Evaluating ozone depletion potentials

SIR—Fisher and co-workers attack the difficult and important issues of ozone depletion potentials[1] and greenhouse warming effects[2] of hydrohalocarbons proposed as environmentally preferable substitutes for the fully halogenated chlorofluorocarbons (CFCs). A significant fraction of hydrohalocarbons are destroyed in the troposphere, so that they deliver substantially less chlorine to the stratosphere per kilogram used and have shorter atmospheric lifetimes than the chemically inert CFCs. The chlorine loading potentials (the amount of chlorine delivered to the stratosphere), the ozone depletion potentials (the change in the ozone column relative to that caused by the reference molecule CFC-11) and lifetimes for other chlorofluorocarbons[3] are given in the table. The shorter lifetimes of the hydrohalocarbons imply that these compounds will be removed more rapidly from the atmosphere than CFCs if production ceases, alleviating concern about possible errors in analysis of their probable environmental impacts.

Nonetheless, accurate estimation of the ozone depletion potentials (ODPs) of alternative compounds requires the use of numerical models with a credible simulation of the physical and chemical processes whereby stratospheric chlorine destroys ozone. Fisher *et al.*[1] based their estimates on gas-phase photochemical-model calculations, which predict a modest maximum ozone depletion of perhaps 5% in the next century based on present chlorofluorocarbon release rates, in sharp contrast to observations of 50% ozone losses during the Antarctic spring[4] and 3–10% in mid-latitudes of the Southern Hemisphere[5]. The role of chlorofluorocarbons in polar ozone depletion has been established by extensive field measurements[5-9], yet the implications of polar ozone loss for the calculation of ODPs were not considered by Fisher *et al.*[1].

Gas-phase photochemical-model calculations predict ozone destruction mainly at middle and low latitudes at altitudes from about 25 to 50 km. Because most of the total column is located at lower levels near 20 km, the corresponding column depletion is at most a few per cent for the present atmosphere. The ODPs derived using gas-phase chemical models are fundamentally related to the chlorine delivered to the stratosphere and subsequently released by the proposed alternative compounds in the ozone destruction region compared to that of CFC-11. This molecule is rapidly broken down in the stratosphere to release its chlorine, whereas some of the other compounds (for example, HCF_2Cl or HCFC-22) have much longer stratospheric lifetimes, and hence release proportionately less chlorine in the ozone-depletion regions predicted by gas-phase models.

But the Antarctic ozone hole is driven by heterogeneous chemistry on the surfaces of polar stratospheric clouds occurring near 10–22 km (refs 5–11), a region where some compounds release far more chlorine. Similar chemistry is found in the Arctic[7]. Past records indicate that only in April are polar stratospheric clouds not present in the atmosphere, so that ozone loss arising from their interaction with chlorine species could occur over much of the year at one pole or the other[5-12]. Air enters the stratosphere largely in the tropics and descends in polar regions. Thus, air reaching the 20-km region above Antarctica has resided longer in the stratosphere and risen higher than that in mid-latitudes, allowing greater release of ozone-destroying chlorine. Observations of long-lived atmospheric tracers suggest rapid downward transport in the Antarctic stratosphere and far lower abundances of N_2O, CH_4, CFC-11, CFC-12 and, by extension, HCFC-22, than predicted by models[13,14] such as those used by Fisher *et al.*[1]. These observations suggest that HCFC-22 will be largely dissociated by the time it arrives in the region of the Antarctic ozone hole, implying that the ozone destruction there exceeds the ODP and may approach the chlorine loading potential for that gas (see table). The impact of polar processes is greater the larger the difference between the ODP and the chlorine loading potential of the alternative compound (see table).

In the Antarctic atmosphere, reactions involving bromine contribute about 20% of the total ozone loss[5,9,11]. Yet Fisher *et al.*[1] note that bromine reactions do not contribute to their ODP calculations. This is because the calculated ozone destruction occurs near 25–50 km, where bromine plays little part, in contrast to that actually observed to take place in polar regions.

If a globally averaged ODP is required for policy formation, such estimates must be based on the physical insight acquired from observations[15] with a view to evaluating errors in numerical models; the implications of polar ozone depletion for global ozone loss cannot be overlooked. As noted by Fisher *et al.*[1], uncertainties in the rate of tropospheric loss of the alternative compounds and hence in the chlorine-loading potentials must also be considered when evaluating the overall uncertainties in ODPs. Fisher *et al.*[1] note the possible role of dilution of the Antarctic ozone hole and transport from the Antarctic to lower latitudes (sometimes called the chemical processor mechanism[12]). The ozone depletion observed in mid-latitudes of the Southern Hemisphere greatly exceeds that explicable by gas-phase photochemistry[5], suggesting that much if not all of the Southern Hemisphere may be influenced by Antarctic ozone depletion. This, in turn, suggests that the Southern Hemisphere ODPs for HCFC-22 and HCFC-142b exceed the estimates by Fisher *et al.*[1] by at least a factor of two (see table). In the Northern Hemisphere, smaller absolute ozone decreases are observed[5] but these are still several times greater than predicted by gas-phase photochemical models and are probably related at least in part to polar chemistry, again implying increases in ODPs for such species.

The physical processes described here indicate that the globally averaged ODP estimates provided by Fisher *et al.*[1] are probably lower limits on the actual ozone depletion by any compound for which the chlorine-loading potential substantially exceeds its ODP. The chlorine-loading potentials represent upper limits that are probably approached in polar regions, with substantial effects spreading to lower latitudes.

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GLOBAL AND HIGH-LATITUDE ODPs, LIFETIMES AND CHLORINE LOADING POTENTIALS

	Global ODP	High-latitude ODP (Θ,S)	High-latitude ODP (Θ,S)/ global ODP	Lifetime (yr)	Chlorine loading potential
HCFC-22	0.03–0.07	0.04–0.09	1.13–1.4	15–25	0.15–0.20
HCFC-123	0.013–0.027	0.019–0.029	1.02–1.1	1.5–2.4	0.017–0.022
HCFC-124	0.013–0.03	0.014–0.04	1.08–1.3	5–10	0.04–0.05
HCFC-141b	0.07–0.14	0.09–0.15	1.03–1.1	6–11	0.10–0.15
HCFC-142b	0.035–0.077	0.04–0.10	1.14–1.4	15–25	0.15–0.20
CFC-12	0.88–0.92	0.90–1.0	1.04–1.3	95–120	1.3–1.9

ODPs from two-dimensional atmospheric models of gas phase reactions.

FISHER *ET AL.* REPLY:—Our ability to forecast future levels of global ozone is limited by current understanding of polar chemical processes. Several chemical mechanisms that are not part of the homogeneous chlorine chemical theory of Molina and Rowland[16] may be unique to the polar region. We agree with Solomon and Tuck that understanding polar processes is central to discussions of policy involving stratospheric ozone.

Solomon and Tuck question whether we have underestimated the ODPs of some chemicals by discussing only global results from homogeneous photochemical models[1]. We did not discuss relative effects on high-latitude stratospheric