Regimes of Nonisothermal Scavenging of Soluble Gaseous Pollutants by Rain in the Atmosphere with Non-Uniform Concentration and Temperature Distribution

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Outline of the presentation

- Motivation and goals
- Fundamentals
- Description of the model
- Results and discussion
- Conclusions
Gas absorption by falling droplets

- $\text{SO}_2$, $\text{CO}_2$, $\text{CO}$ – fossil fuels burning, forest fires
- $\text{NH}_3$ – agriculture
- $\text{CO}_2$, NOx – boilers, furnaces

Henry’s Law:

$$A(g) + H_2O \rightleftharpoons A \cdot H_2O$$

$A \cdot H_2O$ is the species in dissolved state

$$[A \cdot H_2O] = K_H p_A$$
Gas absorption by falling droplets

- SO₂ absorption of boiler flue gas
- HF absorption in the aluminum industry
- In-cloud scavenging of polluted gases (SO₂, CO₂, CO, NOₓ, NH₃)

Scavenging of air pollutions by cloud and rain droplets

Henry’s Law:

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Vertical concentration gradient of soluble gases

- **Gaseous pollutants in atmosphere**
  - \( \text{SO}_2 \) and \( \text{NH}_3 \) – anthropogenic emission
  - \( \text{CO}_2 \) – competition between photosynthesis, respiration and thermally driven buoyant mixing

Fig. 1. Aircraft observation of vertical profiles of \( \text{CO}_2 \) concentration (by Perez-Landa et al., 2007)
Precipitation scavenging of gaseous pollutants by rain

Gaseous pollutants in atmosphere

- SO$_2$ and NH$_3$ – anthropogenic emission
- CO$_2$ – competition between photosynthesis, respiration and thermally driven buoyant mixing

Fig. 2. Vertical distribution of SO$_2$. Solid lines - results of calculations with (1) and without (2) wet chemical reaction (Gravenhorst et al. 1978); experimental values (dashed lines) – (a) Georgii & Jost (1964); (b) Jost (1974); (c) Gravenhorst (1975); Georgii (1970); Gravenhorst (1975); (f) Jaeschke et al., (1976)
Gas absorption by rain:
- Asman, 1995 – uniformly distributed soluble pollutant gas
- Slinn, 1974 – wash out of plums
- Zhang, 2006 – wash out of soluble pollutants by drizzle

Measurements of vertical distribution of trace gases in the atmosphere:
- CH$_3$OH – Cady-Pereira et al., 2012
- NH$_3$ – Georgii & Müller, 1974
- CO$_2$ – Denning et al., 1995; Perez-Landa et al., 2007

Precipitation scavenging of gaseous pollutants by rain in inhomogeneous atmosphere:
- Elperin, Fominykh, Krasovitov & Vikhansky 2011 – Effect of rain scavenging on altitudinal distribution of soluble gaseous pollutants in the atmosphere
- Elperin, Fominykh, Krasovitov 2014 - Nonisothermal scavenging of highly-soluble gaseous pollutants by rain
Criteria of low gradient of concentration and temperature approach applicability (Hales 1972):

\[
\frac{a \cdot m \cdot u \cdot \left| \frac{dc^{(G)}}{dz} \right|}{\beta \cdot c_{gr}^{(G)}} \ll 1
\]

\[
\frac{a \cdot c_{pL} \cdot \rho_{L} \cdot u \cdot \left| \frac{dT^{(G)}}{dz} \right|}{\alpha_{T} \cdot T_{gr}^{(G)}} \ll 1
\]

Velocity of temperature front propagation

\[
U_{T} = \frac{\phi \cdot c_{pL} \cdot \rho_{L} \cdot u}{c_{pG} \cdot \rho_{G}(1 - \phi) + c_{pL} \cdot \rho_{L} \cdot \phi}
\]

Velocity of scavenging front propagation

\[
U_{C} = mI
\]
Description of the model

\[ U_T = 1 \text{ cm} \cdot \text{s}^{-1} \text{ when } I=10 \text{ mm/hour} \]

\[ U_C \propto U_T \text{ when } H_A \text{ is of the order of } 10^2 \text{ M} \cdot \text{atm}^{-1} \]

\[ U_C \ll U_T \text{ gas having low solubility } \text{CO}_2, \text{O}_2 \]

\[ U_C \gg U_T \text{ gas having high solubility } \text{HNO}_3, \text{H}_2\text{O}_2 \]

\[ U_C \propto U_T \text{ moderately soluble gas } \text{methanol } (\text{CH}_3\text{OH}) \]

nitrous acid, hydroxyl radical (OH)
Concentration of the dissolved gas and temperature in a droplet:

\[ c^{(L)}(z) = m c^{(G)}(z) \]  \hspace{1cm} (2)

where

\[ c^{(G)} \quad \text{– concentration of a soluble gaseous pollutant in a gaseous phase} \]

\[ m(T) \quad \text{– solubility parameter} \]

\[ m = m_0 - k_1 \cdot (T - T_0) \]

\[ T^{(L)}(z) = T^{(G)}(z) \]
Description of the model

Total concentration of soluble gaseous pollutant and energy per unit volume in gaseous and liquid phases reads:

\[ c = (1 - \phi) c^{(G)} + \phi c^{(L)} \]  

(3)

\[ E = c_{pG} \cdot \rho_G \cdot (1 - \phi) T^{(G)} + \phi \cdot c_{pL} \cdot \rho_L \cdot T^{(L)} \]

Where \( \phi \) – volume fraction of droplets in the air.

The total flux of the dissolved gas and heat transferred by rain droplets:

\[ q_c = \phi \cdot u \cdot c^{(L)} \]

\[ q_T = \phi \cdot c_{pL} \cdot \rho_L \cdot u \cdot T^{(L)} \]

(4)

where \( u \) – velocity of a droplet.
Equation of mass and energy balance in the gaseous and liquid phases:

\[
\frac{\partial c}{\partial t} = -\frac{\partial q_c}{\partial z} \quad \frac{\partial E}{\partial t} = -\frac{\partial q_T}{\partial z}
\]  

(5)

Combining Eqs. (4) - (5) we obtain:

\[
\frac{\partial x^{(G)}}{\partial t} + U_c(z,t) \frac{\partial x^{(G)}}{\partial z} = 0 \quad \frac{\partial T^{(G)}}{\partial t} + U_T \frac{\partial T^{(G)}}{\partial z} = 0
\]  

(6)

where $U_c(z,t)$ wash-down front velocity, $U_T$ velocity of temperature front propagation.
Initial and boundary conditions:

\[ t = 0 \quad x^{(G)} = f(z) \quad T^{(G)} = g(z) \]  
\[ z = 0 \quad x^{(G)} = x_c^{(G)} \quad T^{(G)} = T_c^{(G)} \]  

(7)

Initial-boundary value problem (6)-(7) is solved by the method of characteristics

Solution:

\[ T^{(G)} = T_0^{(G)} + k_2 \cdot (z - U_T \cdot t) \]  

(8)
Evolution of concentration distribution in the gaseous phase:

\[
\frac{\partial x^{(G)}}{\partial t} + \phi_L \cdot u \cdot (m_0 - k_3 \cdot z + k_3 \cdot U_T \cdot t) \frac{\partial x^{(G)}}{\partial z} = 0
\]  \hspace{1cm} (9)

Initial distribution of concentration is exponential: \( x^{(G)} = x_c^{(G)} \cdot \exp(k_1 \cdot z) \)

\[
x^{(G)} = x_c^{(G)} \exp\left(-\frac{k_4 (c_T - \phi_L u m_0)}{\phi_L u k_3}\right) \times
\exp\left\{ -k_4 U_T t + \frac{k_4 \cdot U_T}{\phi_L u k_3} - \frac{k_4 \cdot m_0}{k_3} \right\} \cdot \exp(k_3 \cdot \phi_L \cdot u \cdot t) \]  \hspace{1cm} (10)

Scavenging coefficient \( \Lambda = -\frac{1}{x^{(G)}} \frac{\partial x^{(G)}}{\partial t} \)  \hspace{1cm} (11)
Description of the model

\[ \Lambda = -\frac{1}{x^{(G)}(t)} \frac{\partial x^{(G)}}{\partial t} = \exp(k_3 \cdot \phi \cdot u \cdot t) \cdot U_{C0} k_4 \left\{ 1 - \frac{\phi_L u k_3}{U_{C0}} (z - U_T t) \right\} \]  

(12)

Scavenging of highly soluble gases \( U_{C0}/U_T >> 1 \)

\[ \Lambda = \exp(k_3 \cdot \phi_L \cdot u \cdot t) \cdot U_{C0} k_5 \left\{ 1 - \phi_L u k_3 z / U_{C0} \right\} \]

Scavenging of gases with low solubility \( U_{C0}/U_T << 1 \)

\[ \Lambda = k_1 \cdot m \cdot I \]  

(13)

where \( I \) – rain intensity
Fig. 3. Evolution of temperature distribution in the atmosphere during rain

Fig. 4. Evolution of temperature distribution in the atmosphere during rain
Results and discussion

Fig. 5. Dependence of scavenging velocity for absorption of methanol by rain vs. time

Fig. 6. Evolution of methanol distribution in the atmosphere caused by rain scavenging
Results and discussion

Fig. 7. Dependence of scavenging coefficient in the vicinity of the ground vs. rain intensity

Fig. 8. Dependence of scavenging coefficient in the vicinity of the ground vs. rain intensity
Results and discussion

Fig. 9. Dependence of scavenging coefficient vs. altitude for methanol wash-out by rain

Fig. 10. Dependence of scavenging coefficient vs. altitude for methanol wash-out by rain
Results and discussion

**Fig. 11.** Comparison of theoretical results with atmospheric measurements

**Fig. 12.** Comparison of theoretical results with atmospheric measurements
It is demonstrated that rain homogenizes initial temperature distribution in the atmosphere in the region between the cloud bottom and the ground, e.g. temperature distribution becomes uniform after several hours of rain having intensity 10 mm/hour.

It is showed that for an arbitrary initial altitudinal distribution of soluble trace gas in the atmosphere with inhomogeneous temperature distribution scavenging coefficient for the wash out of soluble gases by precipitation is time-dependent and height-dependent. Scavenging of soluble gas begins in the upper atmosphere, and scavenging front propagates downwards with the wash-out velocity. Scavenging coefficient in the region between the bottom of a cloud and scavenging front vanishes.

For the exponential initial concentration distribution of soluble trace gases in the atmosphere the scavenging coefficient in the region between the ground and the scavenging front is proportional to rain intensity, solubility parameter for the temperature at the bottom of the cloud and to the growth constant in the initial altitudinal concentration distribution of trace gas.