A DECISION TREE FOR GLOBAL ENVIRONMENTAL IMPACT SCREENING

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OVERVIEW

Global environmental impacts—Ozone Depletion Potential (ODP), Global Warming Potential (GWP), and Atmospheric Lifetime—are of major importance in the development of acceptable halon (and CFC) replacements. In past reports and papers, we have described methods for estimating impacts for tropodegradable halocarbons [1,2]. Here these methods are expanded *to* allow evaluations for all materials, and a decision tree is proposed for screening new chemicals. Although experimentation is needed in making final determinations, the process permits relatively reliable estimations of acceptability without resorting *to* expensive and time-consuming evaluations.

The overall procedure evaluates in turn (1) atmospheric release, (2) hydrolysis, (3) physical removal, (4) photolysis, (5) reaction with hydroxyl free radicals, (6) reaction with tropospheric ozone, (7) other reactions, (8) stratospheric ozone depletion, and (9) global warming, allowing decision points at each stage. Criteria, which may change as the regulatory environment changes, are also considered.

DECISION TREE

The overall methodology for the decision tree can be diagrammed **as** shown in Figure **1,** with details shown in Figure 2. The meaning of the diagram symbols are shown in Figure 3.

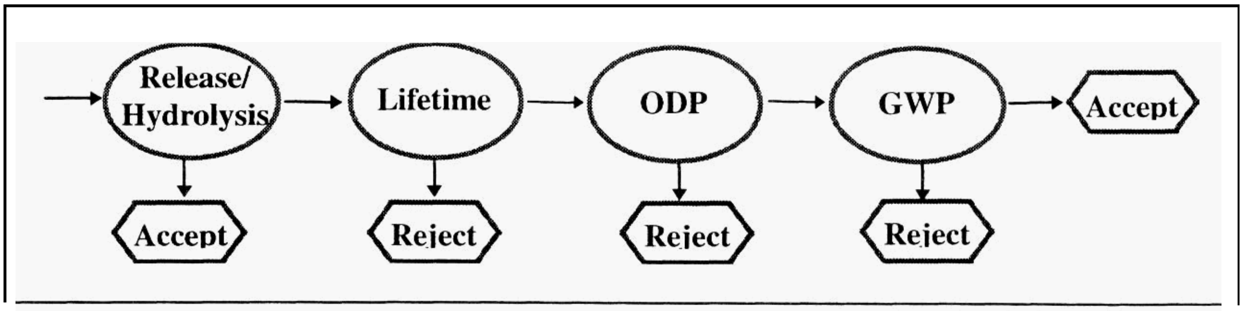

Figure 1. Abbreviated Decision Tree.

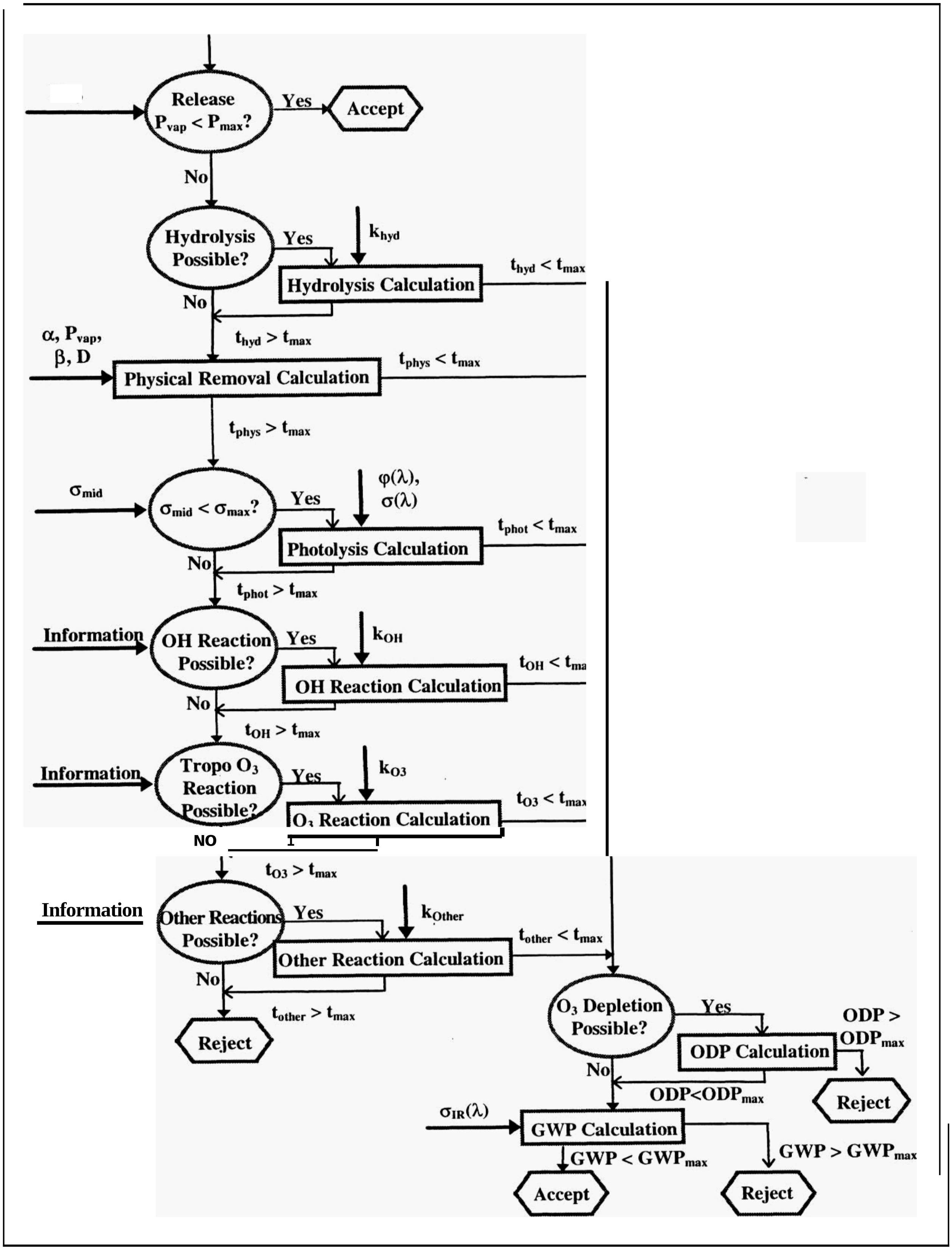

Figure 2. Detailed **Decision** Tree.

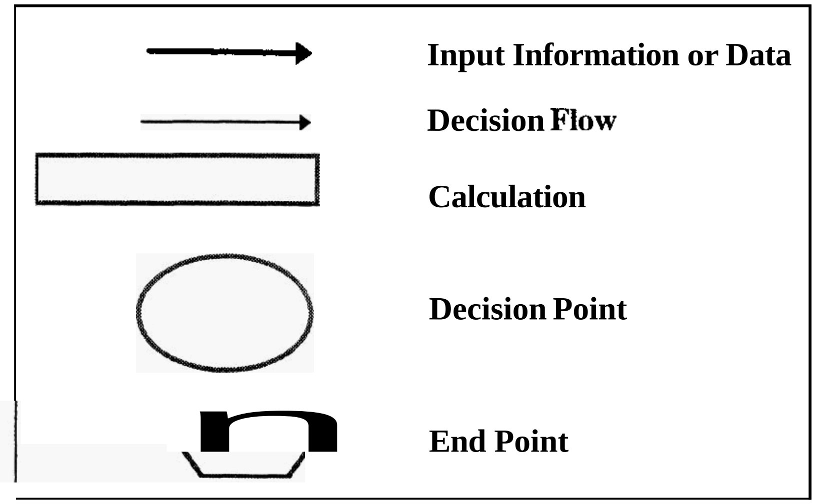

Figure 3. Diagram Symbols.

METHODOLOGY

Decisions are based on whether a calculated (or estimated) atmospheric lifetime (t),[*] Ozone Depletion Potential (ODP), or Global Warming Potential (GWP) is less than or greater than some maximum allowable value (t_{max}, ODP_{max}, GWP_{max}). A major problem is the assignment of maximum allowable values, and this is determined not only by current international environmental regulations, but also by (1) what future regulations are likely, (2) national and local restrictions, **(3)** public perception, and (4) amount of chemical to be produced, which depends on application. Thus, maximum allowable values are not fixed and are subject to debate. The only values that would be acceptable to everyone under all circumstances are zero. Nevertheless, we might make some educated guesses here.

It appears that the atmospheric lifetime of HFC-245fa (6.6 years [3]) may be acceptable to most of the environmental regulatory community. If this is the case, one might take t_{max} to be, perhaps, 10 years. HCFC-123, which has the lowest calculated ODP for the HCFCs, has an ODP of 0.014 based on CFC-11 [4]. Since ODPs of this order of magnitude are of concern (HCFCs are regulated), ODP_{max} must be lower than 0.014. **An** arbitrary value of 0.005 might, therefore, be assigned for ODP_{max}. This may, however, be too high in view of ever increasing regulatory measures. The lowest rigorously calculated GWP for any HCFC, a family of chemicals about which some global warming concern has been expressed, is 90 for a 100-year time horizon based on CO_2 [3]. Thus, one might estimate perhaps 50 for GWP_{max}. These maximum allowable values are not recommended values, but are only taken as a basis for discussion in this paper. As noted earlier, production quantity is extremely important in regulatory action, and chemicals expected to be used in small quantities are likely to have much larger cutoffs than chemicals expected to be used in large quantities.

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[*] To simplify certain equations, we will take all atmospheric lifetimes to be "e-folding" lifetimes, i.e., the time required for the concentration of a compound to decrease to $1/e$ (approximately 0.369) of its initial value.

Release

The first step is to determine whether the vapor pressure (P_{vap}) is sufficient (less than some maximum allowable value P_{max}) to permit release. It has been assumed that anything with a vapor pressure that is measurable using standard techniques (i.e., anything that could evaporate within a finite period of time) is releasable. This includes sublimable solids. Conservatively, this means that only ionic compounds, polymers, and very high molecular weight or certain highly polar solids (e.g., sugars) should be considered as nonreleasable, although compounds that could be readily cleaned up and removed (destroyed) after spillage or use could also be considered nonreleasable.

Hydrolysis

Compounds that are readily hydrolyzed in the atmosphere will have low atmospheric lifetimes. The rate for hydrolytic reaction of a compound C with a concentration [C] in a homogeneous reaction with water with a concentration $[H_2O]$ is given by Equation 1, where k_{hyd} is the hydrolysis rate constant.† In this case, the e-folding atmospheric lifetime is given by Equation 2. One can then

$$\frac{d[C]}{dt} = -k_{hyd}[C][H_2O] \qquad [1]$$

$$t_{1/e} = t_{hyd} = 1/(k_{hyd}[H_2O]) \qquad [2]$$

Effective hydrolysis requires a heterogeneous reaction involving water droplets, since homogeneous hydrolysis is very slow [5]. Thus, hydrolysis is closely related to rainout, a physical removal process discussed below. Some compounds are, however, sufficiently susceptible to hydrolysis that even homogeneous hydrolysis provides effective removal. For example, the carbonyl halides readily undergo hydrolysis to form carbon dioxide and hydrogen halides (Reaction 1). Even in this case, however, the final reactions may be heterogeneous with the carbonyl halides and the HX reaction products acting as nuclei for water droplet formation.

$$O{=}CX_2 + H_2O \rightarrow CO_2 + 2HX \qquad (1)$$

Physical Removal

Physical removal processes include (1) rainout (absorption by water droplets), (2) aerosol scavenging, and (3) solution into oceans [6]. The science of physical removal lags far behind that of the other tropospheric removal processes, and much is qualitative. The input data required for determination (or estimation) of physical removal are α for rainout, P_{vap} for aerosol scavenging, and β and D for solution into oceans. These parameters are defined below.

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†Throughout this paper, equation numbers are inserted in brackets, [], and chemical reaction numbers are placed in parentheses, ().

Rainout

Rainout is believed to be a very effective tropospheric removal mechanism for highly polar compounds such as hydrogen halides (HX, where X represents a halogen atom) and carbonyl halides ($O{=}CX_2$). Absorption by water droplets, "rainout," often occurs with concurrent hydrolysis [7]. For highly hydrophilic compounds such as nitric acid (HNO_3), the global time constant for rainout is about 7 days [8]. As the polarity of a compound decreases, physical removal by water absorption becomes **less** and less effective. For the relatively nonpolar CFCs, HCFCs, HFCs, and PFCs, tropospheric rainout is essentially nonexistent.

Equation 3 has been proposed to estimate the atmospheric lifetime for rainout [9]. Here, a is the solubility coefficient defined by Equation 4. The saturation vapor density is the density of vapor in equilibrium with liquid at a particular temperature (which can be taken as 298 K). Rainout could be significant for highly water-soluble compounds (large values of a) such as alcohols, amines, and carbonyl compounds (esters, carboxylic acids, aldehydes, ketones); however, substitution with fluorine will greatly decrease the solubility and, consequently, the rainout. For example, due to the very low polarity, perfluoroamines such as tris(trifluoromethyl)amine ($N(CF_3)_3$) are likely to have little if any significant removal by rainout.

$$t_{1/e} = t_{phys} \approx \frac{8000}{\alpha} \text{ years} \tag{3}$$

$$\alpha = \frac{\text{solubility (g/L)}}{\text{saturation vapor density (g/L)}} \tag{4}$$

Aerosol Scavenging

Aerosol scavenging involves adsorption of a chemical onto solid particulates. Equation 5 has been advanced to predict the atmospheric lifetime due to aerosol scavenging [9]. Here, P_{vap} is the vapor pressure of a compound in torr at 298 K. Solving for the P_{vap} required to achieve a 10-yr atmospheric lifetime (3.15×10^8 sec), one obtains $P_{vap} = 3 \times 10^{-5}$ torr. For a 1000-yr lifetime (which **is** certain to be unacceptable), the required vapor pressure would be 3×10^{-3} torr. Thus, aerosol scavenging is ineffective for any compound with any significant volatility.

$$t_{1/e} = t_{phys} = 10^{6}(10^{1}P_{vap} + I) \text{ sec} \tag{5}$$

Solution Into Oceans

The lower limit for the tropospheric lifetime due to absorption (solution) into oceans can be estimated by Equation 6 [10]. Here β is the (ocean) water solubility of a gas in moles/m^3-atm (essentially, a Henry's law constant), D is the molecular diffusivity of a gas in water in m^2/year [11], and **z** is the film thickness in the classical stagnant film model for gas exchange. The film thickness is approximately 30×10^{-6} m, and an upper limit on diffusivity at 298 K (giving a lower limit on the lifetime) is approximately 6×10^{-5} cm^2/sec (1.9×10^{-1} m^2/year) [10]. This gives an upper limit on D/z of 6×10^3 m/yr and a lifetime with a lower bound given by Equation 7. This is a lower bound not only because a particularly large value was placed on D/z, but also because of release from the ocean back into the atmosphere, a process not taken into account in this approximation. To obtain a lifetime of less than 10 yrs by this process, one needs compounds with a water solubility greater than 0.5 moles/m^3-atm. The water solubilities of most HCFCs and HFCs are larger than this value; PFCs have water solubilities lower than this value.

$$t_{1/e} = t_{phys} = \frac{3 \times 10^5}{\beta D/z} \qquad [6]$$

$$t_{1/e} = t_{phys} \geq \frac{50}{\beta} \text{ years} \qquad [7]$$

Photolvsis

Photodissociation in the troposphere requires that a compound absorb radiation in the wavelength range from 299 nm to 700 **nm** [6]. The photodissociation rate constant k_{photo} is determined by Equation **8,** where $\sigma(\lambda)$ is the absorption cross section as a function of the wavelength λ, $I(\lambda)$ is the solar intensity as a function of h, and $\varphi(\lambda)$ is the photodissociation quantum yield. Thus, a chemical compound has two characteristics that determine the importance of photolysis: **(1)** the absorption cross section (how well it absorbs electromagnetic radiation encountered in the troposphere) and **(2)** the quantum yield. Both of these are a function **of** the electromagnetic radiation wavelength. The atmospheric lifetime for photodissociation only is then given by Equation **9.**

$$k_{photo} = \int_{290\,nm}^{700\,nm} \sigma(\lambda) I(\lambda) \varphi(\lambda) d\lambda \qquad [8]$$

$$t_{1/e} = t_{phot} = 1/k_{photo} \qquad [9]$$

One might first estimate the possibility for photolysis from σ_{mid}, the absorption cross section at the tropospheric window midpoint for solar radiation, and σ_{max}, the maximum allowable value for this cross section that will result in significant photolysis assuming a quantum yield of 1. If photolysis is possible, then a more rigorous calculation using $\sigma(\lambda)$ and $\varphi(\lambda)$ as input is needed.

Reaction with Tropospheric •OH

Tropospheric hydroxyl free radicals, •OH, may react by abstraction of a hydrogen atom or by addition at a point of unsaturation. If neither hydrogen atoms nor unsaturation is present, one can bypass consideration of reaction with tropospheric •OH as an effective removal mechanism. If reaction is possible, a more detailed calculation is needed.

Rates for hydroxyl free radical reactions with a compound C follow the second-order rate law in Equation 10. Integration gives Equation 11, which can be used **to** estimate lifetimes by assuming pseudo first-order behavior and using a globally averaged hydroxyl free radical concentration ([•OH]) of 9.7 x 10^5 molecules/cm^3 [12].

$$\frac{d[C]}{dt} = -k_{OH}[C][\bullet OH] \qquad [10]$$

$$t_{1/e} = t_{OH} = \frac{1}{k_{OH}[\bullet OH]} \qquad [11]$$

Reaction with Tropospheric Ozone

The analytical procedure for reaction with tropospheric ozone (O_3) is similar to that used for tropospheric hydroxyl free radicals. For halocarbons, ozone reacts almost solely with alkenes. For compounds other than alkenes, one can bypass reaction with tropospheric ozone as an effective removal mechanism. If reaction is possible, a more detailed calculation is needed.

Rates for reactions of ozone with a compound C follow the second-order rate law in Equation 12. Integration gives Equation 13, which can be used to estimate lifetimes by assuming pseudo first-order behavior and using a globally averaged tropospheric ozone concentration ($[O_3]$) of 5.0 x 10^{11} molecules/cm^3 [6].

$$\frac{d[C]}{dt} = -k_{O3}[C][O_3] \qquad [12]$$

$$t_{1/e} = t_{O3} = \frac{1}{k_{O3}[O_3]} \qquad [13]$$

ODP and GWP

The final step, if needed, is to estimate the ODP and GWP and compare the numbers obtained with ODP,,,, and GWP,,, the maximum allowable values. Estimation methods for GWP are nearly nonexistent; however, some estimation methods for ODP have been proposed (in particular, see Reference **6).**

A method for estimating ODPs for non-bromine-containing one- and two-carbon halocarbons has been advanced [13]. The method relates the ODP to two factors, one a reactivity factor related to the number of chlorine atoms in the molecule and the other a survival factor giving the fraction of molecules reaching the stratosphere (and, therefore, related to the atmospheric lifetime). The proposed relationship is shown in Equation 14, where n is the number of chlorine atoms, t is the atmospheric lifetime, and c_1, c_2, and c_3 are parameters to be fit. Here, n^{c_2} is the reactivity factor, $e^{-(c_3/t)}$ is the survival factor, and c_1 is a normalizing constant. This equation gives values that are relatively close to the rigorously calculated ODPs used in fitting the parameters. Since the values for the rigorously calculated ODPs and atmospheric lifetimes used in the parameter fitting have changed since the equation was originally proposed, the reported parameters are not be given in this paper.

$$\mathrm{ODP} = c_1 n^{c_2} e^{-(c_3/t)} \qquad [14]$$

In its present form, Equation 14 is not applicable to bromine-containing compounds. It has, however, been reported that the ODPs for bromine-containing compounds can be estimated from Equation 10 [14]. Here, P is the photolysis factor, which is set equal to 1.0 if there are no special structural features that make the molecule subject to tropospheric photolysis. Otherwise, P **=** 0.180 for **a** bromine geminal to a chlorine (e.g., Br-C-Cl), **P** = 0.015 for geminal bromine atoms

(Br-C-Br), or 0.370 for vicinal bromine atoms (Br-C-C-Br). A is the normalizing constant (0.446), B is 0.740, C is 32.000, and D is 1.120. The hydrogen factor E is 1.000 if there are no hydrogen atoms; otherwise it is 0.0625. #C, #Br, and #Cl are the numbers of carbon, bromine, and chlorine atoms, respectively.

$$\mathrm{ODP} = \mathrm{AEP}[(\#\mathrm{Cl})^{\mathrm{B}} + \mathrm{C}(\#\mathrm{Br})]\mathrm{D}^{(\#\mathrm{C}-1)} \qquad [15]$$

Use of Equation 10 gives, at best, rough approximations, even if the equation is restricted to simple saturated halocarbons. The trends, however, are preserved. It may be that a better fit of parameters could be obtained with a larger set of more recent data as a basis.

ACKNOWLEDGMENT

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