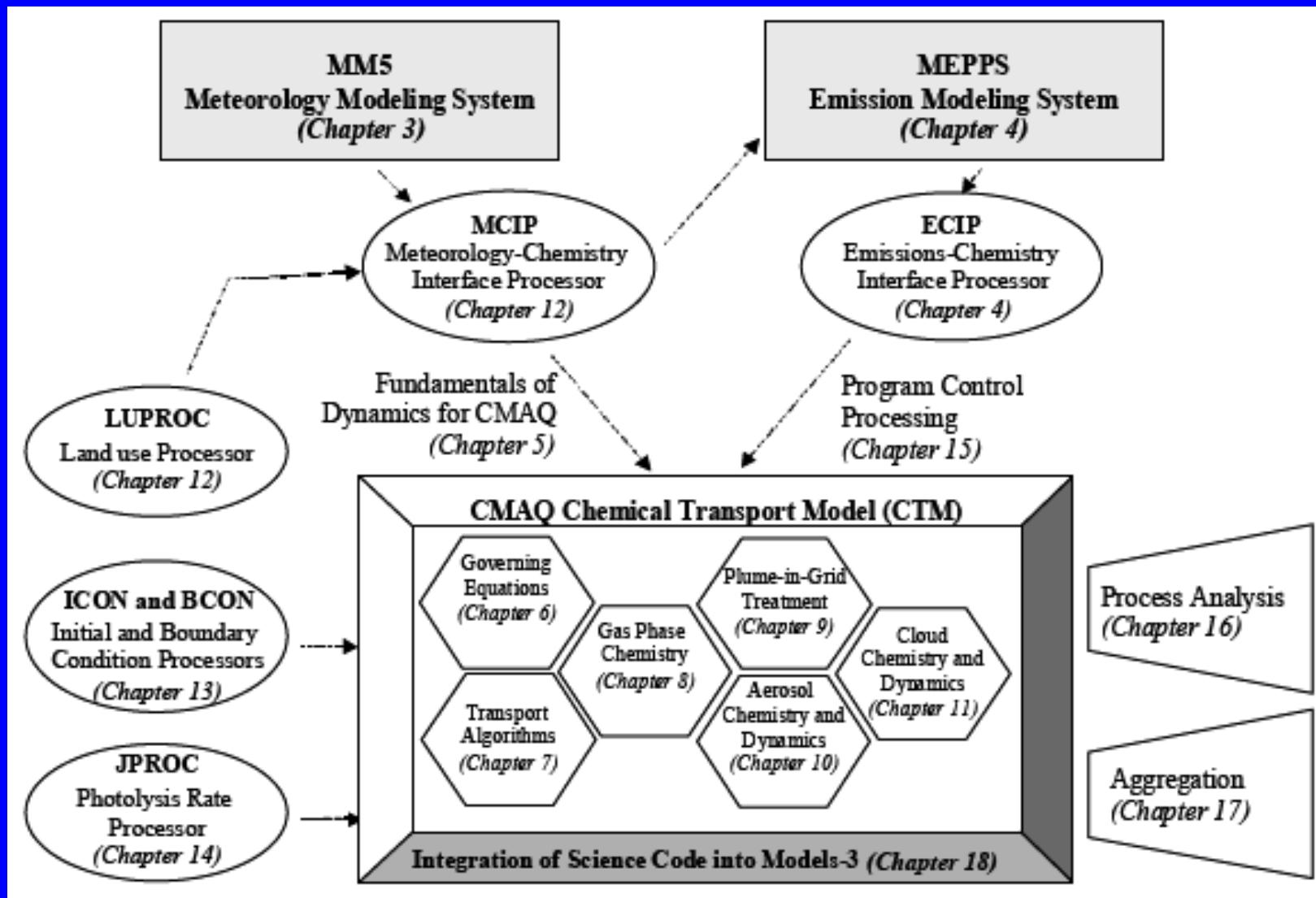


Моделирование газовых примесей и аэрозолей в городском и региональном масштабах

А.Е.Алоян

ИВМ РАН

- Данные об эмиссии
- Метеоданные (динамика атмосферы)
- Кинетические процессы трансформации (фотохимия, нуклеация, конденсация/испарение, коагуляция, гетерогенные процессы)



Dynamics

Chmiestry (gas-liquid)

(nonlinear ODE)

Ion Nucleation

(kinetic theory)

Ternary Nucleation

(thermodynamic theory)

Condensation

(quasilinear equations)

Coagulation

(integro-differential
equations)

Mass-Exchange

at Gas-Particle Interface

(nonlinear ODE)

Computational Grid Size: $(60 \times 60 \times 30 \times 100 \times 30) = 3.24 \times 10^8$

Regional Model

Equations of Atmospheric Hydrodynamics

$$\frac{\partial(\overline{\rho}u_i)}{\partial t} + \frac{\partial(\overline{\rho}u_j u_i)}{\partial x_j} = -\frac{\partial p'}{\partial x_i} - 2\epsilon_{ijk}\overline{\rho}\Omega_j u_k + \delta_{i3}\overline{\rho}g\left(\frac{\vartheta'}{\overline{\vartheta}} + \epsilon q\right) + \frac{\partial\tau_{ij}}{\partial x_j}$$

$$\frac{\partial \rho u_j}{\partial x_j}=0,\quad (j=\overline{1,3})$$

$$\frac{\partial(\overline{\rho}\vartheta)}{\partial t} + \frac{\partial(\overline{\rho}u_j\vartheta)}{\partial x_j} = \frac{L\vartheta}{c_p\overline{T}}\Phi + \frac{\partial H_j}{\partial x_j},$$

$$\frac{\partial(\overline{\rho}q)}{\partial t} + \frac{\partial(\overline{\rho}u_jq)}{\partial x_j} = -\Phi + \frac{\partial Q_j}{\partial x_j},$$

Pollution Transport

The system of equations for the pollution transport and transformation
(Aloyan, 2000; Aloyan et al., 2002)

$$\begin{aligned} \frac{\partial C_i}{\partial t} + u_j \frac{\partial C_i}{\partial x_j} = & F_i^{gas} - P_i^{nucl} - P_i^{cond} + P_i^{phot} \\ & + \frac{\partial}{\partial x_1} K_{11} \frac{\partial C_i}{\partial x_1} + \frac{\partial}{\partial x_2} K_{22} \frac{\partial C_i}{\partial x_2} + \frac{\partial}{\partial x_3} K_{33} \frac{\partial C_i}{\partial x_3}; \\ \frac{\partial \phi_k}{\partial t} + (u_j - \delta_{j3} w_g) \frac{\partial \phi_k}{\partial x_j} = & F_k^{aer} + P_k^{nucl} + P_k^{cond} + P_k^{coag} \\ & + \frac{\partial}{\partial x_1} K_{11} \frac{\partial \phi_k}{\partial x_1} + \frac{\partial}{\partial x_2} K_{22} \frac{\partial \phi_k}{\partial x_2} + \frac{\partial}{\partial x_3} K_{33} \frac{\partial \phi_k}{\partial x_3}. \end{aligned}$$

Where C_i ($i = 1, \dots, N$) and ϕ_k ($k = 1, \dots, M$) are the concentrations of gaseous species and aerosols, respectively; N and M are the numbers of gaseous components and aerosol fractions, respectively.

Photochemistry

The chemical mechanism used in this work is an improved version of that described in Aloyan et al. (1987) and Aloyan et al. (1995). Additional species and chemical reactions were included into the mechanism from the Carbon–Bond Mechanism (CBM–IV) (Gery et al., 1989). The reaction rate constants were taken also from (Anderson 1976; Atkinson and Lloyd, 1984). This approach allows us to describe the intermediate species in more detail, while the computational burden increases only slightly. In total, the resulting hybrid model includes a total of 44 chemical species and 204

$O(^1D)$, $O(^3P)$, O_3 , OH , HO_2 , H , NO_3 , NO , NO_2 , SO_2 , H_2CO , HCO , H_2O_2 , CO , CH_4 , HNO_2 , HNO_3 , SO_3 , SO_2^* , N_2O_5 , CH_3 , CH_3O_2 , CH_3O , CH_3OH , CO_2 , $CH_3O_2NO_2$, $HCOOH$, $HOCH_2O$, $HOCH_2O_2$, CH_3OOH , HO_2NO_2 , CH_3ONO_2 , $ISOP$, XO_2 , $ALD2$, $C2O_3$, PAN , TOL , TO_2 , PAR , OLE , ROR , XO_2N , ETH .

Nucleation

(Kulmala et al., 2000, Hanna, 2002)

Let in the atmosphere under temperature T and pressure P_v we have a binary cluster consisting of n_w water molecules and n_a acid molecules with mole fractions $x_{iw}(i = w; a)$. The particles are also assumed to be of spherical shape and in the aqueous phase. Then, the free energy of new-particle formation in the binary mixture can be represented in the form

$$W = \Delta G = n_w \Delta \mu_w + n_a \Delta \mu_a + A\sigma$$

where ΔG is the change in the Gibbs free energy, A is the surface area, σ is the surface tension, $\Delta \mu_i = \mu_{il}(T; P_v; x_{il}) - \mu_{iv}(T; P_v; x_{iv})$, μ_{il} and μ_{iv} are the chemical potentials in the aqueous and vapor phases, respectively, r^* is the critical radius.

$$r^* = \frac{2\sigma(x^*)w_i(x^*)}{kT \ln \left(\frac{\rho_i^{free}}{\rho_{i,1}^{free}(x^*)} \right)}$$
$$w^* = \frac{4}{3}\pi r^{*2} \sigma(x^*)$$
$$J = Z\rho(1,2) \exp \left[- \frac{w^* - w(1,2)}{kT} \right]$$

Condensation and Coagulation

The kinetic equation for the change of aerosol particle-mass distribution
(Aloyan *et al.*, 1993; Aloyan *et al.*, 1997)

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial g} v_g \phi = J(g, t) + \frac{1}{2} \int_0^g \tilde{K}(g, g_1) \phi_{g-g_1} \phi_{g_1} dg_1 - \phi_g \int_0^\infty \tilde{K}(g, g_1) \phi_{g_1} dg_1$$

where g is the particle mass, J is the nucleation rate, K is the coagulation kernel, v_g is the rate of condensation.

$$v_g = \frac{\alpha \pi d^2 n v_T g^{2/3}}{4(1 + 3d g^{1/3}/8l_1)} \left(1 - \exp \left\{ \frac{\lambda \theta}{kT} \right\} \left[\frac{g_*^{1/3}}{g^{1/3}} - 1 \right] \right)$$

Gas- and Aqueous-Phase Chemistry Model

$$\frac{d[C_g^i]}{dt} = w_{gen,g}^i - w_{loss,g}^i - \left([C_g^i]k_i - [C_{aq}^i] \frac{k_i}{k_H k_b T} \right) L$$

$$\frac{d[C_{aq}^i]}{dt} = w_{gen,aq}^i - w_{loss,aq}^i - \left([C_g^i]k_i - [C_{aq}^i] \frac{k_i}{k_H k_b T} \right) \frac{1}{N_A}$$

$k_i = \left[\frac{r^2}{3D_g} + \frac{4r}{3c_i \alpha_i} \right]^{-1}$ is the coefficient of mass-exchange processes

k_b is the Boltzmann constant, D_g is the diffusion coefficient,
 α_i is the accommodation coefficient, c_i is the mean thermal velocity.

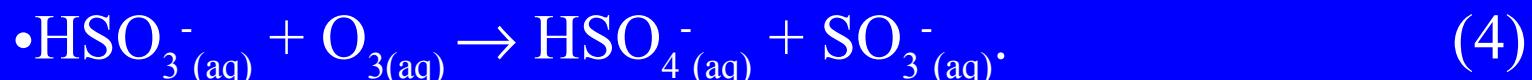
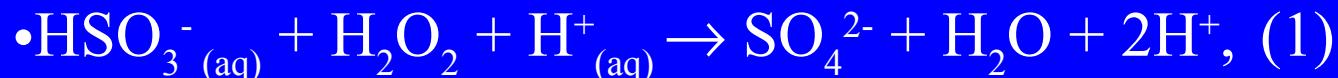
$$K_{H(T)}^i = K_{H(298)}^i \exp\left(-\frac{\Delta_r H_{298}^\circ}{R} \left[\frac{1}{T} - \frac{1}{298} \right]\right)$$
 is Henry's constant,

$\Delta_r H_{298}^\circ$ Is the thermal effect of gas component dissolution at $T = 298$ K

Aqueous-phase chemistry:

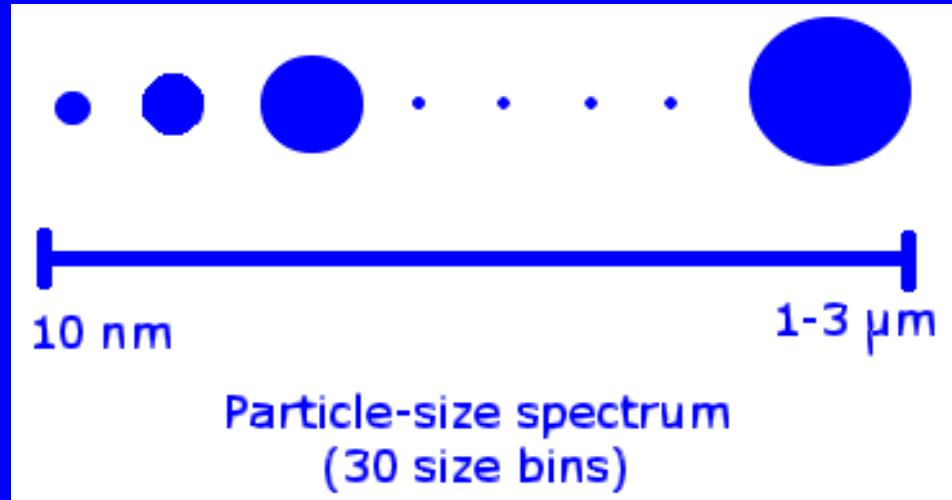
- One-way aqueous-phase chemical reactions: 35
- Aqueous-phase photochemical processes: 6
- Reversible chemical reactions (equilibrium): 21

Sulfite oxidation mechanism:



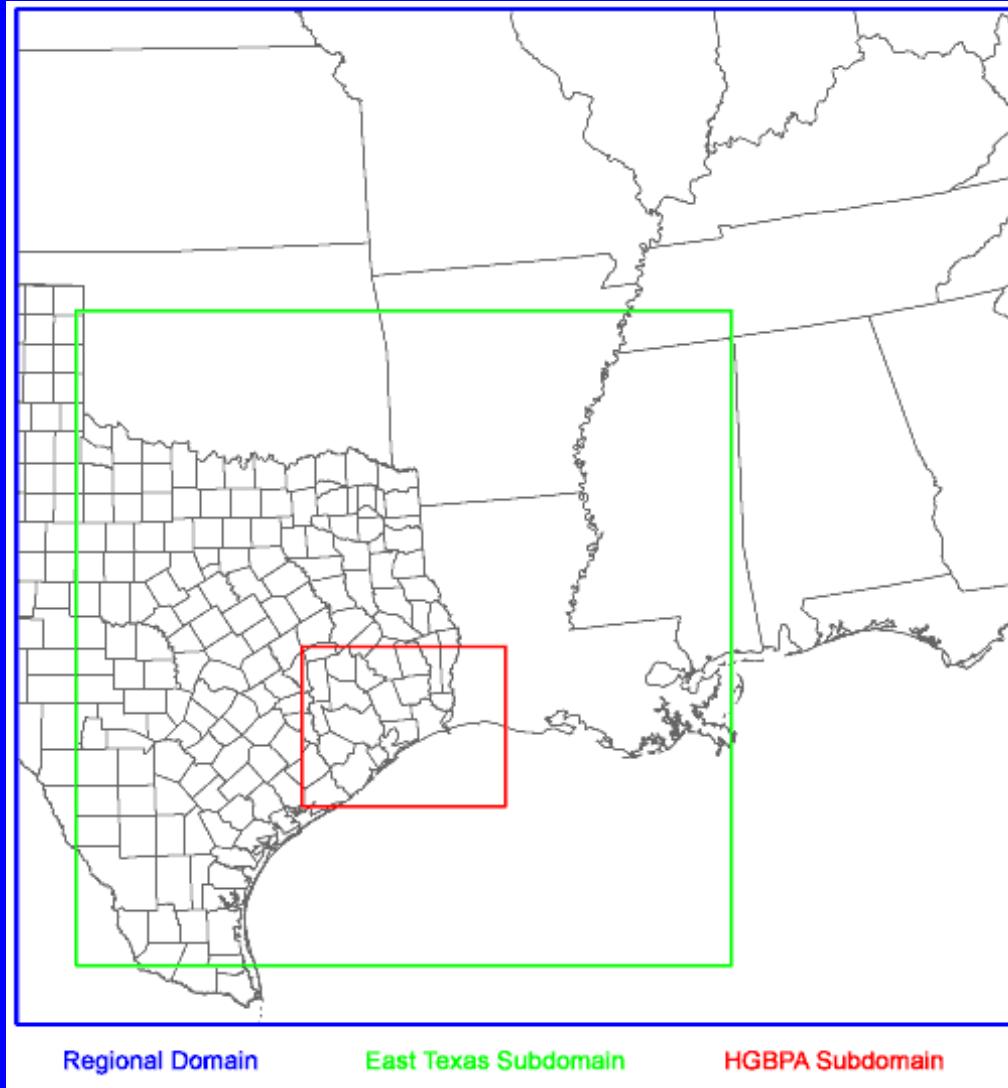
These pathways differ essentially in that the final products of the sulfite oxidation – sulfate ions – are generated directly in reaction (1).

Ion Composition of Aerosol Particles

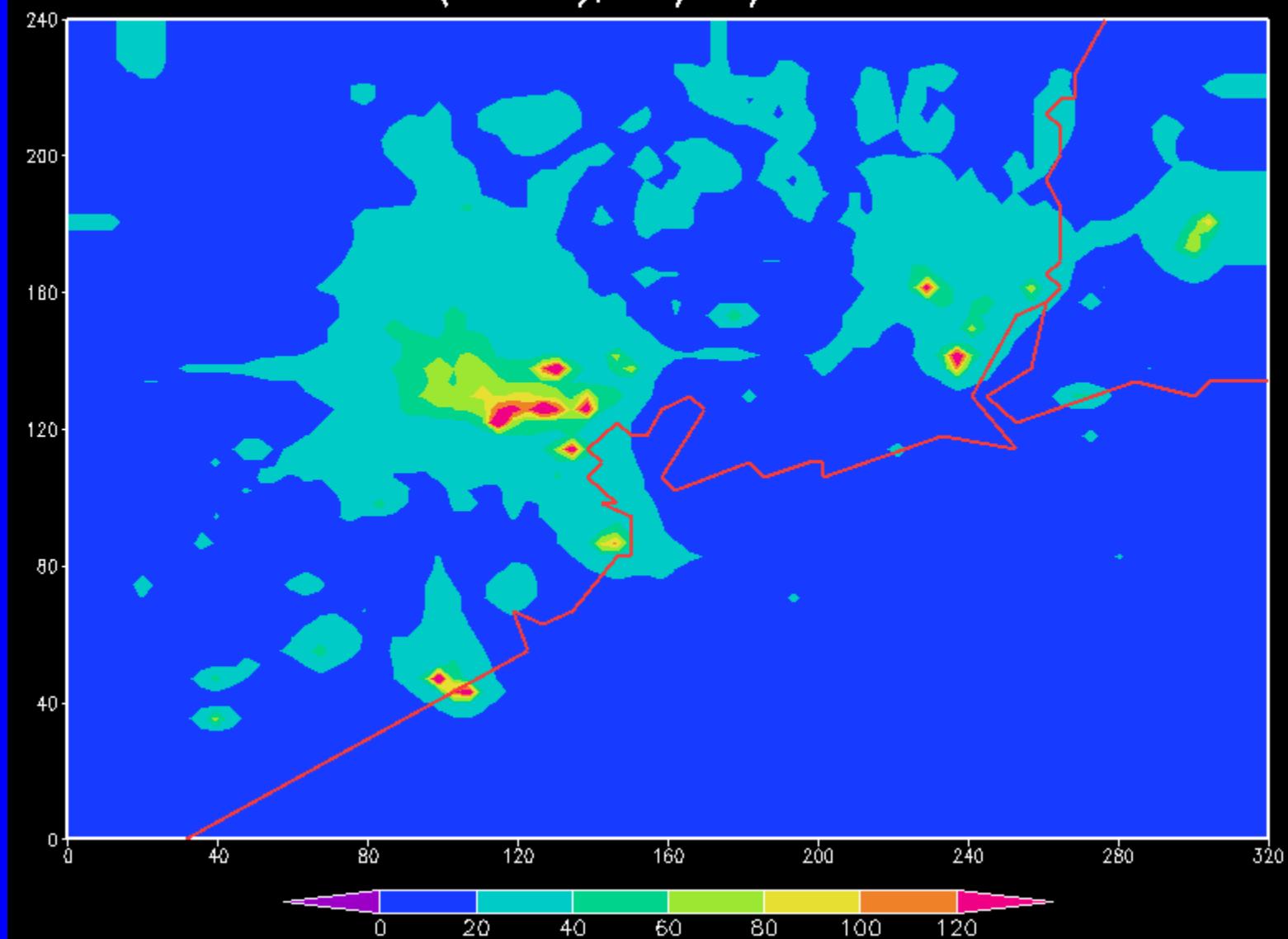


HO_2 , H_2O_2 , O_2 , OH^- , HSO_3^- ,
 H^+ , SO_4^{2-} , O_2^- , SO_3^{2-} , SO_3^- ,
 HSO_5^- , N_2O_5 , NO_3^- , NO_3 , O_3 ,
 SO_2 , HO_2^- , HSO_4^- , SO_5^- , SO_4^- ,
 SO_5^{2-} , $\text{S}_2\text{O}_8^{2-}$, NO_2 , NO ,
 Fe(OH)^{2+} , Fe(OH)_2^+ , Fe^{2+} ,
 Fe^{3+} , $\text{FeOHSO}_3\text{H}^+$, FeSO_4^+ ,
 NO_2^- , HNO_2 , CO_2 , H_2CO_3 ,
 HCO_3^- , H_2SO_4^- .

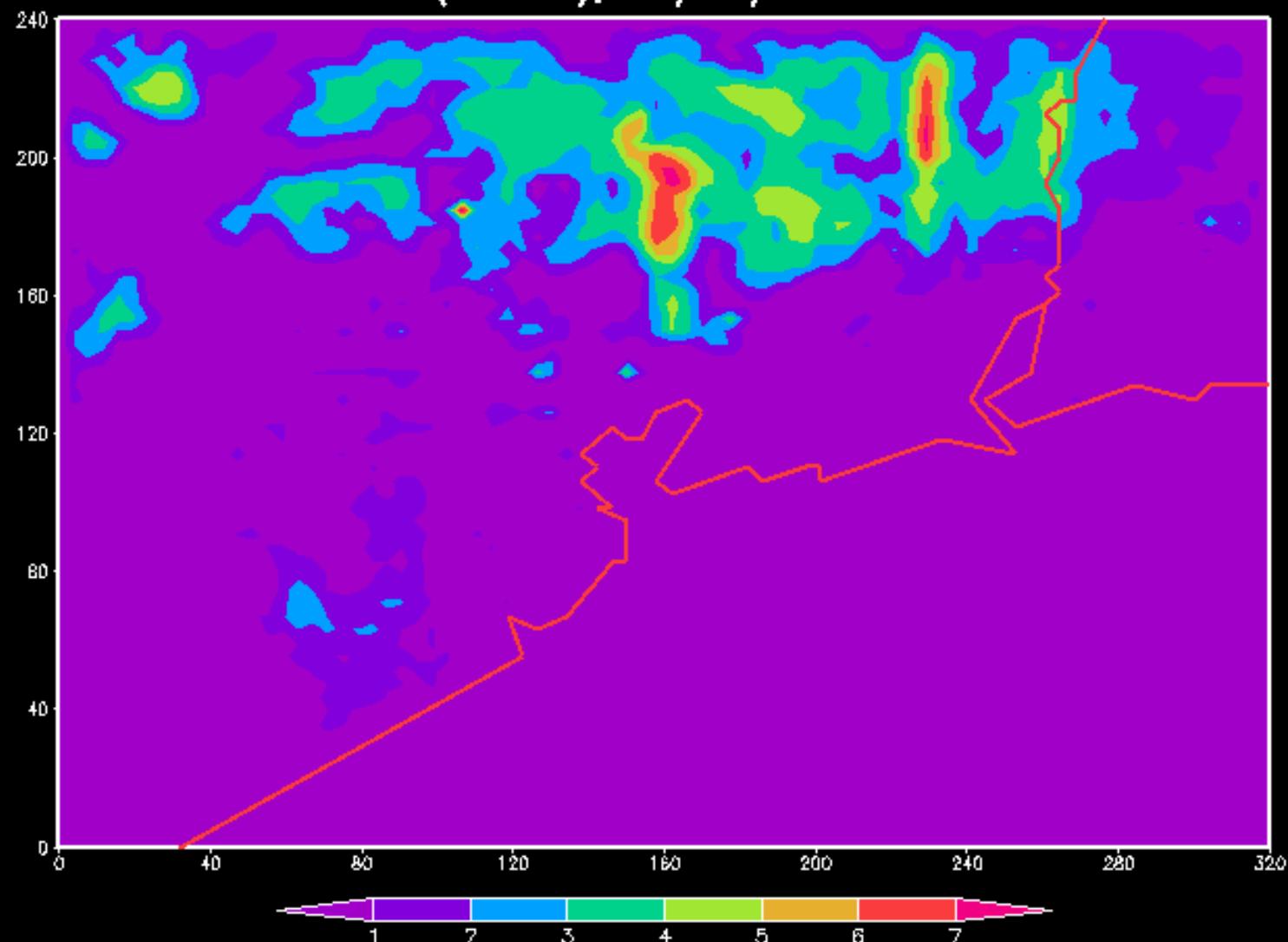
HG modeling domain



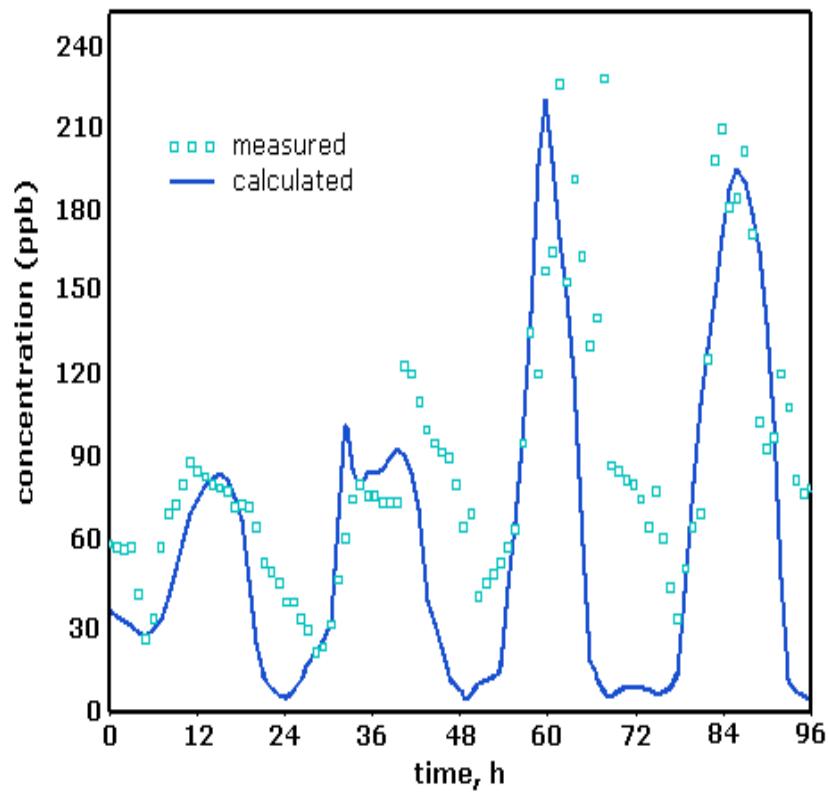
NO₂ (HGBPA), 09/08/1993 12:00



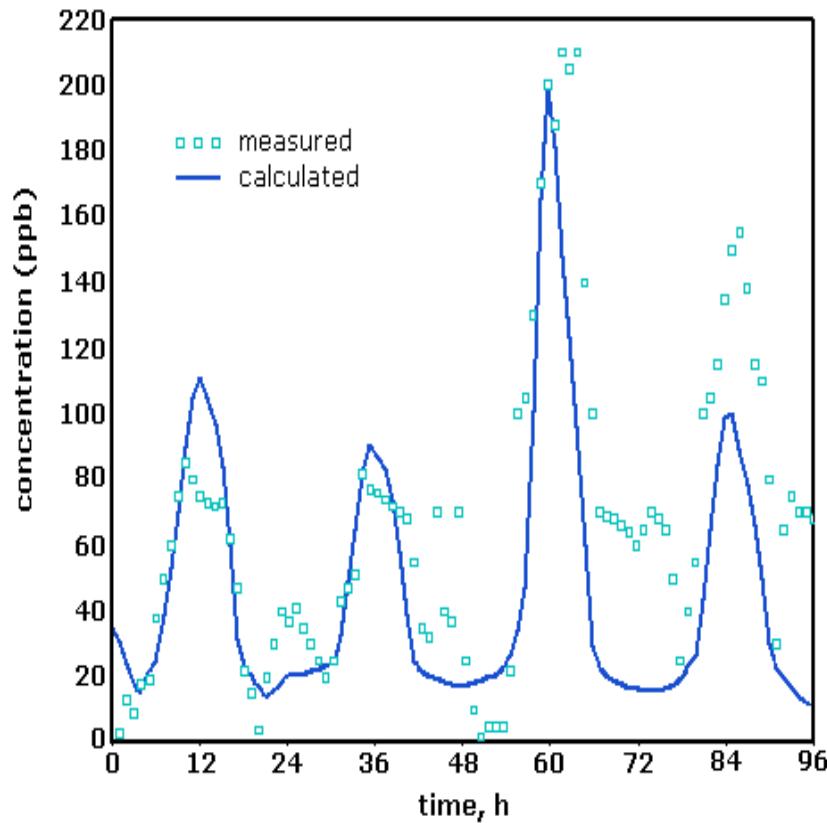
ISOP (HGBPA), 09/08/1993 12:00



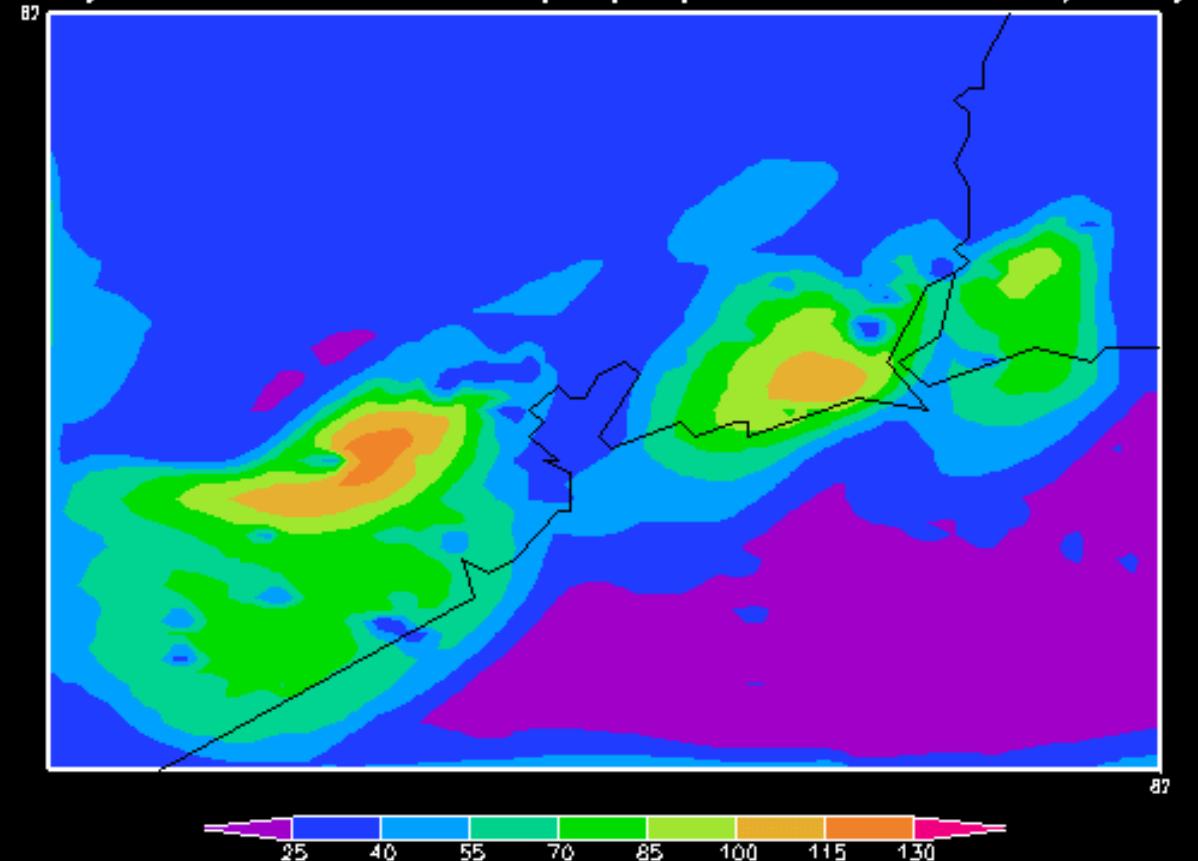
Hourly Average Ozone Concentration (ppb)
Station SPTC, 09/06/93 - 09/09/93



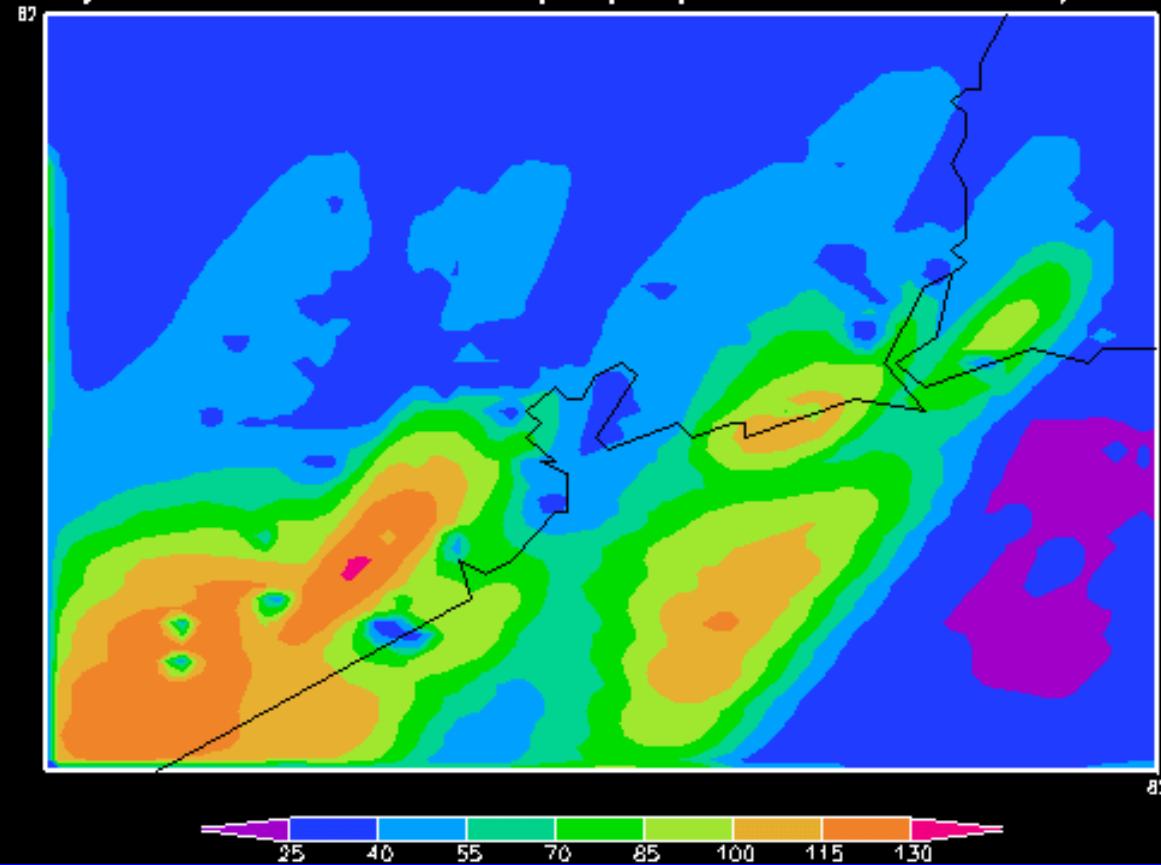
Hourly Average Ozone Concentration (ppb)
Station SBRC, 09/06/93 - 09/09/93



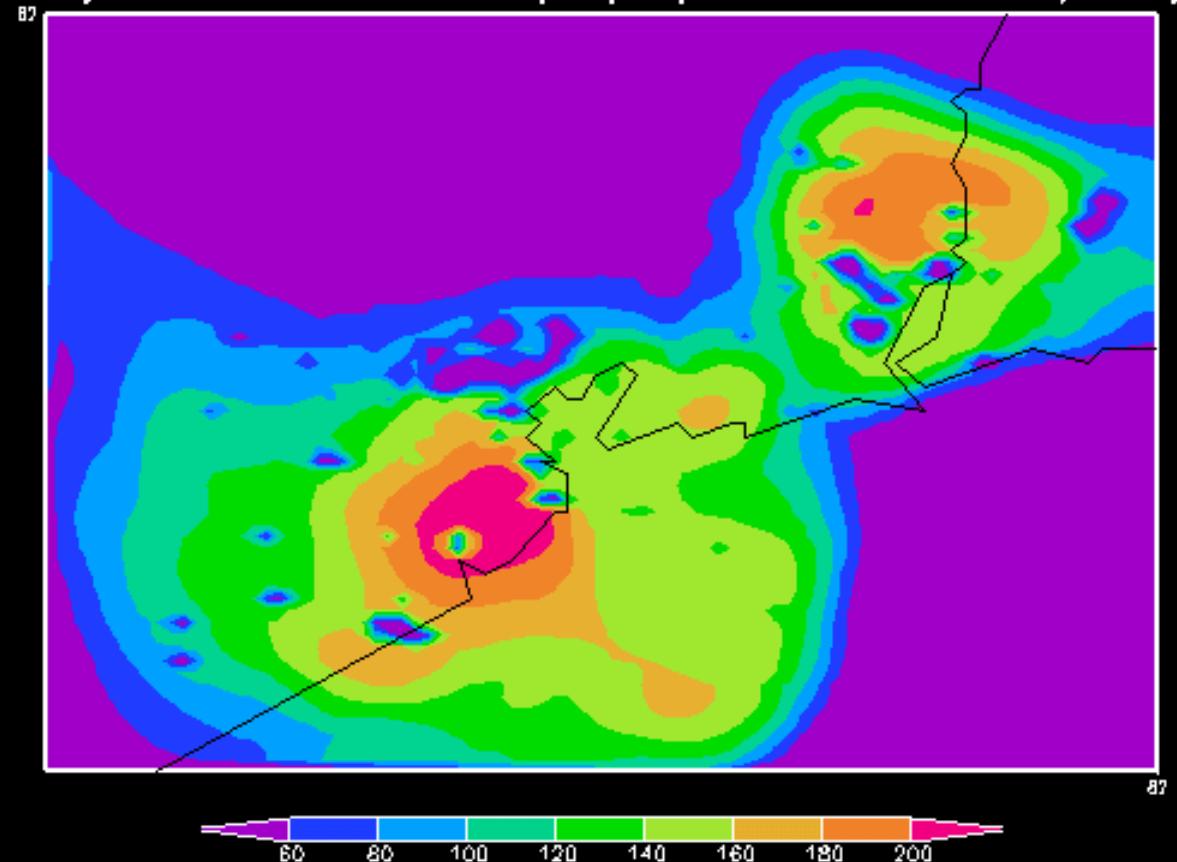
Daily Max One-Hour Ozone, /09/06/93, Max = 121 at {25,27}



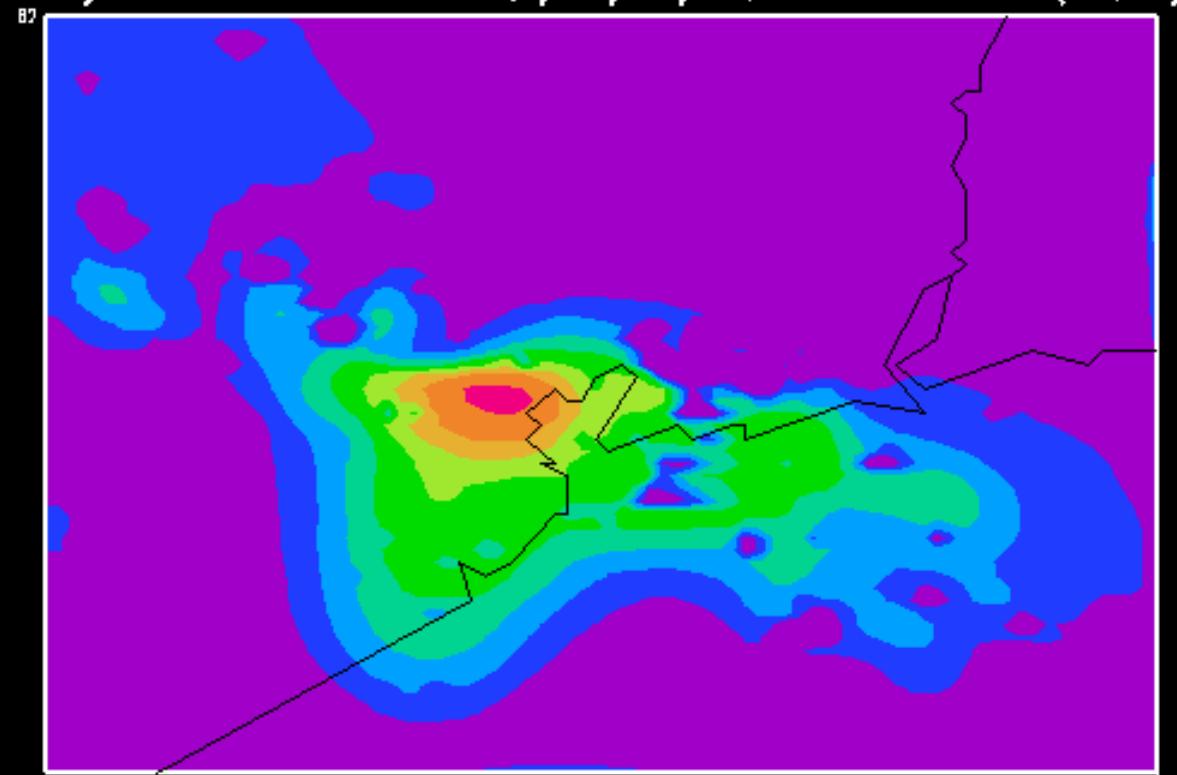
Daily Max One-Hour Ozone, /09/07/93, Max = 121 at {25,27}



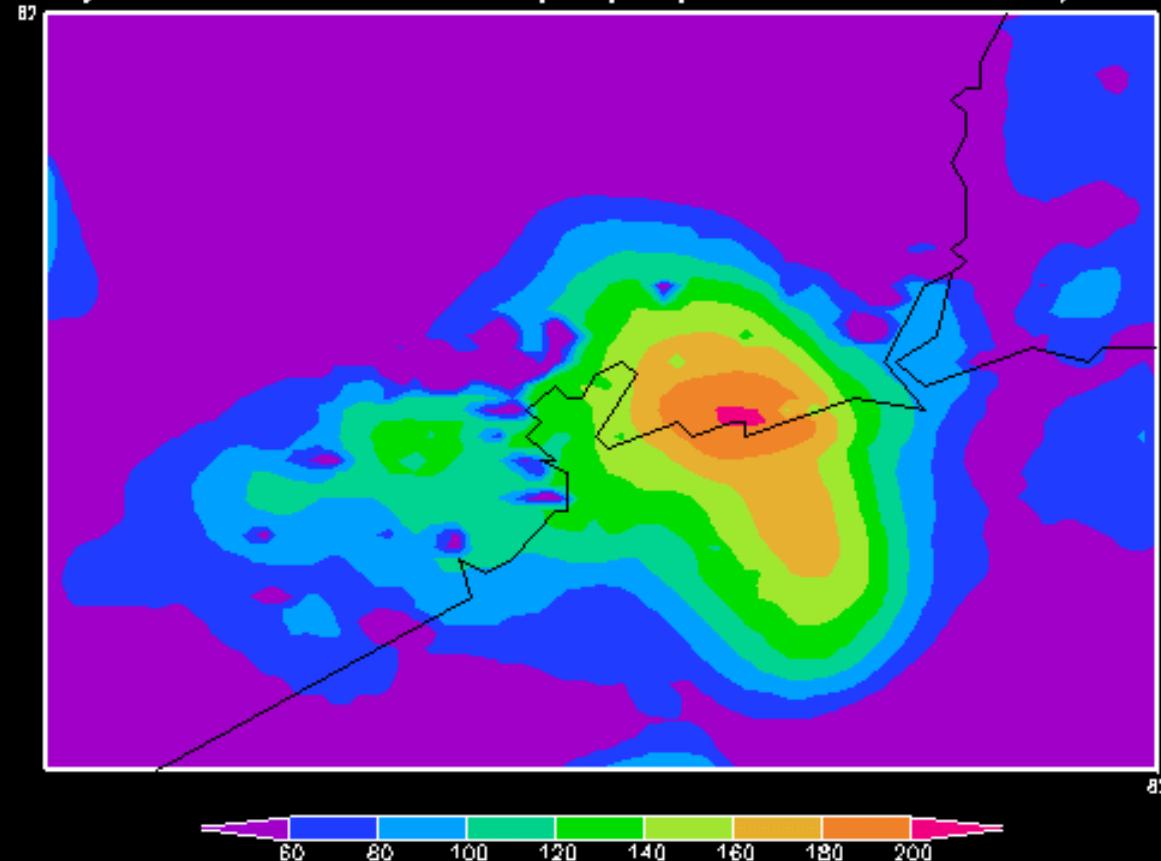
Daily Max One-Hour Ozone, /09/08/93, Max = 220 at {34,21}

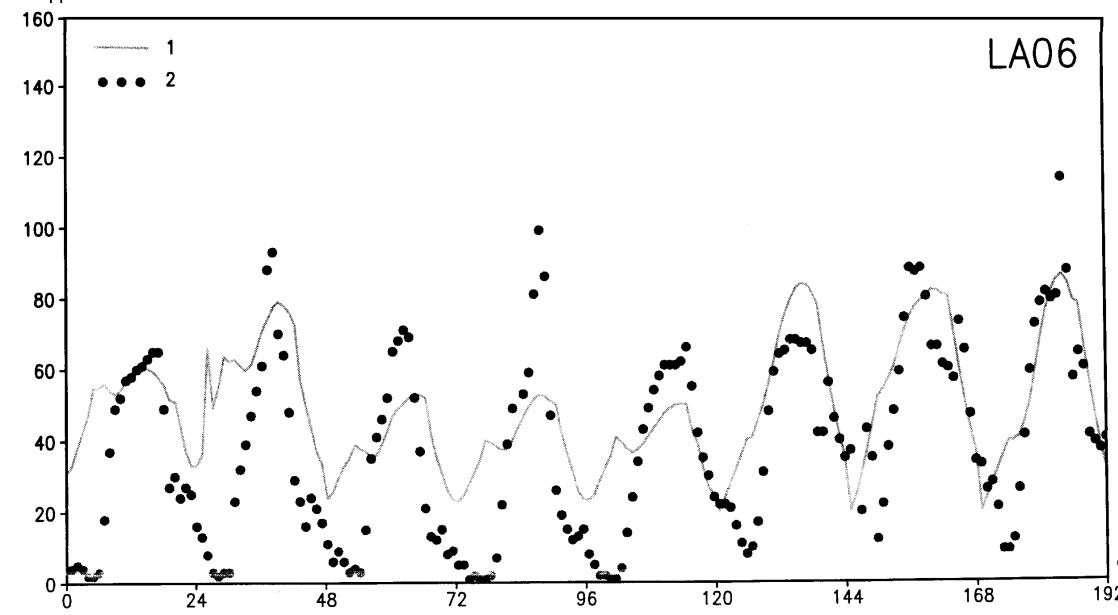
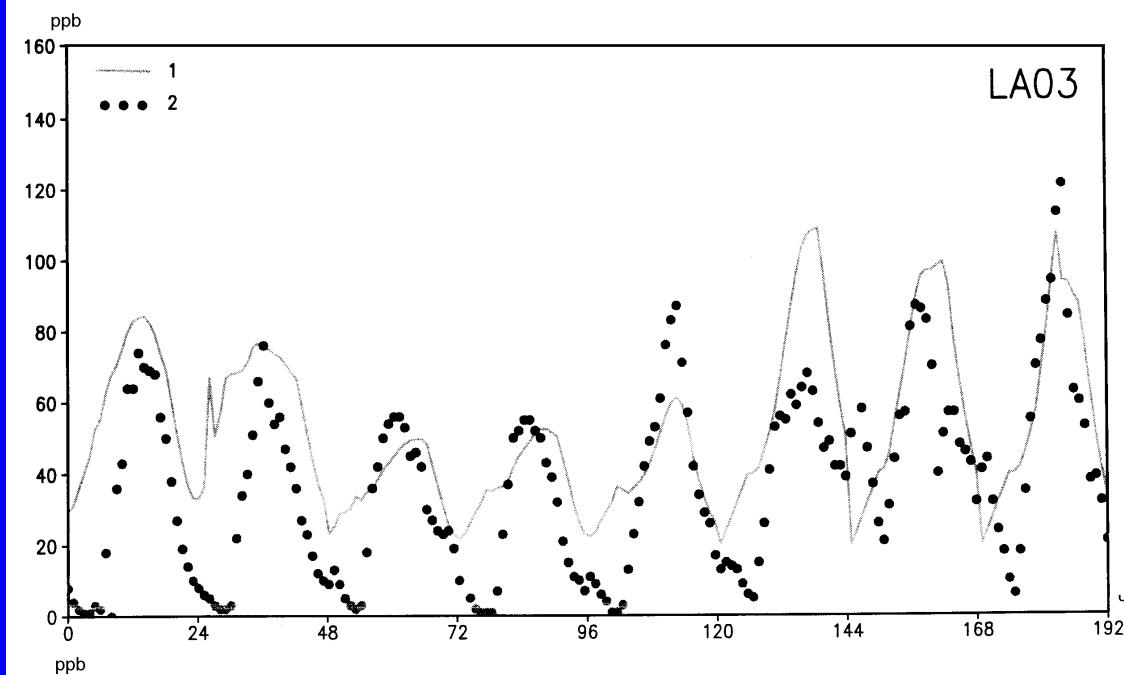


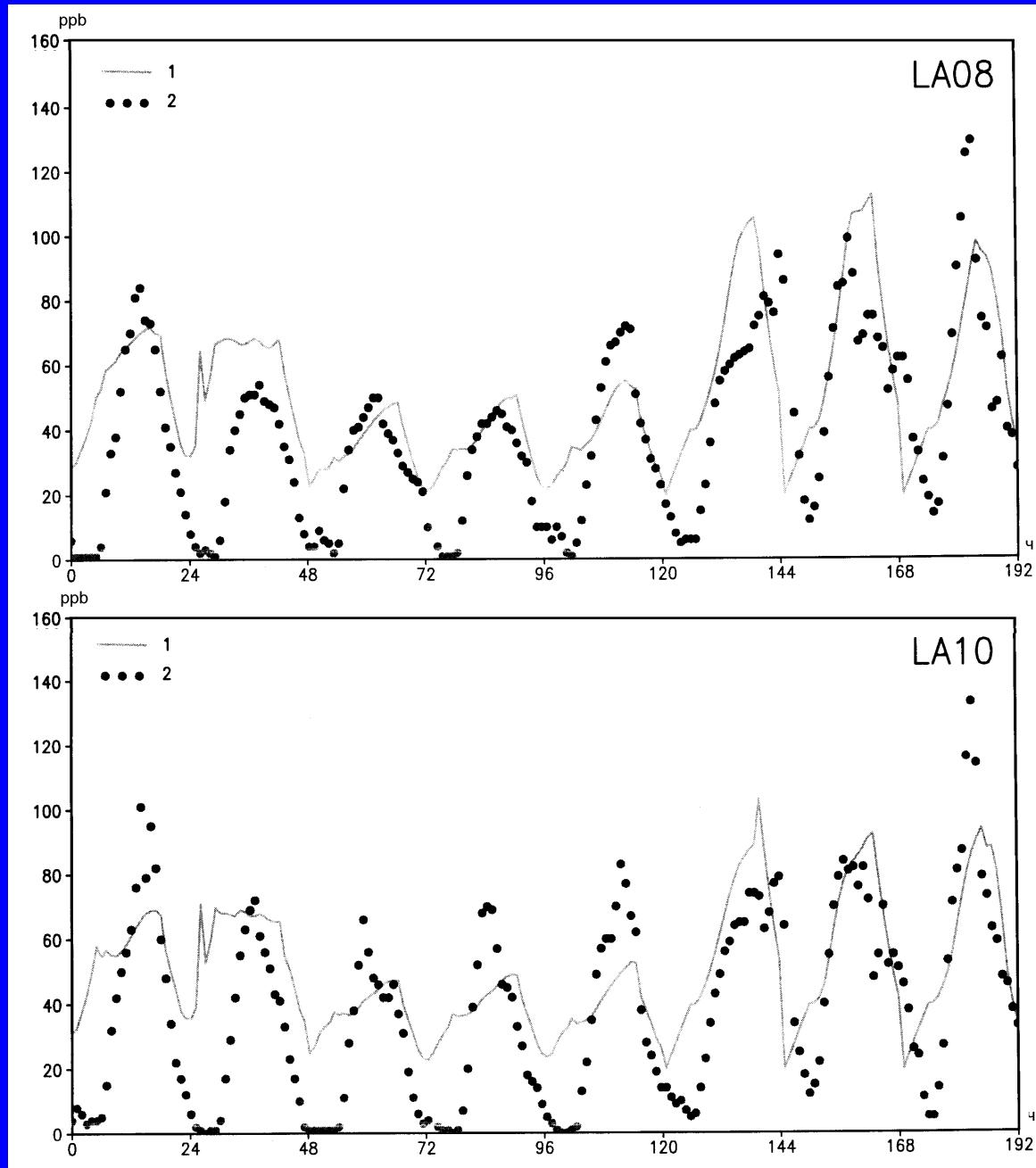
Daily Max One-Hour Ozone, /09/09/93, Max = 205 at (33,31)

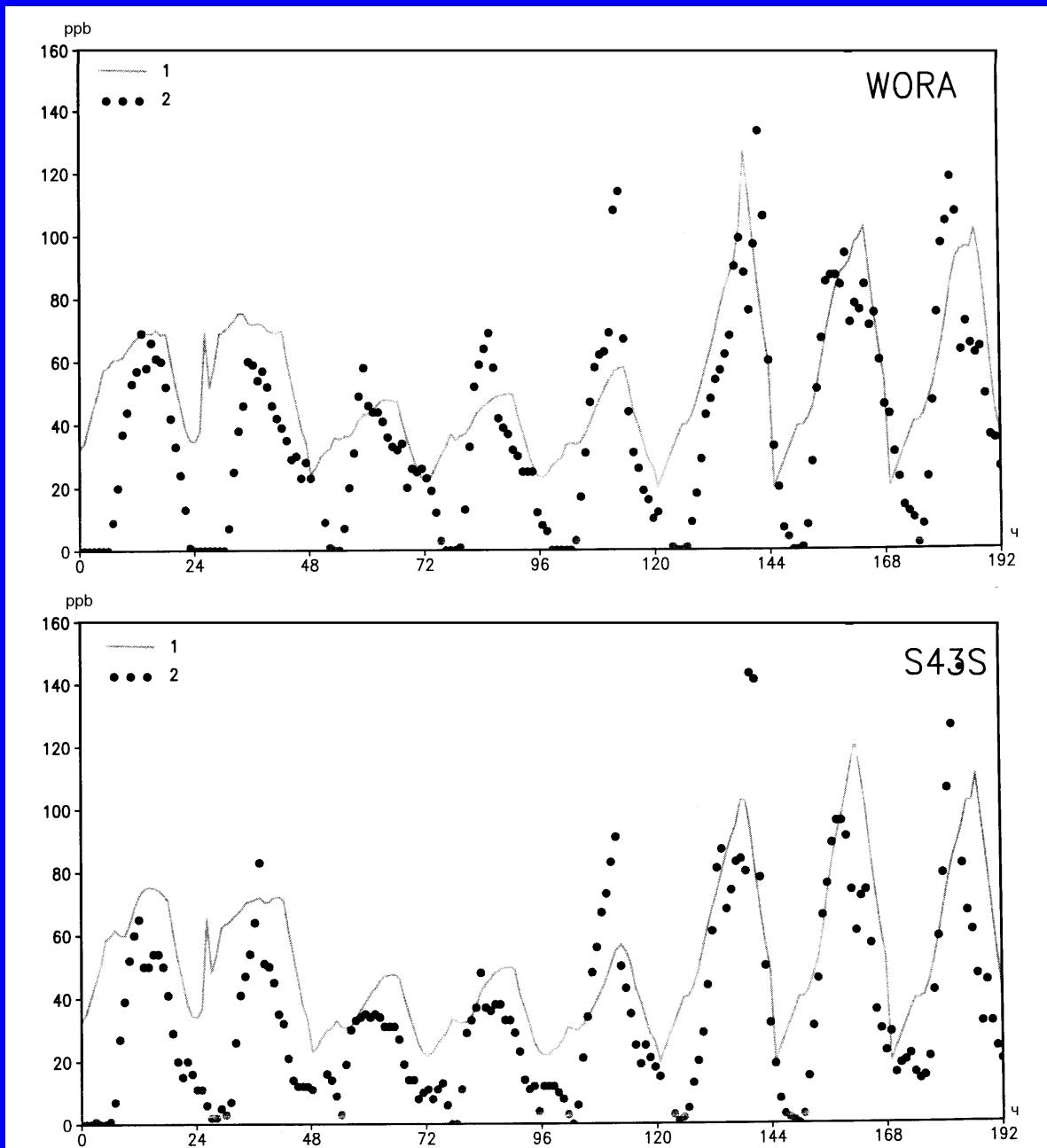


Daily Max One-Hour Ozone, /09/10/93, Max = 202 at {52,29}





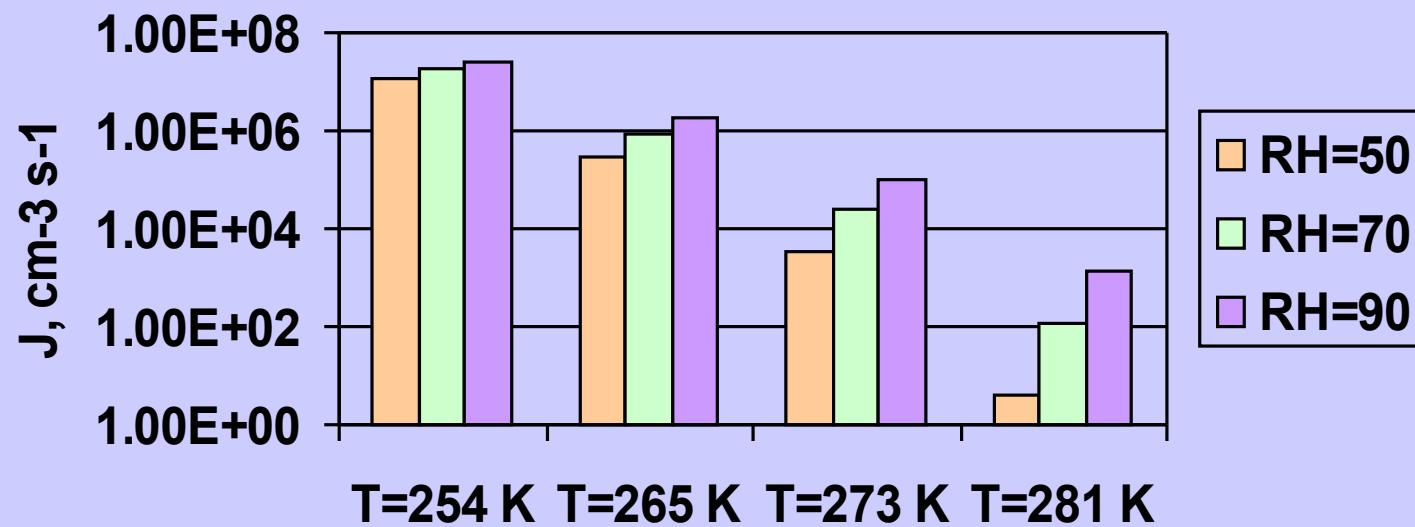




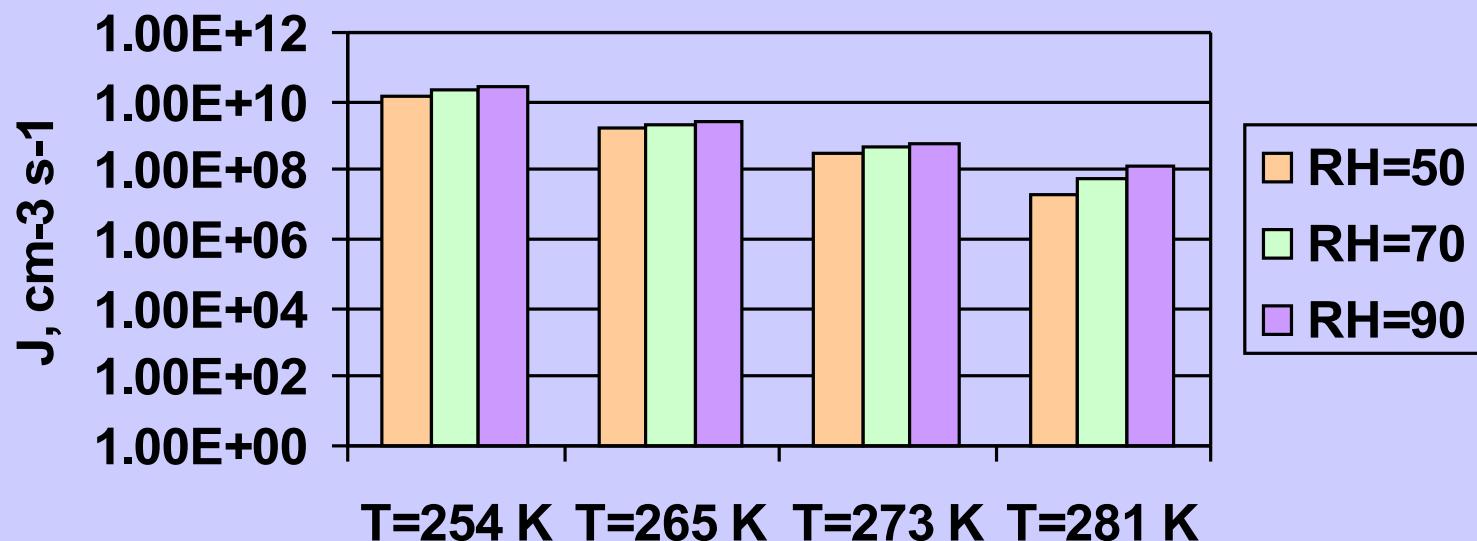
Nucleation rate
at $[H_2SO_4]=1.0E8\text{ cm}^{-3}$
log-scale



Nucleation rate
at $[H_2SO_4]=1.0E9\text{ cm}^{-3}$
log-scale



**Nucleation rate
at $[H_2SO_4]=1.0E10\text{ cm}^{-3}$
log-scale**



Nucleation rate
at $[H_2SO_4]=1.0E11\text{ cm}^{-3}$
log-scale



Critical radius at $[H_2SO_4]=1.0E8\text{ cm}^{-3}$



**Critical radius
at $[H_2SO_4]=1.0E9\text{ cm}^{-3}$**



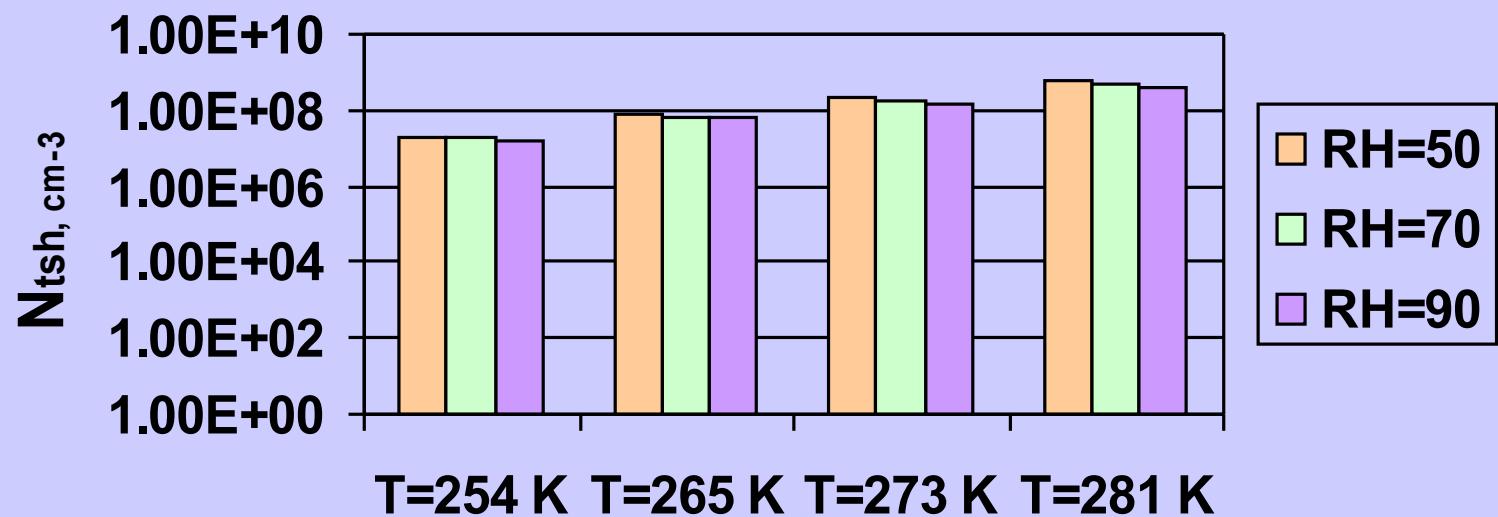
**Critical radius
at $[H_2SO_4]=1.0E10\text{ cm}^{-3}$**



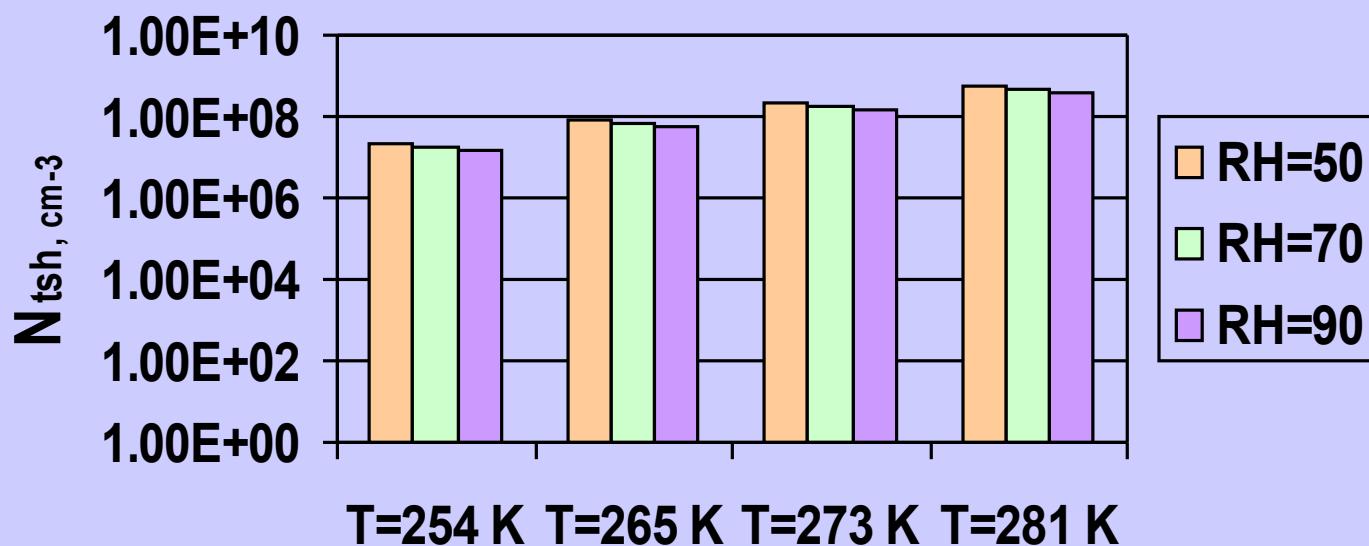
**Critical radius
at $[H_2SO_4]=1.0E11\text{ cm}^{-3}$**



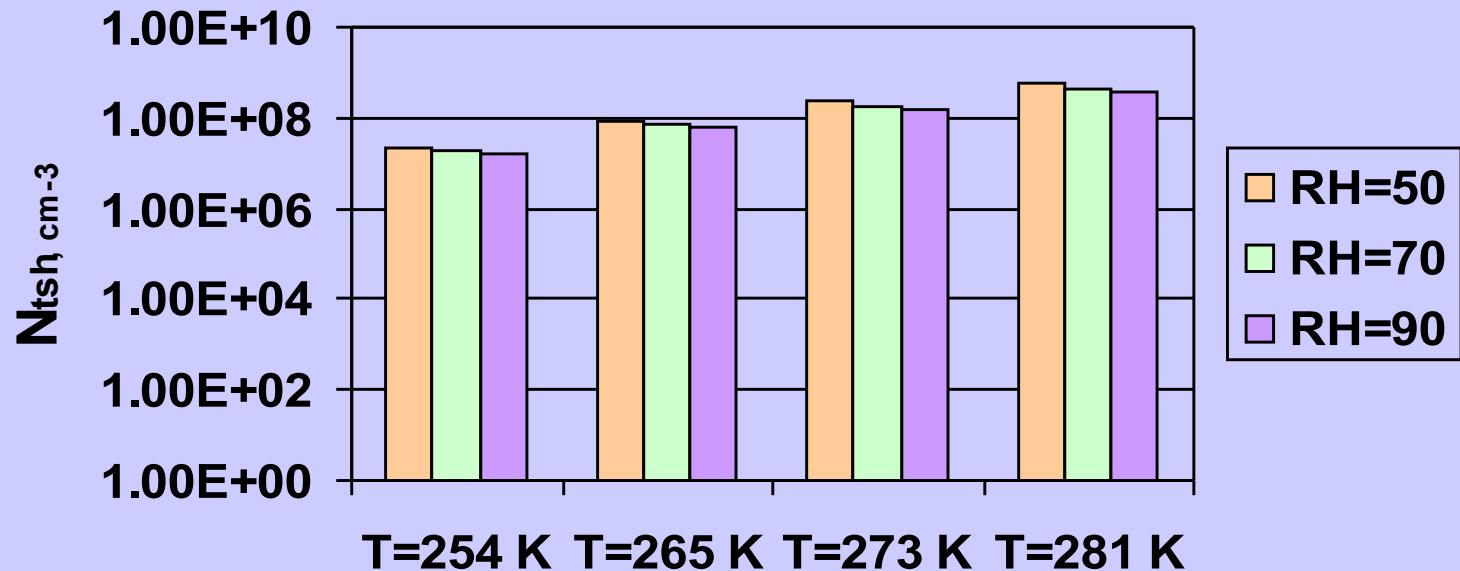
Threshold concentration at $[H_2SO_4]=1.0E8\text{ cm}^{-3}$ log-scale



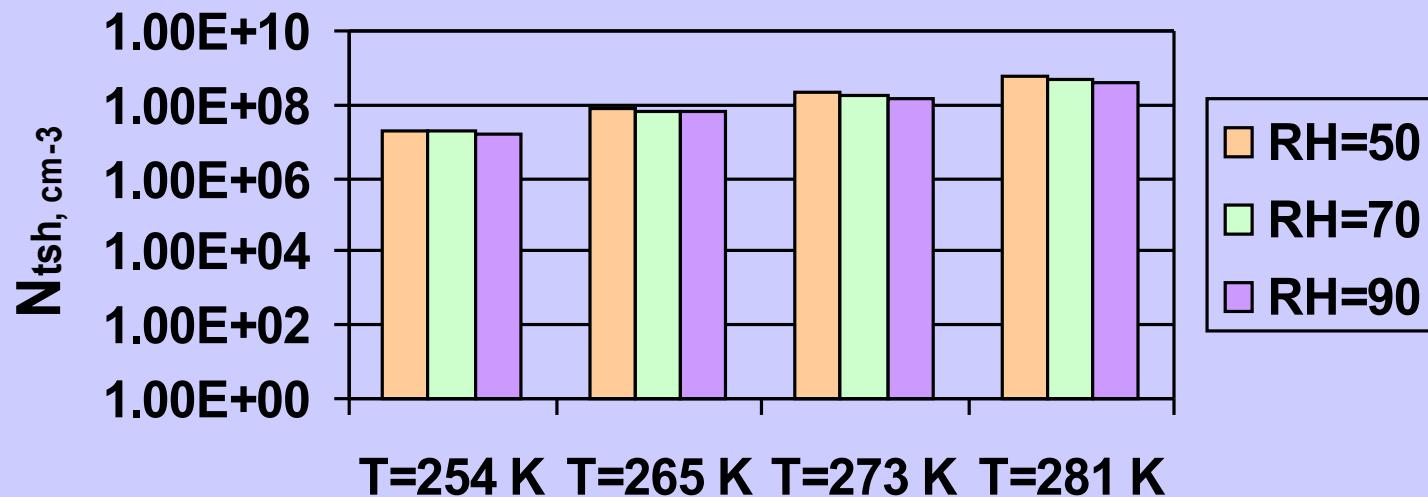
**Threshold concentration
at $[H_2SO_4]=1.0E9\text{ cm}^{-3}$
log-scale**



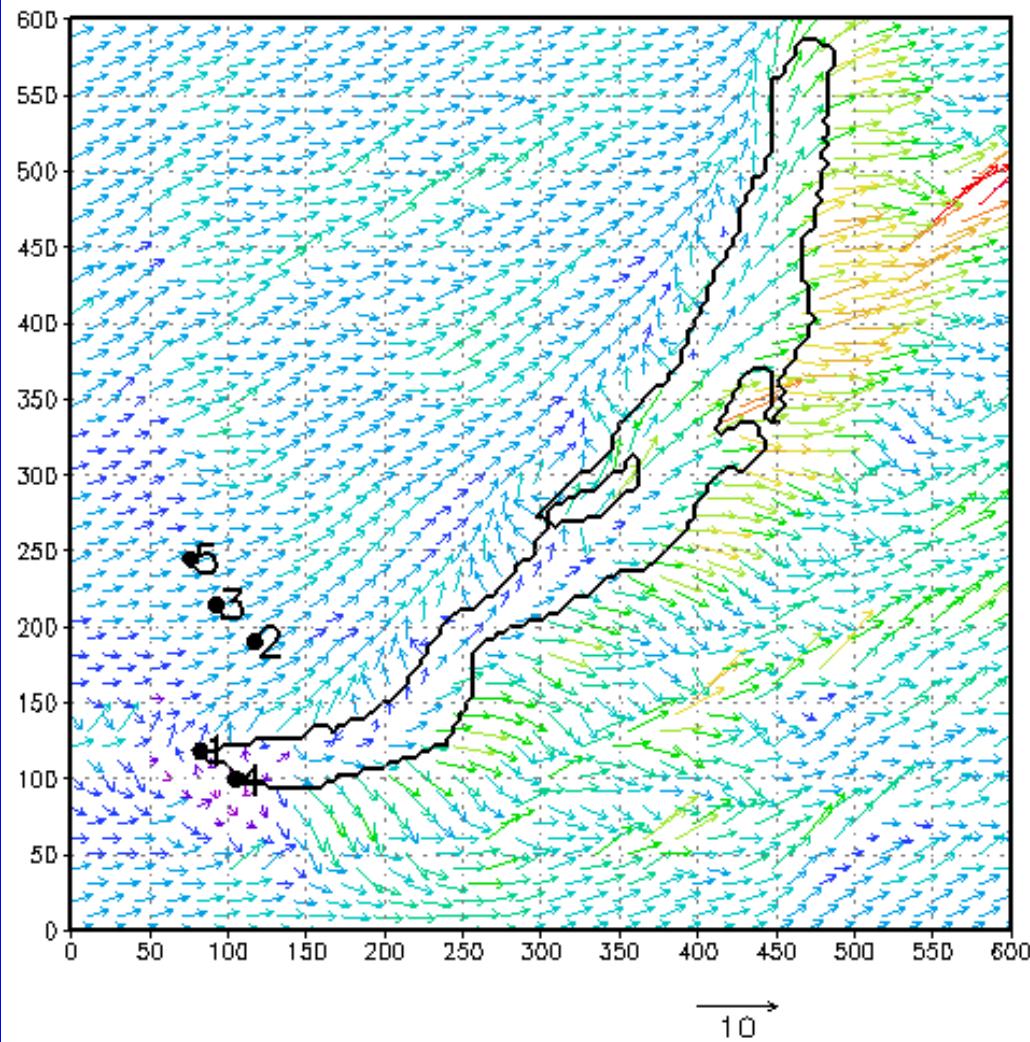
**Threshold concentration
at $[H_2SO_4]=1.0E10\text{ cm}^{-3}$
log-scale**

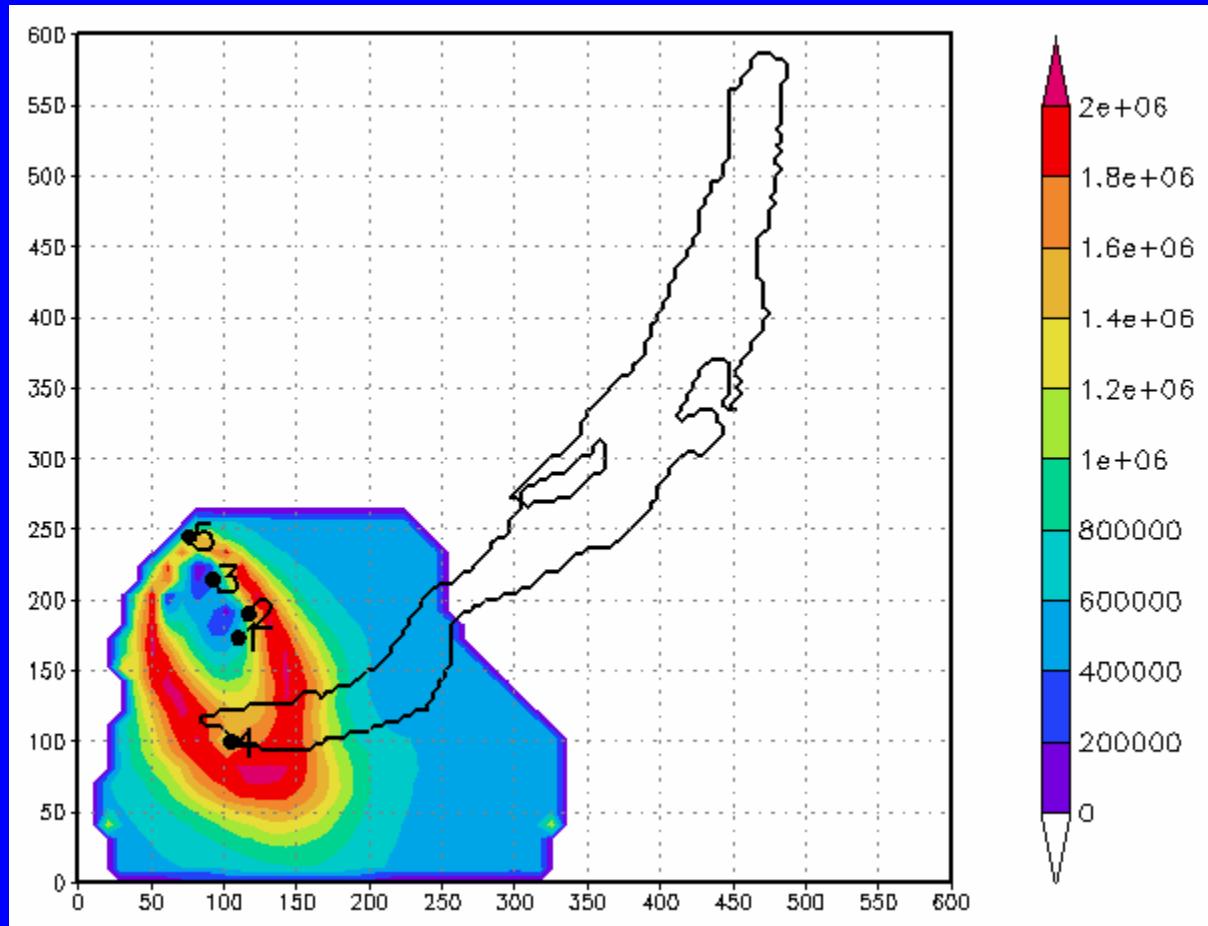


**Threshold concentration
at $[H_2SO_4]=1.0E11\text{ cm}^{-3}$
log-scale**

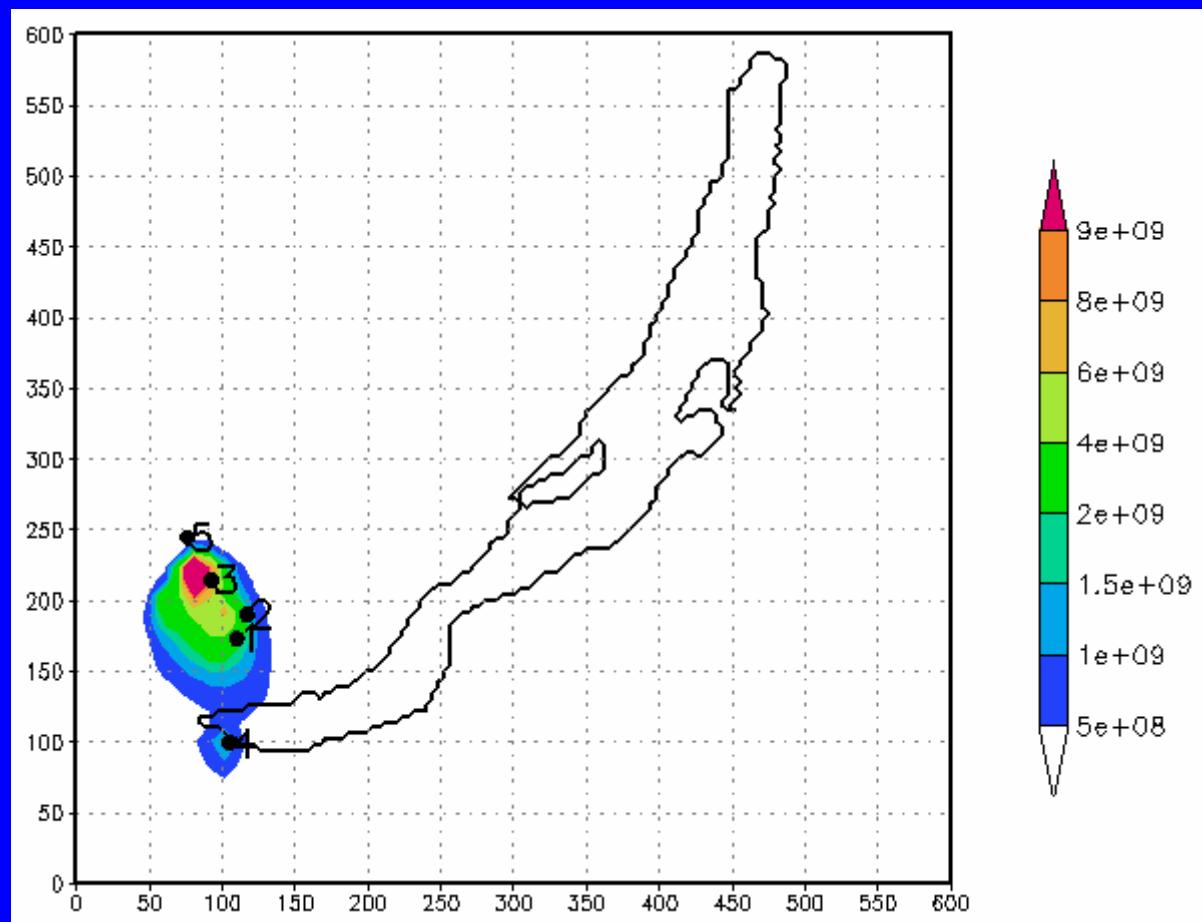


Wind flow field at t=14h

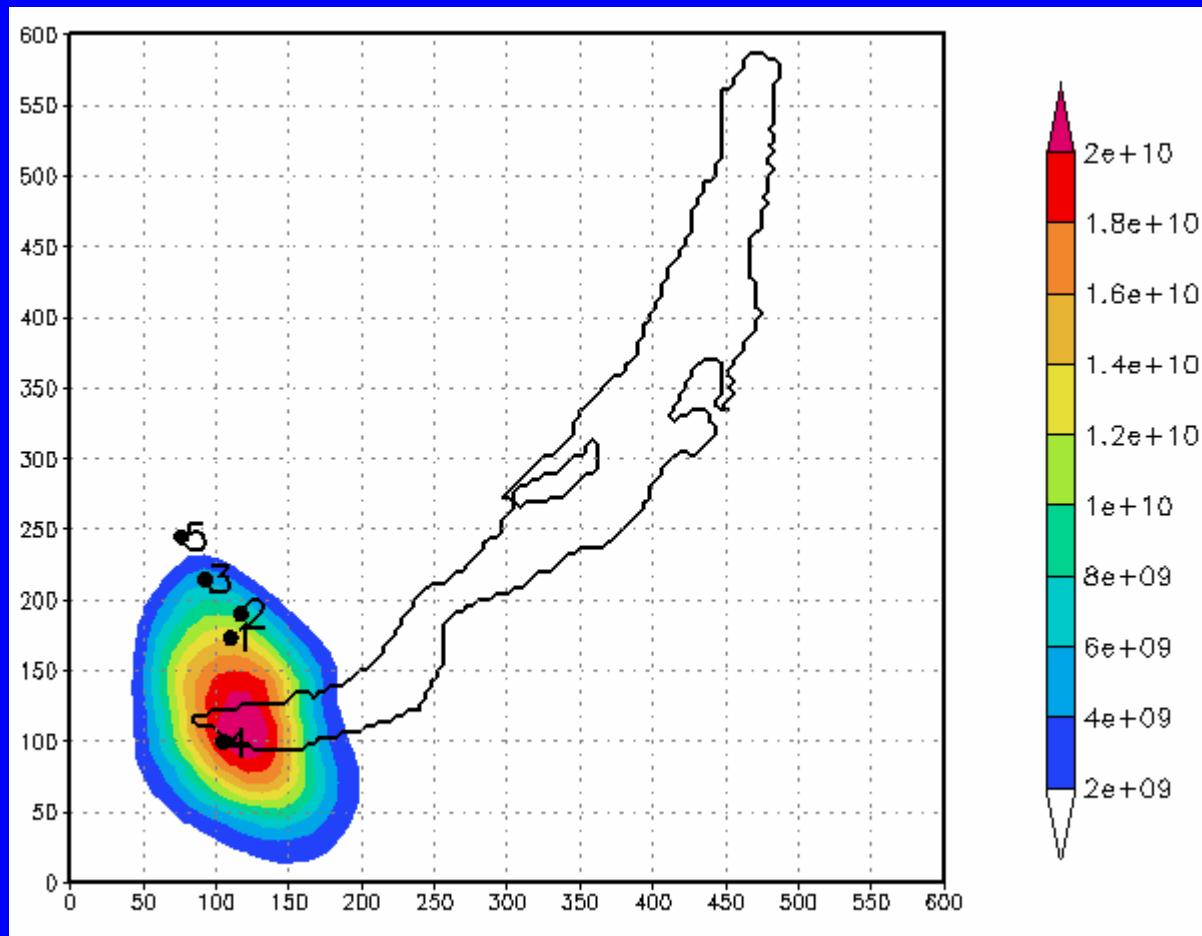




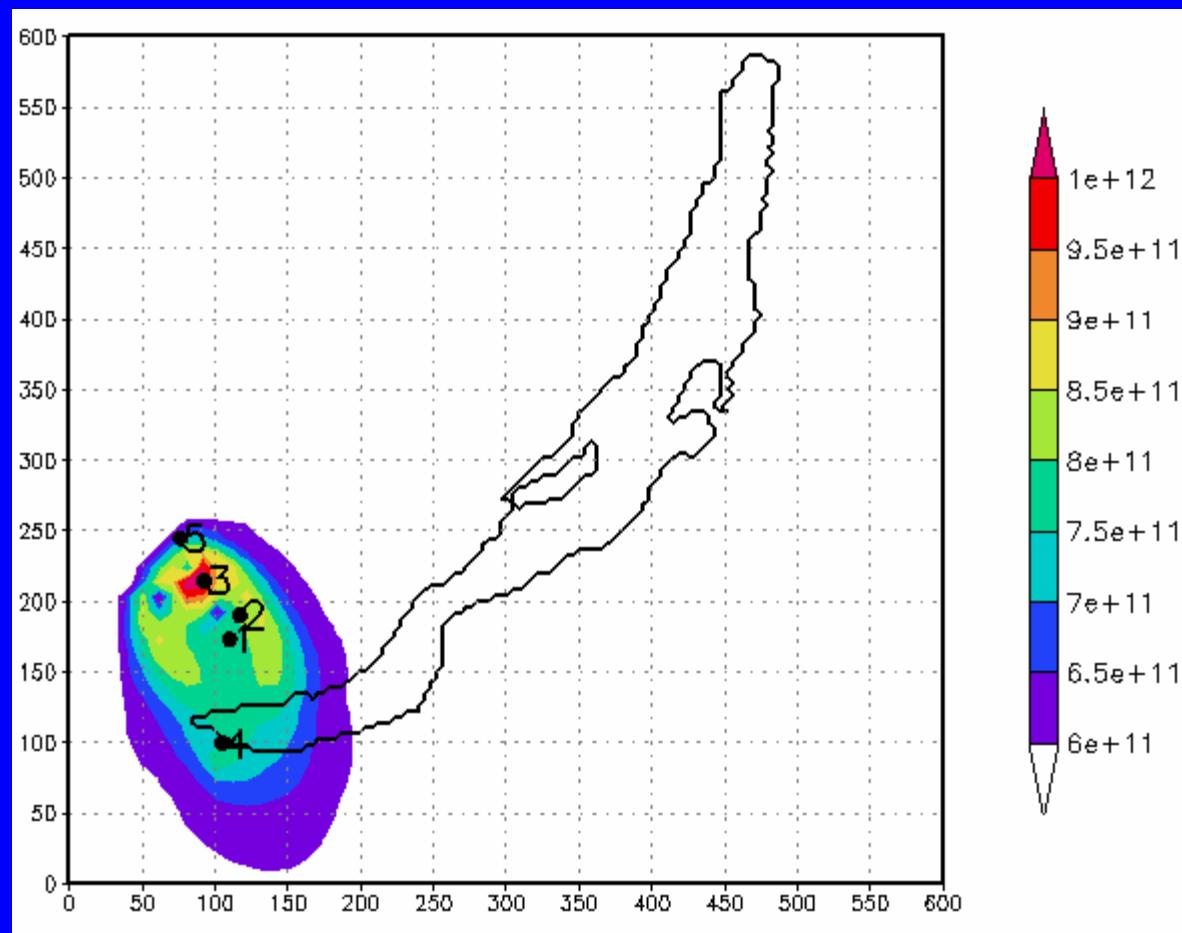
Concentration of OH after 12 h of calculation time_



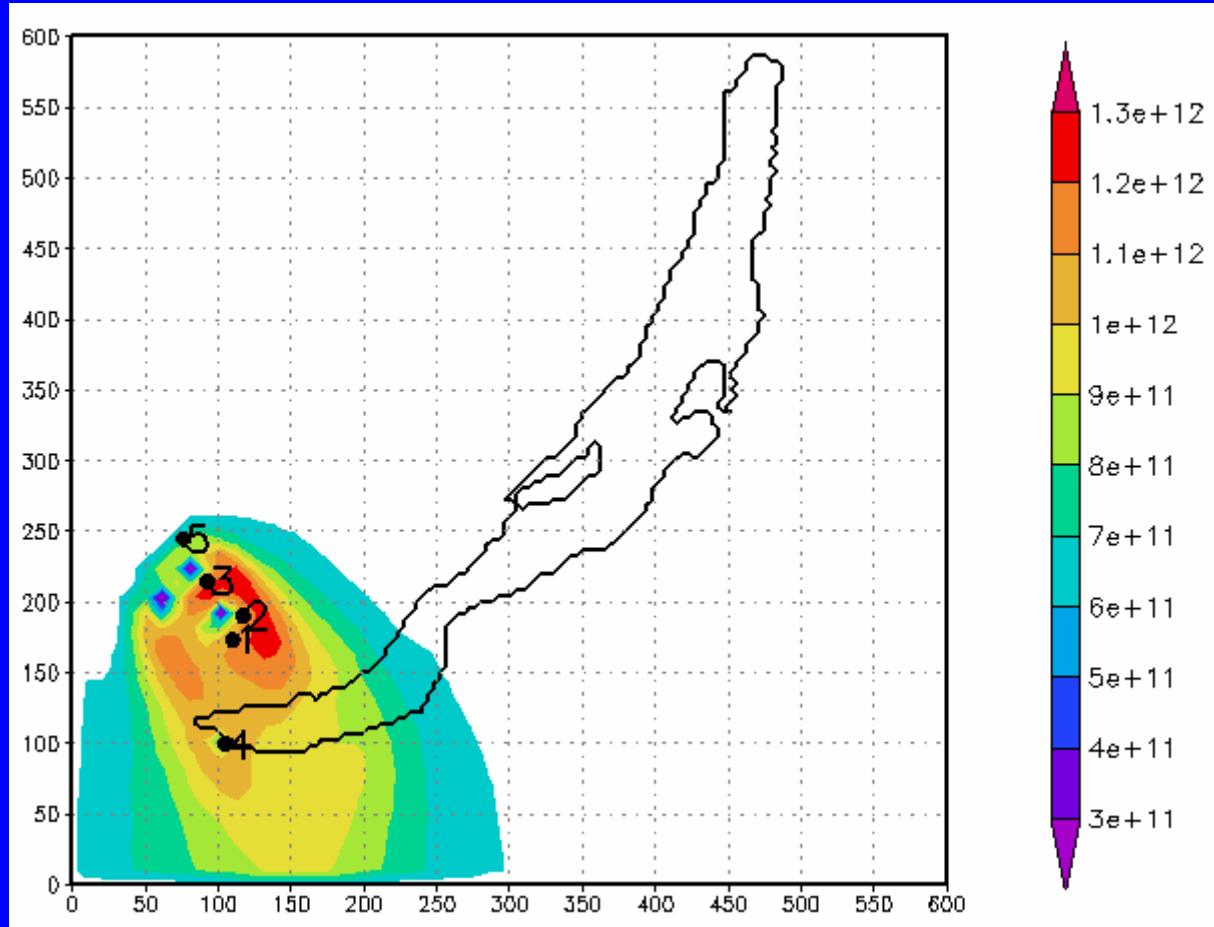
Concentration of H_2SO_4 after 12 h of calculation time_



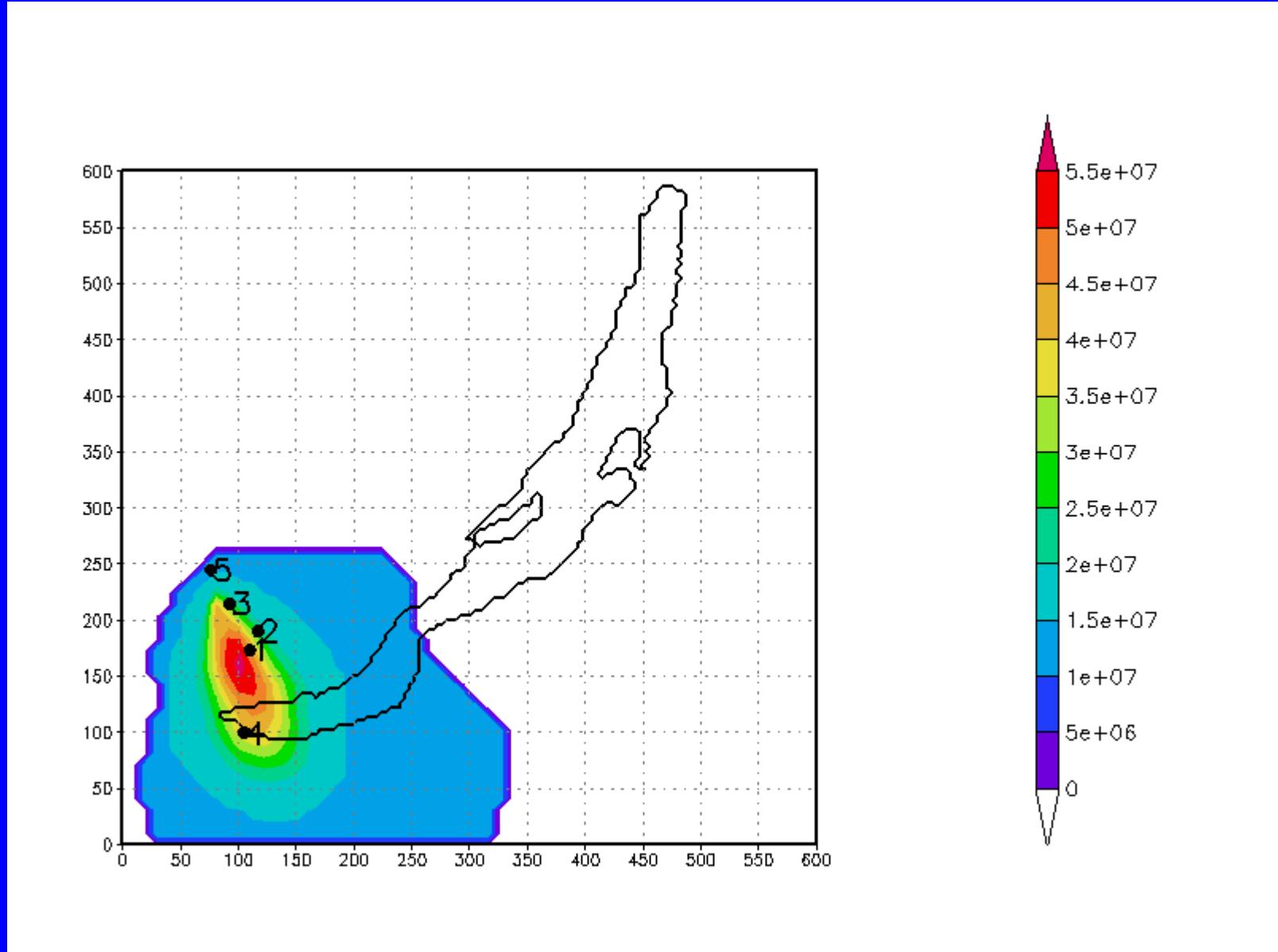
Concentration of HNO_3 after 12 h of calculation time.



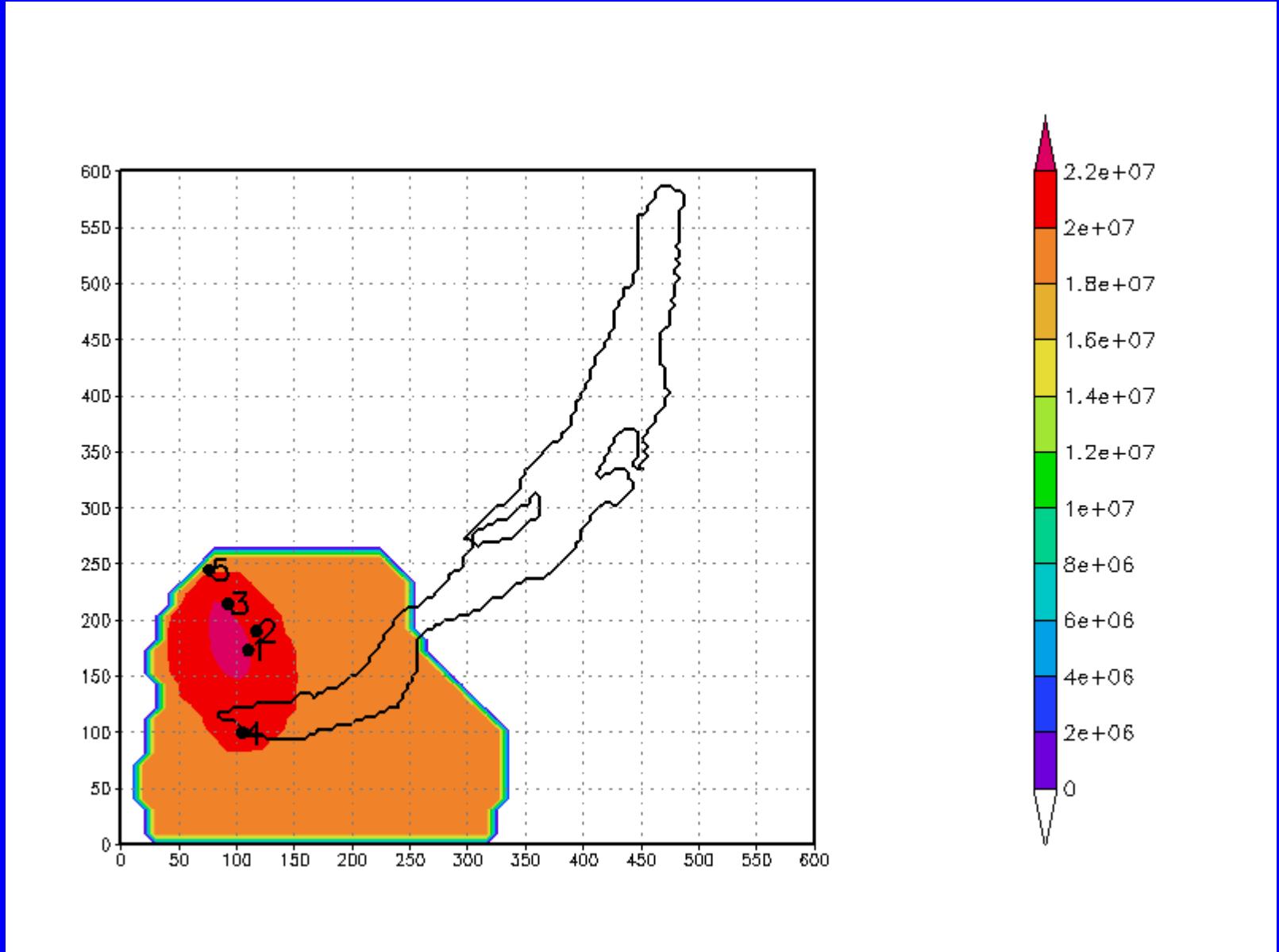
Concentration of O_3 after 12 h of calculation time



Concentration of O_3 after 38 h of calculation time_



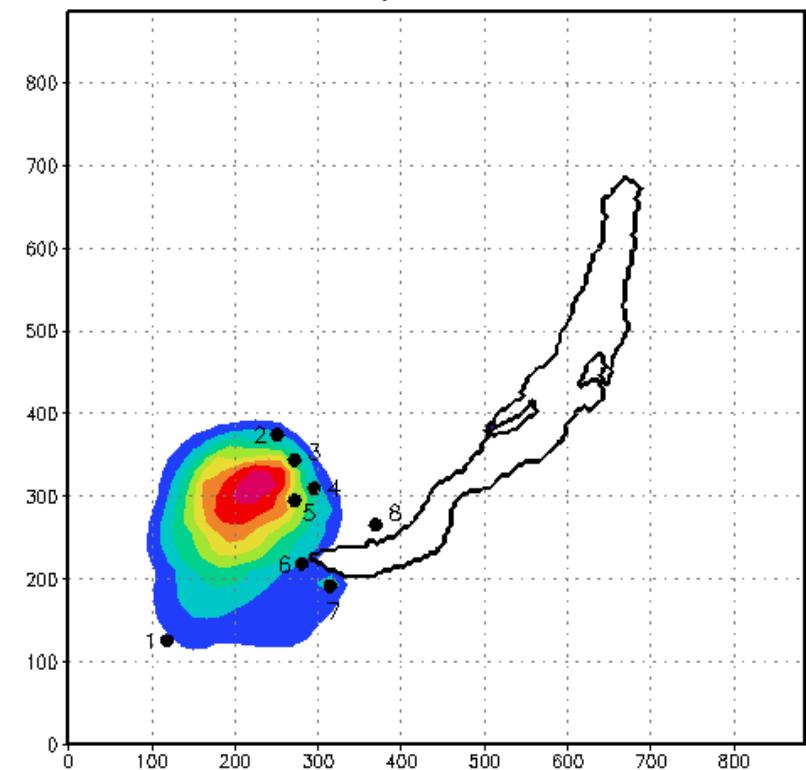
Number concentration of aerosol particles with radius 16 nm after 12 h of the calculation time_



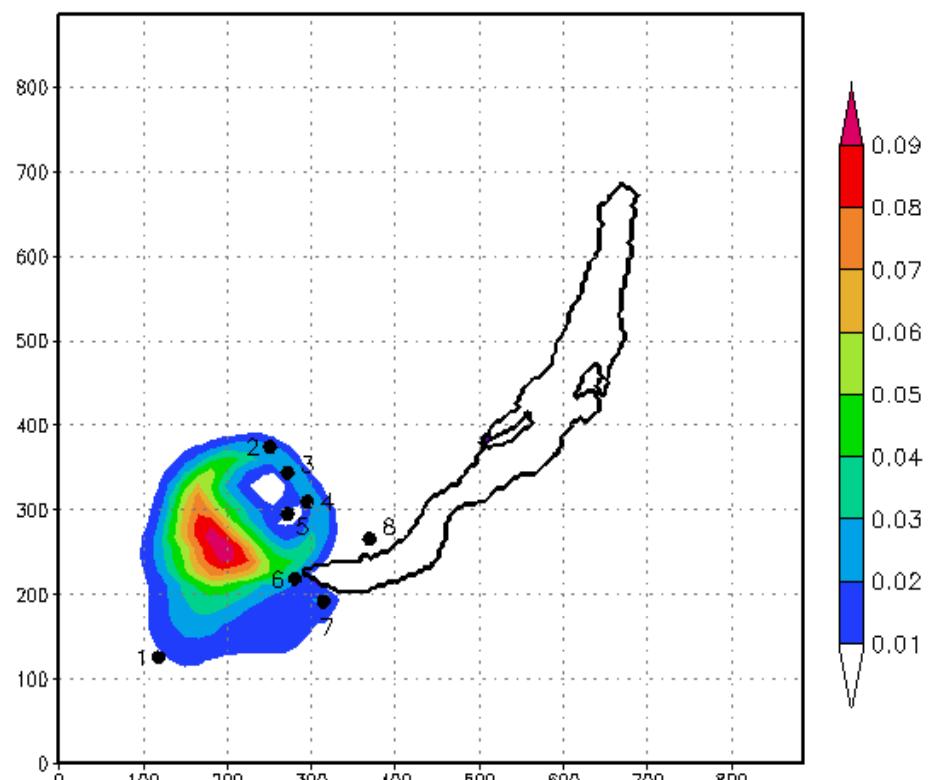
Number concentration of aerosol particles with radius $0.41 \mu\text{m}$ after 12 h of the calculation time_



SO_4^{2-} , 24 h, R1



H^+ , 24 h, R1

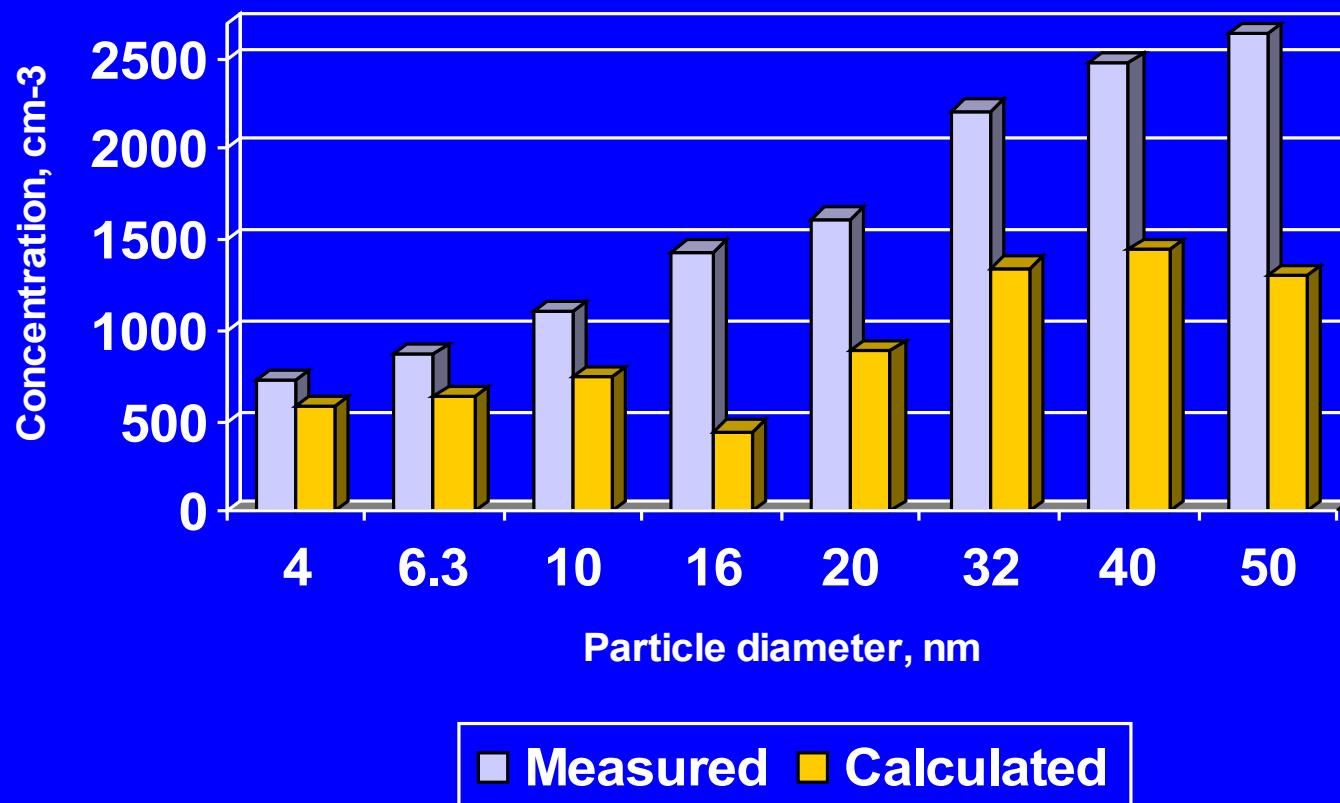


Иркутск (июль, 2003), t = 13 ч

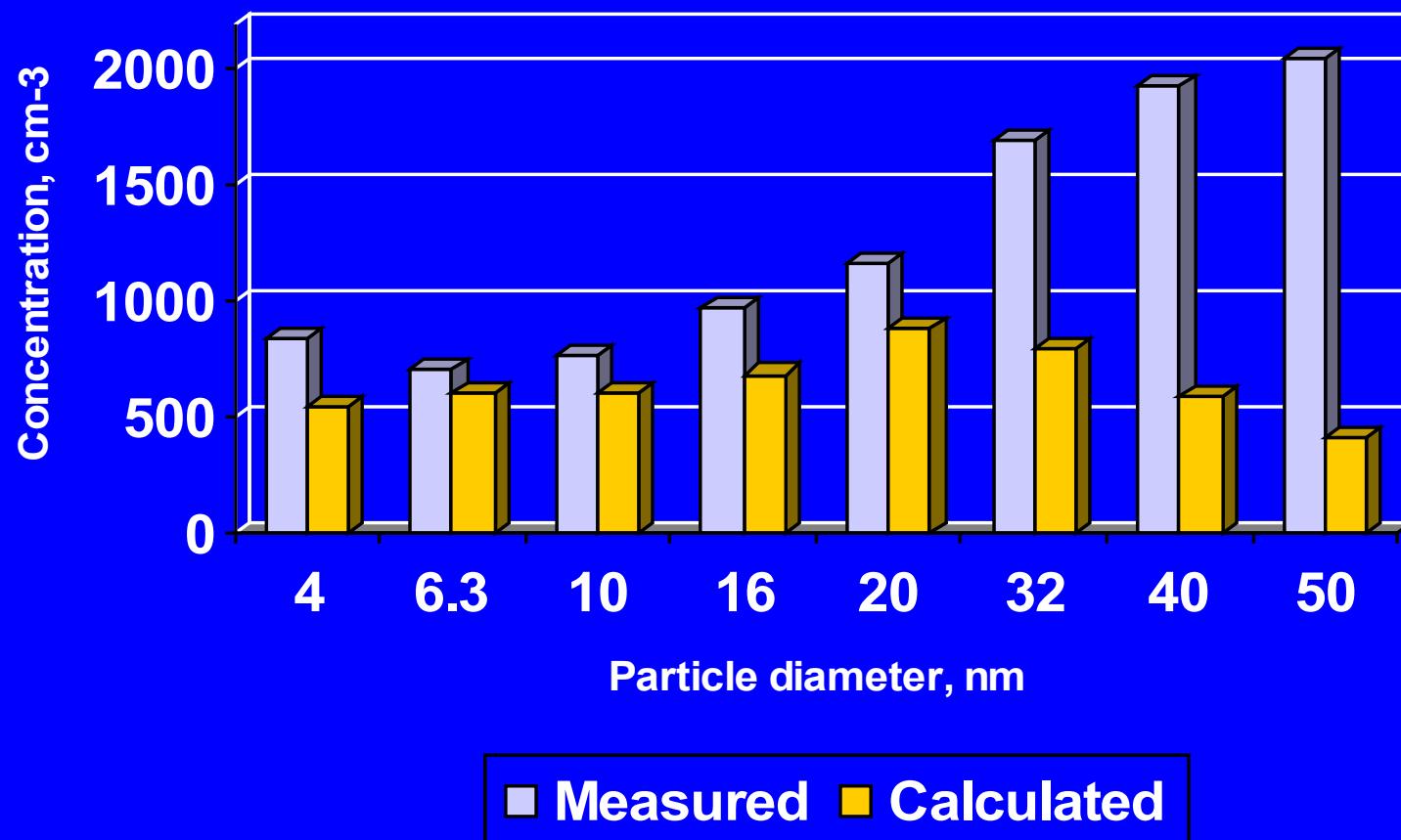
ионы	<i>расчет</i> (мкг/м ³)	<i>измерение</i> (мкг/м ³)
H ⁺	0.0024	0.0081
NH ₄ ⁺	0.7	0.93
NO ₃ ⁻	0.65	0.47
HSO ₄ ⁻	2.66	
SO ₄ ²⁻	0.62	4.33

ИФА - TROICA

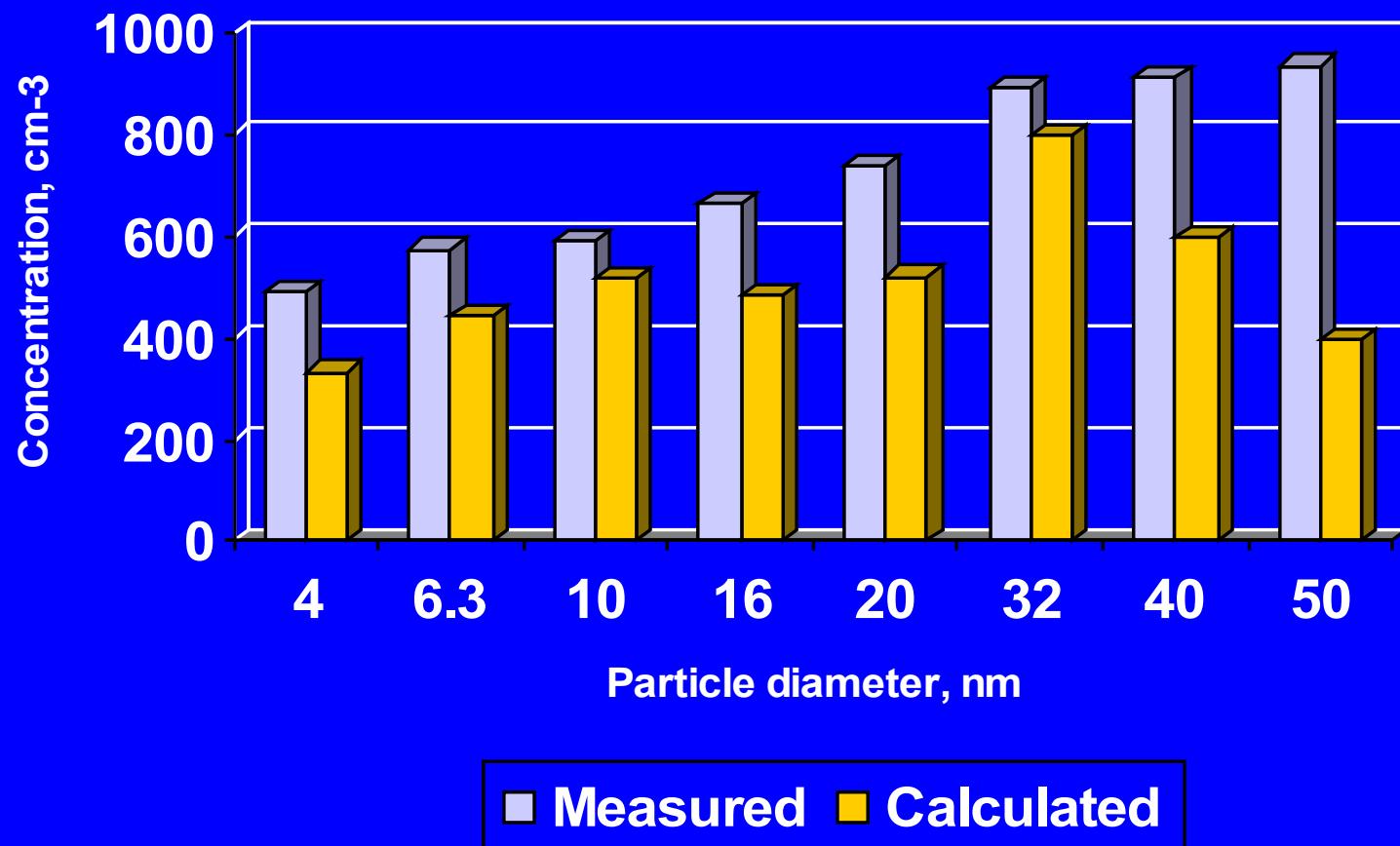
Irkutsk, 22/03/2004



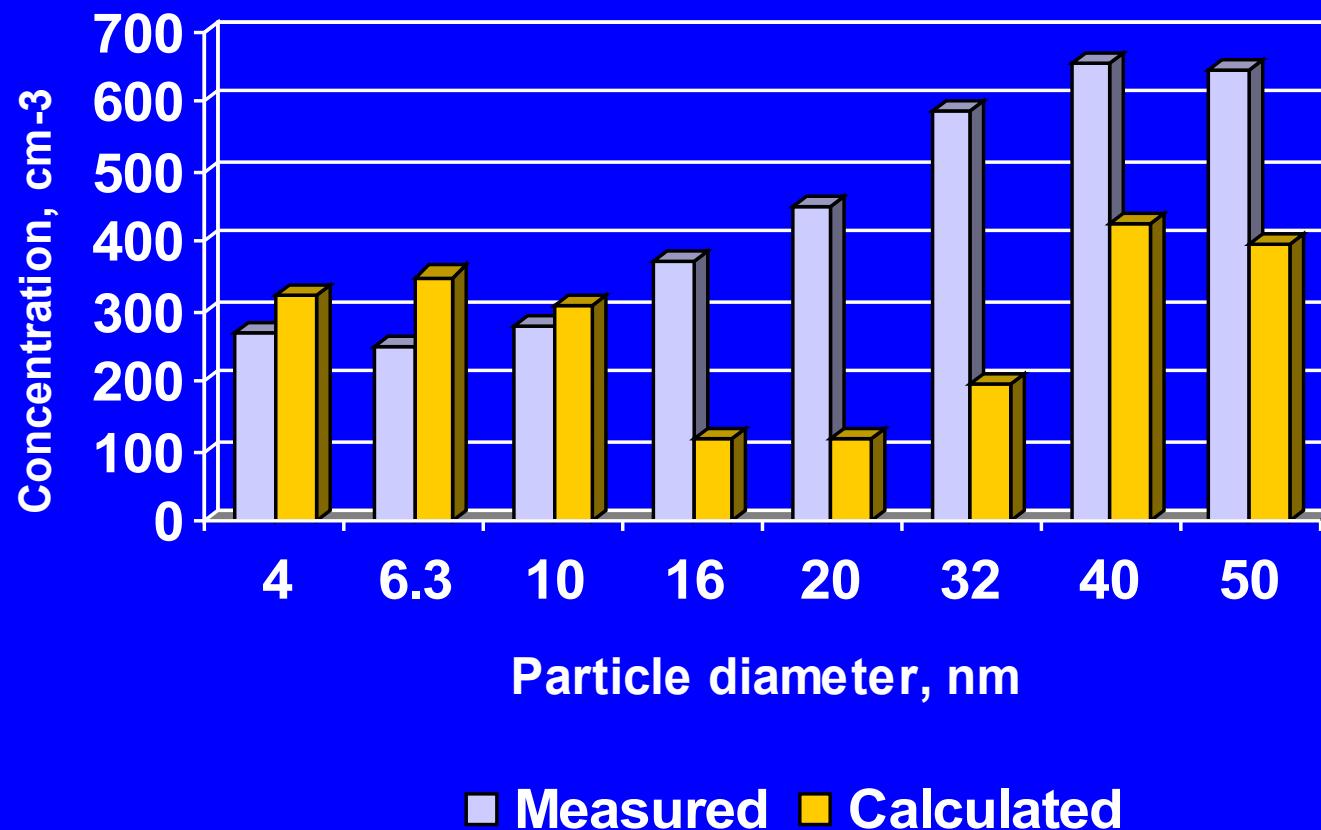
Shelekhovo, 22/03/2004



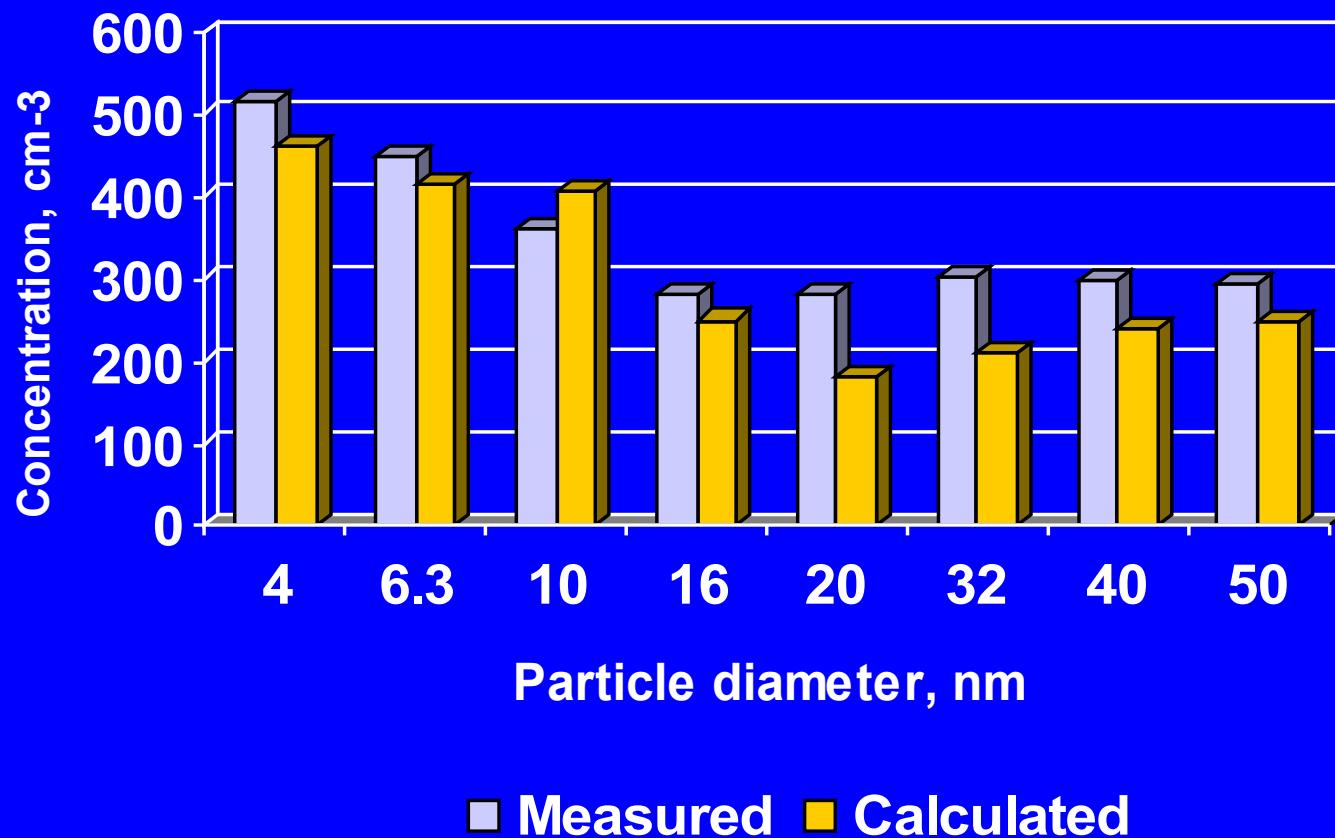
Bol'shoi Lug, 22/03/2004



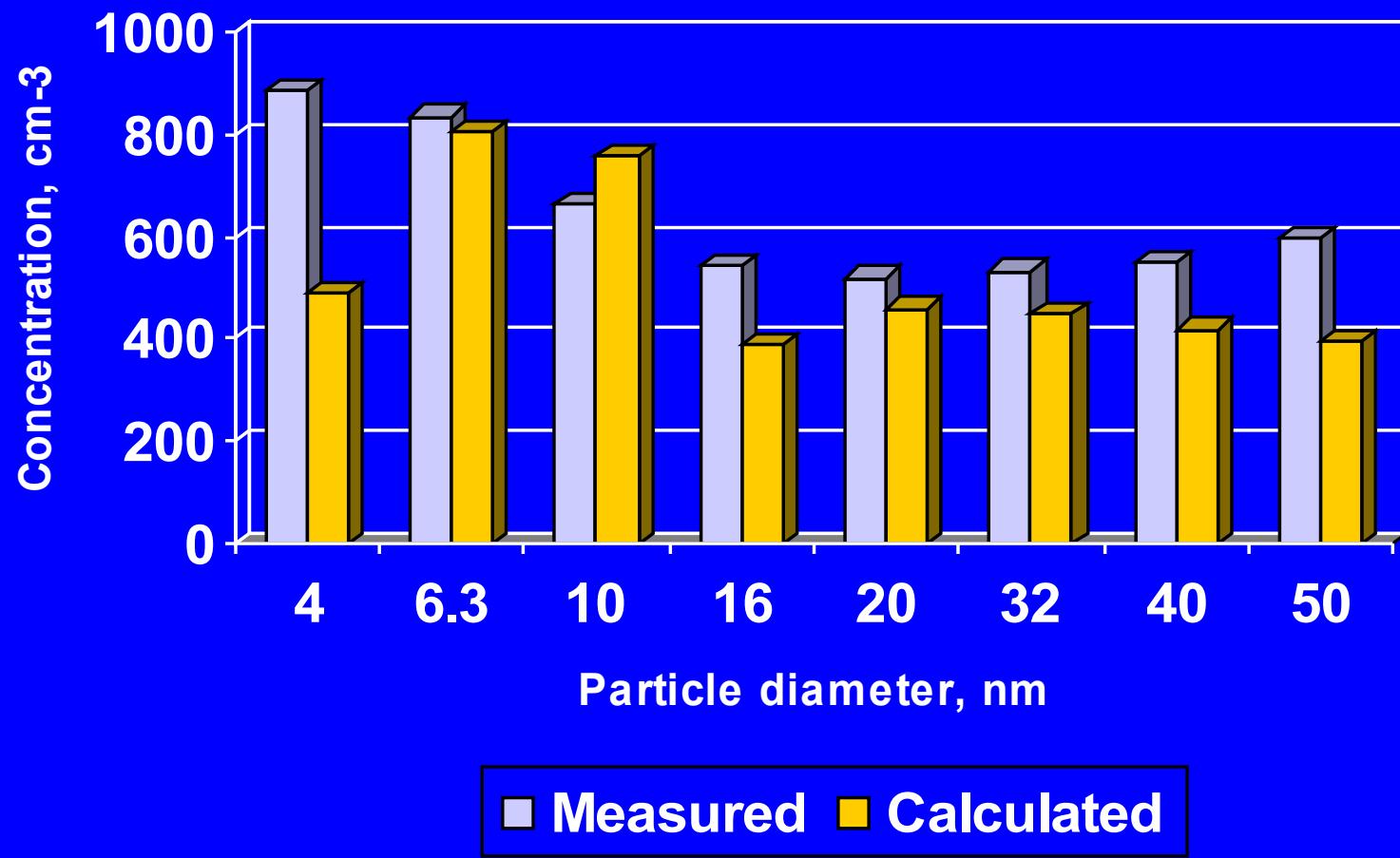
Sludyanka, 22/03/2004



Between Bol'shoi Lug and Slyudyanka, 22/03/2004

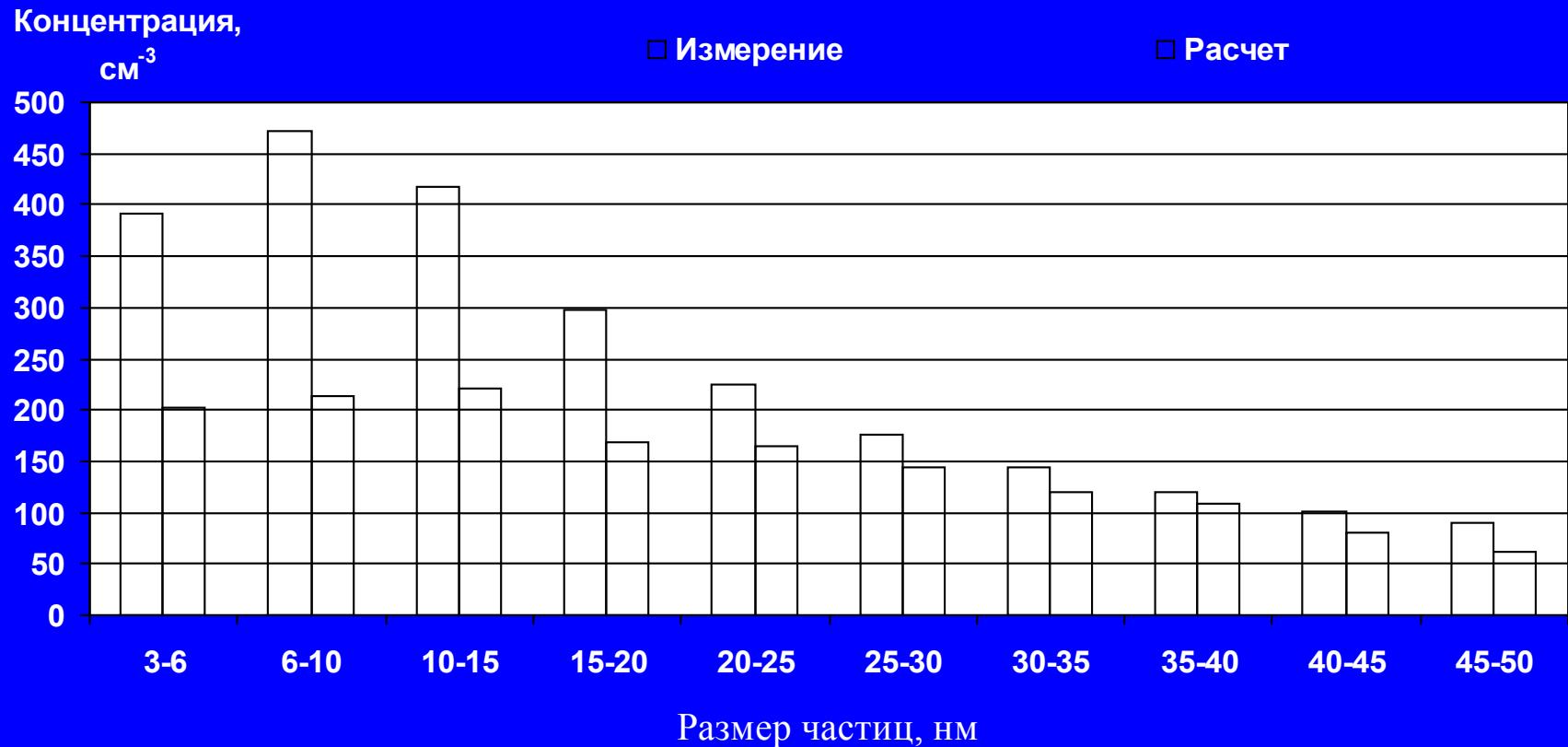


Baykal'sk, 22/03/2004



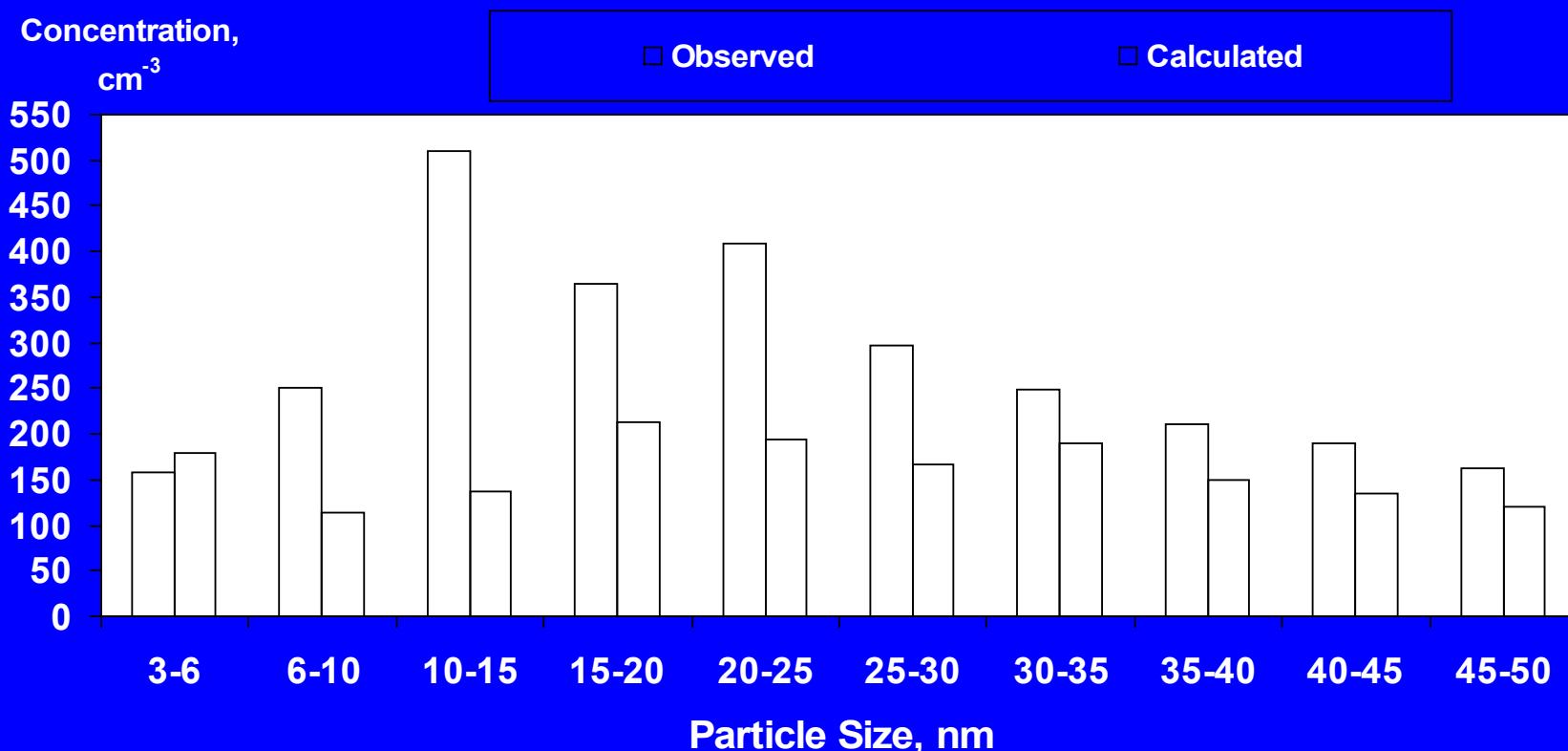
НИФХИ

Листвянка, 26.08.2003, $t = 12$ ч



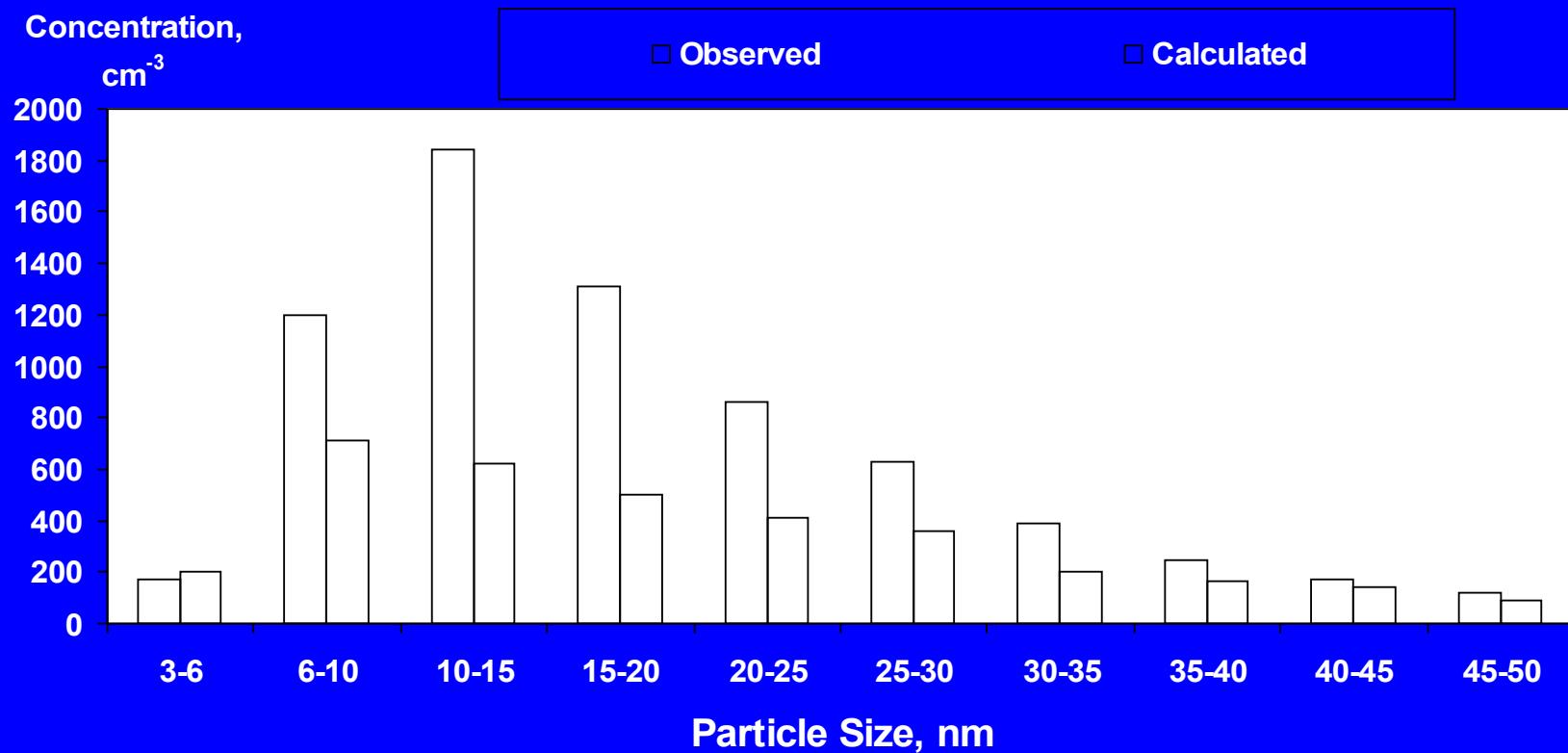
НИФХИ

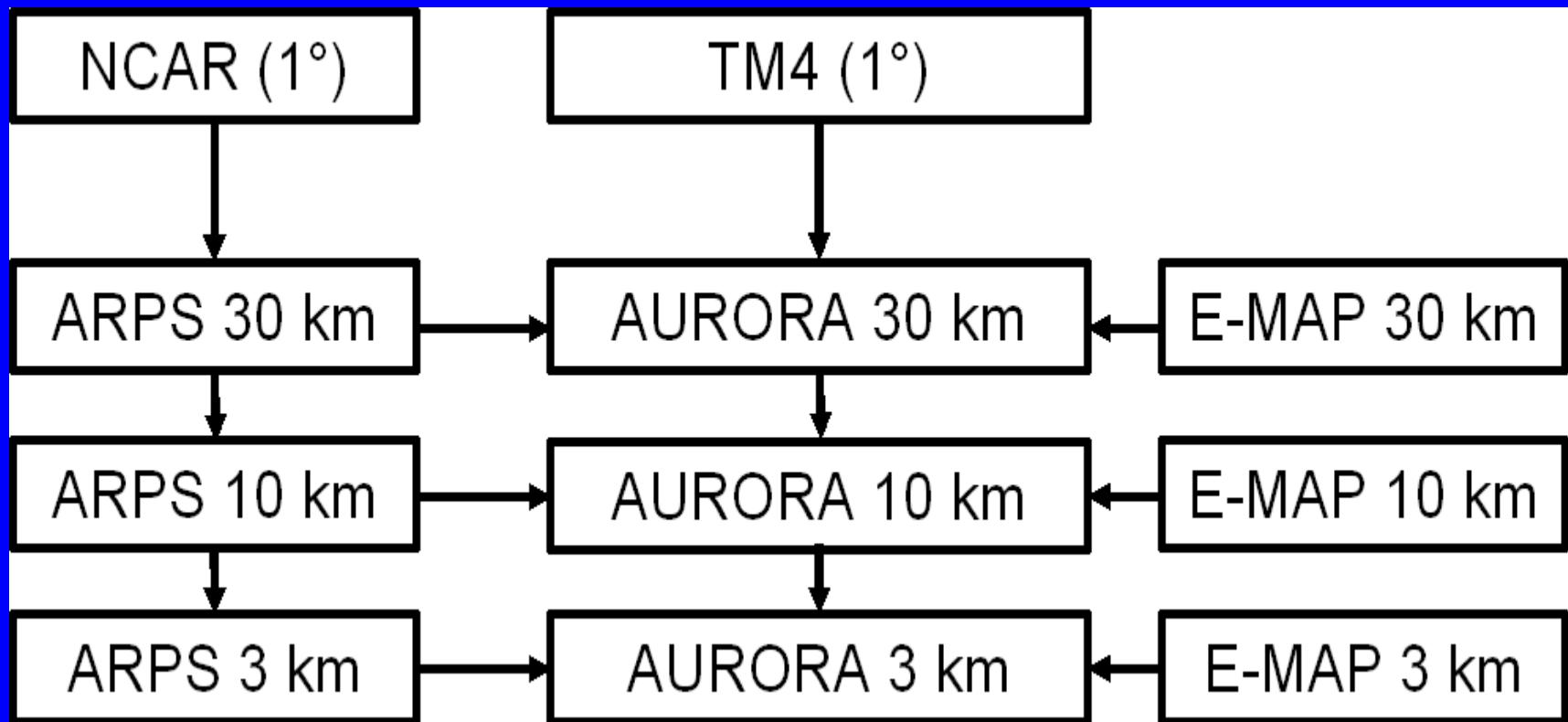
Листвянка, 26.08.2003, $t = 15$ ч



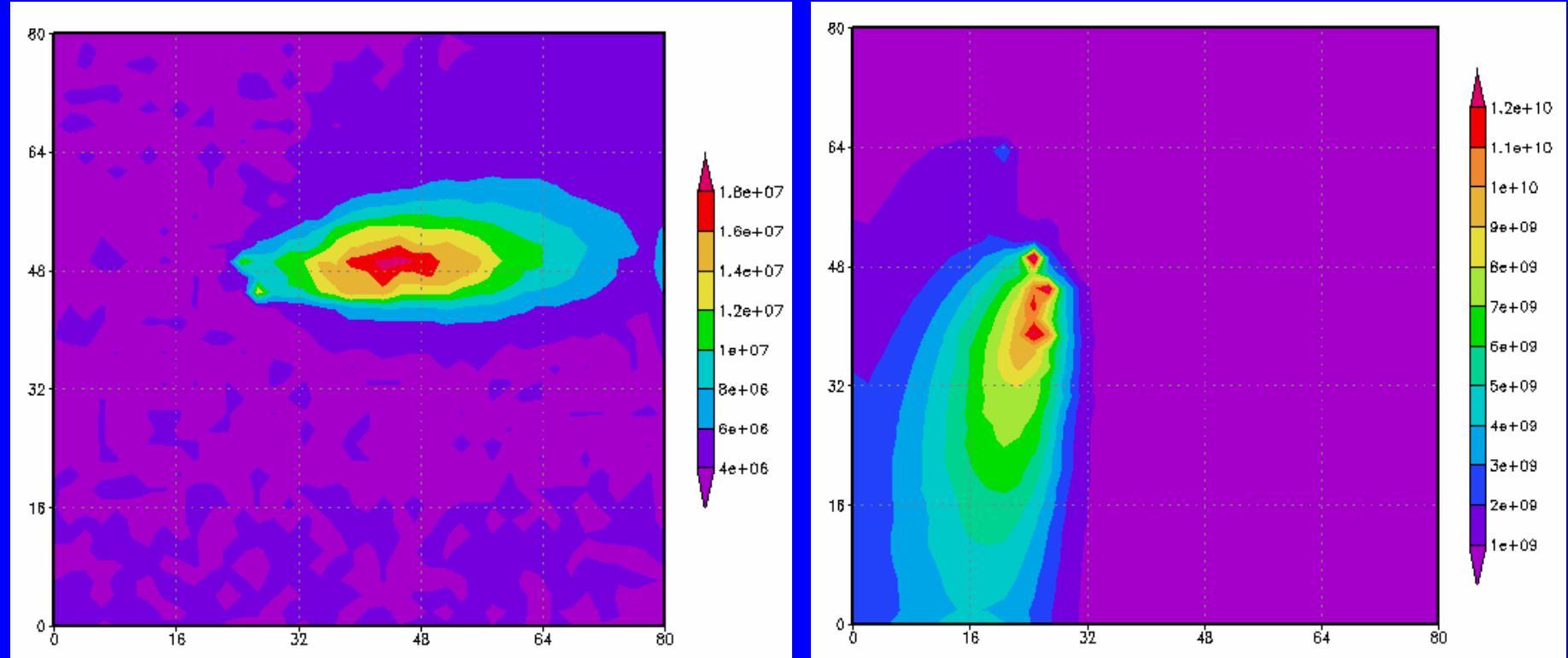
НИФХИ

Листвянка, 26.08.2003, $t = 24$ ч

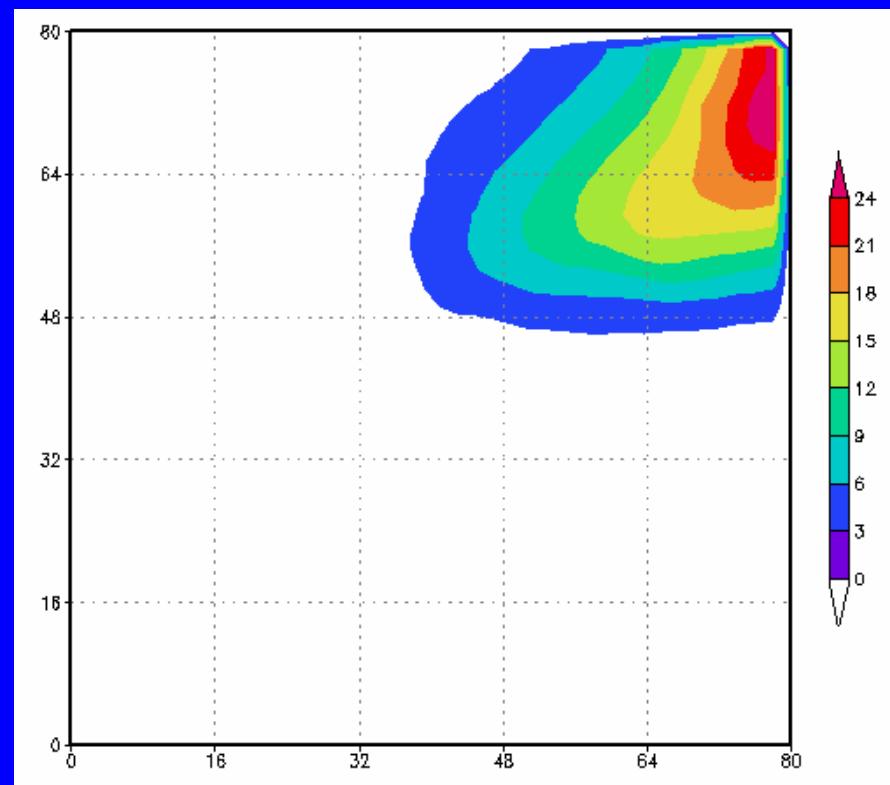
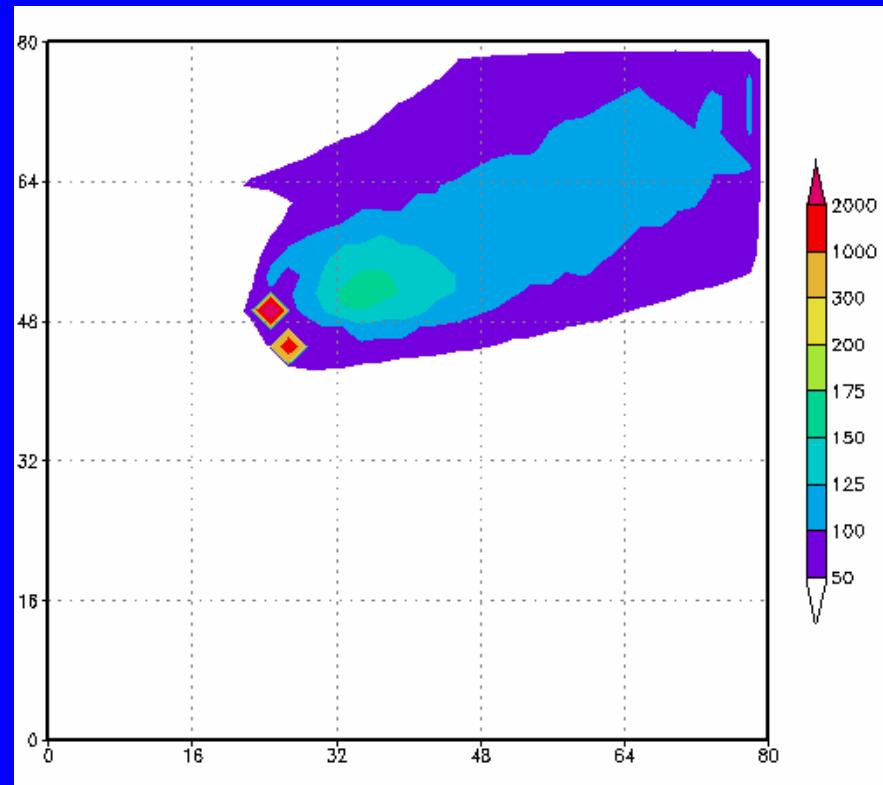




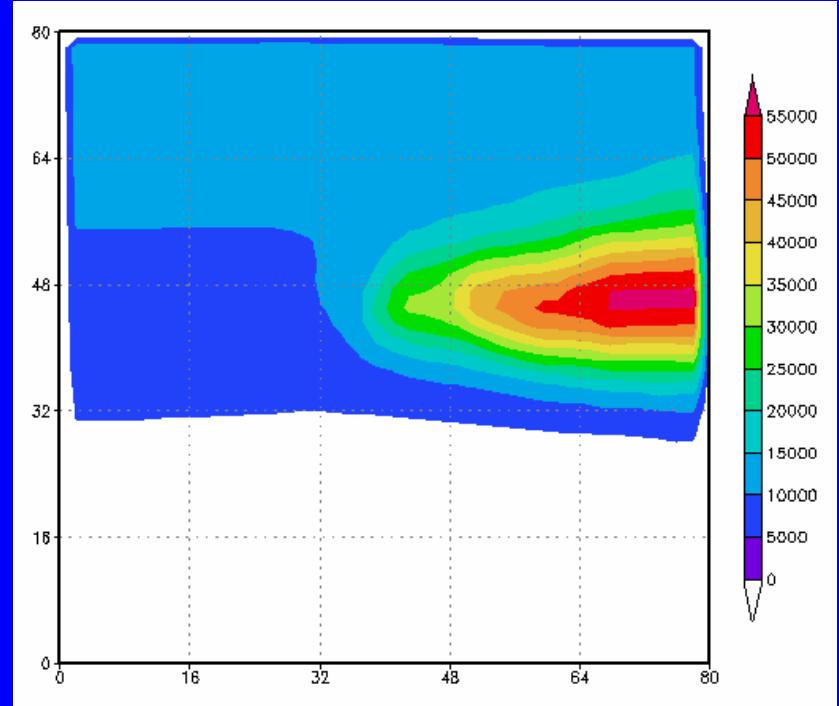
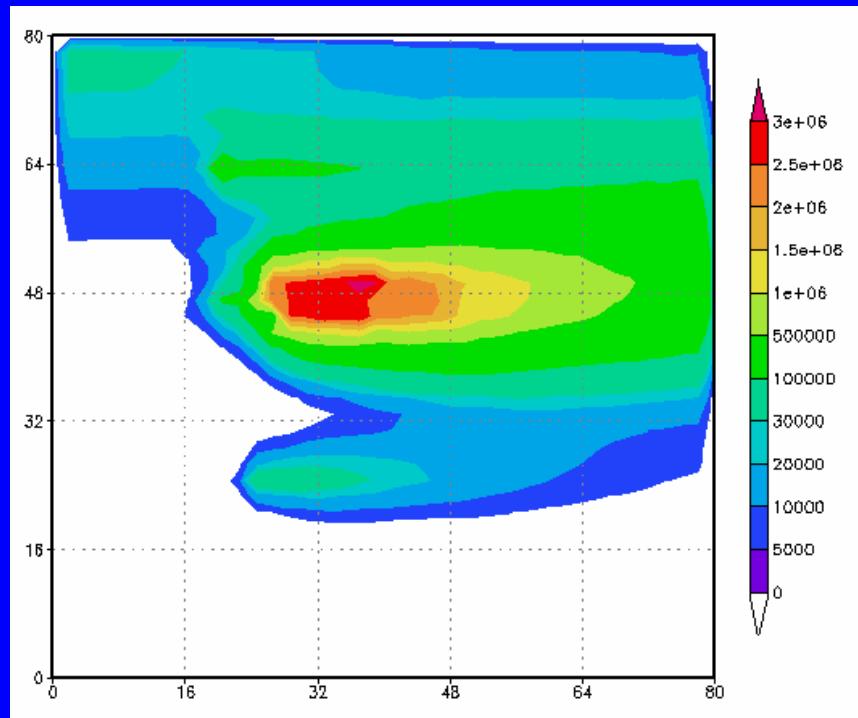
Antwerpen Area



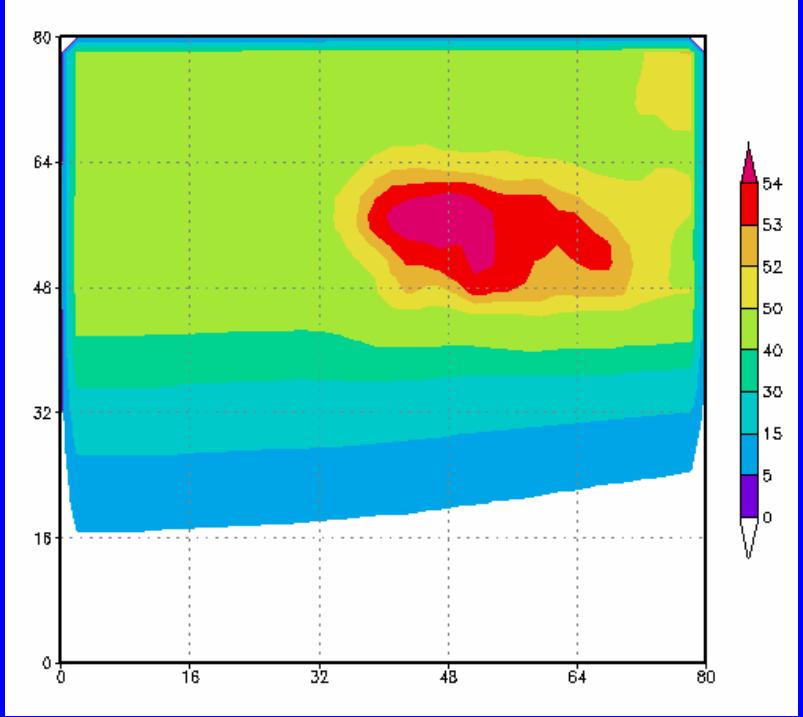
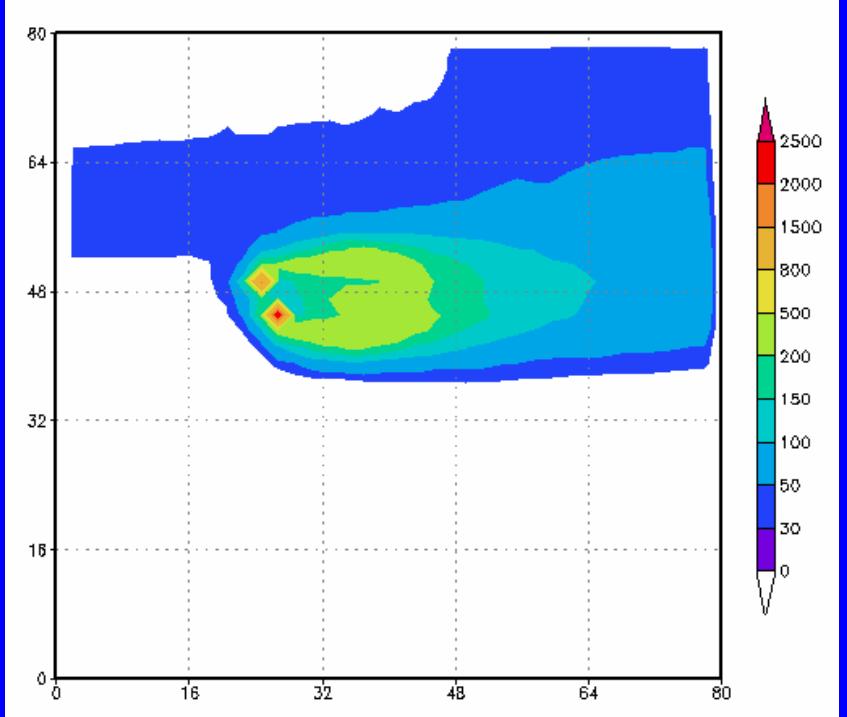
Concentrations of H_2SO_4 at $z = 360$ m after 18 and 30 hours of calculations



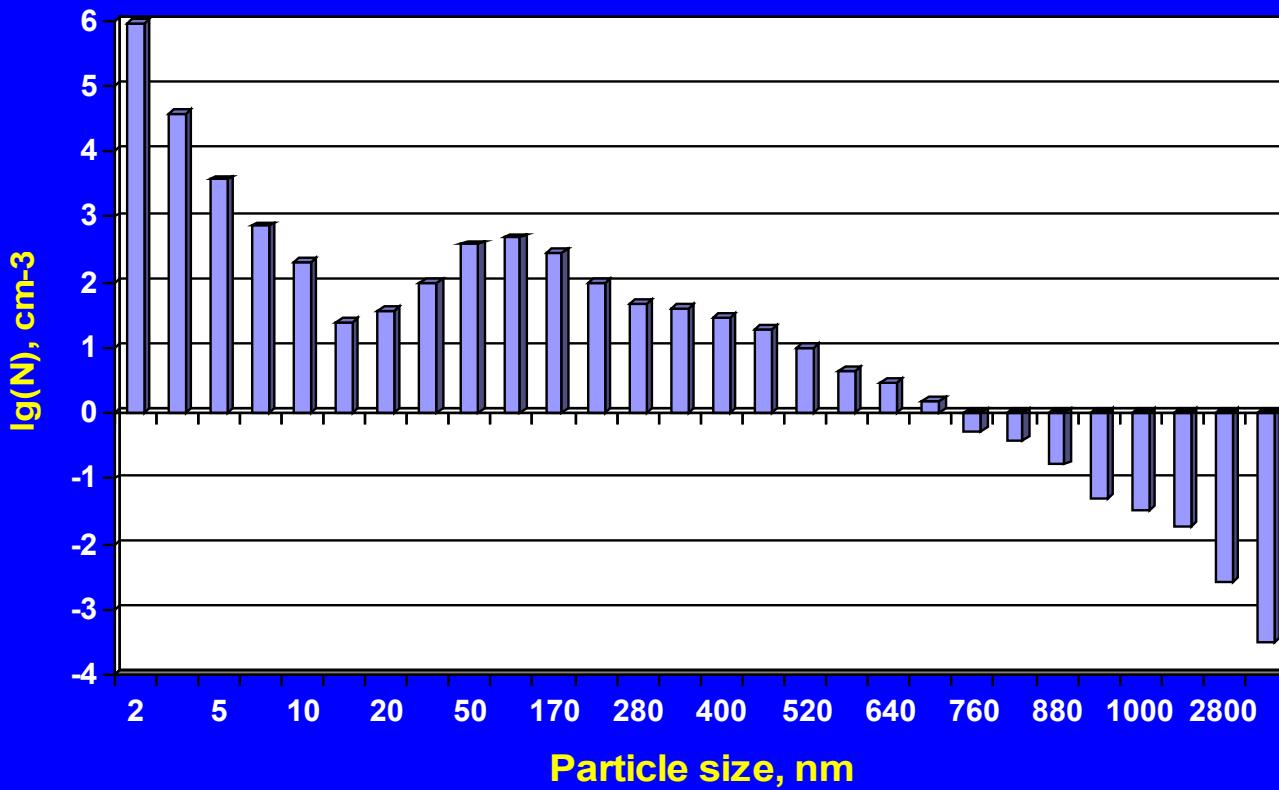
Aerosol (particles of 8 nm of radius) concentration in the (x, y) plane for 12 h at different heights: 28 m and 910 m.



Aerosol (particles of 2nm of radius) concentration in the (x, y) plane for 24 h at different heights: 28 m and 910 m.



Aerosol (particles of 8 nm of radius) concentration in the (x, y) plane for 24 h at different heights: 28 m and 910 m.



Aerosol concentrations (in the logarithmic scale) for the particle size spectrum between 2 nm and 3.4 μm after 30 h (from the start of calculations) at the grid point with coordinates (16, 24, 3).

Conclusions

- The comparison between numerical results and measurement data indicate that the model satisfactorily describes the formation of gas-phase species and aerosols in the atmosphere in the urban and regional scales.
- Due to enhanced concentrations of SO_2 , the modeling domains (the Baikal region including the Irkutsk city, and the Antwerpen area) are characterized by intense formation of nucleation-mode particles.
- The presence of extended forest areas in the Baikal region leads to pose the question of whether there can be other nucleating species, for example, organic compounds.
- The model results indicate that the ion content in aerosol particles is satisfactorily reproduced.

Pollution Transport

Governing equation

$$\frac{\partial \phi}{\partial t} = F_i - \operatorname{div} u\phi + \frac{\partial}{\partial x} K_x \frac{\partial \phi}{\partial x} + \frac{\partial}{\partial y} K_y \frac{\partial \phi}{\partial y} + \frac{\partial}{\partial \sigma} K_\sigma \frac{\partial \phi}{\partial \sigma}$$

Solution domain

$$D_t = D \times [0, T], D = \{(x, y, \sigma) : x \in [-X, X], y \in [-Y, Y], \sigma \in [0, H]\}$$

$$K_z \frac{\partial \phi}{\partial z} = \frac{1}{r_a + r_b + r_c} (\phi - \phi_{surf})$$

Pollution flux in the surface layer

Boundary conditions

$$\phi_i = \phi_i^0 \quad \text{for } t = 0,$$

$$\phi_i = \phi_i^b \quad \text{for } z = H.$$

$$\phi_i|_{\Gamma} = \phi_i^b \quad \text{if } u_n < 0,$$

$$\left. \frac{\partial \phi_i}{\partial n} \right|_{\Gamma} = \phi_i^b \quad \text{if } u_n \geq 0.$$

Consider the functional J of the solution φ :

$$J = \int_0^T dt \int_D p\varphi \, dD$$

where p – is a given function of the form:

$$p = \begin{cases} p_0, & (x, y, z) \in G \\ 0, & (x, y, z) \notin G \end{cases}, \quad p_0 > 0, \quad G \subset D.$$

The functional J describes the total pollution concentration of in a selected subdomain G weighted by the value of p_0 .

Optimization Model

Assume we have n sources of admixtures with emission rates Q_i ($i = 1, 2, \dots, n$) in domain D_t . We select an ecologically significant subdomain $G \subseteq D_t$ and consider the functionals:

$$\alpha_i^c = \int_{t_0}^{t_1} dt \int_G p_i \phi_i(x, t) dG \quad \text{Total concentration in } G$$

$$\alpha_i = \int_{t_0}^{t_1} dt \int_D \phi_i(x, t) dD \quad \text{Total concentration in } D$$

Linear Approximation

Components of the damaging influence of the i -th source in G (ecologically significant area) and D (entire domain):

$$\alpha_i^c = \alpha_i^c f_1(\varphi), \quad \alpha_i = \alpha_i f_2(\varphi)$$

where $f_1(\varphi)$ and $f_2(\varphi)$ are given functions of concentration (risk level), characterizing the amount of damage (on account of economic, ecological, health, etc. criteria).

The total environmental hazard can be written as

$$Y^c = \sum_{i=1}^n \alpha_i^c Q_i (1 - e_i) \quad \text{in } G$$

$$Y_0 = \sum_{i=1}^n \alpha_i Q_i (1 - e_i) \quad \text{in } D$$

where e_i are coefficients of the relative reduction of source rates.

The optimization problem is to find such $\{e_i\}$ that

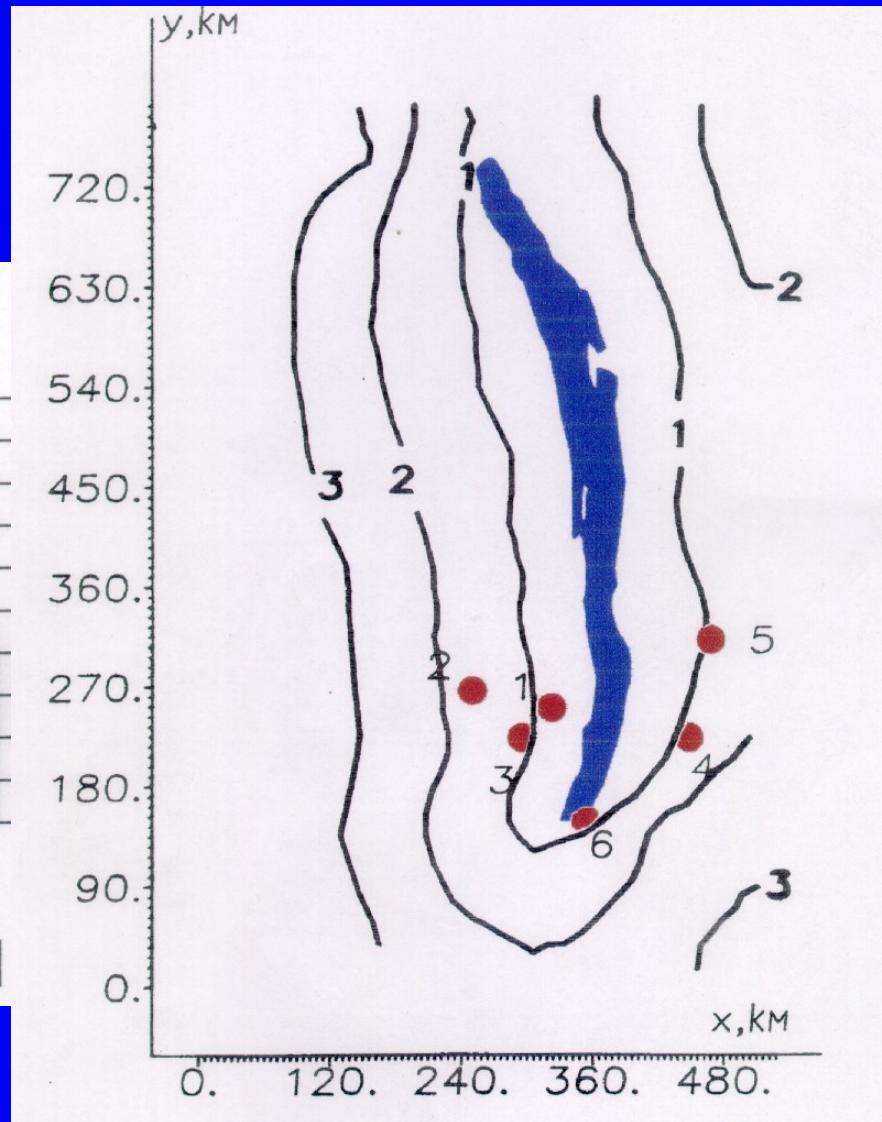
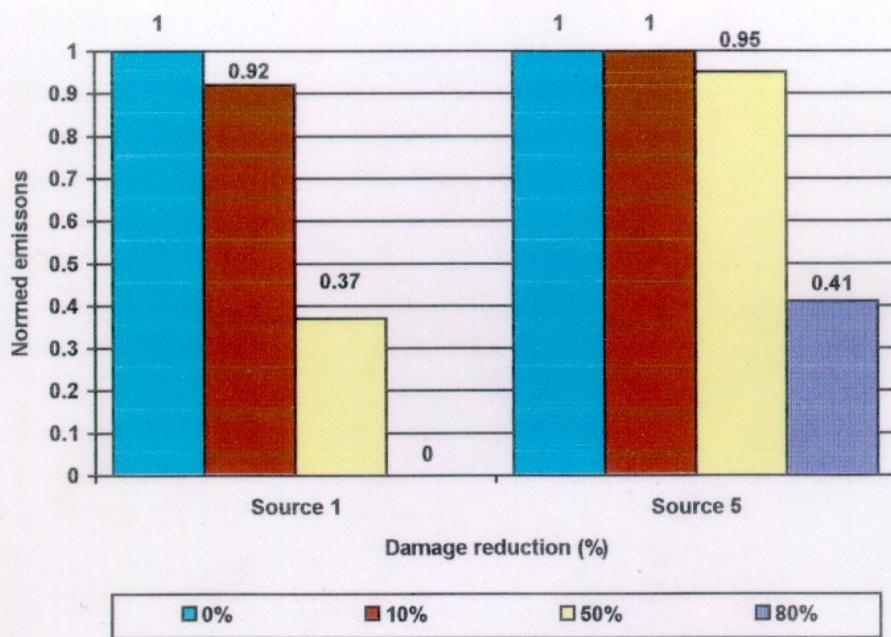
$$Y^c = \sum_{i=1}^n \alpha_i^c Q_i (1 - e_i) \rightarrow \min_{e_i}$$

$$0 \leq e_i \leq 1$$

$$k_1 Y_0 \leq \sum_{i=1}^n \alpha_i Q_i (1 - e_i) \leq k_2 Y_0$$

where k_1 and k_2 are coefficients characterizing the desirable level of damage reduction.

Control of emission source powers



Assessment of Damage

S – the area of forest; Q – the amount of pollution deposited on the forest (e.g., acid deposition); αQ – the fraction of forest destroyed. By *damage*, we mean the costs needed to restore the destroyed fraction of forest. The costs are assumed to be proportional to time and the forest to grow in a geometric progression.

$$S = S(1 - \alpha Q)(1 + \beta)^t$$

$$t = \frac{\ln \frac{1}{1 - \alpha Q}}{\ln(1 + \beta)}, \quad \beta = 0.1$$

Nonlinear Approximation

The dependence of damage to housing stock by dust (x_1) and sulfuric anhydride (mg/m³) (x_2):

$$\ln y = 7.62 + 0.87 \ln x_1 + 1.27 \ln x_2,$$

$$\sum_{i=1}^n (\alpha_i c Q_i)^2 \quad \begin{array}{l} \text{- Damage in the controlled area} \\ G \end{array}$$

$$\sum_{i=1}^n (\alpha_i Q_i)^2 \quad \begin{array}{l} \text{- Damage in the entire area } D \end{array}$$

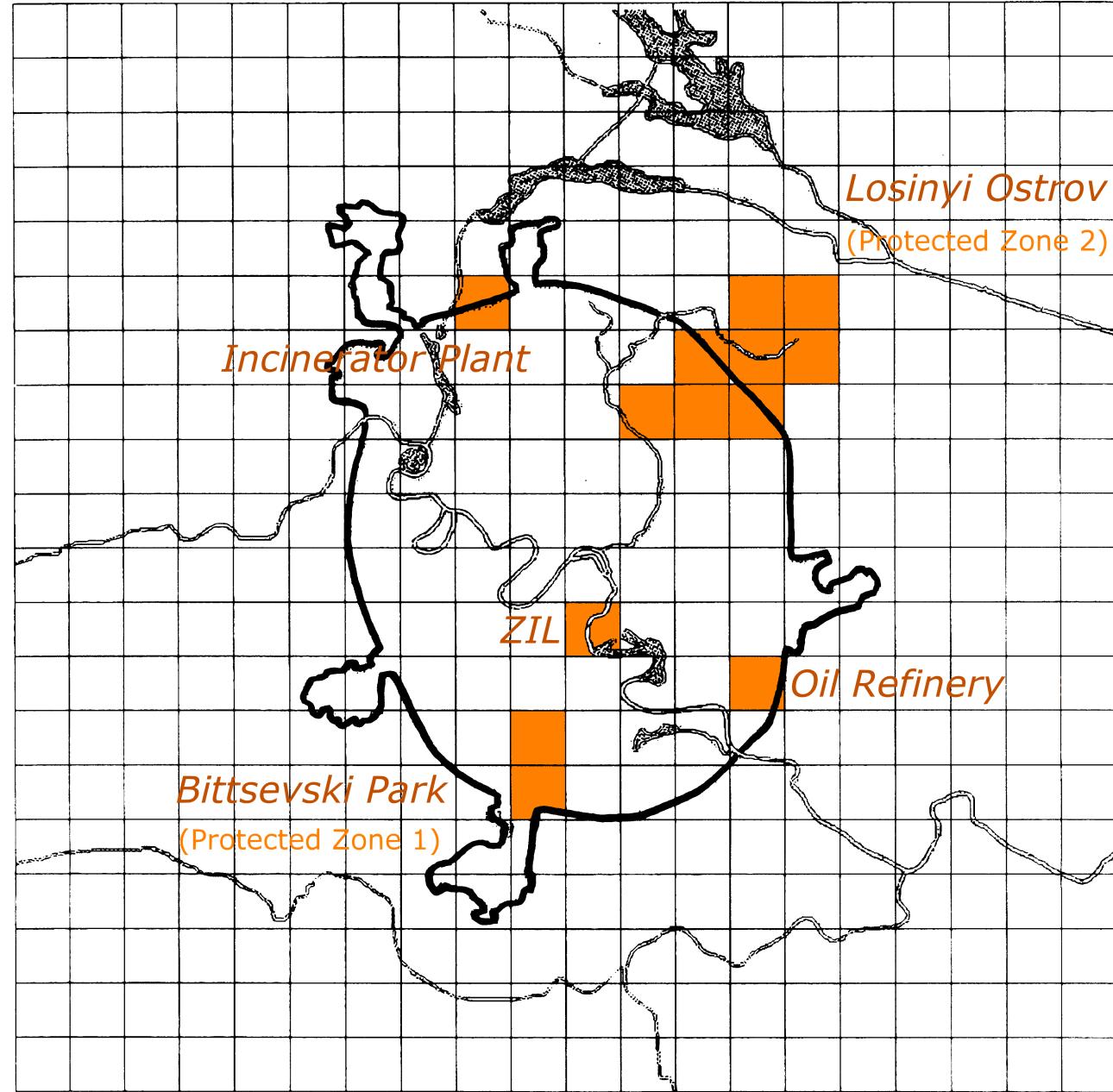
Minimization of Damage

$$\sum (\alpha_i Q_i)^2 \rightarrow \min_{Q_i}$$

under the constraints

$$0 \leq Q_I \leq \bar{Q}_i$$

$$kY_0 \leq \sum_{i=1}^n \bar{\beta}_i Q_i \leq Y_0$$



Protected Zone: Bittsevski Park

<u>Source</u>	Q	Q ⁻	Q/Q ⁻
Oil Refinery	223.78	3278	0.07
Incinerator Plant	1167.13	3514	0.33
ZIL Motor Plant	195.27	3086	0.06

Protected Zone: Losinyi Ostrov

<u>Source</u>	Q	Q ⁻	Q/Q ⁻
Oil Refinery	1446.90	3278	0.44
Incinerator Plant	418.75	3514	0.12
ZIL Motor Plant	3086	3086	0.15