

Interactive comment on “Simulation of trace gas redistribution by convective clouds - Liquid phase processes” by “Y. Yin et al.”

Y. Yin et al.

Received and published: 13 November 2001

Mark Lawrence:

A short discussion of the application of these results to large scale simulations, though not necessary, would help broaden the impact of this work.

The authors:

It is difficult and probably not appropriate to speculate about the details of how the results obtained here for a single cloud can be extended to GCMs. One aspect of our current work is to extend these simulations to representative GCM grid boxes. But equally important is to first of all evaluate the model results for single clouds. So far, our study has revealed more difficulties than solutions to this problem.

Mark Lawrence:

My main criticism regarding the present manuscript is the strong focus on the results at the cloud top, rather than on the integrated results throughout the cloud outflow

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region. At the cloud top, a considerable difference between the continental unsheared, sheared, and equilibrium simulations is seen. The authors justify focusing on this level because in the middle of the cloud, where wet deposition is prevalent, the ratios of the highly soluble tracers to the insoluble tracer are very small (down to $< 1\%$), whereas at the cloud top the soluble tracer mixing ratio are up to 50% of the insoluble tracer values. However, the mixing ratios of all the tracers fall to very low levels at the cloud top, so that even if the relative amounts of the soluble gases are larger at the cloud top, it appears that the absolute amounts are larger in the main outflow region in the middle of the cloud.

The authors:

Plots of the integrated mass above 4 km (or in the main outflow region) have been added and discussed in the revised manuscript.

Mark Lawrence:

For the sake of determining the chemical impact of important gases (such as halogens) which are transported to the upper troposphere, a more relevant parameter to compare would be the integrated mass of tracer between about 4 km (start of the outflow regime) and cloud top (or alternatively between 4 km and the model top). This indicates how much of a real tracer with a given solubility starting in the BL has actually been able to make it to the middle and upper troposphere, and how much has been lost to precipitation scavenging on the way. Based on the plots, I suspect this number will not differ much for the three continental cases considered (Figs. 6 and 12), and will only differ modestly for the marine case (Fig. 8). It is impossible to judge accurately from the plots, due to the small values and opposing curves, and thus it would be very interesting to see what values are found if the authors can perform this integration.

The authors:

We calculated the integrated mass of tracer above 4 km. The results for a highly soluble gas with $H^* = 10^7$ in the 4 cases after 60 min simulation are as follows: The values in this table again indicate that assuming Henry's law equilibrium would have a significant influence on the calculated redistribution of highly soluble gases. This is seen from all

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Table 1: Integrated mass for gas with $H^* = 10^7$

Case	Mass [mol] above 4 km	fraction [%] of insoluble tracer	Mass [mol] in top 0.9 km	fraction [%] of insoluble tracer
1. continental-unsheared	13.47	9.3	1.72	21.3
2. continental-sheared	12.76	11.2	2.13	13.2
3. maritime-sheared	5.84	4.4	1.25	2.4
4. continental-equilibrium	6.42	5.6	0.85	5.3

the 4 columns. In addition, this influence becomes less significant with decreasing gas solubility. This is apparent from the following table, which shows the results for a gas with $H^* = 10^4$.

Table 2: Integrated mass for gas with $H^* = 10^4$

Case	Mass [mol] above 4 km	fraction [%] of insoluble tracer	Mass [mol] in top 0.9 km	fraction [%] of insoluble tracer
1. continental-unsheared	101.36	70.4	6.01	74.6
2. continental-sheared	82.67	72.5	11.52	71.4
3. maritime-sheared	86.04	65.1	31.56	61.2
4. continental-equilibrium	82.60	72.4	11.47	71.1

These results are consistent with those already presented in the manuscript, where we focussed on the upper cloud layers only.

Mark Lawrence:

Once this is done, it may be necessary to reconsider the importance of differences in

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the simulations, in particular if it is found that the consideration of kinetic uptake does not make much difference to the integrated amount of tracer which is transported to above 4 km. If this is the case, can it still be argued that this is important to consider at present in global models?

The authors:

As has been seen from the above table, the equilibrium assumption indeed has a significant influence on the calculated gas redistribution, even when considering a large vertical region at cloud top.

Mark Lawrence:

It will also be interesting to compare the results in that light to those in Crutzen and Lawrence (2000) and Barth et al. (2001). It appears that there is less scavenging in the cloud model results presented here than in our global model runs: the amounts of the $H^* = 10^3$, 10^4 , and 10^5 tracers remaining relative to the insoluble tracer in our global model runs were found to be about 80-90%, 40-60%, and 10-20%, while in Figures 6, 8, and 12 it appears to be 90-95%, 60-80%, and 20-30%. If this difference in the integrated transport amounts cannot be attributed to the neglect of kinetic uptake limitations in the global model, then another reason will need to be proposed and tested, either by the authors or in future studies.

The authors:

The highlighted differences are similar to those expected when non-equilibrium effects are neglected.

It is interesting to compare the results here to those from Crutzen and Lawrence (2000) and Barth et al. (2001). Barth et al. showed that the highly soluble tracers ($H^* = 10^5$ and $H^* = 10^{12}$) were reduced by 40-60% compared to the passive tracer in the outflow region. The values calculated in this study in the region above 4 km are 16.8% and 29% for the maritime case and the continental cases, respectively. The fact that the results from the maritime case are much closer to those reported by Crutzen and Lawrence (2000) implies that the rainfall rate, which depends on the cloud parameterization, was very efficient in the model used by Crutzen and Lawrence.

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Barth et al. attributed the difference between their results and those by Crutzen and Lawrence to the size-dependence of the averaging region and parameterization of the microphysical processes in their study. They also indicated that an overestimate of the loss of highly soluble species in the upper troposphere by larger-scale models was also responsible for the difference. In addition, the results reported here and by Barth et al. (2001) were obtained under specific thermodynamic conditions. The clouds and precipitations produced under these conditions were different from those reported by Crutzen and Lawrence (2000) for monthly mean values. The differences in clouds and precipitation properties could lead to a big difference in scavenging efficiency.

Mark Lawrence:

A final point with respect to considering the values at the cloud top: a peak in the ratio of soluble to insoluble tracers a km above the cloud top, where relatively little vertical transport should be occurring. Do the authors have an explanation for this peak? Could it be due to numerical diffusion of the very low tracer mixing ratios?

The authors:

Firstly, we note that we have not drawn important conclusions from the gas abundances 1 km above cloud top. All of our conclusions are based on abundances within the visible part of the cloud.

The peak in the ratio of the soluble to insoluble tracers a km above the cloud top is caused mainly by the very low abundance of the insoluble tracer. Numerical diffusion will be active in any model of this form, and it will tend to produce soluble/insoluble tracer ratios which are not necessarily small above the cloud top.

Mark Lawrence:

The point is also made that the mixing ratios of the soluble tracers below the cloud in the case assuming Henry's Law equilibrium (Fig. 12) are much lower than those in the case considering kinetic uptake (Fig. 6). In this case, integrating the amount below 4 km would also be illustrative to make clear how large this difference is. Is this difference mainly due to below-cloud scavenging? This would make sense, since raindrops falling through the layers below the cloud will not reside long, and assuming

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Henry's Law equilibrium would be expected to enhance the uptake. This would be interesting to quantify by performing a mixed experiment with equilibrium uptake within the cloud, but kinetic uptake below the cloud. How do the differences in integrated tracer amounts below 4 km for these two cases compare with the amounts above 4 km? Does this make sense, since the below-cloud region is the source region for the tracers entering the cloud? These additional pieces of information should not be too difficult to compute, but would be quite informative.

The authors:

Yes, the difference is mainly due to scavenging by raindrops below cloud base.

An overall comparison of the results from the equilibrium run and the kinetics run is demonstrated by the ratio of integrated species masses at various altitudes between these two cases. This is shown in a table provided in a later paragraph.

Mark Lawrence:

In comparing Figures 9, 10, and 11, I do not understand why there is generally less tracer in the cloud droplets for the $H^* = 10^4$ case than in both the $H^* = 10^2$ case and the $H^* = 10^6$ case (that is, why there is a minimum in the aqueous phase mixing ratios for $H^* = 10^4$), particularly in the upper part of the cloud. Does this have to do with the tradeoff between the amounts which are lost due to wet deposition (and thus the amount left in gas phase to be taken up into droplets later in the simulation) and the fraction of gas which is taken up, or is there another explanation?

The authors:

The reason is that the units in these figures are different. This has been pointed out in the caption of Figure 9 and is added in Figure 10 in the new version. The unit in Figure 9 is $\mu\text{g/litre}$ (not ng/litre in the original manuscript), and mg/litre in Figs. 10 and 11.

Mark Lawrence:

It would be interesting to see the ratio of the curves in Figure 12 versus those in Figure 6, although comparing integrated amounts above and below 4 km may be nearly as informative.

The authors:

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The ratios of the curves in Figure 12 versus those in Figure 6 for gases with different solubilities at different altitudes are as follows:

Table 3: Ratio of the values in Fig. 12 (equilibrium) to those in Fig. 6 (non-equilibrium).

Altitude [km]	$H^* = 10^2$	$H^* = 10^3$	$H^* = 10^4$	$H^* = 10^5$	$H^* = 10^6$	$H^* = 10^7$
0.0	1.0	1.0	0.92	0.75	0.69	0.66
1.5	1.0	1.0	0.98	0.87	0.77	0.66
3.0	1.0	1.0	0.99	0.87	0.76	0.67
4.5	1.0	1.0	1.0	0.85	0.74	0.54
6.0	1.0	1.0	0.99	0.92	0.78	0.52
7.5	1.0	1.0	1.0	1.0	0.86	0.38

The values in this table indicate that assuming Henry's law equilibrium could lead to underestimation of the gases, especially highly soluble gases, transported to the upper part of the clouds, as well as the mass below cloud base.

Mark Lawrence:

Why isn't point 5 (HO_2) in Figure 13 exactly on the line (since it has no temperature dependence)? The difference looks larger than typical printer misplacement error. Figure 13 would also be interesting for the 6 km maximum in cloud outflow, rather than just at the cloud top.

The authors:

The slight departure of point 5 in Figure 13 from the line is due to the number of points used to plot the line, which is a series of straight lines.

Mark Lawrence:

The statement "Model parameterizations of gas transport through clouds (Crutzen and Lawrence, 2000) assume that the gases have temperature- independent Henry's law constants" *only* applies to the Crutzen and Lawrence (2000) study, as far as I am aware. We assumed no temperature dependence in that study because it was a first

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study of this nature, and we wanted to demonstrate the overall principle of dependence of trace gas transport on solubility for simplified and easy to interpret tracers. In computations with real gases, we recompute the temperature dependent solubility every model timestep (see Lawrence et al., 1999); as far as I am aware, most atmospheric chemistry models also consider the temperature dependence of the solubility. This statement should be reworded appropriately.

The authors:

Ok. This has been done in the text.

Mark Lawrence:

The comparison between HCHO and CH₃OH in Figure 13 is not really sufficient to demonstrate that "for moderately soluble gases the effect increases with increasing enthalpy;" a plot of the deviation versus the enthalpy would be much more informative. Is the dependence nonlinear? CH₃C(O)OOH and CH₃OOH have just barely higher enthalpies than CH₃OH, but appear to be notably further from the line. Also, the gases HNO₂ and SO₂ do not fit this at all; HNO₂ has a larger enthalpy than SO₂, but is much closer to the line. Can these deviations from the general statement be justified (perhaps due to subsequent dissociation in the solution, which could be tested by turning the dissociation off)? The most instructive study, if possible, would be a run with a suite of fictitious tracers with a range of solubilities and enthalpies, and to then produce a 2D contour plot of the deviation from the line with no temperature dependence as a function of both the solubility (at a reference temperature) and the enthalpy.

The authors:

We have run the model with a suite of fictitious tracers with solubilities ranging from 10³ to 10⁶ and enthalpies (exactly, $-\frac{\Delta H}{R}$) ranging from zero (no temperature-dependence) to 5000. The values of the integrated species mass above 4 km and near cloud top level are given in the following tables, varying with both solubility (at a reference temperature 0°C) and the enthalpy. It is clear that the effect by assuming temperature-independence increases with increasing enthalpy, but the dependence of this effect on gas solubility is not obvious. Therefore, the general statement in the manuscript has been modified.

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Table 4: Integrated Species Mass Above 4 km

$-\frac{\Delta H}{R}$ [K]	$H^* = 10^3$	$H^* = 10^4$	$H^* = 10^5$	$H^* = 10^6$
5000	104.15	59.58	23.56	14.52
4000	105.90	64.29	24.85	14.62
3000	107.29	69.12	26.41	14.77
2000	108.37	73.88	28.28	14.96
1000	109.18	78.45	30.52	15.23
0	109.94	82.68	33.14	15.59

Mark Lawrence:

Could one interpret the differences in Figure 13 as being indicative of the "effective average cloud temperature" that a trace gas (or set of trace gases) experiences? By choosing a temperature somewhat below 0°C, the points would all shift towards the right to being in better agreement with the curve. Is there a temperature at which a best fit of the points to the curve is obtained? What (if anything) does this say about the average path of trace gases on their way to the cloud top (where the temperature is much below 0°C)?

The authors:

It is true that choosing a lower effective temperature to plot the Henry's law constant values in Figure 13 would tend to move the 'real gas' points closer to the temperature-independent curve. For the cloud considered in figure 13 the optimal choice of temperature seems to vary between about 0 and -20 C and is sensitive both to the altitude and to the solubility of the gas in question. Due to the nonlinearity of the cloud transport it is generally impossible to collapse the data exactly onto the temperature-independent curve. This nonlinearity is likely to be even more serious for mixed-phase clouds.

Mark Lawrence:

The second-to-last paragraph in the Summary ("We have found...") should be revised

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Table 5: Integrated Species Mass at 7500m Level

$-\frac{\Delta H}{R}$ [K]	$H^* = 10^3$	$H^* = 10^4$	$H^* = 10^5$	$H^* = 10^6$
5000	1.39	0.85	0.49	0.36
4000	1.43	0.92	0.51	0.36
3000	1.46	0.99	0.53	0.36
2000	1.49	1.06	0.56	0.36
1000	1.51	1.13	0.60	0.37
0	1.52	1.20	0.63	0.38

accordingly based on my last three comments (above). Also, in that paragraph, a space is needed between "0° C" and "a".

The authors:

Ok. We have done this in the new version of the text.

Mark Lawrence:

In Figure 14 more of the soluble gas comes from higher altitudes than the insoluble gas; is this mainly due to downdrafts, as indicated in section 4.6 (note that it should be "downdrafts", not "downdraft"), or is there also a significant contribution from evaporating precipitation?

The authors:

Yes, there is also a significant contribution from the evaporating precipitation particles.

Mark Lawrence:

In section 4.6, it is mentioned that the cloud covers 1/3 of the 2D domain, or equivalently 1/9 (10%) of a 3D domain, and that larger clouds would have a greater effect than found here. Although the mean fraction of convective clouds is poorly classified, from various satellite studies it appears likely to be around 10% or less, and thus the results here are probably fairly representative of an "average" situation.

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Good point.

Mark Lawrence:

Plus a number of minor points:

In the introduction, it would be appropriate to already mention the Barth et al. (2001) study, since the two studies are in many ways comparable.

The authors:

Ok. This has been added in the new version.

Mark Lawrence:

Why are the lines in Figure 1c not smoother?

The authors:

The reason is that the values of N_0 and k are different in the CCN formula (Eq.11) for different ranges of supersaturation, which is listed in the newly added Table 2.

Mark Lawrence:

I appreciate that the authors added color to Figure 2 on my recommendation, but it would be wise to also keep the readily-distinguishable line styles from the first draft for the sake of B/W copies.

The authors:

This has been done in the revised version.

Mark Lawrence:

In section 3.1, it would be nice to briefly state the values of N_0 and k which are used, rather than just referring the readers to the previous literature.

The authors:

The values of N_0 and k has been add as a table (Table 2) in the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 1, 125, 2001.

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