2 Pollution problem

2.1 General information

This IVP is a stiff system of 20 non-linear Ordinary Differential Equations. It is the chemical reaction part of the air pollution model developed at The Dutch National Institute of Public Health and Environmental Protection (RIVM) and it is described by Verwer in [Ver94]. The parallel-IVP-algorithm group of CWI contributed this problem to the test set.

The software part of the problem is in the file pollu.f available at [MM08].

2.2 Mathematical description of the problem

The problem is of the form

$$\frac{\mathrm{d}y}{\mathrm{d}t} = f(y), \quad y(0) = y_0, \tag{II.2.1}$$

with

$$y \in \mathbb{R}^{20}, \quad 0 \leq t \leq 60.$$

The function f is defined by

$$f = \begin{pmatrix} -\sum_{j\in\{1,10,14,23,24\}} r_j + \sum_{j\in\{2,3,9,11,12,22,25\}} r_j \\ -r_2 - r_3 - r_9 - r_{12} + r_1 + r_{21} \\ -r_{15} + r_1 + r_{17} + r_{19} + r_{22} \\ -r_2 - r_{16} - r_{17} - r_{23} + r_{15} \\ -r_3 + 2r_4 + r_6 + r_7 + r_{13} + r_{20} \\ -r_6 - r_8 - r_{14} - r_{20} + r_3 + 2r_{18} \\ -r_4 - r_5 - r_6 + r_{13} \\ r_4 + r_5 + r_6 + r_7 \\ -r_7 - r_8 \\ -r_{12} + r_7 + r_9 \\ -r_9 - r_{10} + r_8 + r_{11} \\ r_9 \\ -r_{11} + r_{10} \\ -r_{13} + r_{12} \\ r_{14} \\ -r_{18} - r_{19} + r_{16} \\ -r_{20} \\ r_{20} \\ -r_{21} - r_{22} - r_{24} + r_{23} + r_{25} \\ -r_{25} + r_{24} \end{pmatrix},$$

where the r_i are auxiliary variables, given in Table II.2.1. The values of the parameters k_j are in Table II.2.2. Finally, the initial vector y_0 is given by

$$y_0 = (0, 0.2, 0, 0.04, 0, 0, 0.1, 0.3, 0.01, 0, 0, 0, 0, 0, 0, 0, 0.007, 0, 0, 0)^{\mathrm{T}}.$$

2.3 Origin of the problem

The problem is a chemical model consisting of 25 reactions and 20 reacting compounds. Figure II.2.1 shows the reaction scheme. Writing down the reaction velocities r_j for every reaction equation and making the identification in Table II.2.3, which also lists the concentrations at $t = 0$, one arrives at the system of differential equations (II.2.1). The time interval [0,60] represents the behavior of the reactants sufficiently.

TABLE II.2.1: *Auxiliary variables.*

r_1	=	$k_1 \cdot y_1$	r_{10}	=	$k_{10} \cdot y_{11} \cdot y_1$	r_{19}	=	$k_{19} \cdot y_{16}$
r_2	=	$k_2 \cdot y_2 \cdot y_4$	r_{11}	=	$k_{11} \cdot y_{13}$	r_{20}	=	$k_{20} \cdot y_{17} \cdot y_6$
r_3	=	$k_3 \cdot y_5 \cdot y_2$	r_{12}	=	$k_{12} \cdot y_{10} \cdot y_2$	r_{21}	=	$k_{21} \cdot y_{19}$
r_4	=	$k_4 \cdot y_7$	r_{13}	=	$k_{13} \cdot y_{14}$	r_{22}	=	$k_{22} \cdot y_{19}$
r_5	=	$k_5 \cdot y_7$	r_{14}	=	$k_{14} \cdot y_1 \cdot y_6$	r_{23}	=	$k_{23} \cdot y_1 \cdot y_4$
r_6	=	$k_6 \cdot y_7 \cdot y_6$	r_{15}	=	$k_{15} \cdot y_3$	r_{24}	=	$k_{24} \cdot y_{19} \cdot y_1$
r_7	=	$k_7 \cdot y_9$	r_{16}	=	$k_{16} \cdot y_4$	r_{25}	=	$k_{25} \cdot y_{20}$
r_8	=	$k_8 \cdot y_9 \cdot y_6$	r_{17}	=	$k_{17} \cdot y_4$			
r_9	=	$k_9 \cdot y_{11} \cdot y_2$	r_{18}	=	$k_{18} \cdot y_{16}$			

TABLE II.2.2: *Parameter values.*

k_1	$= 0.350$	k_{10}	$= 0.900 \cdot 10^4$	k_{19}	$= 0.444 \cdot 10^{12}$
k_2	$= 0.266 \cdot 10^2$	k_{11}	$= 0.220 \cdot 10^{-1}$	k_{20}	$= 0.124 \cdot 10^4$
k_3[†]	$= 0.123 \cdot 10^5$	k_{12}	$= 0.120 \cdot 10^5$	k_{21}	$= 0.210 \cdot 10$
k_4	$= 0.860 \cdot 10^{-3}$	k_{13}	$= 0.188 \cdot 10$	k_{22}	$= 0.578 \cdot 10$
k_5	$= 0.820 \cdot 10^{-3}$	k_{14}	$= 0.163 \cdot 10^5$	k_{23}	$= 0.474 \cdot 10^{-1}$
k_6	$= 0.150 \cdot 10^5$	k_{15}	$= 0.480 \cdot 10^7$	k_{24}	$= 0.178 \cdot 10^4$
k_7	$= 0.130 \cdot 10^{-3}$	k_{16}	$= 0.350 \cdot 10^{-3}$	k_{25}	$= 0.312 \cdot 10$
k_8	$= 0.240 \cdot 10^5$	k_{17}	$= 0.175 \cdot 10^{-1}$		
k_9	$= 0.165 \cdot 10^5$	k_{18}	$= 0.100 \cdot 10^9$		

[†] Notice that this constant has a typing error in [Ver94].

1.	NO2	→	NO+O3P	14.	NO2+OH	→	HNO3
2.	NO+O3	→	NO2	15.	O3P	→	O3
3.	HO2+NO	→	NO2+OH	16.	O3	→	O1D
4.	HCHO	→	2 HO2+CO	17.	O3	→	O3P
5.	HCHO	→	CO	18.	O1D	→	2 OH
6.	HCHO+OH	→	HO2+CO	19.	O1D	→	O3P
7.	ALD	→	MEO2+HO2+CO	20.	SO2+OH	→	SO4+HO2
8.	ALD+OH	→	C2O3	21.	NO3	→	NO
9.	C2O3+NO	→	NO2+MEO2+CO2	22.	NO3	→	NO2+O3P
10.	C2O3+NO2	→	PAN	23.	NO2+O3	→	NO3
11.	PAN	→	C2O3+NO2	24.	NO3+NO2	→	N2O5
12.	MEO2+NO	→	CH3O+NO2	25.	N2O5	→	NO3+NO2
13.	CH3O	→	HCHO+HO2				

FIGURE II.2.1: *Reaction scheme.*

TABLE II.2.3: *Identification of variables with species. The square brackets '[ ]' denote concentrations.*

variable	species	initial value	variable	species	initial value
y_1	[NO2]	0	y_{11}	[C2O3]	0
y_2	[NO]	0.2	y_{12}	[CO2]	0
y_3	[O3P]	0	y_{13}	[PAN]	0
y_4	[O3]	0.04	y_{14}	[CH3O]	0
y_5	[HO2]	0	y_{15}	[HNO3]	0
y_6	[OH]	0	y_{16}	[O1D]	0
y_7	[HCHO]	0.1	y_{17}	[SO2]	0.007
y_8	[CO]	0.3	y_{18}	[SO4]	0
y_9	[ALD]	0.01	y_{19}	[NO3]	0
y_{10}	[MEO2]	0	y_{20}	[N2O5]	0

TABLE II.2.4: *Reference solution at the end of the integration interval.*

y_1	$0.5646255480022769 \cdot 10^{-1}$	y_{11}	$0.1135863833257075 \cdot 10^{-7}$
y_2	0.1342484130422339	y_{12}	$0.2230505975721359 \cdot 10^{-2}$
y_3	$0.4139734331099427 \cdot 10^{-8}$	y_{13}	$0.2087162882798630 \cdot 10^{-3}$
y_4	$0.5523140207484359 \cdot 10^{-2}$	y_{14}	$0.1396921016840158 \cdot 10^{-4}$
y_5	$0.2018977262302196 \cdot 10^{-6}$	y_{15}	$0.8964884856898295 \cdot 10^{-2}$
y_6	$0.1464541863493966 \cdot 10^{-6}$	y_{16}	$0.4352846369330103 \cdot 10^{-17}$
y_7	$0.7784249118997964 \cdot 10^{-1}$	y_{17}	$0.6899219696263405 \cdot 10^{-2}$
y_8	0.3245075353396018	y_{18}	$0.1007803037365946 \cdot 10^{-3}$
y_9	$0.7494013383880406 \cdot 10^{-2}$	y_{19}	$0.1772146513969984 \cdot 10^{-5}$
y_{10}	$0.1622293157301561 \cdot 10^{-7}$	y_{20}	$0.5682943292316392 \cdot 10^{-4}$

2.4 Numerical solution of the problem

Tables II.2.4–II.2.5 and Figures II.2.2–II.2.6 present the reference solution at the end of the integration interval, the run characteristics, the behavior of the solution over the interval [0,12] and the work-precision diagrams, respectively. The reference solution was computed by RADAU5 on a Cray C90, using double precision, `work(1) = uround` $= 1.01 \cdot 10^{-19}$, `rtol = atol = h0` $= 1.1 \cdot 10^{-18}$. For the work-precision diagrams, we used: rtol $= 10^{-(5+m/4)}$, $m = 0, 1, \ldots, 32$; atol = rtol; h0 = rtol for BIMD, GAMD, MEBDFDAE, MEBDFI, RADAU and RADAU5.

.

References

[MM08] F. Mazzia and C. Magherini. *Test Set for Initial Value Problem Solvers, release 2.4.* Department of Mathematics, University of Bari and INdAM, Research Unit of Bari, February 2008. Available at http://www.dm.uniba.it/~testset.

[Ver94] J.G. Verwer. Gauss-Seidel iteration for stiff ODEs from chemical kinetics. *SIAM J. Sci. Comput.*, 15(5):1243–1259, 1994.

TABLE II.2.5: *Run characteristics.*

solver	rtol	atol	h0	mescd	scd	steps	accept	#f	#Jac	#LU	CPU
BIMD	10^{-7}	10^{-7}	10^{-7}	9.25	5.63	25	25	572	22	25	0.0039
	10^{-10}	10^{-10}	10^{-10}	11.73	8.73	41	41	1257	27	41	0.0107
DDASSL	10^{-7}	10^{-7}		5.94	4.13	135	135	188	23		0.0039
	10^{-10}	10^{-10}		9.04	5.91	536	532	669	38		0.0107
GAMD	10^{-7}	10^{-7}	10^{-7}	8.16	6.31	23	23	625	23	23	0.0049
	10^{-10}	10^{-10}	10^{-10}	11.35	5.36	36	36	1401	36	36	0.0098
MEBDFI	10^{-7}	10^{-7}	10^{-7}	8.46	6.46	120	118	391	20	20	0.0039
	10^{-10}	10^{-10}	10^{-10}	11.45	9.32	235	235	763	33	33	0.0078
PSIDE-1	10^{-7}	10^{-7}		7.51	4.84	31	29	465	9	124	0.0049
	10^{-10}	10^{-10}		10.64	8.04	63	62	970	12	188	0.0098
RADAU	10^{-7}	10^{-7}	10^{-7}	5.59	3.78	32	29	227	21	32	0.0029
	10^{-10}	10^{-10}	10^{-10}	10.00	7.75	35	35	449	21	35	0.0049
VODE	10^{-7}	10^{-7}		6.61	3.32	149	149	208	4	27	0.0029
	10^{-10}	10^{-10}		8.79	4.78	393	375	528	7	61	0.0059

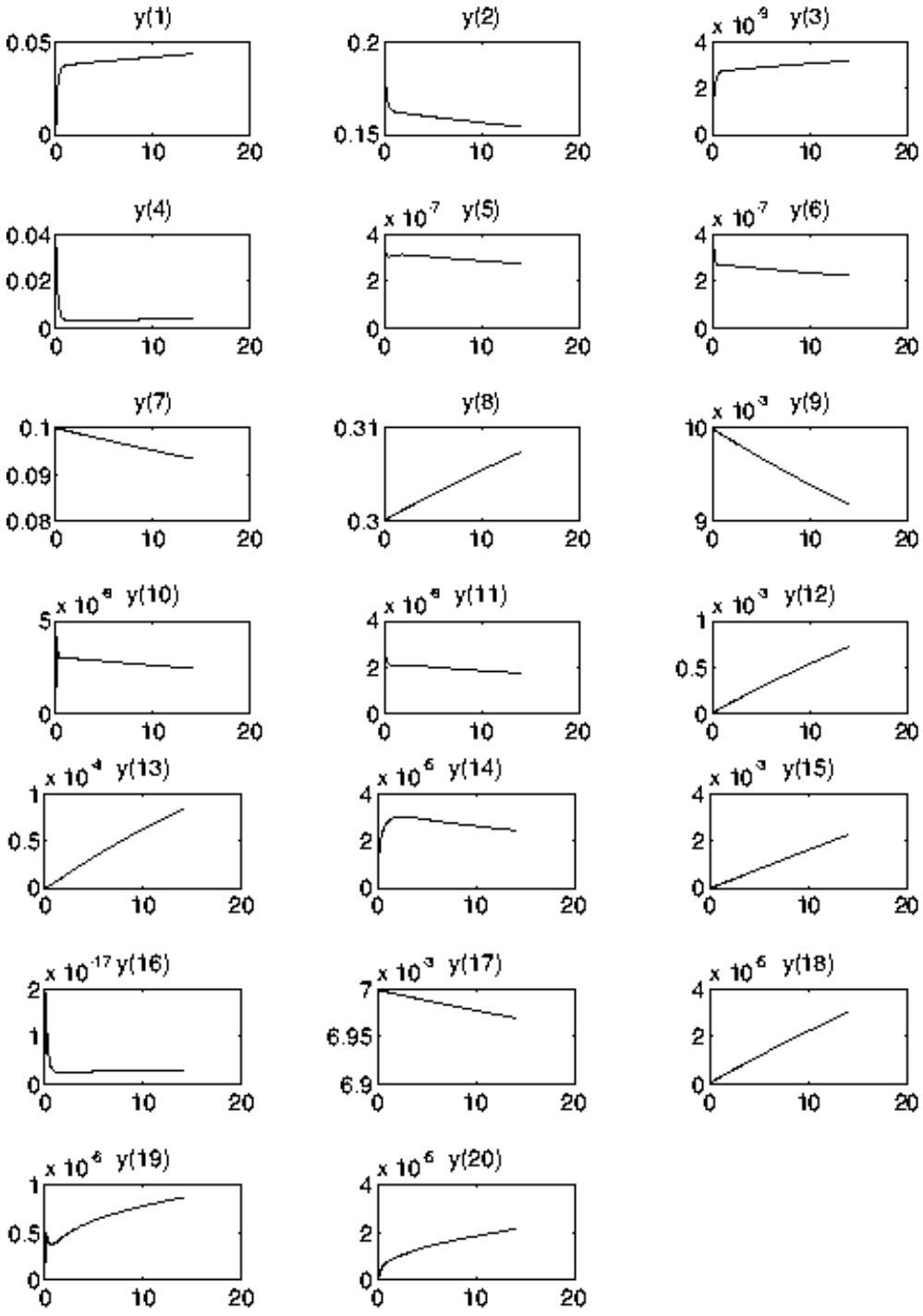


FIGURE II.2.2: *Behavior of the solution over the interval [0,12].*

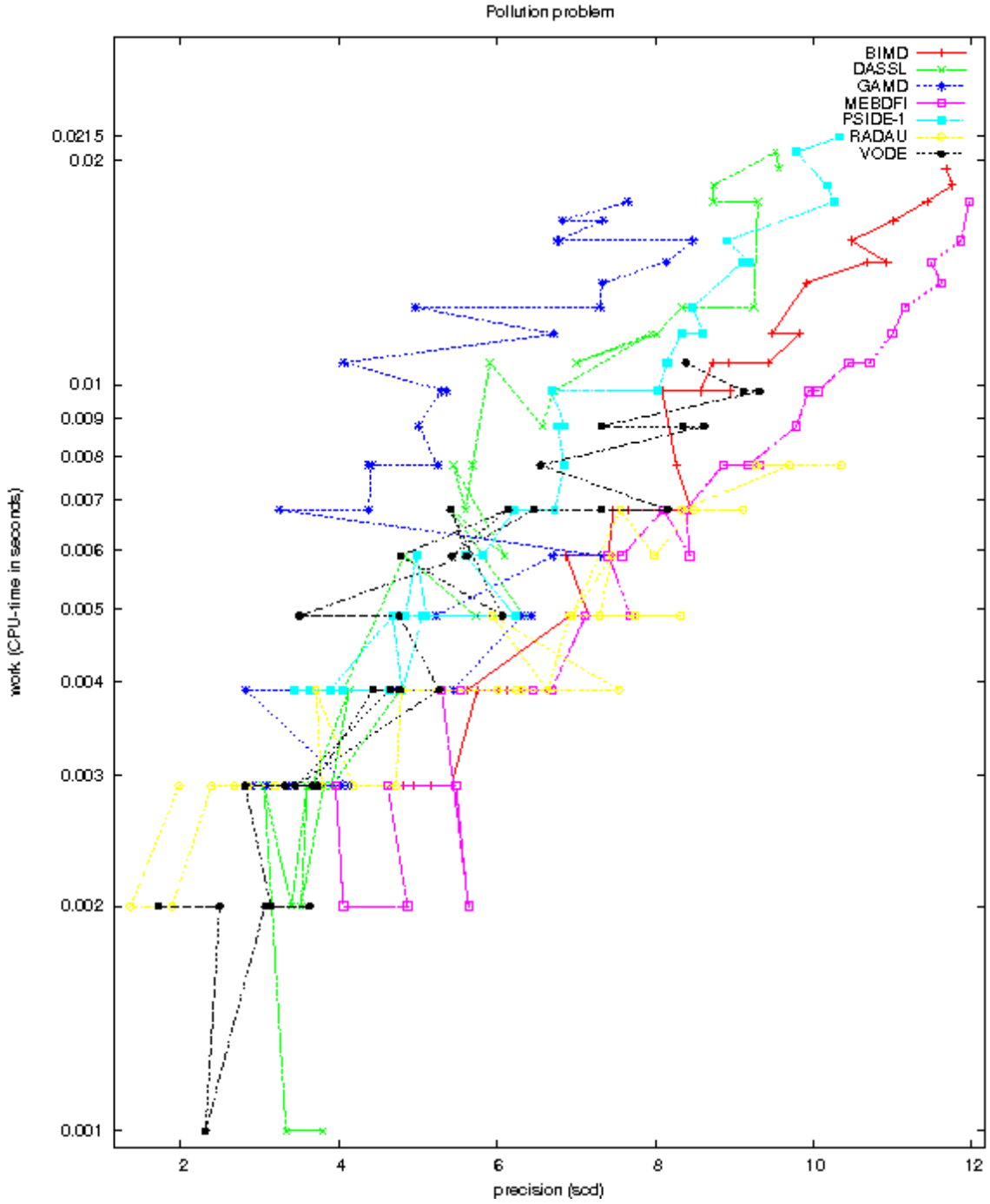
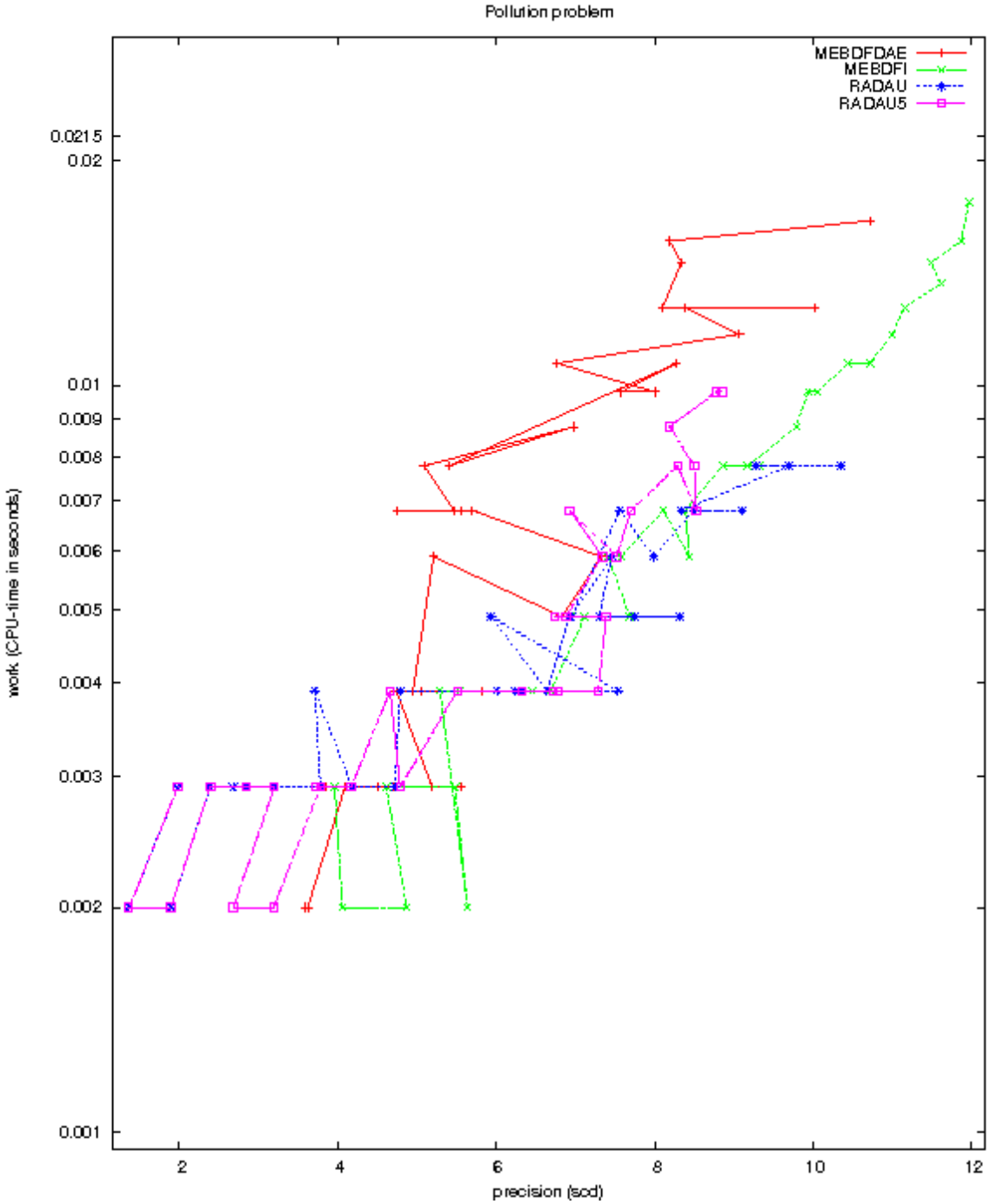


FIGURE II.2.3: *Work-precision diagram (scd versus CPU-time).*



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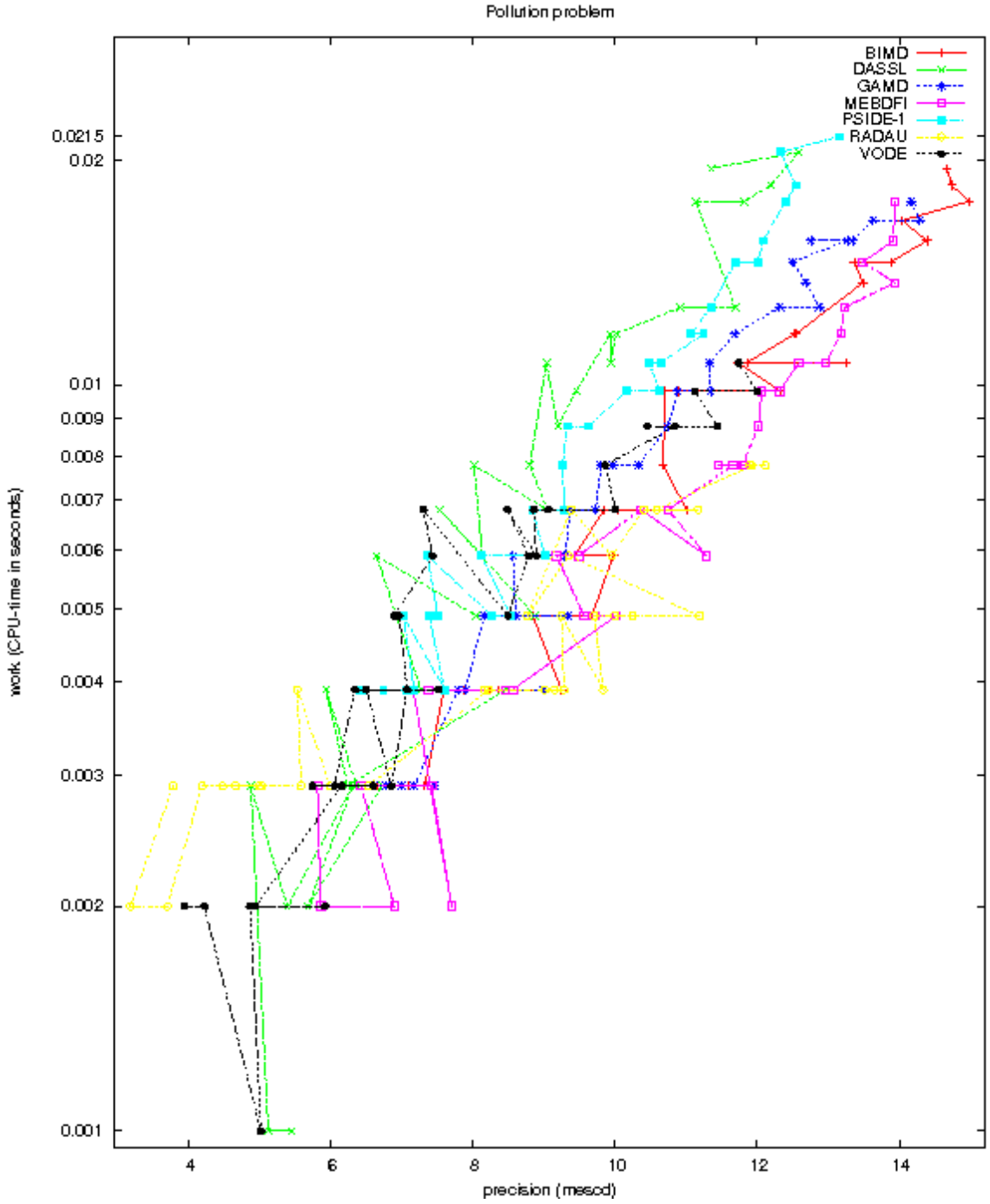

FIGURE II.2.5: *Work-precision diagram (mescd versus CPU-time).*

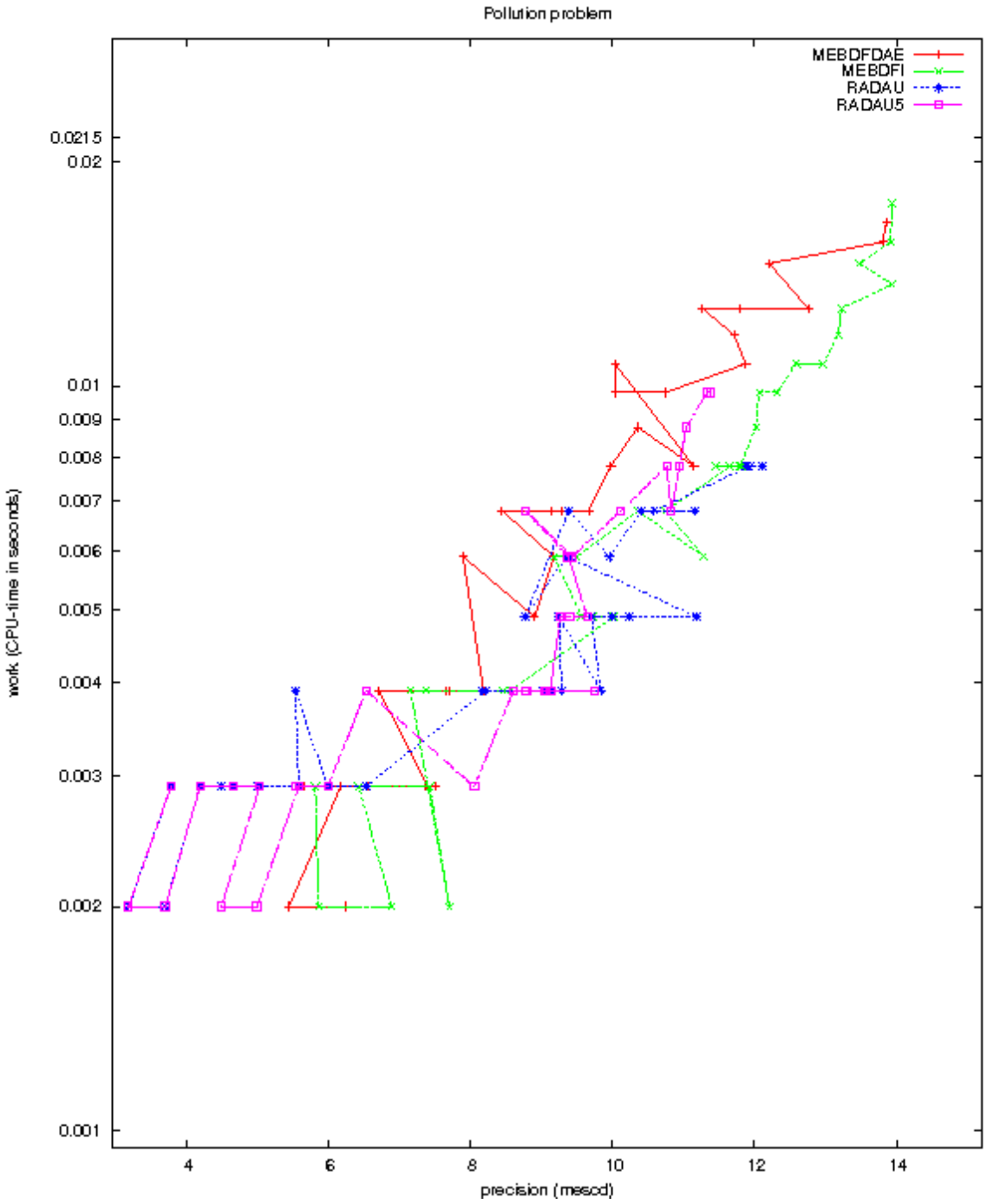

FIGURE II.2.6: *Work-precision diagram (mescd versus CPU-time).*