Wet deposition

Another important process accounting for heavy metal removal from the atmosphere is wet deposition. Particle-bound heavy metals as well as soluble gaseous species are scavenged form the atmospheric air both in cloud environment and below the cloud base. Wet deposition of a substance is described by the equation:

$$\frac{\partial q}{\partial t} = -\Lambda_{wet} q,\tag{1}$$

where Λ_{wet} is the wet deposition coefficient depending on the local precipitation rate R_p .

We used the following expression for the wet deposition coefficient based on measurement data:

$$\Lambda_{wet} = A \left(\frac{R_p}{F}\right)^B,\tag{2}$$

here *A* and *B* are empirical constants;

F is a fraction of the grid cell where precipitation occurs.

We adopt F = 0.3 for convective precipitation and F = 1 for stratiform one following the discussion in [*Walton et al.*, 1988]. The pollutant mixing ratio averaged over a grid cell after the wet deposition is given by:

$$q^{t+\Delta t} = q^t [1 - F(1 - \exp\left(-\Lambda_{wet}\Delta t\right)].$$
(3)

The model distinguishes in-cloud scavenging (ICS) and below-cloud scavenging (BCS).

In-cloud scavenging

In the cloud environment soluble gases dissolve very quickly in the cloud water coming into the equilibrium with the solution, while aerosol particles are taken up by cloud droplets due to nucleation or impaction scavenging. Further collection of cloud drops by falling raindrops leads to removal of the pollutants from the atmosphere. The efficiency of aerosol scavenging by cloud droplets depends upon the cloud liquid water content (LWC). Figure 1 shows the scavenging efficiencies (i.e. the ratio of aerosol concentration in cloud water to its concentration in interstitial air) for Pb and SO₄ measured by *A.Kasper et al.* [1998] as a function of the LWC. For values of the LWC higher than 0.5 g/m³ the efficiency

commonly exceeds 0.8 and it drops down when the LWC become lower 0.1 g/m³. For the approximation of the dependence we used the following expression:

$$\varepsilon_w = \frac{C_w}{C_w + \varepsilon_{w0}},\tag{4}$$

where the liquid water content C_w is in g/m³; constant ε_{w0} is equal to 0.1.



Fig. 1. Efficiency of aerosol scavenging by cloud droplets for lead and sulfate as a function of cloud LWC. Symbols show measurement data from [Kasper et al., 1998], solid line – approximation

Thus for the in-cloud scavenging Equation (3) is transformed to:

$$q^{t+\Delta t} = q^t [1 - \varepsilon_w F(1 - exp (-\Lambda_{wet} \Delta t))], \tag{5}$$

where the scavenging efficiency ε_w for aerosol particles is defined by Eq. (1.66) and $\varepsilon_w = 1$ for aqueous forms.

Parameters of the wet deposition coefficient expression (2) for in-cloud scavenging estimated or measured by different authors are presented in Table 1. Taking into account values in the table and sensitivity calculations we adopted the parameters: $A_{in} = 3 \cdot 10^{-4}$, $B_{in} = 0.8$ for all heavy metal species incorporated into cloud water.

Table 1.6. Parameters of the wet deposition coefficient for in-cloud scavenging
 $(A_{in} \text{ is in units of } s^{-1}; R_p \text{ is in units of } mm/h)$

Reference	$A_{in}(\times 10^{-4})$	B _{in}	Method
<i>Scott</i> , 1982	3.5	0.78	Calculation
<i>Penner et al.</i> , 1991	1.31	1	Estimation *
<i>Brandt et al.</i> , 2002	3.36	0.79	Estimation
Andronache, 2004	3.97	0.81	Measurement **

*- ICS plus BCS of HNO₃ **- Calculations based on measured ICS plus BCS

Below-cloud scavenging

Below the cloud base aerosol particles and soluble gases are collected by falling raindrops and removed from the air. The model parameterization of below-cloud scavenging is mostly based on empirical estimates. Table 2 presents parameters of the wet deposition coefficient for BCS of particles and highly soluble gases based on measurement data. As seen different estimates of A_{below} varies roughly from $0.5 \cdot 10^{-4}$ to $2.5 \cdot 10^{-4}$ s⁻¹; and B_{below} is within the range 0.62-0.79. There is no principal difference between values of the parameters for sub-micron aerosol particles and highly soluble gases. Basing on the data from the table sensitivity and the runs we adopted the values $A_{below} = 1 \cdot 10^{-4}$ and $B_{below} = 0.7$ both particle-bound heavy metals and highly soluble gaseous species (RGM).

Reference	$A_{below} = 1 \cdot 10^{-4}$	B _{below}	Method
Ragland and Wilkening, 1983	1.22	0.63	Estimation
<i>Barries</i> , 1985	1	0.67	Measurement
<i>Jylhä</i> , 1991	1	0.64	Measurement
<i>Asman</i> , 1995	0.52-0.99	0.62	Calculation *
<i>Okita et al.</i> , 1996	1.38	0.74	Measurement
<i>Brandt et al.</i> , 2002	0.84	0.79	Estimation
Andronache, 2003	0.67 - 2.44	0.7	Calculation **

Table 2. Parameters of the wet deposition coefficient for below-cloud scavenging A_{below} is in units of s^{-1} ; R_p is in units of mm/h)

* - for highly soluble gases

** - theoretical calculations based on measured aerosol size spectra

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