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Research Paper

Atmospheric Aerosols: From Chemistry to Climate Change

Dr. Kiran
Associate Professor
PG Department of Chemistry, Mata Gujri College
Sri Fatehgarh Sahib

Abstract
Atmospheric aerosols, suspensions of solid or liquid particles in air, play vital roles in atmospheric chemistry, environmental health, and the global climate system. They originate from both natural and anthropogenic sources, ranging from desert dust and sea salt to combustion-derived soot and secondary organic aerosols. Aerosols influence Earth's radiative balance through scattering and absorption of solar radiation (direct effect) and by modifying cloud properties (indirect effect)[1] . They also affect human health, ecosystems, and biogeochemical cycles[2,3] . Recent advances in measurement techniques, chemical modeling, and remote sensing have significantly improved our understanding of aerosol sources, transformations, and impacts. However, large uncertainties remain regarding aerosol–cloud interactions, organic aerosol formation, and future trends under changing emissions and climate[4] . This review synthesizes current knowledge on aerosol chemistry, environmental and climatic roles, and emerging research directions critical for improved effective mitigation strategies.

I. Introduction

Aerosols are minute particles ranging from nanometers to tens of micrometers that are suspended in the Earth's atmosphere. Despite their small size, they exert profound effects on air quality, human health, and the Earth's energy budget[5]. The global burden of aerosols is influenced by both natural sources—such as dust storms, volcanic eruptions, sea spray, and biogenic emissions—and anthropogenic activities including industrial combustion, vehicular exhaust, biomass burning, and agriculture [6.]

In atmospheric chemistry, aerosols act as active participants rather than passive byproducts. They influence heterogeneous reactions, trace gas lifetimes, and the oxidizing capacity of the atmosphere[2]. Climatically, their impact depends on composition: sulfate aerosols generally cool the atmosphere through light scattering, while black carbon warms it by absorbing solar radiation[7].

Importantly, the relationship between aerosols, climate change, and public health is intricate. Measures to reduce aerosols for health reasons may unintentionally exacerbate global warming if cooling particles like sulfates are reduced[1].

1. Classification and sources of aerosols

1.1 Natural and anthropogenic sources[8-12]

Natural sources include:

- Mineral dust from arid regions[13]
- Sea salt from ocean wave action[5]
- Volcanic aerosols, rich in SO_2 and ash[14]
- Biogenic aerosols such as pollen and oxidized VOCs[2]
- Wildfire smoke, from both natural causes and human ignition[6]

Anthropogenic sources include:

- Fossil fuel combustion, releasing black carbon, organic carbon, and SO_2[15]
- Biomass burning for cooking or land clearing
- Industrial emissions from processes like metal smelting[16]
- Secondary aerosols formed via oxidation of gaseous precursors (e.g., SO_2, NO_x, NH_3, VOCs) [5]

1.2 Primary vs secondary aerosols[17-21]

- Primary aerosols are emitted directly (e.g., soot, dust, sea salt).

- Secondary aerosols form in the atmosphere via gas-to-particle conversion, such as SOA and inorganic salts like ammonium nitrate and sulfate [2]

II. Chemical composition and atmospheric transformations[22-26]

2.1 Major chemical constituents[27-35]

- Sulfate (SO_4^{2-}): Formed from SO_2 oxidation in both gas and aqueous phases[5] . These are strong light scatterers, contributing to cooling[36]

Gas-phase oxidation:
$SO_2 + OH \rightarrow HOSO_2$
$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4$ (sulphuric acid)
The sulphuric acid then nucleates or condenses to form sulfate aerosols.
Aqueous-phase oxidation[37-40]:
In cloud or fog droplets:
SO_2 (dissolved) + $H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons HSO_3^- + SO_3^{2-}$
Oxidation via:
$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H_2O$
$HSO_3^- + O_3 \rightarrow SO_4^{2-} + O_2$
Metal-catalyzed (e.g., Fe^{3+}, Mn^{2+}) reactions
Effect: Sulfate aerosols scatter sunlight, causing cooling.

- Nitrate (NO_3^-): Formed mainly at night from NO_x and ozone reactions, followed by hydrolysis[41]. Semi-volatile and temperature-sensitive.

Gas-phase nighttime reaction:
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_3 + NO_2 \rightleftharpoons N_2O_5$
$N_2O_5 + H_2O$ (on aerosol surface) $\rightarrow 2\ HNO_3$
$HNO_3 + NH_3 \rightarrow NH_4NO_3$ (ammonium nitrate aerosol)
Property: Semi-volatile, especially sensitive to temperature and humidity; tends to dominate in cold seasons.
Through oxidation of nitrogen dioxide (NO_2), then neutralization by ammonia (NH_3).

- Ammonium (NH_4^+): Neutralizes sulfate and nitrate to form salts like $(NH_4)_2SO_4$ and NH_4NO_3[2].

$NH_3 + HNO_3 \rightarrow NH_4NO_3$
$2\ NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
These salts are major components of fine particulate matter ($PM_{2.5}$).

- Organic aerosols[42-55]: Include primary (POA) and secondary (SOA). SOA are formed via VOC oxidation[15] . Their radiative effects depend on chemical makeup.

Primary organic aerosols:: Directly emitted (e.g., biomass burning, vehicles).
Secondary organic aerosols : Formed via atmospheric oxidation of volatile organic compounds.
Secondary organic aerosols formation
Isoprene (C_5H_8) + OH / O_3 / NO_3 → Oxidized products → Condensation → SOA
Effect: Can scatter or absorb light depending on composition; act as cloud condensation nuclei.

- Black carbon (BC)[56-58]: Formed by incomplete combustion, strongly absorbs radiation, and contributes to atmospheric warming and glacial melting[59].

Chemical nature: Pure carbon is physically and optically important.
Reaction (formation via combustion):
$C_xH_\gamma + O_2 \rightarrow CO_2 + H_2O$ + BC (soot) (under limited O_2)
Effect: Strongly absorbs solar radiation → warming, and reduces snow when deposited on ice/snow.

- Mineral dust and sea salt: Act as CCN and participate in heterogeneous chemistry[60]

Mineral dust (from soil):
Composed mainly of silicates (e.g., SiO_2), iron oxides, calcium carbonate ($CaCO_3$).
Can participate in heterogeneous reactions, e.g.:
$CaCO_3 + 2\ HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$
Sea salt (from ocean spray):
Mainly NaCl, Mg^{2+}, Ca^{2+}, SO_4^{2-}, etc.
Reaction example:
$NaCl + HNO_3 \rightarrow NaNO_3 + HCl$

2.2 Transformation processes

- Gas-phase oxidation of VOCs leads to SOA via multi-step reactions involving radicals like OH and $RO_2^\cdot$[9]

Step 1: Volatile organic compound emission

Volatile organic compound such as isoprene (C_5H_8), terpenes (e.g., α-pinene, $C_{10}H_{16}$), and aromatic compounds (e.g., toluene) are emitted from vegetation, fossil fuel combustion, and industrial sources.

α-pinene oxidation by OH

Step 1: Initial attack by OH radical

$C_{10}H_{16}$ (α-pinene) + OH → $C_{10}H_{15}O^{\bullet}$

Step 2: Reaction with O_2

$C_{10}H_{15}O^{\bullet} + O_2 \rightarrow C_{10}H_{15}O_2^{\bullet}$(organic peroxy radical)

Step 3: Reaction with NO or HO_2

With NO (in polluted air):

$C_{10}H_{15}O_2^{\bullet} + NO \rightarrow C_{10}H_{15}O + NO_2$

With HO_2 (in cleaner air):

$C_{10}H_{15}O_2^{\bullet} + HO_2 \rightarrow C_{10}H_{15}OOH + O_2$

Step 4: Formation of low-volatility compounds

These products (like organic hydroperoxides, aldehydes, ketones) condense into aerosol particles:

Low-volatility organics → Condensation/Nucleation →Secondary organic aerosol

Simplified General Pathway:

Volatile organic compound + $OH/O_3/NO_3 \rightarrow RO_2\bullet \rightarrow RO\bullet \rightarrow$ R(=O), R–OH, ROOH → Secondary organic aerosol

Where: $RO_2^{\bullet}$ = Organic peroxy radical

$RO^{\bullet}$ = Alkoxy radical

- Aqueous-phase oxidation of SO_2 forms sulfate in cloud droplets, contributing to acid rain[61-66]

Step-by-step chemical pathway

1. Dissolution of SO_2 in water:

Sulfur dioxide dissolves in water droplets:

$SO_2 (g) \rightleftharpoons SO_2 \cdot H_2O (aq)$

2. Formation o sulfurous acid and its ions:

$SO_2 \cdot H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-}$

So, in aqueous solution, SO_2 exists mainly as bisulfite (HSO_3^-) and sulfite (SO_3^{2-}) ions.

3. Oxidation reactions in aqueous phase[67-77]

These species are then oxidized to sulfate (SO_4^{2-}) by various oxidants present in the cloud water:

Oxidation by hydrogen peroxide (H_2O_2):

This is often the dominant pathway in clouds:

$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O$

Oxidation by ozone (O_3):

More effective at higher pH:

$HSO_3^- + O_3 \rightarrow SO_4^{2-} + O_2 + H^+$

Metal-catalyzed oxidation (e.g., Fe^{3+}, Mn^{2+}):

Common in polluted or mineral-rich clouds:

$HSO_3^- + \frac{1}{2}O_2 \rightarrow SO_4^{2-}$ (catalyzed by Fe^{3+}/Mn^{2+})

Formation of acid rain

Once sulfate (SO_4^{2-}) forms in the droplet, it combines with H^+ to form sulfuric acid:

$SO_4^{2-} + 2 H^+ \rightarrow H_2SO_4$

When these acidified droplets precipitate as rain, they contribute to acid rain, lowering the pH of surface waters and soils.

- Heterogeneous reactions such as N_2O_5 hydrolysis on aerosol surfaces form nitric acid, further contributing to nitrate aerosols and acid deposition[2] .

At night, nitrogen dioxide (NO_2) and ozone (O_3) react to form NO_3 radicals and dinitrogen pentoxide (N_2O_5):

1. Formation of NO_3 and N_2O_5 (gas-phase):

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_3 + NO_2 \rightleftharpoons N_2O_5$ (reversible)

N_2O_5 is relatively stable at night and can be taken up by aerosol surfaces or mineral dust.

2. Heterogeneous hydrolysis of N_2O_5 (on aqueous or solid aerosol surface):

This reaction occurs on the surface of aerosols (e.g., sulfate aerosols, dust, sea salt):

N_2O_5 (g) + H_2O (surface) → 2 HNO_3 (g or aq)

or, dissociatively:

$N_2O_5 + H_2O \rightarrow 2 NO_3^- + 2 H^+$

So this forms: Nitric acid (HNO_3) either in gas phase or dissolved in droplets of nitrate ion (NO_3^-) and protons (H^+), leading to acid rain.

3. Contribution to acid rain:

Once nitric acid is formed, it can be scavenged by cloud droplets and precipitate as acid rain:
$HNO_3 (aq) \rightleftharpoons H^+ + NO_3^-$
When this acidic water reaches the ground, it contributes to acid deposition, affecting soils, vegetation, and aquatic ecosystems.

III. Role in atmospheric chemistry

Aerosols influence the atmospheric oxidizing capacity by altering levels of radicals like $\cdot OH$ and NO_3. For example:

- N_2O_5 hydrolysis removes NO_x, reducing ozone formation[61].
- Polar stratospheric clouds containing aerosols facilitate $ClONO_2$ hydrolysis, releasing Cl radicals that destroy ozone [1].
- Aerosol-phase chemistry regulates methane lifetimes and affects the oxidation of CO and VOCs[78] .

IV. Aerosols and climate: Direct and indirect effects[79]

4.1 Direct radiative effects[80-86]

- Scattering aerosols (sulfate, nitrate, sea salt) cool the planet by reflecting sunlight.
- Absorbing aerosols (black carbon, dust) warm the atmosphere and contribute to "solar dimming" at the surface[1,13 ,].

4.2 Indirect effects[106]

- First indirect effect: Increased aerosol concentrations lead to smaller cloud droplets, increasing cloud albedo (Twomey effect).
- Second indirect effect: Smaller droplets reduce precipitation efficiency, increasing cloud lifetime and enhancing cooling[107].

4.3 Semi-direct effects[87-96]

- Heating by black carbon can evaporate clouds, potentially reducing cloud cover and amplifying warming [103].

V. Health and environmental impacts

Fine particles ($PM_{2.5}$) can penetrate deep into the lungs and bloodstream, leading to diseases such as asthma, cardiovascular illness, and premature mortality[55]. Toxic effects depend on chemical composition—transition metals, black carbon, and organics being particularly harmful.

Environmentally, aerosols:

- Reduce visibility and create haze
- Deposit nutrients like iron and nitrogen into oceans [60]
- Acidify soils and waters via deposition of sulfate and nitrate[1]
- Influence rainfall and water cycles by modifying CCN concentrations[5]

VI. Mitigation and policy implications

Reducing aerosols has dual implications:

- Reducing black carbon benefits both health and climate[59]
- Reducing sulfate may unmask hidden warming, since it currently off sets some greenhouse gas-induced warming[1]
- Integrated policies are essential—e.g., methane reduction helps lower ozone and SOA levels[61]

VII. Future research directions

Key research needs include:

1. Improved molecular understanding of aerosol acidity and volatility[15]
2. Quantification of oxidation pathways for SO_2 and NO_3[16]
3. Advanced cloud-aerosol interaction[97-100] models
4. Enhanced observations in under-sampled regions where aerosol forcing is strongest.[60]
5. New monitoring technologies like drones and real-time sensors[78]

VIII. Conclusion

Aerosols are one of the most complex and important parts of Earth's atmosphere[101-105]. They come from many different sources and go through various chemical changes, interacting across local to global scales. These particles play a key role in environmental chemistry and climate systems. Scientists have made significant progress in understanding how aerosols form, what they are made of, and how they affect the climate and air quality. However, many uncertainties remain especially in how aerosols interact with clouds and in the detailed chemistry of organic aerosols.

Future research must prioritize the integration of in situ field measurements, controlled laboratory studies, mechanistic chemical modeling approaches to constrain aerosol processes across scales. Given the central role of aerosols at the interface of air quality and climate change, a deeper understanding of their physicochemical behavior is not only a scientific imperative but also essential for informing policy on sustainable development, climate mitigation, and public health protection.

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