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*A MATRIX APPROXIMATION TO LARGE SCALE
PHOTOCHEMICAL MODEL CALCULATIONS*

E. Amble

NORWEGIAN INSTITUTE FOR AIR RESEARCH
P.O. BOX 130, N-2001 LILLESTRØM
NORWAY

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SUMMARY

The QSSA model for photochemical reactions in the atmosphere is simulated by a limited system of linear differential equations which can be solved analytically. This permits the use of large time-steps, and the computer time may be reduced by a factor of more than 500, while retaining an overall accuracy which is compatible with other uncertainties and inaccuracies of the total problem.

**A MATRIX APPROXIMATION TO LARGE SCALE PHOTOCHEMICAL
MODEL CALCULATIONS**

In the present report an attempt has been made to simulate the complex photochemical model of a polluted atmosphere in order to save computational time so that the model can be used for pollution transport problems in more than one dimension over great areas and distances.

In an article "Quasi-Steady-State Approximation in Air Pollution Modeling: Comparison of Two Numerical Schemes for oxidant prediction" in the International Journal of Chemical Kinetics, Vol. X, 971-994 (1978), E. Hesstvedt, Ø. Hov, and I. Isaksen have published a numerical method to solve the set of differential equations describing the chemical development in a polluted atmosphere, the QSSA-method.

This model has been taken as a norm for the following attempt to develop a simplified matrix model to simulate the chemical development given by the QSSA method. The number of chemical substances explicitly handled in the matrix model, is limited to the following 10 components:

SO_2 , SO_4 , HNO_3 , C_4H_{10} , $\text{C}_6\text{H}_5\text{CH}_3$, CH_3COOH , PAN, O_3 , H_2O_2 and $\text{NO}_x = \text{NO}_2 + \text{NO}$.

Four tests have been made, all of them with the same procentual composition of the input pollutants, corresponding to the average composition found for several countries in Europe, but with four different intensities:

	fact=1	fact=2	fact=3	fact=4	
SO_2	4.19	8.38	12.56	16.75	T/km ² /year
NO_x	1.18	2.36	3.53	4.71	"
C_4H_{10}	0.57	1.14	1.71	2.28	"
$\text{C}_6\text{H}_5\text{CH}_3$	0.97	1.95	2.92	3.89	"

The QSSA-method was used to calculate the development of the concentrations of the ten components for fact = 1,2,3 and 4 with constant input pollution over several days and nights. The system reached a "daily equilibrium" within 7-10 days for all values of fact, i.e. the same oscillating values repeated themselves from day to day. In order to investigate this oscillation and the effect of nonlinear components in the QSSA model, the radiation was averaged over 24 hours and the calculation repeated with this constant radiation for the four values of fact. In all cases, all the variables ended up with constant values within 7-10 days.

All of the runs began at 12.00 on day No. 1, with the same starting conditions as used in the QSSA program and with the input pollution corresponding to fact 2 and with normally changing radiation until 00 a.m. on day 2, which is the starting point for the different runs with constant average radiation. The radiation corresponds to the radiation on latitude 55⁰ at midsummer. TA mixing height of 1 km was used.

If it is assumed that the photochemical reactions of the ten chosen compounds can be described by a set of linear differential equations, then

$$X' = P + A + BX \quad (1)$$

where

X is the vector of concentrations of the 10 chemical components

P is the production into the system of the 10 components

A is an adjustment vector

B is a 10x10 matrix describing the influence of the components on each other

This system of equations can be solved analytically, and the solution is:

$$x = -B^{-1}(P+A) + e^{Bt}(x_0 + B^{-1}(P+A)) \quad (2)$$

If $\lim_{t \rightarrow \infty} e^{Bt} = 0$ and $x_\infty = -B^{-1}(P+A)$

then

$$x_t = x_\infty + e^{Bt}(x_0 - x_\infty) \quad (3)$$

We wish now to determine the elements in A and B to give the best fit to the QSSA method. Choose $t = 1$ to correspond to 24 hours. Differentiation of (3) gives

$$[e^B]_{i,j} = \frac{\Delta x(1)_i}{\Delta x(0)_j} \quad i, j = 1 \dots 10$$

The ratio $\Delta x(1)_i / \Delta x(0)_j$; is then determined by the QSSA method for all values of i and j . If $[e^B]_{i,j}$ is set equal to these values, then all the first order partial differentials $\frac{\delta x_i}{\delta x_j}$ will be the same as for the QSSA-method. From the matrix e^B the matrix $B = \ln(e^B)$ can be found, and the vector A is calculated from the equation $x_\infty = -B^{-1}(P+A)$, which gives $A = -P - B \cdot x_\infty$. The vector A and matrix e^B has been calculated for the four values of fact. They are not constant, most of the elements change linearly with the value of fact. In all cases $\lim_{n \rightarrow \infty} (e^B)^n = 0$.

The eigenvalues of the matrix B have all negative real parts which correspond to an exponential approach to a limiting value of addends with different relaxation times, the longest of them is 55 hours. A set of complex conjugated eigenvalues correspond to a damped oscillating addend with a 6 hour relaxation time and a period of 150 hours.

The development of the concentrations of the most reactive components, O_3 , H_2O_2 , NO_x and $C_6H_5CH_3$ in the time between day 2, 00 am and day 4, 00 am, have been calculated for the values 1, 2 and 3 of the emission variable (fact), both with the QSSA

method and with the matrix method. The results are listed together with the percentage deviations in the Tables 1, 2 and 3. The components which are not listed, have all smaller deviations.

If a smaller timestep is of advantage, say 6 hrs., then the matrix e^B must be replaced by the 4th root of e^B . Within the validity of the matrix representation, some conclusions can be drawn, for example: the variation of the concentration of the i 'th component due to a change in the input of the j 'th component is

$$\frac{\partial x_i(t)}{\partial P_j} = \left[(e^{Bt} - I) \cdot B^{-1} \right]_{i,j}$$

where I is the 10×10 unit matrix.

Table 1: (fact=1).

Day	Hour	C_6H_xR		H_2O_2		
		QSSA	Matrix	QSSA	Matrix	
2	0	1.066	1.066(10)	2.177(11)	2.177	
	4	6.933	6.990(9)	1.931	1.938	4%
	8	5.220	5.423	1.772	1.795	
	12	4.590	4.721	1.670	1.693	1%
	16	4.366	4.412	1.597	1.615	
	20	4.295	4.288	1.542	1.555	
3	0	4.282	4.249	1.499	1.507	1%
	4	4.290	4.247	1.465	1.470	
	8	4.304	4.261	1.438	1.440	
	12	4.316	4.278	1.417	1.417	0%
	16	4.327	4.295	1.401	1.399	
	20	4.334	4.310	1.388	1.384	
4	0	4.339	4.323	1.378	1.373	0%
		↓	↓	↓	↓	
		4.298	4.379	1.337	1.335	0%

Day	Hour	O_3		NO_x		
		QSSA	Matrix	QSSA	Matrix	
2	0	7.676(11)	7.676 ^s	3.877(10)	3.877	
	4	9.391	9.559	2.776	2.240	-19%
	8	1.066(12)	1.065	2.144	1.869	-13%
	12	1.150	1.140	1.917	1.773	-8%
	16	1.208	1.195	1.839	1.744	
	20	1.251	1.237	1.812	1.734	
3	0	1.285	1.270	1.802	1.732	-4%
	4	1.312	1.297	1.799	1.733	
	8	1.333	1.319	1.799	1.736	
	12	1.353	1.338	1.799	1.739	-3%
	16	1.367	1.353	1.799	1.743	
	20	1.380	1.366	1.800	1.746	
4	0	1.390	1.377	1.800	1.749	-3%
		↓	↓	↓	↓	
		1.438	1.439	1.784	1.765	-1%

Table 2: (fact=2).

Day	Hour	C_6H_xR			H_2O_2		
		QSSA	Matrix		QSSA	MATRIX	
2	0	1.066(10)	1.066		2.177(11)	2.177	
	4	8.913(9)	8.717	-2%	1.924	1.941	1%
	8	7.981	7.845		1.738	1.769	
	12	7.650	7.505	-2%	1.603	1.638	2%
	16	7.591	7.418		1.503	1.537	
	20	7.636	7.442		1.428	1.458	
3	0	7.710	7.506	-3%	1.371	1.397	2%
	4	7.784	7.579		1.327	1.350	
	8	7.846	7.646		1.294	1.313	
	12	7.894	7.704	-2%	1.270	1.285	-1%
	16	7.930	7.751		1.251	1.263	
	20	7.955	7.789		1.237	1.247	
4	0	7.972	7.818	-2%	1.227	1.235	
		↓	↓		↓	↓	
		7.914	7.916	0%	1.216	1.214	0%

Day	Hour	O_3			NO_x		
		QSSA	Matrix		QSSA	Matrix	
2	0	7.676(11)	7.676		3.877(10)	3.877	
	4	9.364	9.532	2%	3.584	3.225	-10%
	8	1.085(12)	1.099		3.275	3.026	
	12	1.207	1.216	1%	3.161	2.990	-5%
	16	1.306	1.312		3.140	3.007	
	20	1.387	1.392		3.153	3.039	
3	0	1.455	1.458	0%	3.174	3.069	-3%
	4	1.512	1.514		3.194	3.096	
	8	1.560	1.562		3.210	3.118	
	12	1.602	1.603	0%	3.222	3.136	-3%
	16	1.637	1.638		3.230	3.150	
	20	1.667	1.667		3.236	3.162	
4	0	1.693	1.693	0%	3.240	3.171	-2%
		↓	↓		↓	↓	
		1.844	1.849	0%	3.220	3.202	-1%

Table 3: (fact=3).

Day	Hour	C_6H_xR			H_2O_2		
		QSSA	Matrix		QSSA	MATRIX	
2	0	1.066(10)	1.066		2.177	2.177	
	4	1.102	1.027	-7%	1.922	1.941	1%
	8	1.126	1.030		1.724	1.755	
	12	1.154	1.051	-9%	1.573	1.608	2%
	16	1.181	1.077		1.457	1.493	
	20	1.205	1.103		1.367	1.402	
3	0	1.224	1.125	-8%	1.298	1.331	3%
	4	1.239	1.144		1.246	1.267	
	8	1.250	1.155		1.206	1.234	
	12	1.256	1.168	-7%	1.175	1.202	2%
	16	1.260	1.176		1.153	1.177	
	20	1.261	1.182		1.136	1.159	
4	0	1.261	1.186	-6%	1.124	1.145	2%
		↓	↓		↓	↓	
		1.223	1.184	-3%	1.128	1.132	0%

Day	Hour	O_3			NO_x		
		QSSA	Matrix		QSSA	Matrix	
2	0	7.676	7.676(11)		3.877(10)	3.877	
	4	9.290	9.664	4%	4.441	4.070	-8%
	8	1.076	1.132(12)		4.621	4.272	
	12	1.206	1.271	5%	4.749	4.450	-6%
	16	1.319	1.389		4.848	4.593	
	20	1.418	1.488		4.924	4.704	
3	0	1.503	1.573	5%	4.980	4.787	-4%
	4	1.577	1.646		5.016	4.848	
	8	1.643	1.708		5.038	4.892	
	12	1.700	1.763	4%	5.047	4.924	-2%
	16	1.751	1.810		5.049	4.945	
	20	1.796	1.851		5.044	4.960	
4	0	1.836	1.886	3%	5.035	4.970	-1%
		↓	↓		↓	↓	
		2.114	2.125	1%	4.878	4.953	+2%

The figures 1 and 2 depict the concentrations of the same chemical components for the 10th day: (a) calculated with the QSSA-method with a normally changing daily radiation, (b) calculated with the QSSA-method with a constant, averaged radiation and (c) x_{∞} from the matrix calculation. The pollution input into the system corresponds to fact=4.

The cyclic functions have been Fourier-analysed. The mean value $C_0/2$ together with the amplitude of the first and second harmonics, c_1 and c_2 , and the time for the maximum of the first harmonic are given in the figures. The first harmonic dominates for all the variables.

If the radiation is approximated with the expression $\alpha_0/2 + \alpha_1 \cos 2\pi t$, and if the matrix is separated in a photo-insensitive matrix C and a photosensitive part D, the set of linear differential equations can be written as

$$x' = P + A + Cx + D \cdot x (\alpha_0/2 + \alpha_1 \cos 2\pi t) \quad (5)$$

$$x' = P + A + (C + \alpha_0/2 \cdot D) \cdot x + \alpha_1 D \cdot x \cdot \cos 2\pi t \quad (6)$$

The matrix $(C + \alpha_0/2 \cdot D)$ can be found as described above for the different values of α , and the matrix D is the derivative of the matrix $(C + \alpha_0/2 \cdot D)$ with respect to $\alpha_0/2$.

If the 2nd and higher harmonics are neglected and $x = x_{\infty} + x_1$ for the 10th day, the solution of x_1 becomes,

$$x_1 = x_1^{\infty} + U \cos 2\pi t + V \sin 2\pi t \quad (7)$$

The vectors x_1 , x_{∞} , U and V as well as the amplitude and phase angle of the first harmonic can be found as functions of α , C and D. The daily variation of the variables can be found in a

similar way also if the system has not reached equilibrium. It is of course possible, if desired, to operate with two or more photosensitive matrixes, for example a short wave and a long wave matrix, and to increase the number of harmonics taken into account. The harmonic Fourier coefficients of the radiation can easily be found for different latitudes and times of year. Thus, a simple parameterization of geographical position is possible.

The computational time for the matrix method is less than 0.5 o/oo of the computational time for the QSSA-method for calculation of the concentrations from one day to the next.

For a large pollution transport problem, the matrix model permits one to follow the development in large steps, for instance from one day to the next, without following the detailed daily development for all grid elements in the system. If, however, the emissions change considerably during the day, it may be more appropriate to use a time interval which is more compatible to the grid size, for instance 6 hours in a 150 km x 150 km grid. For certain grid elements where a more detailed information is wanted, the amplitude and the phase-angle for the first harmonic can be calculated.

It should be remembered that in the present case the matrix-method is used as an approximation to describe the overall connection between a limited number of substances in an atmosphere which is in equilibrium with a constant radiation and a constant input of pollutants. The method should be tested over a wide range of pollution situations in order to get either a sufficiently dense set of matrixes or to find out how the different matrix elements change with the degree of pollution.

The obtained reduction in computational time has to be paid for with a reduction in the resulting accuracy. The intention is that this method shall be an aid to solve large pollution transport problems. The required accuracy of the matrix method will then be determined by the accuracy of the other components of the total problem.

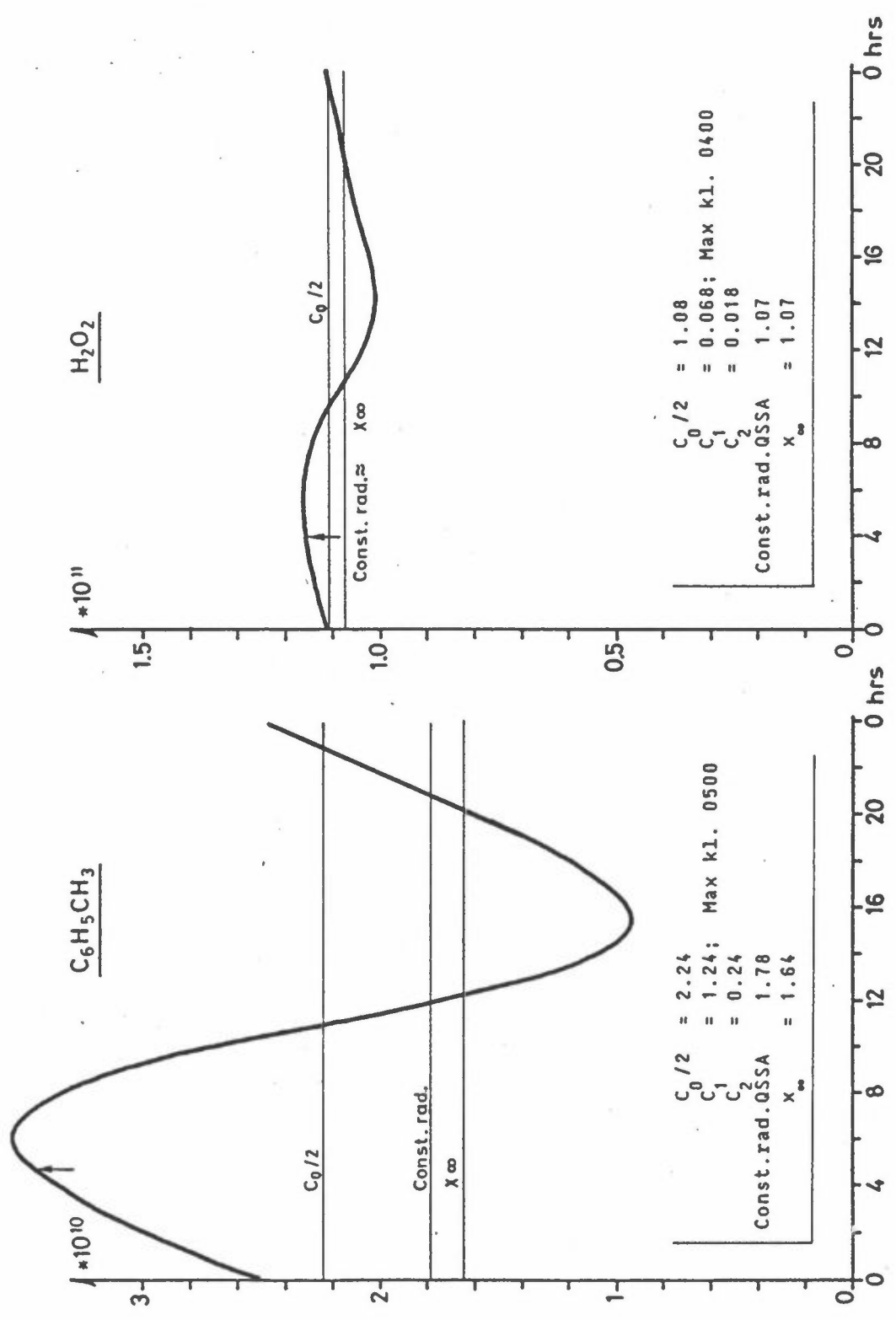


Fig. 1: Concentration on the 10th day, molecules per cm^3 . Fact=4.

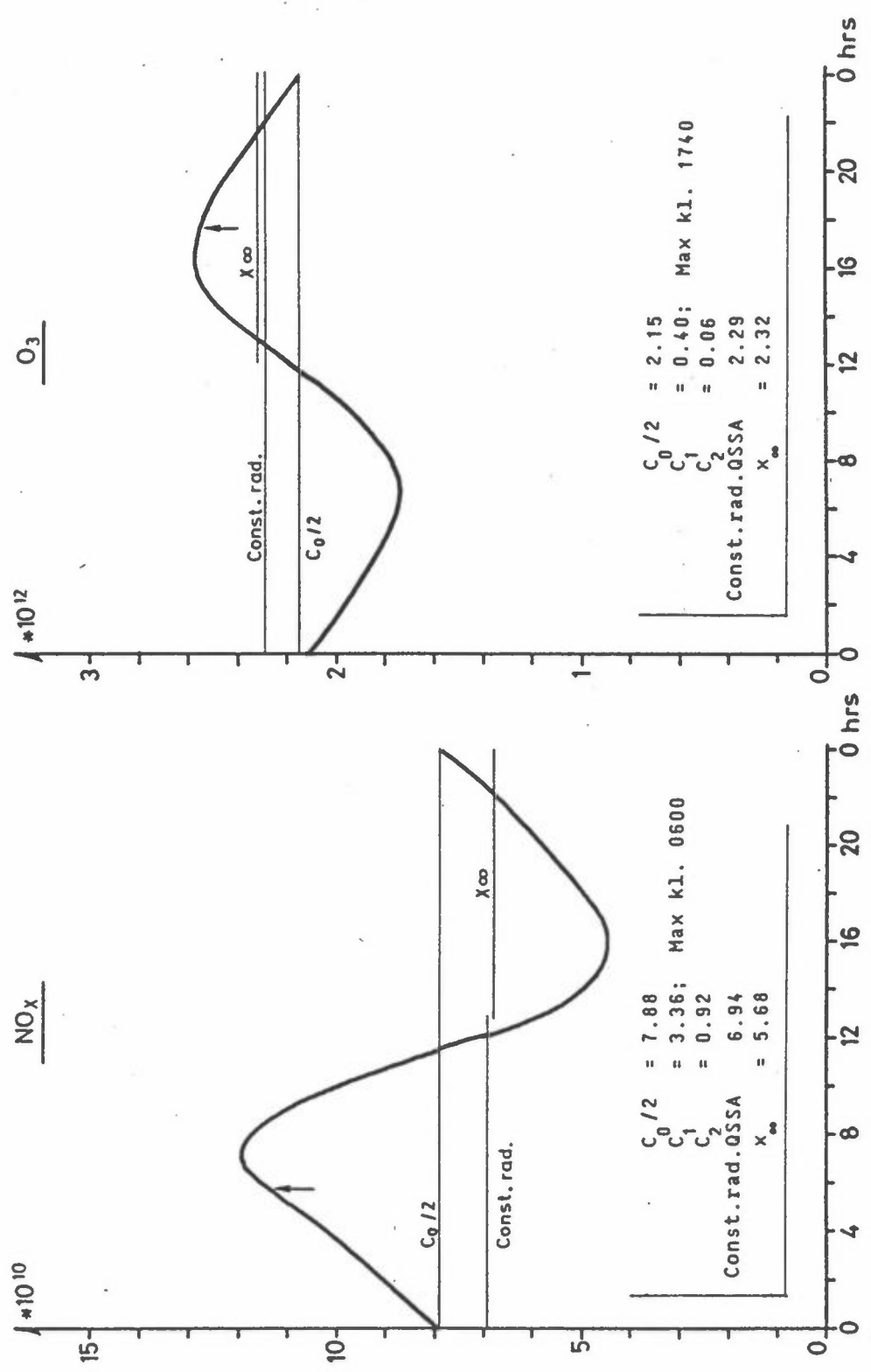


Fig. 2: Concentration on the 10th day, molecules per cm^3 . Fact=4.

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