Abstract

Although they are currently unregulated, atmospheric ultrafine particles (<100 nm) pose health risks because, e.g., their capability to penetrate deep into the respiratory system. Ultrafine particles, often minor contributors to atmospheric particulate mass, typically dominate aerosol particle number concentrations. We simulated the response of particle number concentrations over Europe to recent estimates of future emission reductions of aerosol particles and their precursors. We used the chemical transport model PMCAMx-UF, with novel updates including state-of-the-art descriptions of ammonia and dimethylamine new particle formation (NPF) pathways and the condensation of organic compounds onto particles. These processes had notable impacts on atmospheric particle number concentrations. All three emission scenarios (current legislation, optimized emissions, and maximum technically feasible reductions) resulted in substantial (10–50%) decreases in median particle number concentrations over Europe. Consistent reductions were predicted in Central Europe, while Northern Europe exhibited smaller reductions or even increased concentrations. Motivated by the improved NPF descriptions for ammonia and methylamines, we placed special focus on the potential to improve air quality by reducing agricultural emissions, which are a major source of these species. Agricultural emission controls showed promise in reducing ultrafine particle number concentrations, although the change is nonlinear with particle size.

Introduction

Atmospheric aerosol particles have a detrimental effect on air quality, causing respiratory and cardiovascular health problems, as well as premature deaths.(1, 2) Consequently, the
amount of particulate matter in the atmosphere is monitored and controlled, usually focusing on the mass of particles with diameters of <2.5 μm (PM$_{2.5}$) or <10 μm (PM$_{10}$), although new air quality metrics such as PM$_1$ have also been suggested. Less focus has been placed on particle number concentration, of which a large fraction consists of ultrafine particles with diameters of <100 nm. However, there are indications that ultrafine particles, which can penetrate deep into the lungs, cells, and blood circulation, can be even more harmful to human health than the larger particles. A reduction of 10000 cm$^{-3}$ in ultrafine particles has been suggested to decrease all-cause mortality by 0.1–2.1%, although this estimate is subject to a large uncertainty because of a lack of long-term studies of the concentrations, population exposure, and effects of these particles.

A significant fraction of the ultrafine particle number originates from new particle formation (NPF). Sulfuric acid is a central compound involved in atmospheric NPF, and it is known that additional base compounds help stabilize the small sulfuric acid-containing clusters. Ammonia is the most abundant atmospheric base, and as such, the ternary sulfuric acid–ammonia–water pathway is important for atmospheric NPF. Methylamines, including monomethylamine (MA), dimethylamine (DMA), and trimethylamine (TMA), have atmospheric concentrations that are orders of magnitude lower than those of ammonia, but methylamines are stronger bases and thus more effective in stabilizing sulfuric acid clusters. Specifically, dimethylamine has been shown to enhance formation rates by 1000-fold compared to ammonia, and consequently, the sulfuric acid–dimethylamine NPF pathway should be included in large-scale models describing aerosol numbers.

Agriculture, specifically animal husbandry, is the largest anthropogenic source of ammonia, MA, DMA, and TMA. Ammonia contributes strongly to PM$_{2.5}$, and ammonia emission reductions have the potential to reduce significantly the aerosol particle mass over Europe. Because of the participation of ammonia and methylamines in atmospheric NPF, agricultural emission control measures have the potential to improve air quality also by reducing particle number concentrations.

Impacts of European air quality policies on regional-scale particle number concentrations have been previously studied using the chemical transport model PMCAMx-UF. The model is particularly well-suited for the study of number concentrations, as it simulates the dynamics of aerosol particle populations explicitly starting from nanometer-scale sizes. Ahlm et al. used PMCAMx-UF to study the response of predicted number concentrations to future European emission scenarios from the first Thematic Strategy on Air Pollution (TSAP) report by the International Institute of Applied Systems Analysis (IIASA). Since then, IIASA has further developed its emission scenarios, and the TSAP reports 16a and 16b are the latest to outline future scenarios for each European Union member nation up to the year 2030. These scenarios are guided by the European Commission’s Clean Air Policy Package aiming to reduce the mortality driven by air pollution by 52% by 2030 compared to 2005. Three emission scenarios are presented in TSAP reports 16a and 16b. They include new versions of two earlier scenarios familiar from the first TSAP report, (1) the scenario following the current legislation (CLE) and (2) the scenario corresponding to maximum technically feasible reductions (MTFR), and a newer addition, (3) an optimized scenario designed to meet the air quality improvements proposed.
in the Clean Air Policy Package (OPT). The emission data for all these new scenarios are divided by country.

The PMCAMx-UF model has also received updates since the work of Ahlm et al.\(^\text{(22)}\) A key improvement has been made to the description of the sulfuric acid–ammonia–water NPF pathway.\(^\text{(27)}\) The new NPF scheme uses a look-up table of formation rates calculated with the cluster kinetic model ACDC (Atmospheric Cluster Dynamics Code\(^\text{(28)}\)) using quantum chemistry input data for cluster evaporation rates. In this work, we have also included the sulfuric acid–DMA NPF pathway in PMCAMx-UF, again utilizing ACDC with input from quantum chemistry to calculate the formation rates. These NPF schemes are free of any semiempirical scaling parameters and explicitly account for the coagulational losses due to scavenging by larger particles. Accordingly, they provide more realistic responses to future changes in the concentrations of NPF precursor gases as well as primary particles than have been available before. We have also included a new description of the organic contribution to ultrafine particle growth in PMCAMx-UF,\(^\text{(29)}\) which is important for capturing the lifetimes of the particles produced by NPF.

Here we use the updated PMCAMx-UF, which is first evaluated against observational data, to assess the effect of the new IIASA future scenarios on particle number concentrations over Europe. On the basis of the scenarios, we apply country-based scaling factors for the emissions, which will allow for improved predictions of the local changes in future particle number concentrations compared to what would be possible using domain-based scaling factors. Motivated by the new NPF schemes involving ammonia and amines, we further examine the specific potential of agricultural emission control measures to reduce particle number concentrations and improve air quality.

### Methods

#### PMCAMx-UF Description

The three-dimensional regional chemical transport model PMCAMx-UF simulates both particle mass and number concentrations\(^\text{(27, 30)}\) (see also the Supporting Information). The descriptions of vertical and horizontal advection and dispersion, wet and dry deposition, and gas-phase chemistry are based on the publicly available CAMx air quality model. For aerosol microphysics, including NPF, condensation, and coagulation, PMCAMx-UF uses the Dynamic Model for Aerosol Nucleation (DMAN\(^\text{(31)}\)), which tracks the aerosol mass and number distributions using the Two-Moment Aerosol Sectional (TOMAS) algorithm\(^\text{(32)}\) with the particles divided into 41 logarithmically spaced bins between 0.8 nm and 10 μm.

The version of PMCAMx-UF used here includes 15 aerosol species, including the new surrogate amine species, as well as five secondary organic aerosol (SOA) species. The SOA species and the amine species are new additions to the DMAN module not present in previously published PMCAMx-UF work.\(^\text{(27, 30)}\) The updated DMAN module simulates explicitly the mass transfer of sulfuric acid, ammonia, amine, and the five SOA species, while water is assumed to be in equilibrium. The rest of the aerosol components do not explicitly participate in the mass transfer within DMAN. The TOMAS algorithm handles the condensation of all the condensing species, but while ammonia,\(^\text{(31)}\) the newly added amine,
and the five SOA species condense dynamically, the calculation of sulfuric acid condensation and NPF is performed using the pseudo-steady-state approximation method. (33)

**Condensation of SOA**

Four surrogate SOA species have existed in PMCAMx-UF previously, but they did not contribute to ultrafine particle growth. Patoulias et al. (29) developed an updated version of the DMAN box model, which included a SOA precursor species using the volatility basis set framework. The SOA implementation in the PMCAMx-UF version used here follows the approach of Patoulias et al. (29) in which the SOA precursors condense according to the TOMAS algorithm. Their chemical aging occurs through a reaction with the hydroxyl radical, which reduces the volatility of the organic vapor by 1 order of magnitude. However, instead of the 12 volatility bins used by Patoulias et al. (29) in PMCAMx-UF there are four semivolatile SOA precursor bins with saturation concentrations of 1, 10, 100, and 1000 μg m\(^{-3}\), and one extremely low-volatility species with a saturation concentration equal to 10\(^{-3}\) μg m\(^{-3}\) at 298 K. Furthermore, the rate constant for the chemical aging of the SOA precursors (\(k\)) is assumed to equal 2.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}, which has been found to lead to more realistic SOA production when both anthropogenic and biogenic SOA are aged. (34) The least volatile of the semivolatile species is converted to the extremely low-volatility surrogate species, which is necessary to match observed particle growth (29) and motivated by observational data on low-volatility SOA. (35)

**Treatment of Amines within PMCAMx-UF**

The amine species is treated as a surrogate compound describing MA, DMA, and TMA, as the data available for amine emissions and atmospheric concentrations are currently scarce. The land-based emissions of these methylamines are tied to ammonia emission sources, and thus, we follow the approach of Bergman et al. (15) and assume the amine emissions to be equal to the ammonia emissions scaled by a factor of 0.0057, which is the ratio of MA, DMA, and TMA emissions to ammonia emissions. (18) Besides being removed by condensation and NPF, the amine species is removed through wet deposition, according to the Henry’s law constant of TMA, (36) and through a gas-phase reaction with the OH radical with the rate constant of the TMA–OH reaction. (18) TMA is chosen here as it is the most abundant of these three methylamines in the gas phase; however, the rate constants and atmospheric half-lives are quite similar for MA, DMA, and TMA.

A version of the ISORROPIA II model, modified to include an amine species, is used within in-cloud cells to calculate the gas-particle partitioning of the amine species. The amine species is then distributed to size bins above the activation diameter (\(\sim 80 \text{ nm}\)). In out-of-cloud cells, the DMAN module is called, and within the module, the amine species behaves like DMA. DMA condensation is treated dynamically using the TOMAS algorithm, with an accommodation coefficient of 1, and like ammonia, it is assumed to be nonvolatile in the sense that a zero saturation vapor pressure is assumed when calculating the driving force of condensation. However, an upper limit to the condensation of ammonia and amines is set as the amount needed to neutralize sulfuric acid in the particles. As a stronger base DMA is expected to be preferred over ammonia in the particles, so the amine species is given priority.
over ammonia and condenses first. However, as the amine concentration is quite low, the amount of ammonia in the particles is not significantly affected by this procedure.

Finally, the ACDC-based sulfuric acid–DMA NPF pathway has been added to DMAN to represent the effect of amine species on NPF, operating simultaneously with the existing ACDC-based ternary sulfuric acid–ammonia–water pathway and the classical nucleation theory-based parametrization of the sulfuric acid–water pathway. Using evaporation rates from quantum chemistry, ACDC was used to calculate a comprehensive set of formation rates at different H$_2$SO$_4$ and DMA concentrations, temperatures, and coagulation loss rates due to scavenging by larger particles (condensation sink), and the results are implemented in PMCAMx-UF as a look-up table. Water is not included in the H$_2$SO$_4$–DMA scheme to reduce complexity, as the effect of water on the formation rates is likely to be minor.

Further details can be found in the Supporting Information.

Model Simulations and Emission Scenarios

We applied PMCAMx-UF in the European domain, a 5400 km $\times$ 5832 km region with 36 km $\times$ 36 km grid resolution, using the meteorological input corresponding to the period from May 1 to 29, 2008. The emission inputs corresponding to the base case simulation were the emissions termed “new emissions” by Baranizadeh et al. and included hourly gridded emissions of particulate matter and gases from both anthropogenic and natural sources. The anthropogenic particle emissions included both the pan-European particle number emission and carbonaceous aerosol inventories, while the anthropogenic gas emissions included land emissions from the GEMS data set as well as international shipping emissions. The natural particle and gas emissions combined emissions from ecosystems based on the MEGAN model, marine emissions, and wildfire emissions.

It is important to note that the future scenarios simply scaled the anthropogenic part of these emissions for the affected species (see below).

In addition to the base case simulation with unaltered emissions for the May 2008 period, model simulations were performed in which the anthropogenic fraction of the PMCAMx-UF 2008 emissions was scaled to represent five different future emission scenarios. To calculate the scaling factors, data for the IIASA CLE, OPT, and MTFR scenarios, available in the GAINS database, were utilized. The scaling factors were simply the fractional change in emissions between years 2005 and 2030 as given in the GAINS database. The species whose emissions were affected included NH$_3$, SO$_2$, VOCs, NO$_x$, and particulate matter. The GAINS data are divided by country, and separate scaling factors were calculated for each of the 28 European Union (EU) member nations. The GAINS database also includes projected emissions following current legislation for several non-EU countries. We scaled the emissions from these countries accordingly, using the current legislation scaling factors for these countries in all future scenarios.

Three of the simulations corresponded directly to the IIASA scenarios. The last two simulations were performed to assess the effects of agricultural emission control measures. These runs used the scaling factors of the CLE scenario for everything except ammonia (and consequently amine) emissions, but the NH$_3$ emissions were scaled in the first simulation (NH$_3$-OPT) by the OPT scaling factors and by MTFR factors in the other simulation (NH$_3$-OPT).
The NH₃ scaling factors scaled the emissions of the amine species, as well, as the amine enters the model as a fraction of the ammonia emissions. While other anthropogenic sources of ammonia exist and agricultural activities cause emissions other than ammonia, this procedure is a reasonable approximation: agricultural control measures govern the NH₃ reductions in GAINS, and these measures make at most a small contribution to the reduction of other emissions.

The scaling factors for NH₃, SO₂, VOCs, and PM₂.₅ for the different countries are shown in Figure 1. The grid cell center point coordinates determined the country whose scaling factor was applied for a given grid cell. For grid cells with centers over the sea and countries not included in the GAINS database, the emissions were left unchanged. The VOC scaling was applied to the anthropogenic fraction of all of the modeled VOC species with anthropogenic emissions (see the Supporting Information). The PMCAMx-UF particle emissions include sizes of ≥10 nm, and the PM₂.₅ scaling factors were applied uniformly for all size bins below 2.5 μm, as size-resolved information about the emission changes was not available. Although the particulate emissions in TSAP reports 16a and 16b focus on PM₂.₅, the GAINS database contains both PM₂.₅ and PM₁₀ emission data. We therefore applied scaling factors (separate from the PM₂.₅ factors) also for the particle emissions in the size range from 2.5 to 10 μm calculated on the basis of the difference between PM₁₀ and PM₂.₅ emissions in the GAINS database. A map of these scaling factors, along with the NOₓ factors (used for NO and NO₂), is shown in the Supporting Information (see Tables S1–S3).

Particle Number Size Distribution Data for Model Evaluation

Observational data on particle number size distributions from the EUCAARI (European Aerosol Cloud Climate and Air Quality Interactions) project(40, 46) for the period of May 2008 have been used for model evaluation both in the original application of PMCAMx-UF to Europe(21) and after the updates of Baranizadeh et al.(27) Because the current model version has incorporated new features, including an additional NPF pathway, we evaluated the model predictions again using observational data from seven EUCAARI sites: Aspvreten (Sweden), Cabauw (The Netherlands), Hyytiälä (Finland), Ispra (Italy), Mace Head (Ireland), Melpitz (Germany), and Vavilhill (Sweden). The particle size distributions were measured using either a differential mobility particle sizer (DMPS) or a scanning mobility particle sizer (SMPS).

Results and Discussion

Model Evaluation

Figure 2 shows the comparison between the model predictions and the measurements at the EUCAARI sites for the hourly mean concentration of particles of >10 nm (N₁₀), >50 nm (N₅₀), and >100 nm (N₁₀₀). The agreement between the model and observations has improved compared to what was reported by Baranizadeh et al.(27) While there is still a tendency to overpredict N₁₀ and slightly underestimate N₁₀₀, both the agreement with observations [in terms of normalized mean bias (NMB)] and the scatter [in terms of normalized mean error (NME)] for N₁₀ (NMB = 77%, and NME = 96%) and N₁₀₀ (NMB = −3%, and NME = 48%) have improved compared with those of Baranizadeh et al.(27)
reported NMBs of 113 and −45% and NMEs of 131 and 52% for \( N_{10} \) and \( N_{100} \), respectively. This is due to a large extent to the addition of new condensable vapors.\(^{27}\) \( N_{50} \), which was previously slightly underpredicted (NMB = −9%),\(^{27}\) is now somewhat overpredicted (NMB = 23%), but the agreement remains fairly good (see also Table S4).

There is very little information available about atmospheric amine concentrations,\(^{18}\) and evaluating modeled concentrations against observations is hampered by the sparsity of available measurement data.\(^{15, 16}\) For the work presented here, this kind of evaluation is even more difficult as we are limited to locations within and around Europe, and furthermore, only a few of the available observed data correspond to the simulation month (May). Nonetheless, the modeled amine concentrations seem to be in reasonable agreement with observations (see the Supporting Information and Table S5) and similar in magnitude to those of previous modeling efforts.\(^{15, 16}\) Further model evaluation can be found in the Supporting Information.

### IIASA Emission Scenarios and Particle Number Concentrations

Figure 3 shows the median number concentrations of both \( N_{\text{tot}} \) and \( N_{100} \) for the base case simulation and for the three IIASA scenarios, while the fractional changes between the scenarios and the base case simulation are shown in Figure 4 (see the Supporting Information for mean number concentrations). The first two simulation days were omitted from the analysis to minimize the effects of the initial conditions. In general, all of the scenarios lead to improved air quality in the form of reduced concentrations of both \( N_{\text{tot}} \) and \( N_{100} \) for most of EU-28, with a larger decrease in particle number resulting from the scenarios with more stringent emission controls. For the CLE scenario, much of Europe exhibits a decrease in \( N_{\text{tot}} \) in the range of 10–20%, while the other scenarios result in many areas with a decrease of ≥50%. A particularly large decrease in \( N_{\text{tot}} \) occurs over Eastern Europe in countries such as Romania and Bulgaria. Interestingly, the emission reductions of both particulate matter and the gases relevant to NPF in the model are not notably different in these countries compared to other nations (Figure 1). However, the reduction in VOC emissions is somewhat larger, affecting the concentrations of the organic species participating in particle growth. A possible explanation for the greater relative decrease in \( N_{\text{tot}} \) in eastern Europe is the slower growth due to lower concentrations of condensing vapors, which allows more of the smaller particles to be lost by coagulation.

A notable exception to the improved air quality is predicted for the Nordic countries, where \( N_{\text{tot}} \) remains mostly unchanged or even slightly increased, despite the reduction in emissions of both particles and the NPF precursor gases. This is likely explained by a simultaneous decrease in the condensation sink with the decrease in the already low aerosol precursor emissions in these relatively clean areas. Part of the increase in \( N_{\text{tot}} \) in Denmark and southern Sweden can be attributed to NPF in nearby marine areas. Although the emissions over marine areas are unchanged from the baseline in 2008, an increase in \( N_{\text{tot}} \) is predicted in many coastal sea areas, particularly the North Sea and the Baltic Sea. This is because the decrease in \( N_{100} \) over the continental regions leads to fewer large particles being transported to the marine areas, resulting in a smaller condensation sink (Figure 4) and more favorable conditions for NPF. Other continental areas with an increase in \( N_{\text{tot}} \) include some of the...
eastern countries outside of the EU, for which ammonia emissions are increased compared to the 2008 baseline. For Turkey, in which $N_{\text{tot}}$ increases, the scenarios include an increase in $SO_2$ and PM emissions, as well. While the reductions in particle concentrations in various parts of Europe are often substantial (Figure 4), median percentage changes for the whole domain are more modest because the increases at certain areas, especially outside of the EU, cancel out the decreases at other locations. For the whole domain, $N_{100}$ is reduced by 22% (CLE) to 34% (MTFR), while the change in $N_{\text{tot}}$ is only from 2% to 6% depending on the scenario (see also Table S6).

Figure 5 shows the fractional change in median particle number concentrations (see the Supporting Information for the change in mean number concentrations) due to agricultural amine and ammonia emission control measures beyond current legislation, i.e., the change from the CLE simulation to the NH$_3$-OPT and NH$_3$-MTFR simulations. The decrease in $N_{\text{tot}}$ is $\sim$10% for much of Europe, with $>20\%$ decreases in some regions, mainly for the NH$_3$-MTFR simulation. The magnitude of the decrease in $N_{\text{tot}}$ is consistent with the fact that only the ammonia and amine emissions have changed. The corresponding decrease from the baseline emissions is for many countries $\sim$10% for CLE and $\sim$30–40% for MTFR.

The results are promising in terms of the potential of NH$_3$ and methylamine reductions to improve air quality by reducing total particle number concentrations. However, the decrease is smaller for $>10$ nm particles, $\sim5\%$ for a large part of EU-28, and $N_{100}$ even shows an increase of $\geq10\%$ in many areas. The primary particle emissions are unchanged between these simulations, so the increase in the number of large particles is a result of more newly formed particles surviving and growing to larger sizes by condensation. Sulfuric acid operates under the pseudo-steady-state approximation, where all of the produced sulfuric acid (which is unchanged due to same $SO_2$ emissions) is either condensed or used in NPF. As the particle formation rates decrease, less sulfuric acid is used in NPF and, more importantly, the remaining sulfuric acid and other condensable vapors are distributed among fewer particles. This leads to faster growth for the smallest particles, and consequently fewer particles lost to coagulation. Here the organic species participate in the growth of the new particles, and the first steps of particle formation are driven by sulfuric acid, water, ammonia, and amines. Recent laboratory results suggest that oxidized organics may also participate in the initial particle formation process.(47) This may change the sensitivity of the particle concentrations to $SO_2$, VOC, ammonia, and amine emissions.(11)

Our simulations suggest substantial decreases in particle number concentrations as a result of expected future EU emission policies in Central Europe and the British Islands. In Turkey, however, precursor emissions and hence particle number concentrations are expected to increase in the future. Very little decrease, or even some increase, in particle numbers is expected in the Nordic countries, despite decreasing emissions. On the basis of our simulations, which use new NPF schemes involving amines and ammonia, agricultural emissions show potential in reducing the number concentrations of especially the smallest ultrafine particles. The response of the particle size distribution to agricultural ammonia and amine emissions is nonlinear, because of the nonlinear dynamics of the particle populations. It is also evident via comparison of the NH$_3$-OPT and NH$_3$-MTFR scenarios in Figure 5 that local changes in particle number concentrations are quite nonlinear with respect to changes.
in the level of the applied agricultural emission reductions. To fully unravel the importance of methylamines for atmospheric aerosol populations requires detailed and spatially resolved emission information, and therefore, more work in constraining their emissions and concentrations is needed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Pope CA, Dockery DW. Health effects of fine particulate air pollution: Lines that connect. J Air Waste Manage Assoc. 2006; 56:709–742.
2. Ambient air pollution: A global assessment of exposure and burden of disease Technical Report World Health Organization; Geneva: 2016.
3. Fuzzi S, Baltensperger U, Carslaw K, Decesari S, Denier Van Der Gon H, Facchini MC, Fowler D, Koren I, Langford B, Lohmann U, Nemitz E, Pandis S, Riipinen I, Rudich Y, Schaap M, Slowik JG, Spracklen DV, Vignati E, Wild M, Williams M, Gilardoni S. Particulate matter, air quality and climate: Lessons learned and future needs. Atmos Chem Phys. 2015; 15:8217–8299.
4. Asmi A, Wiedensohler A, Laj P, Fjaeraa A-M, Sellegrin K, Birnili W, Weingartner E, Baltensperger U, Zdimal V, Zikova N, Putaud J-P, Marinoni A, Tunved P, Hansson H-C, Fiebig M, Kivekas N, Lihavainen H, Asmi E, Uleciecicis V, Aalto PP, Siewetlicki E, Kristensson A, Mihalopoulos N, Kalivitis N, Kalapov I, Kiss G, De Leeuw G, Henzing B, Harrison RM, Beddows D, O’Dowd C, Jennings SG, Flentje H, Weinhold K, Meinhardt F, Ries L, Kulmala M. Number size distributions and seasonality of submicron particles in Europe 2008–2009. Atmos Chem Phys. 2011; 11:5505–5538.
5. Oberdörster G, Oberdörster E, Oberdörster J. Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles. Environ Health Perspect. 2005; 113:823–839. [PubMed: 16002369]
6. Araujo JA, Barajas B, Kleinman M, Wang X, Bennett BJ, Gong KW, Navab M, Harkema J, Sioutas C, Linis AJ, Nel AE. Ambient particulate pollutants in the ultrafine range promote early atherosclerosis and systemic oxidative stress. Circ Res. 2008; 102:589–596. [PubMed: 18202315]
7. Terzano C, Di Stefano F, Conti V, Graziani E, Petroiani A. Air pollution ultrafine particles: Toxicity beyond the lung. Riv Eur Sci Med Farmacol. 2010; 14:809–821.
8. Hoek G, Beelen R, Eeftens M, Meliefste K, de Vrieze G, Briggs D, Cyrys J, Forsberg B, Madsen C, Nieuwenhuijsen M, Liu S, de Nazelle A, Brunekreef B. Air pollution exposure in Europe – assessment in the ESCAPE study. Epidemiology. 2009; 20:S254.
9. Korhonen P, Kulmala M, Laaksonen A, Viisanen Y, McGraw R, Seinfeld JH. Ternary nucleation of H2SO4, NH3, and H2O in the atmosphere. J Geophys Res. 1999; 104:26349–26353.
10. Kulmala M, Pirjola L, Makela JM. Stable sulphate clusters as a source of new atmospheric particles. Nature. 2000; 404:66–69. [PubMed: 10716441]
S, Sengupta K, Simon M, Sipila M, Smith JN, Stozhkov Y, Tome A, Tröstl J, Wagner PE, Wimmer D, Winkler PM, Worsnop DR, Carslaw KS. Global atmospheric particle formation from CERN CLOUD measurements. Science. 2016; 354:1119–1124. [PubMed: 27789796]

10Olenius T, Kupiainen-Maättä O, Ortega IK, Kurtén T, Vehkamäki H. Free energy barrier in the growth of sulfuric acid-ammonia and sulfuric acid-dimethylamine clusters. J Chem Phys. 2013; 139:084312. [PubMed: 24007002]

11Almeida J, Schoebesberger S, Kärten A, Ortega IK, Kupiainen-Maättä O, Praplan AP, Adamov A, Amorim A, Bianchi F, Breitenlechner M, David A, Dommen J, Donahue NM, Downard A, Dunne E, Duplissy J, Elhert J, Franchin A, Guida R, Hakala J, Hansel A, Heinritzi M, Henschel H, Jokinen T, Junninen H, Kajos M, Kangasluoma J, Keskinen H, Kupea A, Kurten T, Kvashin AN, Laaksonen A, Lehtipalo K, Leiminger M, Leppa J, Loukonen V, Makhmutov V, Mathot S, McGrath MJ, Nieminen T, Olenius T, Onnela A, Petäjä T, Riccobono F, Rissanen M, Rondo L, Ruuskanen T, Santos FD, Sarnela N, Schallhart S, Schnitzhofer R, Seinfeld JH, Simon M, Sipila M, Stozhkov Y, Stratmann F, Tomé Á, Tröstl J, Tsagkogeorgas G, Vaattovaara P, Vissani Y, Virtanen A, Vrtala A, Wagner PE, Weingartner E, Wex H, Williamson C, Wimmer D, Ye P, Yli-Juuti T, Carslaw KS, Kulmala M, Curtius J, Baltensperger U, Worsnop DR, Vehkamäki H, Kirkby J. Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere. Nature. 2013; 502:359–363. [PubMed: 24097350]

12Glasoe WA, Voltz K, Panta B, Freshour N, Bachman R, Hanson DR, McMurry PH, Jen C. Sulfuric acid nucleation: An experimental study of the effect of seven bases. J Geophys Res Atmos. 2015; 120:1933–1950.

13Bergman T, Laaksonen A, Korhonen H, Malila J, Mielonen T, Lehtinen KEJ, Kühn T, Arola A, Kokkola H. Geographical and diurnal features of amine-enhanced boundary layer nucleation. J Geophys Res Atmos. 2015; 120:9606–9624.

14Yu F, Luo G. Modeling of gaseous methylamines in the global atmosphere: impacts of oxidation and aerosol uptake. Atmos Chem Phys. 2014; 14:12455–12464.

15Aneja VP, Schlesinger WH, Erisman JW. Effects of agriculture upon the air quality and climate: Research, policy, and regulations. Environ Sci Technol. 2009; 43:4234–4240. [PubMed: 19603628]

16Ge X, Wexler AS, Clegg SL. Atmospheric amines - Part I. A review. Atmos Environ. 2011; 45:524–546.

17Backes AM, Aulinger A, Bieser J, Matthias V, Quante M. Ammonia emissions in Europe, part II: How ammonia emission abatement strategies affect secondary aerosols. Atmos Environ. 2016; 126:153–161.

18Megaertiis AG, Fountoukis C, Charalampidis PE, Pilinis C, Pandis SN. Response of fine particulate matter concentrations to changes of emissions and temperature in Europe. Atmos Chem Phys. 2013; 13:3423–3443.

19Fountoukis C, Riipinen I, Denier Van Der Gon HAC, Charalampidis PE, Pilinis C, Wiedensohler A, O’Dowd C, Putaud JP, Moerman M, Pandis SN. Simulating ultrafine particle formation in Europe using a regional CTM: Contribution of primary emissions versus secondary formation to aerosol number concentrations. Atmos Chem Phys. 2012; 12:8663–8677.

20Ahlm L, Julin J, Fountoukis C, Pandis SN, Riipinen I. Particle number concentrations over Europe in 2030: The role of emissions and new particle formation. Atmos Chem Phys. 2013; 13:10271–10283.

21Amann A, editor. Future emissions of air pollutants in Europe. Current legislation baseline and the scope for further reductions 2012TSAP Report 1, version 1.0

22Proposals for a Directive of the European Parliament and of the Council on the reduction of national emissions of certain atmospheric pollutants and amending DirectiveEuropean Commission; Brussels: 20132003/35/EC Technical Report

Environ Sci Technol. Author manuscript; available in PMC 2019 January 16.
27Baranizadeh E, Murphy BN, Julin J, Falahat S, Reddington CL, Arola A, Ahlm L, Mikkonen S, Fountoukis C, Patoulias D, Minikin A, Hamburger T, Laaksonen A, Pandis SN, Vehkamaki H, Lehtinen KEJ, Riipinen I. Implementation of state-of-the-art ternary new-particle formation scheme to the regional chemical transport model PMCAMx-UF in Europe. Geosci Model Dev. 2016; 9:2741–2754.

28Olenius T, Halonen R, Kurten T, Henschel H, Kupiainen-Maättä O, Ortega IK, Jen CN, Vehkama ‘hi, Riipinen I. New particle formation from sulfuric acid and amines: Comparison of monomethylamine, dimethylamine, and trimethylamine. J Geophys Res Atmos. 2017; 122:7103–7118.

29Patoulias D, Fountoukis C, Riipinen I, Pandis SN. The role of organic condensation on ultrafine particle growth during nucleation events. Atmos Chem Phys. 2015; 15:6337–6350.

30Jung JG, Fountoukis C, Adams PJ, Pandis SN. Simulation of in situ ultrafine particle formation in the eastern United States using PMCAMx-UF. J Geophys Res. 2010; 115:D03203.

31Jung J, Adams PJ, Pandis SN. Simulating the size distribution and chemical composition of ultrafine particles during nucleation events. Atmos Environ. 2006; 40:2248–2259.

32Adams PJ, Seinfeld JH. Predicting global aerosol size distributions in general circulation models. J Geophys Res. 2002; 107:4370.

33Pierce JR, Adams PJ. A computationally efficient aerosol nucleation/condensation method: Pseudo-steady-state sulfuric acid. Aerosol Sci Technol. 2009; 43:216–226.

34Murphy BN, Pandis SN. Exploring summertime organic aerosol formation in the eastern United States using a regional-scale budget approach and ambient measurements. J Geophys Res Atmos. 2010; 115:D24216.

35Ehn M, Thornton JA, Kleist E, Sipila M, Junninen H, Pullinen I, Springer M, Rubach F, Tillmann R, Lee B, Lopez-Hilfiker F, Andres S, AciR I-H, Rissanen M, Jokinen T, Schoebesberger S, Kangasluoma J, Kontkanen J, Nieminen T, Kurten T, Nielsen LB, Jørgensen S, Kjaergaard HG, Canagaratna M, Dal Maso M, Berndt T, Petaja T, Wahner A, Kerminen V-M, Kulmala M, Worsnop DR, Wildt J, Mentel TF. A large source of low-volatility secondary organic aerosol. Nature. 2014; 506:476–479. [PubMed: 24572423]

36Sander R. Compilation of Henry’s law constants (version 4.0) for water as solvent. Atmos Chem Phys. 2015; 15:4399–4981.

37Vehkamaki H, Kulmala M, Napari I, Lehtinen KEJ, ‘Timmreck C, Noppel M, Laaksonen A. An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions. J Geophys Res. 2002; 107:4622.

38Ortega IK, Kupiainen O, Kurten T, Olenius T, Wilkmäni O, McGrath MJ, Loukonen V, Vehkamaki H. From quantum chemical formation free energies to evaporation rates. Atmos Chem Phys. 2012; 12:225–235.

39Denier van der Gon HAC, Visschedijk AHJ, Johansson C, Hedberg Larsson E, Harrison R, Beddows D. Size resolved pan European anthropogenic particle number inventory TNO; The Hague, The Netherlands: 2009EUCAARI Deliverable Report D141 available on request from EUCAARI project office

40Kulmala M, Asmi A, Lappalainen HK, Baltensperger U, Brenguier J-L, Facchini MC, Hansson HC, Hov Ø, O’Dowd CD, Pöschl U, Wiedensohler A, Boers R, Boucher O, De Leeuw G, Denier Van Der Gon HAC, Feichter J, Krejci R, Laj P, Lihavainen H, Lohmann U, McFiggans G, Mentel T, Pilinis C, Riipinen I, Schulz M, Stohl A, Swietlicki E, Vignati E, Alves C, Amann M, Ammann M, Arabas S, Artaxo P, Baars H, Beddows DCS, Bergström R, Beukes JP, Bilde M, Burkhart JF, Canonaco F, Clegg SL, Coe H, Crumeyrolle S, D’Anna B, Decesari S, Girardoni S, Fischer M, Fjæraa AM, Fountoukis C, George C, Gomes L, Halloran P, Hamburger T, Harrison RM, Herrmann H, Hoffmann T, Hose C, Hu M, Hyvarinen Å, Hörrak U, Innamaa Y, Iversen T, Josipovic M, Kanakidou M, Kiendler-Scharr A, Kirkevag A, Kiss G, Klimont Z, Kolmoken P, Koppula M, Kristjansson J-E, Laakso L, Laaksonen A, Labowmote L, Lanz VA, Lehtinen KEJ, Rizzo LV, Makonen R, Manninen HE, McMeekeing G, Merikanto J, Minikin A, Mirme S, Morgan WT, Nemitz E, O’Donnell D, Panwar TS, Pawlowska H, Petzold A, Piazzolla JF, Pino C, Plass-Duemer C, Prevot ASH, Pryor S, Reddington CL, Roberts G, Rosenfeld D, Schwarz J, Selend O, Selegre K, Shen XJ, Shiraiwa M, Siebert H, Sierau B, Simpson D, Sun JY, Topping D, Tunved P, Vaattovaara P, Vakkari V, Veefkind JP, Visschedijk A, Vuollekoski H, Vuolo R, Wehner Environ Sci Technol. Author manuscript; available in PMC 2019 January 16.
B, Wildt J, Woodward S, Worsnop DR, Van Zadelhoff G-J, Zardi AA, Zhang K, Van Zyl PG, Kerminen V-M, Carslaw KS, Pandis SN. General overview: European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI)-integrating aerosol research from nano to global scales. Atmos Chem Phys. 2011; 11:13061–130143.

41 Visschedijk AJH, Zandveld P, Denier van der Gon HAC. A high resolution gridded European emission database for the EU integrated project GEMS. Netherlands Organization for Applied Scientific Research; The Hague, The Netherlands: 2007 TNO Report 2007 A R0233/B

42 Guenther A, Karl T, Harley P, Wiedinmyer C, Palmer PL, Geron C. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos Chem Phys. 2006; 6:3181–3210.

43 O’Dowd CD, Langmann B, Varghese S, Scannell C, Ceburnis D, Facchini MC. A combined organic-inorganic sea-spray source function. Geophys Res Lett. 2008; 35:L01801.

44 Sofiev M, Vankevich R, Lanne M, Koskinen J, Kukkonen J. On integration of a Fire Assimilation System and a chemical transport model for near-real-time monitoring of the impact of wild-land fires on atmospheric composition and air quality. WIT Trans Ecol Environ. 2008; 119:343–351.

45 Sofiev M, Lanne M, Vankevich R, Prank M, Karppinen A, Kukkonen J. Impact of wild-land fires on European air quality in 2006–2008. WIT Trans Ecol Environ. 2008; 119:353–361.

46 Kulmala M, Asmi A, Lappalainen HK, Carslaw KS, Pöschl U, Baltensperger U, Hov O, Brenquier J-L., Pandis SN, Facchini MC, Hansson H-C, Wiedensohler A, O’Dowd CD. Introduction: European Integrated Project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI)-integrating aerosol research from nano to global scales. Atmos Chem Phys. 2009; 9:2825–2841.

47 Kirkby J, Duplissy J, Sengupta K, Frege C, Gordon H, Williamson C, Heinritzi M, Simon M, Yan C, Almeida J, Trostl J, Nieminen T, Ortega IK, Wagner R, Adamov A, Amorim A, Bernhammer A-K, Bianchi F, Breitenlechner M, Brike S, Chen X, Craven J, Dias A, Ehrhart S, Flagan RC, Franchin A, Fuchs C, Guida R, Hakala J, Hoyle CR, Jokinen T, Junninen H, Kangasluoma J, Kim J, Krapf M, Kurten A, Laaksonen A, Lehtipalo K, Makkonen T, Mathot S, Molteni U, Onnela A, Perakyla O, Piel F, Petajä T, Praplan AP, Pringle K, Rap A, Richards NAD, Riipinen I, Rissanen MP, Rondo L, Sarnela N, Schobesberger S, Scott CE, Seinfeld JH, Sipila M, Steinr G, Stozhkov Y, Stratmann F, Tome A, Virtanen A, Vogel AL, Wagner AC, Wagner PE, Weingartner E, Wimmer D, Winkler PM, Ye P, Zhang X, Hansel A, Dommen J, Donahue NM, Worsnop DR, Baltensperger U, Kulmala M, Carslaw KS, Curtius J. Ion-induced nucleation of pure biogenic particles. Nature. 2016; 533:521–526. [PubMed: 27225125]

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Figure 1.
Scaling factors calculated from the IIASA CLE, OPT, and MTFR scenarios for the year 2030 for NH3, SO2, PM2.5, and VOC emissions. Note that for countries outside the EU member nations the scaling factor is the same for each scenario. For scaling factors for NOx and particles with sizes between 2.5 and 10 μm, see the Supporting Information.
Figure 2.
Comparison between the predicted and measured hourly average particle number concentrations N10, N50, and N100 at seven EUCAARI stations: Aspvreten (Sweden), Cabauw (The Netherlands), Hyytialä (Finland), Ispra (Italy), Mace Head (Ireland), Melpitz (Germany), and Vavihill (Sweden). The lines correspond to 1:1 (-) and 1:2 and 2:1 (---) ratios. The model predictions are from the base case simulation.
Figure 3. Median ground-level total particle number concentration $N_{\text{tot}}$ for the base case and the CLE, OPT, and MTFR scenarios (top panels). Median ground-level concentration of $>100$ nm particles ($N_{100}$) (bottom panels).
Figure 4.
Predicted fractional change in median $N_{\text{tot}}$ (top panels) and $N_{100}$ (bottom panels) between the CLE, OPT, and MTFR scenarios and the base case.
Figure 5.
Predicted fractional change in median $N_{tot}$, $N_{10}$, and $N_{100}$ between the runs with additional agricultural reductions and the CLE scenario. The left panels show the changes when ammonia is reduced according to the OPT scenario while others follow the CLE scenario ($NH_3$-OPT). The right panels show the changes when ammonia is reduced according to the MTFR scenario while others follow the CLE scenario ($NH_3$-MTFR).