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Chlorine Compounds and Stratospheric Ozone

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with food reinforcement to habituate them to the general experimental situation. The animals were then given 12 trials each day in a T-maze in which entrance into an arm with an olfactory stimulus (1 percent amyl acetate solution) led to food reward (4). The criterion was 22 correct responses in 24 trials. Animals were again given free access to food upon reaching criterion, and behavioral testing ended with measurement of activity by means of an Animex meter (5) over a 90-minute period. Throughout the study each lesion group was tested concurrently with a nonlesion control group (3). The animals were killed by spinal destruction of the nucleus should lead to motor variables. Motor difficulties observed (7) in some animals in all the lesion groups may have restricted their maximum running speeds. Activity, as measured during the 90-minute test period, was positively correlated with

Table 1. Summary of noradrenaline concentration and T-maze performance data; S.E.M., standard error of mean.

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Noradrenaline, cortex and hippocampus (ng/g) (mean ± S.E.M.)</th>
<th>T-maze, days to criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>7</td>
<td>291 ± 15</td>
<td>8–16</td>
</tr>
<tr>
<td>One-stage</td>
<td>3</td>
<td>269 ± 19</td>
<td>11</td>
</tr>
<tr>
<td>Two-stage</td>
<td>4</td>
<td>308 ± 20</td>
<td>10.5</td>
</tr>
<tr>
<td>One-stage total lesion</td>
<td>8</td>
<td>52 ± 5</td>
<td>12.5</td>
</tr>
<tr>
<td>Two-stage total lesion</td>
<td>Partial</td>
<td>157 ± 17</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>65 ± 16</td>
<td>7</td>
</tr>
</tbody>
</table>

Chlorine Compounds and Stratospheric Ozone

The potentially serious impact of man-made chlorofluoromethanes (CF<sub>3</sub>Cl<sub>2</sub>) on stratospheric O<sub>3</sub> is now documented in the scientific literature (1–3). In our recent report (2) we showed that the potential size of this atmospheric perturbation is large, so large that chemical control of the stratosphere will eventually pass to the chlorine oxides (ClO<sub>x</sub>) that arise from CF<sub>3</sub>Cl<sub>2</sub> usage. According to our calculations, the ClO<sub>x</sub> sink for stratospheric O<sub>3</sub> can be expected to dominate natural sinks for O<sub>3</sub> by 1985 or 1990. This time dependence is striking. Time scales of decades arise from our current knowledge of atmospheric mixing rates, and from the present belief (1–3) that the only significant mechanism by which nature can break apart CF<sub>3</sub>Cl<sub>2</sub> and CFCl<sub>3</sub> is by stratospheric photodissociation brought about by ultraviolet radiation. One purpose of this technical comment is to facilitate the readers' efforts
to verify our calculations (2). Several statistics and definitions require clarification, and one minor error should be noted by those who desire to check our work exactly. The CF₂Cl₃ mixing ratio shown for the year 2005 in figure 2 of (2) does not result from a steady model 2 emission rate of 2 x 10⁵ cm⁻² sec⁻¹ at ground as the text implies. In fact, the text should read “5 x 10⁷” on page 1166, column 1, line 46. Also we erroneously used a doubling time of 2.64 years in our computer computations, not 3.5 years as we stated. Consequently, we projected the total CF₂Cl₃ flux at ground level to be 5.2 x 10⁵ cm⁻² sec⁻¹ in late 1975 instead of the proper value, 4.2 x 10⁵ cm⁻² sec⁻¹. We have repeated our calculations for model 3 with the proper 3.5-year doubling time, a 5.05-year e-folding time. Although model 3 is more strongly affected than models 1 and 2, we find with these corrections only small changes in the model 3 results: the column O₃ destruction rate peaks around 1990, as before, at a value of about 1.55 x 10³¹ molecule sec⁻¹ integrated over the globe. In our report (2) we showed a peak value (figure 1) of about 1.81 x 10³¹ molecule sec⁻¹.

It should be noted that our presumed present stratospheric ClX (total concentration of gaseous chlorine compounds including Cl₂, ClO, and HCl) background accounts for more than half of the model 3 O₃ destruction rate and that stratospheric ClX concentrations are not well known (4). On the other hand, we must emphasize that uncertainties in the present ClX background do not affect the conclusions of our report (2). It is extremely important to learn present ClX values. Otherwise, future ClX increases will be impossible to document, whether due to chlorine release from CF₂Cl₄, ClX injection by volcanoes, or HCl from the proposed Space Shuttle system (5).

Also our reference 11 in (2) presents 1973 CF₂Cl₂ and CFCl₃ production statistics as current. These quantities, 4.5 x 10⁸ kg and 2.7 x 10⁸ kg, respectively, are DuPont's estimates of the 1973 annual global production. Presumably, the 1974 figures are larger.

The three paragraphs immediately above should assist others in repeating our calculations. Because of the potential seriousness of this problem, such checks are desirable. Similar reexamination of Crutzen's recent assessment of the expected O₃ depletion (3) are also to be encouraged. The sensitivity of model calculations to parameters such as the characterization of atmospheric transport through eddy diffusion coefficients, chemical reaction rates, and assumed background concentrations of certain species (for example, OH) must be ascertained. Researchers must re-examine stratospheric photochemical schemes for completeness: Have important gas-phase or heterogeneous reactions been overlooked? The search for alternative natural sinks (6) for CF₂Cl₃ should continue as we indicated (2) in reference 10. Researchers should also investigate the atmospheric fate of the fluorine atoms released from CF₂Cl₃. No direct effect on stratospheric O₃ is expected (1–3), but reactions involving fluorine atoms may disrupt natural cycles of hydrogen-containing species and they may present possibilities for monitoring the CF₂Cl₃ effect.

Perhaps more important, atmospheric measurements of background gaseous concentrations are needed for OH, atomic oxygen, the nitrogen oxides, and the chlorine oxides, and, obviously, continued monitoring of O₃ is necessary. Short of observing O₃ decreases directly, the most telling measurement would be of ClO, its present abundance and its rate of increase. To assess the impact of HCl from the Space Shuttle, stratospheric OH data would also be useful.

Stratospheric profiles of CF₂Cl₂, CFCl₃, and CCl₄ are also needed immediately. As all these studies are formulated and completed, the appropriate industrial and governmental bodies may decide intelligently on questions of the regulation and control of CF₂Cl₄ production.

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References and Notes
4. C. B. Farmer [Can. J. Chem. 52, 1544 (1974)] has presented data from infrared measurements which implied an upper limit on the HCl mixing ratio (volume to volume) of 2 x 10⁻¹⁰ in the lower stratosphere. There is reason to believe that HCl is the dominant ClX species in the lower stratosphere. Later C. B. Farmer (paper presented at the 3rd Conference on the Climatic Impact Assessment Program, Cambridge, Mass., 27 February 1974) presented lower stratospheric infrared data which implied an HCl mixing ratio of 8 x 10⁻¹¹ but noted that overlapping CH₃ bands confound data interpretation. Improved instrumentation may be needed to obtain reliable stratospheric ClX data.
5. Each Space Shuttle launch will deposit 5 x 10⁹ to 10¹⁰ kg of HCl in the stratosphere (“Environmental Statement for the Space Shuttle Program” [NASA, Washington, D.C., July 1973]). At the projected launch rate of 50 shuttles per year, we calculate that the globally averaged HCl input rate is at least 100 times smaller than the corresponding chlorine injection rate due to continued CF₂Cl₄ usage at the 1973 levels.
6. P. S. Liu and P. G. Slater [Nature (Land.) 247, 181 (1974)] have established that the flux of CFCl₃ from the atmosphere to the ocean is about 2 percent of the industrial production rate.
7. We thank Dr. S. C. Liu for his extremely careful reading of our report (3), and for several helpful discussions on how to assist other readers. We acknowledge similar assistance from Prof. D. D. Davis, This research was supported by NASA grant NGR 23-065-516 and by the Climatic Impact Assessment Program, Department of Transportation, through NSF grant GA-4326.

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