Atmospheric Aerosols

Lecture 8

Sahraei

Physics Department

Razi university

https://sci.razi.ac.ir/~sahraei

AEROSOL CHEMICAL COMPOSITION

Atmospheric aerosol particles contain sulfates, nitrates, ammonium, organic material, crustal species, sea salt, metal oxides, hydrogen ions, and water.

From these species sulfate, ammonium, organic and elemental carbon, and certain transition metals are found predominantly in the fine particles.

Crustal materials, including silicon, calcium, magnesium, aluminum, and iron, and biogenic organic particles (pollen, spores, plant fragments) are usually in the coarse aerosol fraction.

Nitrate can be found in both the fine and coarse modes.

nitric acid/ammonia reaction for the formation of ammonium nitrate, → Fine nitrate

the product of coarse particle/nitric acid reactions. → coarse nitrate

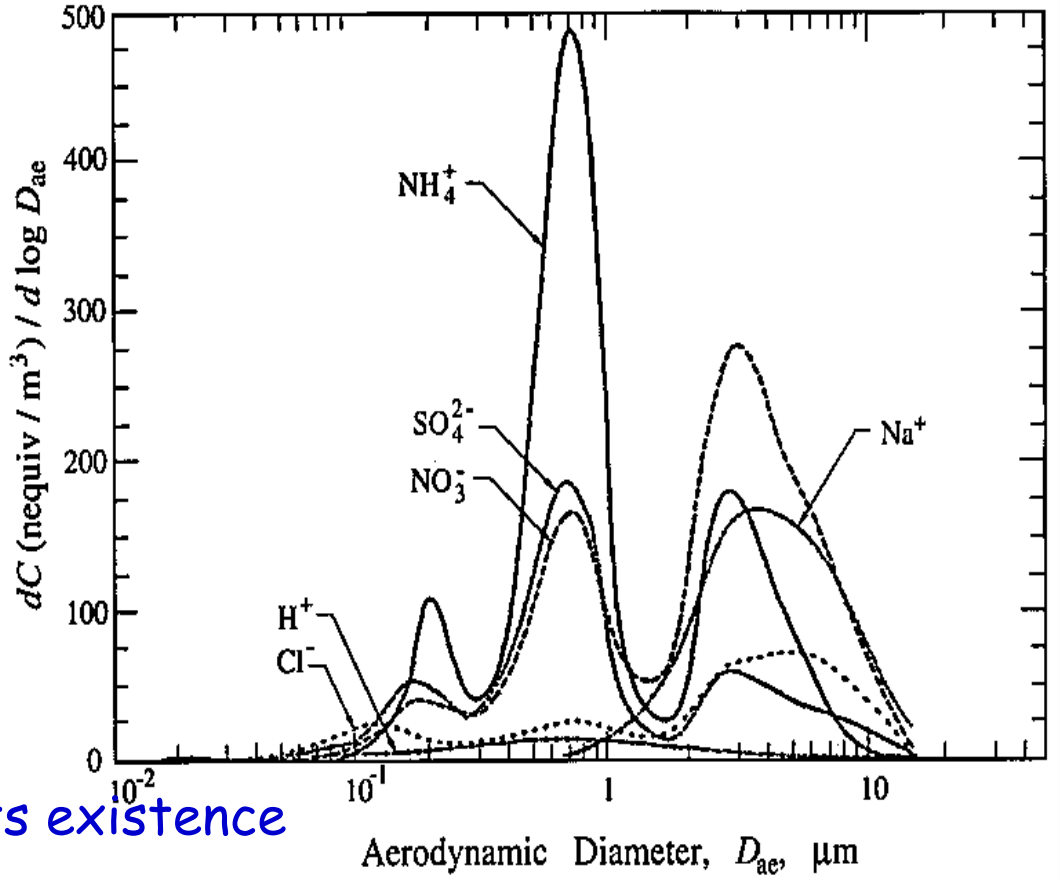
A typical urban aerosol size/composition distribution is shown in this Figure (Wall et al. 1988).

Measured size distributions of aerosol sulfate, nitrate, ammonium, chloride, sodium, and hydrogen ion in Claremont, CA (Wall et al. 1988).

These results indicate that sulfate, nitrate, and ammonium have two modes in the 0.1-1.0 μm size range (the condensation and droplet modes), and a third one over 1 μm (coarse mode).

The condensation mode has a peak around 0.2 μm and is the result of condensation of secondary aerosol components from the gas phase.

The droplet mode peaks around 0.7 μm in diameter and its existence is attributed to heterogeneous



Concentrations (ng m -3) and Size Distribution of Various Elements Found in Atmospheric Particles

Fe_2O_3

Fe_3O_4

Al_2O_3

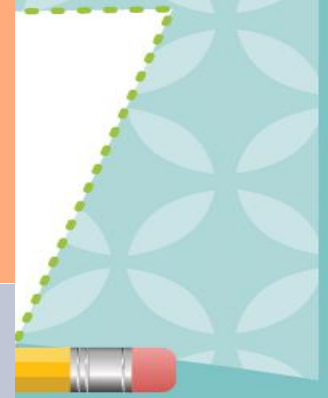
Element	Mode[a]	Concentration (ng m^{-3})		
		Remote	Rural	Urban
Fe	F and C	0.6–4,200	55–14,500	130–13,800
Pb	F	0.01–65	2–1,700	30–90,000
Zn	F	0.03–450	10–400	15–8,000
Cd	F	0.01–1	0.4–1,000	0.2–7,000
As	F	0.01–2	1–28	2–2,500
V	F and C	0.01–15	3–100	1–1,500
Cu	F and C	0.03–15	3–300	3–5,000
Mn	F and C	0.01–15	4–100	4–500
Hg	—	0.01–1	0.05–160	1–500
Ni	F and C	0.01–60	1–80	1–300
Sb	F	0–1	0.5–7	0.5–150
Cr	F and C	0.01–10	1–50	2–150
Co	F and C	0–1	0.1–10	0.2–100
Se	F and C	0.01–0.2	0.01–30	0.2–30

[a]F = fine mode; C = coarse mode.

Source: Schroeder et al. (1987).

Comparison of Ambient Fine and Coarse Particles

	Fine Particles	Coarse Particles
Formation pathways	Chemical reactions Nucleation Condensation Coagulation Cloud/fog processing	Mechanical disruption Suspension of dusts
Composition	Sulfate Nitrate Ammonium Hydrogen ion Elemental carbon (EC) Organic compounds Water Metals (Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc.)	Resuspended dust Coal and oil fly ash Crustal element (Si, Al, Ti, Fe) oxides $CaCO_3$, NaCl Pollen, mold, spores Plant, animal debris Tire wear debris
Solubility	Largely soluble, hygroscopic	Largely insoluble and non-hygroscopic
Sources	Combustion (coal, oil, gasoline, diesel, wood) Gas-to-particle conversion of NO_x, SO_3, and VOCs Smelters, mills, etc.	Resuspension of industrial dust and soil Suspension of soil (farming, mining, unpaved roads) Biological sources Construction/demolition Ocean spray
Atmospheric lifetime	Days to weeks	Minutes to days
Travel distance	100s to 1000s of km	< to 10s of km



Composition of Sea-salt

Species	Percent by Weight
Cl	55.04
Na	30.61
SO_4^{2-}	7.68
Mg	3.69
Ca	1.16
K	1.1
Br	0.19
C (noncarbonate)	$3.5 \times 10^{-3} - 8.7 \times 10^{-3}$
Al	$4.6 \times 10^{-4} - 5.5 \times 10^{-3}$
Ba	1.4×10^{-4}
I	1.4×10^{-4}
Si	$1.4 \times 10^{-4} - 9.4 \times 10^{-3}$
NO_3^-	$3 \times 10^{-6} - 2 \times 10^{-3}$
Fe	$5 \times 10^{-5} - 5 \times 10^{-4}$
Zn	$1.4 \times 10^{-5} - 4 \times 10^{-5}$
Pb	$1.2 \times 10^{-5} - 1.4 \times 10^{-5}$
NH_4^+	$1.4 \times 10^{-6} - 1.4 \times 10^{-5}$
Mn	$2.5 \times 10^{-6} - 2.5 \times 10^{-5}$
V	9×10^{-7}

$$H_2SO_4(g) + 2NaCl \rightarrow Na_2SO_4 + 2HCl(g)$$

Reactions on sea-salt particles modify its chemical composition;

for example, sodium chloride reacts with sulfuric acid vapor to produce sodium sulfate and hydrochloric acid vapor leading to an apparent "chloride deficit" in the marine aerosol.

AEROSOL CHEMICAL COMPOSITION

Inorganic species

Primary : Metals, insoluble minerals, ammonium

Secondary : Sulfates and nitrates

Organic species

Primary : Soot (Impure graphite), polar (e.g. alkanoic acids), and non polar organics (PAH, alkanes…)

Secondary : mainly polar organics (multi-functional compounds)

+ Water

ORGANIC ATMOSPHERIC AEROSOLS

Elemental Carbon (EC)

Black carbon or graphitic carbon

Emitted during combustion processes

Organic Carbon (OC)

Primary OC, directly emitted by sources

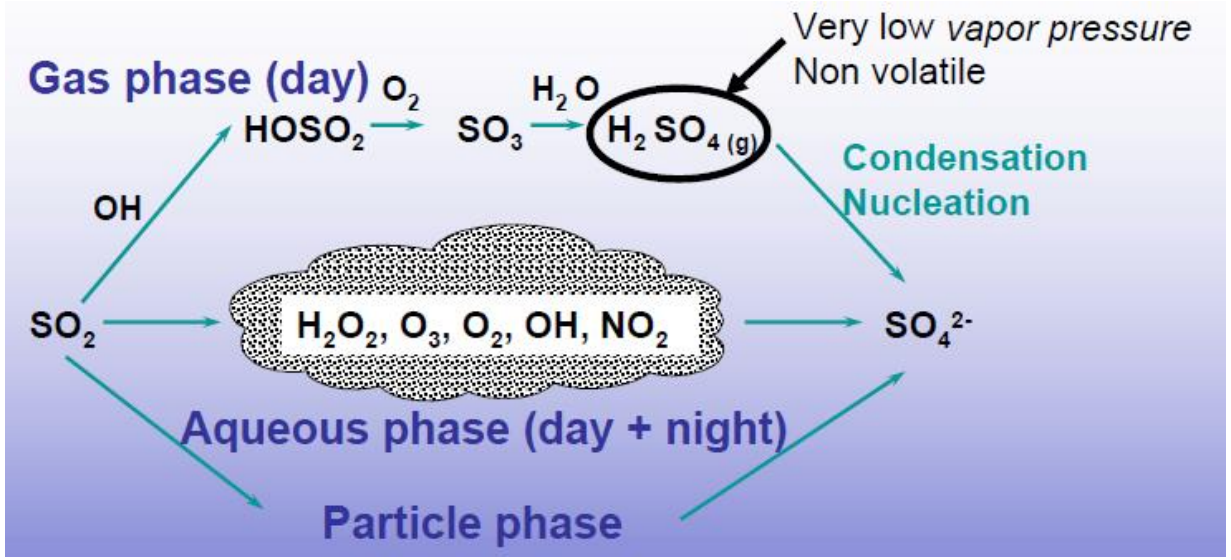
Secondary OC, formed *in-situ* by condensation of low-volatility products of the photo-oxidation of hydrocarbons

ORIGIN OF SULFATES

Oxidation of SO_2

Over continents: SO_2 emissions from man-made activities (fossil fuel combustion) & volcanoes

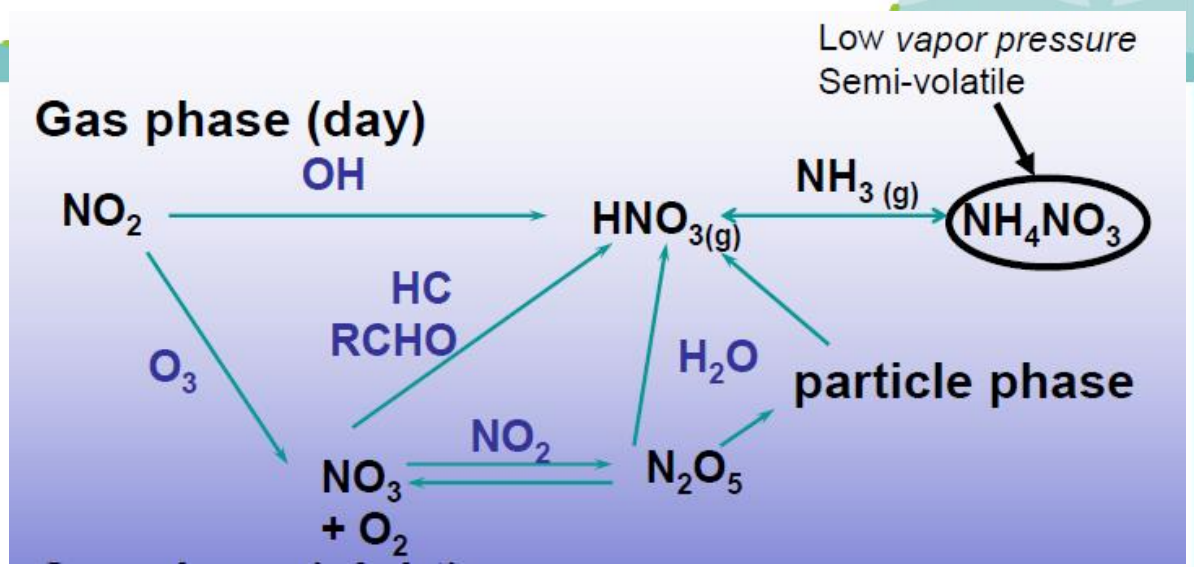
Over oceans: Marine phytoplankton produces dimethyl sulfide (DMS) which oxidises in SO_2



ORIGIN OF NITRATES

Oxidation of NO2

Nitrate ions (I)



Man-made origin: fossil fuel combustion

Natural origin : soil, lighting

Gas phase (night)

NO_2 is converted to HNO_3 mainly in the gas phase

HNO_3 reacts with NH_3 to form ammonium nitrate

Nitrates found in/on both coarse and fine particles:
the origins are not the same. (Fine origin shown above)

Most SO_2 is converted in sulfate either in the gas phase or in the aqueous phase

Both processes produce sulfate aerosol mainly in fine mode (Ø < 2.5 µm)

NITRATE IONS (2)

One origin of nitrate on coarse particles:

$$NaCl\ (s) + HNO_3\ (g) \longrightarrow HCl + NaNO_3\ (s)$$

(This process is important in coastal areas)

AMMONIUM IONS

NH_3 directly emitted in the atmosphere

Man-made origin: sewage, fertilized lands

Natural origin: soil, animals

NH3 reacts with sulfates & nitrates

The preferred form for ammonium in the aerosol phase is ammonium sulfate $(NH_4)_2SO_4$

Each sulfuric acid molecule is looking for two ammonia molecules (neutralization)

If there is not enough ammonia present, sulfuric acid exists either as H_2SO_4 (aq) or NH_4HSO_4

METALS

Man made sources : incorporated in the particle in early stage of particle formation from combustion process

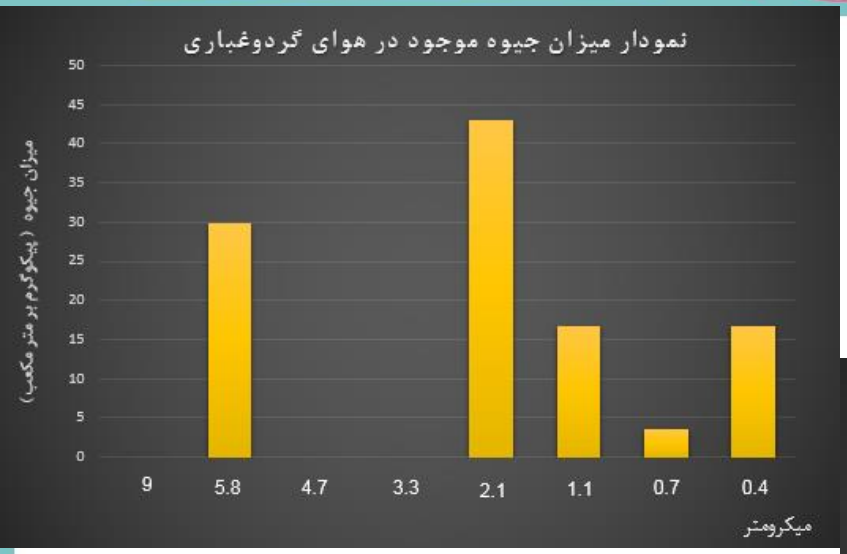
Natural sources: volcanoes + soil erosion

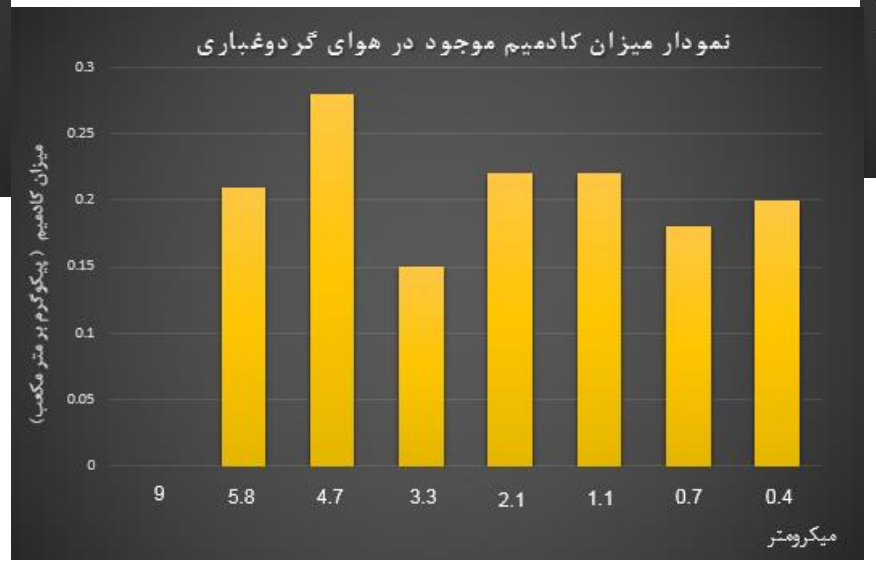
Fine mode : Pb, Zn, Fe, Cd, As…

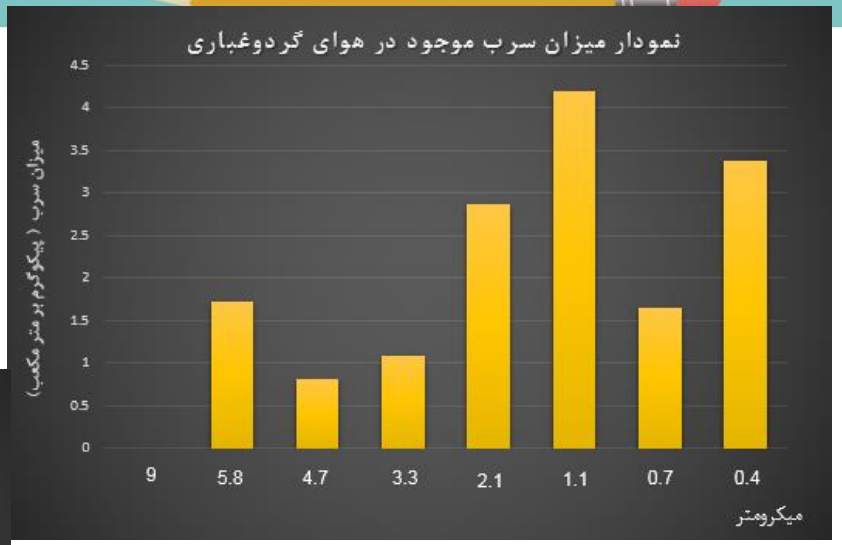
Coarse mode : Ca, Mg, Al, Ti,

Fine & Coarse mode: Na, K, Fe, V, Cr, Co, Ni, Mn, Cu

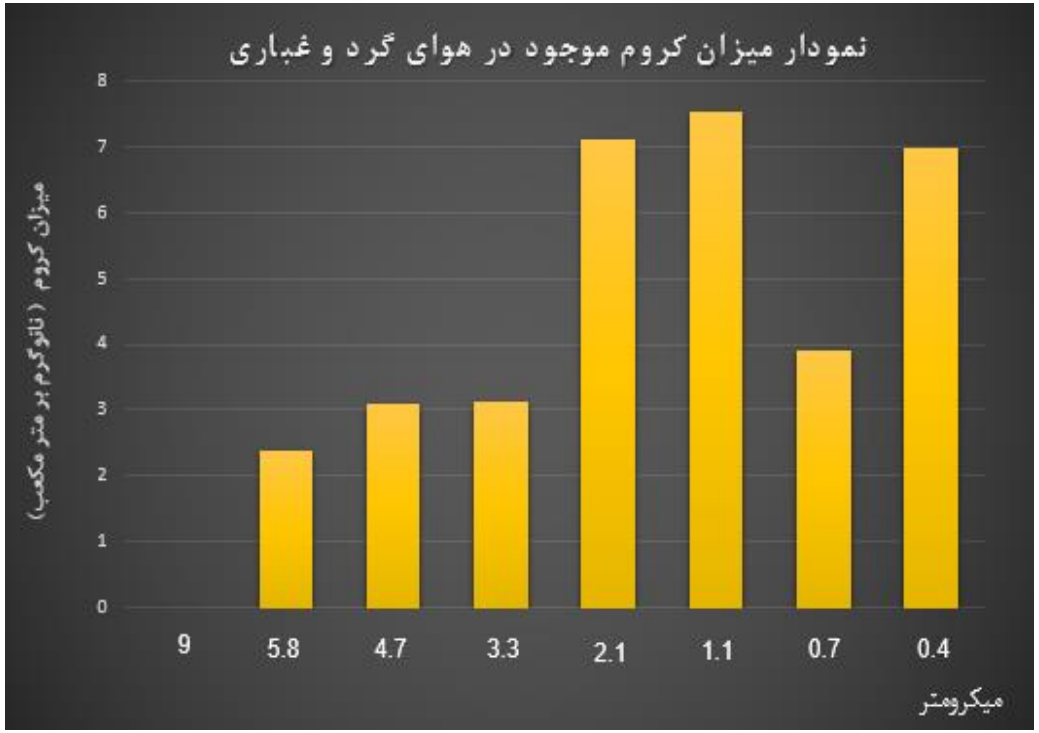
تعیین ترکیبات شیمیایی ذرات گردوغبار

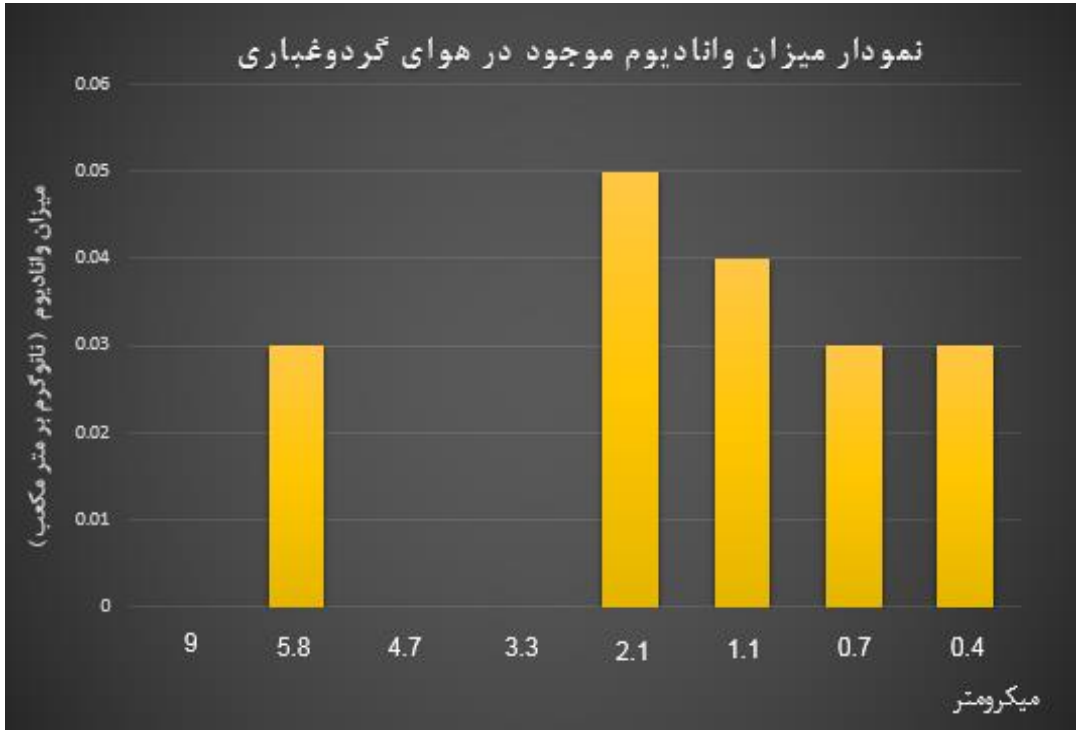




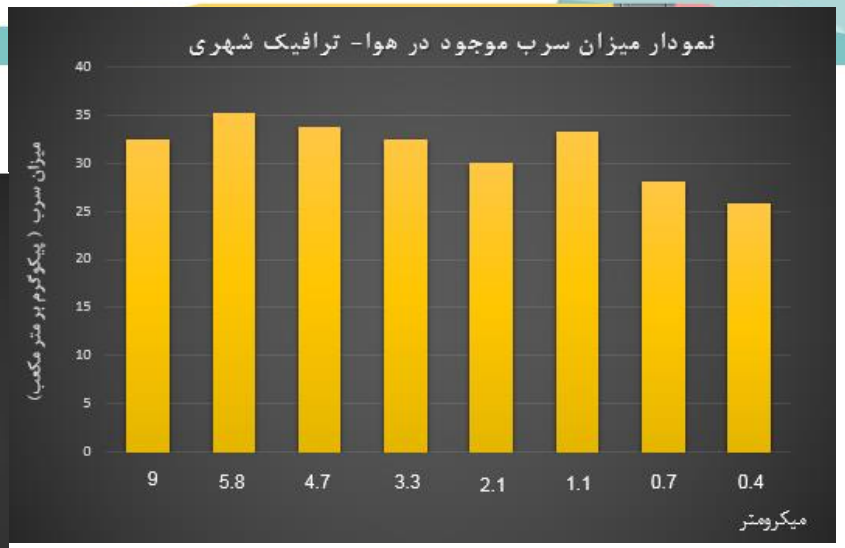


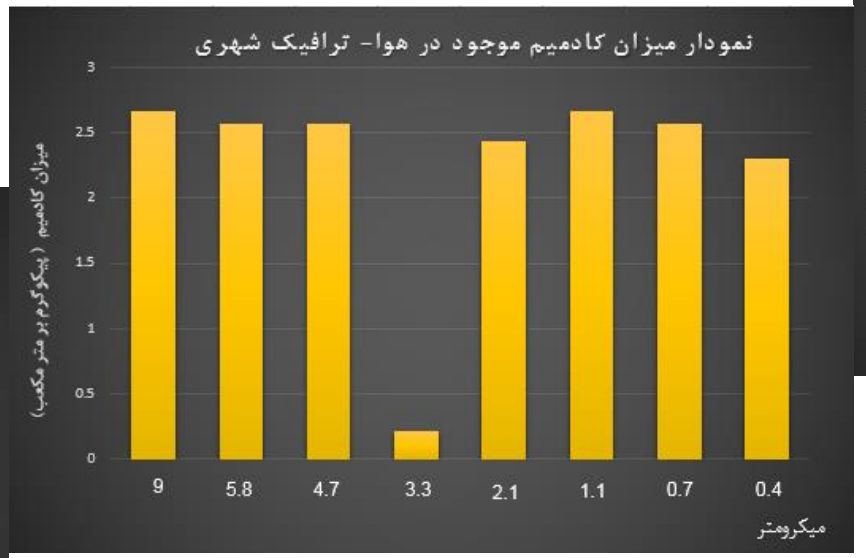
تعیین ترکیبات شیمیایی ذرات گردوغبار

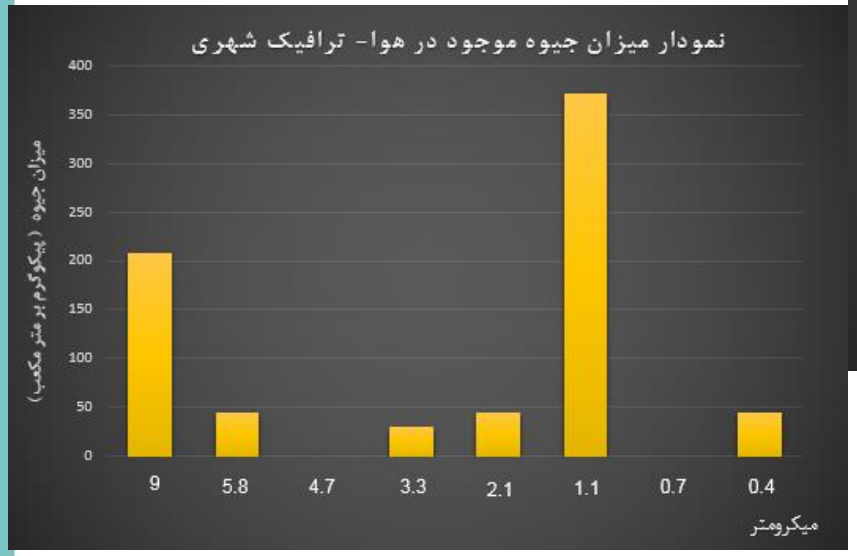




تعیین ترکیبات شیمیایی ذرات آلاینده در ترافیک شهری







مقایسه ترکیبات شیمیایی ذرات آلاینده در شرایط گردوغبار و ترافیک شهری