Atmospheric Degradation of Amines (ADA)

Amines in aerosol — A review
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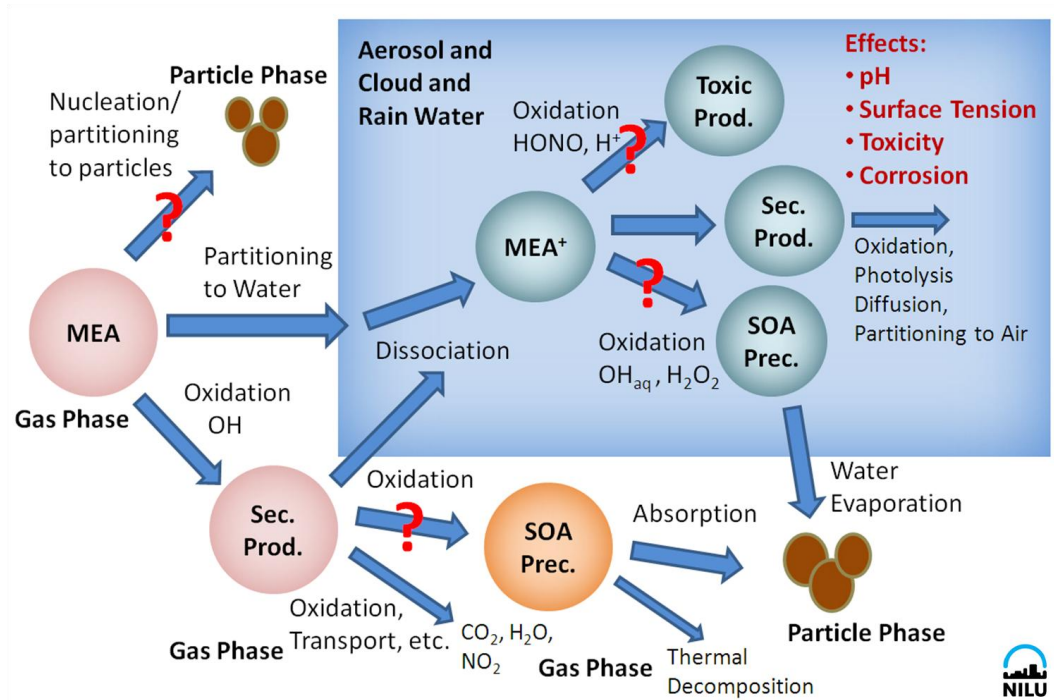
Matthias Karl

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Possible multiphase pathways of 2-aminoethanolamine (MEA) in the troposphere (by Matthias Karl, presented at the INTROP final conference, 14-17 April, 2009).

Preface

Studies on the emission from amine-based CO_2 capture mimic facilities indicate the simple alkane-amines as process degradation products of the more complex amines used in CO_2 capture. These small amines will therefore always be emitted with the cleaned flue gas to the atmosphere no matter which parent amine is used in the absorber, and they may present the major environment and human health problem linked to the implementation of amine-based CO_2 capture. Quantitative knowledge about the atmospheric fate of simple alkane-amines such as CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$ and $(CH_3CH_2)_3N$, including their partitioning to particles and droplets and their contribution to the formation of new particles, is therefore prerequisite to an Environmental Impact Assessment of amine-based CO_2 capture.

The overall objective of the ADA-2010 project is to contribute to the understanding of the atmospheric degradation of amines emitted to the atmosphere from CO_2 capture plants. The specific objectives are:

- To identify the gas phase photochemical degradation products resulting from emission of amines under natural atmospheric conditions.

- To quantify the main products in the gas phase photo-oxidation of amines emitted to air.

- To verify/update existing atmospheric photo-oxidation schemes for amines to account for all products formed under natural conditions.

- To assess the conditions for aerosol formation during the gas phase degradation of amines emitted to air, and to characterize and quantify the aerosol formation.

This report contains a review of the role of amines in the atmospheric aerosol.

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Executive Summary

A Literature review of amines in atmospheric aerosols is presented. The review focuses on methylamine, dimethylamine and trimethylamine, but is not restricted to these alkylamines. Instead it was aimed at giving a broad overview of the current knowledge on amine compounds in aerosol particles and their role in the life cycle of aerosols.

In the Sixties and Seventies of the past century, Public concern on the carcinogenic potential of N-nitroso compounds directed research into the formation and degradation of nitrosamines and related N-nitroso compounds in the condensed phase. Scientific publications from that time still form the basis of the understanding of nitrosamines chemistry on particles. In the last years an increasing number of publications on experimental lab studies, field measurements, and computational work on amines and other nitrogen containing organic compounds became available. Scientific publications from the last decade conclude that amines play an important role in the formation of new aerosol particles and can significantly contribute to the particulate mass of the ambient submicron aerosols in urban, remote continental, and marine air.

Inhalation exposure to nitrogen containing organic aerosol is associated with adverse health effects. Although several well-founded epidemiological studies consistently demonstrated that inhalation of ambient particulate matter (PM) is associated with mortality and morbidity, and specifically with chronic respiratory and cardiovascular diseases, the adverse health effects of secondary organic aerosols, such as those originating from the photo-oxidation of amines are still poorly studied.

The review revealed that there is a knowledge gap with respect to acute and chronic toxic effects of particulate amides and imines, and only little is known about their chemical formation mechanisms.

Amines in aerosol – A review

1 Literature Review of Amines in Aerosols

1.1 Overview

Amines are emitted from a variety of anthropogenic sources including agricultural animal operations,[1] automobile emissions,[2] waste treatment facilities,[3] biomass burning,[4] and industrial uses.[5] Recently emissions of amines from oceanic phytoplankton have been suggested.[6] The lifetime of alkylamines in the atmosphere ranges from a few hours to tens of hours. Since amines do not undergo direct photolysis, their reactions with atmospheric oxidants such as the hydroxyl radical (OH), ozone, and nitrate radical (NO_3) are the main removal paths for amines. Early photo-oxidation experiments in the seventies have shown that amine reactions result in the formation of both volatile and condensed products.[7] Amines have shown a propensity to form aerosols[8-9] which could have important implications for health in the local environment. Aerosols are also known to affect visibility [10] and climate change.[11] Particulate amines and secondary oxidation products from amines in the particle phase have been associated with adverse health impacts of aerosol particles.

The present review is structured as follows:

Particles and Processes:
- Atmospheric nanoparticles
- Secondary Organic Aerosol
- Aminium Salts
- Cloud Condensation Nuclei

Atmospheric Environments:
- Urban Environment and Agriculture
- Forests
- Marine Environment

Toxicity:
- Toxicity of particulate amines
- Toxicity of secondary oxidation products

List of abbreviated alkyl amines:

MMA: methylamine
EA: ethylamine
PA: propylamine
BA: butylamine
DMA: dimethylamine
DEYA: diethylamine
TBA: tributylamine
TMA: trimethylamine
TEYA: triethylamine

1.2   Particles and Processes

Recent field measurements and lab experiments have shown that amine compounds can be a significant portion of the aerosol mass.[9, 12-13] However, the chemistry that leads to particulate amines is not well understood. It appears that the chemistry that is involved in the formation of particles from amines depends on the class of amine reacted. For example, Murphy *et al.*[8] found that tertiary amines in particular form higher yields of aerosols than the primary and secondary amines.

In this section we summarize the major types of aerosols and the relevant aerosol dynamics and aerosol chemistry processes of amine-related aerosols. The lifecycle of aerosols formed by the processing of amine emissions is constituted of:

1) nucleation of new particles,
2) growth of particles by condensation and reactive uptake,
3) cloud processing,
4) dry deposition and wet scavenging.

The first process leads to the formation of atmospheric nanoparticles, i.e. clusters and particles with sizes below 20 nm diameter (section 1.2.1). Amines may be taken up and/or condense onto small particles enabling them to grow further to Aitken mode and accumulation mode size (section 1.2.2 and 1.2.3). When the size of a particle reaches a critical size in diameter and the particles are hygroscopic, they can be activated into cloud condensation nuclei (CCN) and form seeds to cloud formation. The role of amines in the formation of CCN and the processing of amine-particles in clouds are discussed in section 1.2.4. Finally, aerosols are removed from the atmosphere by dry and wet deposition. Particulate amines are considered to be removed relatively fast by wet scavenging due their good solubility in water.[14-15]

1.2.1   Atmospheric Nanoparticles

In remote boreal forest studies, Mäkelä and coworkers [16] found a strong positive correlation between new particle formation events and the concentration of dimethylammonium (the ionic component of dimethylamine). In the event samples, nucleation mode (5-30 nm diameter) particle dimethylammonium (DMA^+) was found to be present exceeding the concentrations found in the non-event samples, indicating that DMA^+ seems to be present in the particle phase during the particle formation periods and/or during the subsequent particle growth. From a large-scale field study in Tecamac (Mexico) it was concluded that aminium compounds, cations with the structure R_3NH^+ formed by protonation of an amine, with R being an alkyl group or H, contributed to the growth of freshly nucleated particles (8-30 nm diameter).[17] The observed growth of fresh particle was consistent with the postulated mechanism of growth through the formation of stable organic salts (aminium salts with organic and inorganic acids).[8, 18] Another recent modeling study suggested that amines may be an important contributor to organic salt formation in the atmosphere.[19] Since the saturation

vapour pressure of low molecular-weight amines found in the atmosphere are too high for such compounds to contribute to condensational growth of small particles, the acid-base reaction of gas phase amines with strong inorganic or organic acids to form essentially non-volatile organic salts and/or the reactive uptake of gas phase amines into liquid droplets and subsequent formation of organic salts in the particulate phase are the likely mechanisms. In summary, the few field studies that included the analysis of the chemical composition of nucleation mode particles suggest that gas phase amines are strongly involved in post-nucleation growth.[16-17, 20-21]

It has also been speculated that amines directly participate in the first steps of nucleation, i.e formation of dimer clusters with sulphuric acid. Murphy et al.[8] reported that for a nucleation process involving nitric acid, amines such as diethylamine may be more effective than ammonia in forming new particles. These authors[8] found that for aminium nitrate salts, amines generally partitioned back to the gas-phase as gas-phase amines were reacted away, leaving ammonium nitrate in the particle-phase; while for an aminium sulfate salt, MMA appeared to displace ammonia, resulting in almost complete conversion to methyl aminium sulfate.[19] Based on ab-initio calculations, Kurtén et al.[22] concluded that short-chained aliphatic amines like dimethylamine could be more important than ammonia in enhancing neutral and especially ion-induced sulfuric acid-water nucleation in the atmosphere, even though their atmospheric concentrations are usually 2-3 orders lower than that of ammonia. Dimethylamine was found to enhance the addition of sulfuric acid to the clusters considerably more effectively than ammonia, with the difference in standard free energies being approximately 5 kcal/mol for the neutral clusters and 7 kcal/mol for the charged clusters. Results from a follow-up computational study confirmed the potential of DMA to enhance atmospheric sulfuric acid nucleation much more effectively than ammonia does.[23] The study also showed that under all tropospherically relevant conditions, practically all DMA-containing two-acid clusters remain almost completely unhydrated, i.e. are not associated with water molecules. A recent flow tube study by Lloyd et al.[24] demonstrated that TMA can be taken up by ammonium nitrate particles, leading to an exchange of TMA for ammonia in the particles. They suggest that this exchange is also possible in the atmosphere when particles are exposed to an amine concentration on the order of 1 ppb for a few hours. Bzdek et al.[25] very recently investigated the displacement of ammonium bisulfate and ammonium nitrate by MMA, DMA, and TMA in very small clusters of 1-2 nm diameter. According to Bzdek et al.,[25] complete conversion of ammonium to aminium in the small clusters happens in less than a second. Even for ambient amine concentrations of a few pptv, i.e. further distant from an amine point source, complete conversion is expected to occur within several seconds to minutes. An important implication for the atmosphere is, that salt components in atmospheric sub-3nm clusters (the so-called pool of neutral and ionic clusters which is continuously present in the atmosphere) are likely to be amine salts rather than ammonia salts, even when ambient ammonia concentrations are much higher than those of amines.

1.2.2 Secondary Organic Aerosol

Gas phase aliphatic amines may play a significant role in secondary aerosol formation via photo-oxidation and gas-to-particle conversion in regions with high amine concentrations.[8, 18] Both oxidation reactions of amines with the OH radical and acid-base reactions between amines and acids commonly present in the atmosphere (i.e. nitric acid and sulfuric acid) and in the emissions appear to play roles in the formation and chemistry of organic nitrogen-containing particle phase species. In a comprehensive particle study on several aliphatic amines, Murphy *et al.*[8] demonstrated that only the two tertiary amines studied (trimethylamine and triethylamine) formed significant non-salt organic aerosol (i.e. low-volatile condensable organics and secondary organic aerosol) when oxidized by OH or ozone. However, the non-salt organic aerosol fraction appeared to be more stable than the alkylaminium nitrate salts and did not quickly repartition back to the gas phase.[8]

In this review, the term "Secondary Organic Aerosol", short SOA, refers to particles that form by the gas/particle partitioning of semi-volatile or low volatile compounds produced in the oxidation of amines by OH, O_3, and NO_3. In the available literature these particles are also referred to as non-salt organic aerosol. The formation of (organic) aminium salts is described in section 1.2.3.

Contrary to primary and secondary amine, tertiary amines form significant amounts of SOA. An early interesting finding by Angelino *et al.*[18] which was later confirmed by Erupe *et al.*,[26] was the presence of trialkylamine-N-oxides in particles generated from TEA. It has been well documented in the synthetic organic chemistry and biochemistry literature that tertiary amines can be readily oxidized to trialkylamine-N-oxides. The discovery of trialkylamine-N-oxides in aerosols thus provided first evidence that oxidation products of alkylamines can partition to the condensed phase of aerosol particles.

While very little aerosol formation was observed in the reaction of primary amines (MMA, EA, PA, BA) with O_3,[8, 27] it is meanwhile evident that high mass yields of SOA are formed in the reaction of primary, secondary, and tertiary amines with the nitrate radical (NO_3).[26, 18, 27] The reaction of TMA with NO_3 radicals was reported to produce mostly SOA and only to a minor extent aminium salts.[26] The nitrate radical is the most important atmospheric oxidant of amines during nighttime, and thus it can be concluded that emissions of tertiary alkylamines might be an important source of SOA during night. In experiment chambers, the NO_3 radical is usually produced by injecting a mixture of ozone and NO_2 into the dark chamber, according to:

$$O_3 \text{ (g)} + NO_2 \text{ (g)} \rightarrow NO_3 \text{ (g)} + O_2 \text{ (g)} \qquad \text{(R1)}$$
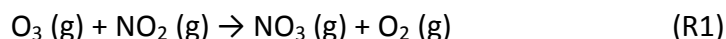
Erupe *et al.*[26] extended on the work by Silva *et al.*[9] and investigated the nighttime chemistry of TMA, TEA, and TBA. Based on low aerosol mass spectrometer (AMS) signal intensities of nitrate ions (m/z 30 and 46) they concluded that formation of aminium salt with nitric acid was minimal during their experiments. High mass fragments were associated with the formation of di-hydroxylated amides in the aerosol,[26] which show lower vapour pressures than the corresponding aldehydes. In the reaction of TMA with NO_3 radicals

obviously dimers or possibly oligomers are formed,[26, 9] which also contribute to the high molecular weight mass fraction of the aerosol. In particular, aerosol generated from TMA exhibits oligomeric properties.

Once bound to particles, amines may undergo several steps of oxidation and accretion reactions. Angelino *et al.*[18] speculate on the presence of dimethyl nitramine in the aerosol generated from TMA, a finding which is of interest since it could originate from the conversion of particulate nitrosamines by light. It could also originate from the partitioning of gas-phase produced dimethyl nitramine into the particles. Zahardis *et al.*[28] found that particulate primary amines exposed to high ozone concentrations were oxidized to stabilized amine oxide or alkylhydroxylamine favoring the formation of nitrosamines. Particulate nitrosamines subsequently oxidize to the nitroalkane. This pathway is very different from the gas phase, where amine oxide or alkylhydroxylamine fragment to various other oxidation products like aldehydes and imines. Due to the related health concern, possible presence of nitrosamine in particles should be addressed in future studies.

Imines were detected as reaction products in both wet and dry particles.[29] Formation of particulate imines is suggested to occur similar to the formation of a Schiff base. It seems to involve the formation of a stable carbinolamine intermediate which subsequently decomposes on particle surfaces, promoted in slightly acidic conditions (pH 4-5), ultimately leading to particulate imine.[27-30] Imine formation via a heterogeneous/multiphase reaction on particle surfaces could occur under certain conditions in the troposphere.[29]

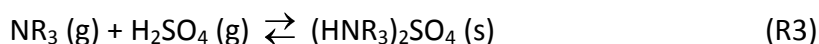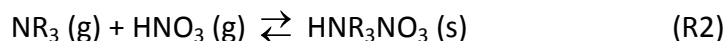### 1.2.3   Aminium salts with organic and inorganic acids

Short alkyl chain aliphatic amines have relatively high vapour pressures and their presence in the aerosol phase is thus most likely to occur in the form of alkyl aminium salts. In the presence of water on the pre-existing particles, the salts will get dissolved and the amines will be converted into their corresponding ionic form, effectively removing them from the gas phase. Amine-related particles collected during a field study in Atlanta, GA (US EPA Supersite) in 1999 showed a diurnal behavior, indicating their semi-volatile nature.[18] This observation would be consistent with postulated acid-base equilibrium reactions in analogy to reactions between ammonia (NH_3) and gas-phase acids.[8] Depending on ambient temperature and relative humidity, particle-bound amines could repartition to the gas phase.

Pitts *et al.*[7] found that for both DEYA and TEYA, the nitrate ion accounted for approximately 50% by weight of the aerosol and qualitatively concluded that a major fraction of the aerosol generated from triethylamine consisted of aminium nitrate. In photo-oxidation experiments, four to six times higher aerosol mass loads were formed from TEYA than from DEYA,[7] probably indicating largely different dissociation constants of the formed aminium nitrate salts.
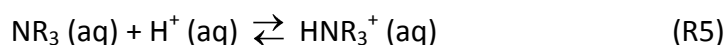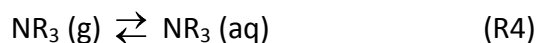
Recent field measurements have shown that aminium salt formation occurs in aged organic carbon particles in Riverside, California,[31] and in the Central Valley

region of California;[32] both of these sites are downwind of bovine sources (cattle farming). An extensive laboratory study of aliphatic amines focused on the roles of both salt formation and oxidation chemistry in gas-particle partitioning.[8] That study confirmed that alkylammonium sulfate and nitrate salts form from alkylamines and that gas-phase oxidation of the amine alkyl groups can lead to low-volatility oxidation products that can physically partition into particles, *i.e.* can be considered to form SOA.

Alkylamines react with strong inorganic acids like nitric acid and sulfuric acid in a reversible thermodynamic equilibrium reaction, according to:

$$NR_3 \text{ (g)} + HNO_3 \text{ (g)} \rightleftarrows HNR_3NO_3 \text{ (s)} \qquad \text{(R2)}$$

$$NR_3 \text{ (g)} + H_2SO_4 \text{ (g)} \rightleftarrows (HNR_3)_2SO_4 \text{ (s)} \qquad \text{(R3)}$$

The equilibrium of these two reactions depends on temperature, relative humidity, and particle acidity.[31, 8] In addition to gas-to-particle conversion by equilibrium reactions, reactive uptake into liquid aerosol may also occur. The heterogeneous uptake (also referred to as reactive uptake or heterogeneous reaction) involves as a first step the equilibrium partitioning of the amine according to Henry's Law (R4; described by a Henry coefficient) and as second step a liquid phase reaction (R5) that leads to the dissolved aminium ion:

$$NR_3 \text{ (g)} \rightleftarrows NR_3 \text{ (aq)} \qquad \text{(R4)}$$

$$NR_3 \text{ (aq)} + H^+ \text{ (aq)} \rightleftarrows HNR_3^+ \text{ (aq)} \qquad \text{(R5)}$$

The occurrence of the heterogeneous reaction of alkylamines in the atmosphere is supported by analysis of the chemical composition of nanoparticles.[17]

The heterogeneous uptake of three alkylamines (MMA, DMA, TMA) on sulfuric acid droplets has been investigated very recently by Wang *et al.*[33] Uptake coefficients (γ) of alkylamines in the range of 2.0×10^{-2} to 4.4×10^{-2} have been found for the irreversible uptake of amines into sulfuric acid droplets at different temperatures. Measured uptake coefficients for the three alkylamines are comparable. The selective accumulation of dimethyl aminium salt observed in the atmosphere is therefore likely due to other causes: the thermodynamic equilibrium of secondary aminium salts may be favored in less acidic aqueous droplets (most ambient sub-micrometer particles are partly or completely neutralized by ammonia). Aminium particles have been found to be enriched in the sub-micrometer fraction of marine aerosols supporting the mechanism of heterogeneous uptake of gas-phase amines into acidic ultrafine particles.[34] A further interesting finding is that amines can displace ammonium cations in ammonium nitrate, ammonium bisulfate, and ammonium sulfate particles,[24, 8, 25] which may lead to enhanced aminium concentrations in ambient particles although concentrations of ammonia in the atmosphere are usually 2-3 orders of magnitude higher than concentrations of alkylamines.

1.2.4 Cloud Condensation Nuclei

Organic salt formation from the reactive uptake of amines increases the effective van't Hoff factor of the solute, thereby decreasing the water vapor saturation required for a particle to develop into a cloud condensation nuclei (CCN). A laboratory study of the reactive uptake of ammonia onto slightly soluble organic acid particles found that this process can significantly increase the CCN activity and hygroscopic growth of these particles.[35] As described in section 1.2.3, reactive uptake into liquid droplets can also occur with gas phase amines and it can thus be inferred that aminium salts will enhance the CCN activity of organic acids thereby contributing to haze, fog, and cloud droplet formation. Amine salts are also hypothesized to have contributed to significant hygroscopic growth observed in a plume from an animal husbandry area in California.[32]

It is also known that amines currently used in CO_2 capture lower the surface tension of water droplets.[36-38] By lowering the surface tension, the activation barrier for the growth of small droplets into cloud droplets is lowered.[39] Surface-active compounds may have a significant potential to increase cloud droplet number concentration and thus radiative forcing of clouds.[40-41] Based on a simple implementation of Köhler theory and a simplified parameterization of the surface tension of droplets containing amines, Karl[42] suggested that the concentration of dissolved amine will determine the number of small water droplets that become activated into CCN. For a given population of accumulation mode particles and a gas phase concentration of 0.1 ppbV 2-aminoethanol (MEA), the size threshold for the activation (activation diameter) was calculated to be 0.2 μm (at a supersaturation of 0.1 %). The activation diameter was reduced to 0.14 μm when the MEA gas phase concentration was increased to 1 ppbv, and at the same time, the number concentration of CCN increased from 600 cm^{-3} to 1380 cm^{-3}.

Amino acids are molecules containing an amine group, a carboxylic acid group and a side chain that varies between different amino acids. Amino acids are thus a chemically similar class to amines. A recent laboratory study indicates that amino acids are effectively activated into cloud condensation nuclei when present as single-compound particles and also in mixed particles with ammonium sulphate.[43] In general, amino acids can be considered to be good CCN.

Once present in clouds, methylamine (MMA) may react with aqueous glyoxal to form high molecular mass oligomers along with smaller amounts of 1,3-dimethylimidazole and light-absorbing compounds.[44] The involved aqueous phase reactions are 1st order in each reactant: rate-limiting imine formation (= first reaction step) is followed by rapid dimer and oligomer formation, glyoxal irreversibly traps volatile amine compounds in the aerosol phase, converting them into oligomers, which - after evaporation of the cloud - contributes to secondary organic aerosol production.

1.3 Atmospheric Environments

Scientific interests into the biogeochemical cycle of nitrogen led to the recognition that organic nitrogen in the form of amino acids and amines play an important role in aquatic nitrogen cycling. During the seventies and eighties amine emissions have been studied, mostly in regions of strong sources like livestock-farming and waste treatment facilities, because of the potential carcinogenicity of their reaction products, in particular of the nitrosamines. Among various speculative pathways for atmospheric degradation of methylamines it was postulated that nitrous oxide (N_2O) can form in substantial amounts.[1] Nitrous oxide is the main naturally occurring regulator of stratospheric ozone. Nitrous oxide is also a major greenhouse gas which contributes to global warming.

Over the last decade, growing interest about the role of amino acids, amines, and proteinaceous material in aerosols triggered laboratory and field research on particulate organic nitrogen with the aim to establish a link between biogenic emissions and climate and to better understand the role of these aerosols in climate change.

1.3.1 Urban Environments and Agriculture

Tan *et al*.[12] have found in one episodic wintertime event of elevated PM2.5 in an urban environment that organic amines were evident in the particles. In urban areas sources of gas-phase amines could derive from municipal wastewater treatment [45] or from agriculture.[18] It was also suggest that vehicle emissions contribute to amines in urban air,[2] however emission rates of aliphatic amines from catalyst-equipped cars have found to be low.[46] During a wintertime episode, hydrocarbon type particles from traffic emission were transformed into amine-type particles, suggesting that particulate amines were formed through gas-to-particle partitioning of gas-phase amines onto the surface of existing particles.[12] Indications of salt formation with nitric acid and sulfuric acid on the particles were also found by Tan *et al*.[12] A study of organic aerosol conducted 2005 in California by Pratt and Prather [13] revealed that the contribution of secondary species to aged organic particles was more than 50 %. Among the secondary aerosol species were ammonium sulfate, ammonium nitrate, and amines. For aged organic aerosol, about 10 % of the particulate nitrate was found to be in the form of non-volatile aminium nitrate salts.[31] Combined field measurements and lab experiments have shown that amine compounds can be a significant portion of aerosol mass especially during the night-time.[9]

Agricultural regions are an important source of amines to the atmosphere. Though amine emission rates from animal husbandry sources are typically two to three orders of magnitude lower than those of ammonia,[1] particulate amines significantly contribute to particle matter mass in plumes from animal husbandry (feedlot) sources in which particulate amine concentrations are estimated to be at least 14–23 % of that of particulate ammonium.[32]

1.3.2 Forests

The amines are known to be end products of the microbial turnover of proteinaceous labile organic matter (e.g. humic substances), for instance released during the decomposition of litter on the forest ground. Mäkelä et al.[16] found the presence of dimethyl aminium (DMA$^+$) during particle bursts (nucleation events) in sub-30 nanometer particles collected at a boreal forest site (Hyytiälä, southern Finland). Other methylamines (such as monomethylamine and trimethylamine) were not identified in the samples. The measurements by Mäkelä et al.[16] showed that DMA$^+$ is present during and/or shortly after the particle formation events occurred, while it was almost absent during the times when no event occurred. In the non-event aerosol, particulate dimethylamine concentrations were less by a factor of about 50. Measurements of DMA$^+$ were correlated with sulfate concentrations in particles and thus salt formation of dimethyl aminium sulfate and/or dimethyl aminium bisulfate was suggested to be involved in nucleation of fresh particles. Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) measurements of positive and negative ion mass spectra obtained from nanoparticles collected during new particle formation event on April 9, 2007, in Hyytiälä, show the presence of protonated MMA, with minor peaks associated with protonated DMA and TMA.[20] Formation of organic aminium salts is suggested to explain a significant amount (23 %) of the observed growth of nanoparticles during new particle event in boreal forests.[20]

1.3.3 Marine Environments

Aliphatic amines represent a class of organic nitrogen compounds that play important roles in some aspects of aquatic nitrogen cycling. They appear to be ubiquitous in marine organisms, where many are used in osmoregulation. Methylamines may be produced by phytoplankton via enzymatic breakdown of intracellular quaternary amine osmotic effectors such as choline and glycine betaine.[47] Yang et al.[48] observed several aliphatic amines in coastal and estuarine seawater and sediment pore waters, including n-propylamine, isopropylamine, diethylamine, n-butylamine and pyridine. Due to their volatility, methylamines are capable of transfer across the air-sea interface and consequently a certain fraction of dissolved amines in surface water will escape to the atmosphere. The methylamines MMA, DMA, and TMA were found in clean air of remote coastal areas.[49] Of the three methylamines (MMA, DMA, and TMA), DMA has been found to in highest atmospheric concentrations in the remote marine atmosphere,[49] which contradicts with the fact that it is the least volatile methylamine. Subsequent reaction with sulfuric acid or strong organic acids may lead to the formation of aminium salts that contribute significantly to the mass of submicrometre marine aerosols.[6, 50-51, 14] Relevant concentrations of dimethyl- and diethyl aminium salts (DMA$^+$ and DEYA$^+$) were measured in submicrometre marine aerosol collected over the North Atlantic during periods of enhanced biological activity (plankton blooms) and aminium salts have been found to be a dominant part of the water-soluble organic nitrogen in these particles.[6] Dialkylamines are stronger bases than mono- and trialkylamines, thus salt

formation is more favoured. In photo-oxidation experiments on the reaction of nitric acid with amines it was shown that among primary, secondary, and tertiary methyl and ethyl amines, only diethyl aminium nitrate significantly accumulated in the particle phase.[8] Thus the selective enrichment of dialkyl aminium in marine aerosols [6, 51] compared to mono- and trialkyl aminium is in agreement with thermodynamic predictions.

Methylamines may be removed from the marine atmosphere by other chemical and biological degradation mechanism and by wet and dry deposition. Hence long range atmospheric transport of amines as suggested by Gorzelska and Galloway [50] is indeed questionable. High amine concentrations in the aerosol phase are found during phytoplankton blooms which supports the marine biological origin of amines over oceans.[6, 34, 51] Gibb *et al.*[14] investigated the nitrogen cycles of ammonia and methylamines over the Arabian Sea and suggested that only a small fraction of the marine produced amines end up in the particle phase as large fractions of amines are photo-oxidized or washed out by rain. Salt formation of gaseous amines with sulfuric acid seems to be the predominant gas-to-particle conversion process for amines in marine environments.[51] Amine salts (aminium sulfate, aminium bisulfate, etc.) have sufficiently low vapor pressures to partition to the aerosol phase; moreover, they exhibit greater water-solubility as compared to other particulate organic nitrogen species.[15]

1.4   Toxicity

A developing area of interest regarding the relationship between the adverse health effects associated with particles suspended in the troposphere is an understanding of how particle chemical composition influences different biological effects in organisms. Although several long-year epidemiological studies consistently demonstrated associations of ambient particulate matter (PM) with mortality and morbidity, particularly with chronic respiratory and cardiovascular diseases,[52-53] the health effects of secondary organic aerosols are still poorly characterized. Although health effects have been related to mass concentrations, it is likely that both particle size and composition affect particle toxicity.[54]

Identification of the toxic constituents of PM responsible for the particle-related adverse health effects has become an area of active investigation. Epidemological evidence and laboratory studies have indicated that organic carbon may be associated with the effect of PM on mortality.[55] However, a number of studies have found no pronounced relation of inflammatory responses with SOA.[56-57] A limited number of experimental studies has suggested that combined exposure to solid particles or liquid aerosols and reactive gases such as O_3, SO_2, HNO_3, or various aldehydes can cause increased airway effects as compared to the effects of the individual gaseous substances.[58-62]

Several toxicology studies have demonstrated that particulate organic nitroso-containing compounds can be associated with adverse health effects. Hamoir et al.[63] studied the effect of positively charged amine-modified, and negatively

charged carboxylate-modified ultrafine polystyrene particles on microvascular permeability in rabbit lungs. The results showed higher effect of the positively charged ultrafine particles, hence suggesting a role of chemical composition and surface reactivity. However, current knowledge on toxicity of particles from amine oxidation is scarce. There are indications that nitroso-compounds on particles are semivolatile[64] and therefore nitrosamines, nitrosamides, and nitramines might be transferred from the gas-phase to particles and vice versa.

1.4.1 Toxicity of Particulate Amines

In a study of acute toxicity and primary irritation by Myers and Ballantyne [65] using different classes of amines, larger amounts were applied occluded to skin, resulting in quite severe irritation. In particular, aliphatic amines, cycloamines, phenylamines, cyclic amines, and the unsaturated amine produced moderately severe cutaneous irritation, while less irritation occurred with alkanolamines and amine salts. Little or no irritation to the eyes resulted from ocular installation of the investigated amine salts. Based on LD50 values, saturated short- and long-chain aliphatic amines were of moderate to high toxicity by peroral (rat) and percutaneous (rabbit) routes, while amine salts and sulfatoamines were the least toxic of the studied amine classes.[65] Hussain and Fraizer [66] found an overall low in vitro toxicity of ethanolamine nitrate in primary hepatocytes from rats. On the other hand, Nemmar et al.[67] found that particles coated with amines produced a significant increase in the rate of blood clots when installed in the trachea of hamsters. Treatment of rats with low doses of heterocyclic amine mixtures in food resulted in enhanced hepatocarcinogenesis.[68-69]

High levels of atmospheric contamination due to the re-suspension of pyrite particles from the mining waste slurry were recorded in the Guadiamar valley after the toxic spill of Aznalcóllar, SW Spain. Major high-particulate events occurred during the extraction of the pyrite-rich mud layer, which covered an extensive area of the valley. The highest concentrations of aromatic amines in ambient aerosols were recorded in August 1998 during the pyrite slurry extraction in the proximity of the Aznalcázar sampling site.[70] Although health hazards associated with the presence of these aromatic amines are unknown, the acute toxicity of the collected particles exceeded that of urban aerosols.[70]

1.4.2 Toxicity of Secondary Oxidation Products

Among the secondary oxidation products from amines, several potentially toxic groups of compounds can be found in the particulate phase, e. g. amides,[71] imines, and N-nitroso compounds. The formation of potentially toxic imines from the reaction of particles containing a primary amine with atmospheric gas-phase aldehydes has been reported.[29, 27] Carcinogenic N-nitroso products derive from many different amino compounds, including most secondary and tertiary amines, but also secondary and tertiary amides, N-substituted ureas, guanidines, and urethanes. The most common N-nitroso compounds such as N-nitroso dimethylamine (NDMA) are derived from either secondary amines or their N-

acylated analogues. A report from US EPA[72] suggests that significant formation of nitrosamines on particles could occur in the plume of amine emission sources, containing both mildly acidic aerosol and elevated concentrations of secondary amines. Animal studies have shown that exposure to increased levels of nitrosamines (and even certain nitrogenous precursors) can lead to increased rates of cancer.[73] To my knowledge no adequate human studies on the relationship between NDMA and cancer have been reported.

Aqueous acidic solutions of nitrite salts or nitrous acid at pH<5 are the best known nitrosating media[74-75] The rate of nitrosation of most secondary amines is roughly proportional to the square of nitrite concentration and shows a maximum at pH 3 to 3.4. Assuming optimum pH conditions on the surface of ambient aerosol particles, the rate of nitrosation of dimethylamine in ambient air can be estimated by: [76]

$$RATE(DMA)=[nitrite]^2 \ percent/hour$$

Where [nitrite] is the concentration (molarity) of total nitrite (NO_2^-) on the aerosol surface. The nitrosation potential of amines in the condensed phase can be influenced by the amine basicity, substrate concentration, thiocyanate ion, chloride ion, acetate ion, formaldehyde, pH, and other factors.[72] The formation of nitrosamines from aqueous solutions of nitrite salts and secondary amines may be mediated by bacteria.[77]

Small amounts of nitrosodimethylamine can be formed in the reactions of acidifed nitrite with either quarternary methylammonium salts ($R_3NH^+Y^-$) or trimethylamine-N-oxide under conditions of high reagent concentrations and high temperatures.[78-79] Suprisingly, it was shown that trimethylamine-N-oxide is more reactive than TMA itself.[80] Very little is known about the mechanism of these reactions and they are probably not relevant under atmospheric conditions.

More recently, indications for the formation of nitrosamines as intermediate in the heterogeneous reaction of particle-bound primary aliphatic amines with ozone were found.[28]

In general, nitrosamines are considered to be thermally stable in the condensed phase in alkaline or mildly acidic medium. In prolonged contact with strong acids they decompose by hydrolysis.[72] This has implications for the atmosphere, since strongly acidic aerosol occur only in extremely polluted conditions, e.g. in plumes from power plants. Thus in ambient continental and remote air, particulate nitrosamines can be considered stable towards thermal degradation. N-nitrosamines undergo photochemical decomposition in sunlight limiting their lifetime in the atmosphere. Dialkylnitrosamines are stable towards ultraviolet (UV) irradiation in neutral solution, however in the presence of dilute acid, dialkylnitrosamines undergo various photochemical reactions.[81]

A further indication for the potential stability of N-nitroso compounds in particles is the discovery of these compounds in ambient aerosol particles. Kneip et al.[64] found that the total molar N-nitroso concentrations in New York City air were comparable to the total concentrations of polycyclic aromatic hydrocarbon (PAH)

compounds. It is worth noting, that members of the chemical class of N-nitrosamines range from high vapour pressure liquids to rather non-volatile solids. The potential of N-nitroso compounds to re-evaporate from the particles would increase the possible inhalation exposure and allows for the transportation of these hazardous compounds over longer distances before their release to the gas phase. Measurement of potentially toxicological important N-nitroso and nitrite-containing compounds in both the fine particulate (PM2.5) and gas phases in samples collected in Provo, Utah, indicate that the majority of the N-nitroso and nitrite organic compounds present in fine particulate matter in the studied urban area are semivolatile organic compounds.[82]

Examination of inhalable airborne particulate matter (PM$_{10}$) collected in the working environment of four rubber factories using a high-volume sampler equipped with a cascade impactor revealed trace amounts of genotoxic nitrosamines (N-nitrosodimethylamine: 0.10–0.98 µg/m^3; N-nitrosomorpholine: 0.77–2.40 µg/m^3) and PAH were present in air samples.[83] Some extracts from the collected filter samples, particularly those obtained from the finest fractions (<0.5 µm), were mutagenic with the Ames test and genotoxic with the Comet assay.[83]

The particulate matter of the tobacco smoke elicits benign and malignant tumors on the skin of mice and rabbits, sarcoma in the connective tissue of rats, and carcinoma in the lungs of rats upon intratracheal instillation.[84] The particular phase of tobacco smoke contains at least 3,500 chemical compounds and a high proportion of them are toxic, carcinogens or mutagens.[85] There are at least 50 carcinogens in cigarette smoke that have been evaluated by the International Agency for Research on Cancer (IARC) to be carcinogenic.[86, 84] Among the multiple carcinogenic compounds, tobacco-specific N-nitrosamines (TSNA) have been shown to be of special significance. TSNA are found only in tobacco products, and are highly carcinogenic. They form in the nitrosation of tobacco alkaloids (*Nicotiana* alkaloids), e.g. nicotine, nornicotine, anabasine, and anatabine. These carcinogenics are present in tobacco, tobacco smoke, and environmental tobaccos smoke. TSNA are created during fermentation, curing, ageing, and burning of the tobacco leaf. In addition, smokeless tobacco contains N-nitrosodiethanolamine (NDELA), which is formed from diethanolamine, a contamination product in tobacco.[87]

1.5   Summary

Amine compounds can constitute a siginificant fraction of submicron ambient aerosols, in particular in urban air and close to agricultural sources. It is evident from both field experiments and computational studies that amines have the propensity to contribute to new particle formation. The tendency of amines to form particulate salts with nitric acid and sulphuric acid has a stabilizing effect on small nucleated clusters and thus enables their further growth. Organic salt formation potentially also enhances the hygroscopic growth of aerosol particles and facilitates their activation into cloud droplets. Contrary to primary and secondary amine, tertiary amines form significant amounts of SOA. The discovery

of trialkylamine-N-oxides in aerosols provided first evidence that gas phase oxidation products of alkylamines can partition to the condensed phase of aerosol particles. Significant SOA formation was observed in the oxidation of alkylamines with the nitrate radical rendering amines a potential important nighttime source of SOA. Particulate amines may undergo several steps of oxidation and accretion reactions. Particulate phase oxidation of amines may lead to the formation of potentially toxic products such as imines and nitrosamines. While particulate aminium salts commonly show low or no toxicity, the formation of N-nitroso compounds in the condensed phase increases the toxicity of particles and is associated with carcinogenesis. Due to their semivolatile nature, N-nitroso compounds could evaporate from the particles and thus increase the inhalation exposure to these carcinogenic substances. In general, there is a lack of information about the acute and chronic toxic effects of particulate amides and imines, and also the chemical mechanisms leading to their presence in aerosol particles are currently not fully understood.

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Norwegian Institute for Air Research
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Gassnova SF
Dokkvegen 19
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ABSTRACT
This report presents a comprehensive review of current literature on the abundance of amines in atmospheric aerosols. The review spans over the whole life cycle of aerosols, showing the relevance of amine-related aerosol dynamic processes in each stage of the cycle. Amine compounds can constitute a siginificant fraction of submicron ambient aerosols, in particular in urban air and close to agricultural sources. It is evident from both field experiments and computational studies that amines have the propensity to contribute to new particle formation. Particulate phase oxidation of amines leads to the formation of potentially toxic products such as imines and nitrosamines. In general, there is a lack of information about the acute and chronic toxic effects of particulate amides and imines, and also the chemical mechanisms leading to their formation in aerosol particles are currently not fully understood.

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ABSTRACT (in Norwegian)
Denne rapporten presenterer en omfattende gjennomgang av aktuell litteratur om betydning av aminer i atmosfæriske aerosoler. Gjennomgangen spenner over hele livsløpet av aerosoler, viser relevansen av amin-relaterte partikkel prosesser i hvert stadium av syklusen. Amine forbindelser kan utgjøre en ganske stor del i submicron parten av aerosoler, særlig i urbane luft og nær landbruket kilder. Det fremgår av både feltforsøk og beregningsorientert studier som aminer har tilbøyelighet til å bidra til ny partikkel formasjon. Oksidasjon av aminer i partikler fører til dannelse av potensielt giftige produkter, for eksempel imines og nitrosaminer. Generelt mangler informasjon om akutte og kroniske toksiske effekter av amides og imines i partikler, og kjemiske mekanismer som fører til dannelsen i aerosol partikkler er ikke kjent god nok.

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