Better protection of the ozone layer

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How can we extend the Montreal Protocol to other ozone-depleting chemicals, such as fuel from the Space Shuttle and pharmaceuticals, when the life cycles of these compounds and the scales of the industries are different?

INTERNATIONAL agreements have been enacted to protect the ozone layer by regulating the release of chlorine- and bromine-bearing chemicals such as the chlorofluorocarbons and the halons. One of the criteria by which such chemicals are assessed and regulated is the ozone depletion potential (ODP)[1–5]. But because more and more chemicals are turning out to be ozone-depleting, we believe that a more refined approach is needed for effective and equitable control. Here, we address ways to extend international agreements to include other contemporary ozone-depleting chemicals whose applications and life cycles are very different from synthetic halocarbons used in the industries already singled out for concern, such as refrigeration, insulation and fire-fighting applications.

During the past decade, an international regime has emerged for limiting the consumption of chemicals believed to carry chlorine (Cl) and bromine (Br) into the upper atmosphere (stratosphere) (see box). The Convention on the Protection of the Ozone Layer (Vienna, 1985) was followed in 1987 by the Montreal Protocol, subsequently amended in 1990 (London amendment) and in 1992 (Copenhagen amendment). The governments that have signed these treaties are committed to phase out the production and consumption of CFCs (chlorofluorocarbons) and halons (brominated hydrocarbons), and to limit the production of their substitutes (for example hydrochlorofluorocarbons, HCFCs) in the expectation that the stratospheric concentration of chlorine and bromine can thereby be reduced. Ultimately, the goal is to reverse the observed downward trend of global ozone, and to limit the possible consequential damage to the biosphere from increased ultraviolet radiation. The adherence of governments to these agreements, which have the status in international law of formal treaties, is mirrored in national legislation such as the US Clean Air Act (1992).

The evolving protocols have given precedence to controlling synthetic CFCs and halons used in applications such as electronic and metal cleaning, foam blowing and refrigeration (CFCs); and fire extinguishers (halons). These chemicals are released in the lower atmosphere (the troposphere), but are sufficiently long-lived that they can be transported to the stratosphere where most of them are broken down by ultraviolet radiation, producing highly reactive Cl and Br radicals that are chiefly responsible for the catalytic destruction of stratospheric ozone. Because the timescale of mixing in the troposphere is less than the residence time of these halocarbons, the effect on ozone (as measured by the ODP) does not depend exactly on where, when and how they are released.

But there are other more direct and effective means by which chlorine can enter the stratosphere. These include solid-fuel rocket motors in the Space Shuttle launches, which deposit chlorine directly in the stratosphere. Prudence, as well as consistency, requires that these sources should also be evaluated under the same criteria (for example, ODPs) to determine their contributions, if any, to ozone depletion. Before the Copenhagen meeting, the scientific community was asked to quantify the impact of other atmospheric emissions such as solid rocket motors[6], stratospheric aircraft[7] and use of methyl bromide (CH_3Br)[8] in agricultural activities. But no ODPs were calculated for solid rocket motors and stratospheric aircraft. Based on the findings on CH_3Br, a freeze on its production beginning in 1995 was adopted in the Copenhagen amendment.

What follows is a demonstration that some potential ozone-depleting substances have life cycles that differ qualitatively as well as quantitatively from the chemicals now controlled by the agreements. We discuss what factors should be considered when developing a strategy for control of compounds whose applications and life cycles are very different from the CFCs. Specifically, we look for ways to ensure that the resulting strategy is practical (can it be applied easily?), effective (does it omit chemicals whose net impact may be comparable to individual HCFCs or CFCs?), and equitable (does it ban or impose excessive penality on uses that

Chronology of ozone-protection agreements

THE Vienna Convention for the Protection of the Ozone Layer was agreed in March 1985 and entered into force in September 1988. It was set up with the intention of preventing any further damage to the ozone layer by "recognising the possibility that world-wide emissions and use of fully halogenated chlorofluorocarbons (CFCs) and other chlorine-containing substances can significantly deplete and otherwise modify the ozone layer, leading to potentially adverse effects on human health, crops, marine life, materials and climate, and recognising at the same time the need to further assess possible modifications and their potentially adverse effects."

It was also agreed that negotiations would continue on the development of a protocol to control equitably global production, emissions and use of CFCs. From this, the Montreal Protocol, an international agreement to phase out ozone-depleting substances, was agreed in 1987.

■ 1987. Montreal Protocol on Substances that Deplete the Ozone Layer. It was agreed that global action was needed to phase out CFCs and halons.

■ 1989. First meeting of the parties to the Protocol in Helsinki. Declaration adopted calling for CFCs and halons to be phased out by 2000.

■ 1990. Second meeting of the parties to the Protocol in London. Agreement to phase out CFCs, halons and carbon tetrachloride by 2000 and methyl chloroform by 2005. Financial mechanism set up to assist developing countries.

■ 1991. New European regulation 594/91 came into force. CFCs to be phased out within the European Communities by 1997.

Second meeting of the parties to the Vienna Convention and third meeting of the parties to the Montreal Protocol.

■ 1992. Fourth meeting of the parties to the Montreal Protocol in Copenhagen. Parties agreed to bring forward phase-out dates for CFCs, carbon tetrachloride and methyl chloroform to 1996; halons to be phased out by 1994. Controls agreed for methyl bromide and HCFCs.

■ 1993. Fifth meeting of the parties to the Montreal Protocol. It was agreed that there would be no essential uses for halons in 1994. Multilateral fund replenished.

Third meeting of the parties to the Vienna Convention. □

Source: UK Department of the Environment.

have relatively small effects on the ozone layer?). We will use three examples to illustrate these points: chlorine deposited by the solid-fuel rockets from the Space Shuttle launches; CH_3Br used in soil fumigation; and brominated compounds in pharmaceutical use.

Ozone depletion potentials

First defined for CFCs a decade ago, the ODP is an index measuring the time-integrated ozone depletion caused by specific quantity of a chemical relative to that caused by the same quantity of the chlorofluorocarbon CFC-11 (the fully substituted methane $CFCl_3$). The definition presumes the chemical is ultimately released into the atmosphere. Policy makers and industry representatives have since asked scientists to extend and calculate ODPs for HCFCs[2] and the halons[3,5]. Total chlorine loading of the atmosphere[9] has also been used to assess the global ozone loss caused by these chemicals, either separately or in combination for specific emission predictions. The amount of chlorine in the stratosphere not still tied up in the parent halocarbon is defined as the stratospheric chlorine loading[10]. To understand the relation between ODP and chlorine loading, it is necessary to examine the life cycles of the halocarbons.

The life cycles of the halocarbons are illustrated in the figure. These halocarbons are, in general, relatively long-lived and thus well mixed in the troposphere. They cycle between the troposphere and stratosphere where a portion of the compound is dissociated during repeated excursions into the stratosphere and the troposphere. The Cl and Br atoms formed in the stratosphere participate in catalytic cycles removing ozone until, on average after 3 years, they are transported back to the troposphere. The Cl and Br atoms in the troposphere, either produced *in situ* by degradation of the halocarbons or transported from the stratosphere, are assumed to be removed quickly by rain out or surface deposition. For CFCs, almost all the chlorine atoms are produced in the stratosphere. The HCFCs react with hydroxyl radicals (OH) and thus are destroyed readily (on a timescale of a few years to decades) in the troposphere. As a result, they contribute less to the stratosphere chlorine loading on a per-molecule-emitted basis.

Numerical simulations using photochemical models indicate that the time-integrated stratospheric chlorine loading is a good proxy for cumulative ozone loss[9,10]. We have used a simple two-box model (with tropospheric and stratospheric compartments) to calculate, as a function of time after release, the amounts of chlorine still tied up in the undissociated halocarbons in the troposphere (B_T) and stratosphere (B_S), as well as the quantity of free chlorine in the stratosphere (C, stratospheric chlorine loading). The differential equations describing the evolution over time of the three reservoirs are

$$\frac{dB_T}{dt} = -\frac{B_T}{L_T} - \frac{B_T f - B_S}{\tau_t}$$

$$\frac{dB_S}{dt} = -\frac{B_S}{L_S} - \frac{B_S - B_T f}{\tau_t} \quad (1)$$

$$\frac{dC}{dt} = -\frac{C}{\tau_t} + \frac{B_S}{L_S}$$

where L_T and L_S are the tropospheric and stratospheric lifetimes for chemical loss of the halocarbons and τ_t is the turnover time for replacing stratospheric air by tropospheric air. In calculating the exchange flux, the tropospheric burden is scaled by a factor $f = 0.15/0.85$ (assuming here that 15% of the atmospheric mass is in the stratosphere) so that the flux is proportional to difference in the mixing ratios. We select $\tau_t = 3$ yr, consistent with Holton's[11] derivation of 2.5 yr for the turnover of air above 100 mbar. Based on two-dimensional model results[12], we select $L_T = 1{,}000$ yr and $L_S = 5$ yr for CFC-11.

Assuming $B_T(0) = 1$ kg chlorine in the form of CFC-11, $B_S(0) = C_{F\text{-}11}(0) = 0$, the burdens (in kg chlorine) for year t are

$$B_T(t) = 0.930\exp[-t/46.5] + 0.070\exp[-t/1.75] \quad (2a)$$

$$B_S(t) = 0.107\,(\exp[-t/46.5] - \exp[-t/1.75]) \quad (2b)$$

$$C_{F\text{-}11}(t) = 0.068\exp[-t/46.5] + 0.090\exp[-t/1.75] - 0.158\exp[-t/3] \quad (2c)$$

The integrated chlorine loading (p.p.t.v.-year) for emission of 1 kton (1×10^6 kg) of CFC-11 is obtained by integrating equation (2c) and multiplying by 0.81.

$$IC_{F\text{-}11}(t) = 2.33\,(1 + 0.16\exp[-t/3] - 1.11\exp[-t/46.5] - 0.05\exp[-t/1.75])\ \text{p.p.t.v.-year} \quad (3)$$

The ODP of a compound X can be approximated as the ratio $IC_X(t)/IC_{F\text{-}11}(t)$, where $IC_X(t)$ is the integrated chlorine loading due to 1 kiloton release of X calculated using appropriate L_T and L_S. The steady state ODP corresponds to the ratio in the limit as $t \to \infty$.

Regulating halocarbons

The Protocol to date has focused on limiting the production of halocarbons used in traditional applications. The list of products containing controlled species (annex D of the Protocol) specifies automobile and truck air-conditioning units; domestic and commercial refrigeration equipment; aerosol products (except medical aerosols); portable fire extinguishers; insulation boards, panels and pipe covers; and pre-polymers. The list of controlled species (annexes A–C) is mainly limited to synthetic fluorochlorocarbons or bromocarbons with no known natural sources.

Although the Protocol recognizes the ODP as a measure of the environmental danger, the lists of controlled species in the annex are not grouped by ODP values. Rather, the species were classified according to chemical type, by use and by when they were included in the Protocol. However, the ODP values are used explicitly in the following way. Instead of imposing production limits on an individual chemical, the control is applied to groups of chemicals. Within each group, the production of each chemical can be traded after appropriate weighting by its ODP value. The Protocol states that "each Party shall, for each group of substances ... determine its calculated levels of Production by (i) multiplying its annual *production* of each controlled substance by the ozone depleting potential specified ...; (ii) adding together, for each such Group, the resulting figures." Under the Copenhagen amendment, the annual production limit on the transition substances (HCFCs) are specified as the 1989 production plus 3.1% of the ODP weighted annual production of the CFCs in the same year.

Although it is not explicitly stated, a reading of the protocols and the US Clean Air Act suggests that their formulations are based on considerations of both ODP and chlorine loading from the current emission rates. There is agreement to phase out production of the CFCs (annex A group I and annex B group I) and CCl_4 (annex B group II) by 1996; and halons (annex A group II) by this year. These compounds all have ODPs of about 0.5 or larger. The atmospheric (1/e folding) lifetimes of these compounds are 30 years or longer (with the exception of halon-1211). Once introduced into the atmosphere, these chemicals will continue to release Cl/Br atoms into the stratosphere over their respective lifetimes. Thus, even if their production is stopped immediately, it will take many decades (until the chemicals are purged from the atmosphere) before the chlorine concentration can return to the level of about 2,000 p.p.t.v. which existed before the ozone hole[10].

In the Copenhagen (1992) amendment, there is a proposal to phase out the substitute HCFCs (annex C) by the year 2030, and to impose stringent limitations on production rates during the interim period. The HCFCs, with atmospheric lifetimes of about 15 years or less, are more rapidly purged from the atmosphere and thus allow for more rapid decay of stratospheric chlorine once use of the

chemicals is phased out. One rationale for controlling HCFCs with ODPs as small as 0.02 is that the short-term relative impact of such species is much larger than suggested by the steady-state ODP[4].

Methyl chloroform (CH_3CCl_3, annex B group III), a compound that fits loosely with the definition of HCFC (but without fluorine), has an atmospheric lifetime of about 6 years and an ODP of 0.12. It is due to be phased out in 1996. This decision was presumably made because the very large production rate contributes significantly to the chlorine loading of the current atmosphere. Chemicals in another class — methylene chloride (CH_2Cl_2), perchloroethylene (C_2Cl_4) and trichloroethylene (C_2HCl_3) — have annual productions comparable to that of CH_3CCl_3, but have not yet been regulated, presumably because they have much shorter lifetimes, smaller ODPs and give rise to smaller chlorine loading.

Some countries have formulated unilateral regulations based mainly on the calculated values of ODPs. Under the US Clean Air Act, any chemical with an ODP larger than 0.2 can be classified as a class I substance. Unless they are in current production, such chemicals may not be manufactured. Heavy fines (up to $25,000 per violation per day) can be imposed for any intentional venting of these materials; and indeed the Environmental Protection Agency is currently seeking large fines from 28 individuals and businesses for such violations[13]. This ODP cut-off is applied independently of the amount released, the argument being that the combined effects from a large variety of ozone-depleting chemicals, even though produced in small quantities, will add up and must be regulated as a collective industry. The ODP cutoff is also applied regardless of how the chemicals will be used. As illustrated by the examples that follow, this approach may be problematic when extended to control chemicals outside the traditional CFC industries because the ODP may depend sensitively on end-use, which in turn determines the life cycle or fate of the chemicals.

ODP of solid rocket fuel

Most scientific studies and early regulations have focused on chemicals whose atmospheric life cycles and participation in ozone depletion are similar to that of CFC-11. The chlorine loading from Space Shuttle launches requires a somewhat different approach. The solid rocket fuel is composed of 16% by weight of aluminum, 70% of ammonium perchlorate (NH_4ClO_4), and 14% of a polymer matrix. Combustion gives rise to the exhaust of HCl into the atmosphere. Each launch emits approximately 200 tons (200,000 kg) Cl out of a total fuel load of 1,700 tons (750 tons of liquid fuel and 950 tons of solid fuel). About one-third of the solid rocket motor exhaust, or 68 tons of Cl, is deposited in the stratosphere (defined here as altitudes above 15 km) per launch (see figure). The Shuttle emissions are removed from the stratosphere with a residence time of 3 years. The average integrated chlorine loading in the stratosphere per kton NH_4ClO_4 used as fuel is given by

$$IC_{SS}(t) = 0.318\,(1.0 - \exp[-t/3]) \quad \text{p.p.t.v.-year} \qquad (4)$$

The behaviour of the chlorine loading is more comparable to that of HCFCs, as the atmospheric recovery is relatively rapid following cessation of emissions.

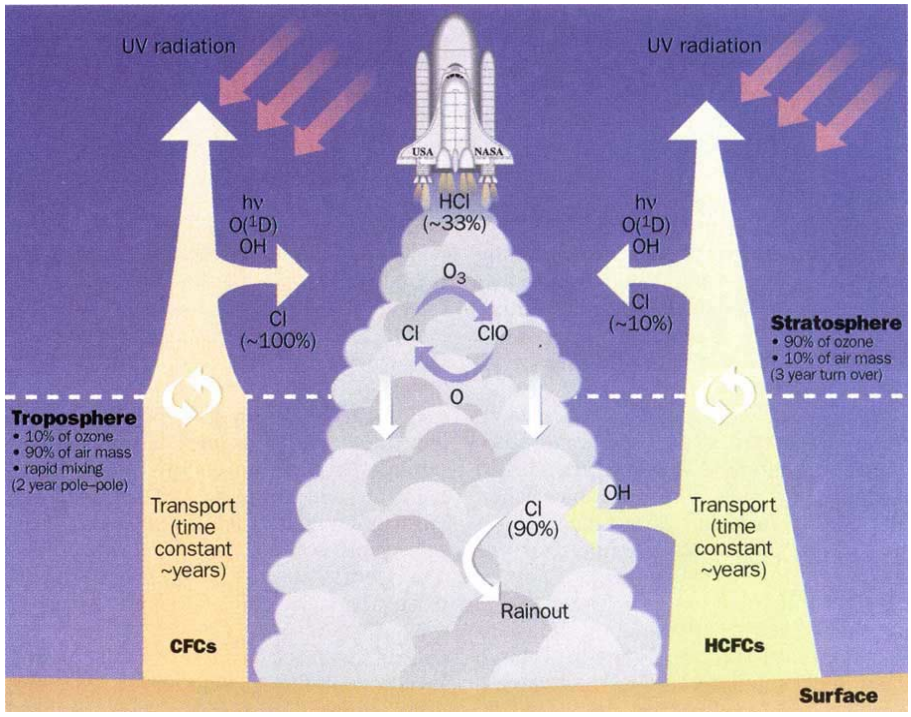
The time-dependent ODP is approximately $IC_{SS}(t)/IC_{F\text{-}11}(t)$. The ratio of the lead coefficients gives the steady-state ODP value of 0.14. Note that the calculated ODP remains above 0.2 for 50 years. As is also obvious from the equations, the time-dependent ODP is very large for a short time after emission because the impact of the Space Shuttle is immediate whereas CFC-11 (and other HCFCs) take years to reach the stratosphere.

One ambiguity in using equation (4) to calculate the ODP for the rocket fuel lies in what is meant by "emission of 1 kton". If we restrict ourselves to the emission of stratospheric HCl (the primary form of chlorine in the exhaust), then the coefficient in equation (4) is larger and the steady state ODP becomes 1.3. On the other hand, if we consider the emissions to be the total fuel load (liquid plus solid), then the coefficient in equation (4) scales down and the ODP becomes 0.05. There is no precedent for using a similar definition to reduce the ODP of a CFC used as an aerosol propellant (when the ODP is defined as the original ODP discounted by the weight fraction of the CFC in the spray-can product).

How do the total anticipated emissions from the Space Shuttle launches compare with chlorine loading expected from the substitute HCFCs to be used in refrigeration, or against the CFC background expected over the next decades? Previous assessments[6,14] showed that a launch rate of one Shuttle per month over several years would increase stratospheric chlorine loading by about 3 p.p.t.v. (as much as 10 p.p.t.v. at northern mid latitudes). This could be compared with a chlorine loading of about 3,000 p.p.t.v. generated by the CFCs emitted over the past several decades. Because the chlorine loading is expected to decrease, we believe that it is more appropriate to use another measure. A 10 p.p.t.v. contribution is comparable to a loading of 30 p.p.t.v. expected from a continuous annual release of 50 kton of a typical HCFC (1 Cl atom, 10-year lifetime, atomic weight 100), and of the same order as the contribution from the annual use of CFCs and HCFCs by some developing countries.

Application-sensitive chemicals

Before the establishment of recovery practice for recycling or destruction, the



Life cycles of CFCs, HCFCs and solid rocket fuel (NH_4ClO_4). Chlorine can either be carried into the stratosphere by atmospheric transport of CFCs, HFCs and by Space Shuttle exhaust. The main difference between CFCs and HCFCs is that most (~90%) HCFCs are removed in the troposphere by hydroxyl radicals (OH). In the case of Space Shuttle, approximately one-third of the fuel (NH_4ClO_4) is burnt in the stratosphere, producing HCl.

applications of the CFCs (apart from use as feedstock to produce other chemicals) are such that, except for a time delay of up to a few decades (the so-called banking time), all the material produced is eventually released to the atmosphere (very little is destroyed during applications). The Protocol recognizes this and explicitly exempts the amount used in feedstock, and the amount recaptured for recycling and destruction, from being counted as production in the basket approach within each group. In extending the control strategy to a wider class of compounds, however, we find that some usage may result in having only part of the applied material released to the atmosphere because the compound is partially destroyed in the application. For example, when used as a soil fumigant, about 10 to 50% of the CH_3Br undergoes prompt chemical transformation in the soil and is not released to the atmosphere[8]. These values are based on several model calculations and limited measurements. If a large fraction of the compound were destroyed (without emitting Cl or Br into the atmosphere) during its application and a portion of the chemical emitted to the atmosphere were destroyed by exchange with the Earth's surface or the ocean, should we extend the existing definition of ODP which currently only focuses on the atmospheric portion of a compound's life cycle? By defining the ODP over an extended life cycle, we will be able to include whatever effects are associated with the differences in life cycles and thus provide a more meaningful measure of relative ozone depletion. In any case, the amount destroyed during any application should be quantified and counted as 'amount destroyed' by approved technologies.

Small-use chemicals

Although the Protocol contains provisions to exempt small medical use of existing CFCs, there is no uniform guideline for assessing new drugs. Many specialized pharmaceuticals contain bromine. Because a Br atom is about 40 times more efficient than a Cl atom in removing ozone[3], the ODPs of these compounds are about the same as the CFCs even if their lifetimes are many times shorter. Although these compounds do pose a short-term risk to the ozone layer, they are expected to have very small annual production (a few tons). How should production of such unique, beneficial drugs be controlled while protecting the ozone layer?

Proposed strategy

We have discussed here several ideas that have been considered implicitly in formulating the control strategy in the Protocol to limit the chlorine loading expected from long-lived halocarbons used in traditional industries. As the list of potential ozone-depleting substances grows, the protection of the ozone layer may require extension of the Protocol to the release of Cl and Br in the stratosphere in connection with other human activities. To this end, it is necessary to follow an approach that relies on our scientific understanding of stratospheric ozone and the life cycles of the compound in question. The aim is to provide sound, long-term protection for the ozone layer, while having a less capricious impact on technological development. The guidelines and the rationale follow.

■ Register all industrially produced chlorine- and bromine-bearing compounds that can potentially put reactive chlorine and bromine species into the stratosphere, and determine their ODPs taking into account the product life cycles. We need to identify all potential sources of stratospheric chlorine and bromine.

■ Ban or place stringent limits on the production of those compounds with long atmospheric lifetimes (lifetime threshold to be determined). Using only short-lived compounds will allow for a reasonably rapid recovery of the atmosphere should unforeseen factors, such as volcanoes or other unanticipated global changes, suddenly enhance chlorine-driven ozone depletion.

■ Set a predetermined goal for the recovery of stratospheric ozone, and thus a schedule for stratospheric chlorine levels (or chlorine plus bromine equivalent measure). Define a market basket approach for the use of all Cl- and Br-bearing chemicals so that the ODP-weighted emissions meet this schedule.

The idea of an ODP-weighted basket is not new. It is part of the protocol in calculating the production within each group of chemicals and in specifying the limit for substitutes. What is different here is the extension to other, non-CFC sources of stratospheric pollution by using an ODP-weighted emission basket that can be tied directly to stratospheric chlorine loading. For the CFCs and HCFCs, the ODP-weighted emission gives results equivalent to those for the ODP-weighted production after exempting feedstock, and recapture for recycling and destruction. However, the particular use of a compound becomes important when evaluating non-volatile chlorinated chemicals, such as the NH_4ClO_4 in Space Shuttle fuel, which are not expected to put reactive chlorine into the stratosphere unless they are used in highly specific ways. For example, static tests of the shuttle engine on the ground should not affect stratospheric ozone. In such cases, the distinction between production and emission becomes important. Extending the existing definition of ODP over a product life cycle could help reconcile this difficulty.

Future prospects

The broad outline proposed here aims to impose taxes or to place caps on the different end-uses of a compound in which part of the chemical is destroyed. It allows for limited use of any Cl- and Br-bearing compounds considered beneficial to society whose values and costs are to be determined by market forces or by national priorities.

The global limit on ODP-weighted emissions can be agreed by parties to the Protocol and each country can choose the manner in which it limits combined emissions of chloro- and bromocarbons (by taxation, by free-market auction of permits or by explicit caps for specific compounds). The permit trading being used for controlling SO_2 emissions in the United States[15] may be a viable approach to setting the pollution fees involved in releasing ozone-depleting chemicals. Chlorine-free rocket fuels are being developed as alternatives to NH_4ClO_4 (ref. 16). The pollution fee system could help to translate the environmental pay-off into more concrete terms.

The rationale for the control of other ozone-depleting substances unrelated to the chlorine and bromine chemical cycles (for example, nitrogen fertilizer, which produces nitrous oxide as a degradation product) is far more complicated and, we believe, needs to be understood further before being regulated. □

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