

Shell Structure of Aged Atmospheric Aerosols

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Abstract

Atmospheric aerosols in the course of their residence time are aging by condensation and evaporation processes as well as reaction processes predominantly taking place at the particle's surface. By analysis of experimental data, mostly impactor sampling and investigation of individual particles, it was found that not only the whole size spectrum but also the structure of an individual particle are dominated by the specific vapour pressures of the contributing substances. It was found that heavy volatile substances are in the core of aged particles and volatile substances near the surface. From inside to outside a shell-structure of substances with rising volatility is built up.

Keywords: Aged aerosols, specific vapour pressure, shell-structure

1. Sources

Primary aerosols originate of anthropogenic and natural sources. Anthropogenic sources mostly result of fossil fuel combustions. Natural sources are induced by geogenic, oceanic and biogenic emissions.

Secondary aerosols are produced by gas-to-particle conversions of reactive gases which also are emitted by anthropogenic and natural sources. In the course of their reaction pathways these gases are transformed into compounds of increased molecular weight until their vapour pressure is low enough to be transformed into particle phase. Secondary aerosol mass mostly is produced by precursor gases like SO₂ into sulphate, NO_x into nitrate, NH₃ into ammonium and volatile organics into heavy volatile particulate compounds.

2. Compositional Aging

Atmospheric particles in the size range between 0,1 and 1 µm diameter have the longest residence time. Substances which are enriched in this size range can be transported from industrial areas to remote areas of the globe. However, due to interactions of the aerosols with different sources and permanent dry and wet removing processes the concentration and composition is changing.

In Tab. 1 the concentrations and compositions of particulate matter in particles below 2,5 µm (PM_{2,5}) at sites of different air quality are listed. The urban measurements were made in

Frankfurt (M), the rural sampling site is in Germany and the remote-site is near the coast in Norway. The relative contribution of sulphate from urban-roadside to remote is increased from 16 % to 34 %. The sulphate mass predominantly consists of secondary aerosols. Therefore sulphur is the dominant element in remote particulate matter.

In the case of organic carbon (OC), elementary carbon (EC) and metal oxides the relative contributions from urban to remote sites significantly are decreasing.

The water content of PM from urban to remote is increasing. For PM at remote sites larger water-soluble fractions are observed.

3. Particle Structure

The atmospheric residence time of a particulate substance beside meteorological parameters depends on its Mass Median Diameter (MMD). The MMD's of particulate substances were determined by impactor measurements. With the aid of an 8-stage Andersen impactor the size-fractionated concentrations of many substances by use of GC-FID, GC-ECD, GC-MS, IC, AAS, ICP-MS, PIXE and NA were measured. It was found that every particulate substance has a specific MMD which is largely invariant of the different sampling sites. The MMD is related with the residence time τ :

$$(1) \quad \frac{1}{\tau} = \frac{v_o}{2H} \left[\left(\frac{MMD}{0,6 \mu m} \right)^2 + \left(\frac{0,6 \mu m}{MMD} \right)^2 \right] + \frac{1}{\tau_{wet}}$$

τ_{wet} is the wet residence time which is given by the atmospheric water cycle (Jaenicke 1978). Under Middle European conditions the yearly mean of τ_{wet} is 6 days.

According to equation (1) particles with a diameter of 0,6 μm have the longest residence time:

$$(2) \quad \frac{1}{\tau} = \frac{v_o}{H} \quad \begin{array}{l} v_o = \text{deposition velocity} \\ H = \text{mixing height} \end{array}$$

Under Middle European conditions the constants have the yearly average values:

$$V_o = 0,1 \text{ cm/s and } H = 1000 \text{ m}$$

Thus we get a mean residence time of 11,6 days for particles of 0,6 μm diameter. Therefore, particles of this size are exposed to long aging processes. After travelling several days these particles become a mixture of anthropogenic and natural sources. It was observed that Saharian dust particles were mixed with oceanic emissions and furthermore with anthropogenic emissions of European industrial areas (Artiñano et al. 2003). Similar events were observed in Asia when Kosa Aerosols originating of Mongolian deserts are transported over China and the bordering ocean to Japan (Mori et al. 2003). In this case desert minerals are mixed with carbonaceous and sulphuric material in China, seasalt-ions over the ocean and nitrate in industrial areas of Japan.

By sputtering the surface of individual aerosol particles the relative frequency of elements in function of depth was analysed (Dlugi 1978). Furthermore particles were investigated by Scanning Electron Microscopy (Moreno et al. 2003). It was found that heavy volatile substances (metal oxides, minerals) are accumulated in the core of the particles and nitrates and organic compounds near the surface. Sulphate and elementary carbon was found between surface and core.

It was found that aged particles have a shell-structure dominated by the specific vapour pressure of the contributing substances.

The substances of the particle along the radius r are built up in shells according to their specific vapour pressures p_s :

$$(3) \quad r \sim p_s; \quad p_s < 1 \text{ Pa}$$

By use of the boiling point T_B and the freezing point T_F it is possible to assess p_s for heavy volatile substances like metal oxides and minerals (Müller 2003).

$$(4) \quad \lg p_s = -\frac{c(T_F + T_B)}{2T} \lg T + 14 \quad T_F, T_B, T \text{ in Kelvin}$$

The calibration factor c is between 3 and 4. By use of $c = 3.5$, for all substances the order of magnitude of p_s can be determined.

Most substances in $PM_{2.5}$ are semi-volatile. These substances partly are in particulate phase and partly in gaseous phase. Empirically, it was found that gas/particle partitioning also depends on the specific vapour pressure (Müller 2003).

$$(5) \quad x_p = \tan h \left(\frac{c}{4} \cdot \frac{T_F + T_B}{T} \lg T - 8,4 \right)^2 \quad \frac{c}{4} \cdot \frac{T_F + T_B}{T} \lg T > 8,4$$

$x_p = \text{particle mass fraction}$

$x_g = \text{gaseous mass fraction}$

$x_p + x_g = 1$

If ambient temperature T is rising several particulate substances partially vaporize. If T decreases several substances condensate on the particles' surfaces. Induced by varying temperature in the course of the particles' aging many condensation and evaporation processes take place. Thus a shell-structure of the particles is built up.

Table 1

Concentration and composition of PM_{2,5} (particulate matter with particles below 2,5 µm) at sites of different air quality (urban-roadside, urban residential, rural and remote) in Middle Europe

	urban roadside	urban residential	rural	remote
Mass (yearly mean)	22 µg/m³	18 µg/m³	11 µg/m³	4 µg/m³
sulphate-ions SO ₄ ⁼	16 %	19 %	22 %	34 %
nitrate-ions NO ₃ ⁻	10 %	12 %	15 %	12 %
ammonium-ions NH ₄ ⁺	9 %	12 %	14 %	12 %
chloride-ions Cl ⁻	3 %	1 %	2 %	1 %
metal-ions Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	4 %	4 %	5 %	2 %
organic carbon (OC)	24 %	22 %	16 %	13 %
elementary carbon (EC)	21 %	16 %	10 %	10 %
Metal oxides, minerals	7 %	6 %	5 %	3 %
Water and rest	6 %	8 %	11 %	13 %
	100 %	100 %	100 %	100 %

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