

SULFURYL FLUORIDE (Vikane[®])
RISK CHARACTERIZATION DOCUMENT
Volume III
Environmental Fate

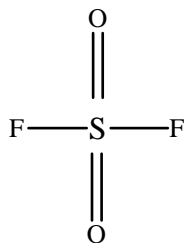
**Environmental Monitoring Branch
Department of Pesticide Regulation
California Environmental Protection Agency**

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ENVIRONMENTAL FATE OF SULFURYL FLUORIDE

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▪ Chemical Description



Common Name:	sulfuryl fluoride
Chemical Names:	sulfuryl fluoride; sulfuric oxyfluoride
Trade Name:	Vikane®
CAS Registry Number:	2699-79-8
Molecular Formula:	F ₂ O ₂ S
Molecular Weight:	102.1

Sulfuryl fluoride is a colorless, odorless gas belonging to the chemical family of inorganic acid halides. It is non-corrosive to metals, stable to light, and thermally stable up to 400 °C when dry. When heated to decomposition in air, very toxic hydrogen fluoride and sulfur dioxide fumes are emitted. Sulfuryl fluoride is soluble in water (750 ppm at 25 °C, pH 7), and is also soluble in common organic solvents such as ethanol, toluene, and carbon tetrachloride (British Crop Protection Council, 1994; Lewis, 1991; O'Neil, 2001; Royal Society of Chemistry, 1994; U.S. Environmental Protection Agency Office of Toxics, 1985). Additional physical and chemical properties are summarized in Table 1.

Fish and wildlife data on the ecological effects to non-target organisms are not available. Because sulfuryl fluoride is a gas, it is not feasible to develop such data in accordance with U.S. Environmental Protection Agency guidelines. Therefore, basic wildlife toxicology tests and ecological effects risk assessments were not required (U.S. Environmental Protection Agency, 1985).

Table 1. Physical and chemical properties of sulfuryl fluoride (Dow Agro Sciences, 2001; Kenaga, 1957).

Physical/Chemical Property	Value
Melting Point	-136 °C
Boiling Point	-55 °C
Vapor Pressure	1.16 x 10 ⁴ mm Hg (20 °C)
Water Solubility	750 ppm (25 °C, pH 7)
Soil Adsorption Coefficient (K _{oc})	6.1 cm ³ /g
Henry's Law Constant (K _h)	3.28 x 10 ⁻² atm-m ³ /mol
Octanol-water Partition Coefficient (K _{ow})	2.57

▪ **Regulation**

Sulfuryl fluoride has been classified as a federally restricted use pesticide for the acute inhalation hazard and possible acute toxicity hazard in humans criteria (U.S. Environmental Protection Agency, 2002). Consequently, it was designated a restricted material pursuant to section 14005.5 of the Food and Agricultural Code. Other criteria for a restricted material designation in this section include posing a danger to public health, or a hazard to crops, domestic animals, farm workers, or the environment. Restricted materials are possessed and used by persons only under permit of the county agricultural commissioner.

The Birth Defect Prevention Act (Stats. 1984, Ch. 669, § 1) mandates the listing of sulfuryl fluoride in section 6198.5 of Title 3, California Code of Regulations. The 200 priority pesticide active ingredients listed in this section are suspected of being hazardous to people, and have widespread use and significant data gaps. All data requirements for sulfuryl fluoride have been submitted to the Department of Pesticide Regulation (DPR).

▪ **Use Profile**

Sulfuryl fluoride is a non-systemic insecticide/rodenticide used for the fumigation of sealed structures and their contents (construction materials, furnishings, and household effects) such as dwellings (including mobile homes), buildings, barns, vehicles, fumigation chambers, rail cars, and surface ships in port. There were no registered uses involving direct application of sulfuryl fluoride to agricultural crops, edible commodities, or feed. The U.S. Environmental Protection Agency, however, granted permanent tolerances for its use in post-harvest fumigation of walnuts and raisins in 2004 (U.S. Environmental Protection Agency, 2004). Sulfuryl fluoride is registered to control existing infestations of insects and related pests such as drywood termites, powder post beetles, old house borers, death watch beetles, bedbugs, cockroaches, clothes moths, rats, and mice (Dow Agro Sciences, 2000; Thomson, 2000). Vikane®, the only end-use

product as of September 10, 2004, is marketed as a liquefied gas in pressurized steel cylinders (99.8 % sulfuryl fluoride).

Full pesticide use reporting in California was implemented by DPR in 1990. All agricultural use must be reported monthly to the county agricultural commissioners. The county agricultural commissioners forward these data to DPR, who annually compiles and makes available a pesticide use report. Agricultural use is defined as including applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way. Although use in structural pest control is excluded from the definition, the use of pesticides designated as restricted materials pursuant to section 14005.5 of the Food and Agricultural Code must be reported. For non-agricultural applications, detailed information such as base meridian/township/range/section is not provided.

Figure 1 is a graphical representation of total pounds of sulfuryl fluoride used in California from 1993 through 2004. Total use ranged from 1,502,091 pounds in 1993 to 3,270,698 pounds in 2004. The average annual use for this reporting period was 2,342,485 pounds. Sulfuryl fluoride is used in all California counties. Table 2 and Figure 2 show use by county from 1999 through 2004 for counties with annual use over 60,000 pounds. Use of sulfuryl fluoride occurs throughout the year. Table 3 and Figure 3 show monthly use for 1999 through 2004 (DPR PUR Database).

Figure 1. Sulfuryl fluoride reported use from 1993 through 2004 (DPR PUR Database).

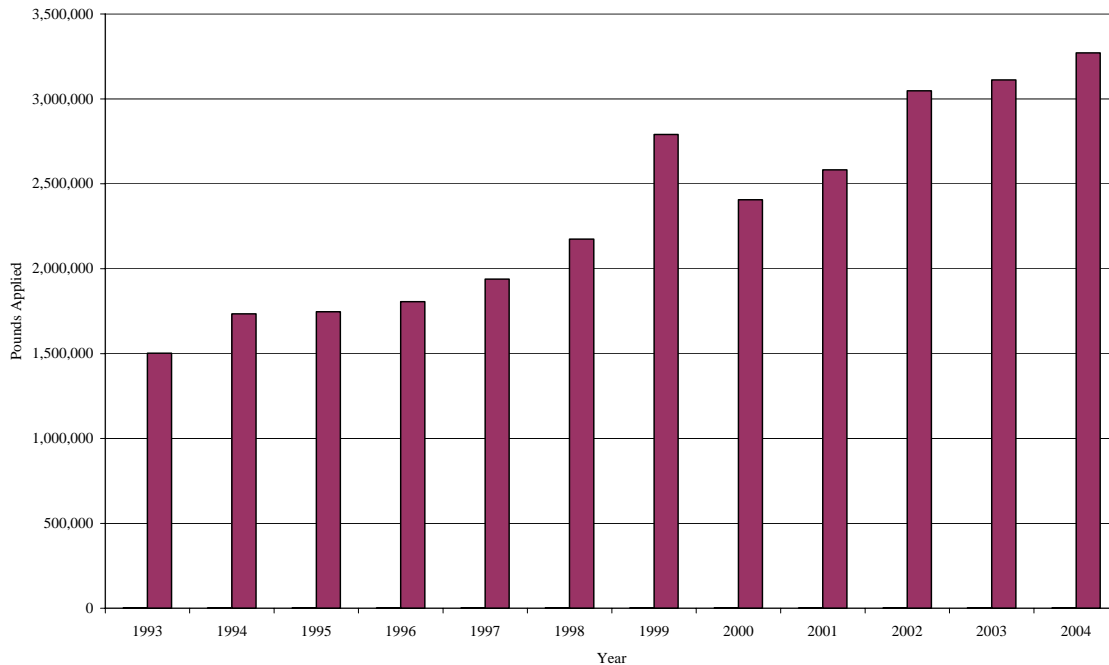


Table 2. Sulfuryl fluoride use by county from 1999 through 2004 for counties with annual use over 60,000 pounds (DPR PUR Database).

County	Pounds Applied					
	1999	2000	2001	2002	2003	2004
LOS ANGELES	924,560	806,192	970,514	1,180,047	1,179,533	1,172,073
ORANGE	466,694	401,705	424,410	460,257	465,854	471,725
RIVERSIDE	60,888	65,823	68,205	84,920	85,504	109,624
SAN BERNARDINO	65,623	72,120	94,850	94,336	96,442	110,173
SAN DIEGO	385,621	371,728	368,295	441,987	420,133	507,175
SANTA BARBARA	75,864	101,523	68,460	67,879	69,467	89,555
SANTA CLARA	348,223	163,556	149,792	172,909	262,555	205,014
VENTURA	110,019	121,268	91,279	100,452	82,064	128,621

Figure 2. Sulfuryl fluoride use by county from 1999 through 2004 for counties with annual use over 60,000 pounds(DPR PUR Database).

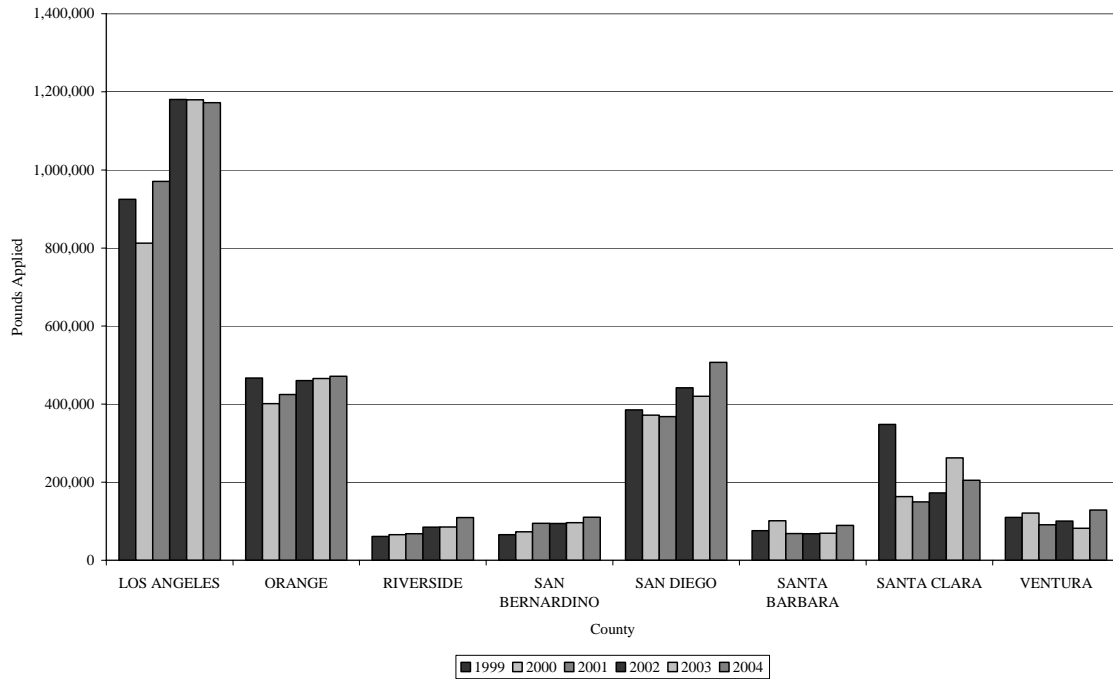
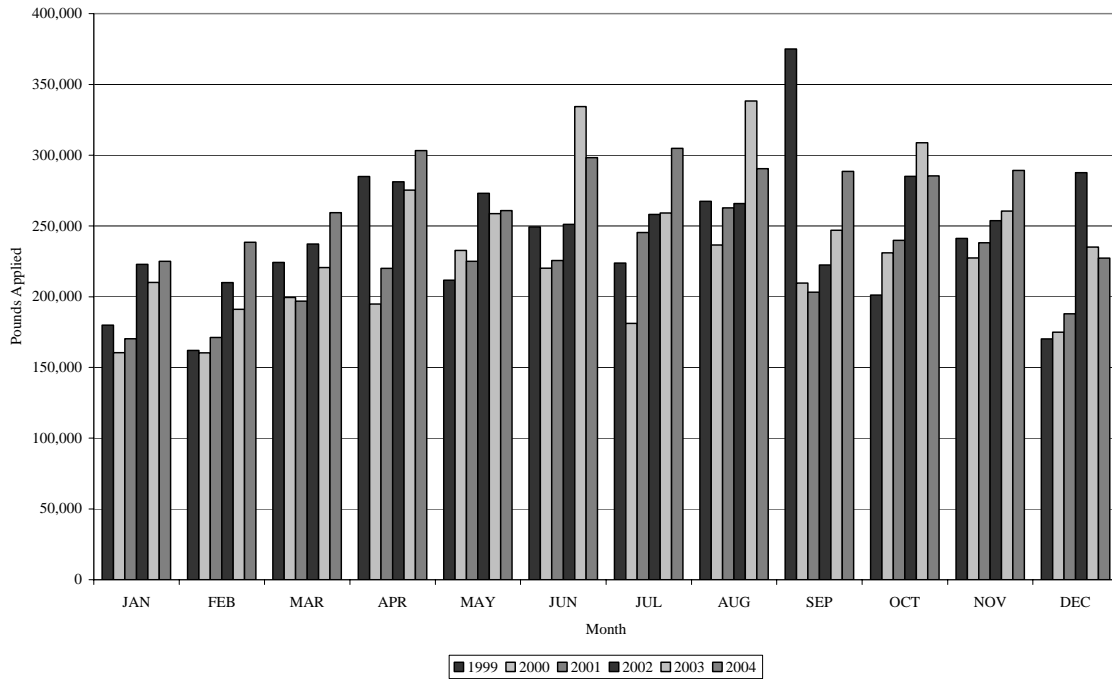


Table 3. Sulfuryl fluoride use by month from 1999 through 2004 (DPR PUR Database).

Month	Pounds Applied					
	1999	2000	2001	2002	2003	2004
JAN	179,834	160,416	170,225	222,873	210,017	224,987
FEB	162,015	160,289	171,134	209,864	191,111	238,385
MAR	224,130	195,438	196,833	237,214	220,530	259,424
APR	285,000	194,342	220,012	281,138	275,334	303,159
MAY	211,533	232,685	224,886	273,011	258,684	260,851
JUN	249,326	220,102	225,631	251,060	334,321	298,241
JUL	223,716	181,141	245,243	258,170	259,138	304,786
AUG	267,484	236,445	262,752	265,702	338,349	290,456
SEP	374,980	207,176	203,207	222,319	246,920	288,610
OCT	201,058	231,002	239,846	285,104	308,741	285,390
NOV	241,076	226,863	238,150	253,724	260,455	289,182
DEC	170,162	174,711	187,921	287,703	235,069	227,228

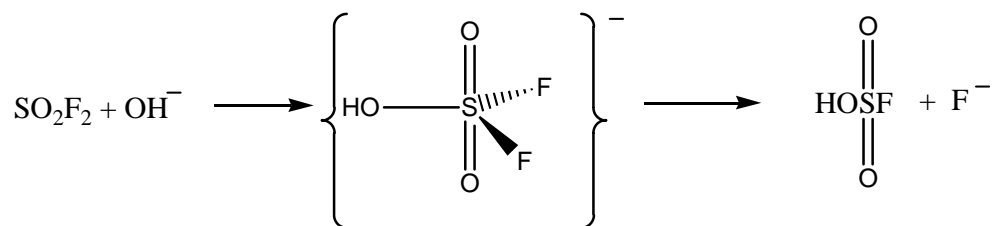
Figure 3. Sulfuryl fluoride use by month from 1999 through 2004 (DPR PUR Database).



▪ **Environmental Fate**

Fate in Water

Sulfuryl fluoride is slowly hydrolyzed in water under neutral conditions. Under alkaline conditions, however, it undergoes rapid hydrolysis. Fluorosulfuric acid (HSO_3F) is formed via nucleophilic attack on the S atom, with displacement of an F ion (Cady and Misra, 1974; Cotton and Wilkerson, 1988; U.S. Environmental Protection Agency, 1993):



The net reaction is:



The rate law may be written as $d[\text{SO}_2\text{F}_2]/dt = -k[\text{SO}_2\text{F}_2][\text{OH}^-]$. At constant pH, $d[\text{SO}_2\text{F}_2]/dt = -k'[\text{SO}_2\text{F}_2]$, where $k' = k[\text{OH}^-]$.

Hydrolysis rates of sulfuryl fluoride in water and in 0.01M HCl have been reported (Cady and Misra, 1974). It was found that at 25 °C, a solution of sulfuryl fluoride in water became increasingly acidic and the concentration of fluoride ion increased due to the slow reaction:



The rate in water or in 0.01M HCl was much higher than the rate of reaction with OH^- ion. It was therefore concluded that sulfuryl fluoride reacts with water as well as with OH^- ion. Sulfuryl fluoride hydrolysis rates and half-lives at various environmentally-relevant pHs are listed in Table 4.

Table 4. Sulfuryl fluoride hydrolysis rates at various environmentally – relevant pH values (Cady and Misra, 1974).

pH	Rate (s^{-1})	Half-life (hours)
5.9 (cloud water)	2.6×10^{-6}	74
7.0 (neutral water)	4.0×10^{-5}	7.0
8.3 (seawater)	1.2×10^{-3}	0.16

Fate in Soil and Biota

Data addressing the fate of sulfuryl fluoride in soil and biota is not available. That data was not required for re-registration due to sulfuryl fluoride's chemical properties and its registration for strictly indoor uses (U.S. Environmental Protection Agency, 1985). Following application and aeration of treated structures, sulfuryl fluoride is dissipated into the atmosphere in the gaseous state. There would be little likelihood that residues would leach to ground water.

Fate in the Atmosphere

Sulfuryl fluoride enters the atmosphere in the gas phase. Once present, it may be transformed and then removed through photolysis and/or reactions with atmospheric radicals (OH and NO₃) or ozone (O₃). The potential for human exposure to sulfuryl fluoride in the vapor phase and subsequent transformation products is therefore related to its rate of dispersion and to its atmospheric lifetime with respect to removal from the atmosphere. A search of the open science literature, however, produced no citations relevant to its fate in the atmosphere. The Estimation Programs Interface (EPI) Suite™ is a Windows® based series of physical/chemical property and environmental fate estimation models developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation. AOPWIN™, an individual model in EPI Suite™, estimates the gas-phase reaction rate for the reaction between a chemical and OH, the most prevalent atmospheric oxidant (Meylan and Howard, 1993). The model also determines if NO₃ reaction will be important, and gas-phase O₃ reaction rates are estimated for olefins and acetylenes. Atmospheric half-lives are automatically calculated using assumed average OH and O₃ concentrations. AOPWIN™ used on sulfuryl fluoride resulted in a prediction of no reaction with the OH radical. In addition, there were no structure matches in the model's experimental database. Although it is possible that sulfuryl fluoride does not react with OH radicals, NO₃ radicals, and O₃, no experimental data are available to confirm this. No data appear to be available concerning the ultraviolet/visible absorption spectrum of sulfuryl fluoride (NIST, 2005). By analogy with other fluorine-containing compounds, it is likely that sulfuryl fluoride does not absorb solar radiation in the actinic region relevant to the troposphere (290-800 nm) and hence that sulfuryl fluoride does not photolyze in the troposphere.

The rates at which sulfuryl fluoride is removed from the atmosphere by dissolution and/or reaction in the oceans and in cloud water were estimated using mathematical formulas to simulate the transfer of gases from the atmosphere to the aqueous phase (Wine and Chameides, 1989). The atmospheric lifetime with respect to dissolution and/or degradation in seawater was estimated to be 22 years. Cloud water was found to be of no importance as an atmospheric sink. The atmospheric lifetime with respect to dissolution and/or degradation in cloud water was estimated to be 1.25 x 10⁷ years. Based on the vapor pressure and aqueous solubility data, rain-out (wet deposition) of sulfuryl fluoride is estimated to be of no importance.

The desorption of gaseous sulfuryl fluoride from 13 representative structural and household commodities have been evaluated (Scheffrahn et al., 1987). Concrete blocks, gypsum/cardboard drywall, wood, fiberglass insulation, polystyrene insulation, topsoil,

carpet padding, polyester cushion fiber, wool fabric, cotton fabric, leather baseball gloves, latex baby bottle nipples, and plastic toy soldiers were fumigated in a 4.3 m³ chamber at 36 mg/L (8.6 ppm, approximate maximum label rate for drywood termites) and 360 mg/L (86 ppm) for 20 hours. During aeration, airborne levels desorbing were determined at 2, 8, and 26 hours, and 5, 20, and 40 days by gas chromatography of the headspace in sealed commodity vials. It was found that 9 of the 13 commodities fumigated at the maximum rate desorbed less than 5 ppm sulfuryl fluoride into the atmosphere at 2 hours. At 26 hours after the start of aeration, all commodities except polystyrene insulation desorbed less than 5 ppm. Several commodities were still off-gassing after 5 days. Desorption half-lives for selected commodities up to 5 days post-aeration ranged from 9.3 hours for latex baby bottle nipples to 36 hours for polyester cushion fibers.

In summary, little or no data on sulfuryl fluoride's environmental and atmospheric loss processes are available. There are no experimental data to allow an assessment of whether or not sulfuryl fluoride undergoes photolysis in the troposphere or whether it reacts with OH radicals, NO₃ radicals, or O₃. For sulfuryl fluoride, the oceans appear to be the only important atmospheric sink. Because of its long atmospheric lifetime with respect to dissolution and/or degradation in sea water, it will be transported throughout the global atmosphere. The potential for sulfuryl fluoride to contribute to the greenhouse effect is a subject for future research. Because of the lack of any data to suggest otherwise, its ability to absorb infrared radiation (NIST, 2005) and its potentially long atmospheric lifetime with respect to photolysis and homogeneous gas-phase reactions to dissolution and/or degradation in sea water make sulfuryl fluoride a good candidate for a greenhouse gas.

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