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OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

Date: January 13, 2004

Subject: PP#1F06312 – Sulfuryl Fluoride. Section 3 Registration for the Post-harvest Fumigation of Stored Cereal Grains, Dried Fruits, and Tree Nuts, and Fumigation of Grain Milling Establishments. Summary of Analytical Chemistry and Residue Data.

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RC 01/04

Executive Summary

Sulfuryl fluoride is being proposed as a methyl bromide replacement to control post-harvest insect and rodent pests in stored grain, dried fruit, and tree nut commodities and in grain milling establishments. Sulfuryl fluoride is a fumigant and, in the form of ProFume™, is formulated as 99+% active ingredient. The fumigation rate for sulfuryl fluoride is the product of the fumigant concentration and exposure time. The maximum target rate is 1500 mg·hr/L for normal atmospheric fumigations and 200 mg·hr/L for vacuum fumigations. Double fumigations are recommended for insect infestations where eggs may be present, with the second fumigation timed to control newly hatched, immature stages. The proposed label specifies that all food commodities be aerated for a minimum of 24 hours prior to the foods entering commerce.

Tolerances are currently established under an experimental use permit for residues of sulfuryl fluoride in/on walnuts and raisins (40 CFR 180.575) and for residues of inorganic fluoride resulting from the use of either sulfuryl fluoride or cryolite (40 CFR 180.145). Sulfuryl fluoride is highly reactive and breaks down to form sulfate and fluoride anions. Parent sulfuryl fluoride and the fluoride anion are the residues of concern for both the tolerance expression and risk assessment purposes.

Storage stability data were not submitted for sulfuryl fluoride. Samples were analyzed for sulfuryl fluoride residues as rapidly as possible following the post-fumigation aeration period. Because the storage interval was very short, storage stability data are not needed for sulfuryl fluoride, per se. Storage stability data for fluoride anion indicate that fluoride is stable in wheat grain, corn grain, corn meal, raisins, and walnuts for up to 140 days. Fluoride residues decline in wheat flour at a rate of 0.3% per day. It is unclear whether this reflects a true dissipation of fluoride from the samples or an increase in "bound" residues. Background residues of fluoride in the control samples for all commodities in the storage stability study decrease with time and the rate appears to be of the same order of magnitude as that observed for wheat flour. How this decline of fluoride anion in the control samples relates to residues in treated commodities or to the regulation of fluoride anion is unclear at this time.

The petitioner has proposed separate methods for the analysis of sulfuryl fluoride and fluoride anion. Residues of sulfuryl fluoride are extracted with water, allowed to volatilize, and then determined by a GC/ECD method that uses headspace analysis. Based on validation data, the limit of detection (LOD) is 0.004 ppm and the limit of quantitation (LOQ) is 0.008 ppm (0.02 ppm for corn grain and wheat germ). The method for the analysis of fluoride anion uses aqueous buffered extraction and a fluoride-selective electrode with the double-known-addition technique for quantifying residues. The petitioner initially reported that the LOD and LOQ for the fluoride method are 0.2 and 0.5 ppm, respectively. Following the independent laboratory validation, the LOQ for the fluoride method was increased to 2 ppm. The petitioner has not demonstrated that either method is capable of extracting incurred residues from cereal grain commodities. Both methods have been reviewed by the Agency's Analytical Chemistry Branch, which recommended that (1) the petitioner radiovalidate both methods and (2) OPP accept the analytical methods without a laboratory validation based on the submitted data (Method Review Memorandum, D. Wright, D282408, 8/14/03).

The proposed tolerances are based on minimal data. Although the petitioner submitted a large quantity of data from studies investigating the effects of various fumigation parameters on sulfuryl fluoride and/or fluoride anion residue levels, very few studies were conducted according to the proposed label directions. In examining the residue data, HED has pooled data across various fumigation parameters when those parameters appear to have little effect on residue levels.

Cereal Grains. Generally, residues of sulfuryl fluoride were below the limit of quantitation in the cereal grain commodities following fumigation at ~1500 mg·hr/L and an active aeration period of 24 hours. Occasionally, quantifiable residues of sulfuryl fluoride were found in/on wheat grain (maximum residue = 0.095 ppm), rice grain (0.025 ppm), rice hulls (0.057 ppm), corn grain (0.026 ppm), corn grits (14.4 ppm). All samples of fumigated corn oil had quantifiable residues of sulfuryl fluoride, with a maximum residue of 7.84 ppm. Apparent residues of sulfuryl fluoride were less than the LOQ in all control samples. For cereal grains, residues of fluoride anion were greater than the LOQ in all commodities except corn oil. Fluoride residues increase with multiple fumigations and appear to be recalcitrant, not declining following longer aeration intervals. Fluoride residues from mill fumigation studies were generally greater than those that resulted from laboratory fumigation studies of cereal grain commodities. Following a single fumigation at ~1500 mg·hr/L, maximum residues ranged from 5.3 ppm (corn grain) to 104 ppm (wheat germ). Measurable fluoride anion residues occurred in most control samples; the residue levels varied from one commodity to another and ranged from 0.03 to 2.08 ppm.

Processing studies conducted with whole grain corn and whole grain wheat showed that residues of fluoride concentrate in wheat shorts (1.26X), wheat bran (2.56X), wheat germ (4.82X), and corn "impurities" (5.49X). Impurities are described as being similar to aspirated grain fractions. The processed cereal grain commodities were generated using simulated commercial practices. Sulfuryl fluoride analyses were not done for commodities processed from treated grain samples. This is not considered to be a data gaps since sulfuryl fluoride is not expected to survive the milling process.

Dried Fruits and Tree Nuts. In dried fruits and tree nuts, residue levels of sulfuryl fluoride varied based on the commodity and the treatment regime. For most commodities, residues had dissipated to <2.1 ppb within 6 days of active aeration (1.5 chamber volumes/min) following fumigation. Sulfuryl fluoride residues were more persistent in commodities with higher oil content (e.g, walnuts, pecans, almonds), typically requiring closer to 14 days for residues to dissipate to <2.1 ppb. At the same fumigation rate, residues of sulfuryl fluoride were greater following vacuum fumigation versus treatment at ambient pressure. In oily commodities, multiple fumigations resulted in higher residues of sulfuryl fluoride at a given aeration time. Pooled across all of the variables addressed in this study, sulfuryl fluoride residues ranged from <2.1 ppb to 6030 ppb (6.03 ppm). Residue levels of fluoride were measured only after residues of sulfuryl fluoride had dissipated to below detectable levels; therefore, the effect of aeration time on fluoride levels cannot be assessed from these data. Generally, fluoride residues appear to be more dependent on the number of fumigations than on the treatment rate, treatment pressure, or commodity. Overall, fluoride residue levels ranged from <1.4 ppm to 21.8 ppm.

Recommendations

The residue chemistry databases for both sulfuryl fluoride and fluoride anion are considered marginally adequate to set tolerances based on the proposed use pattern. As a condition of registration, HED is recommending that further residue data are collected to ensure that the tolerances being recommended by HED are appropriate.

Residue Chemistry Deficiencies

- The number of cereal grain magnitude of the residue studies conducted at the maximum proposed use rate is marginally adequate. Residue data for both sulfuryl fluoride and fluoride anion should be submitted. The data should be from samples in at least three different grain mills that were treated according to the proposed maximum use. The matrices to be analyzed should include raw and processed commodities of wheat, rice, sorghum, and corn, including corn oil.
- The number of dried nut and tree fruit magnitude of the residue studies conducted at the maximum proposed use rate is marginally adequate. Residue data for both sulfuryl fluoride and fluoride anion should be submitted for representative commodities for these two groups. Samples should be treated according to the proposed maximum use.
- Both HED and the Analytical Chemistry Branch are concerned about the ability of the analytical methods to extract incurred residues. Data showing the ability of the sulfuryl fluoride and fluoride anion methods to extract and accurately quantify incurred residues in raw and processed cereal grain matrices should be submitted. Furthermore, HED is requesting that the sulfuryl fluoride method be validated for corn oil. If the current method proves to be acceptable for corn oil, then the requested label restriction (see below) can be lifted and HED will recommend that a tolerance be established for corn oil.
- The sulfuryl fluoride method has not been shown to be specific to sulfuryl fluoride. An interference study for sulfuryl fluoride should be submitted.
- Cereal grain commodities, including aspirated grain fractions, are significant livestock feed items. Feeding studies were not submitted to determine the extent of secondary residues that may occur in livestock commodities. HED is requesting data showing the transfer of fluoride from feedstuffs into livestock commodities. A feeding study is not being requested for sulfuryl fluoride.
- A revised Section F (Proposed Tolerances) is required.

HED notes that data are sufficient to set sulfuryl fluoride and fluoride anion tolerances provided that the following modifications are made to the label:

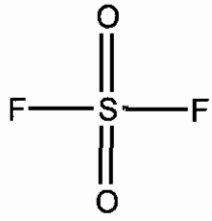
- The total fumigation rate shall not exceed 1500 mg·hr/L at ambient pressure or 200 mg·hr/L under reduced pressure.
- Active aeration of at least 24 hours at not less than 1 chamber volume/min shall occur for all commodities prior to their entering commerce. This requirement does not apply to mill fumigations since practices to ensure worker safety will result in adequate aeration.

- Corn oil shall be removed from the premises prior to fumigation.

Provided such label changes are made, HED is recommending a conditional registration with the sulfuryl fluoride and fluoride anion tolerances shown in Table 5.

Background

Dow AgroSciences has requested permanent tolerances for residues of sulfuryl fluoride and fluoride anion resulting from the post-harvest fumigation of stored cereal grains, cereal grain processed commodities, dried fruit, and tree nuts. Sulfuryl fluoride is a potential methyl bromide replacement. Dow AgroSciences was recently given an experimental use permit for the post-harvest fumigation of walnuts and raisins.



Sulfuryl fluoride is a highly volatile compound with a boiling point of -55°C and a vapor pressure of 0.02 Torr. At 20°C, sulfuryl fluoride has a vapor density of 4.3 g/L (heavier than air) and is both colorless and odorless. The log K_{OW} is estimated to be 0.41. Sulfuryl fluoride has a very low solubility in water (0.075 g/100 g). Solubility in other solvents are 0.78 g/100 g in Wesson oil, 1.74 g/100 g in acetone, and 2.12 g/100 g in chloroform.

860.1200 Directions for Use

Table 1. Summary of Directions for the Post-harvest Use of Sulfuryl Fluoride from the Proposed Label.

Applic. Timing, Type, and Equip.	Formulation [EPA Reg. No.]	Applic. Rate (mg·hr/L)	Max. No. Applic. per Season	Max. Seasonal Applic. Rate (mg·hr/L)	Aeration (hours)	Use Directions and Limitations
Post-harvest fumigation of sealed mills, warehouses, chambers, and other storage structures.	ProFume [62719-XXX]	1500 (ambient pressure) 200 (vacuum fumigation)	2	3000 (ambient pressure) 400 (vacuum fumigation)	24	Food commodities must be aerated for 24 hours prior to entering commerce.

The proposed label has sufficient information to allow the Agency to evaluate the residue trials in light of the proposed use patterns. Prior to registration, HED is requesting that the label and use manual be modified to specify a maximum fumigation rate of 1500 mg·hr/L at ambient pressure or 200 mg·hr/L at reduced pressure, that commodities be actively aerated (not less than 1 chamber volume/min) for at least 24 hours prior to their entering commerce, and that corn oil be removed from any premises prior to fumigation.

860.1300 Nature of the Residue - Plants

DER: None
MARC Decision Memo: None

Nature of the residue studies have not been submitted for sulfuryl fluoride. Following application, sulfuryl fluoride breaks down to form sulfate and fluoride anion. Sulfate is not of toxicological concern. Fluoride anion is of toxicological concern due to potential skeletal fluorosis. The residues of concern for both tolerance enforcement and risk assessment purposes are sulfuryl fluoride and fluoride anion. The lack of nature of the residue studies is not considered to be a deficiency and no further data are required to fulfill this guideline.

860.1300 Nature of the Residue - Livestock

DER: None
MARC Decision Memo: None

As with plants, sulfuryl fluoride would be expected to hydrolyze to form sulfate and fluoride anions. The residues of concern in livestock are sulfuryl fluoride and the fluoride anion; however, due to the nature of the sulfuryl fluoride molecule, HED believes it is unlikely that secondary residues of sulfuryl fluoride will occur in livestock commodities. The lack of nature of the residue studies is not considered to be a deficiency and no further data are required to fulfill this guideline.

860.1340 Residue Analytical Methods

DER: M. Doherty, 1/13/04, MRID 45632902 (Sulfuryl Fluoride; 45632902.der.wpd)
M. Doherty, 1/13/04, MRID 45603901 (Fluoride anion; 45603901.der.wpd)

Sulfuryl Fluoride. The proposed method utilizes headspace analysis to quantitate residues of sulfuryl fluoride. Residues of sulfuryl fluoride are extracted with water in an air-tight blender. The samples are agitated in the blender for five minutes to transfer residues of the highly volatile sulfuryl fluoride from the grain commodity to the headspace above the sample. The headspace is then analyzed for residues of sulfuryl fluoride by injecting an aliquot into a gas chromatograph with electron-capture detection (GC/ECD). The method has been validated using fortification/ recovery experiments on wheat, corn, and rice commodities. Fortification levels ranged from 0.008 to 0.08 ppm (0.2 ppm for wheat). Average recoveries and standard deviations were 88 ± 14% for wheat, 94 ± 16% for corn, and 82 ± 11% for rice. Standard deviations at the 0.008-ppm fortification level ranged from 0.00099 to 0.00129 ppm, resulting in calculated limits of detection and quantification of approximately 0.003 and 0.010 ppm, respectively. There were no apparent residues of sulfuryl fluoride in the control samples. Due to the gaseous nature of sulfuryl fluoride, fortifications were made to the headspace above the commodities and not to the commodities themselves. The method has not been radiovalidated and it is unclear if the method will successfully extract incurred residues. The method has not been shown to be specific to sulfuryl fluoride. It is likely that the method would extract and detect other volatile halogenated compounds (e.g., methyl bromide).

The method underwent an independent laboratory validation. After a considerable amount of consultation between the confirming laboratory and Dow AgroSciences, the laboratory was able to successfully validate the method for wheat grain (average recovery = 104 ± 10%) and wheat flour (94 ± 10%). Other cereal grain commodities were not tested.

The method has been reviewed by the Agency's Analytical Chemistry Branch (ACB; D. Wright Jr., D282408, 8/14/2003). Although the ACB concurs with HED regarding the ability of the method to extract incurred residues and recommends that the petitioner radiovalidate the method, they recommend that OPP accept the data and that an Agency method validation is not required at this time (D. Wright, D282408, 8/14/2003). Furthermore, HED notes that although control samples of corn oil were analyzed, the method was not validated for corn oil. Due to the physicochemical properties of sulfuryl fluoride, oily commodities are the most likely to bear residues following fumigation. In addition to radiovalidation of the method, HED requests that the method performance be verified for corn oil.

Fluoride Anion. The method consists of homogenizing and shaking the sample in the presence of water and total ionic strength adjusting buffer, centrifuging the sample, and analyzing an aliquot of the supernatant with a fluoride-selective electrode. Quantitation of fluoride residues is achieved using a double-known-addition technique.

The method was validated by the petitioner using whole grain wheat, whole grain corn, wheat flour, and corn oil. Two independent laboratory validations were performed; the first used whole grain wheat and wheat flour, and the second used corn oil and raisins. Recovery of fluoride was comparable across all tested commodities and between the petitioner validations and the independent laboratory validations. Generally, recovery of fluoride fell within the acceptable range of 70-120% after values were corrected for background levels of fluoride in control samples. Initial laboratory validation experiments showed limits of detection (LOD) and quantification (LOQ) of approximately 0.2 and 0.5 ppm, respectively. During the independent laboratory validation, the LOQ was increased to 2.0 ppm.

As with the sulfuryl fluoride method, the ability of the method to extract incurred residues has not been demonstrated. HED requests that the petitioner characterize the efficacy of the method with respect to incurred residues.

Conclusions. Both the sulfuryl fluoride and the fluoride anion methods have undergone review by the Agency's ACB. The ACB recommends that the methods be radiovalidated and that they be accepted without a full method validation.

860.1360 Multiresidue Methods

DER: None

Multiresidue method studies have not been submitted to the Agency. Based on their physicochemical properties, neither sulfuryl fluoride nor fluoride anion are likely to be suitable for the multiresidue techniques currently in use. The lack of multiresidue studies is not considered to be a deficiency and no further data are required to fulfill this guideline.

860.1380 Storage Stability

DER: M. Doherty, 1/13/04, MRID 45510302 (45510302.der.wpd)

Sulfuryl Fluoride. Storage stability data for sulfuryl fluoride were not submitted. Sulfuryl fluoride analysis of field trial samples was completed very shortly following the fumigation/aeration of the grain commodities. Storage stability data are not required to support the sulfuryl fluoride residue analysis for the field trial samples because of this short storage interval.

Fluoride Anion. Samples of wheat grain, wheat flour, corn grain, corn meal, raisins, and walnuts were individually homogenized and fortified with an aqueous fluoride solution to a concentration of 20 ppm fluoride. The fortified samples were stored at ambient temperatures for 30 days and then placed into frozen (-20°C) storage for the remainder of the study. On Day 0 and approximately Day 35, Day 75, Day 105, and Day 140 after fortification, the storage stability samples, along with a control sample, a reagent blank, and two daily concurrent recovery samples, were analyzed for fluoride anion. Fluoride residues were extracted using an aqueous solution and analyzed using a fluoride ion selective electrode. The reported LOQ for the method is 0.6 ppm for wheat grain, 0.3 ppm for wheat flour, and 0.5 ppm for corn grain. LOQs for other matrices were not given.

Residues of fluoride anion were stable for the duration of the study (~140 days) in wheat grain, corn grain, corn meal, raisins, and walnuts. In wheat flour, however, fluoride residues exhibited a continual decline throughout the study, with only 55% remaining at 140 days. Regression of the residue data indicates a loss of approximately 0.3% per day. The study design does not permit determination of whether or not the loss reflects dissipation of the fluoride residues or an increase in "bound" residues. This loss should be taken into account when interpreting the results of residue studies in wheat flour. HED will not assume that fluoride anion is stable in all commodities. Furthermore, HED notes that the residues in the control samples for all matrices indicate a loss of fluoride with time and that this loss appears to be of the same order of magnitude as that observed in wheat flour. The significance of this trend as it relates to storage stability and field trial results is unclear at this time.

Conclusions. The storage stability data support the storage intervals and conditions for samples from the field trial and processing studies.

860.1400 Water, Fish, and Irrigated Crops

DER: None

There are no proposed uses for sulfuryl fluoride that would result in residues in fish or irrigated crops. A discussion of the 860.1400 guideline is not germane to this petition.

860.1460 Food Handling

DER: None

There are no proposed uses for sulfuryl fluoride in or around food handling areas. A discussion of the 860.1460 guideline is not germane to this petition.

860.1480 Meat, Milk, Poultry, and Eggs

DER: None

Studies describing residues of sulfuryl fluoride and fluoride anion in meat, milk, poultry, and eggs have not been submitted to the Agency. Due to the nature of the sulfuryl fluoride molecule, HED believes it is unlikely that secondary residues of sulfuryl fluoride will occur in livestock commodities. The ability of fluoride anion to be transferred from animal feeds to livestock commodities is unclear. Since cereal grain commodities, including aspirated grain fractions, are a major cattle and poultry feed item, HED is requesting that livestock feeding studies be done for the fluoride anion.

860.1500 Crop Field Trials

DER: M. Doherty, 1/13/04, MRID 45396301 (45396301.der.wpd)
M. Doherty, 1/13/04, MRID 45510303 (45510303.der.wpd)
M. Doherty, 1/13/04, MRID 45510304 (45510304.der.wpd)

Cereal Grains

Table 2. Summary of Sulfuryl Fluoride Residues in Cereal Grains. Residue data have been pooled across treatment rate and loading factor. The proposed use pattern is a maximum of 2 fumigations, with a total rate not to exceed 1500 mg·hr/L, and a 24-hour aeration period. Data from more than 2 fumigations or aeration periods greater than 1 day have not been included in this table.

Crop	Form	Location	Temp. (°C)	Fumigation No.	Aeration (days)	n	Sulfuryl Fluoride Residues (ppm)			
							Min	Max	Mean	Std Dev
Corn	Starch	Lab	22	1	1	2	<0.008	<0.008	<0.008	0.000
Corn	Flour	Lab	22	1	1	2	<0.008	<0.008	<0.008	0.000
Corn	Grain	Lab	22	1	1	2	<0.020	0.026	0.023	0.004
Corn	Grits	Lab	22	1	1	2	<0.008	14.400	7.204	10.177
Corn	Meal	Lab	22	1	1	2	<0.008	<0.008	<0.008	0.000
Corn	Oil	Lab	22	1	1	2	5.848	7.840	6.844	1.409
Rice	Bran	Lab	22	1	1	2	<0.008	<0.008	<0.008	0.000
Rice	Hulls	Lab	22	1	1	2	0.056	0.057	0.057	0.001
Rice	Grain	Lab	22	1	1	2	0.016	0.025	0.021	0.007
Rice	Polished	Lab	22	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	Bran	Lab	22	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	Flour	Lab	30	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	Flour	Lab	10	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	Flour	Lab	22	1	1	10	<0.008	<0.008	<0.008	0.000
Wheat	Flour	Lab	22	2	1	2	<0.008	0.009	0.009	0.001
Wheat	Germ	Lab	22	1	1	10	<0.020	<0.020	<0.020	0.000

Crop	Form	Location	Temp. (°C)	Fumigation No.	Aeration (days)	n	Sulfuryl Fluoride Residues (ppm)			
							Min	Max	Mean	Std Dev
Wheat	Germ	Lab	30	1	1	2	<0.020	<0.020	<0.020	0.000
Wheat	Germ	Lab	10	1	1	2	<0.020	<0.020	<0.020	0.000
Wheat	Germ	Lab	22	2	1	2	<0.020	<0.020	<0.020	0.000
Wheat	Grain	Lab	22	1	1	10	<0.008	0.090	0.021	0.026
Wheat	Grain	Lab	10	1	1	2	0.032	0.033	0.033	0.000
Wheat	Grain	Lab	30	1	1	2	0.013	0.014	0.013	0.001
Wheat	Grain	Lab	22	2	1	2	0.086	0.095	0.091	0.007
Wheat	Red dog	Lab	22	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	Shorts	Lab	22	1	1	2	<0.008	<0.008	<0.008	0.000

Table 3. Summary of Fluoride Anion Residues in Cereal Grains. Residue data have been pooled across loading factor and aeration time. The proposed use pattern is a maximum of 2 fumigations, with a total rate not to exceed 1500 mg·hr/L, and a 24-hour aeration period. Data from rates less than ~1000 or greater than ~1800 mg·hr/L or from more than 2 fumigations have not been included in this table. Bolded rows indicate the maximum residue for each crop/commodity.

Crop	Commodity	Location	Temp. (°C)	Fumig. No.	Rate[A] (mg-hr/L)	n	Fluoride Anion Residues (ppm)			
							Min	Max[B]	Mean	SD
Barley	Grain	Lab	30	1	1646	4	2.76	3.05	2.88	0.13
Barley	**Grain**	**Mill**	**Amb.[C]**	**1**	**1012**	**4**	**4.27**	**9.25**	**6.27**	**2.37**
Barley	Grain	Mill	Amb.	1	1798	2	6.49	7.96	7.23	1.04
Corn	Flour	Lab	22	1	1500	4	14.90	19.20	17.10	2.26
Corn	Flour	Mill	Amb.	1	1012	4	17.20	24.10	19.35	3.19
Corn	**Flour**	**Mill**	**Amb.**	**1**	**1798**	**2**	**22.70**	**24.10**	**23.40**	**0.99**
Corn	Grain	Lab	30	1	1436	4	1.31	1.64	1.43	0.15
Corn	Grain	Lab	22	1	1500	4	2.07	2.26	2.18	0.09
Corn	Grain	Lab	30	1	1504	4	0.76	1.41	1.00	0.28
Corn	Grain	Mill	Amb.	1	1012	4	1.00	2.05	1.39	0.48
Corn	**Grain**	**Mill**	**Amb.**	**1**	**1012**	**4**	**1.03**	**5.31**	**2.43**	**2.00**
Corn	Grain	Mill	Amb.	1	1798	2	1.19	1.52	1.36	0.23
Corn	Grain	Mill	Amb.	1	1798	2	1.71	1.86	1.79	0.11
Corn	**Grits**	**Lab**	**22**	**1**	**1500**	**4**	**7.74**	**9.17**	**8.57**	**0.69**
Corn	Meal	Lab	22	1	1500	4	5.24	6.30	5.82	0.49
Corn	Meal	Mill	Amb.	1	1012	4	10.50	21.00	14.83	4.66
Corn	**Meal**	**Mill**	**Amb.**	**1**	**1798**	**2**	**21.60**	**26.40**	**24.00**	**3.39**
Corn	**Oil**	**Lab**	**22**	**1**	**1500**	**4**	**<0.50**	**<0.50**	**<0.50**	**0.00**
Corn	**Starch**	**Lab**	**22**	**1**	**1500**	**4**	**3.82**	**5.35**	**4.60**	**0.84**
Oats	Grain	Lab	30	1	1560	4	7.00	8.27	7.54	0.53
Oats	**Grain**	**Mill**	**Amb.**	**1**	**1012**	**4**	**6.82**	**15.25**	**9.78**	**3.77**
Oats	Grain	Mill	Amb.	1	1798	2	12.50	14.00	13.25	1.06
Rice	**Bran**	**Lab**	**22**	**1**	**1500**	**4**	**24.20**	**28.50**	**25.90**	**1.96**
Rice	Brown	Lab	30	1	1599	4	2.16	2.38	2.24	0.10
Rice	**Brown**	**Mill**	**Amb.**	**1**	**1012**	**4**	**3.84**	**11.80**	**6.78**	**3.60**
Rice	Brown	Mill	Amb.	1	1798	2	6.24	7.29	6.77	0.74
Rice	**Grain**	**Lab**	**22**	**1**	**1500**	**4**	**5.49**	**8.46**	**6.93**	**1.43**
Rice	**Hulls**	**Lab**	**22**	**1**	**1500**	**4**	**23.40**	**32.80**	**27.53**	**4.76**
Rice	Polished	Lab	22	1	1500	4	1.30	1.60	1.44	0.13
Rice	Polished	Lab	30	1	1547	4	1.83	2.03	1.96	0.09
Rice	**Polished**	**Mill**	**Amb.**	**1**	**1012**	**4**	**3.21**	**16.10**	**7.44**	**5.85**
Rice	Polished	Mill	Amb.	1	1798	2	7.64	10.70	9.17	2.16
Wheat	**Bran**	**Lab**	**22**	**1**	**1500**	**4**	**34.00**	**37.10**	**35.95**	**1.38**
Wheat	Flour	Lab	22	1	1000	2	19.30	21.10	20.20	1.27
Wheat	Flour	Lab	10	1	1500	2	14.60	15.70	15.15	0.78
Wheat	Flour	Lab	22	1	1500	18	21.50	44.70	32.57	6.18
Wheat	Flour	Lab	30	1	1500	2	33.40	37.80	35.60	3.11
Wheat	Flour	Lab	22	2	1500	2	62.50	62.60	62.55	0.07

Crop	Commodity	Location	Temp. (°C)	Fumig. No.	Rate[A] (mg-hr/L)	n	Fluoride Anion Residues (ppm)			
							Min	Max[B]	Mean	SD
Wheat	Flour	Mill	Amb.	1	1012	4	21.20	49.70	36.48	12.14
Wheat	Flour	Mill	Amb.	1	1798	2	46.4	49.30	47.85	2.05
Wheat	Flour, Semolina	Mill	Amb.	1	1012	4	13.10	27.30	21.63	6.46
Wheat	Flour, Semolina	Mill	Amb.	1	1798	2	25.50	28.40	26.95	2.05
Wheat	Flour, Unbleached White	Mill	Amb.	1	1012	4	22.90	51.50	37.50	14.89
Wheat	Flour, Unbleached White	Mill	Amb.	1	1012	4	26.00	57.00	39.33	13.17
Wheat	Flour, Unbleached White	Mill	Amb.	1	1798	2	41.70	45.30	43.50	2.55
Wheat	Flour, Unbleached White	Mill	Amb.	1	1798	2	40.40	49.30	44.85	6.29
Wheat	Flour, Whole	Mill	Amb.	1	1012	4	22.40	32.90	26.83	4.50
Wheat	**Flour, Whole**	**Mill**	**Amb.**	**1**	**1012**	**4**	**28.10**	**82.30**	**44.83**	**25.48**
Wheat	Flour, Whole	Mill	Amb.	1	1798	2	35.60	40.40	38.00	3.39
Wheat	Flour, Whole	Mill	Amb.	1	1798	2	40.50	48.20	44.35	5.44
Wheat	Germ	Lab	22	1	1000	2	55.30	58.60	56.95	2.33
Wheat	Germ	Lab	10	1	1500	2	17.40	18.60	18.00	0.85
Wheat	Germ	Lab	22	1	1500	18	41.60	104.00	67.01	17.86
Wheat	Germ	Lab	30	1	1500	2	72.30	82.60	77.45	7.28
Wheat	**Germ**	**Lab**	**22**	**2**	**1500**	**2**	**121.00**	**158.00**	**139.50**	**26.16**
Wheat	Germ	Mill	Amb.	1	1012	4	33.40	41.10	38.10	3.31
Wheat	Germ	Mill	Amb.	1	1012	4	41.40	89.70	64.88	24.32
Wheat	Germ	Mill	Amb.	1	1798	2	55.90	63.30	59.60	5.23
Wheat	Germ	Mill	Amb.	1	1798	2	78.80	85.90	82.35	5.02
Wheat	Grain	Lab	22	1	1000	2	1.52	1.74	1.63	0.16
Wheat	Grain	Lab	10	1	1500	2	0.79	0.91	0.85	0.08
Wheat	Grain	Lab	22	1	1500	18	1.47	4.08	2.47	0.84
Wheat	Grain	Lab	30	1	1500	2	2.79	2.96	2.88	0.12
Wheat	Grain	Lab	22	2	1500	2	5.02	5.02	5.02	0.00
Wheat	Grain	Lab	30	1	1713	4	3.38	4.84	4.06	0.62
Wheat	Grain	Lab	30	1	1768	4	1.93	2.24	2.08	0.13
Wheat	Grain	Lab	30	1	1769	4	2.64	3.50	3.03	0.44
Wheat	Grain	Mill	Amb.	1	1012	4	2.98	6.54	4.49	1.57
Wheat	Grain	Mill	Amb.	1	1012	4	2.12	8.36	4.53	2.68
Wheat	**Grain**	**Mill**	**Amb.**	**1**	**1012**	**4**	**3.61**	**23.60**	**9.19**	**5.30**
Wheat	Grain	Mill	Amb.	1	1798	2	4.84	5.65	5.25	0.57
Wheat	Grain	Mill	Amb.	1	1798	2	4.79	5.80	5.30	0.71
Wheat	Grain	Mill	Amb.	1	1798	2	4.73	6.06	5.40	0.94
Wheat	**Red dog**	**Lab**	**22**	**1**	**1500**	**4**	**31.70**	**33.30**	**32.50**	**0.67**
Wheat	**Shorts**	**Lab**	**22**	**1**	**1500**	**4**	**31.90**	**35.50**	**34.18**	**1.57**

[A] For the grain mills, application rates were grouped into categories of <300 mg•hr/L, >300 mg•hr/L and <1200 mg•hr/L, and > 1200 mg•hr/L. The statistics listed for application rate and residue levels are for samples within each application rate grouping.
[B] Due to the design of this study, the maximum residue level and the highest average residue levels are identical.
[C] Amb. = Ambient Temperature

MRID 45396301. Studies were conducted to determine the magnitude of sulfuryl fluoride and fluoride anion residues in/on stored grain commodities following fumigation of the commodities with sulfuryl fluoride. The studies were designed to investigate the effects of temperature (10, 22, or 30 °C), number of fumigations (1-4), fumigation rate (250, 1000, 1500, or 2500 mg·hr/L), fumigation chamber loading (1, 10, 50, or 80% of capacity), and aeration time (1, 4, or 7 days; active aeration at approx. 1 chamber volume/min) on sulfuryl fluoride and fluoride anion residues. Residues of sulfuryl fluoride were analyzed using a GC/ECD headspace method. Residues of fluoride anion were analyzed using a fluoride ion selective electrode following the double standard addition technique.

For sulfuryl fluoride, residues were independent of fumigation rate, number of

fumigations, temperature, and chamber loading factor. After one day of aeration, residues of sulfuryl fluoride were <LOQ in many commodites and <0.1 ppm in all commodities except corn grits (14.4 ppm maximum) and corn oil (7.8 ppm maximum). Following four days of aeration, residues of sulfuryl fluoride were <LOQ in all matrices except corn oil (2.6 ppm maximum) and wheat grain (0.04 ppm maximum; 10 °C only). Quantifiable residue of sulfuryl fluoride persisted in these two commodities even after 7 days of aeration (wheat grain treated at 10 °C only).

For anionic fluoride, residues were independent of chamber loading and aeration time. Residues vary significantly from one commodity to another, with maximum residues observed in wheat germ and wheat flour. The residue values in these commodities are positively correlated with the fumigation rate, fumigation temperature, and the number of fumigations. Quantifiable residues of fluoride anion were found in all matrices except corn oil (<0.5 ppm), further demonstrating the stability of parent sulfuryl fluoride in that matrix.

A large amount of data was submitted to characterize the effects of the fumigation parameters on residue levels. However, within a given set of parameters (i.e., a use pattern), there is very little replication. Pooling data across parameters that do not significantly affect residue levels can be done to increase the number of replicates. Even so, replication is only marginally sufficient to support tolerances for some of the use patterns conducted in this study.

MRID 45510303. Controlled laboratory and operational grain mill fumigations using sulfuryl fluoride were conducted with whole cereal grains (hard red winter wheat, soft red winter wheat, durum wheat, medium grain brown rice, medium grain white rice, white field corn, popcorn, barley, and oats) and representative processed commodities (wheat germ, wheat flour, and corn meal; grain mill fumigations only) in order to determine the magnitude of sulfuryl fluoride and fluoride anion residues that occur following treatment with sulfuryl fluoride. In the laboratory, commodities were fumigated for 24 hours at either 200 mg·hr/L or 1500 mg·hr/L and then aerated for 24 hours prior to analysis. In the grain mills, fumigations were for 24 hours at either ~280 mg·hr/L, ~1000 mg·hr/L, or ~1800 mg·hr/L and were followed by a 24-hour active aeration interval. Residues of sulfuryl fluoride were determined using GC/ECD headspace analysis (laboratory studies only). Samples of the laboratory- and the grain mill-treated commodities were analyzed for fluoride anion using aqueous extraction and fluoride selective-ion electrode. Sulfuryl fluoride analysis was completed immediately after the 24-hour aeration period.

Following the 24-hour aeration interval, residues of sulfuryl fluoride were less than the LOQ (0.008 ppm) in all laboratory-fumigated commodities, with the exception of one white corn subsample fumigated at the 1500-mg·hr/L rate. Residues in that sample were 0.019 ppm and dissipated to < 0.008 ppm by 48 hours after fumigation. Residues of sulfuryl fluoride were not determined in samples from the grain mills.

Residues of fluoride anion were dependent upon the sulfuryl fluoride treatment rate. Residues in whole grains from the laboratory fumigations ranged from <0.5 ppm to 2 ppm at the 200-mg·hr/L rate and from 1 ppm to 8 ppm at the 1500-mg·hr/L rate. Residues in/on grains from

the mill fumigations ranged from 1 ppm to 8 ppm at the lower rate (~280 mg·hr/L) and from 1 ppm to 24 ppm at the higher rates (~1000 - 1800 mg·hr/L). Residues in processed commodities were higher than those in whole grains and ranged from 7 ppm to 50 ppm at the lower rate and from 11 ppm to 90 ppm at the higher rate. Although there is a fairly high degree of variability across treatment replicates, the bulk of the variability in the residue levels appears to be due to properties of the commodities themselves.

There are no specific guidelines regarding the number of trials and replicates required for post-harvest pesticide uses. In the laboratory, two fumigation levels were used (200 and 1500 mg·hr/L) for each commodity and there were four replicates per fumigation level. In the grain mills, three fumigation levels were used (~280, ~1000, and ~1800 mg·hr/L) for each grain and processed commodity and three samples were collected per fumigation. This is equivalent to one trial at each fumigation level for each commodity. Given the residue picture from the entire available database, HED considers this to be a marginally acceptable number of trials for supporting sulfuryl fluoride or fluoride anion tolerances.

Dried Fruit and Tree Nuts

Table 4. Summary of Residue Data from Crop Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Fumigation Rate, mg·hr/L (cumulative rate)	Aeration Time, days	Residue Levels*				
				n	Min.	Max.	Mean	Std. Dev.
Sulfuryl Fluoride, ppb								
A - Almond	1	203	1	4	8.90	12.40	11.03	1.55
A - Almond	1		2	5	1.05	2.10	1.26	0.47
A - Dates	1	208	1	4	1.05	1.05	1.05	0.00
A - Dried Plums	1	219	1	4	1.05	1.05	1.05	0.00
A - Figs	1	197	1	5	1.05	7.20	4.41	2.19
A - Pecans	1	199	1	5	32.20	60.30	46.40	10.85
A - Pecans	1		2	4	17.30	25.30	21.90	3.40
A - Pecans	1		5	4	4.80	7.40	5.53	1.25
A - Pecans	1		8	4	1.05	1.05	1.05	0.00
A - Pistachios	1	214	1	4	1.05	1.05	1.05	0.00
A - Raisins	1	221	1	4	1.05	1.05	1.05	0.00
A - Walnuts	1	217	1	4	67.80	79.00	72.58	5.05
A - Walnuts	1		5	4	1.05	2.10	1.84	0.53
A - Walnuts	1		8	4	1.05	1.05	1.05	0.00
B - Almond	1	1534	1	4	28.00	40.00	33.50	4.93
B - Almond	2	1538 (3072)	1	4	44.00	75.00	57.50	13.63
B - Almond	2		2	5	22.00	55.00	35.20	13.81
B - Almond	2		5	2	7.00	8.10	7.55	0.78
B - Almond	3	1488 (4560)	1	4	107.00	128.00	121.00	9.49
B - Almond	3		5	4	14.00	18.00	15.50	1.91
B - Almond	3		8	4	1.05	2.10	1.84	0.53
B - Almond	3		15	4	1.05	1.05	1.05	0.00
B - Dates	1	1484	1	4	6.10	8.30	7.28	1.09
B - Dates	2	1504 (2988)	1	4	1.05	2.10	1.58	0.61

Table 4. Summary of Residue Data from Crop Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Fumigation Rate, mg·hr/L (cumulative rate)	Aeration Time, days	Residue Levels*				
				n	Min.	Max.	Mean	Std. Dev.
B - Dates	3	1493 (4481)	1	4	5.20	7.10	6.10	0.79
B - Dates	4	1503 (5984)	1	4	8.60	15.00	11.65	2.65
B - Dates	4		5	4	7.50	11.00	9.13	1.45
B - Dates	5	1491 (7475)	1	4	13.00	23.00	16.75	4.35
B - Dates	5		2	4	7.50	19.00	13.88	5.54
B - Dates	5		5	4	5.50	16.00	8.85	4.88
B - Dates	5		8	6	1.05	8.00	3.69	2.93
B - Dates	5		15	4	1.05	1.05	1.05	0.00
B - Dried Plums	1	1575	1	4	1.05	1.05	1.05	0.00
B - Dried Plums	2	1504	1	5	1.05	1.05	1.05	0.00
B - Dried Plums	3	1516	1	5	1.05	2.10	1.47	0.58
B - Dried Plums	4	1521	1	4	1.05	1.05	1.05	0.00
B - Figs	1	1462	1	4	33.00	41.00	37.00	4.08
B - Figs	2	1498 (2960)	1	4	11.00	15.00	13.00	1.63
B - Figs	2		2	4	2.10	9.30	5.58	4.02
B - Figs	2		5	2	4.50	5.60	5.05	0.78
B - Pecans	1	1533	1	4	2224.00	2688.00	2407.50	199.71
B - Pecans	1		5	4	99.00	105.00	102.75	2.63
B - Pecans	1		15	4	15.00	20.00	16.50	2.38
B - Pecans	2	1452 (2985)	1	3	4146.00	5532.00	4906.00	702.65
B - Pecans	2		15	4	12.00	16.00	13.75	1.71
B - Pecans	3	1510 (4495)	1	4	4276.00	6030.00	4950.50	842.09
B - Pecans	3		2	4	1304.00	3915.00	2564.00	1187.76
B - Pecans	3		5	4	199.00	261.00	228.50	27.50
B - Pecans	3		8	4	57.00	69.00	62.75	6.65
B - Pecans	3		15	4	1.05	1.05	1.05	0.00
B - Pistachios	1	1517	1	4	252.00	303.00	277.25	22.37
B - Pistachios	1		5	4	18.00	29.00	23.25	4.57
B - Pistachios	2	1507 (3024)	1	4	51.00	70.00	63.25	8.73
B - Pistachios	2		5	4	1.05	1.05	1.05	0.00
B - Pistachios	3	1506 (4530)	1	4	35.00	56.00	44.75	10.81
B - Pistachios	3		2	4	8.10	16.00	12.25	3.85
B - Pistachios	3		5	4	1.05	1.05	1.05	0.00
C - Almond	1	218	1	4	12.00	20.00	15.50	4.12
C - Almond	1		2	4	1.05	8.80	4.56	3.62
C - Almond	1		4	4	1.05	1.05	1.05	0.00
C - Pecans	1	206	1	4	1095.00	1306.00	1182.50	91.03
C - Pecans	1		2	4	369.00	462.00	419.75	46.35
C - Pecans	1		5	4	39.00	55.00	48.00	6.83
C - Pecans	1		8	5	4.50	7.20	5.64	1.04
C - Pecans	1		15	4	1.05	1.05	1.05	0.00
C - Pistachios	1	202	1	5	13.00	26.00	18.20	5.36
C - Pistachios	1		2	4	1.05	1.05	1.05	0.00
C - Walnuts	1	183	1	4	569.00	640.00	602.50	30.09

Table 4. Summary of Residue Data from Crop Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Fumigation Rate, mg·hr/L (cumulative rate)	Aeration Time, days	Residue Levels*				
				n	Min.	Max.	Mean	Std. Dev.
C - Walnuts	1		2	4	290.00	425.00	362.00	57.17
C - Walnuts	1		5	4	90.00	101.00	94.50	4.80
C - Walnuts	1		8	4	24.00	29.00	26.75	2.63
C - Walnuts	1		15	4	1.05	1.05	1.05	0.00
Fluoride Anion (ppm)								
A - Almond	1	203	2	4	3.20	3.77	3.42	0.26
A - Dates	1	208	6	4	0.70	0.70	0.70	0.00
A - Dried Plums	1	219	1	4	0.70	0.70	0.70	0.00
A - Figs	1	197	1	5	0.70	0.70	0.70	0.00
A - Pecans	1	199	8	4	0.70	1.20	0.95	0.29
A - Pistachios	1	214	5	4	1.20	2.91	1.63	0.86
A - Raisins	1	221	5	5	0.70	0.70	0.70	0.00
A - Walnuts	1	217	9	4	0.70	0.70	0.70	0.00
B - Almond	1	1534	1	4	4.07	5.96	4.66	0.89
B - Almond	2	1538 (3072)	5	4	6.65	7.97	7.37	0.68
B - Almond	3	1488 (4560)	15	4	9.07	9.90	9.51	0.37
B - Dates	1	1484	4	4	0.70	0.70	0.70	0.00
B - Dates	2	1504 (2988)	5	4	0.70	1.20	0.95	0.29
B - Dates	3	1493 (4481)	5	4	1.20	1.20	1.20	0.00
B - Dates	4	1503 (5984)	4	4	0.70	2.74	1.46	0.89
B - Dates	5	1491 (7475)	15	4	1.20	3.09	1.67	0.95
B - Dried Plums	1	1575	2	4	0.70	0.70	0.70	0.00
B - Dried Plums	2	1504 (3079)	2	4	0.70	1.20	1.08	0.25
B - Dried Plums	3	1516 (4595)	4	4	0.70	2.56	1.42	0.80
B - Dried Plums	4	1521 (6116)	5	4	1.20	3.14	1.69	0.97
B - Figs	1	1462	6	4	1.20	1.20	1.20	0.00
B - Figs	2	1498 (2960)	5	4	0.70	2.43	1.26	0.82
B - Pecans	1	1533	13	4	7.72	9.59	8.57	0.79
B - Pecans	2	1452 (2985)	13	4	13.80	17.40	15.45	1.50
B - Pecans	3	1510 (4495)	16	4	19.80	21.80	20.83	1.02
B - Pistachios	1	1517	7	4	3.58	4.56	4.10	0.42
B - Pistachios	2	1507 (3024)	6	4	9.98	12.60	11.05	1.11
B - Pistachios	3	1506	5	4	13.20	17.90	15.70	2.05

Table 4. Summary of Residue Data from Crop Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Fumigation Rate, mg·hr/L (cumulative rate)	Aeration Time, days	Residue Levels*				
				n	Min.	Max.	Mean	Std. Dev.
		(4530)						
C - Almond	1	218	7	4	0.70	0.70	0.70	0.00
C - Pecans	1	206	16	4	0.70	1.20	1.08	0.25
C - Pistachios	1	202	3	4	0.70	1.20	0.83	0.25
C - Walnuts	1	183	15	4	0.70	1.20	0.83	0.25

*Note that residues are expressed as ppb for sulfuryl fluoride and ppm for fluoride anion. For purposes of calculating the summary statistics, ½ LOD or ½ LOQ values were used as follows: sulfuryl fluoride ½ LOD = 1.05 ppb, ½ LOQ = 2.1 ppb; fluoride anion ½ LOD = 0.7 ppm, ½ LOQ = 1.2 ppm.

Supervised post harvest fumigation trials were conducted with walnuts, pistachios, pecans, almonds, dates, figs, dried plums, and raisins. Single fumigations were carried out at normal atmospheric pressure or under vacuum conditions at rates of approximately 200 mg•hr/L. Additionally, multiple fumigations (2-5) were conducted, each at approximately 1500 mg•hr/L. For each treatment/crop combination, 2 replicate fumigations were made and 2-3 samples were collected from each replicate. The trials monitored residues of sulfuryl fluoride and fluoride anion, as well as the time required for sulfuryl fluoride residues to dissipate to < LOQ (4.2 ng/g). Sulfuryl fluoride residues were analyzed using a head space method; fluoride anion was analyzed using a fluoride selective-ion electrode and a double-known-addition technique. Residue levels of sulfuryl fluoride varied based on the commodity and the treatment regime. For most commodities, residues had dissipated to <2.1 ppb within 6 days of aeration (1.5 chamber volumes/min) following fumigation. Sulfuryl fluoride residues were more persistent in commodities with higher oil content (e.g, walnuts, pecans, almonds), typically requiring closer to 14 days for residues to dissipate to <2.1 ppb. At the same fumigation rate, residues of sulfuryl fluoride were greater following vacuum fumigation versus treatment at ambient pressure. In oily commodities, multiple fumigations resulted in higher residues of sulfuryl fluoride at a given aeration time. Pooled across all of the variables addressed in this study, sulfuryl fluoride residues ranged from <2.1 ppb to 6030 ppb (6.03 ppm). Residue levels of fluoride were measured only after residues of sulfuryl fluoride had dissipated to below detectable levels; therefore, the effect of aeration time on fluoride levels cannot be assessed from these data. Generally, fluoride residues appear to be more dependent on the number of fumigations than on the treatment rate, treatment pressure, or commodity. Overall, fluoride residue levels ranged from <1.4 ppm to 21.8 ppm.

Conclusions. Significant data gaps are associated with these studies. The majority of the maximum fluoride residue levels were found in samples from the grain mill fumigations. Replication within those studies was low and there is a fairly high degree of variation in the residue results. Furthermore, laboratory studies show that fluoride levels accumulate with successive fumigations and the grain mill samples were subjected to only one fumigation. HED is requesting that the petitioner conduct fumigations in at least 3 different grain mills. The studies should include raw and processed commodities of wheat, rice, sorghum, and corn, including corn oil, and both sulfuryl fluoride and fluoride anion should be included in the analyses.

Despite these deficiencies, the submitted residue data are considered sufficient for granting a conditional registration for sulfuryl fluoride and for establishing sulfuryl fluoride and fluoride anion tolerances. Provided the label is changed such that (1) the total fumigation rate does not exceed 1500 mg·hr/L under ambient conditions or 200 mg·hr/L under reduced pressure conditions, and (2) corn oil must be removed from the premises prior to fumigation, the submitted data are sufficient to set sulfuryl fluoride and fluoride anion tolerances for stored cereal grain commodities, dried fruits, and tree nuts.

To determine appropriate tolerance levels for fluoride in/on wheat and corn commodities, HED has taken the maximum fluoride residue resulting from a single fumigation of between ~1000 and ~1800 mg·hr/L from the appropriately pooled data. The resulting residue level was then corrected for fumigation rate when the maximum residue occurred at a rate below 1500 mg·hr/L. Based on the available data, HED believes that tolerance levels shown in Table 5 are appropriate.

860.1520 Processed Food and Feed

DER: M. Doherty, 1/13/04, MRID 45396301 (45396301.de1.wpd)

As part of a study examining the effects of various fumigation parameters on the residue levels of sulfuryl fluoride and fluoride anion in cereal grains, the petitioner included a processing study describing levels of fluoride anion in commodities obtained from the processing of treated wheat and corn grain.

Wheat and corn grain were fumigated under controlled conditions at a rate of 1500 mg·hr/L. Following a 24-hour aeration period, the grain samples were analyzed for fluoride anion levels and shipped to Texas A&M University for processing. Wheat bran and wheat germ showed concentration factors of 2.56X and 4.82X, respectively. Fluoride anion residues in other processed wheat commodities were less than or equal to those in the whole grain. Of the corn commodities, only aspirated grain fractions ("impurities") showed a concentration (5.49X) of fluoride residues. The processed cereal grain commodities were produced using simulated commercial practices.

Conclusions. The submitted data indicate that fluoride anion residues concentrate in wheat bran, wheat germ, and corn aspirated grain fractions, and that tolerances separate from those of the unprocessed grains may be appropriate for those commodities. For wheat bran and wheat germ, the tolerances derived from the direct fumigation of those commodities are sufficient to cover residue increases that result from the processing of treated grain. HED is recommending a tolerance for corn, aspirated grain fractions of 55 ppm based on the ~5.5X processing factor and the corn grain tolerance of 10 ppm. HED has used the tolerance value rather than the highest average residue as the basis for the recommended tolerance due to uncertainties in the dataset. Based on the available data, tolerances based on direct-treatment are sufficient to cover residue increases that may result from the processing of treated whole grains.

860.1850 Confined Accumulation in Rotational Crops

DER: None

The requested uses for sulfuryl fluoride are for post-harvest fumigation. There are no rotational crop issues associated with that use pattern and a discussion of the 860.1850 guideline is not germane to this petition.

860.1900 Field Accumulation in Rotational Crops

DER: None

The requested uses for sulfuryl fluoride are for post-harvest fumigation. There are no rotational crop issues associate with that use pattern and a discussion of the 860.1900 guideline is not germane to this petition.

860.1550 Proposed Tolerances

Due to the simplicity of the sulfuryl fluoride molecule and its breakdown products, the Metabolism Assessment Review Committee has not been consulted in determining the residues of concern for this chemical. Tolerances have been proposed for both sulfuryl fluoride and fluoride anion. These are the residues of toxicological concern. Temporary tolerances have been established under 40 CFR 180.575 (sulfuryl fluoride) and 180.145 (fluoride anion) in order to support an experimental use permit for sulfuryl fluoride fumigation of walnuts and raisins. The petitioner has requested that 40 CFR parts 180.575 and 180.145 be amended as indicated in Table 5. In many cases, HED has recommended higher tolerances than those proposed by the petitioner. HED's tolerance recommendations are also in Table 5. There are no international harmonization issues associated with this petition.

Table 5. Tolerance Summary for Sulfuryl Fluoride			
Commodity	Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments (correct commodity definition)
Sulfuryl Fluoride			
Barley, bran	None	0.05	Translated from wheat, flour
Barley, flour	None	0.05	Translated from wheat, flour
Barley, grain	0.01	0.10	Translated from wheat, grain
Barley, pearled	None	0.05	Translated from wheat, flour
Corn, aspirated grain fractions	None	0.05	Translated from wheat, flour
Corn, field, flour	0.01	0.01	–
Corn, field, grain	0.04	0.05	–
Corn, field, grits	0.01	15.0	–
Corn, field, meal	0.01	0.01	–
Corn, field, refined oil	9	None	Recommend use restriction on corn, oil.
Corn, pop, grain	0.04	0.05	–
Millet, grain	0.05	0.10	Translated from wheat, grain
Oat, flour	0.08	0.05	Translated from wheat, flour
Oat, grain	0.01	0.10	Translated from wheat, grain
Oat, rolled	0.08	0.10	Translated from wheat, grain
Rice, bran	0.01	0.01	–
Rice, brown	0.01	None	Covered by rice, grain
Rice, grain	0.04	0.05	–
Rice, hulls	0.08	0.10	–
Rice, polished	0.01	0.01	–
Rice, wild, grain	0.05	0.05	–
Sorghum, grain	0.05	0.10	Translated from wheat, grain
Triticale, grain	0.05	0.10	Translated from wheat, grain
Wheat, bran	0.01	0.05	Translated from wheat, flour
Wheat, flour	0.03	0.05	–
Wheat, germ	0.01	0.02	–
Wheat, grain	0.05	0.10	–
Wheat, milled by-products	0.01	0.05	Translated from wheat, flour
Wheat, shorts	0.01	0.05	Translated from wheat, flour
Nut, tree, group 14	6	3.0	–

Commodity	Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments (correct commodity definition)
Fruit, dried	—	0.05	A dried fruit group tolerance was not proposed. Tolerances for "fruit, dried" should be proposed and the individual listings omitted.
Dates	0.03	See Fruit, dried	–
Figs	0.05	See Fruit, dried	–
Plums, dried	0.01	See Fruit, dried	–
Raisins	0.01	See Fruit, dried	–
All other dried fruits	0.05	See Fruit, dried	–
Fluoride			
Barley, bran	98	45.0	–
Barley, flour	98	45.0	–
Barley, grain	10	15.0	–
Barley, pearled	98	45.0	–
Corn, aspirated grain fractions	98	55.0	–
Corn, field, flour	26	35.0	Translated from 24 ppm at 1012 mg·hr/L
Corn, field, grain	7	10.0	–
Corn, field, grits	10	10.0	–
Corn, field, meal	28	30.0	Translated from 21 ppm at 1012 mg·hr/L
Corn, field, refined oil	3	None	Recommend use restriction on corn, oil.
Corn, pop, grain	7	10.0	–
Millet, grain	24	40.0	–
Oat, flour	98	75.0	–
Oat, grain	17	25.0	–
Oat, rolled	98	75.0	–
Rice, bran	31	30.0	Translated from 11.8 ppm at 1012 mg·hr/L
Rice, brown	14	20.0	–
Rice, grain	10	12.0	–
Rice, hulls	35	35.0	–
Rice, polished	18	25.0	–
Rice, wild, grain	24	12.0	–
Sorghum, grain	24	40.0	–
Triticale, grain	24	40.0	–
Wheat, bran	40	40.0	–
Wheat, flour	10	125.0	–

Commodity	Proposed Tolerance (ppm)	Recommended Tolerance (ppm)	Comments (correct commodity definition)
Wheat, germ	98	130.0	Translated from 89.7 ppm at 1012 mg·hr/L
Wheat, grain	25	40.0	–
Wheat, milled by-products	98	130.0	Translated from wheat, germ
Wheat, shorts	38	40.0	–
Nut, tree, group 14	30	10.0	–
Fruit, dried, except grape, raisins	—	3.0	A dried fruit group tolerance was not proposed. Tolerances for "fruit, dried" should be proposed and the individual listings omitted.
Dates	5	See Fruit, dried	–
Figs	5	See Fruit, dried	–
Plums, dried	5	See Fruit, dried	–
Raisins	5	7.0	**Grape, raisin** - This tolerance is higher than other dried fruits because of the potential for fluoride residues from cryolite on this commodity.
All other dried fruits	5	See Fruit, dried	–

cc: M. Doherty, RAB2 Reading File

Sulfuryl Fluoride/078003
DACO 7.2.1, 7.2.2, and 7.2.3/OPPTS 860.1340/OECD IIA 4.2.5, 4.2.6 and 4.3
Residue Analytical Method – Sulfuryl Fluoride in Cereal Grains

Primary Evaluator — Michael A. Doherty, Ph.D. — Date: 1/13/04
Chemist
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Peer Reviewer — William Drew — Date:
Chemist
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Approved by — R. Loranger — Date: 1/16/04
Richard A. Loranger, Ph.D.
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STUDY REPORTS:

45632902. Davis, B. (03/05/02) Independent Laboratory Validation of Dow AgroSciences LLC Method "Determination of Residues of Sulfuryl Fluoride in Corn, Wheat and Rice Commodities by Gas Chromatography with Electron Capture Detection," as included in Lab Report Code: 011057, Appendix B, "Magnitude of the Terminal Fluoride Ion Level in Cereal Grain Commodities Fumigated with Sulfuryl Fluoride": Lab Project Number: 010114. Unpublished study prepared by Dow AgroSciences LLC. 72 pages.

EXECUTIVE SUMMARY:

The proposed method utilizes headspace analysis to quantitate residues of sulfuryl fluoride in whole cereal grains as well as processed products. Residues of sulfuryl fluoride are extracted from the grain commodities with water in an air-tight blender. The samples are agitated in the blender for five minutes to transfer residues of the highly volatile sulfuryl fluoride from the grain commodity to the headspace above the sample. The headspace is then analyzed for residues of sulfuryl fluoride by injecting an aliquot into a gas chromatograph with electron-capture detection (GC/ECD). The method has been validated using fortification/recovery experiments on wheat, corn, and rice commodities. Fortification levels ranged from 0.008 to 0.08 ppm (0.2 ppm for wheat). Average recoveries and standard deviations were 88 ± 14% for wheat, 94 ± 16% for corn, and 82 ± 11% for rice. Standard deviations at the 0.008-ppm fortification level ranged from 0.00099 to 0.00129 ppm, resulting in calculated limits of detection and quantification of approximately 0.003 and 0.010 ppm, respectively. There were no apparent residues of sulfuryl fluoride in the control samples. Due to the gaseous nature of sulfuryl fluoride, fortifications were made to the headspace above the commodities and not to the commodities themselves. The method has not been radiovalidated and it is unclear if the method will successfully extract weathered residues. The method has not been shown to be specific to sulfuryl fluoride. It is likely that the method would extract and detect other volatile halogenated

compounds (e.g., methyl bromide).

The method underwent an independent laboratory validation. After a considerable amount of consultation between the confirming laboratory and Dow AgroSciences, the laboratory was able to successfully validate the method for wheat grain (average recovery = 104 ± 10%) and wheat flour (94 ± 10%). Other cereal grain commodities were not tested.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the method data are classified as scientifically acceptable. HED notes that although control samples of corn oil were analyzed, the method was not validated for corn oil. Due to the physicochemical properties of sulfuryl fluoride, oily commodities are the most likely to bear residues following fumigation. This method has undergone review by BEAD's Analytical Chemistry Branch, which recommended that radiovalidation be conducted and that OPP accept the method for enforcement purposes.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document (DP Barcode D283007).

COMPLIANCE:

Signed and dated GLP, quality assurance, and data confidentiality information were provided. The only noted deviation was that the GLP status of the sulfuryl fluoride standard is unknown.

A. BACKGROUND INFORMATION

TABLE A.1. Test Compound Nomenclature

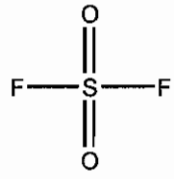
Compound	Chemical Structure
Sulfuryl Fluoride	
Common name	Sulfuryl fluoride
Company experimental name	Sulfuryl fluoride
IUPAC name	
CAS name	
CAS #	002699-79-8
End-use product/EP	Profume; Vikane

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound [Note: add columns as needed]		
Parameter	Value	Reference
Melting point/range	-136°C	Vikane MSDS
pH	Not Provided	
Density	Not Provided	
Water solubility	1.67 g/L	Vikane MSDS
Solvent solubility	Not Provided	
Vapor pressure (10°C)	9150 mm Hg	Vikane MSDS
Dissociation constant (pK_a)	Not Provided	
Octanol/water partition coefficient Log(K_{OW})	Not Provided	
UV/visible absorption spectrum	Not Provided	

B. MATERIALS AND METHODS

B.1. Data-Gathering Method

B.1.1. Principle of the Method:

Because of the volatile nature of sulfuryl fluoride and the headspace analysis technique of this method, the extraction process is carried out in blender jars whose lids have been modified to provide an air-tight seal to the jar and to provide access to the headspace through a standard GC septum.

To validate the method, 25 grams of grain commodity (10 grams in the case of low-density commodities) are transferred to the blender jar. To the jar is added 200 ml of HPLC-grade water. The jar is then sealed with the modified lid. Sulfuryl fluoride stock standard is then injected into the system to fortify the samples and the sample/water mixture is blended for 5 minutes. The sample is then allowed to equilibrate for 5 minutes prior to analysis. Following the equilibration period, an aliquot of the headspace is removed via the GC septum in the lid and injected directly into a gas chromatograph equipped with an electron-capture detector (GC/ECD).

TABLE B.1.1. Summary Parameters for the Analytical Enforcement Method Used for the Quantitation of Sulfuryl Fluoride Residues in Cereal Grains.	
Method ID	GRM 01.12
Analyte(s)	Sulfuryl Fluoride
Extraction solvent/technique	Water/homogenization
Cleanup strategies	None

Instrument/Detector	GC/ECD: Injection Method: Splitless Injection Volume: 100 µL Injector Temp.: 150 °C Column: Varian PLOT - Poraplot Q - 25 m x 0.53 mm (capillary column) Oven Temp.: 70 °C (isothermal) Detector: 63Ni Electron Capture Detector Temp.: 250 °C
Standardization method	External
Stability of std solutions	Not provided in the report. The standard is a gas and should be stable in its original container for an extended period of time. Sulfuryl fluoride is, however, highly reactive and is not expected to remain stable once it is removed from the cylinder.
Retention times	1.13 minutes

B.2. Enforcement Method

The proposed enforcement method is the same as the data gathering method.

C. RESULTS AND DISCUSSION

C.1. Data-Gathering Method

Table C.1.1. Recovery of Sulfuryl Fluoride from Cereal Grain Commodities using the Sulfuryl Fluoride Headspace GC/ECD Method.

Matrix	Sulfuryl Fluoride		
	Fortification Level, ppm	Recoveries, %* (n<70 or >120)	Mean ± SD, % (n)
Wheat commodities	0.008	53 - 153 (10)	90 ± 16 (82)
	0.080	75 - 114 (0)	88 ± 8 (56)
	0.020 (germ only)	65 - 126 (3)	86 ± 14 (22)
	0.20 (germ only)	67 - 92 (1)	79 ± 8 (10)
Corn commodities	0.008	81 - 129 (7)	102 ± 13 (42)
	0.080	58 - 118 (7)	87 ± 15 (54)
Rice commodities	0.008	52 - 105 (5)	81 ± 12 (31)
	0.080	67 - 99 (1)	83 ± 9 (32)

* Due to the number of samples, individual recovery values are not listed. Individual values can be found on pages 22-32 of the method study volume.

Average recovery of sulfuryl fluoride is acceptable at all fortification levels and for all tested matrices. The standard deviations for the recoveries are within acceptable limits. There does not appear to be any significant affect of matrix or fortification level upon recovery. The recovery of sulfuryl fluoride described in the independent laboratory validation is similar to that found during method validation.

Based on the submitted data, it is not possible to ascertain the efficiency of the method.

Neither radiovalidation data nor metabolism studies and their associated methods have been submitted to the Agency. For both the method validation and independent laboratory validation studies, sample headspace was fortified and then sampled. While HED realizes that this experimental design was used due to the nature of sufluryl fluoride, we don't believe that the recovery results from those studies reflect the ability of the method to extract weathered residues.

TABLE C.1.2. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Sulfuryl Fluoride Residues in Cereal Grains.

Analyte	Sulfuryl Fluoride
Equipment ID	Specially constructed air-tight extraction jars. GC/ECD Capillary Column (Poraplot Q - 25 m x 0.53 mm; Varian)
Limit of quantitation (LOQ)	The method has a lower limit of method validation of 0.008 ppm. Based on recovery variability at the 0.008-ppm fortification level, the method has calculated limits of detection and quantification of approximately 0.003 and 0.010 ppm, respectively. The calculated limits are based on 3x and 10x the standard deviation of the method's response at 0.008 ppm.
Limit of detection (LOD)	0.003 ppm (see LOQ, above)
Accuracy/Precision	Recoveries range from 52 - 153%. The extremes in that range occurred at the lower limit of validation (0.008 ppm). Recoveries and variances are more typically acceptable at fortification levels of 0.08 ppm and above.
Reliability of the Method/ [ILV]	An independent laboratory method validation [ILV] was conducted to verify the reliability of the method. The values obtained are indicative that the method is reliable.
Linearity	The example standard curve provided with the submission showed good linearity over the range 0.004 to 0.080 ppm. The coefficient of determination (r2) for the example curve is 0.994 and is based on six injections at each concentration (0.004, 0.008, and 0.080 ppm).
Specificity	There are no peaks at the retention time of interest in control samples; however, an interference study has not been conducted to determine if the method will distinguish the analytes of interest from other agrochemicals that may co-occur in the matrix. Based on the simplicity of the method and lack of any cleanup, it is likely that other volatile, halogenated compounds (e.g., methyl bromide) could interfere with the analysis. It is unknown whether or not the system would provide adequate chromatographic separation between sulfuryl fluoride and any potentially interfering compounds.

C.2. Enforcement Method

The proposed enforcement method is the same as the data gathering method.

C.3. Independent Laboratory Validation

An independent laboratory validation was conducted for this method using wheat grain and wheat flour. The validation was performed by Minnesota Valley Testing Laboratories, Inc. (1126 N. Front Street; New Ulm, MN 56073). There was considerable communication between the validating laboratory and Dow AgroSciences. The communications were by telephone or electronic mail and dealt with a number of troubleshooting issues, including use of specialized

equipment, non-reproducible calibration curves, advice on sample processing and sample integrity, assurance of gas dilution calculations, and a failed wheat grain trial. The validating laboratory suggests that the method be revised to specify side-port needles, since they experienced problems with other needle types becoming clogged with debris. No other revisions were recommended.

Table C.3.1. Recovery of Sulfury Fluoride from Wheat Grain and Wheat Flour using the Sulfuryl Fluoride Headspace GC/ECD Method during the Independent Laboratory Validation.

Matrix	Fortification Level (ppm)	Recoveries (%)	Mean ± SD
Wheat Grain	0.0083	112, 108, 113, 114, 113	112 ± 3
	0.0789	85, 93, 102, 98, 97	95 ± 6
Wheat Flour	0.0083	94, 95, 86, 95, 97	93 ± 4
	0.0789	98, 74, 105, 90, 108	95 ± 13

D. CONCLUSION

Method GRM 01.12 appears to be suitable as a tolerance enforcement method based on fortification recovery data. HED is concerned that the ability of the method to extract weathered fluoride residues has not been demonstrated. BEAD's Analytical Chemistry Branch has reviewed the method and concurs with HED's concern. Their recommendation is that the petitioner radiovalidate the method and that OPP accept the method for tolerance enforcement purposes (D. Wright, D282408, 8/14/2003). HED notes that although control samples of corn oil were analyzed, the method was not validated for corn oil. Due to the physicochemical properties of sulfuryl fluoride, oily commodities are the most likely to bear residues following fumigation and we recommend that the method be validated using corn oil.

E. REFERENCES

Method Review – PP#1F6312. Sulfuryl Fluoride in/on Cereal Grain Commodities. Request for Tolerance Method Validation. DP Barcode: D282408. D. Wright, Jr. 8/14/2003.

F. DOCUMENT TRACKING

RDI: MADoherty (12/9/03); WDrew (10/28/03); RALoranger (10/27/03)
Petition Number(s): PP#1F06312
DP Barcode(s):
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Sulfuryl Fluoride/078003
DACO 7.2.1, 7.2.2, and 7.2.3/OPPTS 860.1340/OECD IIA 4.2.5, 4.2.6 and 4.3
Residue Analytical Method – Fluoride in Cereal Grains

Primary Evaluator	Michael A Doherty Michael A. Doherty, Ph.D. Chemist Registration Action Branch 2, HED (7509C)	Date: 1/13/04
Peer Reviewer	WJ Drew William Drew Chemist Registration Action Branch 2, HED (7509C)	Date:
Approved by	R. Loranger Richard A. Loranger, Ph.D. Branch Senior Scientist Registration Action Branch 2, HED (7509C)	Date: 1/16/04

STUDY REPORTS:

45603901. Davis, B. (02/07/02) Independent Laboratory Validation of Dow AgroSciences LLC Method "Residue Method Validation for the Determination of Fluoride Anion in Corn, Wheat, Corn Oil and Flour," as included in Lab Report Code: 011057, Appendix A, "Magnitude of the Terminal Fluoride Ion Level in Cereal Grain Commodities Fumigated with Sulfuryl Fluoride." Lab Project Number: 010115. Unpublished study prepared by Dow AgroSciences LLC. 63 pages.

45632901. Lala, M. and Randolph, R. (03/12/02) Independent Laboratory Validation for Corn Oil and Raisins using Dow AgroSciences Method GRM 01.17–"Determination of Fluoride Anion in Corn, Wheat, Corn Oil and Flour." Lab Project Number: 1404. Unpublished study prepared by Dow AgroSciences LLC. 65 pages.

EXECUTIVE SUMMARY:

The petitioner, Dow AgroSciences, has proposed an analytical method for the enforcement of fluoride tolerances in cereal grain commodities. The method consists of homogenizing and shaking the sample in the presence of water and total ionic strength adjusting buffer, centrifuging the sample, and analyzing an aliquot of the supernatant with a fluoride-selective electrode. Quantitation of fluoride residues is achieved using a double known addition technique.

The method was validated by the petitioner using whole grain wheat, whole grain corn, wheat flour, and corn oil. Two independent laboratory validations were performed using whole grain wheat and wheat flour, and corn oil and raisins. Recovery of fluoride was comparable across all tested commodities and between the petitioner validations and the independent laboratory validations. Generally, recovery of fluoride fell within the acceptable range of 70-

120% after values were corrected for background levels of fluoride in control samples. Initial laboratory validation experiments showed limits of detection (LOD) and quantification (LOQ) of approximately 0.2 and 0.5 ppm, respectively. During the independent laboratory validation, the LOQ was increased to 2.0 ppm.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the analytical method data are classified as scientifically acceptable. The ability of the method to extract weathered residues has not been demonstrated and HED questions the corn oil validations due to the fortification procedures. The method has been evaluated by OPP Analytical Chemistry Branch (ACB). The ACB concurred with HED's concerns about the fortification procedure, but could not recommend an alternate fortification method. The ACB recommended that the method be validated with respect to weathered residues and that the method be accepted for enforcement purposes.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP Barcode D283007.

COMPLIANCE:

Signed and dated GLP, quality assurance, and data confidentiality information were provided for both volumes. The only noted deviation was that the GLP status of the sodium fluoride standard is unknown.

A. BACKGROUND INFORMATION

Sulfuryl fluoride is a fumigant pesticide being proposed as a methyl bromide replacement for control of insect pests in a number of scenarios. It breaks down to form sulfate and fluoride anion. This document addresses fluoride anion only.

TABLE A.1. Test Compound Nomenclature

Compound	F^-
Common name	Fluoride
Company experimental name	-none-
IUPAC name	Fluoride
CAS name	Fluoride
CAS #	16984-48-8
End-use product/EP	Profume

TABLE A.2. Physicochemical Properties of Fluoride

Parameter	Value	Reference
Melting point/range	No physical/chemical properties were provided for ionic fluoride.	
pH		

TABLE A.2. Physicochemical Properties of Fluoride		
Parameter	Value	Reference
Density		
Water solubility (__°C)		
Solvent solubility (mg/L at __°C)		
Vapour pressure at __°C		
Dissociation constant (pK_a)		
Octanol/water partition coefficient Log(K_{OW})		
UV/visible absorption spectrum		

B. MATERIALS AND METHODS

B.1. Data-Gathering Method

B.1.1. Principle of the Method:

Samples of commodity are homogenized and shaken in the presence of water and total ionic strengh adjusting buffer (TISAB). Following centrifugation, the extract is analyzed for fluoride ion using a fluoride-selective electrode. Residues are quantified using the double known addition (DKA) technique. To validate the method, control samples of whole grain wheat, whole grain corn, wheat flour, and corn oil were fortified with fluoride (as sodium fluoride dissolved in water) to concentrations of 0.5, 2, 5, 20, or 50 ppm. Details regarding equilibration times or conditions were not provided in the submission.

TABLE B.1.1. Summary Parameters for the Analytical Method Used for the Quantitation of fluoride Residues in cereal grains.	
Method ID	GRM 01.17
Analyte(s)	Fluoride anion
Extraction solvent/technique	Water
Cleanup strategies	Centrifugation
Instrument/Detector	Fluoride-selective electrode
Standardization method	Double known addition
Stability of std solutions	Details not provided. Standards are sodium fluoride prepared in ultra-pure water. Standards are presumed to be stable.
Retention times	Not applicable

B.2. Enforcement Method

The proposed enforcement method is the same as the data gathering method.

C. RESULTS AND DISCUSSION

C.1. Data-Gathering Method

Table C.1.1. Recovery of Fluoride Anion from Cereal Grain Commodities and Raisins			
Matrix (Background F^- concentration)	Fluoride Anion		
	Fortification Level (ppm)	Recoveries (%)*	Mean ± SD
Whole Grain Wheat (0.260 ppm)	0.5	80, 68, 66, 90, 68, 88, 93	79 ± 11
	2	98, 99, 93	97 ± 3
	5	94, 85, 91	90 ± 4
	50	74, 85, 70	76 ± 8
Whole Grain Corn (0.182 ppm)	0.5	102, 95, 97, 101, 104, 121, 94	102 ± 9
	2	101, 99, 105	102 ± 3
	5	103, 98, 106	102 ± 4
	50	93, 101, 101	98 ± 4
Wheat Flour (0.116 ppm)	0.5	93, 97, 101, 102, 106, 91, 106	99 ± 6
	2	100, 96, 106	101 ± 5
	5	99, 97, 102	99 ± 2
	50	90, 103, 96	96 ± 7
Corn Oil (0.105; 0.0392 for samples marked †)	0.5	100, 85, 104, 118, 107, 101, 116	104 ± 11
	2	123, 120, 120, 102†, 103†, 103†	112 ± 12
	5	110, 119, 100†, 95†, 99†	105 ± 10
	50	116, 114, 127	119 ± 7

*Recovery values are corrected for background levels of fluoride anion.

Neither radiovalidation of this method nor metabolism data for sulfuryl fluoride have been submitted to the Agency. Therefore, HED cannot ascertain the efficiency of the method for extracting weathered residues of fluoride ion from the cereal grain commodities. HED does not believe that the recovery experiments involving corn oil are valid. Corn oil was fortified with fluoride dissolved in water. Because of the imiscibility of water and oil, HED does not believe that fluoride residues were transferred to the oil prior to extraction. It is likely that the fortification solution remained separated from the oil and then combined with the aqueous extraction solvent during the extraction process.

HED was initially concerned with the possibility of interference from other ions in the extraction solution. In the manual for the fluoride electrode used in the validation studies, the manufacturer (Thermo Orion) states, "Most cations and anions do not interfere with the response of the fluoride electrode to fluoride. Anions commonly associated with fluoride, such as Cl^-, Br^-, I^-, SO_4^{2-}, HCO_3^-, PO_4^{3-}, and acetate, do not interfere with electrode operation. The OH^- ion is an electrode interference." Part of the function of the TISAB is to buffer the pH, so variations in OH^- concentration should not interfere with accurate sample analysis. The selectivity of the electrode in combination with the use of the TISAB allays our concerns about interferences. The method cannot distinguish whether or not measured fluoride residues are a result of fumigations with sulfuryl fluoride.

TABLE C.1.2. Characteristics for the Data-Gathering Analytical Method Used for the Quantitation of Fluoride Anion Residues in Cereal Grain Commodities.	
Analyte	Fluoride anion
Equipment ID	Fluoride-selective electrode (Orion)
Limit of quantitation (LOQ)	2.0 ppm (Note: Original method validation indicated an LOQ of 0.5 ppm; however, it was raised to 2 ppm based on the independent laboratory validation)
Limit of detection (LOD)	0.2 ppm
Accuracy/Precision	The reported recoveries and variability obtained during method development validation and independent laboratory validation are comparable and generally acceptable. A few recovery values fell outside the 70 - 120% range recommended in the guidelines.
Reliability of the Method/ [ILV]	An independent laboratory method validation [ILV] was conducted to verify the reliability of method No. GRM001.17 for the determination of fluoride residues in cereal grain commodities. The values obtained are indicative that the method is reliable.
Linearity	The DKA technique, in essence, produces a standard curve within each sample. The addition of two known amounts of analyte to the sample are used to calibrate the ion-selective electrode meter each time a sample is run. Linearity is not an issue for this method.
Specificity	Interference study data have not been submitted to the Agency. The ion-selective electrode used in the method is selective for fluoride.

C.2. Enforcement Method

The enforcement method is the same as the data-gathering method.

C.3. Independent Laboratory Validation

The ILV was conducted according to guideline specifications. During the course of conducting the validation, the laboratory was not able to reproduce the 0.5-ppm limit of quantitation reported by the petitioner and recommended that the LOQ be increased to 2 ppm.

Table C.3.1. Recovery of Fluoride Anion from Wheat Grain, Wheat Flour, Corn Oil, and Raisins during the Independent Laboratory Validation.

Matrix (Background F^- Concentration)	Fluoride Anion		
	Fortification Level (ppm)	Recoveries (%)*	Mean ± SD
Wheat Grain (2.08)	2	108, 113, 92, 97, 107	104 ± 9
	10	84, 100, 105	97 ± 11
	20	102, 107, 106, 107, 95	103 ± 5
Wheat Flour (0.460)	2	105, 94, 87, 98, 91	95 ± 7
	10	97, 96, 92	95 ± 3
	20	99, 108, 95, 92, 99	98 ± 6
Corn Oil (0.048)	2	101, 104, 101, 90, 97	99 ± 6
	20	101, 106, 99, 99, 98	101 ± 3

Raisins (0.640)	2	92, 81, 90, 87, 102	91 ± 8
	20	85, 83, 90, 87, 90	87 ± 3

*Recovery values are corrected for background levels of fluoride anion.

D. CONCLUSION

Method GRM 01.17 appears to be suitable as a tolerance enforcement method based on fortification recovery data. HED is concerned that the ability of the method to extract weathered fluoride residues has not been demonstrated. BEAD's Analytical Chemistry Branch has reviewed the method and concurs with HED's concern. Their recommendation is that the petitioner validate the method with respect to weathered residues (radiolabeling is not a viable option for F) and that OPP accept the method for tolerance enforcement purposes (D. Wright, D282408, 8/14/2003).

E. REFERENCES

Method Review – PP#1F6312. Sulfuryl Fluoride in/on Cereal Grain Commodities. Request for Tolerance Method Validation. DP Barcode: D282408. D. Wright, Jr. 8/14/2003.

F. DOCUMENT TRACKING

RDI: MADoherty (10/16/03); WDrew (10/28/03); RALoranger (10/27/03)
Petition Number(s): PP#1F06312
DP Barcode(s):
PC Code: 078003

Template Version September 2003

Sulfuryl Fluoride/078003
DACO 7.3/OPPTS 860.1380/OECD IIA 6.1.1 and IIIA 8.1.1
Storage Stability - Fluoride in Cereal Grains, Dried Fruit, and Tree Nuts

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STUDY REPORTS:

45510302. D. R. Foster. (9/21/2001) Storage Stability of Fluoride in Cereal Grain and Flour, Dried Fruit (Raisin), Nuts (Walnuts), and Corn Grain and Meal: Lab Study ID: 010017. Unpublished study prepared by Dow AgroSciences. 45 pages.

EXECUTIVE SUMMARY:

Samples of wheat grain, wheat flour, corn grain, corn meal, raisins, and walnuts were individually homogenized and fortified with an aqueous fluoride solution to a concentration of 20 ppm fluoride. The fortified samples were stored at ambient temperatures for 30 days and then placed into frozen (-20°C) storage for the remainder of the study. On Day 0 and approximately Day 35, Day 75, Day 105, and Day 140 after fortification, the storage stability samples, along with a control sample, a reagent blank, and two daily concurrent recovery samples, were analyzed for fluoride anion. Fluoride residues were extracted using an aqueous solution and analyzed using a fluoride ion selective electrode. The reported LOQ for the method is 0.6 ppm for wheat grain, 0.3 ppm for wheat flour, and 0.5 ppm for corn grain. LOQs for other matrices were not given.

Residues of fluoride anion were stable for the duration of the study (~140 days) in wheat grain, corn grain, corn meal, raisins, and walnuts. In wheat flour, however, fluoride residues exhibited a continual decline throughout the study, with only 55% remaining at 140 days. Regression of the residue data indicates a loss of approximately 0.3% per day. The study design does not permit determination of whether or not the loss reflects dissipation of the fluoride residues or an increase in "bound" residues. This loss should be taken in to account when interpreting the results of residue studies in wheat flour. HED will not assume that fluoride anion is stable in all commodities. Furthermore, HED notes that the residues in the control samples for all matrices indicate a loss of fluoride with time and that this loss appears to be of the

same order of magnitude as that observed in wheat flour. The significance of this trend as it relates to storage stability is unclear at this time.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the storage stability data are classified as scientifically acceptable

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document (DP Barcode D283007).

COMPLIANCE:

The petitioner has provided signed and dated GLP, quality assurance, and data confidentiality information. The only noted deviation to GLP standards is the GLP status of the analysis of the sodium fluoride analytical standard. This deviation is not expected to impact the outcome of this storage stability study.

A. BACKGROUND INFORMATION

Sulfuryl fluoride is a fumigant pesticide being proposed as a methyl bromide replacement for control of insect pests in a number of scenarios. It breaks down to form sulfate and fluoride anion. This document addresses fluoride anion only.

TABLE A.1. Test Compound Nomenclature	
Compound	F^-
Common name	Fluoride
Company experimental name	-none-
IUPAC name	Fluoride
CAS name	Fluoride
CAS #	16984-48-8
End-use product/EP	Profume

TABLE A.2. Physicochemical Properties of Fluoride		
Parameter	Value	Reference
Melting point/range	No physical/chemical properties were provided for ionic fluoride.	
pH		
Density		
Water solubility (__ °C)		
Solvent solubility (mg/L at __ °C)		
Vapour pressure at __ °C		
Dissociation constant (pK_a)		
Octanol/water partition coefficient Log(K_{ow})		
UV/visible absorption spectrum		

B. EXPERIMENTAL DESIGN

B.1. Sample Handling and Preparation

Sample Preparation. Samples of wheat grain, corn grain, raisins, and walnuts were homogenized with a hammermill. Wheat flour and corn meal did not undergo any homogenization or other preparation.

Fortification. Ten grams of each matrix were placed into glass jars and fortified using 1 mL of a 200 µg/mL aqueous fluoride solution (salt unspecified).

Storage. Following fortification, samples were stored at room temperature (~ 20 °C) for the first 30 days of the storage stability study. After 30 days, the samples were transferred to frozen storage (approximately -20°C) for the remainder of the study in an effort to retard mold and fungal growth on the samples. Samples were removed from frozen storage for analysis at approximate time points of 35, 75, 105, and 140 days after fortification.

B.2. Analytical Methodology

Residues of fluoride were extracted using 100 mL of HPLC-grade water + ionic strength adjustment buffer with CDTA (1+1; *further details of the extraction solution were not provided*). The samples were shaken (~ 15 minutes), allowed to settle, and then centrifuged (10 minutes, 2000 RPM). For the walnut samples, an aliquot of the extract was further centrifuged and the resulting top layer was removed by aspiration. Residues of fluoride anion were analyzed with a fluoride selective electrode using the double-known-addition (DKA) technique. The reported LOQ for the method is 0.6 ppm for wheat grain, 0.3 ppm for wheat flour, and 0.5 ppm for corn grain. LOQs for other matrices were not given.

C. RESULTS AND DISCUSSION

Samples were analyzed for fluoride residues using the proposed tolerance enforcement method. The ability of the method to extract weathered fluoride residues has not been assessed. It is likely to be adequate for purposes of this study.

With the exception of wheat flour, residues of fluoride appear to be stable in all tested commodities. In wheat flour, fluoride residues declined at a rate of approximately 0.3% per day ($p=0.001$; see Appendix 1). Whether this is an actual loss of fluoride from the sample or an increase in "bound" residues is unclear at this time. Furthermore, HED notes that the residues in the control samples for all matrices indicate a loss of fluoride with time and that this loss appears to be of the same order of magnitude as that observed in wheat flour.

TABLE C.1. Summary of Concurrent Recoveries of Fluoride from Cereal Grains, Tree Nuts, and Dried Fruit.

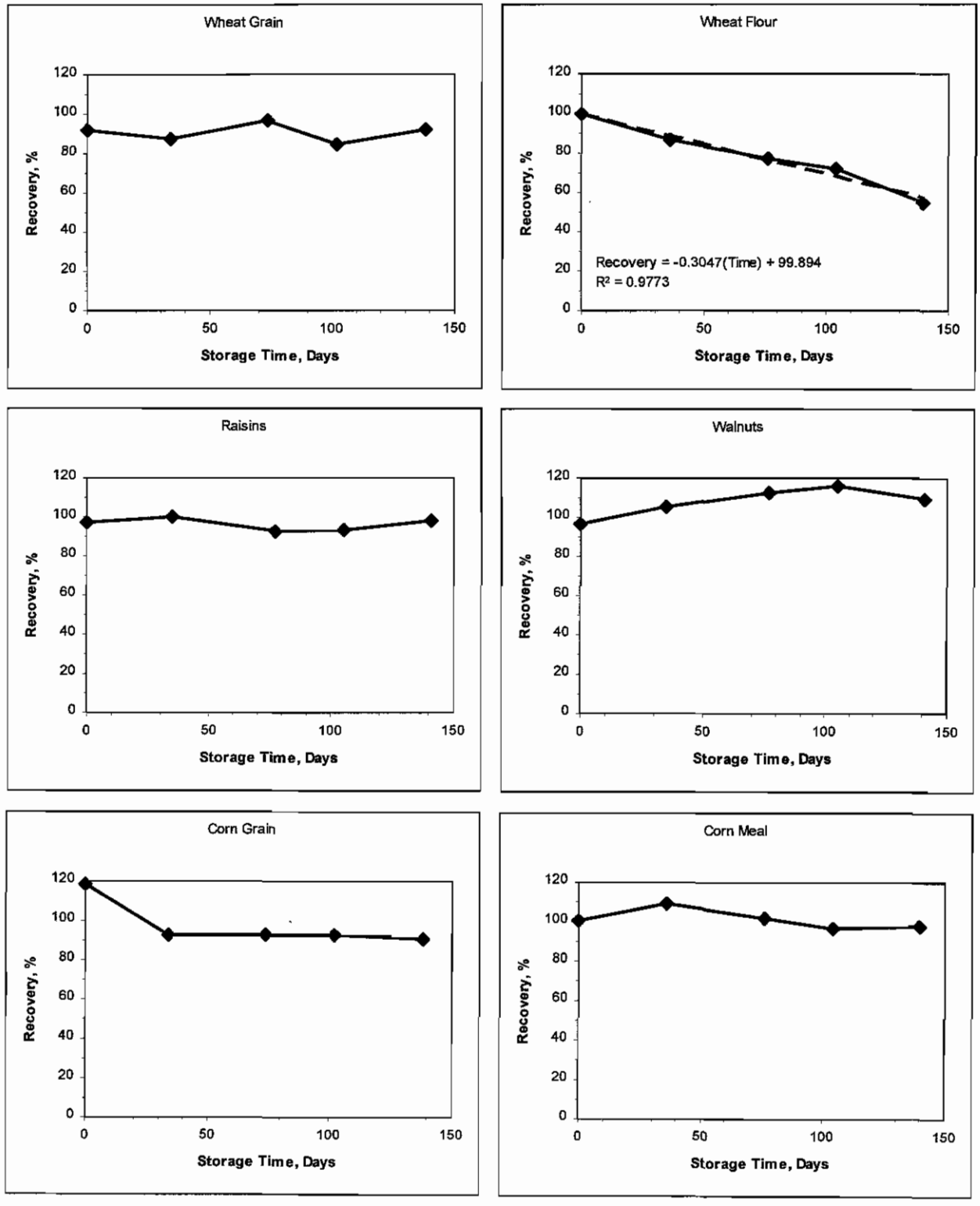
Matrix	Spike level (mg/kg)	Storage Interval (days)	Sample size (n)	Recoveries (%)	Mean ± std dev
See Table C.2.					

Table C.2. Storage Stability of Fluoride Anion in Agricultural Commodities

Commodity	Spike Level (ppm)	Storage Period (days)	Storage Temp. (°C)	Residue in Control (ppm)	Concurrent Recovery (%)	Residue in Stored Sample (ppm)	Corrected Recovery (%)[A]
Wheat Grain	20	0	Ambient	0.994	105	20.6, 20.1	93, 91
		34	-20	0.532	99	19.8, 16.0	97, 78
		74	-20	0.488	97	19.6, 18.8	99, 95
		102	-20	0.278	95	18.2, 15.0	94, 75
		138	-20	0.175	93	17.3, 17.3	92, 92
Wheat Flour	20	0	Ambient	1.180	111	21.9, 24.9	93, 107
		36	-20	0.729	107	20.8, 17.7	94, 80
		76	-20	0.539	108	14.3, 20.2	64, 91
		104	-20	0.306	101	13.2, 16.4	64, 80
		140	-20	0.261	98	11.0, 10.9	55, 54
Raisin	20	0	Ambient	0.984	102	21.2, 20.2	100, 95
		35	-20	0.885	98	20.0, 20.7	98, 102
		77	-20	0.766	104	20.1, 20.0	93, 92
		105	-20	0.592	95	17.9, 18.9	91, 96
		141	-20	0.505	93	18.8, 18.5	99, 97
Walnut	20	0	Ambient	0.685	91	19.2, 17.7	101, 93
		35	-20	0.693	90	19.6, 19.5	106, 105
		77	-20	0.467	93	22.2, 20.5	118, 108
		105	-20	0.227	85	19.8, 20.2	115, 117
		141	-20	0.176	83	18.3, 18.6	109, 110
Corn Grain	20	0	Ambient	0.654	97	25.0, 22.2	126, 112
		34	-20	0.520	105	19.9, 20.0	93, 93
		74	-20	0.417	102	17.4, 21.3	83, 102
		102	-20	0.242	101	18.9, 19.0	92, 93
		138	-20	0.182	97	17.9, 17.5	92, 89
Corn Meal	20	0	Ambient	0.789	109	21.2, 24.0	94, 107
		36	-20	0.542	101	23.1, 22.0	112, 107
		76	-20	0.422	101	20.5, 21.3	100, 104
		104	-20	0.199	101	20.1, 19.6	98, 96
		140	-20	0.167	96	19.0, 19.0	98, 98

[A] Corrected for fluoride residues in controls and for concurrent recovery. Corrected Recovery = [(Measured Residue in Sample - Measured Residue in Control) ÷ 20 ppm] ÷ (Concurrent Recovery ÷ 100) × 100.

FIGURE C.1. Stability of Fluoride in Stored Grain, Dried Fruit, and Tree Nut Commodities.



D. CONCLUSION

The storage stability data for fluoride are acceptable. Based on the behavior of fluoride in stored wheat flour and observance of "dissipation" from control samples, HED will not assume that fluoride is stable in all commodities.

E. REFERENCES

Analytical Methods: DER 45603901

F. DOCUMENT TRACKING

RDI: MADoherty (10/16/03); WDrew (10/28/03); RALoranger (10/27/03)
Petition Number(s): PP1F06312
PC Code: 078003

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Appendix 1. Regression Analysis for Wheat Flour.

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.988583
R Square	0.977296
Adjusted R Square	0.969728
Standard Error	2.954362
Observations	5

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1127.115	1127.115	129.1341	0.001462
Residual	3	26.18477	8.728255		
Total	4	1153.3			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	99.89404	2.321674	43.02674	2.76E-05	92.50543	107.2827
Time, Days	-0.30469	0.026813	-11.3637	0.001462	-0.39002	-0.21936

Sulfuryl Fluoride/078003
DACO 7.4.1/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Sulfuryl Fluoride and Fluoride in Cereal Grains

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Peer Reviewer — Date:
William Drew
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Approved by — Date: 1/16/04
Richard A. Loranger, Ph.D.
Branch Senior Scientist
Registration Action Branch 2, HED (7509C)

STUDY REPORTS:

45396301. Rick, D., Marty, G., Krieger, S. McGuirk, R. (2000) Evaluation of Sulfuryl Fluoride Fumigation Variables on Residue Levels in Crop Commodities: Laboratory Identification Number: 001103. Unpublished study prepared by Dow AgroSciences LLC 108 p.

EXECUTIVE SUMMARY:

Studies were conducted to determine the magnitude of sulfuryl fluoride and fluoride anion residues in/on stored grain commodities following fumigation of the commodities with sulfuryl fluoride. The studies were designed to investigate the effects of temperature (10, 22, or 30 °C), number of fumigations (1-4), fumigation rate (250, 1000, 1500, or 2500 mg•hr/L), fumigation chamber loading (1, 10, 50, or 80% of capacity), and aeration time (1, 4, or 7 days) on sulfuryl fluoride and fluoride anion residues. Residues of sulfuryl fluoride were analyzed using a GC/ECD headspace method. Residues of fluoride anion were analyzed using a fluoride ion selective electrode following the double standard addition technique.

For sulfuryl fluoride, residues were independent of fumigation rate, number of fumigations, temperature, and chamber loading factor. After one day of aeration, residues of sulfuryl fluoride were <LOQ in many commodites and <0.1 ppm in all commodities except corn grits (14.4 ppm maximum) and corn oil (7.8 ppm maximum). Following four days of aeration, residues of sulfuryl fluoride were <LOQ in all matrices except corn oil (2.6 ppm maximum) and wheat grain (0.04 ppm maximum; 10 °C only). Quantifiable residue of sulfuryl fluoride persisted in these two commodities even after 7 days of aeration (wheat grain 10 °C only).

For anionic fluoride, residues were independent of chamber loading and aeration time. Residues vary significantly from one commodity to another, with maximum residues observed in wheat germ and wheat flour. The residue values in these commodities are positively correlated

with the fumigation rate, fumigation temperature, and the number of fumigations. Quantifiable residues of fluoride anion were found in all matrices except corn oil (<0.5 ppm), further demonstrating the stability of parent sulfuryl fluoride in that matrix.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. A large amount of data was submitted to characterize the effects of the fumigation parameters on residue levels. However, within a given set of parameters (i.e., a use pattern), there is very little replication. Pooling data across parameters that do not significantly affect residue levels can be done to increase the number of replicates.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document (DP Barcode D283007).

COMPLIANCE:

Signed and dated GLP, quality assurance, and data confidentiality information were provided. There is no claim of confidentiality and all phases of the study followed Good Laboratory Practice standards.

A. BACKGROUND INFORMATION

TABLE A.1. Test Compound Nomenclature

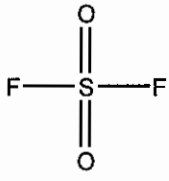
Chemical Structure		F^-
Common name	Sulfuryl fluoride	Fluoride
Company experimental name	Sulfuryl fluoride	-none-
IUPAC name		Fluoride
CAS name		Fluoride
CAS #	002699-79-8	16984-48-8
End-use product/EP	Profume; Vikane	Profume

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound. Properties for fluoride were not available.

Parameter	Value	Reference
Melting point/range	-136°C	Vikane MSDS

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound. Properties for fluoride were not available.

Parameter	Value	Reference
pH	Not Provided	
Density	Not Provided	
Water solubility	1.67 g/L	Vikane MSDS
Solvent solubility	Not Provided	
Vapor pressure (10°C)	9150 mm Hg	Vikane MSDS
Dissociation constant (pK_a)	Not Provided	
Octanol/water partition coefficient Log(K_{OW})	Not Provided	
UV/visible absorption spectrum	Not Provided	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

The fumigations of the grain commodities with sulfuryl fluoride were conducted under laboratory conditions in a series of eight experiments:

Experiment 1- Evaluate the influence of fumigation, sample collection location, and time on fluoride residue levels in the tested commodities. Dosage = 1500 mg•hr/L. Analytes = sulfuryl fluoride and fluoride anion.

Experiment 2- Evaluate the influence of chamber loading on fluoride resiude levels in the tested commodities. Dosage = 1500 mg•hr/L. Chambers loaded to 1, 50, and 80% of chamber capacity. Analyte = fluoride anion.

Experiment 3- Evaluate the influence of dose on commodity residue levels. Dosages = 250 mg•hr/L, 1000 mg•hr/L, and 2500 mg•hr/L. Analytes = sulfuryl fluoride and fluoride anion.

Experiment 4- Evaluate the influence of temperature on commodity residue levels. Dosage = 1500 mg•hr/L. Fumigation temperatures = 10 or 30°C. Analytes = sulfuryl fluoride and fluoride anion.

Experiment 5- Evaluate the influence of repeat fumigations on commodity residue levels. Dosage = 1500 mg•hr/L. 4 fumigations, each at a 7-day interval. Analytes = sulfuryl fluoride and fluoride anion.

Experiment 6- Evaluate the influence of vacuum fumigation on commodity residue levels. Dosage = 1500 mg•hr/L. Each commodity was vacuum-fumigated. Analyte = fluoride anion.

Experiment 7- Evaluate the influence of sulfuryl fluoride concentration and exposure time on commodity fluoride residue levels. Dosage = 1500 mg•hr/L. Analyte = fluoride anion.

Experiment 8- Evaluate the influence of processing on processed commodity residue fluoride levels. Dosage = 1500 mg•hr/L. Analyte = fluoride anion. Data from Experiment 8 are addressed in a separate DER for processed commodities (45396301.de1.wpd).

Table B.1.1. Crop, Fumigation, and Sampling Information

Crop	Matrices	Fumigation[a]				Sampling Procedures			
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L)[b]	Loading Factor (%)	Interval (days)[c]	Location		Number and wt. of samples
							SF	Fluoride	
Experiment 1									
Corn	grain, flour, cornstarch, grits, meal, and oil	22 ± 2.5	1	1500	10	1	Middle	NA	Two, 10-25 g
						4	Middle	Top, Mid, Bottom	
						7[d]	Middle	Middle	
Wheat	grain, bran, flour, shorts, red dog, and germ	22 ± 2.5	1	1500	10	1	Middle	NA	Two, 10-25 g
						4	Middle	Top, Mid, Bottom	
						7[d]	Middle	Middle	
Rice	grain, hulls, polished	22 ± 2.5	1	1500	10	1	Middle	NA	Two, 10-25 g
						4	Middle	Top, Mid, Bottom	
						7[d]	Middle	Middle	
Experiment 2									
Wheat	grain, flour, and germ	22 ± 2.5	1	1500	1	7	NA	Middle	Two, 10-25 g
					50				
					80				
Experiment 3									
Wheat	grain, flour, and germ	22 ± 2.5	1	250	10	1, 4, 7	Middle	Middle[e]	Two, 10-25 g
Wheat	grain, flour, and germ	22 ± 2.5	1	1000	10	1, 4, 7	Middle	Middle[e]	Two, 10-25 g
				2500					
Experiment 4									
Wheat	grain, flour, and germ	10	1	1500	10	1, 4, 7	Middle	Middle[e]	Two, 10-25 g
		30							
Experiment 5									
Wheat	grain, flour, and germ	22 ± 2.5	4[f]	1500	10	1, 4, 7[d]	Middle	Middle[e]	Two, 10-25 g
Experiment 6[g]									
Wheat	grain, flour, and germ	22 ± 2.5	1	1500	10	7	NA	Middle	Two, 10-25 g
Experiment 7									
Wheat	grain, flour, and germ	22 ± 2.5	1	1500	10	7	NA	Middle	Two, 10-25 g

[a] No tank mixes or adjuvants were used.
[b] 1 mg-hr/L = 1 oz-h/1000 cu ft.
[c] After fumigation, all samples were aerated for 24 hours, which is designated Day 1.
[d] Commodities analyzed for sulfuryl fluoride (SF) on day 7 only if SF concentrations in day 4 samples were >LOQ (>8ug/kg).
[e] Fluoride sampled at 7 day interval only.
[f] 7 day interval between fumigations.
[g] Fumigation in experiment 6 was conducted at near-vacuum conditions (~100 mm Hg). Fumigation in all other experiments was conducted at normal atmospheric pressure.

TABLE B.1.2. Trial Numbers and Geographical Locations

NAFTA Growing Region	Crop 1			Crop 2			Crop 3		
	Submitted	Requested		Submitted	Requested		Submitted	Requested	
		Canada	US		Canada	US		Canada	US
Not applicable to a post-harvest use pattern.									

B.2. Sample Handling and Preparation

Following the final fumigation for each of the above-described experiments, the fumigation chambers were aerated with ambient air at approximately 5-10 L/min for 24 hours. The end of the aeration period is designated as Day 1. As rapidly as possible following the aeration period, commodities were analyzed for sulfuryl fluoride for Experiments 1, 3, 4, and 5. Samples were stored at fumigation temperatures and subsequently analyzed for residues of sulfuryl fluoride on Day 4 and Day 7 (if quantifiable residues were found on Day 4). Samples were analyzed for residues of fluoride anion on Day 7 (plus Day 4 for Experiment 1).

B.3. Analytical Methodology

Sulfuryl Fluoride. Residues of sulfuryl fluoride in crop matrices are extracted with water by blending in sealed jars. An aliquot of headspace is removed and immediately injected into a GC equipped with an electron capture detector (ECD). The GC/ECD response is calibrated using an external standard. The reported LOQs for residues of sulfuryl fluoride are 0.008 ppm in/on various grain matrices and 0.02 ppm in/on rice hulls and wheat germ. This method has undergone successful review by the Agency's Analytical Chemistry Branch/BEAD, which has recommended that the method be radiovalidated and that OPP accept the method for tolerance-enforcement purposes.

Fluoride Anion. Residues of fluoride anion in crop matrices are extracted with equal volumes of water and Total Ionic Strength Adjusting Buffer (TISAB) by blending in a homogenizer. A sample of the aqueous layer is removed and centrifuged. A fluoride electrode and a single junction reference electrode are placed in the solution, which is stirred during measurement. During the course of measurement, aliquots of a fluoride standard are added to the solution in two separate steps to complete the double known addition. The reported LOQs for residues of fluoride anion are 0.6 ppm in/on various whole grain matrices, 0.3 ppm in/on corn and wheat flour, cornstarch, corn meal and grits, and rice bran, 0.8 ppm in/on rice hulls and wheat bran, germ, "red dog", and shorts, and 0.5 ppm in/on corn oil. This method has undergone successful review by the Agency's Analytical Chemistry Branch/BEAD, which has recommended that the method be radiovalidated and that OPP accept the method for tolerance-enforcement purposes.

C. RESULTS AND DISCUSSION

There are no recommendations in the OPPTS 860.1500 Guideline pertaining to the number of trials that should be submitted to support post-harvest uses of pesticides. The results from these studies reflect investigations into a number of use-pattern variables and, when taken separately, represent very little replication for a specific use pattern. Pooling data across treatment regimes is appropriate for calculating summary statistics (Tables C.4.1 and C.4.2).

Based on the submitted concurrent recovery data, the analytical method for sulfuryl fluoride is adequate for data collection purposes. The analytical method for fluoride anion regularly produces concurrent recoveries that are highly variable and often well in excess of 100%. Fluoride anion concentrations in untreated samples were below the LOQ for all commodities; therefore, background levels of fluoride do not account for the excessive recoveries of fluoride anion. Despite the high recoveries, the fluoride anion analytical method is adequate for data collection purposes due to the inherent variability of ion-specific electrodes.

Sulfuryl Fluoride. Residues of sulfuryl fluoride in cereal grains appear to be independent of the fumigation dose and chamber loading factor for the doses and factors included in the residue studies. The independence of residues on fumigation dose is likely due to the prevalence of non-quantifiable levels of sulfuryl fluoride in the cereal grains. The independence on loading factor indicates that during the fumigation process, the fumigant was evenly disbursed throughout the fumigation chamber. After one day of aeration, a number of corn, rice, and wheat commodities had quantifiable levels of sulfuryl fluoride (Table 2.3.1). The highest residues were found in corn grits (14.4 ppm) and corn oil (7.8 ppm). Maximum residues in other commodities after one day of aeration were <0.1 ppm. After four days of aeration, residues of sulfuryl fluoride were below the LOQ (0.008 or 0.02 ppm, depending on the commodity) in all tested commodities with the exceptions of corn oil and wheat grain (10 °C only). Quantifiable residue of sulfuryl fluoride persisted in these commodities even after 7 days of aeration (wheat grain from the 10 °C study only).

Fluoride Anion. As with the sulfuryl fluoride residues, residues of fluoride in the cereal grain commodities were independent of fumigation chamber loading. However, fluoride residues are dependent on fumigation dosing level and appear to be positively correlated to fumigation temperature. Residues of fluoride are independent of the aeration time, presumably due to the rapid conversion of labile sulfuryl fluoride residues into stable fluoride anion residues. Fluoride residues are highly dependent on the commodity. The highest residues occurred in wheat flour and germ (Table 2.3.2). The lowest residues were found in corn oil (<0.5 ppm), which further emphasises the stability of parent sulfuryl fluoride in that matrix.

Table C.1. Summary of Concurrent Analytical Method Validation.

Crop Matrix	Fortification Level (ppm)	Recoveries (%)	Mean Recovery ± SD	LOD (ppm)	LOQ (ppm)
Experiment 1 – Sulfuryl Fluoride					
Corn Grain	8.0-80.0	82, 70, 73, 114, 105, 116, 111, 110, 104, 102, 117, 124, 107, 86, 101	101 ± 16	NR	0.008

Crop Matrix	Fortification Level (ppm)	Recoveries (%)	Mean Recovery ± SD	LOD (ppm)	LOQ (ppm)
Corn Flour	8.0-80.0	66, 65, 60, 100, 104, 122, 107, 104, 102, 94, 104, 105, 92, 79, 66	91 ± 19	NR	0.008
Cornstarch	8.0-80.0	91, 90, 82, 82, 85, 88	86 ± 4	NR	0.008
Corn Grits	8.0-80.0	115, 104, 105, 91, 81, 87, 90, 85, 89, 86, 78, 84	91 ± 11	NR	0.008
Corn Oil	8.0-80.0	73, 76, 84, 83, 88, 96, 98, 92, 100, 75, 93, 96	88 ± 9	NR	0.008
Wheat Grain	8.0-80.0	80, 67, 87, 81, 95, 88	83 ± 10	NR	0.008
Wheat Flour	8.0-80.0	97, 90, 95, 87, 84, 86	90 ± 5	NR	0.008
Wheat Bran	8.0-80.0	108, 98, 95, 88, 79, 82	92 ± 11	NR	0.008
Wheat Germ	8.0-80.0	78, 61, 74, 86, 90, 90	80 ± 11	NR	0.02
Wheat Red Dog	8.0-80.0	85, 84, 94, 98, 91, 90	90 ± 5	NR	0.008
Wheat Shorts	8.0-80.0	86, 91, 74, 85, 83, 84	84 ± 6	NR	0.008
Polished Rice	8.0-80.0	100, 104, 89, 93, 97, 90, 84, 66, 61, 72, 76, 89, 91	86 ± 13	NR	0.008
Rice Bran	8.0-80.0	79, 88, 85, 79, 77, 76, 66, 82, 76, 90, 73, 92, 90, 77, 89, 76, 72, 74, 83	80 ± 7	NR	0.008
Experiments 3-5 – Sulfuryl Fluoride					
Wheat Grain	8.0-80.0	146, 111, 96, 96, 82, 115, 94, 84, 91, 96, 91, 89, 84, 109, 102, 88, 82	97 ± 16	NR	0.008
Wheat Flour	8.0-80.0	63, 73, 109, 94, 106, 84, 88, 78, 79, 87, 97, 106, 82, 72, 93, 92, 85, 99	88 ± 13	NR	0.008
Wheat Germ	20.0-200	122, 83, 93, 81, 75, 89, 81, 70, 76, 79, 80, 76, 94, 88, 75, 83	84 ± 12	NR	0.02
Experiment 1 – Fluoride Anion					
Corn Grain	0.5-50	179, 124, 116, 90, 98	121 ± 35	NR	0.6
Corn Flour	0.5-50	183, 139, 103, 76, 114	123 ± 41	NR	0.3
Cornstarch	0.5-50	111, 116, 103, 109	110 ± 5	NR	0.3
Corn Meal	0.5-50	139, 112, 101, 90	110 ± 21	NR	0.3
Corn Grits	0.5-50	136, 106, 91, 99	108 ± 20	NR	0.3
Corn Oil	0.5-50	122, 121, 111, 101, 97	110 ± 11	NR	0.5
Wheat Grain	0.5-50	109, 99, 112, 125	111 ± 11	NR	0.6
Wheat Bran	0.5-50	109, 95, 96	100 ± 8	NR	0.8
Wheat Flour	0.5-50	97, 107, 125	110 ± 13	NR	0.3
Wheat Germ	0.5-50	110, 101, 96	102 ± 7	NR	0.8
Wheat Red Dog	0.5-50	130, 141	136 ± 8	NR	0.8
Wheat Shorts	0.5-50	129, 126, 180	145 ± 30	NR	0.8
Wheat Middlings	0.5-50	129	129	NR	0.8
Wheat Impurities	0.5-50	100	100	NR	0.8
Polished Rice	0.5-50	163, 110	137 ± 37	NR	0.3
Paddy Rice	0.5-50	93, 106	100 ± 9	NR	0.3
Rice Bran	0.5-50	118, 113	116 ± 4	NR	0.3

Crop Matrix	Fortification Level (ppm)	Recoveries (%)	Mean Recovery ± SD	LOD (ppm)	LOQ (ppm)
Rice Hulls	0.5-50	101, 103	102 ± 1	NR	0.8
Experiments 2-7 – Fluoride Anion					
Wheat Grain	2	86, 129, 115, 127, 135, 106, 114, 121, 115, 126, 134, 127, 118, 115, 126, 115	119 ± 12	NR	0.6
Wheat Flour	20	117, 123, 95, 88, 78, 90, 115, 124, 89, 111, 120, 100, 98, 123, 100, 109	105 ± 15	NR	0.3
Wheat Germ	50	121, 124, 90, 129, 78, 75, 101, 104, 86, 124, 113, 109, 108, 98, 106, 101	104 ± 16	NR	0.8

Table C.2. Summary of Storage Conditions			
Matrix	RAC or Extract	Storage Temperature (°C)	Duration (days)
Cereal Grains	RAC	22; 10, 22, and 30 for Experiment 4	8 - 21

Table C.3. Residues of Sulfuryl Fluoride and Fluoride Anion in Cereal Grain Commodities following Post-Harvest Fumigation with Sulfuryl Fluoride.

Crop	Matrix	Fumigation [a]				Sampling Interval (days)	Sulfuryl fluoride Residues (ppm)	Fluoride anion Residues (ppm)
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L) [b]	Loading Factor (%)			
Experiment 1								
Corn	grain	22 ± 2.5	1	1500	10	1	0.0257, 0.020	NA
						4	<0.008, <0.008	2.25, 2.26
						7 [c]	<0.008, <0.008	2.07, 2.13
	flour	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	14.9, 15.4
						7 [c]	<0.008, <0.008	18.9, 19.2
	cornstarch	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	3.82, 5.35
						7 [c]	NA	3.91, 5.30
	meal	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA

Table C.3. Residues of Sulfuryl Fluoride and Fluoride Anion in Cereal Grain Commodities following Post-Harvest Fumigation with Sulfuryl Fluoride.

Crop	Matrix	Fumigation [a]				Sampling Interval (days)	Sulfuryl fluoride Residues (ppm)	Fluoride anion Residues (ppm)
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L) [b]	Loading Factor (%)			
						4	<0.008, <0.008	5.60, 6.30
						7 [c]	NA	5.24, 6.14
	grits	22 ± 2.5	1	1500	10	1	<0.008, 14.4	NA
						4	<0.008, <0.008	9.09, 9.17
						7 [c]	NA	7.74, 8.26
	oil	22 ± 2.5	1	1500	10	1	7.840, 5.848	NA
						4	2.664, 2.511	<0.5, <0.5
						7 [c]	4.384, 3.128	<0.5, <0.5
Wheat	grain	22 ± 2.5	1	1500	10	1	0.009, <0.008	NA
						4	<0.008, <0.008	1.94, 1.92
						7 [c]	NA	1.84, 1.93
	bran	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	36.7, 37.1
						7 [c]	NA	34.0, 36.0
	flour	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	29.9, 29.2
						7 [c]	NA	32.2, 33.5
	shorts	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	35.5, 31.9
						7 [c]	NA	34.8, 34.5
	red dog	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	32.7, 31.7
						7 [c]	NA	33.3, 32.3

Table C.3. Residues of Sulfuryl Fluoride and Fluoride Anion in Cereal Grain Commodities following Post-Harvest Fumigation with Sulfuryl Fluoride.

Crop	Matrix	Fumigation [a]				Sampling Interval (days)	Sulfuryl fluoride Residues (ppm)	Fluoride anion Residues (ppm)
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L) [b]	Loading Factor (%)			
	germ	22 ± 2.5	1	1500	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	56.8, 54.2
						7 [c]	NA	59.0, 52.0
Rice	Paddy rice grain	22 ± 2.5	1	1500	10	1	0.0251, 0.0159	NA
						4	<0.008, <0.008	5.49, 7.80
						7 [c]	NA	5.97, 8.46
	bran	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	28.5, 24.2
						7 [c]	NA	24.6, 26.3
	polished	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	1.47, 1.60
						7 [c]	NA	1.30, 1.40
	hulls	22 ± 2.5	1	1500	10	1	0.0573, 0.0563	NA
						4	<0.008, <0.008	32.8, 23.6
						7 [c]	<0.008, <0.008	30.3, 23.4
Experiment 2								
Wheat	grain	22 ± 2.5	1	1500	1	7	NA	1.95, 2.00
					50			1.78, 1.85
					80			1.47, 1.99
	flour	22 ± 2.5	1	1500	1	7		33.5, 37.8
					50			21.5, 26.4
					80			25.9, 25.7
	germ	22 ± 2.5	1	1500	1	7		43.5, 41.6

Table C.3. Residues of Sulfuryl Fluoride and Fluoride Anion in Cereal Grain Commodities following Post-Harvest Fumigation with Sulfuryl Fluoride.

Crop	Matrix	Fumigation[a]				Sampling Interval (days)	Sulfuryl fluoride Residues (ppm)	Fluoride anion Residues (ppm)
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L)[b]	Loading Factor (%)			
					50			84.1, 83.9
					80			66.3, 73.2
Experiment 3								
Wheat	grain	22 ± 2.5	1	250	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	NA
						7	NA	0.68, 0.65
				1000	10	1	0.00849, <0.008	NA
						4	<0.008, <0.008	NA
						7	NA	1.74, 1.52
				2500	10	1	0.0355, 0.0208	NA
						4	<0.008, <0.008	NA
						7	NA	2.03, 1.85
Wheat	flour	22 ± 2.5	1	250	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	NA
						7	NA	6.88, 7.34
				1000	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	NA
						7	NA	19.3, 21.1
				2500	10	1	0.00825, <0.008	NA
						4	<0.008, <0.008	NA
						7	NA	39.9, 42.8

Table C.3. Residues of Sulfuryl Fluoride and Fluoride Anion in Cereal Grain Commodities following Post-Harvest Fumigation with Sulfuryl Fluoride.

Crop	Matrix	Fumigation [a]				Sampling Interval (days)	Sulfuryl fluoride Residues (ppm)	Fluoride anion Residues (ppm)
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L) [b]	Loading Factor (%)			
Wheat	germ	22 ± 2.5	1	250	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	NA
						7	NA	18.1, 17.1
				1000	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	NA
						7	NA	58.6, 55.3
				2500	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	NA
						7	NA	95.8, 94.2
Experiment 4								
Wheat	grain	10	1	1500	10	1	0.0328, 0.0323	NA
						4	0.0435, 0.0423	NA
						7	0.0210, 0.0192	0.79, 0.91
		30	1	1500	10	1	0.0142, 0.0127	NA
						4	<0.008, <0.008	NA
						7	NA	2.79, 2.96
	flour	10	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	NA
						7	NA	15.7, 14.6
		30	1	1500	10	1	<0.008, <0.008	NA
						4	<0.008, <0.008	NA

Table C.3. Residues of Sulfuryl Fluoride and Fluoride Anion in Cereal Grain Commodities following Post-Harvest Fumigation with Sulfuryl Fluoride.

Crop	Matrix	Fumigation [a]				Sampling Interval (days)	Sulfuryl fluoride Residues (ppm)	Fluoride anion Residues (ppm)
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L) [b]	Loading Factor (%)			
						7	NA	37.8, 33.4
	germ	10	1	1500	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	NA
						7	NA	17.4, 18.6
		30	1	1500	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	NA
						7	NA	72.3, 82.6
Experiment 5								
Wheat	grain	22 ± 2.5	1	1500	10	1	0.0108, 0.0902	NA
						4	<0.008, <0.008	NA
						7 [c]	NA	3.10, 3.94
			2	1500	10	1	0.0953, 0.0860	NA
						4	<0.008, <0.008	NA
						7 [c]	NA	5.02, 5.02
			3	1500	10	1	0.0288, 0.0225	NA
						4	<0.008, <0.008	NA
						7 [c]	NA	6.15, 6.31
			4	1500	10	1	0.0214, 0.0232	NA
						4	<0.008, <0.008	NA
						7 [c]	NA	7.95, 8.00
	flour	22 ± 2.5	1	1500	10	1	<0.008, <0.008	NA

Table C.3. Residues of Sulfuryl Fluoride and Fluoride Anion in Cereal Grain Commodities following Post-Harvest Fumigation with Sulfuryl Fluoride.

Crop	Matrix	Fumigation [a]				Sampling Interval (days)	Sulfuryl fluoride Residues (ppm)	Fluoride anion Residues (ppm)
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L) [b]	Loading Factor (%)			
						4	<0.008, <0.008	NA
						7 [c]	NA	44.7, 34.2
			2	1500	10	1	0.00844, 0.00936	NA
						4	<0.008, <0.008	NA
						7 [c]	NA	62.5, 62.6
			3	1500	10	1	0.00949, 0.008.52	NA
						4	<0.008, 0.00899	NA
						7 [c]	NA	101, 93.7
			4	1500	10	1	0.0129, 0.015.4	NA
						4	0.00837, <0.008	NA
						7 [c]	NA	97.1, 93.2
	germ	22 ± 2.5	1	1500	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	NA
						7 [c]	NA	88.5, 81.9
			2	1500	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	NA
						7 [c]	NA	158, 121
			3	1500	10	1	<0.020, <0.020	NA
						4	<0.020, <0.020	NA
						7 [c]	NA	218, 201
			4	1500	10	1	<0.020, <0.020	NA

Table C.3. Residues of Sulfuryl Fluoride and Fluoride Anion in Cereal Grain Commodities following Post-Harvest Fumigation with Sulfuryl Fluoride.

Crop	Matrix	Fumigation [a]				Sampling Interval (days)	Sulfuryl fluoride Residues (ppm)	Fluoride anion Residues (ppm)
		Temp. (C)	# of appl.	Dose: CT Rate (mg-hr/L) [b]	Loading Factor (%)			
						4	<0.020, <0.020	NA
						7 [c]	NA	235, 222
Experiment 6 [Fumigation in experiment 6 was conducted at near-vacuum conditions (~100 mm HG).]								
Wheat	grain	22 ± 2.5	1	1500	10	7	NA	3.20, 4.08
	flour						NA	33.3, 31.6
	germ						NA	53.7, 54.3
Experiment 7								
Wheat	grain	22 ± 2.5	1	1500	10	7	NA	3.93, 2.91
							NA	2.22, 2.36
	flour	22 ± 2.5	1	1500	10	7	NA	43.4, 39.9
							NA	28.2, 35.3
	germ	22 ± 2.5	1	1500	10	7	NA	104, 90.3
							NA	58.8, 60.1

[a] No tank mixes or adjuvants were used.

[b] 1 mg-hr/L = 1 oz-h/1000 cu ft.

[c] Commodities analyzed for sulfuryl fluoride on Day 7 only if sulfuryl fluoride concentration in Day 4 samples were > LOQ (>0.008 ppm).

Table C.4.1. Summary of Sulfuryl Fluoride Residues in Cereal Grains. Residue data have been pooled across dosage level and loading factor.

Crop	Commodity	Temp. (°C)	Fumigation. No.	Aeration (days)	n	Sulfuryl Fluoride Residues (ppm)			
						Min	Max	Mean	Std Dev
Corn	cornstarch	22	1	1	2	<0.008	<0.008	<0.008	0.000
Corn	flour	22	1	1	2	<0.008	<0.008	<0.008	0.000
Corn	grain	22	1	1	2	<0.020	0.026	0.023	0.004
Corn	grits	22	1	1	2	<0.008	14.400	7.204	10.177
Corn	meal	22	1	1	2	<0.008	<0.008	<0.008	0.000
Corn	oil	22	1	1	2	5.848	7.840	6.844	1.409
Rice	bran	22	1	1	2	<0.008	<0.008	<0.008	0.000
Rice	hulls	22	1	1	2	0.056	0.057	0.057	0.001
Rice	Paddy rice grain	22	1	1	2	0.016	0.025	0.021	0.007
Rice	polished	22	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	bran	22	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	flour	10	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	flour	30	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	flour	22	1	1	10	<0.008	<0.008	<0.008	0.000

Sulfuryl Fluoride/078003
DACO 7.4.1/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Sulfuryl Fluoride and Fluoride in Cereal Grains

Crop	Commodity	Temp. (°C)	Fumigation. No.	Aeration (days)	n	Sulfuryl Fluoride Residues (ppm)			
						Min	Max	Mean	Std Dev
Wheat	flour	22	2	1	2	<0.008	0.009	0.009	0.001
Wheat	flour	22	3	1	2	0.009	0.009	0.009	0.001
Wheat	flour	22	4	1	2	0.013	0.015	0.014	0.002
Wheat	germ	10	1	1	2	<0.020	<0.020	<0.020	0.000
Wheat	germ	30	1	1	2	<0.020	<0.020	<0.020	0.000
Wheat	germ	22	1	1	10	<0.020	<0.020	<0.020	0.000
Wheat	germ	22	2	1	2	<0.020	<0.020	<0.020	0.000
Wheat	germ	22	3	1	2	<0.020	<0.020	<0.020	0.000
Wheat	germ	22	4	1	2	<0.020	<0.020	<0.020	0.000
Wheat	grain	10	1	1	2	0.032	0.033	0.033	0.000
Wheat	grain	30	1	1	2	0.013	0.014	0.013	0.001
Wheat	grain	22	1	1	10	<0.008	0.090	0.021	0.026
Wheat	grain	22	2	1	2	0.086	0.095	0.091	0.007
Wheat	grain	22	3	1	2	0.023	0.029	0.026	0.004
Wheat	grain	22	4	1	2	0.021	0.023	0.022	0.001
Wheat	red dog	22	1	1	2	<0.008	<0.008	<0.008	0.000
Wheat	shorts	22	1	1	2	<0.008	<0.008	<0.008	0.000
Corn	cornstarch	22	1	4	2	<0.008	<0.008	<0.008	0.000
Corn	flour	22	1	4	2	<0.008	<0.008	<0.008	0.000
Corn	grain	22	1	4	2	<0.008	<0.008	<0.008	0.000
Corn	grits	22	1	4	2	<0.008	<0.008	<0.008	0.000
Corn	meal	22	1	4	2	<0.008	<0.008	<0.008	0.000
Corn	oil	22	1	4	2	2.511	2.664	2.588	0.108
Rice	bran	22	1	4	2	<0.008	<0.008	<0.008	0.000
Rice	hulls	22	1	4	2	<0.008	<0.008	<0.008	0.000
Rice	Paddy rice grain	22	1	4	2	<0.008	<0.008	<0.008	0.000
Rice	polished	22	1	4	2	<0.008	<0.008	<0.008	0.000
Wheat	bran	22	1	4	2	<0.008	<0.008	<0.008	0.000
Wheat	flour	10	1	4	2	<0.008	<0.008	<0.008	0.000
Wheat	flour	30	1	4	2	<0.008	<0.008	<0.008	0.000
Wheat	flour	22	1	4	10	<0.008	<0.008	<0.008	0.000
Wheat	flour	22	2	4	2	<0.008	<0.008	<0.008	0.000
Wheat	flour	22	3	4	2	<0.008	0.009	<0.008	0.001
Wheat	flour	22	4	4	2	<0.008	<0.008	<0.008	0.000
Wheat	germ	10	1	4	2	<0.020	<0.020	<0.020	0.000
Wheat	germ	30	1	4	2	<0.020	<0.020	<0.020	0.000
Wheat	germ	22	1	4	10	<0.020	<0.020	<0.020	0.000
Wheat	germ	22	2	4	2	<0.020	<0.020	<0.020	0.000
Wheat	germ	22	3	4	2	<0.020	<0.020	<0.020	0.000
Wheat	germ	22	4	4	2	<0.020	<0.020	<0.020	0.000
Wheat	grain	10	1	4	2	0.042	0.044	0.043	0.001
Wheat	grain	30	1	4	2	<0.008	<0.008	<0.008	0.000
Wheat	grain	22	1	4	10	<0.008	<0.008	<0.008	0.000
Wheat	grain	22	2	4	2	<0.008	<0.008	<0.008	0.000
Wheat	grain	22	3	4	2	<0.008	<0.008	<0.008	0.000
Wheat	grain	22	4	4	2	<0.008	<0.008	<0.008	0.000
Wheat	red dog	22	1	4	2	<0.008	<0.008	<0.008	0.000
Wheat	shorts	22	1	4	2	<0.008	<0.008	<0.008	0.000
Corn	cornstarch	22	1	7	2	NA[A]	NA	NA	NA

Crop	Commodity	Temp. (°C)	Fumigation. No.	Aeration (days)	n	Sulfuryl Fluoride Residues (ppm)			
						Min	Max	Mean	Std Dev
Corn	flour	22	1	7	2	<0.008	<0.008	<0.008	0.000
Corn	grain	22	1	7	2	<0.008	<0.008	<0.008	0.000
Corn	grits	22	1	7	2	NA	NA	NA	NA
Corn	meal	22	1	7	2	NA	NA	NA	NA
Corn	oil	22	1	7	2	3.128	4.384	3.756	0.888
Rice	bran	22	1	7	2	NA	NA	NA	NA
Rice	hulls	22	1	7	2	<0.008	<0.008	<0.008	0.000
Rice	Paddy rice grain	22	1	7	2	NA	NA	NA	NA
Rice	polished	22	1	7	2	NA	NA	NA	NA
Wheat	bran	22	1	7	2	NA	NA	NA	NA
Wheat	flour	10	1	7	2	NA	NA	NA	NA
Wheat	flour	30	1	7	2	NA	NA	NA	NA
Wheat	flour	22	1	7	20	NA	NA	NA	NA
Wheat	flour	22	2	7	2	NA	NA	NA	NA
Wheat	flour	22	3	7	2	NA	NA	NA	NA
Wheat	flour	22	4	7	2	NA	NA	NA	NA
Wheat	germ	10	1	7	2	NA	NA	NA	NA
Wheat	germ	30	1	7	2	NA	NA	NA	NA
Wheat	germ	22	1	7	20	NA	NA	NA	NA
Wheat	germ	22	2	7	2	NA	NA	NA	NA
Wheat	germ	22	3	7	2	NA	NA	NA	NA
Wheat	germ	22	4	7	2	NA	NA	NA	NA
Wheat	grain	10	1	7	2	0.019	0.021	0.02	0.001
Wheat	grain	30	1	7	2	NA	NA	NA	NA
Wheat	grain	22	1	7	26	NA	NA	NA	NA
Wheat	grain	22	2	7	2	NA	NA	NA	NA
Wheat	grain	22	3	7	2	NA	NA	NA	NA
Wheat	grain	22	4	7	2	NA	NA	NA	NA
Wheat	red dog	22	1	7	2	NA	NA	NA	NA
Wheat	shorts	22	1	7	2	NA	NA	NA	NA

[A] NA = Not Analyzed.

Table C.4.2. Summary of Fluoride Anion Residues in Cereal Grains. Residue data have been pooled across loading factor and aeration time.

Crop	Commodity	Temp. (°C)	Fumigation No.	Dosage (mg-hr/L)	n	Fluoride Anion Residues (ppm)			
						Min	Max	Mean	SD
Corn	cornstarch	22	1	1500	4	3.82	5.35	4.60	0.84
Corn	flour	22	1	1500	4	14.90	19.20	17.10	2.26
Corn	grain	22	1	1500	4	2.07	2.26	2.18	0.09
Corn	grits	22	1	1500	4	7.74	9.17	8.57	0.69
Corn	meal	22	1	1500	4	5.24	6.30	5.82	0.49
Corn	oil	22	1	1500	4	<0.50	<0.50	<0.50	0.00
Rice	bran	22	1	1500	4	24.20	28.50	25.90	1.96
Rice	hulls	22	1	1500	4	23.40	32.80	27.53	4.76
Rice	Paddy rice grain	22	1	1500	4	5.49	8.46	6.93	1.43
Rice	polished	22	1	1500	4	1.30	1.60	1.44	0.13
Wheat	bran	22	1	1500	4	34.00	37.10	35.95	1.38
Wheat	flour	10	1	1500	2	14.60	15.70	15.15	0.78

Crop	Commodity	Temp. (°C)	Fumigation No.	Dosage (mg-hr/L)	n	Fluoride Anion Residues (ppm)			
						Min	Max	Mean	SD
Wheat	flour	30	1	1500	2	33.40	37.80	35.60	3.11
Wheat	flour	22	1	250	2	6.88	7.34	7.11	0.33
Wheat	flour	22	1	1000	2	19.30	21.10	20.20	1.27
Wheat	flour	22	1	1500	18	21.50	44.70	32.57	6.18
Wheat	flour	22	1	2500	2	39.90	42.80	41.35	2.05
Wheat	flour	22	2	1500	2	62.50	62.60	62.55	0.07
Wheat	flour	22	3	1500	2	93.70	101.00	97.35	5.16
Wheat	flour	22	4	1500	2	93.20	97.10	95.15	2.76
Wheat	germ	10	1	1500	2	17.40	18.60	18.00	0.85
Wheat	germ	30	1	1500	2	72.30	82.60	77.45	7.28
Wheat	germ	22	1	250	2	17.10	18.10	17.60	0.71
Wheat	germ	22	1	1000	2	55.30	58.60	56.95	2.33
Wheat	germ	22	1	1500	18	41.60	104.00	67.01	17.86
Wheat	germ	22	1	2500	2	94.20	95.80	95.00	1.13
Wheat	germ	22	2	1500	2	121.00	158.00	139.50	26.16
Wheat	germ	22	3	1500	2	201.00	218.00	209.50	12.02
Wheat	germ	22	4	1500	2	222.00	235.00	228.50	9.19
Wheat	grain	10	1	1500	2	0.79	0.91	0.85	0.08
Wheat	grain	30	1	1500	2	2.79	2.96	2.88	0.12
Wheat	grain	22	1	250	2	0.65	0.68	0.67	0.02
Wheat	grain	22	1	1000	2	1.52	1.74	1.63	0.16
Wheat	grain	22	1	1500	18	1.47	4.08	2.47	0.84
Wheat	grain	22	1	2500	2	1.85	2.03	1.94	0.13
Wheat	grain	22	2	1500	2	5.02	5.02	5.02	0.00
Wheat	grain	22	3	1500	2	6.15	6.31	6.23	0.11
Wheat	grain	22	4	1500	2	7.95	8.00	7.98	0.04
Wheat	red dog	22	1	1500	4	31.70	33.30	32.50	0.67
Wheat	shorts	22	1	1500	4	31.90	35.50	34.18	1.57

D. CONCLUSION

Data from these studies indicate that residues of sulfuryl fluoride are not highly dependent upon the treatment rate or loading factor. This is likely due to the combined volatility and high reactivity of the parent compound. Residues of fluoride appear to be independent of the loading factor and the aeration time, indicating that once the sulfuryl fluoride decomposes to form fluoride, that fluoride is rather recalcitrant. Following that line of reasoning, it is not surprising that fluoride content is highly dependent on the treatment rate and number of fumigations.

HED notes that MRID 45510303 also addresses residue levels of fluoride in cereal grain commodities.

E. REFERENCES

Analytical Methods: DER 45603901
Storage Stability: DER 45510302

F. DOCUMENT TRACKING

RDI: MADoherty (10/16/03); WDrew (10/28/03); RALoranger (10/27/03)
Petition Number(s): PP1F06312
PC Code: 078003

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Crop Field Trial - Sulfuryl Fluoride and Fluoride in Cereal Grains

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STUDY REPORTS:

45510303. Rick, D. L., Marty, G. T., Krieger, S. M., Byrne, S. L., Barnekow, D. E. (9/28/2001) Magnitude of the Terminal Fluoride Ion Level in Cereal Grain Commodities Fumigated with Sulfuryl Fluoride: Study ID: 011057. Unpublished study prepared by Toxicology and Environmental Research and Consulting, Dow Chemical Company. 144 pages.

EXECUTIVE SUMMARY:

Controlled laboratory and operational grain mill fumigations using sulfuryl fluoride were conducted with whole cereal grains (hard red winter wheat, soft red winter wheat, durum wheat, medium grain brown rice, medium grain white rice, white field corn, popcorn, barley, and oats) and representative processed commodities (wheat germ, wheat flour, and corn meal; grain mill fumigations only) in order to determine the magnitude of sulfuryl fluoride and fluoride anion residues that occur following treatment with sulfuryl fluoride. In the laboratory, commodities were fumigated for 24 hours at either 200 mg·hr/L or 1500 mg·hr/L and then aerated for 24 hours prior to analysis. In the grain mills, fumigations were for 24 hours at either ~280, ~1000, or ~1800 mg·hr/L and were followed by a 24-hour aeration interval. Residues of sulfuryl fluoride were determined using GC/ECD headspace analysis. Samples from the laboratory- and the grain mill-treated commodities were analyzed for fluoride anion using aqueous extraction and fluoride selective-ion electrode. Sulfuryl fluoride analysis was completed immediately after the 24-hour aeration period.

Following the 24-hour aeration interval, residues of sulfuryl fluoride were less than the LOQ (0.008 ppm) in all laboratory-fumigated commodities, with the exception of one white corn subsample fumigated at the 1500-mg·hr/L rate. Residues in that sample were 0.019 ppm and dissipated to < 0.008 ppm by 48 hours after fumigation. Residues of sulfuryl fluoride were not determined in samples from the grain mill.

Residues of fluoride anion were dependent upon the sulfuryl fluoride treatment rate. Residues in whole grains from the laboratory fumigations ranged from <0.5 ppm to 2 ppm at the 200-mg·hr/L rate and from 1 ppm to 8 ppm at the 1500-mg·hr/L rate. Residues in/on grains from the mill fumigations ranged from 1 ppm to 8 ppm at the lower rate (~280 mg·hr/L) and from 1 ppm to 24 ppm at the higher rates (~1000 - 1800 mg·hr/L). Residues in processed commodities were higher than those in whole grains and ranged from 7 ppm to 50 ppm at the lower rate and from 11 ppm to 90 ppm at the higher rate. Although there is a fairly high degree of variability across treatment replicates, the bulk of the variability in the residue levels appears to be due to properties of the commodities themselves.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified as scientifically acceptable. There are no specific guidelines regarding the number of trials and replicates required for post-harvest pesticide uses. In the laboratory, two fumigation levels were used (200 and 1500 mg·hr/L) for each commodity and there were four replicates per fumigation level. In the grain mills, three fumigation levels were used (~280, ~1000, and ~1800 mg·hr/L) for each grain and processed commodity and three samples were collected per fumigation. Despite the large amount of data, this is equivalent to one trial at each fumigation level for each commodity.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document (DP Barcode D283007).

COMPLIANCE:

The petitioner provided signed and dated Good Laboratory Practice (GLP) and Quality Assurance statements. Noted GLP deviations were aspects of the documentation, commercial application equipment and personnel, and unknown GLP status regarding the purity of the sulfuryl fluoride analytical standard (reported to be 99.8%). It was also noted that the GLP audit only applied to the mill fumigations and not to the subsequent fluoride analyses. It is unclear whether or not the laboratory fumigations were evaluated with respect to GLP compliance. The noted exceptions to GLP are unlikely to significantly impact the study results. As the fluoride analyses were not subjected to GLP audit, it is impossible to conclude whether any potential GLP deviations associated with the analyses would significantly impact the study.

A. BACKGROUND INFORMATION

Sulfuryl fluoride is a fumigant pesticide being proposed as a methyl bromide replacement for control of insect pests in a number of scenarios. It breaks down to form sulfate and fluoride anion.

TABLE A.1. Test Compound Nomenclature

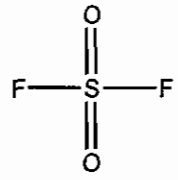
Compound	F^-	
Common name	Fluoride	Sulfuryl fluoride
Company experimental name	-none-	Sulfuryl fluoride
IUPAC name	Fluoride	
CAS name	Fluoride	
CAS #	16984-48-8	002699-79-8
End-use product/EP	Profume	Profume; Vikane

TABLE A.2. Physicochemical Properties of Sulfuryl Fluoride. Note: No physical/chemical properties were provided for ionic fluoride.

Parameter	Value	Reference
Melting point/range	-136°C	Vikane MSDS
pH	Not Provided	
Density	Not Provided	
Water solubility	1.67 g/L	Vikane MSDS
Solvent solubility	Not Provided	
Vapor pressure (10°C)	9150 mm Hg	Vikane MSDS
Dissociation constant (pK_a)	Not Provided	
Octanol/water partition coefficient Log(K_{ow})	Not Provided	
UV/visible absorption spectrum	Not Provided	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

Table B.1.1. Summary of Cereal Grain Fumigation Treatments. All treatments consisted of a single, postharvest fumigation.

Location (City, State, Year)	Crop and Variety	Sample Location	Applic. Rate (mg•hr/L)	Total Applic. Rate (mg•hr/L)
Lab Fumigation	Red Winter Wheat (hard and soft); Durum Wheat; Brown Rice; White Rice; Field Corn (white - human consumed); Popcorn; Barley; Oats	NA	158 - 275	158 - 275 (200 Nominal)
		NA	1261 - 2119	1261 - 2119 (1500 Nominal)

Location (City, State, Year)	Crop and Variety	Sample Location	Applic. Rate (mg•hr/L)	Total Applic. Rate (mg•hr/L)
Star of the West Milling Co., Ligonier, IN (EPA Region 5)	Durum wheat (whole grain, gern, semolina, and flour); Red Winter Wheat, hard and soft (whole grain, whole wheat flour, germ, unbleached white flour); Popcorn; White Field Corn (grain and meal); Yellow Corn Flour; Medium Grain Brown Rice; Medium Grain White Rice; Barley; Oats.	Warehouse	974	974
		1st Floor	1146	1146
		5th Floor	984	984
Stafford County Flour Mills Co., Hudon, KS (EPA Region 5)		1st Floor	1803	1803
		2nd Floor	1793	1793
		4th Floor	943	943
American Rice, Inc., Houston, TX (EPA Region 6)		1st Floor	271	271*
		4.5th Floor	288	288*

*Due to leakage of sulfuryl fluoride from the American Rice mill, the fumigation was ended after approximately 4.5 hours.

TABLE B.1.2. Trial Numbers and Geographical Locations

NAFTA Growing Region	Crop 1			Crop 2			Crop 3		
	Submitted	Requested		Submitted	Requested		Submitted	Requested	
		Canada	US		Canada	US		Canada	US
Not applicable to a post-harvest use scenario									

B.2. Sample Handling and Preparation

Immediately following active aeration of the mill facility for at least 24 hours, aliquots of laboratory samples for sulfuryl fluoride analysis were collected as rapidly as possible and placed into specially designed air-tight blender jars. Each of the remaining samples were placed in an incubator (30°C) to determine residue decline. Samples were scheduled to be sampled at Days 2, 5, 8, 15, and 22 provided that sulfuryl fluoride levels were >LOQ. Once residues were <LOQ, aliquots of the commodities were taken for fluoride anion analysis. Laboratory-fumigated and mill-fumigated samples for fluoride anion analysis were shipped at ambient temperatures to Toxicology & Environmental Research and Consulting (Dow Chemical Co., Midland, MI).

B.3. Analytical Methodology

Residues of sulfuryl fluoride were determined using the headspace analysis methods similar to those described by Hartsell *et al* (1992) and King *et al* (1981). Briefly, samples were transferred to air-tight blender jars that had been fitted with a GC septum assembly. Distilled/deionized water was added to the samples and the samples were homogenized by blending for 5 minutes. After the homogenized samples settled for several minutes, an aliquot of the headspace was removed by syringe and injected into a GC equipped with an electron capture detector. A linear regression of detector response on standard concentration was used to quantify the residues of sulfuryl fluoride. Sample calculations and chromatograms were provided. The LOQ for the method is 0.008 ppm

Residues of fluoride anion were determined using a fluoride selective electrode that was calibrated using the double known addition technique. Commodity samples were blended with distilled/deionized water and "Total Ionic Strength Adjusting Buffer." The samples were centrifuged and the resulting supernatant analyzed for fluoride anion using the fluoride selective electrode. Sample calculations were provided. The LOQ for the method is 0.5 ppm.

Both methods have been evaluated by BEAD's Analytical Chemistry Branch, which recommended that they be validated with respect to weathered residues and that OPP accept the methods for tolerance enforcement purposes.

C. RESULTS AND DISCUSSION

The analytical methods for sulfuryl fluoride and fluoride anion are adequate for data collection purposes based on the reported concurrent recoveries. Storage stability studies indicate that recovery of fluoride in wheat flour decreases with increasing storage time by a rate of approximately 0.3% per day. Due to the short storage intervals (Table C.2), corrections have not been made to fluoride residue levels.

Results from the laboratory study show that residues of sulfuryl fluoride are typically <0.008 ppm following fumigation of stored grains. Measurable residues of sulfuryl fluoride occurred in one corn grain sample from the laboratory studies. As part of the experimental design, residues of sulfuryl fluoride were not measured for samples that were fumigated in the grain mills. Residues of fluoride anion in the grain mill samples were often higher than their laboratory sample counterparts, indicating that there is the potential for higher residues of sulfuryl fluoride than that suggested by the laboratory fumigation data.

Residue data for fluoride anion from the laboratory fumigations show that residues are fairly low in cereal grains (<8.5 ppm at the higher fumigation rate) and that there is relatively little variance in those residues (the largest standard deviation is 0.62 ppm). The fluoride anion residue values in grain samples from the grain mill fumigations were higher and more variable (≤23.6 ± 5.3 ppm). The higher variability is likely due to the less-controlled nature of the mill fumigations versus those conducted in the laboratory. Fluoride anion residues in milled grain fractions (flour, germ, and meal) were consistently higher than residues in the raw grains. Note that the increased residues are not the result of processing since they occurred as a result of direct fumigation of the milled commodities. The fluoride anion results indicate that residues may be pooled within the wheat and corn varieties to increase the replication for those two crops.

Table C.1. Summary of Concurrent Analytical Method Validation.

Crop Matrix	Fortification Level (ppm)	Recoveries (%)	Mean Recovery ± SD
Sulfuryl Fluoride			
Popcorn	10 40	104, 108, 84, 92 83, 101, 105, 101	97 ± 10
White Corn	10 40	87, 94, 87, 94 90, 88, 90, 88	90 ± 3

Crop Matrix	Fortification Level (ppm)	Recoveries (%)	Mean Recovery ± SD
Barley	10 40	95, 97, 93, 109 92, 84, 115, 104	99 ± 10
Oats	10 40	81, 76, 111, 103 88, 81, 100, 73	89 ± 14
Brown Rice	10 40	95, 105, 111, 112 102, 98, 99, 114	104 ± 7
White Rice	10 40	113, 90, 91, 94, 95 112, 63, 95, 93	94 ± 14
Soft Red Winter Wheat	10 40 80	102, 92, 92, 103 95, 90 105	97 ± 6
Hard Red Winter Wheat	10 40	104, 106, 95, 101 101, 108, 96, 98	101 ± 5
Durum Wheat	10 40	100, 104, 100, 98 102, 93, 107, 96	100 ± 5
Fluoride Anion			
Popcorn	5 50 100	104, 102 83 86	94 ± 11
White Corn	5 50	102, 98 88, 84	93 ± 8
Barley	5 50	102, 121 83, 105	103 ± 16
Oats	5 12.5 50 125	114 101 78.4 81.6	94 ± 17
White Rice	5 50	99, 93 88, 84	91 ± 7
Brown Rice	5 50	97, 97 93, 90	94 ± 3
Soft Red Winter Wheat	5 50	109, 118 103, 106	109 ± 7
Hard Red Winter Wheat	5 50	124, 133 110, 94	115 ± 17
Durum Wheat	5 50	111, 103 86, 92	98 ± 11

TABLE C.2. Summary of Storage Conditions (Fluoride analysis only)			
Mill Identification	Storage Temp. (°C)	Actual Storage Duration (days)	Interval of Demonstrated Storage Stability (days)
Star of the West Milling Co., Ligonier, IN (EPA Region 5)	Ambient, approx. 22 °C	15 - 19	Approximately 140 days. Wheat flour showed a dissipation of ca. 0.3% per day for fluoride.
Stafford County Flour Mills Co., Hudon, KS (EPA Region 5)	Ambient, approx. 22 °C	8 - 20	

American Rice, Inc., Houston, TX (EPA Region 6)	Ambient, approx. 22 °C	10 - 21	

Table C.3.1. Residue Data from Fumigations of Grain Crops with Sulfuryl Fluoride: Laboratory Samples.

Location (City, State, Year)	Commodity	Formulation	Total Rate (mg•hr/L)	Aeration Time (days)	Sulfuryl Fluoride (ppm)[A]	Fluoride Anion (ppm)[A]
Laboratory Study	Hard Red Winter Wheat	Profume	235	1	<0.008	0.803
			271		<0.008	0.877
			214		<0.008	0.886
			275		<0.008	0.857
Laboratory Study	Soft Red Winter Wheat	Profume	250	1	<0.008	0.721
			248		<0.008	0.718
			227		<0.008	0.898
			241		<0.008	0.753
Laboratory Study	Durum Wheat	Profume	248	1	<0.008	0.850
			242		<0.008	0.859
			228		<0.008	0.905
			242		<0.008	0.925
Laboratory Study	Brown Rice	Profume	211	1	<0.008	0.561
			213		<0.008	0.611
			218		<0.008	0.576
			207		<0.008	0.563
Laboratory Study	White Rice	Profume	224	1	<0.008	<0.5
			179		<0.008	<0.5
			213		<0.008	<0.5
			196		<0.008	<0.5
Laboratory Study	Field Corn	Profume	238	1	<0.008	<0.5
			193		<0.008	<0.5
			233		<0.008	<0.5
			208		<0.008	<0.5
Laboratory Study	Popcorn	Profume	247	1	<0.008	<0.5
			234		<0.008	<0.5
			246		<0.008	<0.5
			219		<0.008	<0.5
Laboratory Study	Barley	Profume	205	1	<0.008	1.01
			205		<0.008	1.03
			205		<0.008	1.00
			195		<0.008	0.853
Laboratory Study	Oats	Profume	200	1	<0.008	1.87
			158		<0.008	1.76
			184		<0.008	1.81
			167		<0.008	1.85
Laboratory Study	Hard Red Winter Wheat	Profume	1620	1	<0.008	2.64
			2119		<0.008	3.50
			1783		<0.008	3.30
			1553		<0.008	2.66
Laboratory Study	Soft Red Winter Wheat	Profume	1817	1	<0.008	4.84
			1635		<0.008	3.38
			1847		<0.008	3.80
			1553		<0.008	4.21

Location (City, State, Year)	Commodity	Formulation	Total Rate (mg•hr/L)	Aeration Time (days)	Sulfuryl Fluoride (ppm)[A]	Fluoride Anion (ppm)[A]
Laboratory Study	Durum Wheat	Profume	1769	1	<0.008	2.05
			1964		<0.008	2.24
			1718		<0.008	2.11
			1619		<0.008	1.93
Laboratory Study	Brown Rice	Profume	1511	1	<0.008	2.23
			1572		<0.008	2.17
			1728		<0.008	2.16
			1586		<0.008	2.38
Laboratory Study	White Rice	Profume	1706	1	<0.008	2.01
			1465		<0.008	2.03
			1520		<0.008	1.96
			1498		<0.008	1.83
Laboratory Study	Field Corn	Profume	1603	1	<0.008	1.42
			1261		<0.008	1.36
			1501		0.0185[B]	1.31
			1379		<0.008	1.64
Laboratory Study	Popcorn	Profume	1449	1	<0.008	0.764
			1556		<0.008	1.41
			1549		<0.008	0.966
			1460		<0.008	0.879
Laboratory Study	Barley	Profume	1672	1	<0.008	2.79
			1640		<0.008	3.05
			1616		<0.008	2.76
			1656		<0.008	2.92
Laboratory Study	Oats	Profume	1630	1	<0.008	7.39
			1544		<0.008	7.00
			1533		<0.008	7.50
			1534		<0.008	8.27

[A] Average of two replicates.
[B] One replicate from Chamber "7" showed residues of 0.0185 ppm. The other replicate did not have quantifiable residues (<0.008). Residues were <0.008 ppm on Day 2 after fumigation.

Table C.3.2 Residue Data from Fumigations of Grain Crops with Sulfuryl Fluoride: Grain Mill Samples. Note: Sulfuryl fluoride was not analyzed for samples from grain milling facilities.

Location (City, State, Year)	Commodity	Formulation	Total Rate (mg•hr/L)	Aeration Time (days)	Fluoride Anion (ppm)[A]
Star of the West Milling Co., Ligonier, IN	Durum whole wheat	Profume	Control	1	<0.5
			974		3.61
			1146		5.00
			984		23.60
	Durum wheat germ	Profume	Control	1	1.03
			974		46.8
			1146		81.6
			984		89.7
	Durum wheat semolina	Profume	Control	1	<0.5
			974		13.1
			1146		25.9
			984		27.3

Location (City, State, Year)	Commodity	Formulation	Total Rate (mg•hr/L)	Aeration Time (days)	Fluoride Anion (ppm)[A]
	Durum wheat flour	Profume	Control 974 1146 984	1	<0.5 21.2 41.5 49.7
	Hard red winter wheat	Profume	Control 974 1146 984	1	<0.5 2.12 3.89 8.36
	Hard red winter wheat whole flour	Profume	Control 974 1146 984	1	0.59 22.4 32.9 27.2
	Hard red winter wheat unbleached white flour	Profume	Control 974 1146 984	1	<0.5 26.5 51.5 49.1
	Hard red winter and spring wheat germ	Profume	Control 974 1146 984	1	2.0 33.4 38.6 41.1
	Soft red winter wheat	Profume	Control 974 1146 984	1	<0.5 3.59 4.86 6.54
	Soft red winter wheat whole flour	Profume	Control 974 1146 984	1	<0.5 29.5 39.4 82.3
	Soft red winter wheat unbleached white flour	Profume	Control 974 1146 984	1	<0.5 33.9 40.4 57.0
	Popcorn	Profume	Control 974 1146 984	1	<0.5 1.09 1.42 2.05
	White field corn	Profume	Control 974 1146 984	1	<0.5 1.03 2.25 5.31
	White field corn meal	Profume	Control 974 1146 984	1	<0.5 10.5 12.1 21.0
	Yellow corn flour	Profume	Control 974 1146 984	1	<0.5 17.2 18.0 24.1

Location (City, State, Year)	Commodity	Formulation	Total Rate (mg•hr/L)	Aeration Time (days)	Fluoride Anion (ppm)[A]
	Brown rice	Profume	Control 974 1146 984	1	<0.5 3.84 6.95 11.80
	White rice	Profume	Control 974 1146 984	1	<0.5 4.99 5.47 16.10
	Oats	Profume	Control 974 1146 984	1	<0.5 7.88 9.15 15.25
	Barley	Profume	Control 974 1146 984	1	0.61 4.47 7.09 9.25
Stafford County Flour Mills Co., Hudon, KS	Durum whole wheat	Profume	Control 1803 1793 943	1	<0.5 5.80 4.79 4.56
	Durum wheat germ	Profume	Control 1803 1793 943	1	<0.5 78.8 85.9 41.4
	Durum wheat semolina	Profume	Control 1803 1793 943	1	<0.5 25.5 28.4 20.2
	Durum wheat flour	Profume	Control 1803 1793 943	1	<0.5 46.4 49.3 33.5
	Hard red winter wheat	Profume	Control 1803 1793 943	1	0.76 4.84 5.65 3.74
	Hard red winter wheat whole flour	Profume	Control 1803 1793 943	1	<0.5 40.4 35.6 24.8
	Hard red winter wheat *unbleached white flour*	Profume	Control 1803 1793 943	1	<0.5 40.4 49.3 22.9
	Hard red winter and spring wheat germ	Profume	Control 1803 1793 943	1	0.78 55.9 63.3 39.3

Location (City, State, Year)	Commodity	Formulation	Total Rate (mg•hr/L)	Aeration Time (days)	Fluoride Anion (ppm)[A]
	Soft red winter wheat	Profume	Control 1803 1793 943	1	<0.5 4.73 6.06 2.98
	Soft red winter wheat whole flour	Profume	Control 1803 1793 943	1	0.54 48.2 40.5 28.1
	Soft red winter wheat unbleached white flour	Profume	Control 1803 1793 943	1	<0.5 45.3 41.7 26.0
	Popcorn	Profume	Control 1803 1793 943	1	<0.5 1.52 1.19 1.00
	White field corn	Profume	Control 1803 1793 943	1	<0.5 1.71 1.86 1.11
	White field corn meal	Profume	Control 1803 1793 943	1	<0.5 26.4 21.6 15.7
	Yellow corn flour	Profume	Control 1803 1793 943	1	<0.5 22.7 24.1 18.1
	Brown rice	Profume	Control 1803 1793 943	1	<0.5 6.24 7.29 4.54
	White rice	Profume	Control 1803 1793 943	1	<0.5 7.64 10.70 3.21
	Oats	Profume	Control 1803 1793 943	1	0.53 12.50 14.00 6.82
	Barley	Profume	Control 1803 1793 943	1	<0.5 6.49 7.96 4.27
American Rice, Inc., Houston, TX	Durum whole wheat	Profume	Control 271 288	1	<0.5 2.76 2.55
	Durum wheat germ	Profume	Control 271 288	1	0.97 43.4 49.5

Location (City, State, Year)	Commodity	Formulation	Total Rate (mg•hr/L)	Aeration Time (days)	Fluoride Anion (ppm)[A]
	Durum wheat semolina	Profume	Control 271 288	1	<0.5 11.2 12.4
	Durum wheat flour	Profume	Control 271 288	1	<0.5 17.8 15.2
	Hard red winter wheat	Profume	Control 271 288	1	<0.5 2.06 2.13
	Hard red winter wheat whole flour	Profume	Control 271 288	1	<0.5 15.9 15.4
	Hard red winter wheat unbleached white flour	Profume	Control 271 288	1	<0.5 17.6 16.2
	Hard red winter and spring wheat germ	Profume	Control 271 288	1	0.90 34.9 42.1
	Soft red winter wheat	Profume	Control 271 288	1	<0.5 2.50 2.59
	Soft red winter wheat whole flour	Profume	Control 271 288	1	<0.5 19.0 19.3
	Soft red winter wheat unbleached white flour	Profume	Control 271 288	1	<0.5 20.0 14.7
	Popcorn	Profume	Control 271 288	1	<0.5 1.06 1.03
	White field corn	Profume	Control 271 288	1	<0.5 2.07 1.46
	White field corn meal	Profume	Control 271 288	1	<0.5 8.3 6.6
	Yellow corn flour	Profume	Control 271 288	1	<0.5 10.4 12.2
	Brown rice	Profume	Control 271 288	1	<0.5 3.84 2.35
	White rice	Profume	Control 271 288	1	<0.5 2.23 2.42
	Oats	Profume	Control 271 288	1	1.52 7.78 7.46

Location (City, State, Year)	Commodity	Formulation	Total Rate (mg•hr/L)	Aeration Time (days)	Fluoride Anion (ppm)[A]
	Barley	Profume	Control 271 288	1	<0.5 3.48 2.58

[A] Sulfuryl fluoride residues were not measured in the samples from the grain mills.

Table 2.3. Summary of Fluoride Anion Residue Data from Crop Field Trials in Cereal Grains with Sulfuryl Fluoride.[A] All samples are following a 24-hour aeration period.

Commodity	Form	Location	Mean Total Applic. Rate (mg•hr/L)[B]	n	Fluoride Anion Residues (ppm)				
					Min.	Max.	HAFT[C]	Mean	Std. Dev.
Oats	Grain	Lab	177	4	1.76	1.87	1.87	1.82	0.05
Barley	Grain	Lab	203	4	0.85	1.03	1.03	0.97	0.08
Rice, White	Grain	Lab	203	4	<0.5	<0.5	<0.5	<0.5	0.00
Rice, Brown	Grain	Lab	212	4	0.56	0.61	0.61	0.58	0.02
Corn, Field	Grain	Lab	218	4	<0.5	<0.5	<0.5	<0.5	0.00
Corn, Pop	Grain	Lab	237	4	<0.5	<0.5	<0.5	<0.5	0.00
Wheat, Durum	Grain	Lab	240	4	0.85	0.93	0.93	0.88	0.04
Wheat, SRW[D]	Grain	Lab	242	4	0.72	0.90	0.90	0.77	0.09
Wheat, HRW[D]	Grain	Lab	250	4	0.80	0.89	0.89	0.86	0.04
Barley	Grain	Mill	280	2	2.58	3.48	3.48	3.03	0.64
Corn, Field	Grain	Mill	280	2	1.46	2.07	2.07	1.77	0.43
Corn, Pop	Grain	Mill	280	2	1.03	1.06	1.06	1.05	0.02
Oats	Grain	Mill	280	2	7.46	7.78	7.78	7.62	0.23
Rice, Brown	Grain	Mill	280	2	2.35	3.84	3.84	3.10	1.05
Rice, White	Grain	Mill	280	2	2.23	2.42	2.42	2.33	0.13
Wheat, Durum	Grain	Mill	280	2	2.55	2.76	2.76	2.66	0.15
Wheat, HRW	Grain	Mill	280	2	2.06	2.13	2.13	2.10	0.05
Wheat, SRW	Grain	Mill	280	2	2.50	2.59	2.59	2.55	0.06
Barley	Grain	Mill	1012	4	4.27	9.25	9.25	6.27	2.37
Corn, Field	Grain	Mill	1012	4	1.03	5.31	5.31	2.43	2.00
Corn, Pop	Grain	Mill	1012	4	1.00	2.05	2.05	1.39	0.48
Oats	Grain	Mill	1012	4	6.82	15.25	15.25	9.78	3.77
Rice, Brown	Grain	Mill	1012	4	3.84	11.80	11.80	6.78	3.60
Rice, White	Grain	Mill	1012	4	3.21	16.10	16.10	7.44	5.85
Wheat, Durum	Grain	Mill	1012	4	3.61	23.60	23.60	9.19	5.30
Wheat, HRW	Grain	Mill	1012	4	2.12	8.36	8.36	4.53	2.68
Wheat, SRW	Grain	Mill	1012	4	2.98	6.54	6.54	4.49	1.57
Corn, Field	Grain	Lab	1436	4	1.31	1.64	1.64	1.43	0.15
Corn, Pop	Grain	Lab	1504	4	0.76	1.41	1.41	1.00	0.28
Rice, White	Grain	Lab	1547	4	1.83	2.03	2.03	1.96	0.09
Oats	Grain	Lab	1560	4	7.00	8.27	8.27	7.54	0.53
Rice, Brown	Grain	Lab	1599	4	2.16	2.38	2.38	2.24	0.10
Barley	Grain	Lab	1646	4	2.76	3.05	3.05	2.88	0.13
Wheat, SRW	Grain	Lab	1713	4	3.38	4.84	4.84	4.06	0.62
Wheat, Durum	Grain	Lab	1768	4	1.93	2.24	2.24	2.08	0.13
Wheat, HRW	Grain	Lab	1769	4	2.64	3.50	3.50	3.03	0.44
Barley	Grain	Mill	1798	2	6.49	7.96	7.96	7.23	1.04
Corn, Field	Grain	Mill	1798	2	1.71	1.86	1.86	1.79	0.11
Corn, Pop	Grain	Mill	1798	2	1.19	1.52	1.52	1.36	0.23
Oats	Grain	Mill	1798	2	12.50	14.00	14.00	13.25	1.06
Rice, Brown	Grain	Mill	1798	2	6.24	7.29	7.29	6.77	0.74
Rice, White	Grain	Mill	1798	2	7.64	10.70	10.70	9.17	2.16
Wheat, Durum	Grain	Mill	1798	2	4.79	5.80	5.80	5.30	0.71
Wheat, HRW	Grain	Mill	1798	2	4.84	5.65	5.65	5.25	0.57
Wheat, SRW	Grain	Mill	1798	2	4.73	6.06	6.06	5.40	0.94

Commodity	Form	Location	Mean Total Applic. Rate (mg•hr/L)[B]	n	Fluoride Anion Residues (ppm)				
					Min.	Max.	HAFT[C]	Mean	Std. Dev.
Corn, Yellow, Flour	Flour	Mill	280	2	10.40	12.20	12.20	11.30	1.27
Wheat, Durum, Flour	Flour	Mill	280	2	15.20	17.80	17.80	16.50	1.84
Wheat, Durum, Semolina	Flour	Mill	280	2	11.20	12.40	12.40	11.80	0.85
Wheat, HRW Unbleached White Flour	Flour	Mill	280	2	16.20	17.60	17.60	16.90	0.99
Wheat, HRW Whole Flour	Flour	Mill	280	2	15.40	15.90	15.90	15.65	0.35
Wheat, SRW Unbleached White Flour	Flour	Mill	280	2	14.70	20.00	20.00	17.35	3.75
Wheat, SRW Whole Flour	Flour	Mill	280	2	19.00	19.30	19.30	19.15	0.21
Corn, Yellow, Flour	Flour	Mill	1012	4	17.20	24.10	24.10	19.35	3.19
Wheat, Durum, Flour	Flour	Mill	1012	4	21.20	49.70	49.70	36.48	12.14
Wheat, Durum, Semolina	Flour	Mill	1012	4	13.10	27.30	27.30	21.63	6.46
Wheat, HRW Unbleached White Flour	Flour	Mill	1012	4	22.90	51.50	51.50	37.50	14.89
Wheat, HRW Whole Flour	Flour	Mill	1012	4	22.40	32.90	32.90	26.83	4.50
Wheat, SRW Unbleached White Flour	Flour	Mill	1012	4	26.00	57.00	57.00	39.33	13.17
Wheat, SRW Whole Flour	Flour	Mill	1012	4	28.10	82.30	82.30	44.83	25.48
Corn, Yellow, Flour	Flour	Mill	1798	2	22.70	24.10	24.10	23.40	0.99
Wheat, Durum, Flour	Flour	Mill	1798	2	46.40	49.30	49.30	47.85	2.05
Wheat, Durum, Semolina	Flour	Mill	1798	2	25.50	28.40	28.40	26.95	2.05
Wheat, HRW Unbleached White Flour	Flour	Mill	1798	2	40.40	49.30	49.30	44.85	6.29
Wheat, HRW Whole Flour	Flour	Mill	1798	2	35.60	40.40	40.40	38.00	3.39
Wheat, SRW Unbleached White Flour	Flour	Mill	1798	2	41.70	45.30	45.30	43.50	2.55
Wheat, SRW Whole Flour	Flour	Mill	1798	2	40.50	48.20	48.20	44.35	5.44
Wheat, Durum, Germ	Germ	Mill	280	2	43.40	49.50	49.50	46.45	4.31
Wheat, HRW Germ	Germ	Mill	280	2	24.90	42.10	42.10	38.50	5.09
Wheat, Durum, Germ	Germ	Mill	1012	4	41.40	89.70	89.70	64.88	24.32
Wheat, HRW Germ	Germ	Mill	1012	4	33.40	41.10	41.10	38.10	3.31
Wheat, Durum, Germ	Germ	Mill	1798	2	78.80	85.90	85.90	82.35	5.02
Wheat, HRW Germ	Germ	Mill	1798	2	55.90	63.30	63.30	59.60	5.23
White Corn Meal	Meal	Mill	280	2	6.60	8.30	8.30	7.45	1.20
White Corn Meal	Meal	Mill	1012	4	10.50	21.00	21.00	14.83	4.66
White Corn Meal	Meal	Mill	1798	2	21.60	26.40	26.40	24.00	3.39

[A] Residues of sulfuryl fluoride are not reported in this table. Residues of sulfuryl fluoride in all cereal grain matrices one day after fumigation were <0.008 ppm with the exception of one field corn sample bearing residues at 0.0185 ppm. Residues were <0.008 ppm in this sample two days after fumigation. Sulfuryl fluoride residues were not measured for the samples fumigated in the grain mills.

[B] For the grain mills, application rates were grouped into categories of <300 mg•hr/L, >300 mg•hr/L and <1200 mg•hr/L, and > 1200 mg•hr/L. The statistics listed for application rate and residue levels are for samples within each application rate grouping.

[C] HAFT = Highest Average Field Trial. Due to the design of this study, the maximum residue level and the highest average residue levels are identical.

[D] HRWW = Hard Red Winter Wheat; SRWW = Soft Red Winter Wheat

D. CONCLUSION

Residues of sulfuryl fluoride are generally below the LOQ for the analytical method in/on all cereal grain commodities following fumigation at either ca. 200 or 1500 mg·hr/L. Residues of fluoride were quantifiable in most treated commodities. Residue levels were dependent upon treatment rate and on the commodity being assayed and ranged from <0.5 ppm to nearly 90 ppm.

HED notes that MRID 45396301 also addresses residue levels of fluoride in cereal grain commodities.

E. REFERENCES

Analytical Methods: DER 45603901
Storage Stability: DER 45510302

F. DOCUMENT TRACKING

RDI: MADoherty (10/16/03); WDrew (10/28/03); RALoranger (10/27/03)
Petition Number(s): PP1F06312
PC Code: 078003

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Sulfuryl Fluoride/078003
DACO 7.4.1/OPPTS 860.1500/OECD IIA 6.3.1, 6.3.2, 6.3.3 and IIIA 8.3.1, 8.3.2, 8.3.3
Crop Field Trial - Tree Nuts and Dried Fruit

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STUDY REPORTS:

MRID No 45510304. S. L. Byrne, P. L. Hartsell, J. M. Hurley, D. B. Allred, L. M. Carmona, J. Bunnell (2001). Magnitude of the Sulfuryl Fluoride and Terminal Fluoride Ion Levels in Dried Fruit and Tree Nut Commodities Fumigated with Sulfuryl Fluoride: Lab Project Number: 010014.02. Unpublished study prepared by Dow AgroSciences. 181 pages.

EXECUTIVE SUMMARY:

Supervised post-harvest fumigation trials were conducted with walnuts, pistachios, pecans, almonds, dates, figs, dried plums, and raisins. Single fumigations were carried out at normal atmospheric pressure or under vacuum conditions at rates of approximately 200 mg•hr/L. Additionally, multiple fumigations (2-5) were conducted, each at approximately 1500 mg•hr/L. For each treatment/crop combination, 2 replicate fumigations were made and 2-3 samples were collected from each replicate. All samples were aerated for at least 24 hours prior to the first sample being collected for sulfuryl fluoride analysis. The trials monitored residues of sulfuryl fluoride and fluoride anion, as well as the time required for sulfuryl fluoride residues to dissipate to < LOQ (4.2 ng/g). Sulfuryl fluoride residues were analyzed using a head space method; fluoride anion was analyzed using a fluoride selective-ion electrode and a double-known-addition technique. Residue levels of sulfuryl fluoride varied based on the commodity and the treatment regime. For most commodities, residues had dissipated to <2.1 ppb within 6 days of aeration following fumigation. Sulfuryl fluoride residues were more persistent in commodities with higher oil content (e.g, walnuts, pecans, almonds), typically requiring approximately 2 weeks for residues to dissipate to <2.1 ppb. At the same fumigation rate, residues of sulfuryl fluoride were greater following vacuum fumigation versus treatment at ambient pressure. In oily commodities, multiple fumigations resulted in higher residues of sulfuryl fluoride at a given aeration time. Pooled across all of the variables addressed in this study, sulfuryl fluoride residues ranged from <2.1 ppb to 6030 ppb (6.03 ppm). Residue levels of fluoride were measured only after residues

of sulfuryl fluoride had dissipated to below detectable levels; therefore, the effect of aeration time on fluoride levels cannot be assessed from these data. Generally, fluoride residues appear to be more dependent on the number of fumigations than on the treatment rate, treatment pressure, or commodity. Overall, fluoride residue levels ranged from <1.4 ppm to 21.8 ppm.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the residue data are classified as scientifically acceptable. HED notes that the amount of replication present in the study may not be sufficient to support tolerance levels.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document (DP Barcode D283007).

COMPLIANCE:

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. A few deviations from GLP requirements were noted; however, they are not likely to impact the validity of the study.

A. BACKGROUND INFORMATION

TABLE A.1. Test Compound Nomenclature

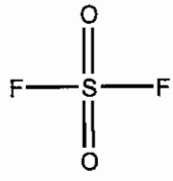
Compound	Chemical Structure
Sulfuryl Fluoride	
Common name	Sulfuryl fluoride
Company experimental name	Sulfuryl fluoride
IUPAC name	
CAS name	
CAS #	002699-79-8
End-use product/EP	Profume; Vikane

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound

Parameter	Value	Reference
Melting point/range	-136°C	Vikane MSDS
pH	Not Provided	
Density	Not Provided	
Water solubility	1.67 g/L	Vikane MSDS

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound		
Parameter	Value	Reference
Solvent solubility	Not Provided	
Vapor pressure (10°C)	9150 mm Hg	Vikane MSDS
Dissociation constant (pK_a)	Not Provided	
Octanol/water partition coefficient Log(K_{OW})	Not Provided	
UV/visible absorption spectrum	Not Provided	

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1 Soil Characterization.				
Trial Identifier (City, State/Year)	Soil characteristics			
	Type	%OM*	pH*	CEC*
These studies examined residues following post-harvest fumigation of commodities. Soil properties are irrelevant to the experimental design and results.				

*These parameters are optional except in cases where their value affects the use pattern for the chemical.

Fumigations were carried out in sealed chambers at 32°C. Fumigations at this temperature were shown in previous studies to produce maximum residues (MRID 45170401).

TABLE B.1.2. Experimental Design of Fumigation Trials. All trials were conducted at 32°C.					
Treatment ID*	EP[1]	Application			
		Fumigation Number	Average Rate, mg·hr/L	RTI[2] (days)	Average Total Rate, mg·hr/L
A - Walnuts	Vikane	1	217	NA	217
A - Pistachios	Vikane	1	214	NA	214
A - Pecans	Vikane	1	199	NA	199
A - Almonds	Vikane	1	203	NA	203
A - Dates	Vikane	1	208	NA	208
A - Figs	Vikane	1	197	NA	208
A - Dried Plums	Vikane	1	219	NA	219
A - Raisins	Vikane	1	221	NA	221
B - Pistachios	Vikane	1 2 3	1517 1507 1506	NA 8 13	4530
B - Pecans	Vikane	1 2 3	1533 1452 1510	NA 19 14	4495
B - Almonds	Vikane	1 2 3	1534 1538 1488	NA 7 7	4560

B - Dates	Vikane	1 2 3 4 5	1484 1504 1493 1503 1491	NA 7 6 8 6	7475
B - Figs	Vikane	1 2	1462 1498	NA 28	2960
B - Dried Plums	Vikane	1 2 3 4	1575 1504 1516 1521	NA 7 8 6	6116
C - Walnuts	Vikane	1	183	NA	183
C - Pistachios	Vikane	1	202	NA	202
C - Pecans	Vikane	1	206	NA	206
C - Almonds	Vikane	1	218	NA	218

* A = 1 Fumigation at normal atmospheric pressure; B = Multiple fumigations at normal atmospheric pressure; C = 1 Fumigation under vacuum.
[1]EP = End-use Product
[2] Retreatment Interval. Commodities were retreated when the concentration of sulfuryl fluoride dissipated to < LOQ.

TABLE B.1.3. Trial Numbers and Geographical Locations

NAFTA Growing Region	Crop 1			Crop 2			Crop 3		
	Submitted	Requested		Submitted	Requested		Submitted	Requested	
		Canada	US		Canada	US		Canada	US
	Not Applicable to a post-harvest use pattern.								

B.2. Analytical Methodology

The analytical methods for sulfuryl fluoride and fluoride anion have been reviewed in DERs for MRIDs 45632902 and 45603901, respectively. The methods have been reviewed by the Agency's Analytical Chemistry Branch which recommended that the methods undergo radiovalidation and that OPP accept them for enforcement purposes.

Sulfuryl Fluoride. The method utilizes headspace analysis to quantitate residues of sulfuryl fluoride. Residues of sulfuryl fluoride are extracted from commodities with water in an air-tight blender. The samples are agitated in the blender for five minutes to transfer residues of the highly volatile sulfuryl fluoride from the commodity to the headspace above the sample. The headspace is then analyzed for residues of sulfuryl fluoride by injecting an aliquot into a gas chromatograph with electron-capture detection (GC/ECD). The method has a reported LOD of 2.1 ppb and a reported LOQ of 4.2 ppb.

Fluoride Anion. The method consists of homogenizing and shaking the sample in the presence of water and total ionic strength adjusting buffer, centrifuging the sample, and analyzing an aliquot of the supernatant with a fluoride-selective electrode. Quantitation of fluoride residues is achieved using a double-known-addition technique. The method has a reported LOD of 1.4

ppm and a reported LOQ of 2.4 ppm.

C. RESULTS AND DISCUSSION

As shown by the concurrent recovery values in Table C.1, the analytical methods used to determine residues of sulfuryl fluoride and fluoride anion are adequate for dried fruits and tree nuts. Recoveries of sulfuryl fluoride were generally lower at the lowest fortification level (4.2 ppb) but are primarily classified as acceptable, ranging from 64 to 114%. At higher fortification levels, recoveries ranged from 79.8 to 110.8%. For sulfuryl fluoride, samples were analyzed on the day of collection. Samples were stored in sealed plastic bags in order to minimize loss of sulfuryl fluoride prior to extraction. It is unclear at this time whether the potential sorption of sulfuryl fluoride to the plastic bag would have a significant impact on residue levels.

Residue levels of sulfuryl fluoride and fluoride anion in dried fruits and tree nuts for the three treatment regimes addressed by this study are shown in Table C.3 and summarized in Table C.4. Residue levels of sulfuryl fluoride varied considerably based on the commodity and the treatment regime. Following fumigation, chambers were actively aerated (approximately 1.5 chamber volumes/min; approximately 40 L/min). For most commodities, residues had dissipated to <2.1 ppb within 6 days of aeration following fumigation. Sulfuryl fluoride residues were more persistent in commodities with higher oil content (e.g, walnuts, pecans, almonds), typically requiring approximately 2 weeks for residues to dissipate to <2.1 ppb. At the same fumigation rate, residues of sulfuryl fluoride were greater following vacuum fumigation versus treatment at ambient pressure. In oily commodities, multiple fumigations resulted in higher residues of sulfuryl fluoride at a given aeration time.

Following a single fumigation, fluoride residues were typically below the limit of quantification in most samples. Noted exceptions are almonds (maximum residue = 5.96 ppm), pistachios (4.56 ppm), and pecans (9.59 ppm). Multiple fumigations resulted in increasing fluoride residues in all commodities.

Due to the variations in the data, it is inappropriate to pool data across the independent variables used in this study and as a result there are only 2 replicates for each fumigation use pattern.

TABLE C.1. Summary of Concurrent Recoveries of Sulfuryl Fluoride and Fluoride Anion from Dried Fruits and Tree Nuts.

Analyte	Matrix	Spike level	Sample size (n)	Mean ± std dev
Sulfuryl fluoride	Almonds	4.2 ng/g	21	64.4 ± 8.6
		21.1 ng/g	18	97.1 ± 11.6
	Dates	4.2 ng/g	6	114.3 ± 8.4
		8.4 ng/g	27	96.6 ± 10.0
	Dried Plums	4.2 ng/g	4	77.4 ± 4.6
		8.4 ng/g	9	97.5 ± 10.8

Analyte	Matrix	Spike level	Sample size (n)	Mean ± std dev
		21.1 ng/g	3	79.8 ± 5.8
	Figs	4.2 ng/g	6	90.9 ± 4.1
		8.4 ng/g	9	102.4 ± 10.7
	Pecans	4.2 ng/g	8	80.1 ± 19.2
		21.1 ng/g	26	110.8 ± 15.6
		105 ng/g	15	94.9 ± 8.2
	Pistachios	4.2 ng/g	9	77.5 ± 14.5
		21.1 ng/g	21	93.0 ± 11.1
		105 ng/g	3	109.2 ± 2.0
	Raisins	4.2 ng/g	3	70.6 ± 5
	Walnuts	4.2 ng/g	12	81.5 ± 12.3
		21.1 ng/g	12	109.9 ± 12.1
Fluoride anion	Almonds	4.8 - 5.2 µg/g	10	98.3 ± 13.5
	Dates	4.8 - 5.2 µg/g	11	85.1 ± 8.7
	Dried Plums	4.8 - 5.2 µg/g	10	88.6 ± 13.6
	Figs	4.8 - 5.2 µg/g	6	91.6 ± 5.8
	Pecans	4.8 - 5.2 µg/g	10	95.6 ± 14.2
	Pistachios	4.8 - 5.2 µg/g	10	101.7 ± 14.1
	Raisins	4.8 - 5.2 µg/g	1	97.3
	Walnuts	4.8 - 5.2 µg/g	4	91.2 ± 14.6

TABLE C.2. Summary of Storage Conditions

Matrix (RAC)	Storage Temp. (°C)	Actual Storage Duration (days)	Limit of Demonstrated Storage Stability (days)
Samples were analyzed for sulfuryl fluoride and/or fluoride anion immediately following the aeration period (see Table C.3 for aeration times).			

TABLE C.3. Residue Data from Post-harvest Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Rate, mg·hr/L (cumulative rate)	Sulfuryl Fluoride (ppb)					Fluoride Anion (ppm)
			Day 1	Day 2	Day 5	Day 8	Day 15	
A - Almonds	1	203	12.4, 10.9, NS, 11.9, 8.9	<2.1, <4.2, <2.1, <2.1, <2.1	NS	NS	NS	3.25, 3.20, NS, 3.44, 3.77 (Day 2)
A - Dates	1	208	<2.1, <2.1, <2.1, <2.1	NS	NS	NS	NS	<1.4, <1.4, <1.4, <1.4 (Day 6)
A - Dried Plums	1	219	<2.1, <2.1, <2.1, <2.1	NS	NS	NS	NS	<1.4, <1.4, <1.4, <1.4 (Day 1)

TABLE C.3. Residue Data from Post-harvest Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Rate, mg·hr/L (cumulative rate)	Sulfuryl Fluoride (ppb)					Fluoride Anion (ppm)
			Day 1	Day 2	Day 5	Day 8	Day 15	
A - Figs	1	197	<2.1, 4.7, 7.2, 4.7, 4.4	NS	NS	NS	NS	<1.4, <1.4, <1.4, <1.4, <1.4 (Day 1, Day 7-3rd sample)
A - Pecans	1	199	43.1, 32.2, 42.8, 53.6, 60.3	25.3, 23.3, NS, 21.7, 17.3	4.8, 7.4, NS, 4.9, 5.0	<2.1, <2.1, NS, <2.1, <2.1	NS	<1.4, <1.4, NA, <2.4, <2.4 (Day 8)
A - Pistachios	1	214	<2.1, <2.1, <2.1, <2.1	NS	NS	NS	NS	<2.4, <2.4, <2.4, 2.91 (Day 5)
A - Raisins	1	221	<2.1, <2.1, NS, <2.1, <2.1	NS	NS	NS	NS	<1.4, <1.4, <1.4, <1.4, <1.4 (Day 5)
A - Walnuts	1	217	74.1, 67.8, 79.0, 69.4	NS	<2.1, <4.2, <4.2, <4.2	<2.1, <2.1, <2.1, <2.1	NS	<1.4, <1.4, <1.4, <1.4 (Day 9)
B - Almonds	1	1534	33, 40, 33, 28	NS	NS	NS	NS	4.07, 4.48, 5.96, 4.13 (Day 1)
	2	1538 (3072)	75, 61, NS, 50, 44	34, 55, 42, 23, 22	8.1, 7.0, NS, NS, NS	NS	NS	7.94, 6.93, NS, 6.65, 7.97 (Day 5)
	3	1488 (4560)	125, 107, 128, 124	NS	14, 18, 14, 16	<4.2, <2.1, <4.2, <4.2	<2.1, <2.1, <2.1, <2.1	9.71, 9.90, 9.07, 9.37 (Day 15)
B - Dates	1	1484	8.3, 6.1, 8.1, 6.6	NSN	NS	NS	NS	<1.4, <1.4, <1.4, <1.4 (Day 4)
	2	1504 (2988)	<2.1, <2.1, <4.2, <4.2	NS	NS	NS	NS	<1.4, <1.4, <2.4, <2.4 (Day 5)
	3	1493 (4481)	7.1, 5.9, 6.2, 5.2	NS	NS	NS	NS	<2.4, <2.4, <2.4, <2.4 (Day 5)
	4	1503 (5984)	15, 12, 8.6, 11	NS	(Day 4) 11, 8.8, 7.5, 9.2	NS	NS	2.74, <1.4, <2.4, <2.4 (Day 4)
	5	1491 (7475)	15, 13, NS, 23, 16, NS	7.5, 11, NS, 19, 18, NS	7.9, 16, NS, 5.5, 6.0, NS	<4.2, <2.1, 8.0, <4.2, <4.2, 6.8	<2.1, <2.1, NS, <2.1, <2.1, NS	<2.4, 3.09, NS, <2.4, <2.4, NS (Day 15)
B - Dried Plums	1	1575	<2.1, <2.1, <2.1, <2.1	NS	NS	NS	NS	<1.4, <1.4, <1.4, <1.4 (Day 2)

TABLE C.3. Residue Data from Post-harvest Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Rate, mg·hr/L (cumulative rate)	Sulfuryl Fluoride (ppb)					Fluoride Anion (ppm)
			Day 1	Day 2	Day 5	Day 8	Day 15	
	2	1504 (3079)	<2.1, <2.1, <2.1, <2.1	NS	NS	NS	NS	<2.4, <2.4, <2.4, <2.4 (Day 2)
	3	1516 (4595)	<4.2, <2.1, <2.1, <4.2, <2.1, <2.1	NS	NS	NS	NS	<1.4, <2.4, NS, <2.4, 2.56, ND (Day 4)
	4	1521 (6116)	<2.1, <2.1, <2.1, <2.1	NS	NS	NS	NS	<2.4, 3.14, <2.4, <2.4 (Day 5)
B - Figs	1	1462	40, 41, 34, 33	NS	NS	NS	NS	<2.4, <2.4, <2.4, <2.4 (Day 6)
	2	1498 (2960)	11, 13, 13, 15	9.3, 8.8, <4.2, <4.2	4.5, 5.6, NS, NS	NS	NS	<1.4, <1.4, <2.4, 2.43 (Day 5)
B - Pecans	1	1533	2224, 2323, 2688, 2395	NS	104, 99, 103, 105	NS	(Day 10) 15, 16, 15, 20	7.72, 8.28, 9.59, 8.68 (Day 13)
	2	1452 (2985)	5040, NS, 5532, 4146	NS	NS	NS	(Day 12) 13, 12, 16, 14	15.0, 17.4, 15.6, 13.8 (Day 13)
	3	1510 (4495)	4276, 5209, 6030, 4287	3157, 3915, 1880, 1304	240, 261, 214, 199	68, 69, 57, 57	<2.1, <2.1, <2.1, <2.1	20.1, 21.8, 19.8. 21.6 (Day 16)
B - Pistachios	1	1517	252, 287, 267, 303	NS	18, 29, 24, 22	NS	NS	3.95, 4.29, 3.58, 4.56 (Day 7)
	2	1507 (3024)	63, 51, 69, 70	NS	<2.1, <2.1, <2.1, <2.1	NS	NS	12.6, 10.7, 9.98, 10.9 (Day 6)
	3	1506 (4530)	36, 35, 56, 52	8.1, 9.9, 16, 15	<2.1, <2.1, <2.1, <2.1	NS	NS	15.0, 16.7, 17.9, 13.2 (Day 5)
C - Almonds	1	218	18, 20, 12, 12	6.3, 8.8, <2.1, <4.2	(Day 3) <2.1, <2.1, <2.1, <2.1	NS	NS	<1.4, <1.4, <1.4, <1.4 (Day 7)
C - Pecans	1	206	1190, 1095, NS, 1306, 1139	369, 392, NS, 456, 462	51, 39, NS, 55, 47	4.5, 7.2, 5.8, 4.9, 5.8	<2.1, <2.1, NS, <2.1, <2.1	<2.4, <1.4, NS, <2.4, <2.4 (Day 16)
C - Pistachios	1	202	17, 26, 21, 13, 14	<2.1, <2.1, NS, <2.1, <2.1	NS	NS	NS	<1.4, <1.4, NS, <1.4, <2.4 (Day 3)

TABLE C.3. Residue Data from Post-harvest Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Rate, mg·hr/L (cumulative rate)	Sulfuryl Fluoride (ppb)					Fluoride Anion (ppm)
			Day 1	Day 2	Day 5	Day 8	Day 15	
C - Walnuts	1	183	591, 569, 610, 640	349, 290, 425, 384	92, 90, 101, 95	25, 24, 29, 29	<2.1, <2.1, <2.1, <2.1	<2.4, <1.4, <1.4, <1.4 (Day 15)

TABLE C.4. Summary of Residue Data from Crop Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Fumigation Rate, mg·hr/L (cumulative rate)	Aeration Time, days	Residue Levels*				
				n	Min.	Max.	Mean	Std. Dev.
Sulfuryl Fluoride, ppb								
A - Almond	1	203	1	4	8.90	12.40	11.03	1.55
A - Almond	1		2	5	1.05	2.10	1.26	0.47
A - Dates	1	208	1	4	1.05	1.05	1.05	0.00
A - Dried Plums	1	219	1	4	1.05	1.05	1.05	0.00
A - Figs	1	197	1	5	1.05	7.20	4.41	2.19
A - Pecans	1	199	1	5	32.20	60.30	46.40	10.85
A - Pecans	1		2	4	17.30	25.30	21.90	3.40
A - Pecans	1		5	4	4.80	7.40	5.53	1.25
A - Pecans	1		8	4	1.05	1.05	1.05	0.00
A - Pistachios	1	214	1	4	1.05	1.05	1.05	0.00
A - Raisins	1	221	1	4	1.05	1.05	1.05	0.00
A - Walnuts	1	217	1	4	67.80	79.00	72.58	5.05
A - Walnuts	1		5	4	1.05	2.10	1.84	0.53
A - Walnuts	1		8	4	1.05	1.05	1.05	0.00
B - Almond	1	1534	1	4	28.00	40.00	33.50	4.93
B - Almond	2	1538 (3072)	1	4	44.00	75.00	57.50	13.63
B - Almond	2		2	5	22.00	55.00	35.20	13.81
B - Almond	2		5	2	7.00	8.10	7.55	0.78
B - Almond	3	1488 (4560)	1	4	107.00	128.00	121.00	9.49
B - Almond	3		5	4	14.00	18.00	15.50	1.91
B - Almond	3		8	4	1.05	2.10	1.84	0.53
B - Almond	3		15	4	1.05	1.05	1.05	0.00
B - Dates	1	1484	1	4	6.10	8.30	7.28	1.09
B - Dates	2	1504 (2988)	1	4	1.05	2.10	1.58	0.61
B - Dates	3	1493 (4481)	1	4	5.20	7.10	6.10	0.79
B - Dates	4	1503 (5984)	1	4	8.60	15.00	11.65	2.65
B - Dates	4		5	4	7.50	11.00	9.13	1.45
B - Dates	5	1491 (7475)	1	4	13.00	23.00	16.75	4.35
B - Dates	5		2	4	7.50	19.00	13.88	5.54
B - Dates	5		5	4	5.50	16.00	8.85	4.88
B - Dates	5		8	6	1.05	8.00	3.69	2.93
B - Dates	5		15	4	1.05	1.05	1.05	0.00

TABLE C.4. Summary of Residue Data from Crop Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Fumigation Rate, mg·hr/L (cumulative rate)	Aeration Time, days	Residue Levels*				
				n	Min.	Max.	Mean	Std. Dev.
B - Dried Plums	1	1575	1	4	1.05	1.05	1.05	0.00
B - Dried Plums	2	1504	1	5	1.05	1.05	1.05	0.00
B - Dried Plums	3	1516	1	5	1.05	2.10	1.47	0.58
B - Dried Plums	4	1521	1	4	1.05	1.05	1.05	0.00
B - Figs	1	1462	1	4	33.00	41.00	37.00	4.08
B - Figs	2	1498 (2960)	1	4	11.00	15.00	13.00	1.63
B - Figs	2		2	4	2.10	9.30	5.58	4.02
B - Figs	2		5	2	4.50	5.60	5.05	0.78
B - Pecans	1	1533	1	4	2224.00	2688.00	2407.50	199.71
B - Pecans	1		5	4	99.00	105.00	102.75	2.63
B - Pecans	1		15	4	15.00	20.00	16.50	2.38
B - Pecans	2	1452 (2985)	1	3	4146.00	5532.00	4906.00	702.65
B - Pecans	2		15	4	12.00	16.00	13.75	1.71
B - Pecans	3	1510 (4495)	1	4	4276.00	6030.00	4950.50	842.09
B - Pecans	3		2	4	1304.00	3915.00	2564.00	1187.76
B - Pecans	3		5	4	199.00	261.00	228.50	27.50
B - Pecans	3		8	4	57.00	69.00	62.75	6.65
B - Pecans	3		15	4	1.05	1.05	1.05	0.00
B - Pistachios	1	1517	1	4	252.00	303.00	277.25	22.37
B - Pistachios	1		5	4	18.00	29.00	23.25	4.57
B - Pistachios	2	1507 (3024)	1	4	51.00	70.00	63.25	8.73
B - Pistachios	2		5	4	1.05	1.05	1.05	0.00
B - Pistachios	3	1506 (4530)	1	4	35.00	56.00	44.75	10.81
B - Pistachios	3		2	4	8.10	16.00	12.25	3.85
B - Pistachios	3		5	4	1.05	1.05	1.05	0.00
C - Almond	1	218	1	4	12.00	20.00	15.50	4.12
C - Almond	1		2	4	1.05	8.80	4.56	3.62
C - Almond	1		4	4	1.05	1.05	1.05	0.00
C - Pecans	1	206	1	4	1095.00	1306.00	1182.50	91.03
C - Pecans	1		2	4	369.00	462.00	419.75	46.35
C - Pecans	1		5	4	39.00	55.00	48.00	6.83
C - Pecans	1		8	5	4.50	7.20	5.64	1.04
C - Pecans	1		15	4	1.05	1.05	1.05	0.00
C - Pistachios	1	202	1	5	13.00	26.00	18.20	5.36
C - Pistachios	1		2	4	1.05	1.05	1.05	0.00
C - Walnuts	1	183	1	4	569.00	640.00	602.50	30.09
C - Walnuts	1		2	4	290.00	425.00	362.00	57.17
C - Walnuts	1		5	4	90.00	101.00	94.50	4.80
C - Walnuts	1		8	4	24.00	29.00	26.75	2.63
C - Walnuts	1		15	4	1.05	1.05	1.05	0.00
Fluoride Anion (ppm)								
A - Almond	1	203	2	4	3.20	3.77	3.42	0.26
A - Dates	1	208	6	4	0.70	0.70	0.70	0.00
A - Dried Plums	1	219	1	4	0.70	0.70	0.70	0.00

TABLE C.4. Summary of Residue Data from Crop Fumigation Trials with Sulfuryl Fluoride.

Treatment ID - Crop	Fumigation Number	Fumigation Rate, mg·hr/L (cumulative rate)	Aeration Time, days	Residue Levels*				
				n	Min.	Max.	Mean	Std. Dev.
A - Figs	1	197	1	5	0.70	0.70	0.70	0.00
A - Pecans	1	199	8	4	0.70	1.20	0.95	0.29
A - Pistachios	1	214	5	4	1.20	2.91	1.63	0.86
A - Raisins	1	221	5	5	0.70	0.70	0.70	0.00
A - Walnuts	1	217	9	4	0.70	0.70	0.70	0.00
B - Almond	1	1534	1	4	4.07	5.96	4.66	0.89
B - Almond	2	1538 (3072)	5	4	6.65	7.97	7.37	0.68
B - Almond	3	1488 (4560)	15	4	9.07	9.90	9.51	0.37
B - Dates	1	1484	4	4	0.70	0.70	0.70	0.00
B - Dates	2	1504 (2988)	5	4	0.70	1.20	0.95	0.29
B - Dates	3	1493 (4481)	5	4	1.20	1.20	1.20	0.00
B - Dates	4	1503 (5984)	4	4	0.70	2.74	1.46	0.89
B - Dates	5	1491 (7475)	15	4	1.20	3.09	1.67	0.95
B - Dried Plums	1	1575	2	4	0.70	0.70	0.70	0.00
B - Dried Plums	2	1504 (3079)	2	4	0.70	1.20	1.08	0.25
B - Dried Plums	3	1516 (4595)	4	4	0.70	2.56	1.42	0.80
B - Dried Plums	4	1521 (6116)	5	4	1.20	3.14	1.69	0.97
B - Figs	1	1462	6	4	1.20	1.20	1.20	0.00
B - Figs	2	1498 (2960)	5	4	0.70	2.43	1.26	0.82
B - Pecans	1	1533	13	4	7.72	9.59	8.57	0.79
B - Pecans	2	1452 (2985)	13	4	13.80	17.40	15.45	1.50
B - Pecans	3	1510 (4495)	16	4	19.80	21.80	20.83	1.02
B - Pistachios	1	1517	7	4	3.58	4.56	4.10	0.42
B - Pistachios	2	1507 (3024)	6	4	9.98	12.60	11.05	1.11
B - Pistachios	3	1506 (4530)	5	4	13.20	17.90	15.70	2.05
C - Almond	1	218	7	4	0.70	0.70	0.70	0.00
C - Pecans	1	206	16	4	0.70	1.20	1.08	0.25
C - Pistachios	1	202	3	4	0.70	1.20	0.83	0.25
C - Walnuts	1	183	15	4	0.70	1.20	0.83	0.25

* Note that residues are expressed as ppb for sulfuryl fluoride and ppm for fluoride anion. For purposes of calculating the summary statistics, ½ LOD or ½ LOQ values were used as follows: sulfuryl fluoride ½ LOD = 1.05 ppb, ½ LOQ = 2.1 ppb; fluoride anion ½ LOD = 0.7 ppm, ½ LOQ = 1.2 ppm.

D. CONCLUSION

These data are intended to address residue levels resulting from the post-harvest fumigation of dried fruits and tree nuts with sulfuryl fluoride. For both the parent compound and the fluoride ion, residues vary considerably between commodities, fumigation rate, fumigation number, and fumigation pressure. Pooling of data across those variables is, therefore, inappropriate. As a result, there are only 2 replicates for each fumigation regime. Generally, quantifiable residues of both sulfuryl fluoride and fluoride anion were more likely to be found in tree nuts than in dried fruit.

E. REFERENCES

Storage Stability: DER 45510302
Methods: DER 45603901

F. DOCUMENT TRACKING

RDI: MADoherty (12/9/03); WDrew (10/28/03); RALoranger (10/27/03)
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Processed Food and Feed - Fluoride in Cereal Grains

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STUDY REPORTS:

45396301. Rick, D., Marty, G., Krieger, S. McGuirk, R. (2000) Evaluation of Sulfuryl Fluoride Fumigation Variables on Residue Levels in Crop Commodities: Laboratory Identification Number: 001103. Unpublished study prepared by Dow AgroSciences LLC 108 p.

EXECUTIVE SUMMARY:

As part of a study examining the effects of various fumigation parameters on the residue levels of sulfuryl fluoride and fluoride anion in cereal grains, the petitioner included a processing study describing levels of fluoride anion in commodities obtained from the processing of treated wheat and corn grain. Residues of sulfuryl fluoride were not analyzed for this study.

Wheat and corn grain were fumigated under controlled conditions at a rate of 1787 and 1565 mg·hr/L, respectively. Following a 24-hour aeration period, the grain samples were analyzed for fluoride anion levels and shipped to Texas A&M University for processing and subsequent fluoride analysis. Fluoride analysis was by aqueous extraction with quantitation by double-known addition fluoride-selective electrode. Sample storage times and conditions are supported by available storage stability data. Samples of raw commodities were processed using simulated standard commercial practices. Wheat bran and wheat germ showed concentration factors of 2.56 and 4.82X, respectively. Fluoride anion residues in other processed wheat commodities were less than or equal to those in the whole grain. Of the corn commodities, only aspirated grain fractions showed a concentration (5.49X) of fluoride residues.

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the data depicting residues in processed foods are classified as scientifically acceptable.

The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document (DP Barcode D283007).

COMPLIANCE:

Signed and dated GLP, quality assurance, and data confidentiality information were provided. There is no claim of confidentiality and all phases of the study followed Good Laboratory Practice standards.

A. BACKGROUND INFORMATION

Sulfuryl fluoride is a fumigant pesticide being proposed as a methyl bromide replacement for control of insect pests in a number of scenarios. It breaks down to form sulfate and fluoride anion. This document addresses fluoride anion only.

TABLE A.1. Test Compound Nomenclature	
Compound	F^-
Common name	Fluoride
Company experimental name	-none-
IUPAC name	Fluoride
CAS name	Fluoride
CAS #	16984-48-8
End-use product/EP	Profume

TABLE A.2. Physicochemical Properties of Fluoride		
Parameter	Value	Reference
Melting point/range	No physical/chemical properties were provided for ionic fluoride.	
pH		
Density		
Water solubility (__°C)		
Solvent solubility (mg/L at __°C)		
Vapour pressure at __°C		
Dissociation constant (pK_a)		
Octanol/water partition coefficient Log(K_{OW})		
UV/visible absorption spectrum		

B. EXPERIMENTAL DESIGN

B.1. Application and Crop Information

Bulk samples of grain were fumigated at 1787 mg·hr/L (wheat) or 1565 mg·hr/L (corn) with sulfuryl fluoride. See DER 45396301 addressing the residues in grain for further details.

B.2. Sample Handling and Processing Procedures

The treated grain samples were processed by Texas A&M University and shipped to Dow Agrochemical for fluoride analysis. Information regarding the storage conditions at the processing facility and the processing techniques used to generate the processed corn and wheat commodities was not included with the submission.

B.3. Analytical Methodology

Method GRM 01.17 was used to analyze fluoride anion residues. The method extracts fluoride into water, and uses a fluoride selective electrode and the double known addition technique to detect and quantify residues. The LOD and LOQ of the method are 0.2 and 2.0 ppm, respectively. The method has undergone review by BEAD's Analytical Chemistry Branch (ACB). The ACB recommended that the method be radiovalidated and that OPP accept the method for tolerance-enforcement purposes.

C. RESULTS AND DISCUSSION

Information regarding storage conditions and intervals were not provided for the processing study. Based on the submitted storage stability data, residues of fluoride may change with storage time. The importance of this potential dissipation as relates to the processing study cannot be determined until further information is provided regarding the handling and storage of the samples used in this study.

Samples were analyzed for fluoride residues using the proposed tolerance enforcement method. The ability of the method to extract weathered fluoride residues has not been assessed; however, based on the recommendations of the ACB, it is likely to be adequate for purposes of this study. Processed commodities were generated using simulated standard commercial practices. Processing factors derived from these commodities should reflect the potential for processing to affect residues of fluoride in actual processed cereal grains.

The submitted data indicate that fluoride anion residues concentrate in wheat bran, wheat germ, and corn aspirated grain fractions, and that tolerances separate from those of the unprocessed grain may be appropriate for those commodities. The actual need for separate tolerances will depend on the residue levels that occur from direct fumigation of the processed commodities. The empirical processing factors for wheat bran (2.56X) and corn aspirated grain fractions (5.49X) are less than the theoretical maximum factors (7.7 and 200X, respectively). The OPPTS Guidelines do not list a theoretical concentration factor for wheat germ.

Table C.1. Summary of Concurrent Analytical Method Validation.					
Commodity	Fortification Level (ppm)	Recoveries (%)	Mean Recovery ± SD	LOD (ppm)	LOQ (ppm)
Concurrent recovery data associated with the processing study were not provided in the submission. Concurrent recoveries for other fluoride analysis associated with MRID 45396301 ranged from 100-145%.				Not Reported	0.3 - 0.8

Table C.2. Summary of Storage Conditions			
Matrix (RAC)	Storage Temp. (°C)	Actual Storage Duration (days)	Interval of Demonstrated Storage Stability (days)
Corn	22	51-52	140
Wheat	22	45-49	138

Table C.3 Residue Data from the Cereal Grain Processing Study with Fluoride.					
RAC	Processed Commodity (F^- in Control)	Total Rate (mg·hr/L)	Aeration Interval (hours)	Residues (ppm)*	Processing Factor
Wheat	Whole Grain (<LOQ)	1787	24	1.19	---
	Flour (<LOQ)			0.45	0.38
	Shorts (0.34)			1.50	1.26
	Bran (<LOQ)			3.05	2.56
	Middlings (<LOQ)			0.72	0.60
	Impurities (0.31)**			1.07	0.90
	Germ (<LOQ)			5.74	4.82
Corn	Whole Grain (<LOQ)	1565	24	1.76	---
	Flour (0.49)			1.29	0.73
	Meal (<LOQ)			1.37	0.78
	Grits (<LOQ)			0.83	0.47
	Oil (<LOQ)			<LOQ	---
	Impurities (<LOQ)**			9.67	5.49
	Wet Oil (<LOQ)			<LOQ	---
	Wet Starch (0.40)			<LOQ	---

* Residue values are the average of two measurements per commodity. Individual residue values were not provided as part of the submission. For commodites with quantifiable fluoride residues in control samples, the residue values reflect the net residue (i.e., the measured residue - control residue).
** Impurities are described as being similar to aspirated grain fractions.

D. CONCLUSION

Some concentration of fluoride residues appears to occur when converting cereal grain treated with sulfuryl fluoride into bran, germ, and aspirated grain fractions.

E. REFERENCES

Analytical Methods: DER 45603901

Storage Stability: DER 45510302

F. DOCUMENT TRACKING

RDI: MADoherty (10/16/03); WDrew (10/28/03); RALoranger (10/27/03)
Petition Number(s): PP1F06312
PC Code: 078003

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