaction between nitric acid, ammonia and sea salt. They have therefore concluded that policy strategies for PM2.5 need to take into account emission reductions for a wide range of PPM components and secondary PM precursors and to focus primarily on the abatement of NH_3. They say further that better understanding of this complex interlinking between emissions and PM formation may help to explain why PM levels have remained constant despite falling PPM emissions.

Similarly Harrison et al. (2013) modelled concentrations of SIA in PM10 at a rural site in Harwell (UK) for a relatively high pollution period (19 March – 19 May 2007). The response of concentrations at Harwell to reductions of precursor emissions (SO_2, NO_x and NH_3) for 1) across the UK only, 2) mainland Europe only, and 3) the whole of Europe has been modelled. As in earlier studies, they showed that the total reductions in SIA concentrations are less than linear with the emission reductions for all precursors.

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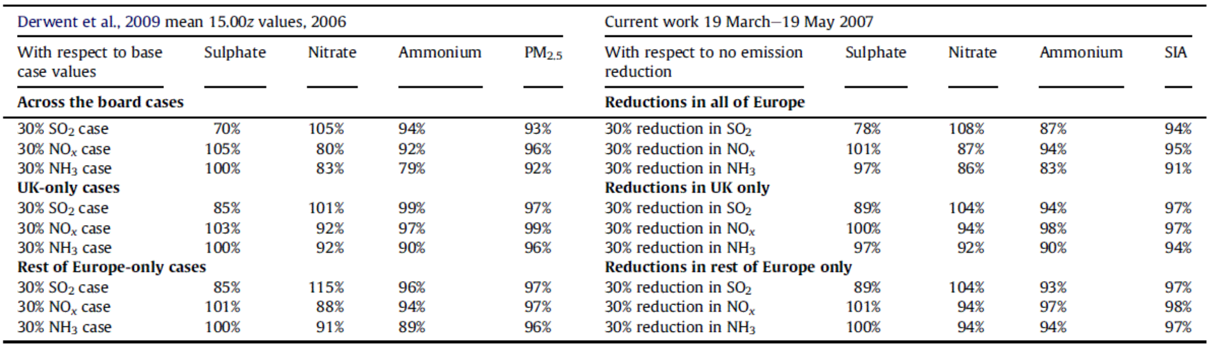
[12] Non Methanic Volatil Organic Compounds

They also showed that the abatement of SO_2 emissions leads to an increase in nitrate concentrations whereas reductions of NO_x lead to increases in sulphate. Further, they predict a low response of nitrate aerosol concentrations to NO_x emission reductions. Table 1 shows the results of this study and compares them with the previous study by Derwent et al. (2009) in terms of concentrations (at the same rural site in Harwell) of sulphate, ammonium and PM2.5 due to 30% emission reductions of SO_2, NO_x or NH_3, and compared to no emission reductions. Both studies give very similar results and the 30% emission reduction of NH_3 over the whole Europe leads to the highest reduction in SIA concentrations (9%) at the modelled site. Comparatively, a 30% reduction in NO_x and SO_2 emissions lead to a 5% and 6% reduction in SIA concentrations, respectively.

Table 1: Comparison of Derwent et al. (2009) and Harrison et al. (2013) concentration results of nitrate, sulphate, ammonium and PM2.5 (compared to reference) due to emission reductions of SO_2, NO_x and NH_3 (Table 1 in Harrison et al., 2013)



Derwent et al., 2009 mean 15.00z values, 2006					Current work 19 March–19 May 2007				
With respect to base case values	Sulphate	Nitrate	Ammonium	$PM_{2.5}$	With respect to no emission reduction	Sulphate	Nitrate	Ammonium	SIA
Across the board cases					**Reductions in all of Europe**				
30% SO_2 case	70%	105%	94%	93%	30% reduction in SO_2	78%	108%	87%	94%
30% NO_x case	105%	80%	92%	96%	30% reduction in NO_x	101%	87%	94%	95%
30% NH_3 case	100%	83%	79%	92%	30% reduction in NH_3	97%	86%	83%	91%
UK-only cases					**Reductions in UK only**				
30% SO_2 case	85%	101%	99%	97%	30% reduction in SO_2	89%	104%	94%	97%
30% NO_x case	103%	92%	97%	99%	30% reduction in NO_x	100%	94%	98%	97%
30% NH_3 case	100%	92%	90%	96%	30% reduction in NH_3	97%	92%	90%	94%
Rest of Europe-only cases					**Reductions in rest of Europe only**				
30% SO_2 case	85%	115%	96%	97%	30% reduction in SO_2	89%	104%	93%	97%
30% NO_x case	101%	88%	94%	97%	30% reduction in NO_x	101%	94%	97%	98%
30% NH_3 case	100%	91%	89%	96%	30% reduction in NH_3	100%	94%	94%	97%

Renner and Wolke (2010) found that a reduction of 50% in the NH_3 regional emissions from agriculture in Germany lead to a maximum reduction of 30% in ammonium nitrate concentrations, while ammonium sulphate remained unchanged.

Another study by Megaritis et al. (2012) found that reducing NH_3 emissions seems to be the most effective control strategy for reducing PM2.5, when compared to reductions of other precursor gases, mainly due to a significant decrease of ammonium nitrate. Their modelling results indicated an average reduction of PM2.5 concentrations over Europe of 5.5% during summer and 4% during winter, due to a 50% reduction in NH_3 emissions. While for a 50% reduction in NO_x and SO_2 emissions, the simulated PM2.5 reductions were, respectively, 5% and 5.1% in summer and 0,4% and 2,6% in winter. Megaritis et al. (2012) findings for winter are consistent with other studies (Tsimpidi et al., 2007; Odman et al., 2009; Aksoyoglu et al., 2011). During summer, the 50% NH_3 emission reduction resulted in a decrease of ammonium by 22% over the entire model domain. Nitrate was reduced by 35% in Western Europe and by 27% in southwest Europe, while the corresponding decrease of total PM2.5 in these areas was 15% and 10%, respectively. Similarly, in winter ammonium was reduced by 24% over the domain, with an average 20% decrease in nitrate concentration. Overall, ammonium nitrate reduction accounts for almost 80% of total PM2.5 reduction in both periods. The reduction of NH_3 produces also a slight decrease of sulphate levels due to the effect of NH_3 on cloud pH and on the rate of in-cloud sulphate production.

Pay et al. (2012) found on the other hand that the continental regions in Europe tend to be HNO_3 limited for nitrate formation, rather than NH_4-limited. They concluded that the formation of SIA in Europe tends to be limited by SO_2 and HNO_3 gaseous precursors due to the relatively high NH_3 emissions, mainly from agriculture, especially in north-western Europe. Therefore, they recommend regulatory strategies in this part of Europe to be focused on the reduction of NO_x and SO_2 rather than NH_3 emissions. The comparison of their modelling results with EMEP measurements has nevertheless shown that the model overestimates the ratio Free ammonia[13]/Total-NO_3 over the Iberian Peninsula and at some coastal stations in north and north-east Europe, indicating that these areas are more NH_4-limited than the model results suggest.

A study in the Netherlands (Weijers et al., 2010) showed that the SIA contribution to PM10 and PM2.5 in the Netherlands is higher than previously thought, pointing to a need to focus more on the mitigation of PM precursors emissions in the Netherlands and in Europe in order to attain PM limit values. They found that SIA dominates the PM composition, especially when increased PM levels occur. The average contribution of SIA to PM10 in the Netherlands was estimated to be 30% to 40%, increasing to between 45% and 55% on days when PM10 was above 40 $\mu g.m^{-3}$ and becoming 25% to 35% when PM10 was less than 40 $\mu g.m^{-3}$. Long-range transport and meteorology are the main factors influencing these higher levels.

2.2.3 ***NH_3 Emission Control and Mitigation Measures***

The best available control measures for mitigation of NH_3 emissions from agriculture are summarized and discussed in this section. This analysis is the background to determine what are feasible scenarios of NH_3 agriculture emission reduction for Europe.

The most important sources of NH_3 emissions in the EU are livestock production, especially animal manures, followed by the application of synthetic nitrogen fertilizers.

Animals utilize only a fraction (5% to 45%) of the available nitrogen (N) in the feeding for the production of meat, milk, eggs and offspring. The greater part is excreted via urine and faeces, which is either stored and managed for some time in manure storage systems, or deposited directly on land and allowed to decompose. Following storage, manure is applied to agricultural land to fertilize crops

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[13] Free ammonia indicator quantifies the amount of ammonia available, after neutralizing SO_4^{2-}, for NH_4NO_3 formation. This indicator is based on the fact that $(NH_4)_2SO_4$ aerosol is the favored form for sulfate. Free ammonia is defined as the total ammonia minus twice the sulfate concentration on a molar basis.

including grasslands. However, only about 30% to 60% of the manure N will be utilized by growing crops for the production of plant protein, and only the protein in the harvested fraction of the crop will feed people or livestock. Therefore, in a livestock farming system less than 10% of the N from manure is exported from the farm as animal products (i.e., meat, milk and eggs), and the greater part is dissipated into the environment (Oenema and Velhof, 2007).

Significant losses of gaseous N compounds occur via volatilization of NH_3. Emissions of NH_3 occur during various stages of the animal production and manure management:

1) Animal feed,
2) Animal manure excreted in housing systems and in pasture,
3) Animal manure in storage systems, and
4) From animal manure applied to cropland.

In addition, NH_3 emissions occur from the application of synthetic nitrogen fertilizers, especially urea- and ammonium-based nitrogen fertilizers. Figure 5 schematically shows the key sources of ammonia from livestock and crop production.

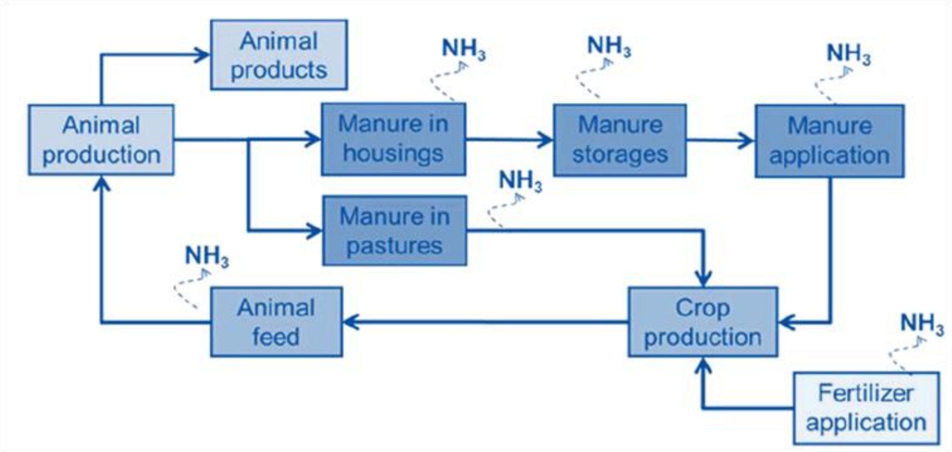

Figure 5: ***Key sources of ammonia from livestock and crop production (Source: Oenema and Velthof, 2012).***

Methods to control and mitigate ammonia emissions from agriculture have been developed and tested for several decades. A range of emission control options is now proven in practice in more and more countries for the major sources of agricultural ammonia emissions (e.g., animal manure and urea fertilizer application). Furthermore and because of learning effects, the practical functioning of these techniques has been improved and costs have declined. This section summarizes a review of the main control and mitigation measures for NH_3 emissions from agriculture reported in Oenema et al (2007), Oenema and Velthof (2007), Witzke and Oenema (2007), Döhler et al (2011), Oenema et al (2011), and most recently in Oenema and Velthof (2012) and UNECE (2012a).

It is important to note that emission reduction efficiencies of the different available abatement measures depend on the chosen reference system and on local factors, such as climate and soil conditions, differences in management practices and in the technical performances of abatement measures. Further, these categories of measures may affect each other's effectiveness and efficiency. The applicability of these measures and their costs will also vary across countries, depending on types of farms, their size, methods commercially available and experience. Costs tend to be higher on small farms in countries with little experience, and lower on large farms in countries with lots of experience.

Ammonia emission abatement measures are categorized as follows (UNECE, 1999):

- Nitrogen management, taking account of the whole nitrogen cycle;
- Livestock feeding strategies;
- Low-emission animal housing systems;
- Low-emission manure storage systems;
- Low-emission manure spreading techniques;
- Possibilities for limiting ammonia emissions from the use of mineral fertilizers.

Nitrogen management

Nitrogen management is seen as an integral measure of the whole nitrogen cycle, which may affect all sources of NH_3 emissions and help to prevent pollution swapping between different sources, nitrogen compounds and environmental compartments. It is based on the premise that decreasing the nitrogen surplus and increasing nitrogen use efficiency contributes to lower emissions of NH_3. On mixed livestock farms, between 10 to 40% of the nitrogen surplus is related to NH_3 emissions, while the remaining part will be lost through N leaching and denitrification (Oenema and Velthof, 2012; UNECE, 2012a).

Oenema et al (2011) provides a conceptual framework for developing integrated approaches to N management. The 'optimum' level of integration depends on many factors (e.g., farm type), and it remains a challenge to define such optima for various situations and cases. The integral approach can be seen as an extension to known abatement options that would allow to avoid losses and to better provide agricultural production (animals, plants) with the needed nitrogen amounts. The principles in the nitrogen management to decrease emissions of N are (UNECE, 2012a):

- All N sources on the farm are fully considered in a coherent whole-farm perspective and a whole N cycle perspective;
- All N sources are stored and handled properly;

- Amounts of N used are strictly according to the needs of growing plants and animals;
- Nitrogen sources are used in a timely manner, using the appropriate techniques, in the appropriate amounts and appropriate place;
- All possible N loss pathways are considered in a coherent manner.

Animal feeding strategies

The quantity of nitrogen excretion in animal faeces and urine is linearly dependent on the intake of nitrogen in food (protein). For example, about 65% of the nitrogen ingested by pigs is not used for growth and is excreted. Feeding according to the protein requirements of the animals reduces the oversupply of protein, leading to a reduction in nitrogen excretions and thus a decrease in ammonia emissions.

Feeding strategies are implemented through:

- phase feeding,
- low-protein feeding, with or without supplementation of specific synthetic amino acids and ruminal bypass protein,
- increasing the non-starch polysaccharide content of the feed,
- supplementation of pH-lowering substances, such as benzoic acid.

Phase feeding is an effective and economically attractive measure. It implies adapting the amount of proteins in the food to the needs of the animals. For instance, young animals and high-productive animals require more protein than older, less-productive animals. In average, this measure leads to a NH_3 emission reduction of 10% for a 1% reduction in the mean protein content in the diet, but efficiencies depend strongly on the animal categories. These strategies decrease ammonia emissions from manure in housing, storage and during application to crop land (UNECE, 2012a).

Low-protein animal feeding is one of the most cost-effective ways to reduce NH_3 emissions. It has no implications on animal health as long as the requirements for all amino-acids are met. It is most applicable to housed animals, as experts have indicated that the practical applicability of feeding strategies to grazing animals is limited (UNECE, 2011). Never the less, emissions from pastures are low and grazing itself is indicated as a measure. For example, total annual emissions (from housing, storage and spreading) from dairy systems may decrease by up to 50% with nearly all-day grazing, as compared to animals that are fully confined (UNECE, 2012a).

Animal housing

The available techniques to reduce NH_3 emissions from animal housing have been well known for decades and apply one or more of the following principles:

Principles	NH_3 emission reduction*
• Decrease the surface area fouled by manure	15-25% in pig housing
• Rapid removal of urine and rapid separation of faeces and urine	25-46%
• Decrease air temperature and velocity above the manure	up to 20%
• Reduce PH of the manure	up to 60% in pig and cattle housing systems
• Reduce temperature of the manure	45-75%
• Dry the manure (e.g., poultry litter)	up to 70%
• Scrubbing ammonia from exhaust air	70-95%
• Decrease housing time by increasing grazing time	10-50%, but some emission swapping

* Oenema and Velthof (2012)

All of these principles are scientifically sound and practically proven. Different housing systems and environmental conditions are required by different animal categories, requiring therefore different techniques for the application of the above-mentioned principles with different results in NH_3 emission reduction.

Manure storage

Measures to reduce NH_3 emissions from manure storage systems apply one or more of the following principles: a) Decreasing the surface area where emissions can take place, i.e., through covering of the storage, encouraging crusting and increasing depth of storages; b) Reducing the pH and temperature of the manure; and c) Minimizing disturbances such as aeration (UNECE, 2012a).

The Nitrates directive requires modified storage conditions and storage times, which has implications on NH_3 emissions and mitigation potentials. The directive demands leak-tight manure storages and sufficient storage capacity, related to longer prohibition periods for manure application. However, the Nitrates directive does not require covered manure storages. Ammonia losses from slurry stores can be minimized by covering open stores. Döhler et al (2011) and Oenema and Velthof (2012) list the main natural and artificial covers solutions and their efficiencies as follows:

- **Natural floating covers**, by allowing the formation of a natural crust, are the simplest and most inexpensive form of slurry store covering. The reduction potential ranges between 30 and 80% for cattle slurry and between 20 and 70% for pig slurry.
- **Artificial floating covers** with chopped straw, peat, bark, etc, (must be at least 10 cm thick and replaced after stirring) can have a higher reduction effect of 40% to 90%. The effectiveness of both

cover variants (natural floating cover and chopped straw) is limited on farms with frequent slurry distribution because the natural floating layer or the straw layer is destroyed temporarily or permanently. It is applicable to large earth-banked lagoons and concrete or steel tanks.

- **Granule covers** have lower material losses than in the case of straw. They float again shortly after the slurry has been stirred. Therefore, only a small amount of the granules is spread with the slurry. However, it is necessary to replace the lost material. Emission losses are reduced by 60% to 90%.
- **Floating sheets** also have a reduction potential from 60% to 90%. Their advantage lies in low maintenance requirements. Precipitation water must be led or pumped into the slurry lying underneath.
- **Floating bodies and solid covers**, such as a concrete cover, a tent roof, or a plastic cover, have the highest reduction potential of up to 95% (60%-95%). Floating bodies are only suitable for liquid pig slurry without a natural floating layer. Solid covers have the longest service life and low maintenance requirements, and avoid rainwater input.

Manure application

Low-emission manure application techniques involve machinery that (i) decreases the exposed surface area of slurries applied to surface soil through band application, injection, incorporation;, and/or (ii) decreases the time that emissions can take place, i.e., buries slurry or solid manures through injection or incorporation into the soil; and (iii) decreases the source strength of the emitting surface, i.e., through lowering the pH and NH_4 concentration of the manure (through dilution). Examples of such application techniques are shown in Table 2.

Known techniques to reduce NH_3 emissions from manure application are now applied at a much larger scale and in more countries, lowering costs, especially for larger farms. The up-scaling has taken place mainly through contractors as many animal farmers in e.g., the Netherlands and Denmark have outsourced manure application to specialized contractors.

The timing of manure application has changed during the last decade as a result of the Nitrates directive. The directive imposes longer prohibition periods for manure application to decrease the risk of nitrate leaching. Ammonia emissions might however increase with longer prohibition periods because manure application is then more concentrated during the growing seasons with higher temperatures and less precipitation (Oenema and Velthof, 2012).

Table 2: Low-emission manure application techniques and NH_3 emission reduction (in %) attained by their implementation.

Measures	Emission reduction*
• The band-spreading of slurry at the soil surface, which deposits the slurry on the soil in parallel bands using **trailing hose**, suitable for arable grassland.	30-35%
• The band-spreading of slurry at the soil surface, which deposits the slurry on the soil in parallel bands using **trailing shoe** methods, suitable for arable grassland.	30-60%
• **Slurry injection - open slots**, suitable for application on grassland and in growing crop stands, with slopes < 15% and low stone content.	60-80% (Oenema and Velthof, 2012) 70% (UNECE, 2012a)
• **Slurry injection - closed slots**, where the slurry is fully covered after injection by closing the slots with press wheels or rollers fitted behind the injection tines. Deeper injection is required when greater volumes of manure are injected to avoid manure oozing to the surface	70-90% (Oenema and Velthof, 2012). 80% (shallow slot 5-10 cm); 90% (deep injection >15cm) (UNECE, 2012a)
• **Incorporation of surface-applied solid manure and slurry into soil**. Applicable in arable soils without vegetation (in pre-sowing season)	When the manure is completely buried within the soil immediately after application: 80-90%. Incorporation within 4 h.: 45-65%. Incorporation within 24 h.: 30% for slurry, 35% for solid manure from cattle and pig and 55% from poultry
• **Dilution of slurry** by at least 50% in low pressure water irrigation systems, suitable for arable grassland.	30%

* Based on Oenema and Velthof (2012), UNECE (2007) and UNECE (2012a).

Fertilizer application

Measures to reduce emissions of NH_3 from the application of urea and ammonium based fertilizers are based on one or more of the following principles (UNECE, 2012a):

- decrease the surface area where emissions may occur, i.e., through band application, injection, incorporation (but a rapid increase in pH in concentrated bands of urea, especially where there is high crop residue, may lead to high emissions due to rise in pH);
- decrease the period emissions may occur, i.e., through rapid incorporation of fertilizers into the soil or via irrigation;
- decrease the source strength of the emitting surface, i.e., through urease inhibitors, blending and acidifying substances;
- ban its use (as in the case of ammonium (bi)carbonate) and substitute by ammonium nitrate.

UNECE (2012a) summarized the ammonia emission reduction techniques for application of urea and their emission reduction potential (in brackets) as follows: 1) Injection (> 80%); 2) Urease inhibitors (> 30%); 3) Incorporation following surface application (> 50%); and 4) Surface spreading with irrigation (> 40%). A ban on ammonium carbonate as fertilizer would eliminate all emissions associated with its application. In addition, the following techniques for the application of ammonium-based fertilizers would lead to the following NH_3 emission reduction potential (in brackets): 1) Injection (> 80%); 2) Incorporation following surface application (> 50%); and 3) Surface spreading with irrigation (> 40%). The emission reduction potential is determined compared to the broadcast application of the urea- and ammonium based fertilizers (UNECE, 2012a).

In conclusion, although there has been less ambition in reducing NH_3 emissions than other PM precursors, there are proven and feasible methods to control and mitigate ammonia emissions from agriculture, including for the major sources of agricultural ammonia emissions. Key mitigation measures include improved storage of manure (e.g., closed tanks) and anaerobic digestion at large farms, improved application of manure on soil (e.g., trailing hose, slot injection) in large farms, and improved application of urea fertilizer or substitution by ammonium nitrate. Furthermore and because of learning effects, the practical functioning of these techniques has been improved and costs have declined. The available measures are technically simple and can cost-effectively be applied in large farms (responsible for 80% of NH_3 emissions), enabling cutting ammonia emissions in the EU27 by about 30% on top of current legislation in 2020 (Amman, 2012).

3 Justification for the topic

The adverse impacts of air pollution on health and on the environment are well recognised worldwide. Despite significant progress made to reduce emissions and mitigate effects of air pollution, air pollution is still an important environmental problem in developed countries and an increasing problem in the developing world, especially in urban areas. Epidemiological studies attribute the most severe health effects from air pollution to particulate matter (PM). Even at concentrations below current air quality standards and guidelines PM is expected to pose a health risk, as scientific evidence does not suggest a threshold below which no adverse health effects would be anticipated when exposed to PM (WHO, 2006a, 2013a).

Particulate matter (PM) prevails as the main air quality problem in Europe as it continues to pose the greatest risk to human health. EEA (2015) estimated that 4.8 million years of life lost (YLL) were caused by fine particulate matter pollution (PM2.5) alone in 2012 in Europe, and the WHO (2014) estimated an average loss of life expectancy of 8.6 months in the European Union due to exposure to PM2.5 resulting from human activities.

Despite the recognised impacts of current PM ambient concentrations and despite the efforts to reduce emissions of PM and its precursor gases, the results of European, national, and local policies lag largely behind its targets and have so far proven ineffective in reducing PM ambient levels and meeting the European PM standards. The EU limit and target values for PM are widely exceeded in Europe. Moreover, the development in annual mean concentrations from 2002 to 2011 indicates a slow decrease in PM10 averaged across Europe, but a small increase in PM2.5 levels measured at regional and, especially, urban background stations was observed from 2006 to 2011 (Guerreiro et al., 2014).

About a third of the European urban population lives in areas where the PM10 daily limit value and the PM2.5 exposure concentration obligation[14] are exceeded. In addition, more than 80% of urban dwellers are exposed to PM10 concentrations exceeding the WHO air quality guideline for PM10 (20 $\mu g.m^{-3}$ as an annual mean) and more than 90% are exposed to PM2.5 levels above the WHO guideline (10 $\mu g.m^{-3}$ as an annual mean) (Guerreiro et al., 2014). Authorities in countries with limited air policy experience are confronted with the challenge of having large populations exposed to high PM ambient concentrations and an increasing incidence in respiratory diseases.

Air quality is a well developed scientific field, with developed analytical methods to monitor and model chosen air pollution indicators and their sources. On the other hand, PM has proven to be a difficult and complex air pollutant to manage. Particulate matter (PM) is a heterogeneous and complex mixture of small particles and liquid droplets, made up of a number of components, such as nitrates and sulphates, organic chemicals, metals, and soil or dust particles, and of varying size from nanometres to

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[14] The PM2.5 exposure concentration obligation is 20 $\mu g.m^{-3}$ as an annual mean.

micrometres. PM in ambient air has many sources, both natural and anthropogenic, and PM may be directly emitted or formed in the atmosphere due to emissions of precursor gases, e.g., SO_2, NO_X, NH_3 and VOCs. In addition, PM size and chemical composition changes in time and space, depending on emission sources and atmospheric conditions.

Road transport, industry and power generation are the main sectors known to be responsible for air pollution. As emission mitigation actions and policies targeting these sectors have been implemented over the last decades, other sectors are emerging as main contributors to PM ambient air concentrations: household combustion as the main emitter of primary PM (PPM10 and PPM2.5) and of BaP, an indicator for carcinogenic PAHs in PM, and agriculture as the main emitter of an important PM precursor, NH_3.

The sector ‘Commercial, institutional and household fuel combustion’ dominates now the emissions of primary PM and BaP, contributing to 43% and to 55% of the total primary PM10 and PM2.5 emissions, respectively, and to 85% of the total BaP emissions in the EU-28 in 2012. In addition, this sector has increased its emissions of BaP, PPM2.5, and PPM10 by, respectively, 24%, 11% and 13%, from 2003 to 2012 in the EU-28. The use of household wood and other biomass combustion for heating is growing in some countries, due to government incentives/subsidies, rising costs of other energy sources, or an increased public perception that it is a 'green' option. Biomass is being promoted as a renewable fuel that can assist with climate change mitigation and contribute to energy security (EEA, 2014b).

PM has recently been classified as carcinogenic (Loomis et al, 2013), but PM is constituted by several chemical compounds that contribute to its carcinogenic and health effects of which PAHs are considered among the most dangerous due to their carcinogenic and mutagenic character. BaP is a marker for the carcinogenic risk of PAHs in ambient air and 90% of BaP in ambient air is adsorbed onto PM. Furthermore, BaP may be used as a marker for emissions from ‘Commercial, institutional and household fuel combustion’, as this emission sector accounts for 85% of all BaP emissions in the EU-28.

As mentioned in chapter 2, while concentrations of PM, NO_2 and O_3 and their health impacts are regularly estimated for the whole of Europe, much less has been done to estimate BaP concentrations, exposure and health effects. It is therefore important to improve the estimation of current BaP concentrations over the whole Europe, and of its associated population exposure and health impacts, in order to discuss necessary mitigation measures targeting emissions of BaP and PAHs.

Another issue is the fact that in Europe about one third of PM10 and half of PM2.5 have an inorganic chemical speciation consisting of: ammonium (NH_4^+), nitrate (NO_3^-) and sulphate (SO_4^{2-}). These species are the product of oxidation of PM precursor gases: ammonia (NH_3), nitrogen oxides (NO_X) and sulphur oxides (SO_X). Although NH_3 by itself is a small fraction of the PM mass, it plays a decisive role by determining the formation of ammonium sulphate ($(NH_4)_2SO_4)$) and ammonium nitrate (NH_4NO_3) as PM constituents. Emissions of the precursor gases NO_x and SO_x have decreased considerably over the last decade (27% and 50%, respectively), while NH_3 emissions have only decreased by 7% from 2002 to 2011. Furthermore, NH_3 emission reduction expected by the Gothenburg Protocol by 2020 (compared to 2005) is only 6% for EU27. Thus, there is less ambition in reducing NH_3 emissions than other PM precursors.

Agriculture was responsible for 93% of the NH_3 emissions in 2011 (EU27) and there are proven and feasible methods to control and mitigate NH_3 emissions from agriculture which could cut its emissions by about 30% on top of current legislation. Thus, agriculture is among the main sources of air pollution and is becoming more important as pollution from industry and transport are generally subject to tighter controls. Furthermore, a limited amount of specific measures can substantially reduce NH_3 emissions.

Today's citizens are generally better informed about air pollution and there is growing political commitment to improve air quality. In order to convert these new attitudes into effective action capable of dealing with the complex and difficult issues connected to the problem of PM, decision makers require scientific evidence on the importance of specific pollutant emissions from specific sectors and of its health impacts. Evaluating the importance of emissions of selected pollutants from the emerging emission sectors, agriculture and household combustion, to PM concentrations and to health effects is an important step towards the selection and implementation of cost-effective mitigation strategies to reduce PM concentrations and related impacts.

3.1 Major hypothesis

The main hypothesis of the proposed PhD is that *the emission sectors of household combustion and agriculture are key sectors contributing to the currently sustained PM levels and related health effects in Europe and must be mitigated in order to achieve compliance with the European PM standards*.

The main hypothesis consists of the following sub- hypothesis:

Sub-hypothesis 1: The European population exposure to BaP and the related incidence in lung cancer is quantifiable, by combining measurements, dispersion modelling and relevant auxiliary data.

Sub-hypothesis 2: The implementation of the Gothenburg Protocol will not alone lead to compliance with PM standards in 2020 throughout Europe.

Sub- hypothesis 3: Effective mitigation measures for the agricultural sector can be identified in order to reduce the contribution of ammonia emissions from agriculture to the exceedances of the European PM standards.

4 Major goal, research questions and tasks

The major goal of this thesis is to apply improved methodologies to investigate the importance of emerging emission sectors to PM and associated BaP and its health impacts, in order to support effective air quality management with focus on particulate matter, including PAHs.

The main research questions are:

- How are emerging emission sectors contributing to the development of PM and Benzo(a)pyrene (BaP) ambient air concentration levels in Europe?
- What are the current health impacts of human exposure to BaP concentrations in Europe?
- Will the Gothenburg Protocol lead to compliance with the European PM standards by 2020?
- What is the potential contribution of feasible reductions of NH_3 emissions from agriculture to reduce inorganic PM formation, and thus PM2.5 and PM10 ambient air concentrations in Europe?

The above mentioned goal will be obtained through the following tasks:

1. Implement an improved approach combining measurements, modelling and auxiliary data for BaP ambient air concentration mapping, in order to overcome the insufficient geographical coverage of BaP measurements and the uncertainties of BaP concentration modelling.
2. Quantify the European population exposure to BaP ambient air concentrations and subsequent health impact as lung cancer incidence in Europe.
3. Determine the effect of the implementation of the Gothenburg Protocol on PM levels in 2020 and evaluate the need for the implementation of further measures to meet the PM standards in Europe.
4. Review feasible mitigation measures to reduce NH_3 emissions from agriculture and their combined emission reduction potential.
5. Quantify the effect of feasible reduction in NH_3 emissions from agriculture on the reduction of PM levels and of exceedances in PM standards in Europe, beyond the implementation of the Gothenburg Protocol in 2020, by combining data from a chemical transport model and measurements.

The work has benefited from the results from research carried out by the candidate and colleagues from the European Topic Centre on Air Pollution and Climate Change Mitigation (ETC/ACM) as part of the candidate’s work for the European Environmental Agency (EEA) within the ETC/ACM, between 2012 and 2015.

During this work and previous 20 years of work within air quality assessment and management, the candidate has obtained expertise and practice within:

- the development, implementation and validation of air quality dispersion models, including meteorological pre-processors and wind-field models;
- the development of modelling quality objectives and systems for benchmarking the quality of modelling results;
- population exposure assessment using different approaches (static/dynamic, outdoor/indoor);
- the development of air quality indicators, including exposure indicators;
- Development, verification, and improvement of air pollutant emission inventories (both bottom-up and top-down approaches);
- Source apportionment: quantification of the contribution of source sectors to air pollutants ambient air concentrations;
- Air quality screening, design of monitoring networks and evaluation of monitoring programmes;
- Quality assurance and quality control of air quality data, including data and trend analysis;
- In depth knowledge of the EU legislation, international protocols, and policies regarding air quality and control of air pollutant emissions in Europe;
- development and implementation of air quality standards;
- environmental impact assessment, particularly focused on impacts air pollutants concentrations and deposition;
- mitigation measures and development of air quality plans and programmes, optimising cost-effectiveness of abatement strategies;
- support the review of European Air Quality Directives and policy development;
- evaluation of effectiveness of implemented policies and measures;
- institutional building: setting up and developing institutions and expertise for air quality assessment and management in developing countries.

Based on knowledge and experience obtained from more than 20 years of work in air quality assessment, air quality management and support to policy development, this thesis aims to contribute to a new perspective to air quality management, focusing on the emerging emission sectors of household combustion and agriculture, towards attaining the main goal of the European Thematic Strategy on Air Pollution, i.e., "levels of air quality that do not give rise to significant negative impacts on, and risks to human health and environment".

4.1 Novelty

The analysis of past policies targeting mostly the transport, industry and energy production sectors, as well as the importance of other emission sectors to the sustained PM levels in Europe, indicates the need to investigate the importance and mitigation potential of the agriculture and household combustion sectors.

Environmental decisions must frequently be made without sufficient data on exposure. In particular, data for toxic air pollutant exposures like PAHs are usually scarcer in geographic and temporal coverage than data for other regulated pollutants such as nitrogen dioxide (NO_2), ozone (O_3) and particulate matter (PM). In order to estimate the population exposure to BaP and its associated health effects in Europe, it is necessary to have the best possible knowledge on the status of the BaP concentrations across Europe. The geographical coverage of BaP measurements is insufficient for preparing a European concentration map and the chemical transport model results are uncertain due mainly to uncertainties in input emission data, and due to lack of measurement data for model validation. The present study attempts to improve the exposure estimate to ambient air BaP concentrations by combining the available measurement data to modelling results from two different chemical transport models. Based on this the health impact of population exposure to ambient air BaP could be estimated.

The current study has evaluated the effect of the full implementation of the Gothenburg Protocol on ambient air concentrations of PM and related exceedances of the European PM standards by 2020. That is crucial information to understand if there is a need for further policies and measures to curb PM exceedances.

Agriculture is by far the most important emitter of ammonia (NH_3). NH_3 is a key component in the formation of secondary inorganic aerosols, which accounts for about half of PM2.5 and one third of PM10 background ambient air concentrations in Europe. This work has strived to find a good method to estimate the effect of feasible reductions of NH_3 emissions from agriculture on exceedances of PM standards in Europe, beyond the implementation of the Gothenburg protocol, compensating for the fact that chemical transport models generally underestimate PM ambient levels.

EXPERIMENTAL PART

5 Part 1: Population exposure to BaP concentrations in Europe

In order to estimate the population exposure to BaP and its associated health effects in Europe, it is necessary to have the best possible knowledge on the status of the BaP concentrations across Europe. The geographical coverage of BaP measurements is insufficient for preparing a European concentration map and the modelling results are uncertain, due mainly to uncertainties in input emission data (see section 5.1.2) and due to lack for measurement data for model validation. In the current work, it is attempted to find an improved approach for BaP mapping in Europe by combining the existent measurement data with modelling results.

5.1 Methodology

The methodology used for the creation of the new BaP concentration map over Europe is similar to the one documented in Horálek et al. (2014a) and previously used to create concentration maps for PM10, PM2.5, O_3, NO_2. The mapping method used is a linear regression model followed by kriging of the residuals produced from that model (residual kriging), as explained further in section 5.1.4. In the linear regression model, the measured data are taken as a dependent variable, while the output concentration data from a chemical transport model and other supplementary data (e.g., altitude, meteorology, population density) are used as independent variables.

5.1.1 *Measurement air quality data*

Monitoring data for BaP concentrations was extracted from the European monitoring database AirBase (Mol and Van Hooydonk, 2012) for stations classified as the type *background* for the areas *rural*, *suburban* and *urban*. *Industrial* and *traffic* station types are not considered, as they represent hot spot concentrations on a different scale than the concentration map produced (10 x 10 km^2). The following European measurements of BaP concentrations in ambient air in 2012 were considered as annual average ($ng.m^{-3}$):

- BaP in PM2.5, aerosol
- BaP in PM10, aerosol
- BaP in PM10, air+aerosol
- BaP, air+aerosol (on PM size cut off)

As mentioned before, most of the BaP is present in PM2.5, not in the coarser fraction of PM10, and the gaseous fraction of the total BaP is quite small. Air base data was supplemented with data for three Slovak urban background stations (SHMI, 2013), and two French stations[15] (provided by INERIS).

Measurements from stations with data coverage of at least 14% (i.e., a minimum of 51 days) valid daily measurements (24 hours samples) in the year of 2012 were used. This corresponds to the minimum time coverage for indicative measurements laid down in Annex IV of Directive 2004/107/EC (EU, 2004). This relatively low requirement for data coverage was adopted in order to use as much available measurement data as possible, as BaP measurements are scarce in large areas in Europe. On the other hand, it allows an increase in the uncertainty of the measurement data used, compared to other pollutants. EC (2001) recommends a sampling frequency of one day every third day of the year, allowing an evenly distributed data sampling and a data coverage of 43%. Furthermore, it says that individual measurements can be expected to have an uncertainty of about +/- 50% at the 95% confidence level. When individual measurements are used for generating annual means, the likely expanded uncertainty arising from reducing daily to once in every 6th day sampling would be between 25 and 30% falling to ~10% when every third day is sampled (EC, 2001).

As stated, sampling should be spread evenly over the weekdays and the year, in order to calculate an annual mean representative of the real value. Two stations in Spain were excluded, as their data covered only two or three consecutive months. In total, 84 rural background and 289 urban/suburban background stations were used, as shown in Figure 6.

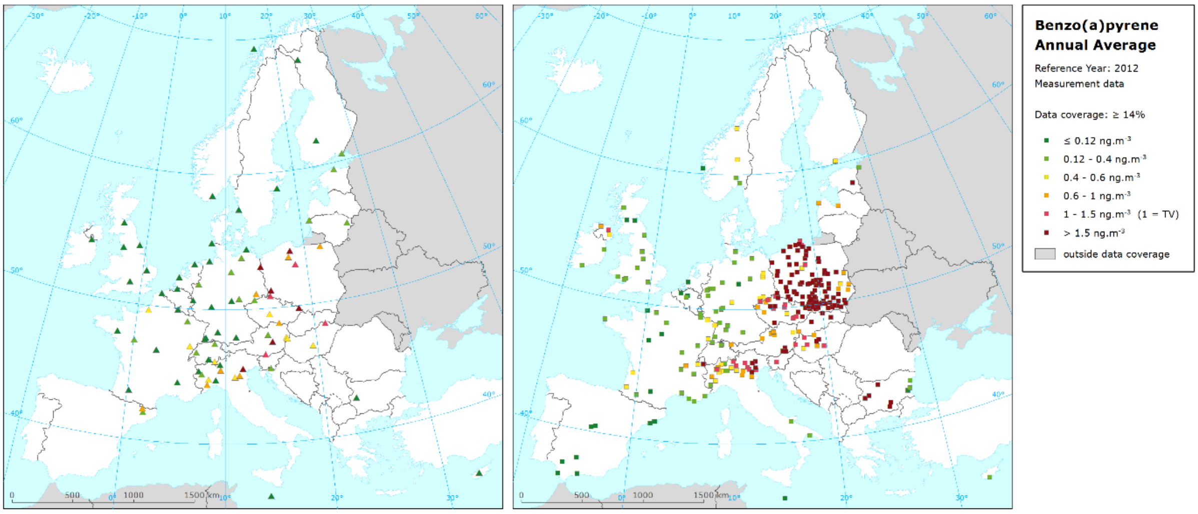

Figure 6: ***Measurement air quality data from rural (left) and urban/suburban (right) background stations. BaP, annual average, 2012.***

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[15] With the station codes: FR01020 and FR24009.

5.1.2 *Chemical transport model data*

Modelled BaP annual mean concentrations for 2012 were used to produce the BaP concentration maps. Results from two different chemical transport models (CTMs) were used for comparison: the EMEP MSC-E model[16] (EMEP, 2014) and the CHIMERE model (Menut et al., 2013).

Emission data used by the models EMEP and CHIMERE

Emissions for 2012 with spatial resolution 50 x 50 km^2 provided by EMEP/CEIP (2014) were used for both model runs. The total estimated BaP emissions by EMEP for modelling purposes for EU28 in 2012 was 241 tonnes[17] (EMEP/CEIP, 2014), while the total BaP emission of the 20 countries[18] that reported BaP emissions in the EU28 was 180 tonnes in 2012 (EEA, 2014a). This considerable difference corresponds to the gap filling estimation done by EMEP in order to obtain a more complete emission inventory for modelling purposes.

The emission data for modelling is based on a combination of official reported data supplemented with expert estimates for missing data and/or for data of low quality. Not reported emissions are gap-filled (by EMEP‘s interpolation routine) in order to create complete sectorial gridded emissions for the whole of the EMEP area so that EMEP is capable of performing dispersion modelling.

The emission data used for dispersion modelling was the estimated emissions of BaP for use in models (EMEP/CEIP, 2014), for both EMEP and CHIMERE models. Considering this data, the main countries contributing to the total EU28 emissions in 2012 were Poland (18 %), Romania (16 %), Germany (13 %), Italy (8 %), Spain (6 %) and Belgium (5 %). In total, these 6 countries account for 66 % of the estimated total EU28 BaP emission in 2012.

Table 3 shows the differences per country between the officially reported emissions of BaP for 2012 and the estimate for modelling purposes.

While the EMEP model uses the EMEP/CEIP (2014) emission data with a spatial resolution 50 x 50 km^2, the CHIMERE model uses the same original data re-distributed within its domain with a higher resolution (0.25° x 0.25°, i.e., circa 20x30 km), based on the spatial distribution of auxiliary data like

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[16] The results were directly provided by EMEP MSC-E using 2012 emissions, the report EMEP (2014) shows preliminary results for 2012 using 2011 emissions.

[17] Meaning that a total emission of 60 tonnes was estimated for 2012 for the remaining 8 countries that did not report: Austria, Belgium, Finland, Greece, Italy, Luxembourg, Portugal and Spain. These 8 countries are estimated to account for 25 % of the total EU28 emissions of BaP in 2012.

[18] The 20 countries that reported BaP emissions for 2012 and included in this total are: Bulgaria, Croatia, Cyprus, the Czech Republic, Denmark, Estonia, France, Germany, Hungary, Ireland, Latvia, Lithuania, Malta, the Netherlands, Poland, Romania, Slovakia, Slovenia, Sweden, and the United Kingdom.

population density. In short, the emission data is the same for both models, but CHIMERE refines its spatial distribution to its finer gridcells.

Table 3: ***BaP emissions in 2012 in the EU28 countries: officially reported and estimated for modelling.***

	Emissions (T/yr)			Emissions (T/yr)	
countries	for models	officially reported	countries	for models	officially reported
AT	2,26	-	HU	9,23	9,19
BE	12,06	-	IE	1,23	1,23
BG	8,95	8,95	IT	18,97	-
CY	0,29	0,29	LT	3,90	3,90
CZ	5,55	5,55	LU	0,26	-
DE	31,60	31,60	LV	4,23	4,23
DK	2,46	2,46	MT	0,02	0,02
EE	4,48	4,48	NL	1,20	1,20
ES	13,57	-	PL	43,51	43,51
FI	5,15	-	PT	0,02	-
FR	5,04	5,04	RO	37,76	37,76
GB	3,51	3,51	SE	4,40	4,40
GR	8,27	-	SI	3,83	3,83
HR	3,41	3,41	SK	5,37	5,37
Total EU28				**240,52**	**179,92**

EMEP MSC-E model output

EMEP MSC-E POP model is a three-dimensional Eulerian multi-compartment chemistry transport model (Gusev et al., 2005) developed to simulate long-range transboundary transport and deposition of selected POPs, including BaP in Europe.

The model considers the main environmental compartments; atmosphere, soil, seawater, and vegetation. It includes basic processes describing POP emission, partitioning between the gaseous and particulate phase, advective transport and turbulent diffusion, wet and dry deposition of POPs in particulate and gaseous phase to the underlying surface, and degradation. For the description of atmospheric transport and deposition of POPs the MSCE-POP model uses the same modules for advective transport and turbulent diffusion of pollutants within the atmosphere as the MSCE-HM model, which are described by Travnikov and Ilyin (2005). The POP deposition processes from the atmosphere to underlying surface are described on the basis of an approach similar to MSCE-HM model and described in Travnikov and Ilyin (2005). For the description of POP exchange with and accumulation in main environmental compartments, the atmospheric module of MSCE-POP model is complemented with additional modules for soil, seawater, and vegetation (Gusev et al., 2005). MSCE-POP model domain covers practically the whole troposphere, upper layer of soil of 20 cm, and seawater compartment within the model grid.

The chemical transport model EMEP MSCE-POP simulates the photodegradation of BaP adsorbed to particulate matter. It uses the calculated value of half-life obtained in Chen et al. (2001) on the basis of

Quantitative Structure-Property Relationship studies (QSPRs) on direct photolysis of BaP in atmospheric aerosol. Its numerical value agrees with the interval of experimentally determined values of BaP half-life due to photodegradation process (Gusev et al., 2006). In addition, the model takes into account the degradation of BaP in the gaseous phase due to reactions with hydroxyl radicals (OH); all other reactions are neglected (Gusev et al., 2005).

The model's output (see Figure 7, left) covers completely the mapping domain (i.e., the area of the EEA member and cooperating countries within the map extent Map_1c, EEA, 2011). The model was run by EMEP MSC-East in its own grid specification in circa 50 x 50 km^2 resolution, and driven by ECMWF meteorology for 2012. EMEP (2014) provides details on the EMEP modelling.

CHIMERE model output

CHIMERE[19] is an Eulerian off-line chemistry-transport model primarily designed to produce daily forecasts of ozone, aerosols and other pollutants and make long-term simulations for emission control scenarios. The key processes affecting the pollutant concentrations and deposition calculated by CHIMERE are emissions, transport (advection and mixing), turbulence, clouds and radiation, aerosols and gases chemistry, and deposition. Gas-phase chemistry is simulated with the original scheme of Lattuati (1997), also called MELCHIOR, describing more than 300 reactions of 80 gaseous species. The evolution of particles follows Warren (1986) and the formation of organic aerosol is described in Bessagnet et al. (2008). A more comprehensive description of the model is given in Menut et al. (2013).

CHIMERE was modified to take into account the partitioning of BaP between the gas phase and the particle phase according to its saturation vapour pressure taken from Gusev et al. (2005). The degradation of BaP in the gaseous phase due to reactions with hydroxyl radicals (OH) is also taken into account.

Air concentrations of BaP for 2012 were simulated by INERIS with the CHIMERE model over Europe with a resolution of 0.25° x 0.25°, i.e., circa 20x30 km^2. The modelling domain is the mapped area of the EEA member and cooperating countries, without Iceland, northern Norway and southern Cyprus (see Figure 7, right).

Data with a 0.25°x0.25° resolution from the European Centre for Medium-Range Weather Forecasts (ECMWF) are used for meteorology. A climatology of MACC for aerosol and gas species are used for boundary conditions (boundary conditions for BaP are set at 0 ng.m^{-3} due to lack of information).

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[19] http://www.lmd.polytechnique.fr/chimere/

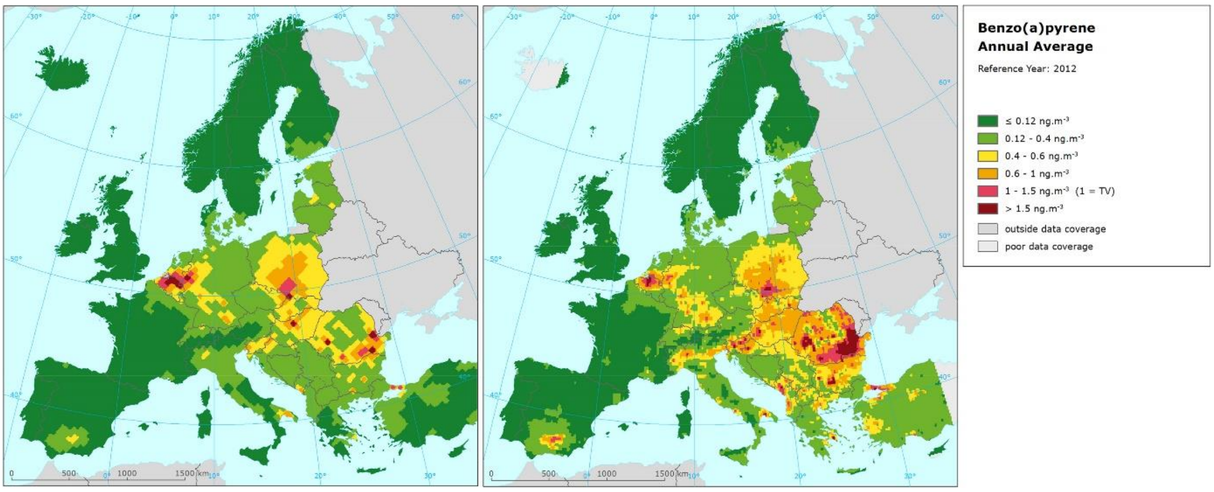

Figure 7: ***Output of chemical transport model EMEP (left, resolution 50x50 km^2) and CHIMERE (right, resolution 20x30 km^2). BaP annual average in 2012.***

In areas of higher emissions, and typically higher population density, the CHIMERE model calculates higher concentrations of BaP than the EMEP model. The main reason for this in the fact that CHIMERE has a higher resolution than EMEP, i.e., smaller gridcells: ca 20x30 km^2 versus EMEP's 50x50 km^2. In areas of higher emissions, typically more densely populated areas, the calculated concentrations are averaged over a smaller gridcell area, leading to higher concentrations.

5.1.3 *Other supplementary data*

The altitude data field (in meters above sea level) is taken from GTOPO30[20] (original resolution 30x30 arc-seconds), which is a global digital elevation model (DEM).

Annual average for 2012 of: 1) wind speed (m/s), surface solar radiation (annual average of daily sum, MWs/m^2), temperature (converted to °C), and relative humidity (%) were used as meteorological parameters. The data was extracted from the Meteorological Archival and Retrieval System (MARS) ERA-interim reanalyses of ECMWF[21] (original resolution 0.25°x0.25°).

Population density (in inhabitants/km^2, census 2001) for the majority of countries is based on data provided by the European Commissions (EC) Joint Research Centre (JRC). The original resolution is 100x100 m^2. For countries and regions lacking JRC data, we used ORNL population data in the 1x1 km^2 resolution.

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[20] https://lta.cr.usgs.gov/GTOPO30

[21] http://www.ecmwf.int/en/research/climate-reanalysis/browse-reanalysis-datasets

5.1.4 *Interpolation*

The interpolation method used is a linear regression model followed by interpolation (kriging) of the residuals produced from that model (residual kriging). Interpolation is carried out according to the relation:

$$\hat{Z}(s_0) = c + a_1.X_1(s_0) + a_2.X_2(s_0) + \cdots + a_n.X_n(s_0) + \eta(s_0) \qquad (1)$$

Where:

$\hat{Z}(s_0)$	is the estimated value of the air pollutant concentration at the point s_o,
$X_1(s_0)$	is the output of the dispersion model at point s_o,
$X_2(s_0)$,…,$X_n(s_0)$	are the other supplementary variables at the point s_o,
c, a_1, a_2,…, a_n	are the selected parameters of the linear regression model calculated at point s_o, based on the data at the points of measurement,
$\eta(s_0)$	is the spatial interpolation of the residuals of the linear regression model at the point s_o calculated based on the residuals at the points of measurement.

The supplementary data for use in the mapping is explored and selected separately for the rural and the urban background areas. In addition, a test is made to decide on the use of a logarithmic transformation of measurement and/or model data, prior to linear regression and interpolation. Denby et al. (2009) recommended to use the log-normal transformed concentrations for the interpolation, particularly when the range of data is large, since the frequency distributions of measured and modelling concentrations are closer to log-normal distributions than to normal distributions. If the test shows better results, one applies a logarithmic transformation of concentrations for air quality measurements and/or the CTM modelling output. Then we apply the multiple linear regression, followed by residual kriging, using:

$$\hat{Y}(s_0) = c + a_1.\ln(X_1(s_0)) + a_2.X_2(s_0) + \cdots + a_n.X_n(s_0) + \eta(s_0) \qquad (2)$$

Where:

$\hat{Y}(s_0)$	is the estimated value of the logarithmical transformed concentration at point s_0.

After the interpolation, the interpolated values are back-transformed by exponentiation with the kriging error:

$$\hat{Z}(s_0) = exp\left\{\hat{Y}(s_0) + \frac{\sigma^2(s_0)}{2}\right\} \qquad (3)$$

Where:

$\hat{Z}(s_0)$	is the estimated back-transformed concentration value at point s_0,
$Y(s_0)$	is the logarithmical transformed concentration at point s_0.
$\sigma(s_0)$	is the kriging error value at point s_0.

The back-transformed standard error of the interpolation is calculated as follows:

$$\delta(s_0) = \sqrt{exp(\sigma^2(s_0) - 1).\, exp\{2Y(s_0) + \sigma^2(s_0)\}} \qquad (4)$$

Where:

$\delta(s_0)$ is the back-transformed standard error of the interpolation at point s_0.

5.1.5 *Merging of rural and urban background maps*

The BaP annual mean concentration map is constructed for the rural and urban areas separately on a grid of 10 x 10 km^2 resolution. The rural map is based on BaP annual mean measurements at rural background stations and the urban map on measurements at urban and suburban background stations. The reason for the separate mapping of rural and urban areas is the assumption that BaP concentrations in general are higher in urban than in the rural areas. However, in some areas the assumption is not valid. For those areas both the rural and the urban background maps are adapted with the use of a joint rural/urban map, which is constructed based on both rural and urban/suburban background stations. Finally, the adapted rural and urban background maps are merged into one combined air quality concentration map using a European-wide population density grid at 1x1 km^2 resolution For the grid cells (1x1 km^2) with a population density lower than a defined value of α_1, the rural map value is used; for grid cells with a population density greater than a defined value α_2, the urban map value is used. For areas with population density within the interval (α_1, α_2) a weighting function of α_1 and α_2 is applied. The value of α_1 is 100 inhabitants/km^2 and α_2 is 500 inhab./km^2.

$$Z(s_0) = \frac{\alpha_2 - \alpha(s_0)}{\alpha_2 - \alpha_1}.\, R(s_0) + \frac{\alpha(s_0) - \alpha_1}{\alpha_2 - \alpha_1}.\, U(s_0) \qquad (5)$$

Where:

$Z(s_0)$ is the resulting value of concentration at the point s_0,

$R(s_0)$ is the concentration at the point s_0 for the rural map,

$U(s_0)$ is the concentration at the point s_0 for the urban map,

$\alpha(s_0)$ is the density of population at the point s_0.

Summarising, the separate rural and urban background maps are constructed at a resolution of 10x10 km^2; their merging however takes place on basis of the 1x1 km^2 resolution population density grid, resulting in a final combined pollutant concentration map on this 1x1 km^2 resolution grid, which is aggregated to a 10x10 km^2.

5.1.6 *Calculation of population exposure*

Population exposure for Europe as a whole is calculated from the BaP annual mean concentration map and population density data, both at 1x1 km^2 resolution. It is expressed by the percentage of total European population living in areas with BaP air concentrations within specific intervals, including below and above the BaP target value (TV = 1 $ng.m^{-3}$). In addition, the European-wide exposure is calculated as the population-weighted concentration, i.e., the average concentration per inhabitant. In addition to the population-weighted concentration for the whole Europe, also the population-weighted concentration for each 10x10 km^2 grid was calculated, which enables to present the population-weighted concentration map in 10x10 km^2 resolution.

The population-weighted concentration was calculated according to the equation:

$$\hat{c} = \frac{\sum_{i=1}^{N} c_i P_i}{\sum_{i=1}^{N} P_i} \tag{6}$$

Where:

$\hat{c}$ is the population-weighted average concentration in the whole Europe or in the given 10x10 km^2 grid cell,

P_i is the population in the i^{th} 1x1 km^2 grid cell,

c_i is the concentration in the i^{th} 1x1 km^2 grid cell,

N is the number of grid cells in Europe as a whole or in the given 10x10 km^2 grid cell.

5.1.7 *Uncertainty analysis of concentration map*

Ordinary kriging provides good estimates, based on spatial statistics, of the uncertainty. Kriging does not directly consider the monitoring uncertainties used, however it does implicitly include these uncertainties in the interpolation. Thus monitoring uncertainty, or correctly the variability between monitors, is implicitly included in the current interpolation uncertainty. These estimates of the residual kriging variance, are used to provide uncertainty estimates of the interpolated air quality maps, as the uncertainty of the kriging is well represented by the kriging variance (Denby et al., 2009).

The uncertainty estimation of the European concentration map is based on cross-validation and on the interpolation standard error map, calculated based on kriging theory.

The cross-validation method computes the quality of the spatial interpolation for each measurement station point from all available information except from the station point under examination, i.e., it withholds one data point and then makes a prediction at the spatial location of that point. This procedure is repeated for all measurement points in the available set. The advantage of this cross-validation technique is that it enables evaluation of the quality of the predicted values at locations without measurements, as long as they are within the area covered by the measurements.

The results of cross-validation are described by the statistical indicators and scatter plots. The indicators used are root mean squared error (RMSE) and bias or the mean prediction error (MPE):

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\hat{Z}(s_i) - Z(s_i)\right)^2} \tag{7}$$

$$bias(MPE) = \frac{1}{N}\sum_{i=1}^{N}\left(\hat{Z}(s_i) - Z(s_i)\right) \tag{8}$$

Where:

$Z(s_i)$	is the measured concentration[22] at the i^{th} point, $i = 1,\ldots, N$
$\hat{Z}(s_i)$	is the estimated concentration[22] at the i^{th} point using other information, without the measured concentration at the i^{th} point,
N	is the number of the measuring points.

In addition to the RMSE expressed in the absolute units, one could express this uncertainty in relative terms by relating the RMSE to the mean air pollution concentration measured at all stations:

$$\boldsymbol{RRMSE = \frac{RMSE}{\bar{Z}}\ .100} \tag{9}$$

where $RRMSE$ is the relative RMSE, expressed in percent,

$\bar{Z}$ is the arithmetic average of the measured concentrations[22] $Z(s_1), \ldots, Z(s_N)$.

RMSE and RRMSE should be as small as possible, and bias should be as close to zero as possible.

The interpolation standard error map is calculated based on the spatial statistics theory (Cressie, 1993). The standard error is calculated as shown in equation 4. The standard error of the combined (rural and urban background) map is calculated from the standard errors of the separate rural and urban background maps, as in De Smet et al. (2011).

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[22] i.e. all measured BaP annual mean concentration(s).

5.1.8 *Estimation of health effects of BaP in Europe*

On the basis of the BaP population exposure estimates as explained in section 5.1.6, the number of lung-cancer incidences due to exposure to ambient air BaP concentrations is calculated for the interpolated maps' domains. BaP has other health impacts, as summarized in section 2.1.1, but other health endpoints lack an adequate exposure-response function in order to estimate the effects.

The exposure –response function recommended by the WHO is used for lung cancer incidence in this study. It is based on epidemiological data from studies with coke-oven workers, for which the unit risk for exposure to BaP was estimated to be 8.7 x 10^{-5} per ng.m^{-3} (WHO 1987, 2000). The unit risk (UR) is defined as "the additional lifetime cancer risk occurring in a hypothetical population in which all individuals are exposed continuously from birth throughout their lifetimes to a concentration of 1 ng.m^{-3} in air" (WHO, 2000). This unit risk value falls within the range of estimated risk of 2.3 - 43 x 10^{-5} per ng.m^{-3}, as summarized by Boström et al (2002).

The number of lung cancer incidences (N) is estimated as follows:

$$\boldsymbol{N = C \cdot Pop \cdot UR_{[BaP]}/L}) \qquad (10)$$

Where:

C is the ambient air concentration of the pollutant

Pop is the exposed population, from

$UR_{[BaP]}$ is the unit risk,

L is the lifetime average exposure.

5.2 Results

5.2.1 *BaP concentrations and uncertainties*

Selection of supplementary data and kriging type

For the BaP concentration map creation, the best variant of the mapping method must to be selected. At first, the set of supplementary data was selected separately for the rural and background areas. Secondly, the need for a logarithmical transformation of measurement and model (CTM) data was examined (section 5.1.4).

The first step is to execute the linear regression analysis for the urban and the rural background stations separately, in order to identify useful supplementary data for use in the residual kriging. For the selection of the useful supplementary data, the backward elimination is used and confirmed by automatic stepwise regression as escribed in Horálek et al. (2007). Both the variants with and without the logarithmical transformation were examined.

The results of the regression analysis are presented in Table 4. The coefficient of determination (R^2) and adjusted R^2 should be as close to one as possible, and standard errors should be as small as possible. However, the standard errors for the linear regression models with and without logarithmical transformation are not mutually comparable, due to the logarithmical transformation. The choice was made based on the best linear regression result. However, this choice might not necessarily provide the best residual kriging result.

The selected linear regression models shown in Table 4 and Table 5 are explained here under.

For rural areas:

1) **EMEP/CHIMERE** is the linear regression model using the BaP measurements in rural background stations as dependent variable and the CTM results as independent variable;
2) **EMEP/CHIMERE, log. transformed** is the linear regression model using the BaP measurements as dependent variable and the CTM results as independent variable, where both the measurements and the CTM results have been previously logarithmic transformed;
3) **EMEP/CHIMERE, altitude, log. transformed** is the same as in 2), with altitude as an independent variable, but altitude has not been logarithmic transformed;
4) **EMEP/CHI., altitude, wind speed, log. transf.** is the same as in 2), with altitude and wind speed as an independent variables which have not been logarithmic transformed.

For urban background areas:

I. **EMEP/CHIMERE** is the linear regression model using the BaP measurements in urban/suburban background stations as dependent variable and the CTM results as independent variable;
II. **EMEP/CHIMERE, temperature** is the linear regression model using the BaP measurements in urban/suburban background stations as dependent variable and both the model results and temperature as independent variables;
III. **EMEP/CHIMERE, log. transf**. is the linear regression model using the BaP measurements in urban/suburban background stations as dependent variable and the model results as independent variable, where both the measurements and the CTM results have been logarithmic transformed;
IV. **EMEP/CHIMERE, temp., log. tr.** is the same as in III, with temperature as an independent variable, but temperature has not been logarithmic transformed;
V. **EMEP/CHIMERE, temp., pop.d., log. tr**. is the same as in III, with temperature and population density as an independent variables, where temperature has not been logarithmic transformed and population density has previously been logarithmic transformed.

Table 4: Statistical indicator values of the selected linear regression models indicating the correlation between observed and calculated annual mean BaP concentrations (2012), using the specified supplementary data.

	rural areas					
linear regression model	**using EMEP**			**using CHIMERE**		
	R^2	**adj. R^2**	**std. err.**	**R^2**	**adj. R^2**	**std. err.**
EMEP/CHIMERE	0.20	0.19	0.76	0.27	0.26	0.73
EMEP/CHIMERE, log. transformed	0.20	0.19	1.29	0.32	0.31	1.20
EMEP/CHIMERE, altitude, log. transformed	0.23	0.21	1.28	0.35	0.33	1.17
EMEP/CHIMERE, altitude, wind speed, log. transf.	0.38	0.35	1.16	0.42	0.40	1.12
	urban background areas					
linear regression model	**using EMEP**			**using CHIMERE**		
	R^2	**adj. R^2**	**std. err.**	**R^2**	**adj. R^2**	**std. err.**
EMEP/CHIMERE	0.25	0.25	2.97	0.18	0.18	3.11
EMEP/CHIMERE, temperature	0.30	0.29	2.88	0.26	0.25	2.96
EMEP/CHIMERE, log. transformed	0.34	0.34	1.19	0.27	0.27	1.25
EMEP/CHIMERE, temperature, log. transf.	0.44	0.44	1.10	0.45	0.45	1.09
EMEP/CHIMERE, temp., popul. density, log. tranf.	0.51	0.50	1.04	0.53	0.52	1.02

For the best variants, the spatial interpolation was executed and mutually compared as presented in Table 5. The comparison is performed using cross-validation, see section 5.1.7. The main indicator is RMSE and the additional ones are bias and linear regression parameters (slope and intercept) from the cross-validation scatterplot. RMSE, bias and the linear regression’s intercept should be as close to zero as possible, R^2 and the linear regression’s slope should be as close to one as possible. The best results are marked in Table 5 by dark green, the second best by light green.

Based on the analysis, the following variants were selected:

- For the rural map: 4) **EMEP/CHIMERE, altitude, wind speed, log. tr.**, i.e., EMEP or CHIMERE model data with logarithmic transformation, altitude and wind speed.
- For the urban background map: IV) **EMEP/CHIMERE, temp., log. tr**., i.e., EMEP or CHIMERE model data with logarithmic transformation, and temperature.

In both cases, the logarithmical transformation is applied to the measurement and CTM data. EMEP and CHIMERE models give quite similar results in rural areas. At the urban background areas, the best performing linear regression model is different for the EMEP and CHIMERE models. When using EMEP data, the linear regression model IV is the best performing variant, while when using CHIMERE data the linear regression model V is the best performing variant.

Table 5: Comparison of different variants of spatial interpolation showing RMSE, bias, R^2 and linear regression from the cross-validation scatter plots of BaP annual mean predicted values, 2012. Unit: ng.m^{-3}, except R^2.

rural areas

spatial interpolation variant	using EMEP				using CHIMERE			
	RMSE	bias	R^2	regr. eq.	RMSE	bias	R^2	regr. eq.
EMEP/CHIMERE	0.70	0.03	0.33	y=0.384x+0.33	0.69	0.03	0.36	y=0.433x+0.31
EMEP/CHIMERE, log. transf.	0.67	0.13	0.44	y=0.568x+0.34	0.62	0.08	0.49	y=0.587x+0.29
EMEP/CHIMERE, alt., wind sp., log. tr.	0.64	0.08	0.44	y=0.477x+0.33	0.60	0.06	0.51	y=0.509x+0.31

urban background areas

spatial interpolation variant	using EMEP				using CHIMERE			
	RMSE	bias	R^2	regr. eq.	RMSE	bias	R^2	regr. eq.
EMEP/CHIMERE	1.98	0.05	0.67	y=0.723x+0.79	2.11	0.09	0.63	y=0.708x+0.88
EMEP/CHIMERE, temperature	1.97	0.03	0.67	y=0.733x+0.73	2.11	0.07	0.63	y=0.716x+0.83
EMEP/CHIMERE, log. tranf.	1.89	-0.01	0.70	y=0.734x+0.69	2.07	0.02	0.64	y=0.723x+0.77
EMEP/CHIMERE, temp., log. tr.	1.84	0.04	0.71	y=0.756x+0.69	2.02	0.08	0.66	y=0.746x+0.76
EMEP/CHIMERE, temp., pop.d., log tr.	2.11	0.22	0.68	y=0.863x+0.58	1.97	0.15	0.70	y=0.836x+0.59

Ultimately, the variant IV (i.e., without population density) was selected for urban background mapping both for EMEP and CHIMERE. This choice was done for two reasons: 1) for consistency (i.e., the same variant is selected for both EMEP and CHIMERE), 2) the negative dependency of the population density (i.e., increasing BaP with the decreasing population density) for which we do not have a clear explanation. This negative dependency might be caused by differences in residential heating behaviour between countries and between rural and urban areas. Temperature is used in the chosen model IV. In the multiple linear regression, with increasing temperature, BaP is decreasing. The main reason for this relation is that domestic heating is the main source of BaP emissions.

Spatial interpolation

Based on the supplementary parameters and the kriging variant selected above, the concentration map of BaP was constructed using both EMEP and CHIMERE model outputs. The maps were created separately for the rural and urban background areas (at 10x10 km^2 resolution), and subsequently combined using population density (at 1x1 km^2 resolution), see sections 5.1.4 and 5.1.5. The combined BaP concentration map has a 10x10 km^2 resolution.

Figure 8 presents the combined final maps for the 2012 BaP annual mean for Europe in a 10x10 km^2 grid resolution, using EMEP and CHIMERE model outputs. Red and purple areas and stations exceed the target value (TV) of 1 ng.m^{-3}. The dark green colour indicates concentrations under the estimated reference level of 0.12 ng.m^{-3}, corresponding to an additional lifetime cancer risk of 1 x 10^{-5}.

Table 6 presents the estimated parameters of the linear regression models (c, a_1, a_2, ... in equation 1) and of the residual kriging (*nugget*, *sill*, *range*), and it includes the statistical indicators of both the regression and the kriging. The adjusted R^2 and standard error are indicators for the fit of the regression relationship, where the adjusted R^2 should be as close to one as possible and the standard error should be as small as possible. RMSE and bias are the cross-validation indicators, showing the quality of the resulting map.

Table 6: Parameters of the linear regression models and of the ordinary kriging variograms (nugget, sill, range) and their statistics of BaP annual average for 2012 in rural and urban areas, using EMEP (left) and CHIMERE (right) model results.

linear regression model + ord. kriging of its residuals	**using EMEP**		**using CHIMERE**	
	rural areas	**urban b. areas**	**rural areas**	**urban b. areas**
	coeff.	**coeff.**	**coeff.**	**coeff.**
c (constant)	1.95	2.81	1.45	3.29
a1 (log. EMEP model 2012)	0.456	0.72		
a1 (log. CHIMERE model 2012)			0.606	0.79
a2 (altitude GTOPO)	-0.00163		-0.00141	
a3 (wind speed 2012)	-0.599		-0.439	
a4 (temperature 2012)		-0.19		-0.26
adjusted R^2	**0.35**	**0.44**	**0.40**	**0.45**
standard error [$ng.m^{-3}$]	**1.16**	**1.10**	**1.12**	**1.09**
nugget	0.62	0.58	0.07	0.08
sill	1.29	1.16	0.69	0.71
range [km]	950	900	250	250
RMSE [$ng.m^{-3}$]	**0.64**	**1.84**	**0.60**	**2.02**
RRMSE [%]	**129%**	**69%**	**121%**	**75%**
bias (MPE) [$ng.m^{-3}$]	**0.08**	**0.04**	**0.06**	**0.08**

Figure 9 presents the difference between the interpolated maps created using EMEP and CHIMERE output data. The main differences are observed in the areas with largest differences between the CTM results and with low density of measurement stations (e.g., Romania). In general, in areas higher population density and higher emissions, the CHIMERE model calculates higher concentrations than the EMEP model due to its higher spatial resolution. The lower EMEP emission and concentration field resolution leads to a smoothing of BaP concentrations over the grid cell and therefore to lower concentrations in these specific areas (see also discussion in section 5.1.2).

Large differences between the CTM results in the areas with high density of measurement stations (e.g., Benelux) do not lead to large differences in the interpolated maps outputs, because the spatial interpolated mapping results are primarily driven by the measurement results.

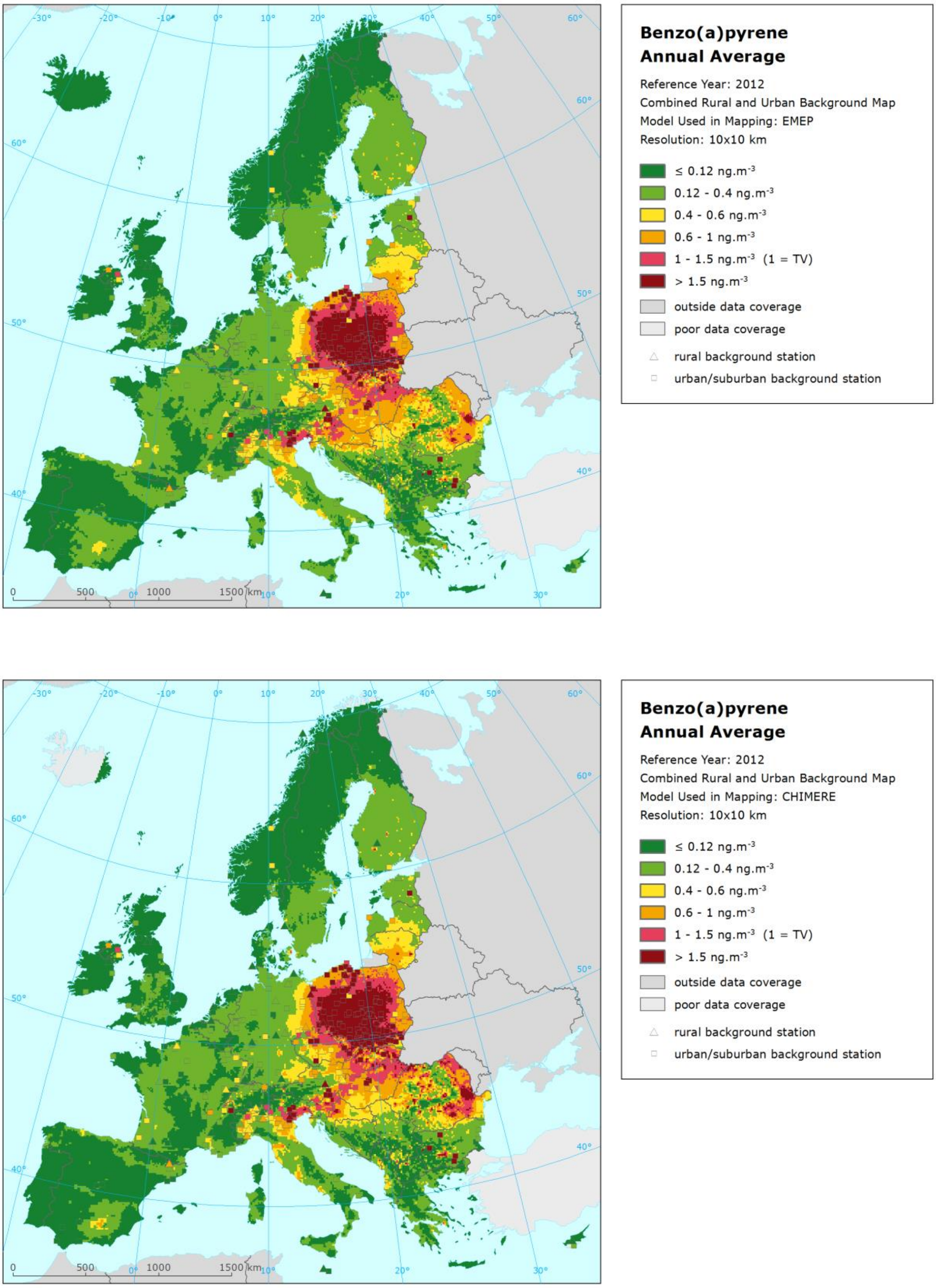

Figure 8: ***Spatial interpolated concentration field of annual mean BaP in 2012 using EMEP (top) and CHIMERE (bottom) models and the measured values at measurement points.***

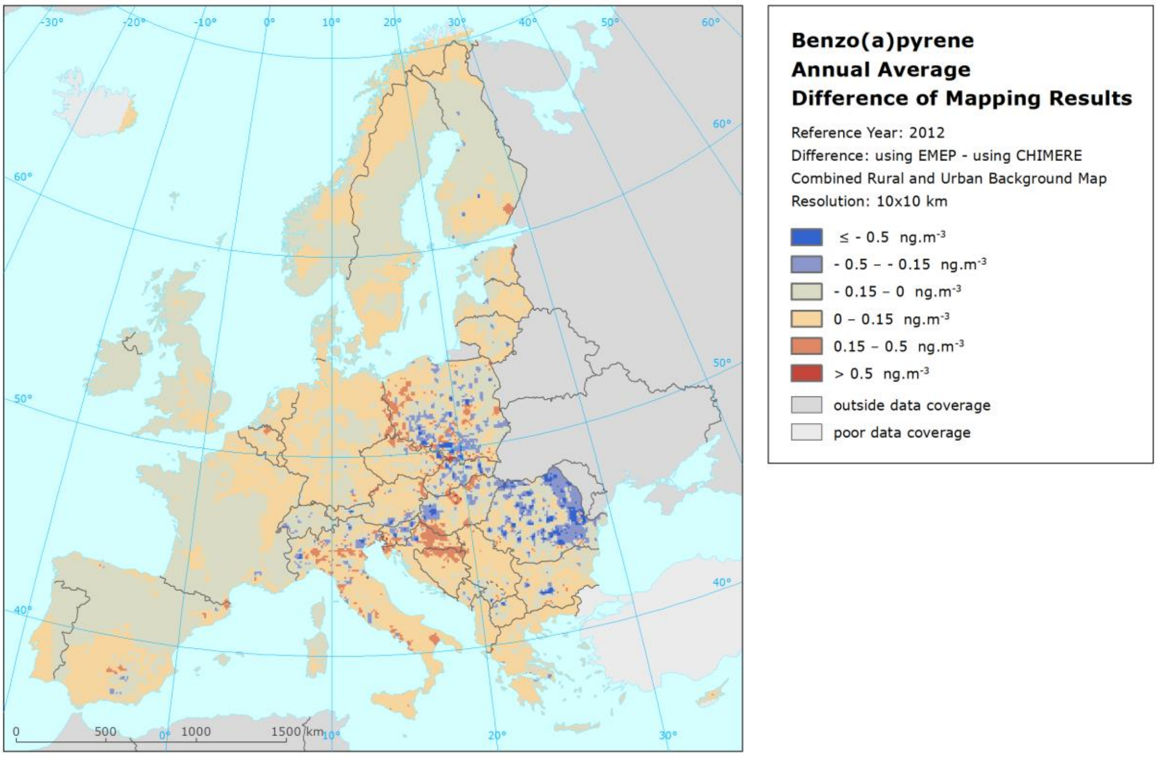

Figure 9: ***Difference of the mapping results of BaP annual average for 2012 using EMEP and CHIMERE models.***

Uncertainties

The air quality directive (EU, 2004) sets the upper and lower assessment threshold (UAT and LAT) of 0.6 and 0.4 ng.m^{-3} for the assessment of BaP concentrations. Monitoring is not required for levels under the LAT (0.4 ng.m^{-3}). These thresholds are quite high compared to an estimated reference level of 0.12 ng.m^{-3}. Thus, BaP concentrations are not measured or the measurement density is very low over large parts of Europe, increasing the uncertainties in the assessment of concentrations and estimation of population exposure.

Uncertainty estimated by cross-validation

Cross-validation simulates and examines the behaviour of the interpolation in the places with no measurement. Using RMSE as the main indicator of uncertainty, the *absolute mean uncertainty* of the final combined map at areas 'in between' the station measurements can be expressed in ng.m^{-3}, see Table 6. RMSE for rural areas is 0.64 ng.m^{-3} for the concentration map using the EMEP model and 0.60 ng.m^{-3} for the map using CHIMERE results. For urban background areas, with higher concentrations, the RMSE is also higher, i.e., 1.8 ng.m^{-3} for the map using EMEP and 2.0 ng.m^{-3} for the map using CHIMERE.

Uncertainty may also be expressed as relative RMSE (RRMSE), i.e., RMSE divided by the mean BaP concentration of all the stations (equation 9). The averaged RRMSE for rural areas is 129% for the EMEP data and domain and 122% for the CHIMERE data and domain. For urban background areas the estimated RRMSE is, respectively, 69% and 75%, for EMEP and CHIMERE modelled data and domain.

The mean measured annual value at the stations is 0.5 ng.m^{-3} for rural background stations and 2.7 ng.m^{-3} for urban/suburban background stations. Both absolute and relative uncertainty values are influenced by these levels. The quality of the map using the CHIMERE model output is slightly better for rural areas, while the quality of the map using the EMEP model output is slightly better for urban background areas.

Figure 10 shows the cross-validation scatter plots, for both rural and urban background areas. R^2 and the slope a (from the linear regression equation $y = a \cdot x + c$) should be as close to one as possible, the intercept c should be as close to zero as possible. The R^2 indicates that for the rural areas about 44% (using EMEP model) or 51% (using CHIMERE model) and for the urban background areas about 71% (using EMEP model) or 66% (using CHIMERE model) of the variability is attributable to the interpolation.

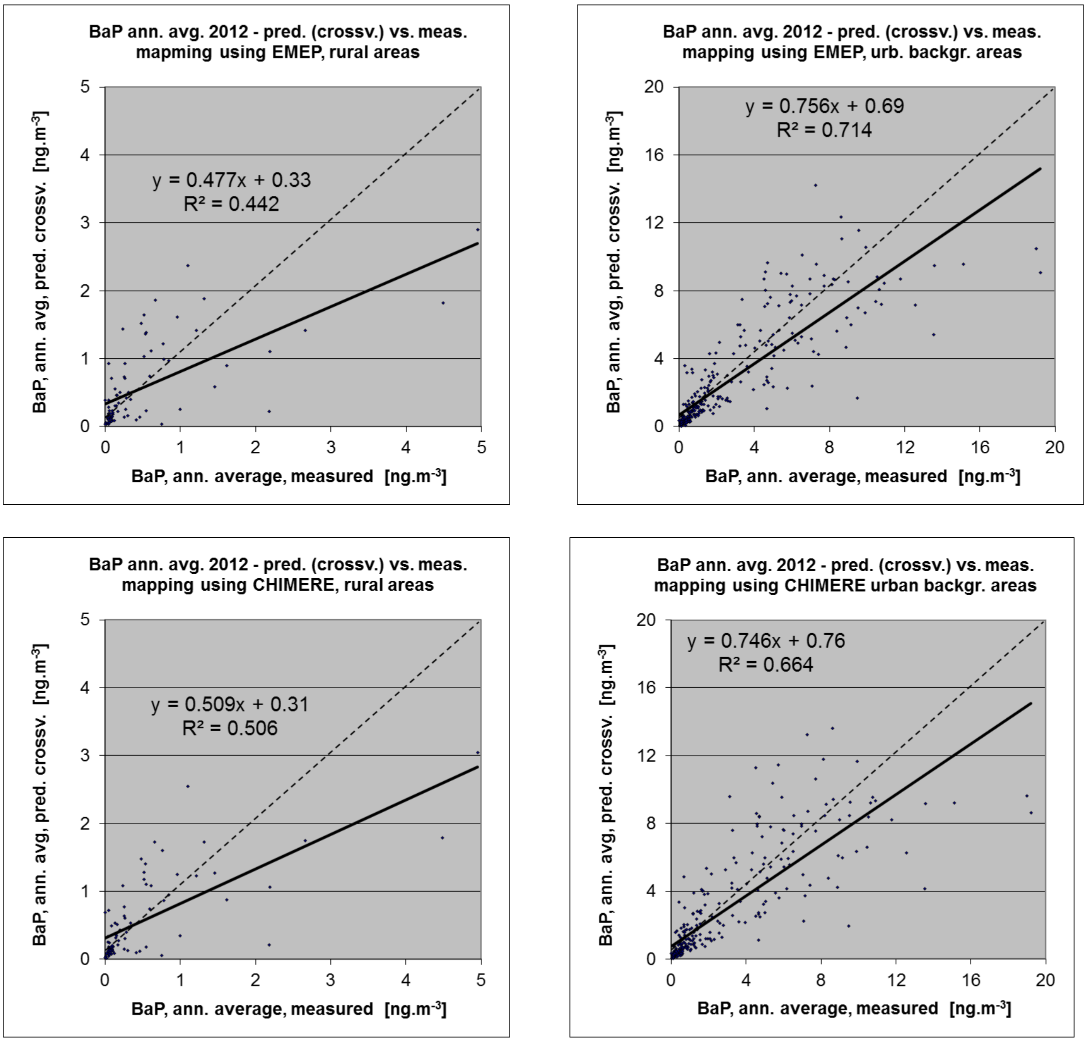

Figure 10: Correlation between cross-validation predicted values and measurements for the BaP annual average map for 2012 created using EMEP (upper) and CHIMERE (lower) for rural (left) and urban (right) areas.

Uncertainty maps based on the kriging theory

In addition to the cross-validation analysis, the uncertainty can also be done based on the kriging theory. The interpolation standard error was calculated for the concentration maps of BaP annual average in 2012 using EMEP and CHIMERE model outputs, as explained in section 5.1.7. In general, the highest uncertainty is in the areas of the highest concentrations, which is overcome when calculating the relative standard error. Figure 11 shows the uncertainty maps, expressed as the relative standard error, calculated by dividing the standard error by the concentration (Figure 8) for each grid cell.

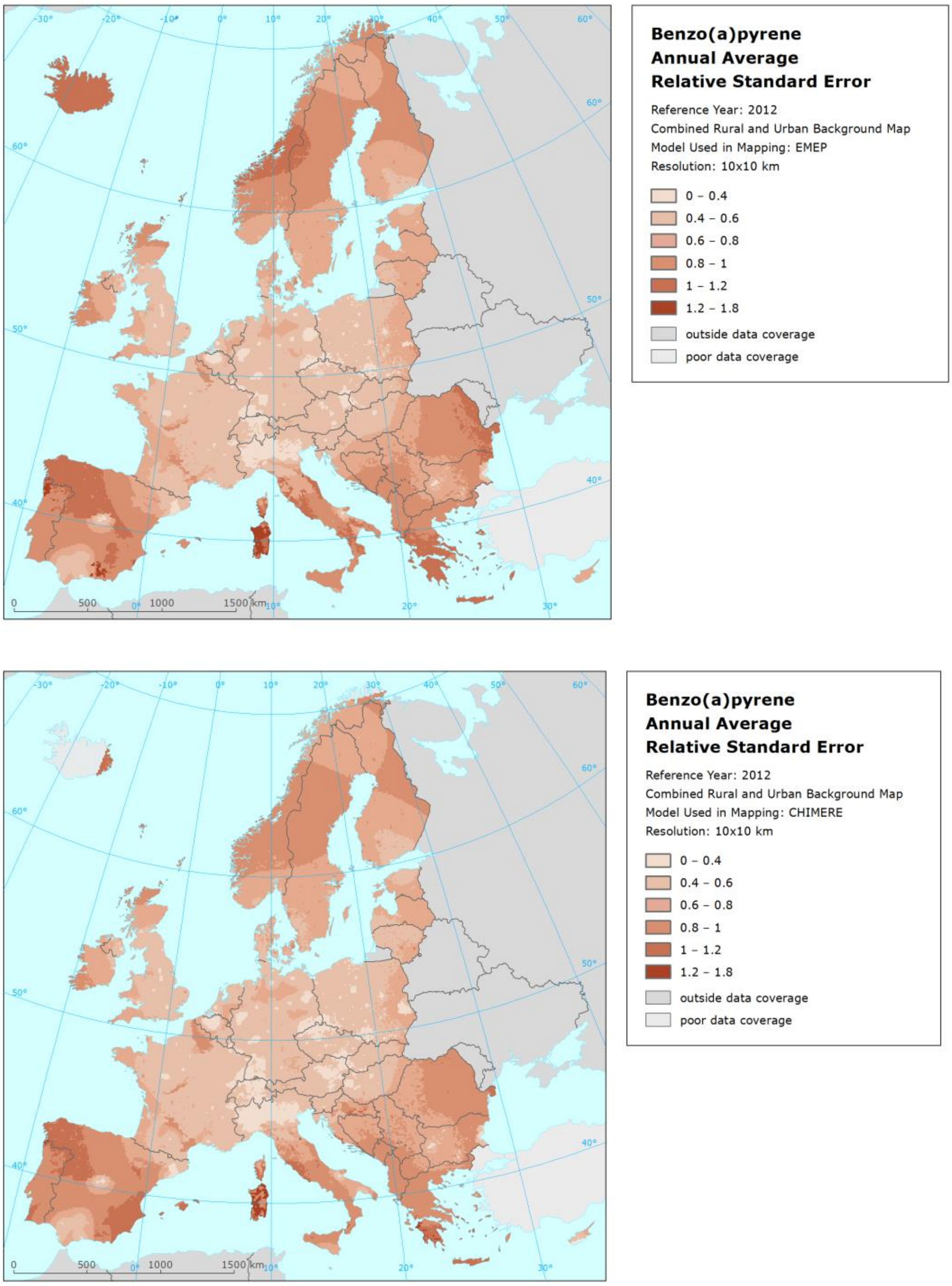

Figure 11: ***Uncertainty map showing interpolation relative standard error for concentration map of BaP annual average in 2012, using EMEP (top) and CHIMERE (bottom) models.***

5.2.2 *Population exposure to BaP*

Exposure of individuals to PAHs occurs through inhalation, ingestion, and absorption through the skin. PAHs emitted to the air may contribute to human exposure by these three different pathways. PAHs in the air may be inhaled, or may be deposed and contaminate the soil, crops and plants, leading to low concentrations of PAHs in food and water. More substantial amounts of PAHs, including BaP, may be found in food, as a consequence of various methods of cooking, preservation and storage. As PAHs are formed in smouldering as well as flaming combustion, "burnt" food contains PAHs, as do smoked foods. Inhalation is the dominant pathway for BaP exposure for smokers, while for non-smokers the main route of exposure is through food (Kim et al., 2013; WHO, 2000; USEPA, 1994). The focus of this section is on the estimation of the European population exposure to ambient BaP concentrations.

The population exposure to BaP concentrations in Europe in 2012 was estimated based on the final combined concentration map (in 1x1 km^2 resolution) and the population density map as explained in section 5.1.6.

Table 7 give the population exposure frequency distribution for a limited number of BaP annual mean concentration ranges, as well as the population-weighted concentration for 2012 for each country and in total. The population-weighted concentration of BaP for the whole Europe (i.e., the average BaP concentration to which the average European inhabitant is exposed to) was about 0.9 ng.m^{-3} in 2012. Note that the population covered is different for the two models, as their modelling domain differs slightly, i.e., for the EMEP model a total population of 516 730 thousand inhabitants is covered, while in the CHIMERE model domain the population covered is 516 169 thousand inhabitants. For the map using CHIMERE, Iceland, northern Norway and southern Cyprus are not included in the calculation, as they're outside the model domain, leading to 561 000 inhabitants not covered by CHIMERE's calculation. Turkey is not included in the calculation due to lacking air quality data.

For the calculation of population exposure the resolution of the CTM output is important, particularly in areas with low measurement density. As explained in section 5.1.2, and specifically in areas of higher population density which are typically the areas of higher emissions due to domestic combustion, concentrations calculated in a small gridcell are higher than in a bigger gridcell. As these areas of higher emissions usually coincide with the areas of higher population density, it has an impact in the outcome of the population exposure. This can be seen in Table 7 for some countries with few measurement stations, but with high emissions and concentrations like Romania and Bulgaria. For small countries the difference in the position of the gridcell boundaries between the CTMs may have as big or greater importance than the resolution.

Figure 13 shows the population-weighted concentration[23] for 2012, with the two different models outputs. It gives a better picture of the population exposure than the concentration maps presented in Figure 8, as it takes into account the population density. It shows that in Baltic countries (especially

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[23] The population weighted concentrations presented with a 10x10 km^2 resolution were calculated for each 10x10 km^2 gridcell by: 1) multiplying concentration with population at each 1x1 km^2 grid cell; 2) summing this product for the hundred gridcells (1x1 km^2) within the 10x10 km^2 gridcell; and 3) dividing this sum by the total population of the 10x10 km^2 gridcell. See equation 6.

Lithuania) some regions of Eastern Europe the population-weighted concentration is very high. People live close to the source, dominated by domestic heating and therefore in areas of higher concentrations than where population density is lower.

About 20 % of the European population has been exposed to BaP annual mean concentrations above the target value (TV) 1 ng.m^{-3} in 2012 and only about 12 % of the European population live in areas with concentrations under the estimated reference level of 0.12 ng.m^{-3} (Table 7). Both the percentage of inhabitants living in the areas above TV and the population-weighted concentration are quite high. As mentioned, the reason for this is the fact that the most of the European population live in urban areas, in general more polluted than the rural areas.

Table 7: Population exposure and population-weighted concentration for BaP annual mean in 2012, based on the interpolated concentration map using EMEP (left) and CHIMERE (right) model outputs.

Country	EMEP							CHIMERE							
	BaP - annual mean, exposed population (%)						BaP conc.	BaP - annual mean, exposed population (%)							BaP conc.
	< 0.12	0.12 - 0.4	0.4 - 0.6	0.6 - 1.0	1.0 - 1.5	> 1.5	Pop. weighted	no data	< 0.12	0.12 - 0.4	0.4 - 0.6	0.6 - 1.0	1.0 - 1.5	> 1.5	Pop. weighted
Andorra	24,06	75,94	0,00	0,00	0,00	0,00	0,11	0,0	16,9	83,1	0,0	0,0	0,0	0,0	0,16
Albania	7,99	19,35	21,01	40,71	10,82	0,12	0,60	0,0	9,5	22,4	20,0	41,3	1,8	4,9	0,64
Austria	1,36	5,15	10,20	64,68	11,12	7,49	0,87	0,0	1,3	6,1	15,7	58,8	7,3	10,7	0,88
Bosnia & Herzeg.	4,49	13,13	10,03	33,64	38,57	0,15	0,81	0,0	5,9	20,0	25,4	36,0	12,5	0,3	0,60
Belgium	4,42	90,36	5,22	0,00	0,00	0,00	0,22	0,0	11,7	88,3	0,0	0,0	0,0	0,0	0,19
Bulgaria	5,78	26,38	7,45	4,91	6,89	48,58	1,78	0,0	8,0	24,5	6,2	5,9	5,7	49,6	2,39
Switzerland	2,66	58,07	18,76	11,16	9,33	0,02	0,45	0,0	2,2	51,0	17,8	15,6	7,7	5,7	0,57
Cyprus	17,63	76,88	0,56	4,93	0,00	0,00	0,21	28,4	71,6	0,0	0,0	0,0	0,0	0,0	0,03
Czech Republic	0,00	1,51	4,55	21,97	36,24	35,72	1,75	0,0	0,0	2,1	5,0	24,6	34,0	34,3	1,72
Germany	0,87	70,57	15,55	11,40	1,05	0,57	0,37	0,0	1,1	70,5	16,0	10,3	1,5	0,5	0,35
Denmark	17,07	23,63	24,07	11,08	24,14	0,00	0,57	0,0	17,2	25,5	19,9	17,4	20,0	0,0	0,56
Estonia	2,77	22,10	13,96	12,21	25,78	23,18	1,04	0,0	2,0	26,9	7,6	13,2	23,5	26,8	1,06
Spain	51,05	45,29	3,64	0,03	0,00	0,00	0,15	0,0	50,0	43,4	5,5	1,0	0,0	0,0	0,15
Finland	2,30	28,50	22,49	20,27	18,22	8,21	0,72	0,0	2,3	28,3	25,9	15,0	14,4	14,1	0,80
France	11,82	79,32	7,89	0,53	0,44	0,00	0,23	0,0	13,3	73,8	11,6	0,7	0,3	0,1	0,24
Greece	13,99	29,07	15,46	40,00	1,06	0,42	0,51	0,0	16,2	29,1	10,1	17,2	27,3	0,0	0,57
Croatia	0,25	14,72	9,26	37,00	29,77	9,00	0,93	0,0	0,4	26,6	21,8	21,4	12,9	16,9	0,82
Hungary	0,00	0,00	1,02	27,38	29,75	41,85	1,56	0,0	0,0	0,0	5,8	23,2	27,9	43,1	1,52
Ireland	41,06	57,46	0,72	0,76	0,00	0,00	0,13	0,0	41,5	57,5	1,0	0,1	0,0	0,0	0,13
Iceland	93,62	6,38	0,00	0,00	0,00	0,00	0,09	96,1	3,9	0,0	0,0	0,0	0,0	0,0	0,00
Italy	3,18	38,02	32,17	16,53	6,06	4,04	0,53	0,0	8,2	38,8	19,4	23,2	6,5	3,9	0,53
Liechtenstein	0,23	19,54	78,94	1,29	0,00	0,00	0,44	0,0	0,2	10,6	8,9	80,3	0,0	0,0	0,65
Lithuania	0,00	4,10	23,13	12,42	6,58	53,77	1,56	0,0	0,0	4,5	22,1	14,5	11,3	47,6	1,65
Luxembourg	7,51	92,49	0,00	0,00	0,00	0,00	0,28	0,0	12,3	87,7	0,0	0,0	0,0	0,0	0,26
Latvia	0,10	18,29	12,16	46,02	9,79	13,64	0,86	0,0	0,1	19,1	14,4	45,9	13,6	6,9	0,80
Monaco	0,00	100,00	0,00	0,00	0,00	0,00	0,26	0,0	0,0	100,0	0,0	0,0	0,0	0,0	0,20
Montenegro	14,95	8,64	4,20	8,51	5,48	58,22	1,54	0,0	13,7	9,7	8,1	10,4	6,6	51,6	2,04
Macedonia, FYRO	11,98	8,21	3,37	26,20	49,07	1,18	0,87	0,0	12,3	7,0	7,3	11,3	19,2	43,0	1,46
Malta	100,00	0,00	0,00	0,00	0,00	0,00	0,09	0,0	100,0	0,0	0,0	0,0	0,0	0,0	0,09
Netherlands	31,47	68,44	0,09	0,00	0,00	0,00	0,15	0,0	19,2	80,8	0,0	0,0	0,0	0,0	0,14
Norway	24,57	47,77	26,46	1,13	0,01	0,07	0,26	0,5	28,9	45,9	22,0	2,3	0,1	0,1	0,26
Poland	0,00	0,05	0,28	6,19	9,28	84,20	4,28	0,0	0,0	0,0	0,3	5,1	10,2	84,4	4,42
Portugal	99,09	0,91	0,00	0,00	0,00	0,00	0,05	0,0	99,1	0,9	0,0	0,0	0,0	0,0	0,04
Romania	0,34	7,68	7,45	12,59	8,11	63,82	2,23	0,0	0,3	6,3	5,4	9,8	9,0	69,1	3,55
Serbia	5,21	12,41	7,13	11,44	48,91	14,90	0,99	0,0	6,0	13,9	7,4	36,5	21,3	15,0	0,93
Sweden	4,71	20,64	14,80	35,07	24,25	0,53	0,67	0,0	6,5	20,9	17,0	42,4	12,7	0,5	0,61
Slovenia	0,00	0,90	4,44	14,26	30,82	49,57	1,54	0,0	0,0	3,4	4,6	15,3	29,3	47,4	1,49
Slovakia	0,00	0,13	0,88	23,65	26,54	48,80	2,15	0,0	0,0	0,1	0,6	20,4	28,5	50,4	2,54
San Marino	0,00	15,37	84,63	0,00	0,00	0,00	0,42	0,0	0,0	5,6	94,4	0,0	0,0	0,0	0,45
United Kingdom	11,53	86,31	0,90	1,27	0,00	0,00	0,22	0,0	13,6	84,5	1,0	0,8	0,0	0,0	0,21
All	**11,66**	**46,73**	**10,44**	**10,71**	**6,82**	**13,64**	**0,84**	**0,11**	**12,57**	**46,12**	**9,78**	**11,00**	**6,14**	**14,28**	**0,92**

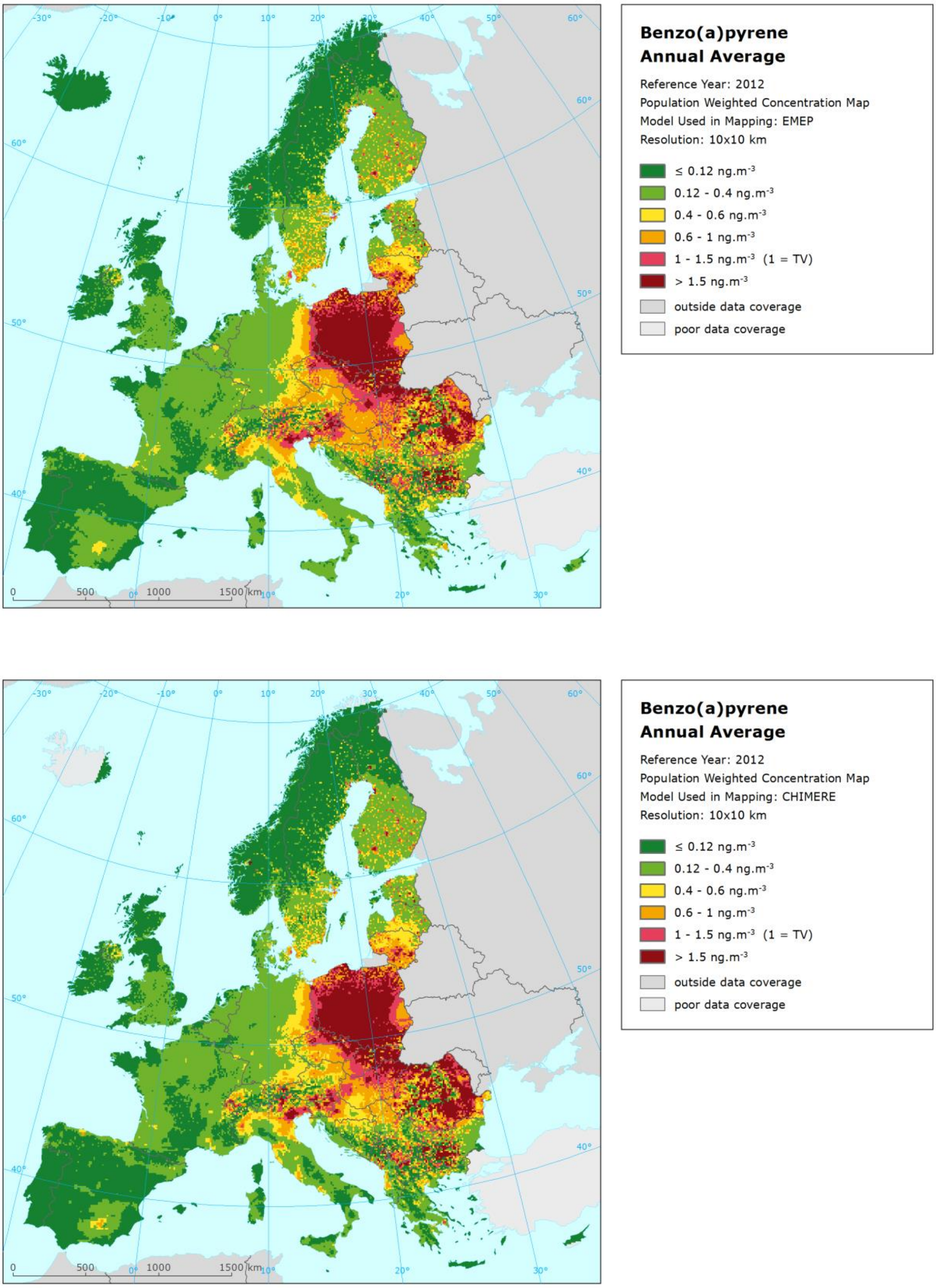

Figure 12: ***Population-weighted concentration field of annual mean BaP in 2012, using EMEP (top) and CHIMERE (bottom) models.***

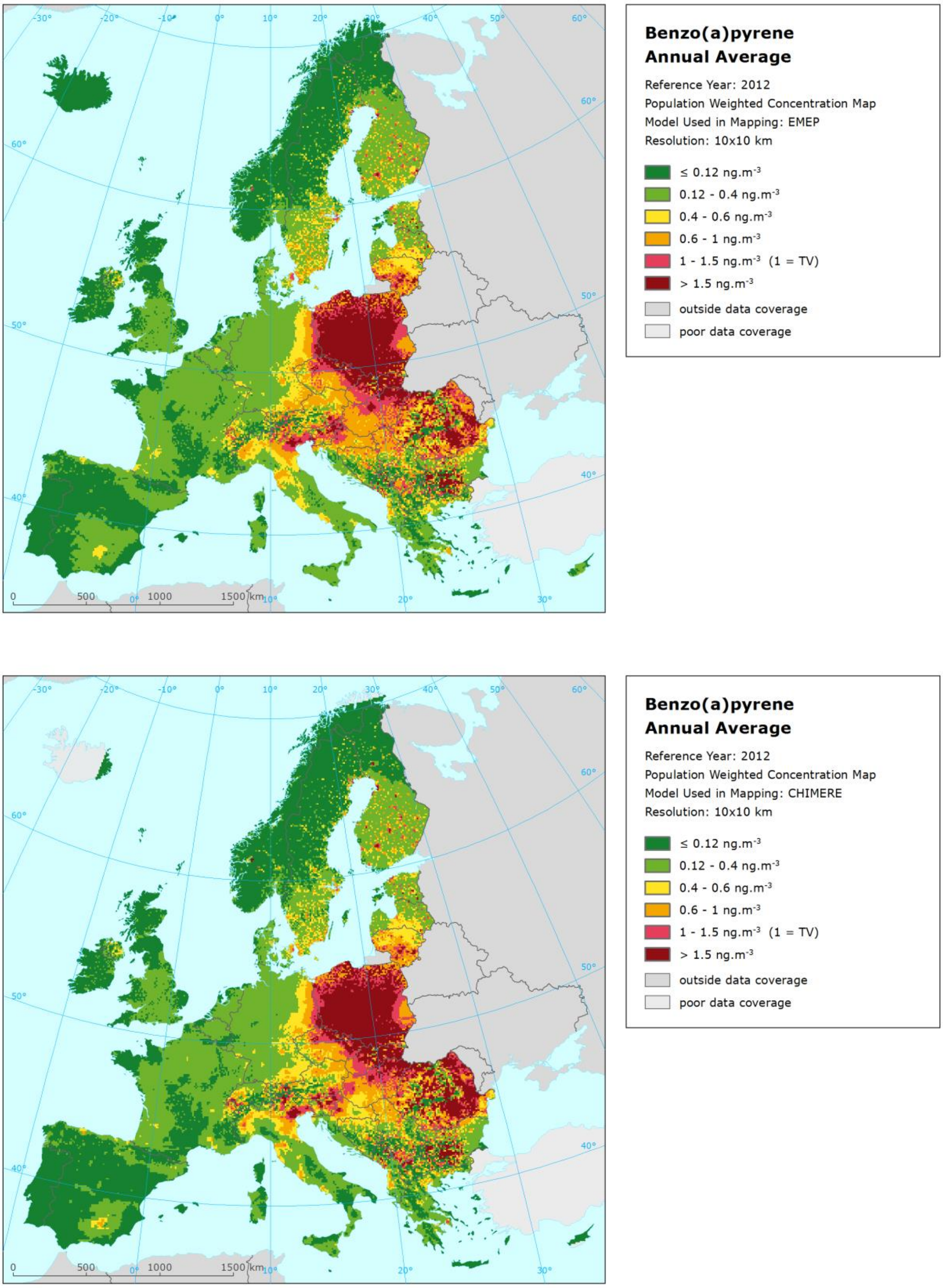

Figure 13: ***Population-weighted concentration field of annual mean BaP in 2012, using EMEP (top) and CHIMERE (bottom) models.***

5.2.3 *Estimation of health effects of BaP in Europe*

On the basis of the BaP population exposure estimates, the number of lung-cancer incidences due to exposure to ambient air BaP concentrations was calculated for the interpolated maps' domains, as explained in section 5.1.8. BaP has other health impacts, as summarized in section 2.1.1, but other health endpoints lack an adequate exposure-response function in order to estimate the effects.

The number of lung cancer incidences was calculated for each country based on the population-weighted concentrations presented in Table 7 and population data for 2012 (01.01.2013) for each country (EUROSTAT, 2015). Lifetime average exposure was set to 70 years, as it was used for the basis of calculation of the $UR_{[BaP]}$ (WHO, 2000).

The estimated number of lung cancer incidences within the whole model domain was about 540 (ranging from 2650 to 140)[24] for the EMEP output results and about 580 (ranging from 2880 to 150) using the CHIMERE model.

Table 8 shows the estimated number of lung cancer incidences per country due to exposure to ambient air BaP concentrations, based on the interpolated concentration map using EMEP and CHIMERE model outputs. Lung cancer incidences are presented as: median, corresponding to the median unit risk 8.7 x 10^{-5} per $ng.m^{-3}$; minimum, corresponding to the median unit risk 2.3 x 10^{-5} per $ng.m^{-3}$; and maximum, corresponding to the median unit risk 43 x 10^{-5} per $ng.m^{-3}$. The largest health impacts can be found in the Eastern European countries, in agreement with the concentration and population exposure maps shown in Figure 8 and Figure 13 . About 50% of the total estimated lung cancer incidences occur in Poland and Romania.

Interpolated maps tend to smooth concentrations and at the resolution (10 x 10 km^2) of the produced interpolated maps the concentrations in urban areas tend to be underestimated. In addition, over large parts of Europe the BaP concentration is assessed to be below the LAT of 0.4 $ng.m^{-3}$, in which case the air quality directive (EU, 2004) does not require monitoring. In these regions, the interpolated concentration map is highly uncertain, as discussed in section 0 and shown in Figure 11. In addition, a fraction of BaP (typically less than 10%, depending on e.g., temperature) is in the gaseous phase and is not taken into account by most of the measurements (see section 5.1.1).

The estimates given above are very likely underestimating the health impacts of ambient BaP since:

- concentrations are underestimated mostly due to the lack of measurement data;

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[24] Within the range of estimated risk of 2.3 - 43 x 10^{-5} per $ng.m^{-3}$ (Boström et al., 2002). It does not include the uncertainties in the concentration maps.

- only intake via inhalation is considered, indirect intake via deposition to soil and water with consequent uptake and bioaccumulation in the food chain plays also an important role;
- the exposure –response function used to estimate lung cancer incidence maybe underestimated. It is based on epidemiological data from studies with coke-oven workers, presumably a male strong/healthy part of the population. The wider population (including children, elderly, sick individuals, woman, etc) may have a more pronounced response to exposure to BaP;
- other health effects than lung cancer (as discussed in section 2.1.1) have not been included in these estimates;
- Any chemical interactions or synergic effects among PAHs and between PAHs and other air pollutants were not considered.

Table 8: ***Estimated number of lung cancer incidences due to exposure to ambient air BaP concentrations, based on the interpolated concentration map using EMEP (left) and CHIMERE (right) model outputs.***

Country	Population	EMEP				CHIMERE			
		BaP conc.	lung cancer incidences			BaP conc.	lung cancer incidences		
		Pop. weighted	median	max	min	Pop. weighted	median	max	min
Andorra	76246	0,11	0	0	0	0,16	0	0	0
Albania	2898782	0,60	2	11	1	0,64	2	11	1
Austria	8451860	0,87	9	45	2	0,88	9	46	2
Bosnia & Herzegovina	3835645	0,81	4	19	1	0,60	3	14	1
Belgium	11161642	0,22	3	15	1	0,19	3	13	1
Bulgaria	7284552	1,78	16	79	4	2,39	22	107	6
Switzerland	8039060	0,45	5	22	1	0,57	6	28	2
Cyprus	865878	0,21	0	1	0	0,03	0	0	0
Czech Republic	10516125	1,75	23	113	6	1,72	23	111	6
Germany	80523746	0,37	37	182	10	0,35	35	175	9
Denmark	5602628	0,57	4	20	1	0,56	4	19	1
Estonia	1320174	1,04	2	8	0	1,06	2	9	0
Spain	46727890	0,15	9	43	2	0,15	9	44	2
Finland	5426674	0,72	5	24	1	0,80	5	27	1
France	65560721	0,23	19	94	5	0,24	19	96	5
Greece	10991400	0,51	7	35	2	0,57	8	39	2
Croatia	4262140	0,93	5	24	1	0,82	4	21	1
Hungary	9908798	1,56	19	95	5	1,52	19	92	5
Ireland	4591087	0,13	1	4	0	0,13	1	4	0
Iceland	321857	0,09	0	0	0	0,00	0	0	0
Italy	59685227	0,53	39	195	10	0,53	40	196	10
Liechtenstein	36838	0,44	0	0	0	0,65	0	0	0
Lithuania	2971905	1,56	6	29	2	1,65	6	30	2
Luxembourg	537039	0,28	0	1	0	0,26	0	1	0
Latvia	2023825	0,86	2	11	1	0,80	2	10	1
Monaco	37600	0,26	0	0	0	0,20	0	0	0
Montenegro	620893	1,54	1	6	0	2,04	2	8	0
Macedonia, FYROM of	2062294	0,87	2	11	1	1,46	4	19	1
Malta	421364	0,09	0	0	0	0,09	0	0	0
Netherlands	16779575	0,15	3	15	1	0,14	3	15	1
Norway	5051275	0,26	2	8	0	0,26	2	8	0
Poland	38062535	4,28	202	1001	54	4,42	209	1034	55
Portugal	10487289	0,05	1	3	0	0,04	1	3	0
Romania	20020074	2,23	55	274	15	3,55	88	437	23
Serbia	7181505	0,99	9	43	2	0,93	8	41	2
Sweden	9555893	0,67	8	39	2	0,61	7	36	2
Slovenia	2058821	1,54	4	20	1	1,49	4	19	1
Slovakia	5410836	2,15	14	72	4	2,54	17	84	5
San Marino	33562	0,42	0	0	0	0,45	0	0	0
United Kingdom	63905297	74,50	17	86	5	0,21	16	81	4
Total	**535310552**	**0,84**	**536**	**2649**	**142**	**0,92**	**582**	**2877**	**154**

6 Part 2: How to limit agriculture's contribution to secondary PM formation in Europe

The objective of this study is to analyse the impact of the Gothenburg Protocol emission reductions and additional ammonia emission reductions on European PM concentrations levels and on the exceedances of the air quality standards for PM. To tackle this issue, a set of model runs were performed for the reference year 2009 and several emissions reduction scenarios, using the EMEP MSC-W model (Simpson et al, 2012), a chemical transport model widely used for policy support in Europe. The model results for a base scenario were validated against measurements. Finally, the analyses of results is based on the impact of NH_3 emission reductions on the reduction of PM concentrations and exceedances across Europe.

6.1 Methodology

The calculations of PM concentrations including NH^{4+}, NO^{3-} and SO_4^{2-} are performed using the 2009 meteorology for the whole year and for all emission scenarios. Emission inputs to dispersion modelling consist in a European emission inventory with a spatial resolution of 0.125°×0.0625°.

6.1.1 *Emission scenarios*

Five simulations were performed based on different emission scenarios: one reference scenario with 2009 emissions, a Gothenburg Protocol scenario (horizon 2020) representing the Gothenburg 2020 protocol emissions, and three more stringent scenarios on ammonia emissions with 10%, 20% and 30% ammonia emission reduction (applied to the Gothenburg emission scenario). The emission scenarios are presented in Table 9. The scenario representing the Gothenburg Protocol emissions was built with the national emission ceiling numbers reported in Annex II issued from UNECE (2012b) (see Table A. 1 to Table A. 6 in Appendix). Coarse PM primary emissions have not been given in the Gothenburg Protocol; estimates for the national emissions of primary coarse PM are obtained from the EMEP webdab emission web site[25] (see Table A. 1 to Table A. 6 in Appendix). To allocate the national emission by activity sector, the same sectoral distribution by pollutant as for the reference year 2009 is applied for these national ceilings.

The spatial patterns of emissions for the different scenarios were estimated based on the spatial patterns of emissions in 2007, in order to take advantage of the high resolution MACC inventory generated by TNO (Kuenen et al., 2011). Prescribed time profiles and height distributions were used following the EURODELTA protocol (*cf* Thunis et al., 2008).

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[25] http://www.ceip.at/ms/ceip_home1/ceip_home/webdab_emepdatabase/

Table 9: Description of emission scenarios

Scenario name in this report	Description
2009REF (or REF)	Official 2009 (from EMEP numbers downloaded on www.emep.int and updated in 2012)
2020GOT (or GOT)	Gothenburg 2020 emissions
2020G10 (or G10)	Gothenburg 2020 + additional 10% reduction for NH_3, EU27 only
2020G20 (or G20)	Gothenburg 2020 + additional 20% reduction for NH_3, EU27 only
2020G30 (or G30)	Gothenburg 2020 + additional 30% reduction for NH_3, EU27 only

The gridded distribution of anthropogenic emissions used were provided by INERIS and were based on a merging of databases from:

- *TNO 0.125°×0.0625° emissions for 2007 from MACC (cf. Kuenen et al., 2011)*
- *EMEP 0.5°×0.5° for 2009 (cf. Vestreng et al., 2007)*
- *Emission data from the GAINS database (see http://gains.iiasa.ac.at/gains)*
- *INERIS expertise on re-gridding with various proxies (population, landuse, Large Point Source data)*

Large point sources from the fine scale (0.125°×0.0625°) TNO-MACC emissions data for 2007 were added to surface emissions. For the various activity sectors (given in SNAP source-sectors[26]) the processing steps were the following:

- SNAP 2: The country emissions were re-gridded with coefficients based on population density and French bottom-up data, the methodology (Bessagnet et al., 2012) was extrapolated to the whole of Europe. For PM2.5 emissions, the annual EMEP totals were kept except for the

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[26] Standardized Nomenclature for Air Pollutants (SNAP) reporting. SNAP 1: Combustion in energy and transformation industries; SNAP 2: Non-industrial combustion plants; SNAP 3: Combustion in manufacturing industry; SNAP 4: Production processes; SNAP 5: Extraction and distribution of fossil fuels and geothermal energy; SNAP 6: Solvents and other product use; SNAP 7: Road transport; SNAP 8: Other mobile sources and machinery ; SNAP 9: Waste treatment and disposal; SNAP 10: Agriculture.

countries[27] CZ, BA, BE, BY, ES, FR, HR, IE, LT, LU, MD, MK, NL, SK, TR. For these countries, PM2.5 emissions from GAINS were used. Additional factors were applied on two Polish regions (×4 or ×8) for PM2.5 and PM10 emissions (Personal communication from IIASA) with formerly coal mining activity. These coalmine regions still show high emissions of PM due to continued domestic uses of coal.

- SNAP 3,7,8,9,10: TNO-MACC emissions spatial distribution was used as proxy to regrid EMEP 0.5°x0.5° annual totals into the finer modelling grid.
- SNAP 1,4,5,6: EMEP 0.5°x0.5° emissions were regridded by adequate proxies ("artificial landuse", data for industries from the European Pollutant Emission Register[28] (EPER)).

For countries where TNO-MACC emissions are not available EMEP 0.5°×0.5° emissions are used (Iceland, Liechtenstein, Malta and Asian countries) and re-gridded with adequate proxies ("artificial landuse", data for industries from the EPER).

The spatial distribution calculated as mentioned above for the year 2007 is scaled by sectors and countries for each emitted pollutant, in order to calculate the emissions for a given scenario listed in Table 9 and the reference year 2009. For maritime emissions and countries not mentioned in the protocol emission ceilings, emissions from IIASA's (2004) 2020 Current Legislation Emissions (CLE) scenario were used. Emissions of CO and emissions of PPM with particle diameter between 2.5 µm and 10 µm (PPMcoarse) were also taken from the same 2020 CLE scenario. Emissions of PPM include elemental carbon, organic material and other anthropogenic dust.

Table 10 shows the total change (in percentage of 2009) in emissions of primary PM and PM precursors due to the implementation of the Gothenburg Protocol in 2020, compared to 2009. The detailed emission data per country can be found in the appendix (Table A. 1 to Table A. 6).

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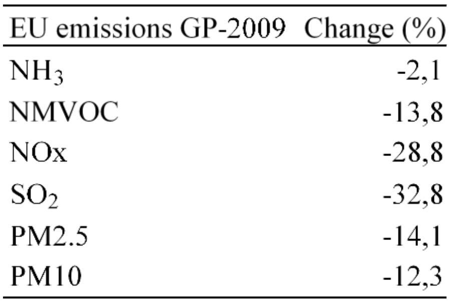
[27] Using ISO 3166-1 alpha-2 codes for the countries.

[28] EPER is a web-based register, enabling the access to emissions to water and air of 50 key pollutants from large and medium-sized industrial point sources in the EU. The register is hosted by the European Environment Agency. http://www.eea.europa.eu/data-and-maps/data/eper-the-european-pollutant-emission-register-4

Table 10: Change in total EU27 emissions due to the Gothenburg Protocol compared to 2009.



EU emissions GP-2009	Change (%)
NH_3	-2,1
NMVOC	-13,8
NOx	-28,8
SO_2	-32,8
PM2.5	-14,1
PM10	-12,3

6.1.2 *Modelling of PM formation and dispersion*

The simulations of the emission scenarios described in Table 9 were performed using the three-dimensional Eulerian chemistry transport model EMEP MSC-W model v4.1.3 for the domain over Europe (from -25°E to 45°E and from 30°N to 70°N), using meteorology data for 2009.

A grid resolution of 0.25° to 0.5° was used, as it has been shown by Cuvelier et al. (2013) to be sufficient to study the effect of additional ammonia emission reduction measures on PM formation and concentrations.

The output species include SIA (here SIA is the sum of ammonium, sulphate and nitrate) and the total PM in both 2.5 and 10 µm fractions (PM10 and PM2.5). The following acronyms for SIA and their precursors is used here:

- NO_3-X : Nitrate for particles with diameter below X µm
- NH_4-X : Ammonium for particles with diameter below X µm
- SO_4-X : Sulphate for particles with diameter below X µm
- HNO_3 : Nitric acid (gas)
- NH_3 : Ammonia (gas)
- TNO_3 : Total nitrate ($TNO_3 = NO_3\text{-}10 + HNO_{3\text{ eq. Nitrate}}$)
- TNH_4 : Total ammonium ($TNH_4 = NH_4\text{-}10 + NH_{3\text{ eq. Ammonium}}$)

In the EMEP model, the PM10 concentration is calculated as follows:

$$PM10 = PPM_{coarse} + PPM_{fine} + SO_4^{2-} + NO_3^{-} + NH_4^{+} + Sea\ Salt + SOA + Dust \qquad (11)$$

The EMEP model includes on-line calculated windblown and road dust and also African dust from boundary conditions; SOA originates from both anthropogenic and biogenic VOC emissions. Further details on the model are given in Simpson et al. (2012).

6.1.3 *Model evaluation*

The model has to demonstrate its reliability as a basis for policy and decision making, and the model predictions of the speciated inorganic PM concentrations calculated in the baseline run (using current emissions) need therefore to be compared and found consistent with observations. The evaluation was carried out using all the available EMEP observations for 2009 (Table 11) that were downloaded from the EBAS database[29]. Only daily observations were used and all the observations are regional background measurements, which is coherent with the resolutions of the models in this exercise.

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[29] EBAS is a database hosting observation data of atmospheric chemical composition and physical properties. EBAS hosts data submitted by data originators in support of a number of national and international programs ranging from monitoring activities to research projects. EBAS is developed and operated by the Norwegian Institute for Air Research (NILU). For a complete list of programmes and projects for which EBAS serves as a database, please consult the information box in the Framework filter of the web interface (http://ebas.nilu.no/)

Table 11: Number and EMEP station code of sites used for the evaluation of model results for each pollutant.

Pollutant	Number of EMEP sites	EMEP stations code (b)
PM10	72	AT02, AT05, AT48, CH01, CH02, CH03, CH04, CH05, CY02, CZ01, CZ03, DE01, DE02, DE03, DE07, DE08, DE09, DE44, DK05, ES01, ES06, ES07, ES08, ES09, ES10, ES11, ES12, ES13, ES14, ES16, ES17, ES78, FR09, FR13, FR15, FR18, GB06, GB36, GB43, GB48, GR02, HU02, IT01, LV10, LV16, MD13, NL07, NL09, NL10, NL91, PL05, SE11, SE12, SE14, SI08, FR09, FR13, FR15, FR18, GB06, GB36, GB43, GB48, GR02, HU02, NL07, NL09, NL10, NL91, SE11, SE12
PM2.5	48	AT02, CH02, CH05, CY02, CZ03, DE02, DE03, DE44, ES01, ES07, ES08, ES09, ES10, ES11, ES12, ES13, ES14, ES16, ES78, FR09, FR13, FR15, FR18, GB36, GB48, GLOB, IE31, IT04, LV10, LV16, NL09, NL10, NL11, NL91, PL05, SE11, SE12, SE14, SI08, FR09, FR13, FR15, FR18, GB36, GB48, IE31, SE11, SE12
SO_4-10 (a)	38	AM01, AT02, CH01, CH02, CH05, CZ01, CZ03, DE44, DK03, DK05, DK08, DK31, ES01, ES07, ES08, ES09, ES10, ES11, ES12, ES13, ES14, ES16, ES17, ES78, FI09, FI17, FI36, FR09, FR13, FR15, GB02, GB06, GB07, GB13, GB14, GB36, GB48, HU02
NO_3-10	47	AM01, AT02, DE44, ES01, ES07, ES08, ES09, ES10, ES11, ES12, ES13, ES14, ES16, ES17, ES78, GB36, GB48, HU02, IE05, IE06, IE08, IT01, KZ01, LV10, LV16, MD13, NL08, NL10, NL11, NL91, NO01, NO15, NO39, NO42, NO55, NO56, PL02, PL03, PL04, PL05, RU18, SK02, SK06, GB36, GB48, NL11
NH_4-10	42	AM01, AT02, DE44, DK03, DK05, DK08, DK31, ES09, ES78, FI09, FI17, FI36, GB36, GB48, HU02, IE05, IE06, IE08, IT01, LV10, LV16, MD13, NL08, NL10, NL11, NL91, NO01, NO15, NO39, NO42, NO55, NO56, PL02, PL03, PL04, PL05, RU18, SK06, GB36, GB48, NL11
TNO_3	47	AT02, CH02, CH05, CZ01, CZ03, DK03, DK05, DK08, DK31, ES01, ES07, ES08, ES09, ES10, ES11, ES12, ES13, ES14, ES16, ES17, FI09, FI17, FI36, FR09, FR13, FR15, HU02, IE01, IT01, LT15, LV10, LV16, MD13, NO01, NO15, NO39, NO55, NO56, PL02, PL03, PL04, PL05, SE05, SE11, SE12, SE14, SI08
TNH_4	42	AT02, CH02, CH05, CZ01, CZ03, DK03, DK05, DK08, DK31, ES01, ES07, ES08, ES09, ES10, ES11, ES12, ES13, ES14, ES16, ES17, FI09, FI17, FI36, FR09, FR13, FR15, HU02, IE01, IT01, LT15, LV10, LV16, MD13, PL02, PL03, PL04, PL05, SE05, SE11, SE12, SE14, SI08
HNO_3	19	AM01, AT02, GB48, HU02, IT01, MD13, NL11, NO01, NO15, NO39, NO42, NO55, NO56, PL05, SK02, SK06, GB48, NL11
NH_3	20	AM01, AT02, DK03, DK05, DK08, DK31, GB48, HU02, IT01, MD13, NL07, NL11, NL91, PL05, SK06, GB48, NL07, NL11, NL91

(a) Sulphate and corrected sulphate (to account for the sea salt contributions) concentrations were used for the comparisons

(b) Information on station locations, altitude and other metadata for these stations can be found at http://ebas.nilu.no/

6.1.4 *Evaluation of the impact of ammonia emission reductions on exceedances of PM standards*

It is known that CTMs generally underestimate PM concentrations, explained by a lack of sources and/or missing processes (Bessagnet et al., 2014). In order to evaluate the influence of NH_3 emission reductions on PM10 concentrations and exceedances, descriptive statistics were applied to compensate for this known underestimation, as described in Table 12. Measured concentrations data stored in AirBase[30] were used, in addition to the model outputs from each scenario (2009REF, 2020GOT, 2020G10, 2020G20, 2020G30). The model outputs were interpolated to extract the modelled concentrations at the Airbase station locations. A delta of concentration at each monitoring site is then calculated, based on the difference of the modelling results from a 2020 scenario and the 2009 REF reference run. This delta is then applied to the 2009 observations to get a better estimate of 2020 concentrations for the various emission scenarios (Table 12). This methodology based on observations and modelling allows determining the evolution of concentrations for all stations typologies.

Table 12: Steps of the calculation of future PM concentrations at the AirBase stations location for the scenario analyses

Step 1: Observational data	**Step 2 : model simulation**	**Step 3**		**Step 4**
AirBase observations 2009 C_k measured concentration at site k	Output model 2009REF Output model 2020GOT Output model 2020G10 Output model 2020G20 Output model 2020G30	Interpolation of modelled concentrations on AirBase stations	C_k^{REF} C_k^{GOT} C_k^{G10} C_k^{G20} C_k^{G30}	$C_k + (C_k^{GOT} - C_k^{REF})$ $C_k + (C_k^{G10} - C_k^{REF})$ $C_k + (C_k^{G20} - C_k^{REF})$ $C_k + (C_k^{G30} - C_k^{REF})$

The focus of this analysis is on the impact of the NH_3 reduction scenarios on PM10 and PM2.5. The air quality Directive (EU, 2008) specifies that the annual mean of PM2.5 must not exceed 20 $\mu g.m^{-3}$ in case of PM2.5 (stage 2 indicative limit value in 2020), and 40 $\mu g.m^{-3}$ in case of PM10. A short-term LV is defined for PM10: the number of days that exceed the daily limit value, fixed at 50 $\mu g.m^{-3}$, must not exceed 35. These limit values were used as indicators to quantify the impact of scenarios. It is noticeable that, according to the Guidance on the Commission Implementing Decision 2011/850/EC (EC, 2013; for EU, 2011) only stations with a data capture larger than 85% are used.

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[30] AirBase is the public air quality database system of the EEA. It contains air quality monitoring data and information submitted by the participating countries throughout Europe.
http://acm.eionet.europa.eu/databases/airbase

6.2 Results

6.2.1 *Model evaluation*

Figure 14 presents the annual mean PM10 and PM2.5 concentrations simulated by the models for 2009. The corresponding measured annual mean concentrations are shown in the figure with coloured circles with the same colour scale.

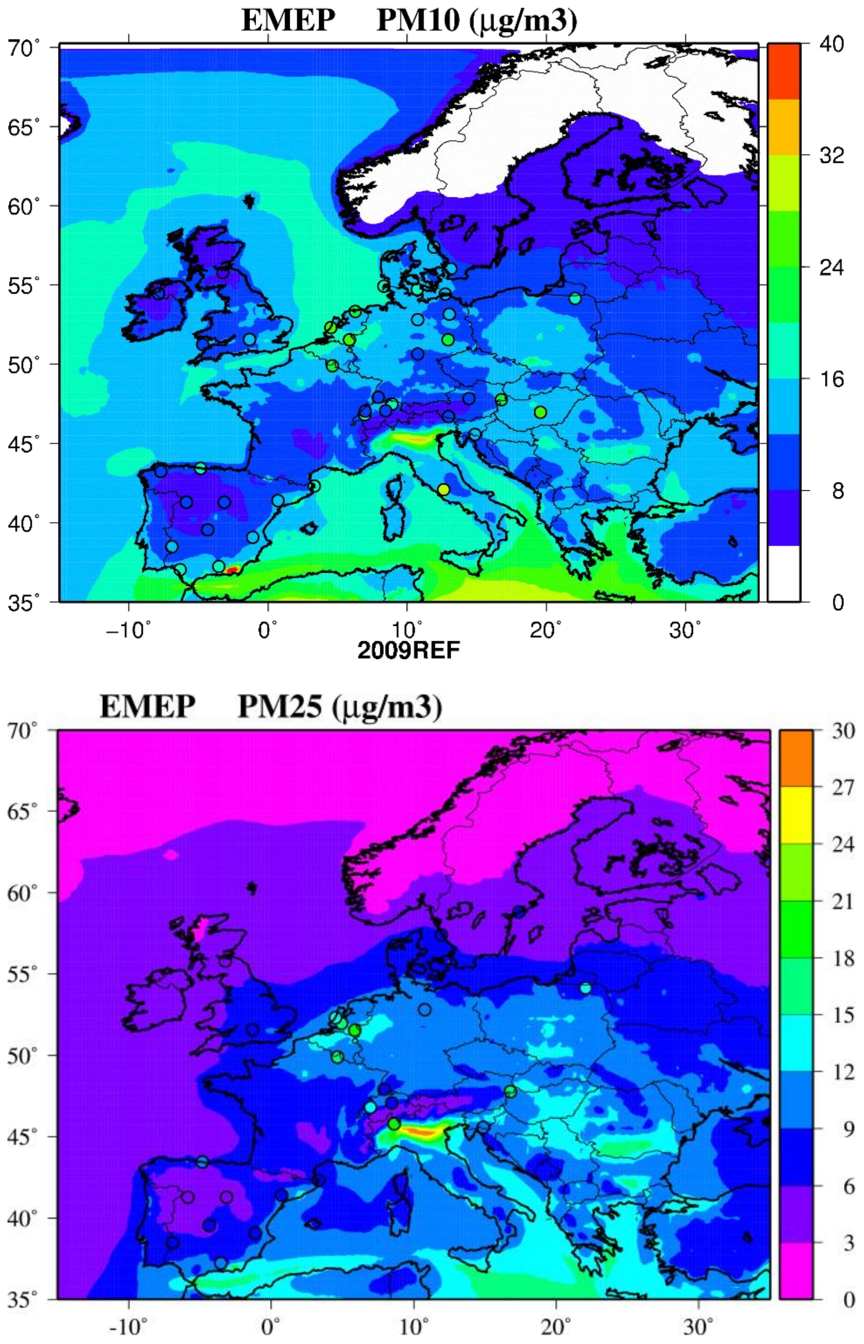

Figure 14: Modelled annual mean PM10 (top) and PM2.5 (bottom) concentrations and measured annual mean concentrations (coloured circles, only stations with at least 75 % of data coverage are plotted) in 2009. Units: µg.m^{-3}.

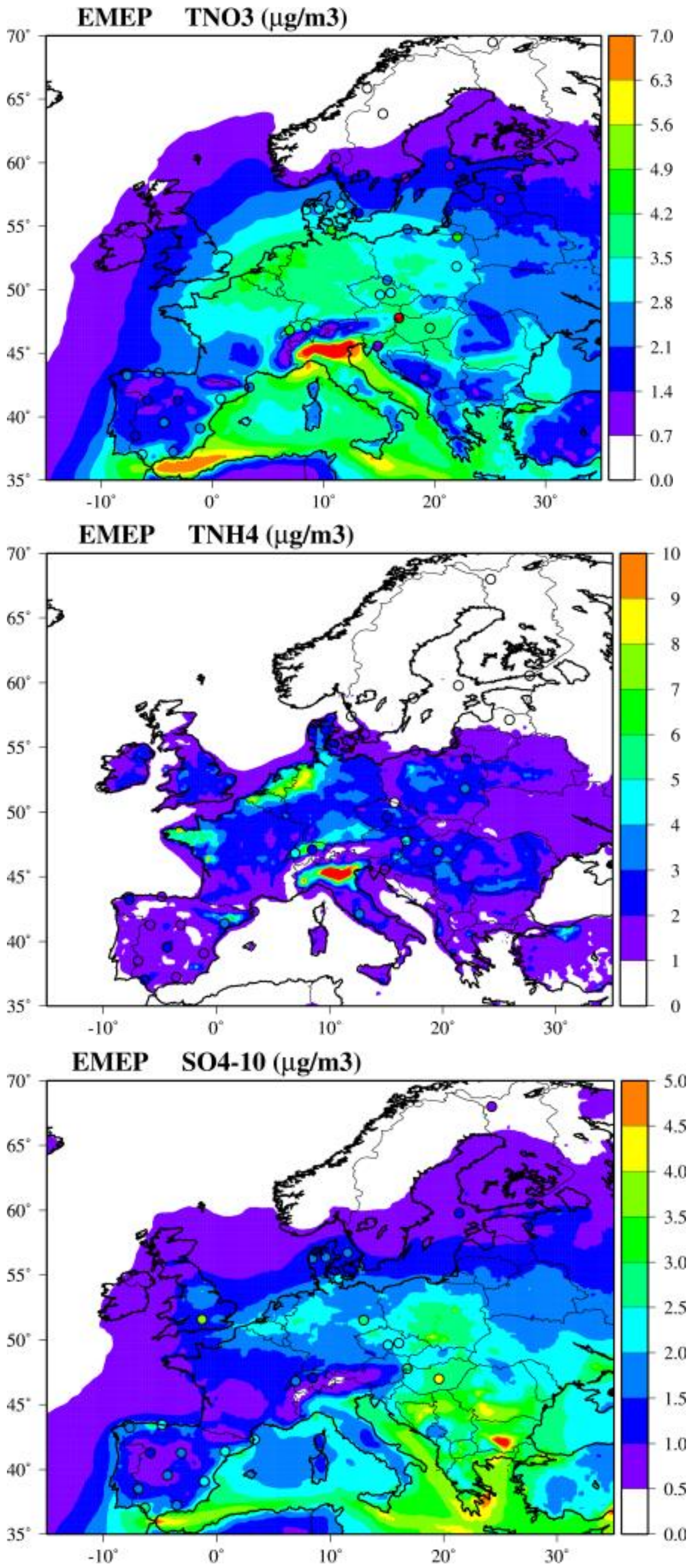

Figure 15: ***Modelled annual mean Total nitrate (TNO_3), Total ammonium (TNH_4) and Sulphate (SO_4-10) concentrations in 2009 (coloured circles are the observations, only stations with at least 75 % of data coverage are plotted). Units: µg.m^{-3}.***

Figure 15 presents the annual averaged Total nitrate (TNO_3), Total ammonium (TNH_4) and Sulphate (SO_4-10) concentrations simulated for 2009. TNO_3 and especially sulphate concentrations are high areas with intense maritime shipping and high NO_x and SO_x emissions (e.g., in the Strait of Gibraltar and over the Mediterranean Sea). The sulphate hotspot in Bulgaria is due to high SO_x emissions from the largest energy complex in South Eastern Europe, the Maritsa Iztok Complex, powered by lignite coal, while the hotspot in Greece is mainly due to emissions from the Port of Piraeus and some power plants in the area. The high concentrations of TNO_3 and TNH_4 in the Pô valley in Italy are due to a combination of high NO_x and NH_3 emissions and topographic and meteorological conditions disfavouring dispersion.

Table 13 summarizes the performance of the model in terms of error statistics as the mean bias, correlation (spatio-temporal) and the root mean square error (RMSE) for the PM, SIA and associated gases (NH_3 and HNO_3), in addition to TNO_3 and TNH_4. As expected, PM10 and PM2.5 concentrations are underestimated by the model (ca 25%), leading to a negative bias, explained by a lack of sources and/or missing processes (*e.g.,* secondary organic aerosols and local dust). On SIA components, the model is able to reproduce annual mean concentrations with a small bias. For TNO_3 and TNH_4 concentrations, EMEP underestimates in average over Europe by 3% and 11%, respectively. Sulphate and HNO_3 concentrations are underestimated by 27%, while NH_4-10 is underestimated by 23% and H_3.-10 by 9%. The hardest compound for EMEP to model is HNO_3, which is underestimated by 31% and has a very low correlation between modelled and measured concentrations (0.21). EMEP is, never the less, a state of art model and its results are comparable to several state of the art CTMs as CHIMERE and LOTOS-EUROS (Bertrand et al., 2014).

Table 13: Performances of the EMEP model in terms of error statistics: observed and modelled annual mean values, mean bias, correlation, Root Mean Square Error (RMSE), number of daily mean observations for comparison (Nb). Units: µg.m^{-3}, except for correlation and Nb.

Pollutant	Observ.	Model	Bias	Corr	RMSE	Nb
PM10	15.65	11.76	-3.89	0.55	10.63	16405
PM2.5	10.71	8.17	-2.54	0.63	7.56	11043
SO_4-10	1.93	1.41	-0.52	0.59	1.49	9975
NH_4-10	1.05	0.81	-0.24	0.50	1.59	9930
NO_3-10	2.02	1.84	-0.18	0.32	4.60	11432
NH_3	2.09	1.52	-0.57	0.71	2.52	3877
HNO_3	1.05	0.72	-0.33	0.21	1.37	3125
TNH_4	1.92	1.70	-0.22	0.52	1.88	13354
TNO_3	2.39	2.32	-0.07	0.34	4.28	15261

SIA concentrations are considerably underestimated by the model during PM pollution episodes and this contributes to the global underestimation of PM2.5 and PM10 concentrations during these events.

Analysing the 10 highest daily mean concentrations at each site, in average EMEP underestimates such high concentrations by 38% for both PM10 and PM2.5, by 42% for TNH_4 and by 32% for TNO_3.

6.2.2 *Impact of NH_3 emissions reduction on annual PM concentrations*

Figure 16 displays the concentration decline throughout Europe between the 2009 situation and the expected situation with Gothenburg Protocol emissions. The results show a slightly higher decrease particularly over the Pô valley in Italy, Greece and Romania. In Spain and the Netherlands, the decrease is very low. In these countries, the small decrease of concentrations is mainly attributed to low reduction in emissions between 2009 and 2020.

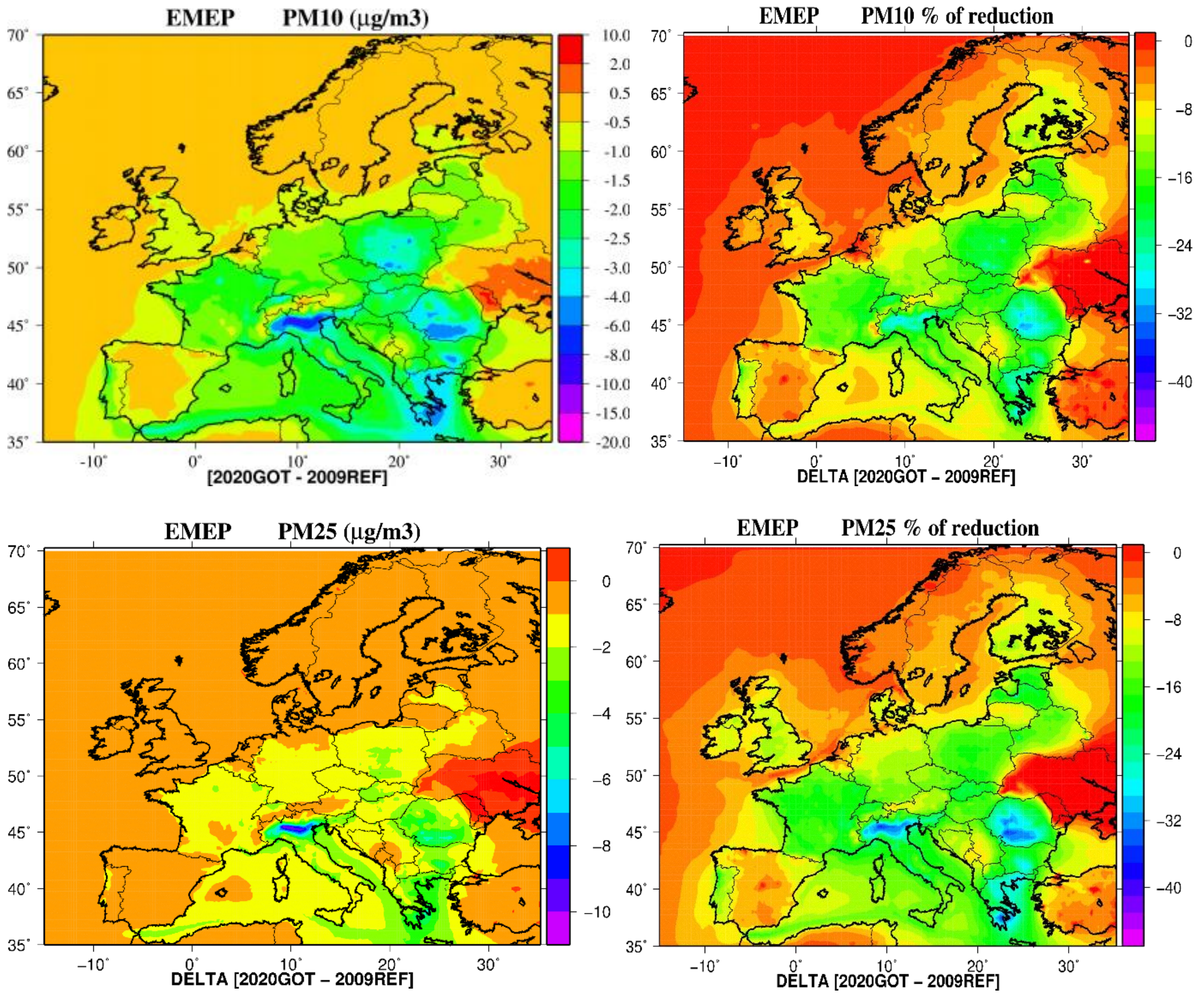

Figure 16: ***Reduction of annual mean PM10 (top) and PM2.5 (bottom) concentrations (left, in µg.m^{-3}) and in percentage (right) for the scenario 2020GOT: difference between scenario and reference (2009REF).***

The Air Quality Directive (EU, 2008) established the national exposure reduction target (NERT) for human exposure to PM2.5, based on the average exposure indicator (AEI) set at the national level. The AEI (representative of general population exposure) is an averaged level of concentrations (in space — per country and time), measured at urban or suburban background monitoring stations over a three-year period, as shown in Figure 17[31]. The Directive requires a considerable reduction in the AEI between 2010 (average 2009-2011) and 2020 (average 2018-2020) for most EU Member States, depending on their levels in 2009-2011. Based on the AEI levels shown in Figure 17[32], PT, IE, ES and LT will have to reduce their levels by 10%; the UK, MT, DK, LV, LU, DE, NL, BE, and FR will have to assure a 15% reduction; and RO, AT, GR, CY, IT, and SI need to reduce their AEI levels by 20%, in order to achieve the NERT (EU, 2008). Finally, HU, CZ, SK, PL, and BG, which have levels above 22 µg.m^{-3}, will have to reduce their levels to a maximum of 18 µg.m^{-3}. This implies a reduction of, respectively, 18%, 32%, ca 28%, 33% and 39% in a decade, which implies a considerable effort in reduction of PPM and PM precursor emissions. As Figure 16 shows, the Gothenburg Protocol will not suffice to achieve such reductions.

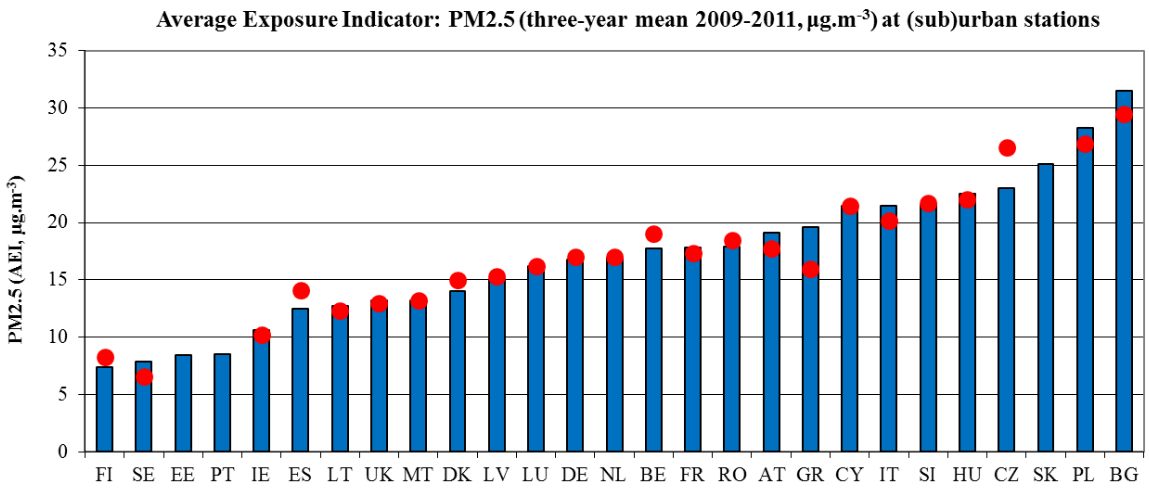

Figure 17: ***Average Exposure Indicator (AEI). Red dots: AEI reported by the countries for 2009-2011, except Poland (for 2010-2011). Bars: calculated AEI based on PM2.5 (µg.m^{-3}) 3-year mean at suburban and urban monitoring stations, 2009-2011. Source: EEA (2013a).***

Figure 18 shows the reduction in PM10 annual mean concentrations due to a further reduction of 10%, 20% and 30% in NH_3 emissions from agriculture over the whole Europe, compared to the Gothenburg emissions scenario. An additional emission reduction of NH_3 has an impact in a large region from the

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[31] The presented levels by the bars are not based on a stable set of stations and for some countries results are based on data for less than three years (e.g. Poland).

[32] The country codes are given in ISO 3166-1 alpha-2 code.

north of France and south East of England to Poland and Romania (Figure 18). The Pô Valley area is greatly influenced by decreases in ammonia emissions. The highest decreases are simulated in Benelux, western part of Germany, northern part of France and north Italy. Note that all the reduction in mass concentration due to NH_3 emission cuts is in the fine fraction, so actually in PM2.5. Even dough these reductions may not seem much as annual mean mass concentration, they are very important in terms of PM10 high concentration episodes, which are the main cause of exceedances of PM10 LVs in Europe (see further analysis in section 6.2.3).

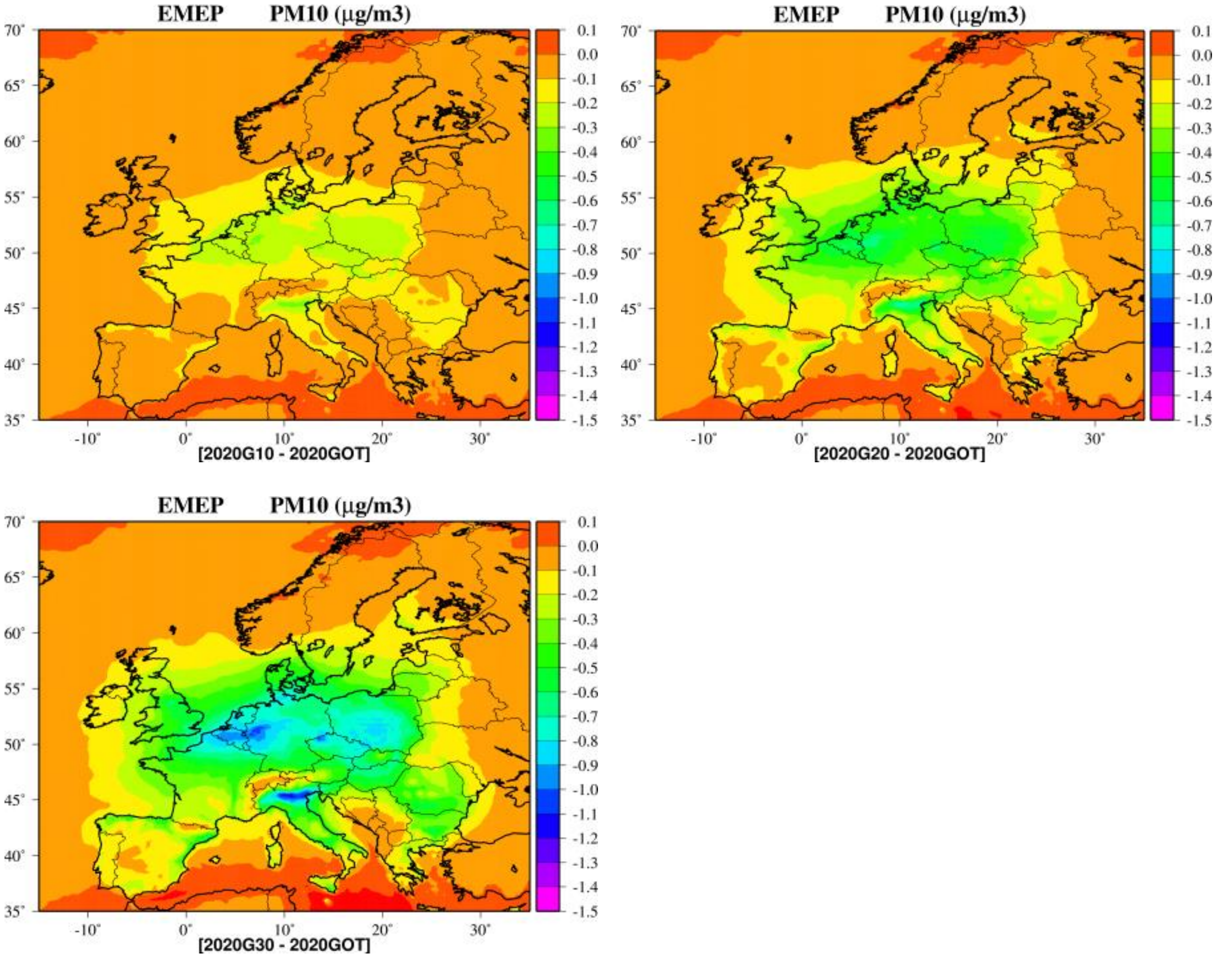

Figure 18: ***Reduction of annual mean PM10 concentrations (µg.m^{-3}) for the scenarios 2020G10, 2020G20 and 2020G30: Delta between scenario and 2020GOT.***

Figure 19 shows the annual mean concentration reduction expected with the scenario 2020G30 in percent points for PM10, PM2.5 and SIA compared to the 2020GOT scenario. The simulations of a further reduction of 30% NH_3 emissions from agriculture, compared to the Gothenburg scenario, indicate that the reduction in annual mean PM2.5 concentration may reach 10% in some areas. The most important reductions (in percentage) are observed over the south of England, north of France, Benelux, Germany, Czech Republic, and Poland, reaching 10% in these regions, also confirmed by the pattern in

SIA reductions. In the south of England, the range of annual mean PM2.5 concentration reduction lies from 6% to 10%. This is close to the values reported by Harrison et al. (2013) with an expected reduction of 9% in a rural site in the south of England with a 30% cut of ammonia emissions in Europe. The percentage reductions of the PM10 annual mean concentrations over Europe are lower than for PM2.5, as expected, ranging from 3% to 8% over most of Europe.

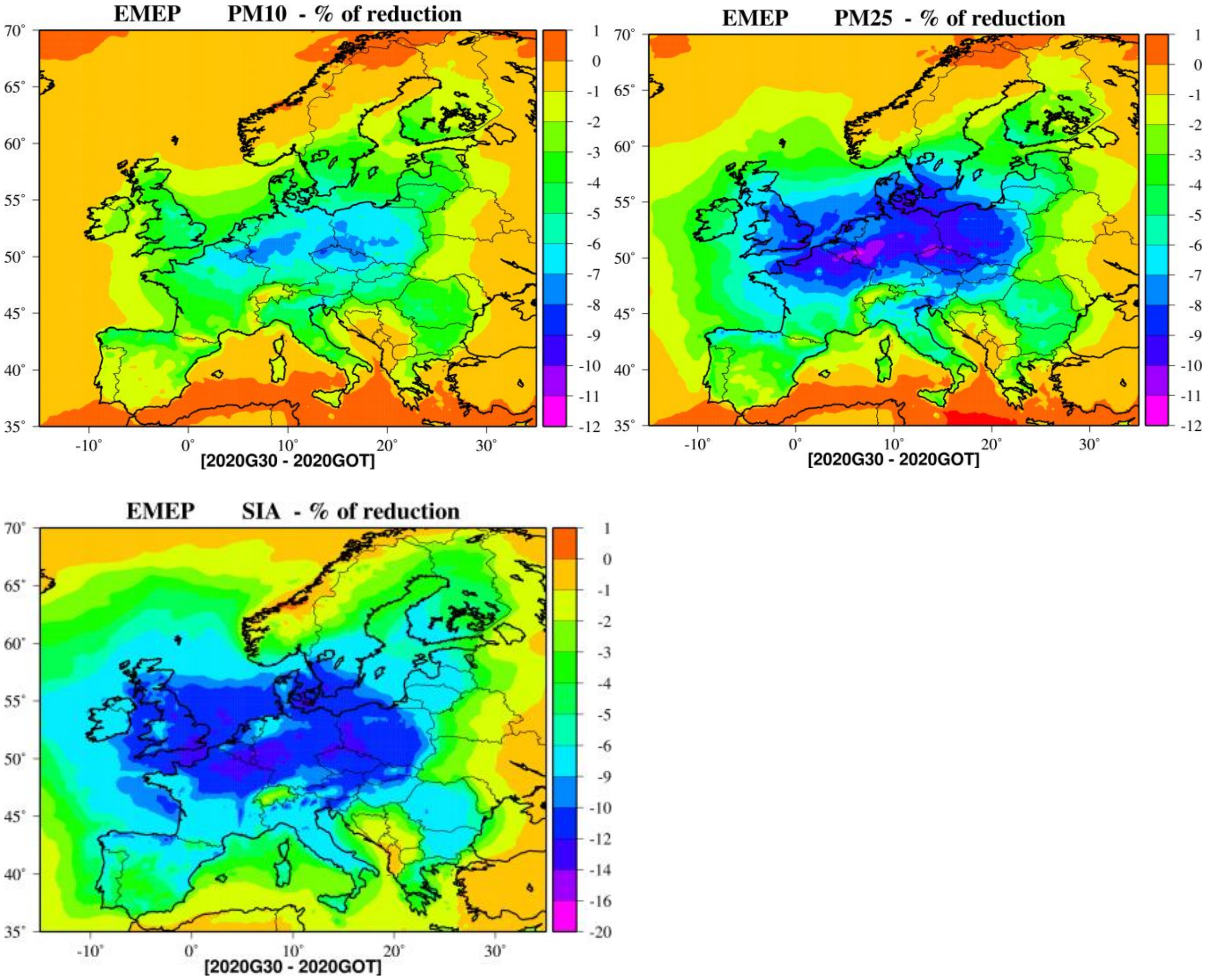

Figure 19: ***Reduction of annual mean PM10, PM2.5 and SIA concentrations (in %) for the scenario 2020G30 compared to 2020GOT emission scenario.***

Figure 20 shows the annual mean concentration reduction expected with the scenario 2020G30 in percentage for PM10, PM2.5 and SIA, compared to the 2009 reference scenario. Such a reduction would largely allow achieving the NERT of[33]: 10% in PT, IE, and LT; 15% in the UK, LV, LU, BE, NL, DE, and FR; 20% in GR, RO, and SI. Furthermore, it would greatly support other countries achieving their

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[33] Using ISO 3166-1 alpha-2 code for countries.

NERT: ES (10%), DK (15%), HU, (18%), AT and IT (20%), SK (28%), CZ (32%), PL (33%), and BG (39%).

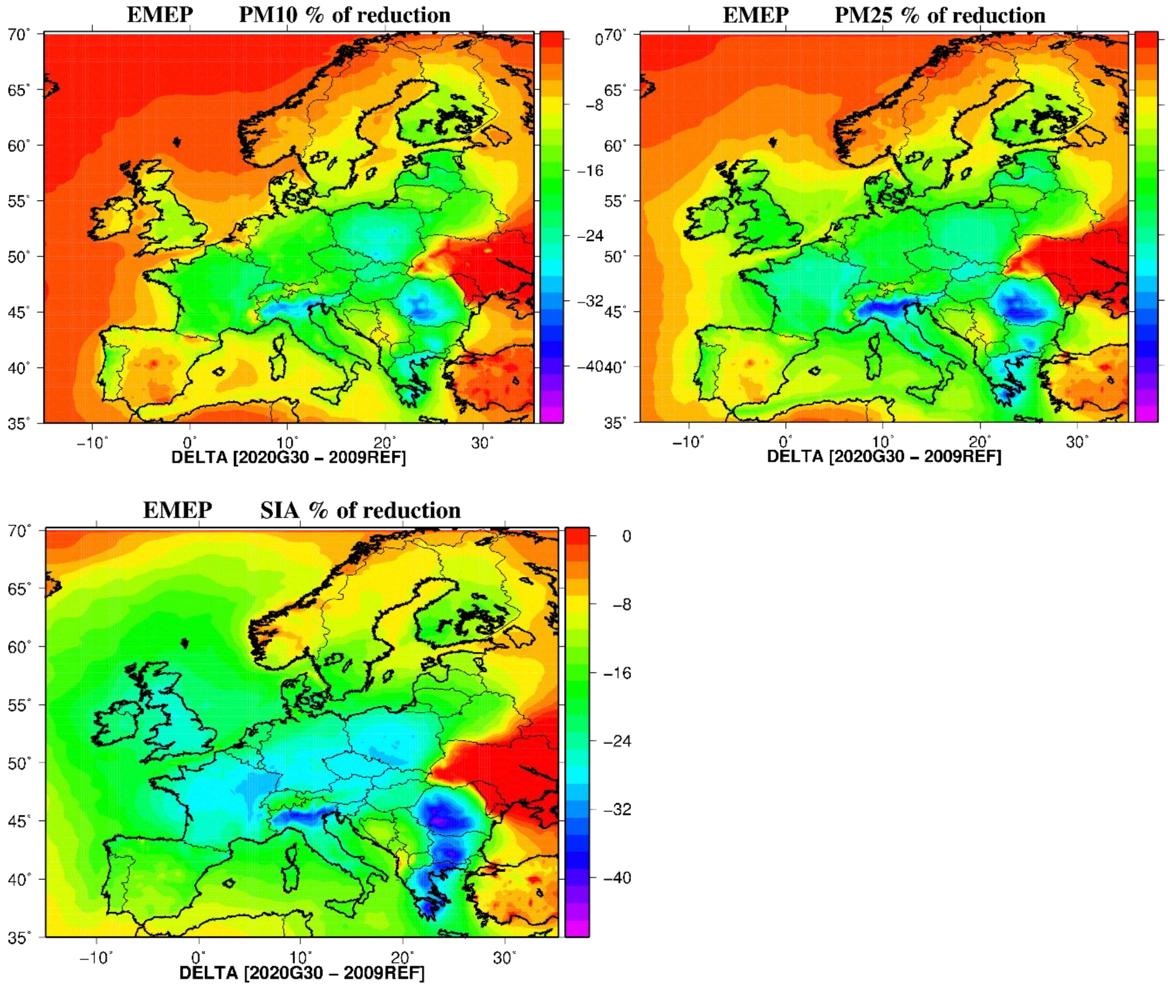

Figure 20: ***Reduction of annual mean PM10, PM2.5 and SIA concentrations (in %) for the scenario 2020G30 compared to 2009 emission scenario.***

The free ammonia is the amount of ammonia available, after neutralizing sulphate, for ammonium nitrate formation mainly. The free ammonia is defined as the difference in molar concentrations of the total ammonium and of sulphate concentrations:

$$\text{F-NH}_x = \boldsymbol{TN}\text{H}_4 - \mathbf{2} \times \boldsymbol{SO_4^{2-}} \qquad (12)$$

Figure 21 (left) shows the annual mean concentrations of free ammonia (*F-NH$_X$*) for the scenario 2020GOT. There is clearly an excess of ammonia in Europe in the scenario 2020GOT, with the highest concentrations of free ammonia over the areas with higher NH_3 emissions. To complete the analysis the G_{ratio} is used (Ansari and Pandis, 1998 in Pay et al., 2012). This ratio indicates whether fine-particle nitrate formation is limited by the availability of HNO_3 or NH_3. All the terms in the following equation are expressed on a molar basis:

$$\boldsymbol{G_{ratio}} = \frac{F\text{-}\boldsymbol{NH_x}}{\boldsymbol{TNO_3}} \tag{13}$$

- $G_{ratio} > 1$ indicates that nitric acid is limiting,
- $G_{ratio} < 0$ indicates the ammonia is severely limiting,
- G_{ratio} between 0 and 1 indicates ammonia is available for reaction with nitric acid, but ammonia is the limiting species.

The map of G_{ratio} in Figure 21 (right) shows that the model simulates a global limitation by the nitric acid with severe limitations over ammonia hot spot emission areas. The model predicts lower G_{ratio} in some countries in Central Europe. This map indicates a general behaviour, even in region with G_{ratio} greater than one, ammonia emission reductions have a significant impact because this ratio is strongly time dependent and can often decrease below 1. A close look at the spatial patterns of G_{ratio} in Figure 21 (right) shows that often, the maximum effect of ammonia emission reductions shown in Figure 19 is located outside the highest G_{ratio}.

Depending on the ambient NH_3 concentration and the NH_x concentration in soil/vegetation, there might be an upward flux (secondary emission) of NH_3 instead of deposition. Such a situation occurs in the high-density emission regions. This process is not included in the EMEP model, which might partly explain the negative bias in NH_3 (caused by over estimating the deposition flux). Due to the lack of this feedback, the model might be more sensitive for NH_3 reductions than what these results show.

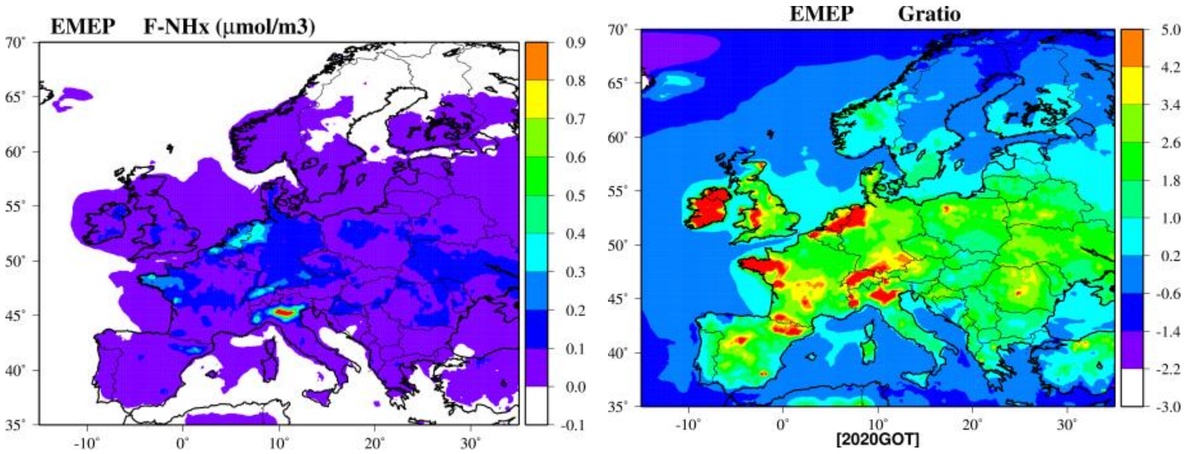

Figure 21: Annual mean concentrations of free ammonia concentrations (left, F-NH_x in µmol.m^{-3}) and the annual mean G_{ratio} (right) in the scenario 2020GOT (red colour for values above the scale maximum).

6.2.3 *Impact of NH_3 emissions reduction on the number of stations in exceedance*

The Air Quality Directive sets an annual and a daily limit values for PM10 for human health protection for, respectively, long-term and short-term effects. The daily LV is the most stringent, i.e., it is most often exceeded (Guerreiro et al., 2014).

Figure 22, Figure 23 and Figure 24 summarize the impact of the Gothenburg Protocol and further reductions in NH_3 emissions on the number of stations exceeding, respectively, the daily LV for PM10 (i.e., more than 35 days above 50 µg.m^{-3}), the PM10 yearly mean LV, and the yearly mean LV for PM2.5. The columns show the number of exceedances per Member State (in EU27) and per monitoring station classification: rural, suburban and urban background stations, and hotspot stations: traffic and industrial. Table 14 summarizes the effect of each scenario on PM10 and PM2.5 exceedances.

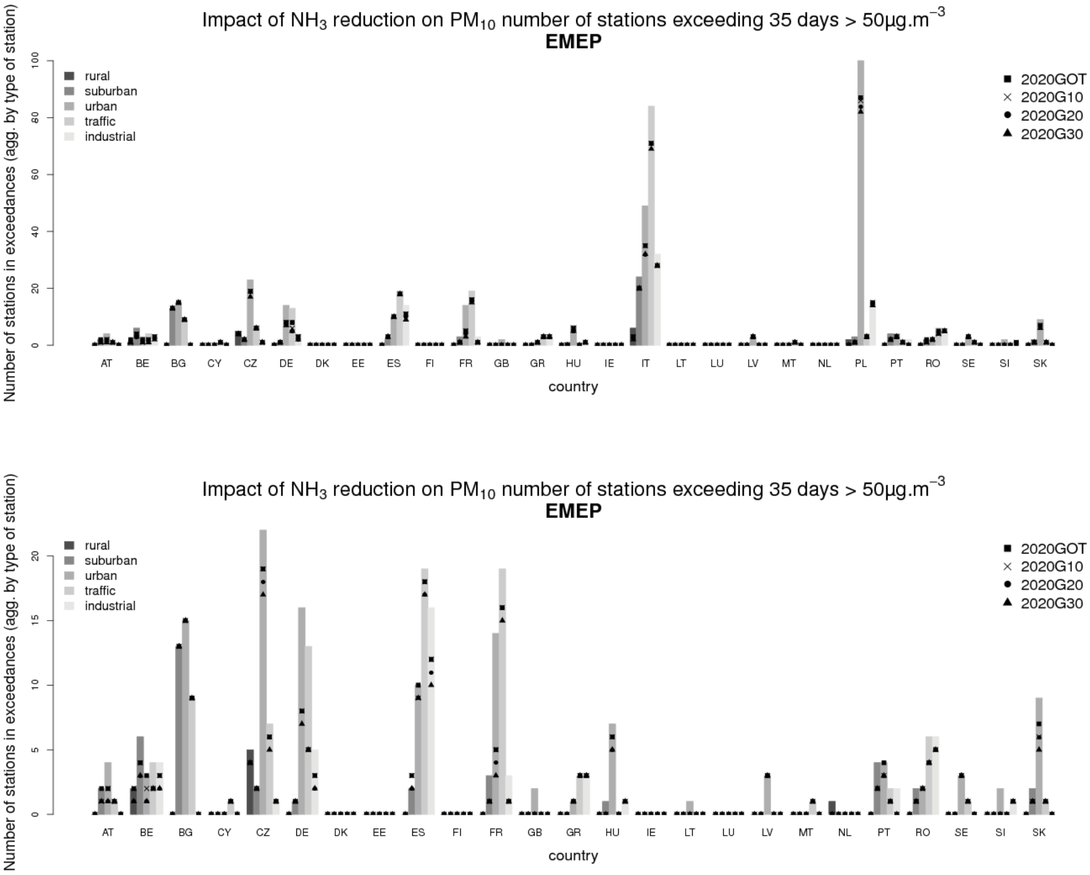

Figure 22: ***Number of PM10 stations exceeding more than 35 days the daily limit value of 50 µg.m^{-3} for the base year 2009, impact of the various scenarios for all EU27 countries (top) and for all EU27 countries except for Italy and Poland (bottom).***

In 2009, 612 monitoring stations exceeded the PM10 daily LV of 50 µg.m^{-3} more than 35 days. According to the modelling results, the number of remaining stations exceeding the PM10 daily LV after the implementation of the Gothenburg Protocol in 2020 is still 486 (Table 14). The results show a clear response of the number of PM10 stations in exceedance of the daily LV to the Gothenburg 2020 protocol emission reductions. On average in EU27, the number of stations exceeding the PM10 LV is reduced by 21% with the Gothenburg Protocol scenario. This reduction in EU27 is mainly driven by the decrease of exceeding stations in Italy, Poland and Germany (see Table A. 7 in Appendix). On the other hand, the results show that further measures must be considered to reduce PM levels across Europe.

A 30% reduction of ammonia emissions in addition to the Gothenburg Protocol scenario enhances the reduction of exceedances in Europe, reducing the number of stations in exceedance of the daily PM10 LV by 40 (i.e 8% of the remaining stations in exceedance with GOT2020 alone, Table 14). Despite the fact that the NH_3 emissions cut are in the agricultural sector and therefore in rural areas, 75% of those stations no longer exceeding the daily limit values are urban, suburban or traffic stations, showing how important regional emissions of NH_3 are for secondary particle formation that impacts on the concentrations in urban areas. The most important reduction of the number of stations in exceedance is occurs in Italy and Poland, because the initial number of exceeding stations is highest in these countries (Table A. 7 in Appendix). The Benelux, West of Germany and North of Italy exhibit the highest concentration decreases expected due to ammonia emission reductions.

It is noteworthy that an additional 10% or 20% agriculture emissions reduction for NH_3 does have a smaller impact in most regions on the number of stations in the exceedance of the PM10 daily limit value (compared to the number of exceedances under the Gothenburg Protocol scenario) than the 30% emission reduction. NH_3 emission reductions of 10%, 20%, 30%, respectively, give a decrease of 8, 24, and 40 exceeding stations compared to the Gothenburg Protocol (Table 14). Thus, the additional G10 scenario does not bring a significant effect on the number of exceeding stations; additional emission reduction (G20 and G30) seems to be more efficient. Clearly, we observe a non-linear effect in the reduction of concentrations or the number of stations exceeding the thresholds values; the reduction of ammonia emissions is more and more efficient from G10 to G30 scenarios, especially to the G30 scenario.

An analysis carried out on scenario impacts shows that the model response on daily exceedances might be underestimated, because the model tends to underestimate the high concentrations of PM components and particularly the nitrate and ammonium concentrations. This indicates that the NH_3 emission reductions would in reality allow a higher degree of compliance with the daily PM10 LV.

Table 14: Influence of the Gothenburg Protocol and further NH_3 emission reductions in the number of stations in exceedance of the PM limit values in the EU27, aggregated by station type.

Number of stations in exceedances		**OBS** [(a)]	**Pvalid**[(b)]	**EMEP**			
				GOT	*G10*	*G20*	*G30*
PM10 limit value : **35 days > 50µg.m^{-3}**	*rural*	16	5.9%	9	9	7	7
	suburban	65	19.7%	51	50	48	48
	urban	267	27.3%	210	204	197	189
	traffic	175	20.3%	143	142	141	136
	industrial	89	19.0%	73	73	69	66
	Total	**612**	**21.0%**	**486**	**478**	**462**	**446**
PM10 limit value : **annual mean > 40 µg.m^{-3}**	*rural*	3	1.4%	2	2	2	2
	suburban	13	4.9%	11	11	11	11
	urban	69	8.9%	51	50	50	49
	traffic	43	6.4%	29	28	28	26
	industrial	13	4.0%	8	8	8	8
	Total	**141**	**6.26%**	**101**	**99**	**99**	**96**
PM2.5 limit value : **annual mean > 20 µg.m^{-3}**	*rural*	7	10.4%	3	2	2	2
	suburban	12	22.6%	8	8	8	8
	urban	48	22.6%	34	33	31	28
	traffic	26	21.3%	19	19	19	19
	industrial	12	25.0%	9	9	9	8
	Total	**105**	**20.9%**	**73**	**71**	**69**	**65**

(a) OBS are the number of stations with observed exceedances in 2009.

(b) P_{valid} is the percentage of exceeding stations among the valid stations (only stations with a data capture larger than 85% are used in calculations).

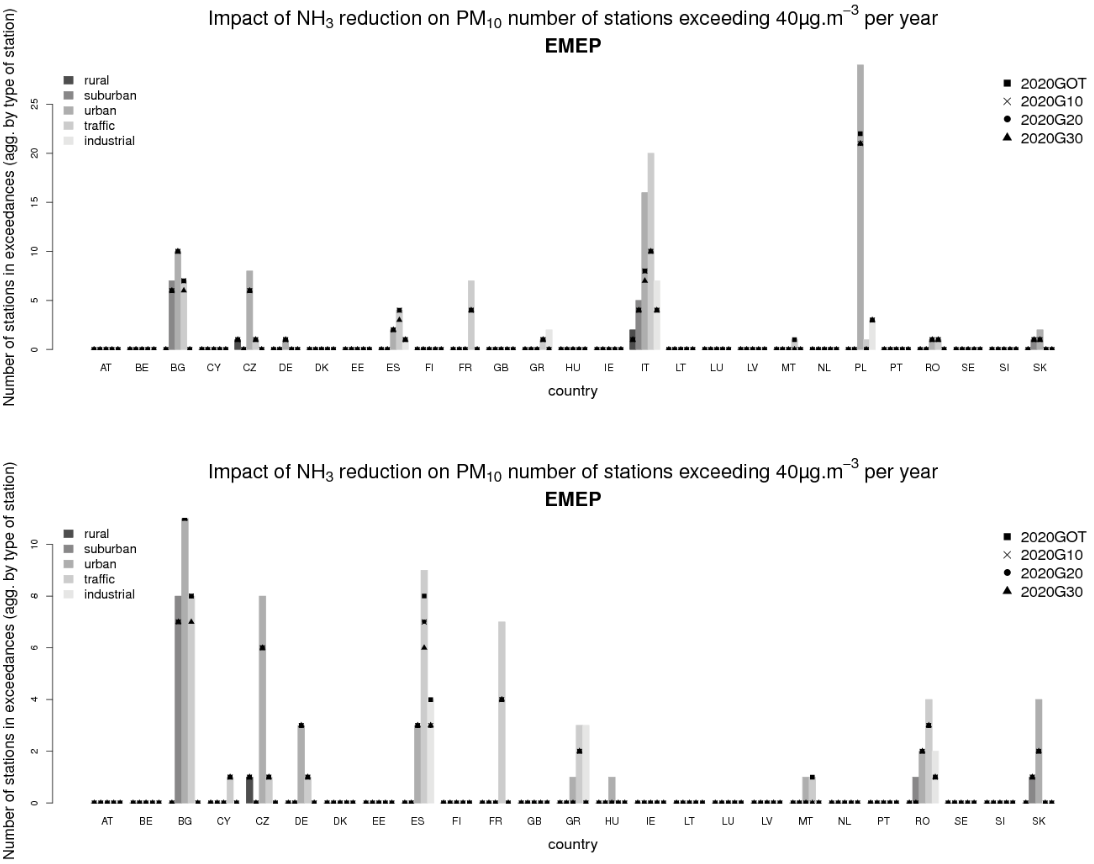

Figure 23: Number of PM10 stations exceeding the annual mean limit value of 40 µg.m^{-3} for the base year 2009, impact of the various scenarios for all EU27 countries (top) and for all EU27 countries except for Italy and Poland (bottom).

The Gothenburg Protocol scenario reduced by 28% the number of stations exceeding the PM10 annual limit value. While for the PM2.5 annual limit value, the Gothenburg Protocol scenario reduced by 30% the number of exceeding stations. The decrease is slightly higher for the PM2.5 limit value because most of the impact of ammonia emission reductions is concentrated in the fine fraction of PM. The effect of further NH_3 emission reductions on exceedances of the annual PM10 LV is less pronounced than for the daily LV, with a reduction of only 5% in the number of stations in exceedance for G30 compared to the GOT scenario. On the other hand, for PM2.5 annual LV, the corresponding reduction is quite significant, reaching 11%.

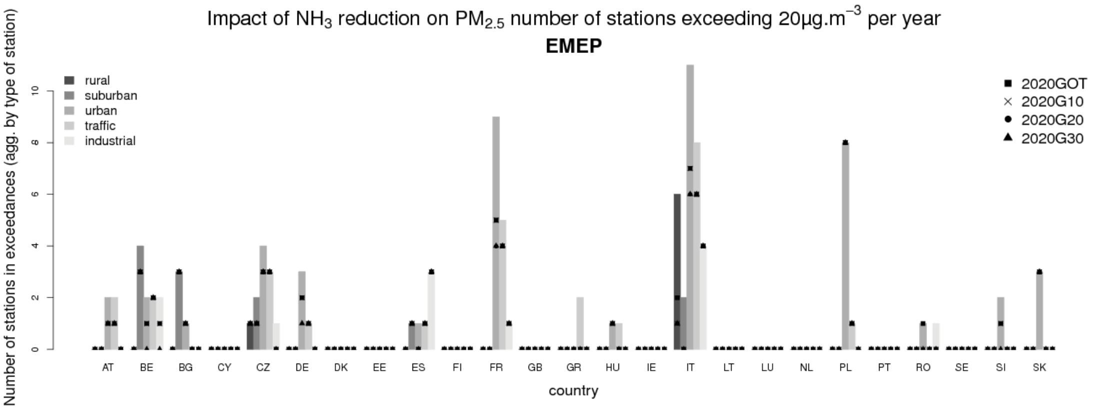

Figure 24: Number of PM2.5 stations exceeding annual mean limit value of 20 µg.m^{-3} for the base year 2009, impact of the various scenarios for all EU27 countries.

7 Conclusions

The major goal of this thesis has been met, as the current work applied improved methodologies to investigate the importance of emerging emission sectors to PM concentrations, as well as BaP concentrations (in PM) and its health impacts, in order to support effective air quality management with focus on particulate matter, including PAHs.

The main hypothesis; the emission sectors of household combustion and agriculture are key sectors contributing to the currently sustained PM levels and related health effects in Europe and must therefore be mitigated in order to achieve compliance with the European PM standards, was confirmed by the current work.

More details on the conclusions from the findings are given in the following sections 7.1 and 7.2.

7.1 Part 1: Household combustion: contribution to BaP emissions and its impact on health

Household combustion is by far the most important emission sector of BaP, contributing 82 % of the total BaP emissions in 2012. The development in the officially reported emissions of BaP from 2003 to 2012 shows that the household combustion sector has been the dominating BaP emission sector over that period and its emissions have increased by 25 % between 2003 and 2012. Household combustion was also responsible for, respectively, 49% and 64% of the total anthropogenic emissions of primary PM2.5 and total PAHs in 2012. In addition, its importance, in percentage share of total emissions, has significantly increased for these pollutants over the last decade.

This study showed that the European population exposure to BaP ambient air concentrations and the related incidence in lung cancer is quantifiable, by combining measurements, the best available information from chemical transport models (CTMs) and relevant auxiliary data, such as altitude, wind speed and temperature, through the use of the spatial interpolation method residual kriging.

The spatial interpolated maps show high 2012 annual mean concentrations of BaP in Eastern Europe, especially Poland and the Czech Republic, as well as in Northern Italy. The population-weighted concentration of BaP averaged over the whole Europe (i.e., the average BaP concentration which the average European inhabitant is exposed to) was about 0.9 ng.m^{-3} in 2012, thus close to the target value of 1 ng.m^{-3}. About 20 % of the European population was exposed to BaP annual mean concentrations above the target value in 2012 and only about 12 % of the European population live in areas with concentrations under the estimated reference level of 0.12 ng.m^{-3}, which corresponds to an additional lifetime cancer risk of 1 x 10^{-5}. The estimated exposure map for Europe shows that the population-weighted concentration of BaP is very high in the Baltic countries (especially Lithuania) and in large regions of Eastern Europe.

In the health impact assessment, the estimated number of lung cancer incidences in 2012 within the whole model area was 540 and 580 using, respectively, EMEP and CHIMERE model data as input to the interpolated concentration maps. The largest health impacts can be found in the Eastern European countries, which is in agreement with the concentration maps. About 50% of the lung cancer incidences due to BaP exposure occur in Poland and Romania. These results are most probably underestimating the health impacts of BaP emitted to ambient air, due mainly to the lack of measurement data in large areas and the fact that only lung cancer by inhalation of BaP is estimated. In addition, it is important to bear in mind that BaP only represents between 5 and 41% of overall carcinogenicity amongst the group of PAH compounds for which data are available (Holland et al., 2001).

The current study shows that PAHs, with BaP as an indicator, should be given more attention when considering air quality management and reduction of air pollution impacts in Europe. Furthermore, it shows that domestic combustion is an increasingly important sector with considerable emissions of PAHs (especially BaP) and primary PM, which requires more attention from an air quality management perspective and better coordination with climate change mitigation policies.

7.2 Part 2: How to limit agriculture’s contribution to secondary PM formation in Europe

The results in this study show that the implementation of the Gothenburg Protocol will be an important step towards compliance with PM limit values (LV) over Europe, but is far from assuring achievement of the specific long-term environmental objectives set by the thematic strategy for 2020 (EC, 2005) and will not suffice to achieve compliance with PM standards in Europe by 2020. The Gothenburg Protocol alone will only contribute to, respectively, a 21%, 28% and 30% reduction in the number of stations in exceedance of the PM10 daily LV, PM10 annual LV and PM2.5 LV in 2020, compared to 2009. Hence, further measures to reduce PM levels across Europe must be considered.

NH_3 is an important precursor for PM whose emissions, mainly from agriculture, have been less reduced over the past decade than for other precursors. On the other hand, a limited amount of specific measures can substantially reduce NH_3 emissions from agriculture, as there are proven and feasible methods to control and mitigate NH_3 emissions from animal manure management and urea fertilizer application. The available measures could cut NH_3 emissions in the EU27 by about 30% on top of the implementation of the Gothenburg Protocol in 2020.

The results of the different NH_3 emission reduction scenarios (i.e., 10%, 20% or 30% reduction beyond the Gothenburg Protocol) show that a greater ammonia emission reduction above 10% enhances the efficiency of the effect on the reduction of PM concentrations and of exceedances of PM limit values.

A further reduction of 30% of NH_3 agriculture emissions beyond the Gothenburg Protocol would contribute to reduce the exceedances of the PM10 daily LV, PM10 annual LV and PM2.5 LV, respectively, by 8 %, 5 %, and 11%, compared to the Gothenburg Protocol. Annual mean PM2.5

concentrations across Europe would also be considerably reduced, especially in Central and Central-Eastern Europe, reaching a 10% reduction in Belgium, Germany, the Czech Republic and Poland, compared to the Gothenburg Protocol implementation alone. This would considerably improve the chances of countries being able to meet their National Exposure Reduction Targets, set by the Air Quality Directive (EU, 2008).

8 Recommendations

Looking at a general framework needed to understand the contribution of emissions to PM and its health impacts, thus achieving a more accurate modelling system, further research is still needed at all levels, i.e.:

1. Mechanisms determining emissions and their quantification and characterisation in space and time;
2. Mechanisms determining chemical transformation of pollutants, including the formation of secondary particles from precursor gasses, as well as mixing and transport in the atmosphere;
3. Mechanisms determining sinks of PM in the atmosphere, including wet and dry deposition and transition of chemical species from aerosol to gas and vice-versa;
4. Understanding human time activity in different micro-environments, including indoors, in order to more accurately estimate human exposure;
5. Understanding the mechanisms of damage and repair of the different components and sizes of PM, including antagonistic and synergetic effects, in the human bodies, taking into account the variability in sensitivities within the human population.

CTMs are used to assess PM levels and evaluate the response of PM concentrations to emission reductions. In addition to meteorological data, they require detailed information on emissions and the atmospheric processes that transform those emissions into ambient concentrations. On the other hand, CTMs generally underestimate PM mass concentrations, explained by a lack of sources and/or missing processes. From the current research, some concrete recommendations can be made, as follows:

- Improve the quality and completeness of the PAH and BaP emission inventories. This would be considerably improved by making reporting of BaP and PAH emissions mandatory, rather than voluntary as is currently the case under the UNECE-LRTAP Convention.
- There is a need for more BaP measurements where measurement density is very low or inexistent, particularly where high concentrations are expected, e.g., in Romania, Bulgaria. This is necessary to improve the quality of the BaP concentration assessment across Europe and consequent health effects, and essential for the validation and improvement of CTMs. Thus, a decrease in the LAT (0.4 ng.m^{-3}), defining the threshold above which BaP must be monitored, should be re-evaluated towards the estimated acceptable risk level (0.12 ng.m^{-3}).
- BaP only represents part of the overall carcinogenicity amongst the group of PAH compounds for which data are available. More research is needed on the mutagenic and carcinogenic potency of the various PAHs and of their ambient air concentrations (e.g., dibenzo[a, l]pyrene), in order to understand the health impacts of the total PAH mixture and correctly estimate exposure risks, using BaP as an indicator for the PAH mixture.

- Better emission models for natural and anthropogenic emissions of PM and precursors, including better temporal and spatial resolution, in order to improve modelling of high PM episodes due to secondary PM formation. A good time/spatial resolution of NH_3 emissions from agriculture is crucial to predict correctly episodes due to SIA formation.
- Better understanding and description of the mechanisms involved in SIA formation and sinks, i.e., inorganic aqueous-phase chemistry in cloud or fog-water droplets; improve deposition schemes and of chemical interactions between species; improve the subgrid-scale treatment of mixing and transport of emission plumes.
- Better understanding of the components and complex mechanisms involved in SOA formation, including the mechanism behind the different VOCs emissions from different vegetation types.
- More research on health effects of specific PM chemical components and size, including SIA.

ABSTRACT

Particulate matter (PM) prevails as the main air quality problem in Europe, as it continues to pose the greatest risk to human health. Despite the recognised impacts of current PM ambient concentrations and despite the efforts to reduce emissions of PM, including polycyclic aromatic hydrocarbons, and PM precursor gases, current policies have so far proven ineffective in reducing PM and benzo(a)pyrene (BaP) ambient levels and meeting the European PM and BaP standards.

Household combustion was identified as a major emission sector of primary PM and BaP, and of increasing importance for PM and BaP concentrations in Europe. This study estimated European population exposure to BaP and the related incidence in lung cancer, by combining measurements, dispersion modelling and relevant auxiliary data (altitude and meteorological data). About 20 % of the European population was exposed to BaP annual mean concentrations above the target value (1 ng.m^{-3}) in 2012 and only about 12 % of the European population live in areas with concentrations under the estimated reference level for acceptable risk (0.12 ng.m^{-3}). The estimated number of lung cancer incidences due to BaP exposure in 2012 was above 500 for the whole Europe, with about 50% of these occurring in Poland and Romania. BaP should thus be given more attention in air quality management.

Agriculture is the main emission sector NH_3, an important PM precursor leading to the formation of secondary inorganic aerosols (SIA). SIA accounts for about one third of PM10 and half of PM2.5 concentrations in regional background ambient air in Europe. The model simulations, combined with measurement data, in this study show that the emission reductions agreed under the revised Gothenburg Protocol (GP) will not be sufficient to achieve compliance with PM standards in Europe in 2020; hence further European measures should be considered. A further reduction of 30% of NH_3 agriculture emissions is achievable by the implementation of currently available mitigation measures. Such an emission reduction would contribute to reduce further the exceedances of the PM10 daily limit value (LV), PM10 annual LV and PM2.5 LV, respectively, by 8 %, 5 % and 11%, compared to implementation of the GP. Annual mean PM2.5 concentrations across Europe would also be further reduced, reaching a 10% reduction in some Central-Eastern European countries, compared to the GP implementation alone.

Domestic combustion and agriculture are key emission sectors in future air quality management aiming at the reduction of health effects from exposure to PM, including BaP.

ABSTRACT (IN POLISH)

Cząstki stałe (PM - particulate matter) stanowią jeden z głównych problemów związanych z zanieczyszczeniem powietrza w Europie, również w kontekście dużego narażenia zdrowia ludzi. Jednakże mimo rozpoznaania skutków aktualnie mierzonych stężeń PM w powietrzu i działań mających na celu ograniczenie emisji PM, jak i ich gazowych prekursorów oraz związków aromatycznych (PAHs), obecne regulacje prawne okazują się niewystarczające do obniżenia stężeń PM i benzo-alfa-pirenu (BaP) w powietrzu do poziomów dopuszczalnych w Europie.

Spalanie paliw w paleniskach domowych jest głównym źródłem emisji pierwotnych PM i BaP. Jest to też główna przyczyna wzrostu stężeń PM i BaP w Europie. W pracy obliczono narażenie ludzi (population exposure) w Europie oraz przypadki wystąpienia nowotworu płuc poprzez połączenie pomiarów z modeleowaniem dyspersji zanieczyszczeń i danymi dodatkowymi, (np. danymi topograficznymi i meteorologicznymi). W roku 2012 około 20 % Europejczyków narażonych było na rocznie uśrednione stężenia BaP przekraczające dozwolone wartości normatywne (1 ng.m^{-3}). Jedynie 12 % ludzi w Europie żyje w rejonach gdzie to stężenie jest poniżej poziomu referencyjnego dla akceptowalnej wartości narażenia (0.12 ng.m^{-3}). Oszacowana liczba przypadków nowotworu płuc w związku z narażeniem na wysokie stężenia BaP w 2012 r. w całej Europie wynosiła ponad 500, z tego 50 % w Polsce i Rumunii. Zatem PaP powinien być szczególnie brany pod uwagę przy zarządzaniu jakością powietrza.

Rolnictwo jest głównym sektorem emitującym NH_3, który jest ważnym prekursorem PM prowadzącym do powstawania w powietrzu cząstek wtórnych (SIA). SIA tworzy jedną trzecią stężeń PM10 i połowę PM2.5 mierzonych w powietrzu w rejonach, gdzie określa się tło stężeń w Europie. Obliczenia modelowe wsparte pomiarami i przedstawione w pracy jednoznacznie wskazują, że wartości redukcji emisji uzgodnione w ramach skorygowanego Protokołu z Geteborga (GP) są niewystrczające dla uzyskania stężeń mieszczących się w ramach wartości normatywnych dla PM w Europie dla roku 2020. Zatem dodatkowe działania zmierzające do redukcji PM będą konieczne. Dodatkowa redukcja 30 % emisji NH_3 w rolnictwie jest możliwa poprzez wprowadzenie obecnie dostępnych metod. Takie działania mogą skutkować dalszą redukcją przekroczeń wartości dopuszczalnych w skali dobowej PM10, w skali rocznej PM10 i PM2.5 odpowiednio 8%, 5 % i 11 % w porównaniu z wprowadzaniem uzgodnień zapisanych w GP. Roczne stężenia PM2.5 w Europie mogą być dalej redukowane , osiągając poziom 10 % redukcji w niektórych krajach Europy Centralnej, w porównaniu jedynie z wprowadzaniem ustaleń z GP.

Paleniska domowe i rolnictwo będą głównymi sektorami emisji zanieczyszczeń powietrza w przyszłości. Sektory te powinny być szczególnie istotne przy działaniach zmierzających do redukcji skutków zdrowotnych związanych z narażeniem na stężenia PM, w tym BaP.

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APPENDIX

2020 emissions ceilings according to the Gothenburg Protocol

Table A. 1: *SO_2 Emissions*

Country	Emission 2009 (kT)	Emission 2005 (kT)	Reduction (%)	Ceiling 2020 (kT)
Austria	17,4	27	26	20,0
Belarus	157,8	79	20	63,2
Belgium	76,7	145	43	82,7
Bulgaria	440,4	777	78	170,9
Croatia	59,3	63	55	28,4
Cyprus	17,9	38	83	6,5
Czech Republic	173,5	219	45	120,5
Denmark	14,3	23	35	15,0
Estonia	54,8	76	32	51,7
Finland	59,2	69	30	48,3
France	289,3	467	55	210,2
Germany	434,7	517	21	408,4
Greece	424,5	542	74	140,9
Hungary	79,7	129	46	69,7
Ireland	32,6	71	65	24,9
Italy	232,1	403	35	262,0
Latvia	4,1	6,7	8	6,2
Lithuania	29,5	44	55	19,8
Luxembourg	2,2	2,5	34	1,7
Malta	8,0	11	77	2,5
Netherlands	37,4	65	28	46,8
Norway	14,5	24	10	21,6
Poland	861,7	1224	59	501,8
Portugal	74,3	177	63	65,5
Romania	459,9	643	77	147,9
Slovakia	64,1	89	57	38,3
Slovenia	10,6	40	63	14,8
Spain	462,6	1282	67	423,1
Sweden	29,6	36	22	28,1
Switzerland	12,4	17	21	13,4
United Kingdom of Great Britain and Northern Ireland	397,3	706	59	289,5

Table A. 2: *NO_x Emissions*

Country	Emission 2009 (kT)	Emission 2005 (kT)	Reduction (%)	Ceiling 2020 (kT)
Austria	187,1	231	37	145,5
Belarus	189,2	171	25	128,3
Belgium	207,5	291	41	171,7
Bulgaria	117,3	154	41	90,9
Croatia	75,9	81	31	55,9
Cyprus	19,6	21	44	11,8
Czech Republic	251,4	286	35	185,9
Denmark	131,5	181	56	79,6
Estonia	30,2	36	18	29,5
Finland	154,7	177	35	115,1
France	1105,5	1430	50	715,0
Germany	1320,9	1464	39	893,0
Greece	381,9	419	31	289,1
Hungary	166,9	203	34	134,0
Ireland	87,4	127	49	64,8
Italy	973,5	1212	40	727,2
Latvia	32,0	37	32	25,2
Lithuania	53,5	58	48	30,2
Luxembourg	43,9	19	43	10,8
Malta	8,9	9,3	42	5,4
Netherlands	280,3	370	45	203,5
Norway	178,7	200	23	154,0
Poland	822,1	866	30	606,2
Portugal	199,0	256	36	163,8
Romania	252,0	309	45	170,0
Slovakia	84,2	102	36	65,3
Slovenia	45,7	47	39	28,7
Spain	943,7	1292	41	762,3
Sweden	153,1	174	36	111,4
Switzerland	79,5	94	41	55,5
United Kingdom of Great Britain and Northern Ireland	1143,3	1580	55	711,0

Table A. 3: NH_3 Emissions

Country	Emission 2009 (kT)	Emission 2005 (kT)	Reduction (%)	Ceiling 2020 (kT)
Austria	63,4	63	1	62,4
Belarus	150,0	136	7	126,5
Belgium	69,1	71	2	69,6
Bulgaria	52,5	60	3	58,2
Croatia	36,9	40	1	39,6
Cyprus	5,2	5,8	10	5,2
Czech Republic	73,0	82	7	76,3
Denmark	75,1	83	24	63,1
Estonia	10,0	9,8	1	9,7
Finland	37,2	39	20	31,2
France	656,2	661	4	634,6
Germany	575,7	573	5	544,4
Greece	62,1	68	7	63,2
Hungary	67,9	80	10	72,0
Ireland	108,4	109	1	107,9
Italy	392,7	416	5	395,2
Latvia	16,5	16	1	15,8
Lithuania	28,3	39	10	35,1
Luxembourg	4,7	5	1	5,0
Malta	1,5	1,6	4	1,5
Netherlands	125,1	141	13	122,7
Norway	22,7	23	8	21,2
Poland	273,4	270	1	267,3
Portugal	47,4	50	7	46,5
Romania	187,7	199	13	173,1
Slovakia	25,1	29	15	24,7
Slovenia	17,7	18	1	17,8
Spain	354,7	365	3	354,1
Sweden	50,1	55	15	46,8
Switzerland	62,8	64	8	58,9
United Kingdom of Great Britain and Northern Ireland	283,0	307	8	282,4

Table A. 4: NMVOC Emissions

Country	Emission 2009 (kT)	Emission 2005 (kT)	Reduction (%)	Ceiling 2020 (kT)
Austria	120,9	162	21	128,0
Belarus	362,0	349	15	296,7
Belgium	105,1	143	21	113,0
Bulgaria	91,3	158	21	124,8
Croatia	77,4	101	34	66,7
Cyprus	11,4	14	45	7,7
Czech Republic	151,2	182	18	149,2
Denmark	89,1	110	35	71,5
Estonia	36,7	41	10	36,9
Finland	111,4	131	35	85,2
France	865,6	1232	43	702,2
Germany	930,6	1143	13	994,4
Greece	212,1	222	54	102,1
Hungary	128,1	177	30	123,9
Ireland	47,7	57	25	42,8
Italy	1131,2	1286	35	835,9
Latvia	60,5	73	27	53,3
Lithuania	66,2	84	32	57,1
Luxembourg	9,4	9,8	29	7,0
Malta	2,6	3,3	23	2,5
Netherlands	152,2	182	8	167,4
Norway	138,4	218	40	130,8
Poland	634,1	593	25	444,8
Portugal	179,7	207	18	169,7
Romania	432,7	425	25	318,8
Slovakia	64,3	73	18	59,9
Slovenia	34,0	37	23	28,5
Spain	672,0	809	22	631,0
Sweden	197,0	197	25	147,8
Switzerland	90,7	103	30	72,1
United Kingdom of Great Britain and Northern Ireland	822,4	1088	32	739,8

Table A. 5: PM2.5 Emissions

Country	Emission 2009 (kT)	Emission 2005 (kT)	Reduction (%)	Ceiling 2020 (kT)
Austria	19,4	22	20	17,6
Belarus	51,8	46	10	41,4
Belgium	15,8	24	20	19,2
Bulgaria	29,0	44	20	35,2
Croatia	10,5	13	18	10,7
Cyprus	2,3	2,9	46	1,6
Czech Republic	20,4	22	17	18,3
Denmark	25,4	25	33	16,8
Estonia	18,6	20	15	17,0
Finland	38,2	36	30	25,2
France	251,4	304	27	221,9
Germany	105,7	121	26	89,5
Greece	62,8	56	35	36,4
Hungary	27,8	31	13	27,0
Ireland	8,5	11	18	9,0
Italy	168,6	166	10	149,4
Latvia	28,3	27	16	22,7
Lithuania	8,6	8,7	20	7,0
Luxembourg	2,2	3,1	15	2,6
Malta	1,4	1,3	25	1,0
Netherlands	15,9	21	37	13,2
Norway	43,9	52	30	36,4
Poland	123,3	133	16	111,7
Portugal	57,2	65	15	55,3
Romania	115,1	106	28	76,3
Slovakia	27,4	37	36	23,7
Slovenia	15,9	14	25	10,5
Spain	75,2	93	15	79,1
Sweden	27,7	29	19	23,5
Switzerland	9,7	11	26	8,1
United Kingdom of Great Britain and Northern Ireland	67,0	81	30	56,7

Table A. 6: PMcoarse & CO Emissions

Country	PMcoarse Emission 2009 (kT)	PMcoarse Emission 2020 (kT)	CO Emission 2009 (kT)	CO Emission 2020 (kT)
Austria	15,3	12,0	631,8	694,6
Belarus	12,8	7,8	990,0	951,1
Belgium	6,7	18,5	380,9	286,5
Bulgaria	19,9	27,7	253,7	392,9
Croatia	4,3	5,4	285,2	514,4
Cyprus	1,3	2,1	20,3	85,0
Czech Republic	15,9	14,5	403,5	437,8
Denmark	6,0	9,8	406,8	309,2
Estonia	4,7	2,4	168,2	105,3
Finland	13,4	6,4	465,5	602,1
France	112,8	86,0	3666,4	4575,6
Germany	81,3	87,0	3011,0	3999,5
Greece	37,2	18,0	591,3	1120,4
Hungary	19,9	12,9	312,8	486,5
Ireland	4,3	6,1	151,9	191,7
Italy	28,9	50,6	2725,3	3085,4
Latvia	4,6	1,9	266,9	133,0
Lithuania	2,4	3,6	169,2	155,5
Luxembourg	0,9	1,2	37,6	37,0
Malta	0,8	0,0	30,8	0,0
Netherlands	13,8	22,8	579,5	678,4
Norway	6,0	5,1	319,8	1542,1
Poland	125,3	51,4	2777,9	3068,3
Portugal	25,8	11,0	486,5	1810,4
Romania	20,9	34,1	1349,3	845,4
Slovakia	3,4	7,8	207,8	231,4
Slovenia	3,0	3,7	150,6	203,5
Spain	32,5	51,7	1686,5	3175,6
Sweden	11,6	9,5	612,2	598,3
Switzerland	10,6	5,3	256,5	331,1
United Kingdom of	46,9	50,3	2317,3	1809,7

Influence of the Gothenburg Protocol and further NH_3 emission reductions in the number of stations in exceedance of the PM10 daily limit value for EU27 countries.

Table A. 7: Number of stations (all types) in exceedance of the PM10 daily LV (more than 35 days above 50 µg.m^{-3}) in 27 EU countries: observed in 2009 (OBS), due to the Gothenburg Protocol (GOT) and due to further NH_3 emission reductions (scenarios G10, G20, G30).

MS	OBS	Emission scenario			
		GOT	G10	G20	G30
AT	7	5	4	3	3
BE	19	14	13	9	9
BG	37	37	37	37	37
CY	1	1	1	1	1
CZ	37	32	32	31	29
DE	35	17	17	16	15
DK	0	0	0	0	0
EE	0	0	0	0	0
ES	47	43	42	39	38
FI	0	0	0	0	0
FR	39	23	23	22	20
GB	2	0	0	0	0
GR	7	7	7	7	7
HU	9	7	7	6	6
IE	0	0	0	0	0
IT	195	156	155	152	148
LT	1	0	0	0	0
LU	0	0	0	0	0
LV	3	3	3	3	3
MT	1	1	1	1	1
NL	1	0	0	0	0
PL	124	107	105	104	99
PT	12	7	6	6	6
RO	16	12	12	12	12
SE	4	4	4	4	4
SI	3	1	1	1	1
SK	12	9	8	8	7
EU27	**612**	**486**	**478**	**462**	**446**

SCIENTIFIC ACHIEVEMENTS

SCIENTIFIC PAPERS (PEER- REVIEWED)

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27. Guerreiro, C., Dam, V.T. (2010) Preliminary results from air quality modelling in Dakar. Kjeller, NILU (NILU OR, 52/2010).

28. Guerreiro, C., Dam, V.T. (2010) A bottom-up air pollution emission inventory for Dakar. Kjeller, NILU (NILU OR, 53/2010).

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30. Guerreiro, C. (2009) Fourteenth EIONET Workshop on Air Quality Management and Assessment. Warsaw, Poland 05-06 October 2009. Proceedings. Bilthoven, European Topic Centre on Air and Climate Change (ETC/ACC Technical paper, 2009/14).

31. Larssen, S., Guerreiro, C. (2008) Thirteenth EIONET workshop on air quality management and assessment, Brugge, Belgium 29-30 September 2008. Proceedings. Bilthoven, European Topic Centre on Air and Climate Change (ETC/ACC Technical paper, 2008/11).

OTHER LECTURES (selected lectures after 2008)

1. Guerreiro, C. (2015) EU air quality limit value exceedances in Europe. Keynote speaker, In: Routes to Clean Air, Air Quality Conference 2015. Institute of Air Quality Management. 22nd-23rd October 2015, Bristol, UK (https://www.the-ies.org/events/routes-clean-air-air-quality).

2. Guerreiro, C., Horálek, J., de Leeuw, F., Couvidat, F. (2015) Mapping BaP concentrations and estimation of population exposure and health impacts. Presented at 20th EIONET Air Quality Management and Assessment Workshop, Ljubljana, Slovenia, October 5-6th 2015 (http://acm.eionet.europa.eu/docs/meetings/151005_eionet_aq_ws/meeting151005.html).

3. Guerreiro, C., Beauchamp, M., Bessagnet, B., Tsyro, S. (2014) EMEP simulations of PM levels in Europe under the Gothenburg Protocol and measures to reduce further ammonia emissions from agriculture. Presented at the Task Force on Integrated Assessment Modelling, 43rd meeting, Helsinki, Finland, May 6-7, 2014. Kjeller, NILU (NILU F, 16/2014).

4. Castell, N., Viana, M., Minguillón, M.C., Guerreiro, C.B., Querol, X. (2014) The use of micro-sensors in air quality monitoring. Presented at the 19th EIONET Air Quality Management and Assessment Workshop, Bern, Switzerland, 30 September - 1 October 2014. Kjeller, NILU (NILU F, 60/2014).

5. Guerreiro, C., de Leeuw, F., Foltescu, V. (2013) Air quality status in Europe. Invited talk at COST Action TD1105 EuNetAir WG1-WG4 meeting on New Sensing Technologies and Methods for Air Pollution Monitoring, Copenhagen, 3-4 October 2013. Kjeller, NILU (NILU F, 74/2013).

6. Guerreiro, C., Foltescu, V., de Leeuw, F. (2013) Air quality in Europe - recent assessments. Presented at 18th EIONET Air Quality Management and Assessment Workshop, Dublin, October 25th 2013. (NILU F, 83/2013).

7. Guerreiro, C., Horálek, J., de Leeuw, F. (2012) Status and trends of NO_2 ambient concentrations and NO_2/NO_X concentration ratios in Europe. Presented at the 8th International Conference on Air Quality - Science and Applications, Athens, 19-23 May 2012. Kjeller, NILU (NILU F, 03/2012).

8. Foltescu, V., Guerreiro, C., de Leeuw, F. (2012) Air quality in Europe - recent assessments. 17th EIONET Air Quality Management and Assessment Workshop, Madrid, Spain, 25th and 26th October 2012. (NILU F, 47/2012).

9. Hak, C., Larssen, S., Randall, S., Guerreiro, C., Denby, B. (2010) Contribution of traffic to urban air quality and mitigation strategies in European Cities. Road dust - health effects and abatement strategies. International conference Stockholm October 18-19, 2010. Kjeller (NILU F, 115/2010).

10. Denby, B., Georgieva, E., Larssen, S., Guerreiro, C., Liu, L., Douros, J., Moussiopoulos, N., Fragkou, L., Gauss, M., Olesen, H., Miranda, A.I., Dilara, P., Thunis, P., Lappi, S., Rouil, L., Lükewille, A., Querol, X., Martin, F., Schaap, M., van den Hout, D., Kobe, A., Silibello, C., Vincent, K., Stedman, J., Gonçalves, M., Pirovano, G., Volta, L., van Pul, A., Ortiz, A.G., Roberts, P., Oettl, D. (2010) Guidance on the use of models for the European air quality directive: an activity for FAIRMODE. Presented at 13th International conference on harmonization within atmospheric dispersion modelling for regulatory purposes. Paris 1-4 June 2010. Kjeller, NILU (NILU F, 14/2010).

11. Guerreiro, C. (2010) Model applications in the European Air Quality Directive. FAIRMODE. Presented at: Air quality modeling: a key policy-driving tool. Aveiro, Portugal, 26 November 2010. Kjeller, NILU (NILU F, 81/2010).

12. Guerreiro, C. (2009) The AirQUIS emission module. Presented at a visit by a South African delegation to NILU, Kjeller, 30 March-3 April 2009. Kjeller, NILU (NILU F, 11/2009).

13. Guerreiro, C. (2009) AirQUIS. The measurement module. Presented at a visit by a South African delegation to NILU, Kjeller, 30 March-3 April 2009. Kjeller, NILU (NILU F, 13/2009).

14. Denby, B., Larssen, S., Guerreiro, C., Douros, J., Moussiopoulos, N., Fragkou, L., Gauss, M., Olesen, H., Costa, A.M. (2008) Guidance on the use of models for the European air quality directive: an activity of FAIRMODE. 13th EIONET Workshop on Air Quality Assessment and Management, Bruges, Belgium, 29 - 30 September 2008. Kjeller, NILU (NILU F, 34/2008).

15. Denby, B., Larssen, S., Guerreiro, C., Douros, J., Moussiopoulos, N., Fragkou, L., Gauss, M., Olesen, H., Miranda, A.I. (2008) Guidance on the use of models for the European air quality directive. The first Plenary Meeting of the Forum for Air Quality Modelling in Europe (FAIRMODE), Cavtat, Croatia, 10 October 2008. Kjeller, NILU (NILU F, 38/2008).