

1 **Authors' Response to Anonymous Referee #1 Interactive**
2 **comment on "Atmospheric lifetimes and ozone depletion**
3 **potentials of trans-1-chloro-3,3,3-trifluoropropylene and**
4 **trans-1,2-dichloroethylene in a three-dimensional model"**

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9 We thank Referee #1 for consideration of our article. Regarding the questions raised in the second
10 paragraph of the review (shown in italics):

11

12 *(1) Everyone recognizes that the ODP value is also dependent on time of the year when the*
13 *emission occurs. It is strange that the authors continue to use uniform emission throughout the*
14 *year, rather than doing 4 seasons. It would be more work, but will provide useful needed*
15 *information.*

16 Our choice of uniform emissions rate throughout the year arises from the intended applications of
17 tCFP and tDCE. In our understanding, rates of release to the atmosphere for industrial cleaning
18 solvents, including compounds for which tCFP and tDCE are being evaluated as replacements, are
19 not subject to well-defined seasonal patterns. While the seasonal dependence of ODP for tCFP and
20 tDCE would be interesting, we have no basis for choosing an emissions time dependence with
21 these compounds. The issue of ODP seasonal dependence for replacement VSLs will hopefully
22 be considered (and the study supported) for future replacement compound candidates whose
23 applications will have seasonal dependence, such as for agricultural fumigants.

24

25 *(2) If a VSL molecule enters the stratosphere, it should release its chlorine atoms near the*
26 *tropopause. Thus, to a very good approximation, there are no local sources and sinks for Cly in the*
27 *stratosphere and changes in Cly mixing ratio due to the VSL should be uniform. Yet the results in*
28 *Figures 2a and 2c show large latitudinal and vertical gradients. One explanation may be that*
29 *there is such a large gradient in Cly across the extra tropical tropopause that there is diffusive*
30 *transport in the model to maintain the gradients. There are publications that argue that the entry*
31 *point to the stratosphere is predominately through the tropical tropopause. Is this diffusive*
32 *transport caused by the high concentration in the extra-tropical troposphere realistic?*

33 Stratospheric entry for long-lived gases usually occurs through the tropical tropopause, but tCFP
34 and especially tDCE are short-enough lived that only minimal fractions of these source gases reach
35 the tropical tropopause layer (TTL) from surface emissions between 30 °N and 60 °N. For tDCE in
36 particular (Fig. 1b), TTL mixing ratios are no greater than 1 ppt, so that very little tDCE reaches
37 the stratosphere through the tropics. Although extratropical cross-tropopause transport in the
38 atmosphere and its representation in models is an ongoing topic of research interest, many studies

39 have pointed out the importance of isentropic transport across the tropopause (e.g. Holton et al.,
40 1995; Lelieveld et al., 1997; Hintsä et al., 1998; Ko et al., 2003; Law et al., 2007). With regard to
41 the model we used, Pan et al. (2007) examined this issue for both MOZART 3 driven by ECMWF
42 operational and reanalysis meteorology fields and for WACCM 3, the climate model which
43 supplied meteorology fields to drive MOZART 3 for this study, by comparison with data collected
44 during the POLARIS measurement campaign. While the reanalysis-driven MOZART 3 indicated
45 excess upper troposphere (UT) mixing into the lower stratosphere (LS) through high LS values of
46 CO and H₂O, the WACCM 3 runs for that study had little such indication of excess UT to LS
47 transport. Because this ODP study used WACCM 3 meteorology to drive MOZART 3, we believe
48 our extratropical UT-LS transport of tCFP, tDCE, and especially Cl_y generated from these source
49 gases reasonable.

50 We believe that for tCFP and tDCE, the Cl_y perturbation in the LS depends on latitude because of
51 transport of Cl_y produced by VLS degradation in the troposphere into the LS by Northern
52 extratropical isentropic mixing. The southward horizontal mixing of the Cl_y perturbation is limited
53 by Cl_y-unperturbed air from the Southern troposphere entering the tropical LS for the Northern
54 midlatitude emissions scenario used in this study. The Cl_y perturbation from tCFP in our Fig. 2a
55 could then be interpreted as a combination of Cl_y from tCFP oxidized in the troposphere and
56 transported to the Northern LS by isentropic mixing with tCFP transported into the LS through
57 tropics and midlatitudes (compare with tCFP in our Fig. 1a) and oxidized within the LS. The Cl_y
58 perturbation from tDCE in Fig. 2c could be interpreted as a combination of Cl_y from tDCE
59 oxidized in the troposphere with Cl_y from tDCE transported to the Northern LS primarily by
60 isentropic mixing and oxidized to Cl_y there. The compound tDCE seems unusual among the
61 various VLSs we have evaluated in that intact transport as tDCE through the tropical tropopause
62 is minimal.

63

64 (3) *In order to get the 1% depletion in the stratosphere, the model must be forced with a high*
65 *emission, resulting in large increase in Cl_y in the troposphere. Does this corrupt the ODP results?*
66 *Should depletion in the troposphere be included in the ODP calculation?*

67 We considered the possibility that such large emissions could alter atmospheric lifetime and ODP
68 results from MOZART, and our test is first discussed in the initial paragraph of page 16644. We

69 performed a second MOZART run for tDCE (the shorter-lived of the two compounds) using 16.7
70 Tg yr⁻¹ emissions, one-third of the 50.0 Tg yr⁻¹ tDCE used in the MOZART run for ODP
71 determination, and found that lifetime calculated from the 50.0 Tg yr⁻¹ run was 6% higher than for
72 the 16.7 Tg yr⁻¹ run (these lifetimes are shown in the latter two rows of Table 1). The O₃ burden
73 perturbations from the two tDCE runs are considered in the final paragraph of the Results section,
74 starting on line 22 of page 16646 and referencing Table 4, although with regard to fraction of O₃
75 burden perturbation in the stratosphere. One-third of the total ΔO₃ burden for the 50.0 Tg yr⁻¹ run is
76 $(9.870+0.361)/3 = 3.410$ Tg, approximately 5% higher than the total ΔO₃ burden for the 16.7 Tg
77 yr⁻¹ run of $(3.192 + 0.061) = 3.253$ Tg. The 5% change in ΔO₃ per unit flux of tDCE (and thus in
78 ODP) is insignificant compared to the uncertainty in the tDCE + OH reaction rate constant
79 measurements.

80 We include the total O₃ column change, not stratosphere-only, in ODP calculation because the
81 absorption of ultraviolet (UV) radiation by O₃ takes place throughout the atmosphere. The concern
82 in O₃ depletion arose from increased exposure of surface lifeforms to UV at wavelengths between
83 300 and 320 nm that are especially effective at causing injuries such as sunburn, cataracts, and
84 mutations. Though O₃ in the middle or upper stratosphere has a somewhat larger cross section
85 toward 300-320 nm UV radiation than it does in the LS or UT because of temperature dependence,
86 all O₃ contributes toward the absorption of damaging solar UV, so that we count O₃ loss at all
87 altitudes toward ODP.

88

89 *(4) Is the ozone response to Cly increase in the troposphere linear or does it saturate? If it*
90 *saturates, are we underestimating the tropospheric ozone depletion per unit mass emitted by using*
91 *such a large emission?*

92 The ΔO₃ burdens shown in Table 4 for the tDCE flux test help to answer this question. If the
93 tropospheric O₃ response to Cl_y from tDCE is linear and the OH field in the troposphere is
94 unaffected by the tDCE flux increase, the tropospheric ΔO₃ burden for 50.0 Tg tDCE yr⁻¹ should be
95 3×3.192 , or 9.576 Tg. The tropospheric ΔO₃ burden shown in the table for 50.0 Tg tDCE yr⁻¹,
96 9.870 Tg, is about 3% higher than that prediction. This suggests to us that the minimal nonlinearity
97 we encounter in this test arises from shifts in tDCE and its Cl_y perturbation to higher altitudes due
98 to tropospheric O₃ loss, instead of a saturation of tropospheric O₃ response to Cl_y which we would

99 have expected to result in a smaller O₃ loss dependence than linear.

100

101 (5) *If the ozone depletion is mostly in the troposphere near the emission region, is the concept of*
102 *using a single number to characterize ozone depletion still useful?*

103 The definition of ODPs for VSLs was established (e.g., by Wuebbles et al., 2001) to be dependent
104 on location of the emissions, so it really is not a single number. Unfortunately the high
105 computational costs prevent us from doing more than a representative set of ODP calculations for
106 each gas. For VSLs, the single-valued ODP for a given location remains useful as an indicator of
107 relative O₃ loss from candidate replacement compounds though ODP is admittedly not a
108 comprehensive scientific description of the atmospheric O₃ effect. The single-value ODP remains
109 part of the initial determination as to whether a candidate replacement compound is
110 environmentally acceptable for use through policy limits on ODP such as the amended Montreal
111 Protocol. Thus, ODP remains an essential guideline for decisions as to whether to produce a
112 candidate compound that could potentially be released to the atmosphere. We have added text to
113 the third paragraph of our Introduction and a new third sentence to the sixth paragraph of our
114 Method to clarify these points in our revised manuscript.

115

116 With regard to the technical comments (third paragraph of review):

117

118 (1) *The statement that much of the ozone loss occurs in the troposphere (50% for tCFP and 96%*
119 *for tDCE) should be included in the abstract.*

120 The abstract (p. 2 lines 10-12) already contains a qualitative statement, but we agree to change that
121 sentence to a more quantitative statement regarding O₃ loss for tCFP and tDCE in the troposphere
122 in the revised manuscript.

123

124 (2) *P. 16643 and p. 16647: On p. 16643, the authors stated that the large flux could lower (my*
125 *word, the authors used the word “alter”) the OH field in a CTM, resulting in overestimation of*
126 *atmospheric lifetime. The authors then continue to state that this is due to reduction in OH*
127 *production associated with ozone depletion. On p. 16647, the authors suggest that the high fluxes*
128 *may saturate the oxidizing capacity in the troposphere, suggesting that OH is suppressed because*

129 of the enhanced loss associated with the reaction with tDCE. Which is it?

130 The statement on p. 16647 originated in an earlier draft and was regrettably not corrected for
131 consistency with that on p. 16643. This is corrected in the revised manuscript.

132

133 (3) P. 16645. The authors claim that comparison of figure 1a and figure 2a suggests that half of
134 Cl_y increase is due to Cl_y transported from the troposphere. I do not think this is justified because
135 in figure 1a, the mixing ratio of the source gas along the tropopause ranges from 25 to 100 ppt,
136 and change in Cl_y is not uniform in the stratosphere.

137 This returns somewhat to question (2) regarding realism of MOZART 3 cross-tropopause transport.
138 In Fig. 1a, tCFP vertical gradients about the tropopause are stronger north of 45 °N than toward the
139 tropics, which we believe is mostly maintained by the downward Brewer-Dobson circulation from
140 the stratosphere because low OH concentrations mean that tCFP oxidation in the North polar
141 tropopause and LS should proceed slowly. Nevertheless, the Cl_y perturbation from tCFP (Fig. 2a)
142 exhibits a maximum greater than 50 ppt for all latitudes north of 35 °N and altitudes higher than
143 the 250 hPa pressure level. We could not devise another explanation for the Cl_y maximum at
144 altitude other than approximately 25 ppt Cl_y produced by tCFP entering the stratosphere through
145 the tropics to be oxidized plus 25 ppt Cl_y originating from tCFP oxidized in the troposphere and
146 crossing into the LS through the Northern midlatitude tropopause. With our existing model
147 outputs, we cannot guarantee that the tropospheric Cl_y did not cross into the LS at polar latitudes,
148 so that we chose the word "suggests" for the manuscript, but for Cl_y from tCFP to cross the
149 tropopause there, it would have to diffuse against the Brewer-Dobson downward circulation, which
150 is unlikely.

151

152 (4) What is the reason for the calculated decrease in ClO_x in figure 2?

153 The annual and zonal $ClO_x = Cl + ClO$ decrease of up to 5% for tCFP (Fig. 2b) and 1% for tDCE
154 (Fig. 2d) is likely due to an increase of NO_2 by up to 5 ppt, or 4%, in the region south of 70 °S
155 between 20 and 40 hPa in the perturbed runs that favored $ClONO_2$ and, through suppression of
156 HO_x , HCl over the ClO_x species and Cl_2O_2 in the Cl_y partitioning. While this is a minor effect
157 overall (and seems to cause little change in O_3 , compare Fig. 3a and Fig. 3b to Fig. 2b and Fig. 2d
158 respectively in the South polar stratosphere), we do not expect it to represent a real effect from

159 tCFP or tDCE, but we are uncertain as to whether this possible artifact in MOZART 3 originates in
160 stratospheric sulfate aerosol and/or polar stratospheric cloud chemistry or in the parameterization
161 of NO generated by solar wind in the upper atmosphere.

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