

Gas/Particle Partitioning of Carbonaceous Substances

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Carbonaceous substances are a main constituent of atmospheric particles. Substances which originate of combustion sources mostly accumulate in the particle size-range between 0,1 and 1 μm diameter. Organic compounds of this size have vapour pressures between 1 and 10^{-10} Pa. Therefore, these compounds under ambient air conditions are semi-volatile, partly they exist in particulate phase and partly in gaseous phase. Semi-volatile p.e. are polycyclic aromatic hydrocarbons (PAHs), pesticides and organochlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs).

Gas/particle partitioning of a substance decisively influences it's atmospheric removal processes. In gas phase removal mostly is induced by photochemical reactions and in particulate phase by dry and wet deposition.

With the aid of impactor sampling and chemical analysis the Mass Median Diameters (MMDs) of many substances were determined. Gas/particle partitioning was measured by sampling with a glass fiber filter backed by polyurethane (PU)-foam.

MMD Vs. Specific Vapour Pressure

Empirically it was found that the Mass Median Diameter MMD of a particulate substance can be quantitatively related to its specific vapour pressure p_s (Pa):

$$(1) \quad MMD = 0,1 \left(1 - \lg p_s \right) \mu\text{m} \quad p_s < 10\text{Pa}$$

It was also found that the p_s of a considered substance can be assessed by use of the freezing point T_F and boiling point T_B :

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

Inserting equation (2) in (1) we get:

$$(3) \quad MMD = 0,1 \left[\frac{c(T_F + T_B)}{2T} \lg T - 13 \right] \quad c \frac{(T_F + T_B)}{2T} \lg T > 13$$

c is a specific factor, for organic compounds varying between 3.7 and 4.2. By use of equation (3) is seen that the MMD is shrinking with increasing temperature.

Gas/Particle Partitioning Vs. Specific Vapour Pressure

By use of many measurements of the last decade it was found, that the mass fraction x_p of a particle-bound compound can be calculated with the tangens hyperbolicus of it's MMD:

$$(4) \quad x_p = \tan h \left(\frac{MMD}{0,6} \right)^2$$

$$x_p = \frac{c_p}{c_p + c_g} \quad \text{particulate mass fraction}$$

$$x_g = \frac{c_g}{c_p + c_g} \quad \text{gaseous mass fraction}$$

c_p and c_g concentrations in particulate phase and gaseous phase

By use of equation (3) we get:

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

If ambient temperature T is rising several particulate substances partially vaporize. If T decreases several substances condensate on the particles surface.

Solubility Vs. MMD

Measurements of particulate substances also demonstrated that the solubility S in water is rising with decreasing MMD:

$$(6) \quad \lg S = \frac{s_i}{MMD}$$

s_i is the specific factor of the considered particulate substance. For MMD the relations (1) and (3) can also be inserted.

Ambient particulate matter of particles below $2.5 \mu\text{m}$ (PM_{2,5}) by roughly $2/3$ is water-soluble and above $2.5 \mu\text{m}$ only by $1/3$.