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ASSESSMENT OF EFFECTS ON VEGETATION OF DEGRADATION PRODUCTS FROM ALTERNATIVE FLUOROCARBONS

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EXECUTIVE SUMMARY

If one assumes that the mass of fluorine (F) deposited under steady-state conditions will have an upper limit of 1.5×10^9 per year and all F returns as hydrogen fluoride (HF) that is uniformly dispersed into global rainfall and is deposited by wet deposition, an upper limit for the concentration of F in precipitation would be about 3 μg per liter (3 ppb).

This quantity of F, with reference to concentration or rate of deposition, is well below that heretofore considered to be of significance with respect to the direct effects on plants of air-borne F from industrial operations. It also represents a 30 to 100% increase in what would be estimated to be natural background (3 to 10 ppb). Moreover, F at this concentration would be passively transported as a complex with essentially no capacity to modify the chemical speciation of elements in rain. The activity of F in rain is principally determined by Ca or Al, and pH and concentration of sulfate ions in precipitation could affect the potential of these elements to alter the activity of F. Nevertheless, Al concentrations in rain at the lower range of pH should be sufficient to complex F derived from the degradation of fluorocarbons.

The wet deposition of 3 ppb HF in rain and a total precipitation of 1000 mm per year would constitute a negligible enrichment of the soil in terms of its normal contents or in comparison to that from perhaps the lowest detectable atmospheric concentration of gaseous F. Nor would this deposition of HF affect the chemistry of acidic soils, and rain with a concentration of HF at least 10^3 greater would be needed to affect the chemistry of alkaline soils.

If one assumes that any or all F returns as a fluorinated acetic acid, the effects cannot be estimated because no data are presently available on the effects or degradation of trifluoroacetic acid in plants. Nevertheless, some species of plants can synthesize monofluoroacetate and omega-fluorooleate and -fluoropalmitate. Despite the great chemical stability of the methylene carbon-fluorine bond, plants can metabolize monofluoroacetate and enzymes capable of degrading it occur in soil microorganisms. This leads to the question of the ultimate fate of trifluoroacetic acid with reference to the possible mechanisms for biological dehalogenation and what end products could occur.

It is recommended that research be directed to: (1) metabolism of trifluoro- and other halidoacetates by plants and microorganisms; (2) phytotoxicity of perchloroacetate and alkylhydroperoxides; (3) bioaccumulation and toxicology of these compounds in components of terrestrial and aquatic ecosystems; (4) further quantitative knowledge of the biogeochemistry of F in natural systems.

1. ASSUMPTIONS

The interaction of the degradation products of fluorocarbons with vegetation could occur in several modes: by direct effects on the plant; by changes mediated by the plant; or indirectly, by an affect on the immediate environment of the plant. For an assessment of any of these, certain assumptions are necessary as to the nature of the environmental exposures that could be expected. Ours will be based upon an envelope with the following boundaries.

Firstly, we shall assume that the mass of fluorine deposited globally per annum under steady-state conditions will have upper and lower limits of 1.5×10^9 and 0.5×10^9 kg, respectively. These values are based on another assumption that upper and lower annual rates for global emissions of fluorocarbons are, respectively, 3×10^9 and 1×10^9 kg with fluorine constituting an average of 50% of the mass of the fluorocarbons.

Secondly, we shall assume that all fluorine (F) returns either as hydrogen fluoride (HF) or as a fluorinated acetic acid. A subsidiary assumption is that the latter occurs as the trifluoro-form although the occurrence of difluoromonochloro- and monofluorodichloro-forms are possibilities and the partitioning of fluorine among them could be considered.

Thirdly, we shall assume that fluorine is deposited by the mode of wet deposition, i.e., by rainout in precipitation. Concomitant assumptions are that this is uniformly dispersed into an average global rainfall of 4.9×10^{17} liters per year (Erchel, 1975). Consequently, upper and lower limits for the concentration of fluorine in precipitation would be, respectively, 3 and 1 μg per liter (3 and 1 ppb).

2. INORGANIC FLUORINE

Concern with the effects of fluorides on plants has been devoted to that resulting from dry deposition (mainly with reference to gaseous HF and secondarily with particulate forms). The occurrence of precipitation as rain or mist and the presence of dew or free water on the foliage has mainly been considered with respect to their effects on the accumulation of air-borne fluoride and not with fluoride in wet deposition. That is, precipitation has been viewed primarily with respect to its facilitation of the solution and subsequent absorption of deposits by the foliar tissues or its elution of deposited fluoride from foliage. (For example: the effects of mist on toxicity of HF and cryolite, McCune et al, 1977; models for the accumulation of fluoride by forage, Craggs and Davison, 1985).

Accordingly, our evaluation of inorganic fluoride from fluorocarbon degradation rests upon a comparison with what is known about the effects of industrial emissions and what could be considered the natural condition.

2.1. HF in precipitation

One problem is to what extent the concentration of fluoride in rain can be partitioned into natural and anthropogenic sources, and then to what extent the products from the atmospheric degradation of fluorocarbons represent an increased burden over that contributed by the other sources. In general, one can come to the conclusion that the assumed quantities of fluoride in rain due to the degradation of fluorocarbons may represent close to the detectable increment of present levels, be deposited as complexes, and have no effect on the chemistry of rain water or on the plant.

2.1.1. Quantity

In a metropolitan area (Yonkers, New York), fluoride concentrations never exceeded 100 ppb and infrequently were greater than 50 ppb in rainfall (Jacobson et al., 1976). In Newfoundland, rain and snow considered free of anthropogenic influence had fluoride averaging less than 10 ppb whereas precipitation enriched by a source (probably by washout) had average concentration of 280 ppb in rain (range of 110 to 580 ppb) and an average of 360 ppb in snow water (range of 110 to 1040 ppb) (Sidhu, 1982). Barnard and Nordstrom (1982) found a difference between coastal and inland sites in the distribution of values. Coastal values ranged from 2 to 24 ppb with a median of 4.2 ppb and were uncorrelated with sodium concentrations; inland values ranged up to 34 ppb with a median of 9.4 ppb. They further concluded, from mass balance considerations, that most of the fluoride in precipitation was anthropogenic in origin rather than from maritime aerosols, volcanic activity (2 to 3 ppb), or soil particles (ca 1 ppb).

2.1.2. Chemistry

Ares (unpublished) has concluded that at the concentrations present in rainfall, fluoride is passively transported as a complex with essentially no capacity to modify the chemical speciation of elements in rain water. Basically, the composition and form of minerals in dust determine, in addition to quantity, the activity of fluoride in rain.

Ares also concluded that the major ions determining the activity of fluoride in solution would be Ca or Al, depending upon the pH. Above pH 5.0, the solubility of Ca and other salts of fluoride limit its activity to a level no greater than 10^{-4} M. Below pH 4.5, hydrates of Al(III) regulate nearly all fluoride at molar ratios of Al:F of greater than 4 by the formation of Al-F complexes.

The solution of sulfate ions in precipitation will secondarily affect Ca and Al and thereby their potential to alter the activity of fluoride. Nevertheless, at the concentrations of fluoride assumed, HF derived from the degradation of fluorocarbons would not alter the acidity or composition of rain.

That Al concentrations in rain should be sufficient to complex fluoride at the lower pH range is deduced from limited data. In the vicinity of Göttingen, levels of Al ranged from 48 to 174 ppb with a mean of 89 ppb (Ruppert, 1975). In the vicinity of Solling, Ares (unpublished) found concentrations of Al in rain ranging from 10 to 1720 with a median of 100 ppb.

2.2. Effects on soil

The fluoride content of normal soils ranges from 20 to 1000 ppm depending upon minerals present, depth in the soil, and content of organic matter, with an average of about 200 ppm (see review by Davison, 1983). Assuming a concentration of 3 ppb in rain and a total precipitation of 1000 mm per year, about 30 gF ha^{-1} would be deposited per year, which is equivalent to an enrichment of about 0.04 ppm (using Davison's bulk density factor for soil). By comparison and using Davison's estimate of deposition velocity, exposure to air averaging 0.05 μgF m^{-3} would result in the deposition of about 380 gF ha^{-1} per year. Consequently, this wet deposition would constitute a negligible contribution to the soil in terms of normal contents or in comparison to that from perhaps the lowest detectable atmospheric concentration of gaseous fluoride.

The data of Ares (1986) would also indicate that wet deposition of HF in the assumed range of concentrations would not affect the soil solution in acidic forest soils. In these, it was estimated that 99.9% of fluoride was complexed with Al, and one could conclude that 3 ppb in rain would not affect the chemistry of the soil. Ares postulated that the solubility of fluoride in alkaline soils (pH 7.2 to 8.2) is controlled by ralstonite ($NaMgAlF_6$) at high Na levels or fluorite (CaF_2) at low Na levels and that rain with a concentration at least 10^3 greater than that assumed in this assessment would be needed to affect the soil chemistry.

In areas subject to airborne fluoride from industrial emissions, enrichment of fluoride and changes in soil chemistry have been observed (Ares, 1978; Fluhler et al., 1982; Polomski et al., 1982; Sidhu, 1982). Nevertheless, it has been concluded that the increased levels of fluoride found in foliage in these areas represents more the result of increased deposition directly to the plant than of uptake from an increased level of fluoride in soil (Braen and Weinstein, 1985; McClenahen, 1976).

2.3. Gaseous HF

By way of comparison, the effects of gaseous fluoride are relatively well known although knowledge is not as plentiful as would be desired for practical applications to environmental quality. Table 1 lists some values for different averaging times of what could be considered protective for three classes of vegetation. Some standards for fluoride are also based on the concentration present in foliar tissue, and Table 2 presents a example of this kind of standard.

The short-term (24-hour) value for highly sensitive plants is based upon the effects of HF on gladiolus or young foliage of conifers, such as spruce, fir, and pine (see reviews by McCune, 1969; Weinstein, 1977). The 1-month value for highly sensitive plants represents what could be protective for grapevines

Table 1. Possible acceptable limits for atmospheric concentrations of gaseous fluoride with reference to effects on vegetation.

Plant Sensitivity class	Concentration (μgF m^{-3}) Averaging time		
	24 hours	1 month	7 months
High	1.6	0.4	0.25
Moderate	3.6	1.5	0.6
Low	10.0	2.5	1.2

Table 2. Standards of the State of Maryland for the concentration of fluoride in vegetation.

Class of vegetation	Concentration of fluoride (μgF per g dry mass)		
Forage for cattle[a]	80	60[b]	35[c]
Field crops	35[d]		
Ornamental plants	40[d]		
Conifers & evergreens (current)	50[d]		
" " (older)	75[d]		
Deciduous trees & shrubs	100[d]		
Grasses & herbs (not grazed)	150[d]		

a) Unwashed samples
b) Mean for two months
c) Mean for 12 months
d) Foliage washed before analysis

based on the work of Doley (1986) with the Chardonnay cultivar of *Vitis vinifera.* The 7-month concentration for highly sensitive plants is based in part on the results of MacLean et al. (1984) as related to the occurrence of suture red spot (SRS) on fruit of peach. This is one of the most sensitive responses of plants to HF and also an economically significant effect. If protection against the occurrence of SRS is not of concern, a higher value such as 0.4 $\mu gF\ m^{-3}$ based upon Doley (1986) could be used.

The averaging periods above were chosen mainly because they represent the exposure regimes used to furnish the experimental data. However, they should also recognize what characteristics of exposure could be operationally significant in the vicinities of the sources and receptors. Given the variability observed in the concentrations of HF in quotidian or weekly cycles and the temporal variations in the susceptibility of plants under ambient conditions, one could propose periods shorter than 24 hours or greater than 24 hours and less than 30 days. With respect to a seven-month value, there is some question as to whether a mean value is appropriate when the median of the population of samples from which it is derived could be zero.

In general one could conclude that atmospheric levels of gaseous fluoride below those considered protective for vegetation would result in greater accumulations of fluoride in foliage and soil than would the wet deposition of HF from fluorocarbon degradation.

3. HYDROGEN CHLORIDE

Although hydrogen chloride could also result from degradation of some compounds proposed as alternatives, it is much less toxic to plants than fluoride. For example, Guderian (1977) recommends a concentrations no greater than 50 $\mu g\ m^{-3}$ as being protective of the most sensitive vegetation. In addition, concentrations of chloride in foliage associated with thresholds for foliar injury are in the range of 0.2 to 2% by dry weight.

4. FLUORO-ORGANIC COMPOUNDS

No data are presently available of the effect of trifluoroacetic acid on plants. Nevertheless, some plants do synthesize monofluoroacetate and some data is available on the degradation of this compound by plants and microbes.

The distribution of fluorine-containing organic molecules in nature appears to be limited to its occurrence as monofluoroacetate (Marais, 1944) and in omega-fluorine homologues, fluorooleate and fluoropalmitate (Peters et al. 1960; Ward et al., 1964). For more details on their distribution see Weinstein et al. (1972). The carbon-fluorine bond in these compounds has extraordinary stability and its slow release is accomplished by refluxing in 20 percent sodium hydroxide or heating at 100C in concentrated sulfuric acid. Complete release occurs only after refluxing in 30 percent sodium hydroxide or by sodium fusion at 400C.

Monofluoroacetate is a naturally-occurring compound in plants, and has been implicated in "lethal synthesis" in many mammals (Peters, 1952), i.e., the biosynthesis of monofluorocitrate from fluoroacetate, which blocks aconitic hydratase and can result in death. It seemed likely that, despite the great chemical stability of the methylene carbon-fluorine bond, there might be enzymes capable of degrading it. The cleavage of the carbon-fluorine bond of monofluoroacetate was first reported by Horiuchi (1962) using extracts from a pseudomonad isolated from soil. Although defluorination occurred, significant defluorination was not reported until Goldman (1965) isolated a pseudomonad from soil that grew on a medium containing monofluoroacetate as the sole carbon source. The results were quickly verified for other soil organisms (Tonomura et al., 1965; Kelly, 1965). The enzyme capable of cleaving the carbon-fluorine bond was a haloacetate halidohydrolase (Goldman and Milne, 1966; Goldman et al., 1968; Goldman, 1969) that catalyzes the reaction

$$XCH_2COO^- + OH^- \rightarrow X^- + HOCH_2COO^-$$

where X = F, Cl, or I.

Preuss et al. (1968, 1969) first reported that higher plants can cleave the methylene carbon-fluorine bond. This was shown by the liberation of $^{14}CO_2$ following incubation with 2-^{14}C-fluoroacetate in germinating seeds of peanut, castor bean, and *Acacia georginae.* Pinto bean seeds were not able to liberate $^{14}CO_2$. In peanut, inorganic fluoride was one product of the reaction. The other was postulated to be glycolic acid. The enzyme that accomplishes defluorination in plants has not been characterized.

The facility by which the carbon-fluorine bond can be cleaved by enzymes found in soil microorganisms and higher plants, leads to the question of the ultimate fate of trifluoroacetic acid (Pattison, 1959), one of the major products of photochemical oxidation of several of the alternative fluorocarbons. It is probable that plant and/or microbial enzymes can remove fluorine atoms from the molecule. Whether dehalogenation will occur as it does with dichloroacetate (Goldman et al., 1968), i.e., removal of both halogen atoms together, or whether it might be a stepwise dehalogenation, with monohalidoacetate as the end product, is not known.

5. RECOMMENDATIONS

It is apparent that the quantities of inorganic fluoride assumed in this discussion are well below those heretofore considered to be of interest with respect to the environmental consequences of industrial operations. They could represent a doubling of what would be estimated to be natural background. Accordingly, research on their possible biogeochemical effects should be directed to the identification of natural systems presently uninfluenced by anthropogenic fluoride and a better understanding of pathways of transport and transformation for fluoride in them.

With reference to the effects of fluoro-organic compounds, it is recommended that research be directed to: (1) metabolism of trifluoro- and other halidoacetates by plants and microorganisms; (2) bioaccumulation and toxicology of these compounds in components of terrestrial and aquatic ecosystems; (3) phytotoxicity of perchloroacetate and alkylhydroperoxides.

Annex A Experts and Reviewers

ANNEX A
EXPERTS AND REVIEWERS INVOLVED IN AFEAS

EXPERTS

R. Atkinson	University of California, Riverside
W.L. Chameides	Georgia Institute of Technology
P.S. Connell	Lawrence Livermore National Laboratory
R.A. Cox	Harwell Laboratory
R.G. Derwent	Harwell Laboratory
D.L. Filkin	E. I. du Pont de Nemours & Co., Inc,
D.A. Fisher	E. I. du Pont de Nemours & Co., Inc.
J.P. Friend	Drexel University
C.H. Hales	E. I. du Pont de Nemours & Co., Inc.
R.F. Hampson	National Institute of Standards and Technology, Gaithersburg
I.S.A. Isaksen	Oslo University
L.S. Kaminsky	State University of New York at Albany
M.K.W. Ko	Atmospheric and Environmental Research, Inc
M.J. Kurylo	National Institute of Standards and Technology, Gaithersburg
R. Lesclaux	University of Bordeaux
D.C. McCune	Boyce Thompson Institute for Plant Research, Ithaca
M.O. McLinden	National Institute of Standards and Technology, Boulder
M.J. Molina	Jet Propulsion Laboratory
H. Niki	York University, Ontario
M.J. Prather	NASA Goddard Institute for Space Studies
V. Ramaswamy	Princeton University
S.P. Sander	Jet Propulsion Laboratory
F. Stordal	Oslo University
N.D. Sze	Atmospheric and Environmental Research, Inc.
A. Volz-Thomas	Kfa Julich
W-C Wang	Atmospheric and Environmental Research, Inc,
L.H. Weinstein	Boyce Thompson Institute for Plant Research, Ithaca
P.H. Wine	Georgia Institute of Technology
D.J. Wuebbles	Lawrence Livermore National Laboratory
R. Zellner	University of Hannover

REVIEWERS

D.L. Albritton	National Oceanic and Atmospheric Administration
J.G. Anderson	Harvard University
R.E. Banks	University of Manchester Institute of Science and Technology
J.J. Bufalini	US Environmental Protection Agency
A.W. Davison	Newcastle University
W.B. DeMore	Jet Propulsion Laboratory
D.D. Des Marteau	Clemson University
R.A. Duce	University of Rhode Island
A. Goldman	University of Denver

EXPERTS AND REVIEWERS INVOLVED IN AFEAS (Continued)

M.R. Hoffman	California Institute of Technology
C.J. Howard	National Oceanic and Atmospheric Administration
N. Ishikawa	F&F Research Centre, Tokyo
J.L. Moyers	National Science Foundation
V. Ramanathan	University of Chicago
A.R. Ravishankara	National Oceanic and Atmospheric Administration
F.S. Rowland	University of California, Irvine
P. Simon	Institut d'Aeronomie Spatiale de Belgique
H.O. Spauschus	Georgia Institute of Technology
S. Solomon	National Oceanic and Atmospheric Administration
A. Tuck	National Oceanic and Atmospheric Administration
R.T. Watson	National Aeronautics and Space Administration
S. Wofsy	Harvard University

Annex B Companies Sponsoring AFEAS

ANNEX B
COMPANIES SPONSORING AFEAS

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LaRoche Chemicals	USA
Montefluos SpA	Italy
Pennwalt Corporation	USA
Racon (Atochem)	USA

Annex C Statement of Work

ANNEX C

STATEMENT OF WORK

Each reviewer should prepare a one page written review of each paper specified with their name in the following. The reviews should be sent to the chairman of the AFEAS science committee as early as possible and fifty copies of the reviews should be brought to the AFEAS conference.

The reviews should address the following questions:

1. Is there significant information relevant to the subject that is not included in the review paper?

2. Are the conclusions supported by the information presented in the review paper?

3. Are the findings reported in the executive summary supported by the information in the body of the paper? Are all of the important points covered in the executive summary? Does the summary provide the correct level of detail or is information included that should be removed?

I. Physical and Chemical Properties:

Since model calculations and evaluations of potential biological and health effects will require the information developed in these reviews as input, Experts answering these questions will be required to submit their review papers by not later than 28 February, 1989.

A. Solubility in Water, Vapor Pressure, Hydrolysis Rates

Based on information in the literature, supplied by AFEAS member companies and available from other sources, what are the recommended temperature dependent values of the solubility in pure water, solubility in sea water, vapor pressure, and hydrolysis rates for each of the HCFCs and HFCs? Expert - Mark McLinden

Reviewer - H.O. Spauschus

B. Reaction Rate Constants

Based on available information, what is the recommended temperature dependent rate constant for reaction of each of the HCFCs and HFCs with hydroxyl and $O(^1D)$? What are the error limits on these rate constants? Experts - Bob Hampson, Mike Kurylo and Stan Sander working together.

Reviewers - W. B. DeMore and A. R. Ravishankara

C. Absorption Cross-Sections

Based on available information, what are the recommended ultraviolet (190-400 nm) and infra-red (primarily in the 8 - 13 m range) cross-sections for each of the HCFCs and HFCs? What are the error limits on these cross-sections? Expert - Mario Molina

Reviewers - P. Simon and A. Goldman

D. Degradation Mechanisms

Based on available information, how will the HCFCs and HFCs degrade in the troposphere after the initial hydrogen atom abstraction by hydroxyl, what are the intermediate and final products and what is the most likely atmospheric lifetime of each of these products? Is it likely that relatively stable fluorine-containing intermediates would be formed? How would the products be removed from the atmosphere? As this is one of the more important set of questions, four experts, or teams of experts, are being asked to address these questions. Experts - Tony Cox and R. Lesclaux working together; Roger Atkinson; Hiromi Niki; and Reinhardt Zellner.

Reviewers - All reviewers should compare the papers to identify inconsistencies and determine if they are due to uncertainties that cannot be resolved without further research or if they are due to errors in one or more of the papers. Specific responsibilities for more extensive reviews are:

J. G. Anderson - papers prepared by R. A. Cox and R. Lesclaux and R. Zellner

J. Bufalini - papers prepared by R. Atkinson and H. Niki

W. B .DeMore - papers prepared by H. Niki and R. Zellner

A.R. Ravishankara - papers prepared by R. Atkinson and R. A. Cox and R. Lesclaux

Each of the following reviewers should prepare a single review of the group of four papers. The group should be reviewed for completeness and consistency. Causes of any inconsistencies should be discussed. Each of these reviewers should suggest a single executive summary based on the four executive summaries.

F. S. Rowland

R. E. Banks

N. Ishikawa

II. Uncertainties in Atmospheric Lifetimes

Experts answering these questions will be required to submit their review papers by not later than 1 April, 1989.

A. Tropospheric Hydroxyl Concentrations

Based on measurements of the isotopic ratio of carbon in atmospheric carbon monoxide, what is the average tropospheric hydroxyl radical concentration and what are the uncertainties in the derived concentration? Given that the rate constant of the reactions of HCFCs and HFCs with hydroxyl are temperature dependent, what is your best estimate of lifetime (with uncertainty limits) of each of the HCFCs and HFCs? Experts - Andreas Volz-Thomas and R. G. Derwent working together.

Given the available data base on methyl chloroform and HCFC-22 (measured atmospheric concentrations and estimated global emissions), what are the calculated atmospheric lifetimes of these compounds and how sensitive are the lifetime to variations in these data, e.g. latitudinal, seasonal, vertical profile? Calculate the effect of a reasonable variation in each of these parameters in turn. Assuming that reaction with OH is the only sink for methyl chloroform and HCFC-22, how do uncertainties in the data base for these compounds extrapolate to influence the derived OH concentration? Extend the sensitivity calculation from effect on lifetime to effect on *OH* and hence on the lifetimes of alternative fluorocarbons. Based on this analysis, what is your best estimate of lifetime (with uncertainty limits) of each of the HCFCs and HFCs.

Are the inferred lifetimes for methyl chloroform and HCFC-22 consistent with the assumption that reaction with OH is the only sink? Is it possible that there is another sink for one or other compound, e.g. hydrolysis of methyl chloroform? Expert - Michael Prather

Reviewer - S. Wofsy
Individual reviews should be prepared for each paper and the conclusions of the papers should be compared. If there are inconsistencies the reviewer should determine if they are due to uncertainties that cannot be resolved without further research or if one or both of the papers contain errors.

B. Hydrolysis

Based on available information on hydrolysis rates, what are the most likely atmospheric lifetimes of methyl chloroform, HCFC-22 and the other HCFCs and HFCs against hydrolysis? (Estimates of average hydroxyl concentrations derived using measurements of methyl chloroform are based on the assumption that there are no other significant atmospheric sinks of methyl chloroform. This question is being asked to determine if that is a valid assumption.) Experts - Paul Wine and Bill Chameides working together.

What are the atmospheric lifetimes of the compounds identified in I.D. against hydrolysis? What are the ultimate products that would be formed in solution? Experts - Paul Wine and Bill Chameides working together.

Reviewers - M. R. Hoffmann and D. D. Des Marteau
In addition to preparing reviews of the papers the reviewers should prepare brief summaries of other potentially important liquid phase reactions involving compounds identified in I.D. and not addressed by AFEAS.

III. Natural Sources

Experts answering these questions will be required to submit their review paper by not later than 1 May, 1989.

What are the source strengths and atmospheric concentrations of compounds containing chlorine and/or fluorine due to natural sources? What are natural concentrations of fluoride in ground water? What are the concentrations of fluoride from natural sources in rain water and surface waters (oceans, rivers, lakes)? What concentrations are found in metropolitan water supplies before and after fluoridation? What are the source strengths of other inorganic compounds that would be converted to acidic compounds in the atmosphere? Expert - J. Friend

Reviewers - J. L. Moyers and R. A. Duce

IV. Model Calculations

Experts answering these questions will be required to submit their review papers by not later than 1 May, 1989.

A. Stratospheric Ozone

Given the information supplied by the experts answering I.B., I.C. and II., what are the calculated ozone depletion potentials (including uncertainties) of the HCFCs? Based on available information, could HFCs contribute to ozone depletion? Experts - Don Fisher, Ivar Isaksen, Dak Sze and Don Wuebbles working together.

Reviewers - S. Solomon and A. F. Tuck

B. Tropospheric Ozone

Given the information supplied by the experts answering I.B., is it likely that the HFCs and HCFCs would contribute to production of photochemical oxidants in the vicinity of release? on a global basis, how would emissions of HCFCs and HFCs (currently, emissions of CFCs are about one billion kilograms per year) compare to natural sources of ozone precursors? Expert - Hiromi Niki.

Reviewer - J. Bufalini

C. Global Warming

Given the information supplied by the experts answering I.B., I.C. and II., what are the halocarbon global warming potentials (including uncertainty limits) of the HCFCs and HFCs? Experts - Don Fisher, Dak Sze, and one other climate modeler, working together.

Reviewer - V. Ramanathan

V. Biological and Health Effects

Experts answering these questions will be required to submit their review papers by not later than I May, 1989.

Based on the answers to these questions in sections I. and II., is it likely that the decomposition products from annual emissions of one billion kg. (an amount that is approximately equal to current emissions of CFCs) could contribute to biological or health effects? The organisms to be considered should range from humans all the way down to microorganisms. The review should address the following topics for each of the classes of degradation compounds on the list:

1. Known acute and chronic affects to all concentrations, but with emphasis on the lowest concentrations for which data are available.

2. Existence of a dose-response threshold.

3. Availability of data on quantitative dose-response relationships.

4. Biochemists reaction mechanisms, if known.

5. Repair mechanisms and/or ability of the organism to adapt.

6. Potential effects at projected concentrations corresponding to hypothetical emissions for a given parent compound of 1 billion kg/year at steady state.

7. Most important research needed to resolve uncertainties relevant to the above items.

   Experts - L. S. Kaminsky; and L. H. Weinstein and D. C McCune working together.

Reviewer - A. Davison
Individual reviews should be prepared for each paper and the conclusion of the papers should be compared. If there are inconsistencies the reviewer should determine if they are due to uncertainties that cannot be resolved without further research or if one or both of the papers contain errors.

REFERENCES

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