Australian Pesticides & Veterinary Medicines Authority

CHEMISTRY AND RESIDUES PROGRAM

RESIDUES EVALUATION REPORT

NCRIS/ATS No.:	59952/37112
Product_name:	Profume Gas Fumigant
Active Constituent(s):	Sulfuryl fluoride
Applicant Name:	Dow AgroSciences Australia Ltd
Purpose of application:	To register a new fumigant product

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EXECUTIVE SUMMARY

Dow AgroSciences Australia Ltd has applied for registration of a new product containing the active constituent sulfuryl fluoride. The product is a gas used for control of insect pests in various situations including grain storages silos and warehouses, in fumigation chambers and food processing facilities such as mills. The product will also be used for seed intended for sowing and for hay fumigation. A number of non-food situations are also specified on the product label, which include fumigation of dwellings, buildings, construction materials, furnishings, machinery, vehicles and shipping containers.

The proposed use pattern for sulfuryl fluoride (at standard temperature and pressure) is a maximum target concentration of **128 g/m^3** with a maximum fumigant dosage of **1500 CT or 1500 g hr/m^3**. The food commodities specified on the draft product label included cereal grains and processed fractions, dried fruit and nuts. The proposed withholding period is 24 hours.

Sulfuryl fluoride residues in varying types of wheat following fumigation (single and repeat fumigations) ranged <0.008 – 0.028 mg/kg. In rice grain (white, brown and polished), sulfuryl fluoride residues ranged <0.008 – 0.025 mg/kg. Sulfuryl fluoride residues in corn ranged <0.008 – 0.026 mg/kg. The range of sulfuryl fluoride concentrations for each of the whole grain commodities was similar, following fumigation for 24 hours and sampling at 1 day after fumigation. The concentrations of sulfuryl fluoride in wheat, following either a single or repeat fumigations, were also similar. On the basis of the data generated for wheat, rice, barley, oats and corn, an MRL of 0.05 mg/kg sulfuryl fluoride is recommended for cereal grains.

Different types of Australian wheat sourced from NSW, Qld, SA and WA were fumigated at 1500 CTP. Fluoride ion residues ranged from 0.5 to 2.1 mg/kg in the fumigated wheat. The trial was non-GLP, however the range of fluoride residues were within the range of concentrations found in overseas trials. The STMR is 0.89 mg/kg and the HR is 2.1 mg/kg. The Australian data are used in the chronic dietary estimates for fluoride, as the results are reflective of concentrations in grain to which Australian consumers are most likely to be exposed.

The data for repeat fumigations vs single fumigations of wheat do not show any clear trends with respect to accumulation of fluoride ion concentrations, therefore the current MRL of 7 mg/kg for fluoride ion in cereal grains would remain appropriate for repeat fumigations, noting that median residues in the Australian trial were 0.89 mg/kg. In addition, a very large proportion of the cereal grains that are produced in Australia are consumed domestically and would not be fumigated more than once, therefore a higher level is not necessarily required for the proposed Australian GAP. Grain that is subjected to repeat fumigations would most likely be exported rather than used for domestic consumption.

In relation to processed grain commodities, a processing study was conducted after fumigation of wheat and corn. Concentration of fluoride ion residues was observed in wheat shorts, bran and germ, with calculated processing factors of 1.2, 2.45 and 4.6, respectively. As wheat bran and wheat germ are traded commodities, it is appropriate to establish individual MRLs for these. The highest residues in Australian wheat were 2.1 mg/kg, therefore fluoride residues in wheat bran and wheat germ are 5.1 mg/kg and 9.66 mg/kg, respectively. An MRL of 10 mg/kg is recommended for wheat germ.

As fumigation of processed fractions could not be accommodated due to the large contribution to the chronic dietary estimate of fluoride ion residues from such commodities

(such as flour, bran, cereal fractions), processed fractions are not supported for inclusion on the label at this time. This may be considered further once FSANZ have undertaken a total modelling of fluoride exposure to all food and water. The commodities that are supported for inclusion on the label are all whole cereal grains, dried fruits and nuts. As peanuts are not part of the Codex crop group Tree Nuts, a separate MRL for peanuts is required.

The estimated chronic dietary intake of sulfuryl fluoride and fluoride ion arising from residues in food is unlikely to exceed the health standards. The estimated short-term (or acute) dietary intake of sulfuryl fluoride arising from residues in food is unlikely to exceed the health standards.

Use of the product in accordance with the above label instructions is unlikely to pose a risk to Australian trade as Codex MRLs for sulfuryl fluoride were established in 2006 for cereal grains and processed fractions, dried fruit and tree nuts. Relevant MRLs have also been established by the USA, Japan and Germany. Users and producer groups however are requested to provide comment through the normal consultation mechanism, which is the APVMA Public Release Summary.

DISCUSSION

1. INTRODUCTION

1.1 Background to the application

Dow AgroSciences Australia Ltd has applied for registration of a new product containing the active constituent sulfuryl fluoride. The product is a gas used for control of insect pests in various situations including grain storages silos and warehouses, in fumigation chambers and food processing facilities such as mills. The product will also be used for seed intended for sowing and for hay fumigation. A number of non-food situations are also specified on the product label, which include fumigation of dwellings, buildings, construction materials, furnishings, machinery, vehicles and shipping containers.

Profume is packaged in a cylinder under pressure and contains 56.7 g of product comprising 99.8% sulfuryl fluoride (SO_2F_2) and 0.2% inert ingredients.

The relevant chemical properties of sulfuryl fluoride are shown below:

Molecular formula	SO_2F_2
Formula weight	102.1
Boiling point	-54 °C
Vapour pressure	1611 kPa at 20 °C
Specific gravity	1.35 at 20 °C

1.2 Label and maximum treatment regime

The proposed use pattern for sulfuryl fluoride (at standard temperature and pressure) is a maximum target concentration of **128 g/m^3** with a maximum fumigant dosage of **1500 CT or 1500 g hr/m^3**. The food commodities specified on the draft product label include cereal grains and processed fractions, dried fruit and nuts.

The product is supplied with a fumigation manual and requires appropriate training prior to use. A 'Fumiguide' is provided with the product, which allows the user to calculate the appropriate dosage for a given size of storage or structure, for vacuum fumigations and tightly sealed structures. Some of the input parameters include the volume of the storage structure, the temperature of the storage, the pressure of the system and the exposure times for effective fumigation. The outputs are the required dosage (CT), the effective concentration for the specified pest(s) and the quantity of the product.

A factor affecting the amount of fumigant needed is the extent of sorption by the commodity. The rate of sorption depends on the commodity; generally commodities with a high oil content such as oilseeds or with a higher surface area to volume ratio will have a higher sorption rate.

Restraints: DO NOT APPLY WHEN THE TEMPERATURE WITHIN THE COMMODITY TO BE FUMIGATED IS BELOW 5 °C.

At low temperatures the efficacy of the fumigant may not be optimal due to a decrease in the pressure; at low temperatures higher dosages may be required unless the storage or structure is heated.

Withholding periods: The proposed withholding period is Nil.

The instructions on the label of the registered product in the US state that for bulk commodities such as grains, *the commodity should be actively aerated for a minimum of 24 hours prior to offering to consumers*.

Aeration and Re-entry: For re-entry purposes, a minimum re-entry period of 6 to 8 hours is specified on the product label, depending on the volume of the structure to be fumigated. For structures fumigated at 16 g/m^3 or less, the re-entry period is a minimum of 6 hours from the start of aeration as specified. For structures fumigated at concentrations greater than 16 g/m^3, the minimum re-entry period specified is a minimum of 8 hours from the start of aeration as specified.

On the basis of the draft re-entry instructions, the proposed withholding period is effectively a minimum of 6 to 8 hours.

1.3 Applicant's proposed MRLs, residue definition and withholding periods

The Applicant has proposed the following MRLs for sulfuryl fluoride and inorganic fluoride in various commodities:

Commodity	SO_2F_2 (mg/kg)	Inorganic F (mg/kg)
Cereal grains		
barley	0.01	10
maize	0.04	7
oats	0.01	17
rice	0.04	10
wheat	0.05	25
other grains	0.05	24
Dried fruit		
dates	0.03	5
dried plums	0.01	5
figs	0.05	5
raisins	0.01	5
other dried fruit	0.05	5
Tree nuts		
almonds	0.2	10
pecans	6	23
pistachios	0.5	18
walnuts	6	30
other tree nuts	6	30

1.4 Current Australian MRLs and residue definition

There are no relevant MRLs for sulfuryl fluoride or an associated residue definition in Australia. However there is an MRL of 7 mg/kg for fluoride ion in cereal grains, fruits and vegetables. The basis of the existing MRLs is unknown.

1.5 Toxicological information

The following toxicological standards have been recommended by the Office of Chemical Safety, Department of Health and Ageing: ADI and ARfD lists current to 31 December 2006.

Compound	Dietary Standard, mg/kg bw		No Observable Effect Level (NOEL), mg/kg bw	Safety Factor	Reference
Sulfuryl fluoride	ADI[1]	0.01	20 ppm (inhalation)		25/8/2006 report

1 http://www.tga.gov.au/docs/pdf/adi.pdf

	ARfD[2]	0.3	31 (300 ppm inhalation)	100	

2. BIBLIOGRAPHY OF DATA

A list of new data provided by the applicant to address the data requirements described in the Requirements Series (Parts 4, 5A and 5B) and/or relevant Residue Guidelines is shown below in Table 1.

There are noted discrepancies between the study list and the studies that were provided and reviewed as part of this application. The additional studies that do not appear on the study list are highlighted in Attachment 1.

2 http://www.tga.gov.au/docs/pdf/arfd.pdf

Table 1: Data List Provided For Profume Gas Fumigant

APVMA Data No	Applicants Ref	Author(s)	Title	Date	Data Type	Data Sub-type
1797	104331	Davis, B.	Independent Laboratory Validation of Dow AgroSciences LLC Method GRM 01.12- Determination of Residues of Sulfuryl Fluoride in Dried Fruit and Tree Nuts by Gas Chromotography with Electron Capture Detection	Mar-02	Residues	Analytical Methods
1796	103384	Davis, B.	Independent Laboratory Validation of Dow AgroSciences LLC Method 'Determination of Residues or Sulfuryl Fluoride in Corn, Wheat and Rice Commodities by Gas Chromatography with Electron Capture Detection,' as included in Lab Report Codes: 0011057, Appendix B, 'Magnitude of the Terminal Fluoride Ion Level in Cereal Grain Commodities Fumigated with Sulfuryl Fluoride'.	Mar-02	Residues	Analytical Methods
1800	135376	Creasy, S.R., Hartsell, R.L., Hurley, J.M., Mukker, G.K., Bunnell, J., Byrne, S.L.	Determination of Residues of Sulfuryl Fluoride as Fluoride in Dried Fruit and Tree Nuts Using a Fluoride Selective Electrode with a Double Known Addiction Calibration Technique	Jun-01	Residues	Analytical Methods
1795	103563	Davis, B.	Independent Laboratory Validation of Dow AgroSciences LLC Method 'Residue Method Valuation 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'.	Feb-02	Residues	Analytical Methods
1887	OR06	Davis, B	Independent Laboratory Validation of Dow AgroSciences LLC Method GRM 01.11 – Determination of Residues of Sulfuryl Fluoride as Fluoride in Dried Fruit and Tree Nuts Using a Fluoride-Selective Electrode with a Double Known Addition Calibration Technique	Apr-02	Residues	Analytical Methods
1886	OR02a	Davis, B	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 Codes: 0011057, Appendix B, 'Magnitude of the Terminal Fluoride Ion Level in Cereal Grain Commodities Fumigated with Sulfuryl Fluoride' AMENDED REPORT	Jun-03	Residues	Analytical Methods
1798	104584	Lala M., Randolph, R	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.	Mar-02	Residues	Analytical Methods
1888	102607	Barnekow, D.E and Foster, D.R	Interim Report-Storage stability of Sulfuryl Fluoride on SKC 1g Anasorb CSC Tubes at Ambient and Frozen Temperature Conditions	Jun-02	Residues	Analytical Methods
1792	103283	Barnekow, D.E.	Evaluation of the Extraction Efficiancy of the Direct Diffusion Fluoride-Ion Selective Probe Analysis Method by Direct Comparison to the Total Fluoride Neutron Activation Anaylisis Technique.	Jun-02	Residues	Analytical Methods
1783	86560	Rick, D.L., Marty, G.T.,	Magnitude of the Terminal Fluoride Ion Level in Cereal Grain Commodities	Sep-01	Residues	Crop Residues Human

		Krieger, S.M., Byrne, S.L., Barnekow, D.E.	Fumigated with Sulfuryl Fluoride			Consumption
1782	79999	Rick, D.L., Marty, G.T., Krieger, S.M., McGuirk, R.J.	Evaluation of Sulfuryl Fluoride Fumigation Variables on Residue Levels in Crop Commodities	Dec-00	Residues	Crop Residues Human Consumption
1791	102816	Bostock, N., Foster, D.R.	Residues of Fluoride Ion Following Fumigation of a Mill with Sulfuryl Fluoride in Grain, Flour and Bran Produced Immediately After Restart of Production and in Commodities Placed in the Mill Prior to Fumigation – North America 2002	Jun-02	Residues	Crop Residues Human Consumption
1781	76344	Hartsell, R.L.	To determine and evaluate the Significance of Sulfuryl Fluoride Residues in Dried Fruits and Tree Nuts Following Fumigation Treatments with Sulfuryl Fluoride at Different Teperatures, Sample Locations, Desorption Rates, Repeated Fumigations, and A comparison of Treatments Done under Vaccum or Normal Atmospheric Pressure – Phase 1	Jun-00	Residues	Crop Residues Human Consumption
1789	102840	Perkins, J.M., Foster, D.R.	Residues of Fluoride Ion in Cereals and Commodities Following Fumigation of a Flour Mill with Sulfuryl Fluride – Italy 2001	July 2002a	Residues	Crop Residues Human Consumption
1793	135284	Machalinski, B.	Fluoride Levels and Distrabution in Hen Eggs with Respect to Selected Biological Parameters	Jan-96	Residues	Crop Residues Human Consumption
1790	102839	Perkins, J.M., Foster, D.R.	Residues of Fluoride Ion in Flour produced immediately after Fumigation of a Mill with Sulfuryl Fluride, Italy – 2001	Jul-02	Residues	Crop Residues Human Consumption
1786	102837	Perkins, J.M., Foster, D.R.	Residue of Fluoride Ions in Cereals following Fumigations of a Flour Mill with Sulfuryl Fluoride – UK 2000	Jun-02	Residues	Crop Residues Human Consumption
1788	102855	Blaschke, U.	Residues of Fluoride Ion Following Fumigation of a Mill with Sulfuryl Fluoride in Flour and Bran produced immediately after restart of Production and in Commodities placed in the Mill prior to Fumigation, Germany – 2002	Jul-02	Residues	Crop Residues Human Consumption
1787	102967	Bostock, N., Foster, D.R.	Residues of Fluoride Ion Following Fumigation of a Mill with Sulfuryl Fluoride in Grain, Flour and Bran that may be retained in Machinery during Fumigation, in Flour and Bran produced immediately after restart of Production and in Commodities placed in the Mill prior to Fumigation, UK – 2002	Jul-02	Residues	Crop Residues Human Consumption
1785	103138	Perkins, J.M., Foster, D.R.	Residue of Fluoride Ions in Cereals following Fumigations of a Flour Mill with Sulfuryl Fluoride – Gemany 2000	Jan-02	Residues	Crop Residues Human Consumption
1784	111349	Byrne, L.L., Hartsell, P.L., Hurley, J.M., Allred, D.B., Carmona, L.M., Bunnel, J.	Magnitude of the Sulfuryl Fluoride and Terminal Fluoride Ion Levels in Dried Fruit and Tree Nut Commoditites Fumigated with Sulfuryl Fluoride	Oct-01	Residues	Crop Residues Human Consumption
1893	111689	Creasy, S.R., Hartsell, P.L. and Hurley, J.M	Determination of Sulfuryl Fluoride and Fluoride Ion Residuals in Corn, Rice, Soybean and Wheat following Fumigation	Dec-01	Residues	Crop Residues Human Consumption
1801	135210	Creasy, S.R., Hartsell, R.L., Hurley, J.M., Carmona, L.M., Byrne, S.L.	Determination of Residues of Sulfuryl Fluoride in Dried Fruit and Tree Nuts by Gas Chromatography with Electron Capture Detection	Jul-01	Residues	Crop Residues Human Consumption
1891	NR09	Rick, D.L., Kreiger, S.M.,	Magnitude of the terminal fluoride ion level in finished food products	Mar-03	Residues	Fate – Storage,

		Mielke, M.S.	fumigated with sulfuryl fluoride			Processing and Cooking
1889	Z40	Prabhakaran, S.K., Schneider, B.	Quality Characteristics of Rice Treated with ProFume* Gas Fumigant (Sulfuryl Fluoride)	Dec-01	Residues	Fate – Storage, Processing and Cooking
1794	104591	Forster, D.R.	Storage Suitibility of Fluoride in Cereal Grain and Flour, Dried Fruit (Rasins), Nuts (Wallnuts), and Corn Grain Meal.	Sep-01	Residues	Fate – Storage, Processing and Cooking
1890	NB18	Scheffrahn, R. H., Osbrink, W. L. A., Hsu, R. C., and Su, N. Y.	Post-Fumigation Fate of Sulfuryl Fluoride: Desorption from Structural Commodities and Transient and Permanent Residue in Protected and Exposed Foodstuffs, Unpublished Report of DowAgroSciences,. (Ref B7.1/01, NB18)	4-Sep-87	Residues	Fate – Storage, Processing and Cooking
1799	135375	Rick, D.L., Marty, G.T., Foster, D.R.	Determination of Fluoride Anion in Corn, Wheat, Corn Oil and Flour with a Fluoride Selective Electrode	Apr-02	Residues	Other Information

3. RESIDUES EVALUATION

3.1 Metabolism

The metabolism of sulfuryl fluoride in plants is not well described. The studies provided did not meet contemporary requirements for plant metabolism studies. However as sulfuryl fluoride is a fumigant, conventional metabolism studies are not required.

Sulfuryl fluoride is converted to sulphate and fluoride ions upon contact with protein molecules:

$$SO_2F_2 + H_2O \rightarrow SO_4^{2-} + 2F^- + 4H^+$$

Sulphate ions are not considered to be of toxicological concern. The residues that are of concern as a result of fumigation are sulfuryl fluoride itself and fluoride ion (or inorganic fluoride), which forms after fumigation.

3.2 Analytical methods and storage stability

Methods for the determination of both sulfuryl fluoride residues and fluoride ion residues were provided for a number of commodities including whole cereal grains and processed fractions, corn and corn oil, dried fruit and nuts.

Fluoride ion was quantified using a fluoride selective electrode with a known double addition technique. The limits of quantitation ranged from 0.5 to 4 mg/kg in a range of commodities that were analysed (section 9).

Sulfuryl fluoride residues in fumigated commodities were determined by head-space determinations using GC/ECD. The limits of quantitation ranged from 4.2 to 8 μg/kg in a range of commodities. The details of the methods and independent laboratory validations are described in section 9 of this report.

The stability of fluoride ion residues in stored fumigated commodities such as wheat grain, wheat flour, raisins, walnuts, corn grain and corn meal was investigated for up to 140 days in freezer conditions. The stability was demonstrated to be acceptable for all commodities with the exception of wheat flour, in which some degradation occurred up to 140 days.

The stability of sulfuryl fluoride residues in stored commodities was demonstrated by sorption of the fumigant in charcoal air sampling tubes and storage of the tubes in both ambient conditions for up to 46 days and under freezer storage conditions for up to 180 days. Under both sets of conditions, the residues of sulfuryl fluoride were demonstrated to be stable. Details of both storage stability studies are described in section 9 of this report.

3.3 Residue definition

The proposed residue definition for sulfuryl fluoride in fumigated commodities is *sulfuryl fluoride*. The terminal residue that forms as a result of sulfuryl fluoride fumigation is inorganic fluoride, which should also be considered as part of the residue for the purposes of monitoring and dietary exposure assessment. However as inorganic fluoride is naturally occurring and is present in the environment, it is not suitable for the purposes of monitoring for compliance.

Therefore, the residue definition for monitoring and compliance purposes is:

Sulfuryl fluoride *sulfuryl fluoride*

And, the residue definition for dietary intake purposes is:

Sulfuryl fluoride and inorganic fluoride ion (both determined separately)

As fluoride ion is already defined in Table 3 of the MRL Standard under ***Fluorine (inorganic salt)***, another entry is not required. The existing entry is:

Fluorine (inorganic salt) *Fluoride ion*

The same definition appears in the Australia New Zealand Food Standards Code.

The relevant entries recommended for inclusion in Table 3 of the APVMA MRL Std are therefore:

Sulfuryl fluoride *sulfuryl fluoride*
(***See also Fluorine (inorganic salt))***

The above definitions are the same as those proposed by the 2005 JMPR and ratified by CAC 2006.

3.4 Residues in foods and animal feeds

3.4.1..Cereal grains and processed commodities

Fumigation studies were conducted under laboratory conditions and in mills in the US and Europe, with CTPs ranging 200 to 2366 mg hr/L. Sulfuryl fluoride residues in grains and processed grain commodities following fumigation at CTPs corresponding to 1500 mg hr/L are tabulated below. The fumigation experiments included single fumigations for a number of commodities, as well as repeat fumigations for wheat only.

Commodity	CTP (values and range) mg hr/L	Range of SO_2F_2 residues (µg/kg)	Range of fluoride residues, mg/kg
Wheat (single fumigation)			
Wheat (AUS)	1500		0.5 – 2.1 (mean 1.08)
Wheat grain (US)	1883 – 1892	<8 – 9	1.84 – 1.94 (mean 1.93, 1.88)
Wheat grain (Ger)	2016		11.4, 14.3
Wheat grain (UK)	1814		12.3 (organic), 14.3 (consort)
Wheat grain (UK)	1595		9.21 (organic), 14.28 (mill blend)
Wheat (Italy)	1387		4.5 (organic), 6.18 (Canadian)
Wheat (US)	1626		9.09
Durum wheat	1500		1.93 – 2.24 (mean 2.08)
	943 – 1803		3.61 – 5.8 (value of 23.6 not selected from that trial)
SRWW	1500		3.38 – 4.84 (mean 4.05)
	943 – 1803		1.42 – 6.06
HRWW	1500		2.64 – 3.5 (mean 3.025)
	943 – 1803		2.12 – 6.54
Wheat (repeat fumigations)	1707 – 2262	<8 – 28	3.1 – 8
Rice (single fumigations)			
Rice grain (US)	2186 – 2240	<8 – 25	5.49 – 8.46
Rice grain (Ger)	2016		6.75
Rice grain (UK)	1814		14.6
White rice	943 – 1803		3.21 – 16.1
	1500		1.83 – 2.03 (mean 1.95)
Rice grain (US)	1626		7.86

Rice (Italy)	1387		3.56
Brown rice	943 – 1803		3.84 – 11.8
Brown rice (UK)	1595		8.35
	1500		2.16 – 2.38 (mean 2.23)
Polished rice	1979 – 2212	<8 (2)	1.3 – 1.6
Barley (single fumigations)			
Barley	943 – 1803		4.27 – 9.25
Barley (Ger)	2106		23.3
Barley (UK)	1814		21
	1595		18.38
Barley (Italy)	1387		11.75
Barley (US)	1626		18.27
	1500		2.76 – 3.05 (mean 2.88)
Oats (single fumigations)			
Oats (US)	943 – 1803		6.82 – 15.25
	1500		7 – 8.27 (mean 7.54)
Corn (single fumigations)			
Corn (US)	1643 – 1726	<8 – 26	2.07 – 2.25
White corn	943 – 1803		1.03 – 5.31
	1500		1.31 – 1.64 (mean 1.43)
Popcorn	943 – 1803		1 – 2.05
	1500		0.76 – 1.41 (mean 1.00)

Sulfuryl fluoride residues in varying types of wheat following fumigation (single and repeat fumigations) ranged <0.008 – 0.028 mg/kg. In rice grain (white, brown and polished), sulfuryl fluoride residues ranged <0.008 – 0.025 mg/kg. Sulfuryl fluoride residues in corn ranged <0.008 – 0.026 mg/kg. The range of sulfuryl fluoride concentrations for each of the whole grain commodities was similar, following fumigation for 24 hours and sampling at 1 day after fumigation. The concentrations of sulfuryl fluoride in wheat, following either a single or repeat fumigations, were also similar.

Combining the sulfuryl fluoride residues in various grains, the values are in rank order: <0.008, 0.008, 0.009 (3), 0.011, 0.016, 0.020, 0.021, 0.022, 0.023, 0.025, 0.026, 0.028 mg/kg; the estimated STMR is 0.018 mg/kg and the highest residue (HR) is 0.028 mg/kg. On the basis of the data generated for wheat, rice, barley, oats and corn, an MRL of 0.05 mg/kg sulfuryl fluoride is recommended for cereal grains.

Different types of Australian wheat sourced from NSW, Qld, SA and WA were fumigated at 1500 CTP. Fluoride ion residues ranged from 0.5 to 2.1 mg/kg in the fumigated wheat. The trial was non-GLP, however the range of fluoride residues were within the range of concentrations found in overseas trials. The fluoride ion residues are in rank order: <0.5, 0.56, 0.56, 0.59, 0.63, 0.80, 0.84, 0.86, 0.87, 0.88, 0.89, 0.91, 0.96, 1.1, 1.2, 1.2, 1.5, 1.9, 1.9, 2.0, 2.1 mg/kg. The STMR is 0.89 mg/kg and the HR is 2.1 mg/kg. The Australian data are used in the chronic dietary estimates for fluoride, as the results are reflective of concentrations in grain that Australian consumers are most likely to be exposed to. In varying wheat varieties used in trials conducted in Europe and in the US, fluoride residues ranged 1.42 – 14.3 mg/kg.

The data for repeat fumigations vs single fumigations of wheat do not show any clear trends with respect to accumulation of fluoride ion residues , therefore the current MRL of 7 mg/kg for fluoride ion in cereal grains would remain appropriate for repeat fumigations, noting that median residues in the Australian trial were 0.89 mg/kg. In addition, a very large proportion of the cereal grains that are produced in Australia are consumed domestically and would not be fumigated more than once, therefore a higher level is not necessarily required for the proposed Australian GAP. Grain that is subjected to repeat fumigations would most likely be exported rather than used for domestic consumption.

In trials conducted overseas, fluoride ion residues in barley grain ranged 2.76 – 23.3 mg/kg; fluoride ion residues in oats ranged 7 – 15.25 mg/kg. In rice grain, fluoride ion residues ranged 1.3 – 16.1 mg/kg and in corn (including popcorn) fluoride ion residues ranged 0.76 – 5.31 mg/kg. Overall, the fluoride ion residues in grains ranged from 0.76 – 23.3 mg/kg (including analysis of replicate samples).

The fluoride ion concentrations in cereal grains are in rank order: 1, 1.43, 1.52, 1.86, 1.92, 1.94, 1.96, 2.05, 2.08, 2.23, 2.25, 2.26, 2.8, 2.88, 2.92, 3.08, 3.1, 3.56, 3.59, 3.94, 4.05, 4.5, 5, 5.02, 5.02, 5.31, 5.49, 5.65, 5.8, 5.9, 6.06, 6.15, 6.18, 6.31, 6.54, 6.75, 7.29, 7.54, 7.8, 7.86, 7.95, 7.96, 8, 8.35, 9.09, 9.21, 9.25, 10, 10.7, 11.4, 11.75, 11.8, 12.3, 14, 14.28, 14.3, 14.3, 14.6, 15.25, 16.1, 18.27, 18.38, 21 and 23.3 mg/kg.

In relation to processed grain commodities, a processing study was conducted after fumigation of wheat and corn (section 8.1). Concentration of fluoride ion residues was observed in wheat shorts, bran and germ, with calculated processing factors of 1.2, 2.45 and 4.6, respectively. As wheat bran and wheat germ are traded commodities, it is appropriate to establish individual MRLs for these. The highest residues in Australian wheat were 2.1 mg/kg, therefore fluoride residues in wheat bran and wheat germ are $2.1 \times 2.45 = 5.1$ mg/kg and $2.1 \times 4.6 = 9.66$ mg/kg, respectively. MRLs of 7 and 10 mg/kg are recommended for wheat bran and wheat germ, respectively. As the existing MRL of 7 mg/kg for cereal grains remains appropriate, an MRL of 10 mg/kg is required for wheat germ only.

For chronic dietary exposure, using the STMR of 0.89 mg/kg from Australian trials and the processing factors of 2.45 for wheat bran and 4.6 for wheat germ, lead to STMR-Ps of 2.18 mg/kg for bran and 4.09 mg/kg for germ.

The proposed label directions for fumigation include both whole grains as well as processed commodities. In the following table are shown residues of sulfuryl fluoride and fluoride ion concentrations in processed commodities. Data for repeat fumigations of wheat flour and wheat bran are included.

Commodity	Range of CTP mg hr/L	Range of SO_2F_2 residues (µg/kg)	Range of fluoride residues (mg/kg)
Wheat flour (single fumigations)			
Wheat flour (US)	1718, 1719	<8 (2)	29.2 – 33.5
Durum flour (US)	943 – 1803		21.2 – 49.7 (mean 40.3)
HRWW flour	943 – 1803		22.4 – 40.4 (mean 30.6)
HRWW white flour	943 – 1803		22.9 – 51.5 (mean 39.9)
SRWW flour	943 – 1803		28.1 – 82.3 (mean 44.7)
SRWW white flour	943 – 1803		26 – 57 (mean 40.7)
Wheat flour (Ger.)	2016		55
Wheat flour (UK)	1814		55
Wheat flour (organic, UK)	1595		51.09
Cracked wheat grain/flour	1595		52.59
Semolina flour (UK)	1595		82.99
Wheat flour (Ger.)	1484		28.66
Wheat flour (Italy)	1387		40.82
Wheat flour (US)	1626		42.94
Wheat flour (repeat fumigations)			
Wheat flour (US)	1404 – 2056	<8 – 15	34.2 – 101
Wheat bran (single fumigation)			
Wheat bran (US)	1717	<8 (2)	34 – 37.1
Wheat germ (single fumigation)			

Wheat germ (US)	1428 – 1482	<20 (2)	52 – 59
Durum germ (US)	943 – 1803		41.4 – 89.7 (mean 70.7)
HRWW germ (US)	943 – 1803		33.4 – 63.3 (mean 45.3)
Wheat germ (repeat fumigations)			
Wheat germ (US)	1290 – 2230	<20 (8)	81 – 235
Corn meal (single fumigation)			
White corn meal (US)	943 – 1803		10.5 – 25.4 (mean 17.9)
Yellow corn meal (US)	943 – 1803		17.2 – 24.1 (mean 20.8)
Corn meal (US)	1928 – 2195	<8 (2)	5.24 – 6.30
Corn flour (single fumigation)	1621 – 1657	<8 (2)	15.4 – 19.2
Corn grits (single fumigation)	1842 – 2248	<8, 14	7.74 – 9.17
Corn oil (single fumigation)	1540 – 2366	5850, 7840	<5 (4)
Maize flour (single fumigation)			
Maize flour (Ger.)	2016		38.5
Maize flour (UK)	1814		55.5
Maize flour (UK)	1595		70.09
Maize flour (Ger.)	1484		14.06
Maize flour (Italy)	1387		24.27
Maize flour (US)	1626		37.34
Rice bran & hulls			
Rice bran (single fumigation)	2096 – 2295	< 8 (2)	24.2 – 28.5
Rice hulls (single fumigation)	1541 – 2061	56, 57	23.4 – 32.8

Sulfuryl fluoride residues in fumigated wheat flour (single and repeat fumigations), wheat bran and wheat germ ranged <0.008 – 0.02 mg/kg. Similar concentrations were found in fumigated corn flour and grits and rice bran. The highest sulfuryl fluoride residues were present in rice hulls and corn oil at levels of 0.057 mg/kg and 7.8 mg/kg, respectively. The recommended MRL of 0.05 mg/kg for cereal grains will accommodate residues of sulfuryl fluoride in most processed fractions that are used for human foods and/or traded, with the exception of corn oil.

Fluoride ion concentrations in wheat flour ranged from 21 to 83 mg/kg following single fumigations and up to 101 mg/kg following repeat fumigations. Fluoride ion concentrations in wheat flour are in rank order: 28.66, 29.2, 29.9, 30.6, 34.2, 39.9, 40.3, 40.7, 40.82, 42.94, 44.7, 44.7, 51.09, 52.59, 55, 55, 62.5, 62.6, 82.99, 93.2, 93.7, 97.1 and 101 mg/kg. The estimated STMR is 44.7 mg/kg fluoride ion in wheat flour.

Fluoride ion concentrations in wheat bran following a single fumigation were 34 to 37 mg/kg. Residues in wheat germ following single fumigations ranged from 33 to 90 mg/kg; upon repeat fumigations, fluoride ion concentrations ranged from 81 to 235 mg/kg. Fluoride ion concentrations in wheat germ are in rank order: 45.3, 54.2, 56.8, 70.7, 81.9, 88.5, 121, 158, 201, 218, 222 and 235 mg/kg. The estimated STMR is 104.7 mg/kg for wheat germ.

The MRL of 40 mg/kg recommended for wheat bran (as a result of processing of fumigated wheat) also accommodates fluoride ion concentrations that may be present in fumigated wheat bran. The MRL of 70 mg/kg recommended for fluoride ion in wheat germ however does not accommodate concentrations that may be present in wheat germ that is fumigated. Therefore an MRL of 120 mg/kg is recommended for fluoride ion in wheat germ.

Fluoride ion concentrations in processed corn commodities ranged from <5 up to 25 mg/kg and in maize flour from 14 to 70 mg/kg. The fluoride ion concentrations in maize flour are in rank order: 14.06, 24.27, 37.34, 38.5, 55.5 and 70.09 mg/kg. The estimated STMR is 38 mg/kg for maize flour. An MRL of 75 mg/kg is recommended for maize flour.

Although in the paragraphs above MRLs have been recommended for processed commodities, if the estimated chronic dietary exposure is not acceptable, then the fumigation of processed commodities may be excluded and/or restricted on the proposed label directions.

3.4.2. Dried fruit and nuts

Studies on the fumigation of dried fruits and nuts were conducted in the US. Studies included single as well as repeat fumigations (up to 5 successive fumigations) with sampling following each of the fumigations. The results of the residues analyses are tabulated below:

Commodity	Range of CTP mg hr/L	Range of SO_2F_2 residues µg/kg	Range of fluoride residues (mg/kg)
Raisins (single and repeat fumigations)	2502 – 2535	<1 – <4.2	<2.2 (days 4 & 7 samples)
Figs (single and repeat fumigations)	1441 – 1513	11 – 41	<1.4 – <2.4 (day 6 & 7 samples)
Dates (single and repeat fumigations)	1447 – 1518	<2.1 – 23	<1.4 – 3.09 (days 5 to 16 samples)
Dried plums (single and repeat fumigations)	1486 – 1611	<2.1 – <4.2	<1.4 – 3.14 (day 3 and 6 samples)
Walnuts (single and repeat fumigations)	2500 – 2550	44.1 – 4811	2.3 – 25.8 (day 7 samples)
Pistachios (single and repeat fumigations)	1496 – 1519	35 – 303	3.95 – 17.9
Pecans (single and repeat fumigations)	1443 – 1539	2224 – 6030	19.8 – 21.8
Almonds (single and repeat fumigations)	1485 – 1558	28 – 128	4.07 – 9.71 (days 2 to 16 samples)

As the proposed label directions do not preclude multiple fumigations, the data for repeat fumigations are considered as part of the MRL determination. The data for walnuts were generated with a higher CTP than indicated on the proposed product label and higher than that used to generate data for other tree nuts. However the range of residues are within the values observed for pecans (which are similar to walnuts) that were treated at the proposed CTP. As use on peanuts is also proposed on the draft label, a separate MRL is required for peanut which is classified as an oilseed.

On the basis of the data presented above, the following MRLs are recommended:

Commodity	Sulfuryl fluoride	Fluoride ion
Dried fruit (raisins, figs, dates, dried plum)	0.07 mg/kg	5 mg/kg
Tree nuts (almonds, walnuts, pecans, pistachios)	7 mg/kg	30 mg/kg
Peanut	7 mg/kg	30 mg/kg

For the purposes of dietary intake assessment (acute and chronic), an HR of 0.043 mg/kg sulfuryl fluoride is recommended for dried fruit. For tree nuts, HRs of 4.8, 0.3, 6 and 0.13 mg/kg are recommended for walnuts, pistachios, pecans and almonds, respectively. Sulfuryl fluoride residues in tree nuts are in rank order: 0.033, 0.044, 0.045, 0.057, 0.063, 0.121, 0.277, 1.534, 2.407, 3.08, 4.79, 4.81, 4.91 and 4.95 mg/kg; the estimated STMR is 0.91 mg/kg.

For chronic intake assessment, the fluoride ion concentrations in dried fruit are in rank order: <1.4 (7), <2.2 (3), <2.4 (4), 2.56, 2.74, 3.09 and 3.14 mg/kg. The estimated STMR is <2.2 mg/kg for dried fruit.

The fluoride ion concentrations in nuts are in rank order: 2.3, 2.91, 4.56, 5.96, 7, 7.2, 7.97, 9.59, 9.71, 12.35, 12.6, 17.9, 21.8 and 25.8 mg/kg. The estimated STMR is 8.79 mg/kg for nuts.

3.5 Animal transfer studies and required animal commodity MRLs

Very little information on the transfer of sulfuryl fluoride from feed commodities to animal commodities such as meat, milk, eggs was provided by the Applicant. A published paper on the transfer of fluoride from drinking water to hen eggs was submitted, however as it was not directly relevant to the transfer from fumigated commodities, the paper was not considered relevant to the current application.

As sulfuryl fluoride is unlikely to be transferred to animal commodities such as milk, eggs, meat and offal, animal commodity MRLs for sulfuryl fluoride are not considered necessary. There may be transfer of fluoride ion into milk, meat and other commodities as a result of fumigated grain commodities being fed to livestock. However as inorganic fluoride ion is naturally present in milk and meat commodities, it would not be practical to establish inorganic fluoride MRLs for compliance or trade purposes.

The 2005 JMPR estimated the livestock dietary burden for inorganic fluoride, however determined that animal commodity MRLs could not be established as livestock feeding studies were not provided. As there are no established MRLs for inorganic fluoride in animal commodities for trade purposes, in this case it is not considered necessary to establish such MRLs for compliance with domestic standards. There are no existing standards for animal commodities in the Food Standards Code.

3.6 Fat solubility and potential for bioaccumulation

The repeat fumigation studies confirmed that sulfuryl fluoride and fluoride ion concentrations were higher in commodities that had a high fat content. For example some of the nuts, which have a higher fat content than dried fruits (walnuts, pecans and pistachios), had high fluoride concentrations compared to dried fruits that were also subjected to repeat fumigations. This accumulation effect is important to note when considering the proposed label directions and the possibility of repeat fumigations of commodities that may be stored for prolonged periods.

4. DIETARY RISK ASSESSMENT

The following health standards have been recommended by the Office of Chemical Safety, Department of Health and Ageing and/or the JMPR (ADI and ARfD lists as of December 2006).

Compound	Dietary Standard, mg/kg bw		No Observable Effect Level (NOEL), mg/kg bw	Safety Factor	Reference
Sulfuryl fluoride	ADI[3]	0.01	20 ppm (inhalation)		25/8/2006 report
	ARfD[4]	0.3	31 (300 ppm inhalation)	100	

4.1 Chronic dietary exposure assessment

The chronic dietary exposure to sulfuryl fluoride and fluoride ion is estimated by the National Estimated Daily Intake (NEDI) calculation encompassing all registered/temporary uses of the chemical and the mean daily dietary consumption data derived from the 1995 National

3 http://www.tga.gov.au/docs/pdf/adi.pdf
4 http://www.tga.gov.au/docs/pdf/arfd.pdf

Nutrition Survey of Australia. The NEDI calculation is made in accordance with WHO Guidelines[5] and is a conservative estimate of dietary exposure to chemical residues in food.

The NEDI for fluoride ion was estimated using Upper Levels of Intake[6] (UL) of fluoride as recommended by the Australian NH&MRC and published in the Nutrient Reference Values for Australia and New Zealand[7] for different age groups.

For adults, the recommended Upper Level of Intake is 10 mg fluoride/day (for men and women of all age groups, ranging 19 years to >70 years). This is equivalent to 0.15 mg/kg bodyweight/day. As part of the chronic estimate, the exposure from fluoride in drinking water must also be included. The total intake of water (including water from foods as well as fluids) ranges 1.8L to 2.6L/day for adults[8]. A mean value of 2.2L/day is used to represent the mean intake of drinking water for the chronic dietary exposure assessment for fluoride ion. The concentration of fluoride in drinking water as recommended by the NH&MRC is 1 mg/L[9]. NH&MRC Drinking Water Guidelines (2004) state that *"based on health considerations, the concentration of fluoride in drinking water should not exceed 1.5 mg/L"*.

For children, the recommended Upper Level of Intake ranges from 1.3 to 2.2 mg fluoride/day for children aged 1 to 8 years old. To correlate with the same age and bodyweight range used by FSANZ for children (2 to 6 years of age, mean bodyweight 19 kgs), an Upper Level of 1.9 mg fluoride/day is used (equivalent to 0.1 mg/kg bw/day as calculated from reference bodyweights and reported UL values). The total intake of water (including water from foods as well as fluids) ranges 1L to 1.2L/day for children aged 1 to 8 years old [10]. A value of 1.2L/day is used to represent the mean intake of drinking water for the chronic dietary exposure assessment for fluoride ion.

Using all of the above reference values and the calculated STMRs for cereal grains, dried fruits and nuts and STMR-Ps for wheat bran and wheat germ leads to NEDI estimates equivalent to 71% of the UL for children and 25% of the UL for the general population (7 years and above). These estimates do not include the use of sulfuryl fluoride to fumigate processed commodities, as the resulting concentrations of fluoride ion in processed commodities are likely to exceed the UL, from exposure from all sources of food and water. Drinking water alone comprises 89% of the estimated fluoride exposure for children and 88% for the general population. The drinking water exposure approximates 63% of the UL for children and 22% of the UL for adults. A total diet exposure assessment of fluoride is yet to be completed by FSANZ and will occur during the period from registration to promulgation of the MRLs into the Food Code.

The NEDI for sulfuryl fluoride is equivalent to 2.4% of the ADI. This only includes use on cereal grains, dried fruit, peanuts and tree nuts.

5 Guidelines for predicting dietary intake of pesticide residues, WHO, 1997.

6 Upper Level of Intake is defined as the highest average daily nutrient intake likely to pose no adverse health effects to almost all individuals in the general population. Nutrient Reference Values for Australia and New Zealand, NH&MRC Publication 2006.

7 Nutrient Reference Values for Australia and New Zealand, NH&MRC Publication 2006. Table 9: Minerals – Copper, Chromium, Manganese, Fluoride, Sodium and Potassium. 2006.

8 Nutrient Reference Values for Australia and New Zealand, Table 4: Macronutrients and Water.

9 NH&MRC 1991.

10 Nutrient Reference Values for Australia and New Zealand, Table 4: Macronutrients and Water.

DIAMOND Modelling[11]: DIAMOND Modelling of chronic dietary exposure is also performed on new chemicals, and chemicals with estimated dietary exposure greater than 90% of the ADI. The DIAMOND model estimated the chronic dietary exposure of sulfuryl fluoride as XX% of the ADI for the general population.

It is concluded that the chronic dietary exposure of sulfuryl fluoride and fluoride ion is acceptable.

4.2 Acute dietary exposure assessment

The acute dietary exposure is estimated by the National Estimated Short Term Intake (NESTI) calculation. The NESTI calculations are made in accordance with the deterministic method used by the JMPR[5] with 97.5th percentile food consumption data derived from the 1995 National Nutrition Survey of Australia. NESTI calculations are conservative estimates of acute exposure (24 hour period) to chemical residues in food.

The NESTIs for all relevant commodities are summarised in the following table. The highest acute dietary intake was estimated at 3% of the ARfD. It is concluded that the acute dietary exposure of sulfuryl fluoride is acceptable.

Commodity/Food	% ArfD (2 to 6 years)	% ArfD (general population)
Cereal grains and processed fractions	>0.2	>0.2
Dried fruit	>0.1	>0.1
Peanuts	4	>3
Tree nuts	3	3

5. RESIDUE RELATED ASPECTS OF TRADE

Cereal grains are considered as major export commodities[12] and the overall risk to export trade is considered to be small. However, use of sulfuryl fluoride may result in detectable residues in tree nuts dried fruits and the Applicant should be responsible for informing the growers/ producers/ stakeholders of any potential risks to the industry.

5.1 Commodities exported

The commodities that are considered as major export commodities in accordance with Part 5B of Ag MoRaG are cereal grains and associated commodities and dried fruit.

5.2 Destination and Value of Exports

The total exports of Australian cereal grains were estimated at 16,000 kt for 2005 – 2006 and 15, 779 kt for 2004 – 2005 for wheat; export of coarse grains were estimated at just over 6,000 kt for 2005 – 2006 and 5264 kt for 2004 – 2005.

The 8 largest export markets for Australian cereal grains (including wheat) by value are shown below (Australian Commodity Statistics 2005; ABARE Food Statistics 2006).

Destination	Value, $ million	
	2004 – 2005	2005 – 2006
Japan	617	425

11. DIAMOND: The DIamond Modelling Of Nutritional Data is a computer dietary modelling program based upon statistical software that is used by FSANZ.

12 Part 5B of the Vet Requirements Series and Ag Requirements Series, Overseas Trade Aspects of Residues in Food Commodities, August 2004.

China	943	342
Malaysia	198	168
Korea	323	270
Saudi Arabia	329	346
Thailand	111	130
Indonesia	545	588
UAE	94	159

In relation to export of dried fruit and nuts, the following statistics were available. Almonds and macadamias produced during 2004 – 2005 were valued at 77 and 119 million $AUS, respectively. This relates to 12 and 32 kt production, respectively. For dried vine fruit, 30 kt were produced during 2005 – 2006 and of that 7 kt was exported; the value of the exported fruit and market destinations was not available.

As sulfuryl fluoride is proposed as a methyl bromide replacement, not all shipments of Australian grain or domestic grain will be fumigated, while there is a quarantine and pre-shipment preference for methyl bromide. Also as grain is a bulked and blended commodity, it is likely that fumigated and non-fumigated lots may be bulked prior to processing.

As separate MRLs are not proposed for processed cereal grain commodities, as processed commodities themselves are not to be fumigated (in accordance with proposed directions for use), further consideration of trade of processed commodities is therefore not required.

5.3 Overseas registration and approved label instructions

The applicant indicated that sulfuryl fluoride fumigants products are registered for use on cereal grains, dried fruit and nuts in several countries including USA, Germany and Italy.

5.4 Comparison of Australian MRLs with Codex and overseas MRLs.

The Codex Alimentarius Commission (Codex) is responsible for establishing Codex Maximum Residue Limits (CXLs) for pesticides. Codex CXLs are primarily intended to facilitate international trade, and accommodate differences in Good Agricultural Practice (GAP) employed by various countries. Some countries may accept Codex CXLs when importing foods. Sulfuryl fluoride was evaluated by the 2005 JMPR and CXLs were established by CAC in 2006. MRLs or tolerances established overseas are compared to the proposed Australian MRLs for sulfuryl fluoride in the table below.

Commodity	**Sulfuryl Fluoride MRLs/Tolerances (mg/kg)**				
	Australia	**Japan***	**US**	**Codex**	**Germany****
Cereal grains	0.05	0.1	–	0.05	0.05
Corn grain	–	0.05	0.05	–	–
Rice	–	0.04	0.04	–	–
Rice polished	–	–	0.01	–	–
Barley, millet, oats, sorghum, triticale, wheat	–	–	0.1	–	–
Barley bran, wheat bran	–	–	0.05	–	–
Cereal brans	–	–		0.1	–
Rice bran	–	–	0.01	–	–
Wheat germ	–	–	0.02	0.1	–
Tree nuts	7	3	3	3	10
Peanuts	7	0.5	0.5	–	–
Dried fruit	0.07	1	0.05	0.06	0.05

* Japanese provisional list updated February 2007; MRLs were not listed for processed fractions.
** EU MRLs have not been established for sulfuryl fluoride.

There is a noticeable difference in the value established for tree nuts both in Australia and Germany, compared to the Codex value. It is noted that animal commodity MRLs have been established for sulfuryl fluoride in the USA, where specific commodities are fumigated in accordance with US GAP. The commodities and MRLs are: dried egg 1 mg/kg; cheese 2 mg/kg; hog meat 0.02 mg/kg; cattle meat, dried 0.01 mg/kg.

5.5 Potential risk to trade

Export of treated produce containing detectable residues of sulfuryl fluoride may pose a risk to Australian trade in situations where (i) no residue tolerance (import tolerance) is established in the importing country or (ii) where residues in Australian produce are likely to exceed a residue tolerance (import tolerance) established in the importing country.

For grains, nuts and dried fruits, as MRLs have been established by Codex, USA and some EU countries, there is likely to be general acceptance of fumigated commodities by a number of importing markets. For cereal grains, the export destinations are also likely to accept Codex Industry comment is required however on the discrepancy between the proposed Australian MRL for tree nuts and peanuts and the Codex MRL for tree nuts and lack of MRL for peanuts.

The overall risk to export trade in animal commodities is considered to be negligible, as fumigation of animal commodities is not proposed in the directions for use of the product.

The relevant industry groups should be given the opportunity to comment on the perceived level of risk and whether any industry-initiated strategies are required to manage the risk. The opportunity to comment will be facilitated through the public consultation process, by response to the Public Release Summary.

6. CONCLUSIONS

Dow AgroSciences Australia Ltd has applied for registration of a new product containing the active constituent sulfuryl fluoride. The product is a gas used for control of insect pests in various situations including grain storages silos and warehouses, in fumigation chambers and food processing facilities such as mills. The product will also be used for seed intended for sowing and for hay fumigation. A number of non-food situations are also specified on the product label, which include fumigation of dwellings, buildings, construction materials, furnishings, machinery, vehicles and shipping containers.

The proposed use pattern for sulfuryl fluoride (at standard temperature and pressure) is a maximum target concentration of **128 g/m^3** with a maximum fumigant dosage of **1500 CT or 1500 g hr/m^3**. The food commodities specified on the draft product label included cereal grains and processed fractions, dried fruit and nuts. As fumigation of processed fractions could not be accommodated due to the large contribution to the chronic dietary estimate of fluoride ion residues from such commodities (such as flour, bran, cereal fractions), processed fractions are not supported for inclusion on the label at this time. This may be considered further once FSANZ have undertaken a total modelling of fluoride exposure to all food and water. The commodities that are supported for inclusion on the label are all whole cereal grains, dried fruits and nuts. As peanuts are not part of the Codex crop group Tree Nuts, a separate MRL for peanuts is required. The proposed withholding period is 24 hours.

The estimated chronic dietary intake of sulfuryl fluoride and fluoride ion arising from residues in food is unlikely to exceed the health standards. The estimated short-term (or acute) dietary intake of sulfuryl fluoride arising from residues in food is unlikely to exceed the health standards.

Use of the product in accordance with the above label instructions is unlikely to pose a risk to Australian trade as Codex MRLs for sulfuryl fluoride were established in 2006 for cereal grains and processed fractions, dried fruit and tree nuts. Relevant MRLs have also been established by the USA, Japan and Germany. Users and producer groups however are requested to provide comment through the normal consultation mechanism, which is the APVMA Public Release Summary.

APPENDICES

7. METABOLISM

The metabolism of sulfuryl fluoride is not well described in plants or animals. The studies provided did not meet contemporary requirements for plant metabolism studies and are therefore not reported further.

8. MAGNITUDE OF RESIDUES IN CROPS, LIVESTOCK AND PROCESSED COMMODITIES

Cereal Grains

8.1. Evaluation of Sulfuryl Fluoride Fumigation Variables On Residue Levels In Crop Commodities, Rick, D.L., Marty, G.T., Krieger, S.M. and McGuirk, R.J. Dow AgroSciences LLC, Study ID 001103, 27 December 2000. (Ref. 1).

In this study, hard red winter wheat, rice and corn and their respective processed fractions were exposed to controlled fumigations of sulfuryl fluoride. Additional experiments were conducted using whole grain wheat, wheat flour and wheat germ to determine the effect of different fumigation conditions on the rate of sulfuryl fluoride desorption and resulting fluoride levels in the commodities. The overall experimental conditions included:

1. controlled fumigation
2. loading factor (as a % of the structure capacity)
3. dose of sulfuryl fluoride (CTP)
4. exposure temperature
5. repeat fumigations
6. vacuum fumigation
7. sulfuryl fluoride concentration with constant CTP
8. the effect of processing whole wheat and corn

For each experiment, there were two replicate exposure chambers and one control chamber for each commodity tested. In most of the experiments (except #2) the commodities were loaded to occupy approximately 10% of the total fumigation chamber. Due to intrinsic differences in the densities of the various whole grain commodities and their processed fractions, the equivalence in volumetric loading between commodities would not equate to equivalence in weight loading.

The results of the controlled fumigation from experiment 1 and experiments 2 to 7 are tabulated below. Values of sulfuryl fluoride for each fumigated commodity are reported as corrected for recovery. Values of fluoride are reported as ‘net concentrations’, i.e. measured fluoride concentration in fumigated commodity — concentration in untreated control sample. As the fluoride concentrations in the control samples were <LOQ in most cases, the reported values were not adjusted.

Experiment 1: CT = 1500 mg hr/L or 1500 g hr/m^3; concentration 62.5 mg/L; exposure time 24 hours. Samples were taken from the middle of the structure on days 1, 4 and 7. Two replicate results and one control result is reported for each commodity tested at each time point.

Commodity	Measured concentrations in the chamber		Fluoride concentration (mg/kg)			SO_2F_2 concentration (mg/kg)		
	SO_2F_2 (mg/L)	CTP (mg hr/L)	Day 4	Day 7	Controls*	Day 1	Day 4	Day 7
Whole corn	69.9	1643	2.25	2.07	<0.6	0.0257	<0.008	<0.008
	73.4	1726	2.26	2.13		0.020	<0.008	<0.008
Corn flour	67	1621	14.9	18.9	<0.3	<0.008	<0.008	<0.008
	68.5	1657	15.4	19.2		<0.008	<0.008	<0.008
Cornstarch	62.6	1534	3.82	3.91	<0.3	<0.008	<0.008	NA
	87.6	2146	5.35	5.3		<0.008	<0.008	NA
Corn meal	79.3	1928	5.6	5.24	<0.3	<0.008	<0.008	NA
	90.3	2195	6.3	6.14		<0.008	<0.008	NA
Corn grits	75.5	1842	9.09	7.74	0.329	<0.008	<0.008	NA
	92.1	2248	9.17	8.26		0.0144	<0.008	NA
Corn oil	97.8	2366	<0.5	<0.5	<0.5	7.84	2.66	4.38
	63.6	1540	<0.5	<0.5		5.85	2.51	3.13
Whole grain rice	86.1	2186	5.49	5.97	<0.6	0.0251	<0.008	NA
	88.2	2240	7.80	8.46		0.0159	<0.008	NA
Rice bran	82.8	2096	28.5	24.6		<0.008	<0.008	NA
	90.7	2295	24.2	26.3		<0.008	<0.008	NA
Polished rice	87.8	2212	1.47	1.3	<0.6	<0.008	NA	NA
	78.5	1979	1.60	1.4		<0.008	NA	NA
Rice hulls	81.8	2061	32.8	30.3	<0.8	0.0573	<0.02	<0.02
	61.2	1541	23.6	23.4		0.0563	<0.02	<0.02
Whole grain wheat	73.9	1892	1.94	1.84	<0.6	0.009	<0.008	NA
	73.6	1883	1.92	1.93		<0.008	<0.008	NA
Wheat bran	67.3	1717	36.7	34	<0.8	<0.008	<0.008	NA
	67.3	1717	37.1	34.8		<0.008	<0.008	NA
Wheat flour	67.9	1719	29.9	32.2	<0.3	<0.008	<0.008	NA
	67.9	1718	29.2	33.5		<0.008	<0.008	NA
Wheat germ	59	1482	56.8	59	<0.8	<0.02	<0.02	NA
	56.9	1428	54.2	52		<0.02	<0.02	NA
Wheat red dog	72.3	1779	32.7	33.3	<0.8	<0.008	<0.008	NA
	65.9	1622	31.7	32.3		<0.008	<0.008	NA
Wheat shorts	71.8	1760	35.5	34.8	<0.8	<0.008	<0.008	NA
	70.4	1726	31.9	34.5		<0.008	<0.008	NA

<LOQ fluoride = <0.3 to <0.8 mg/kg depending on the commodity type and weight. LOQ SO_2F_2 = 0.02 for rice hulls and wheat germ and 0.008 for other commodities.
NA = Not analysed.

<u>Experiments 2 to 7</u>: Residues of SO_2F_2 and fluoride in whole wheat resulting from varying conditions of fumigation.

Expt. No.	Experimental design	Measured concentrations in the chamber		Fluoride concentration (mg/kg) Day 7 only		SO_2F_2 concentration (mg/kg)		
		SO_2F_2 (mg/L)	CTP (mg hr/L)	Treated	Control	Day 1	Day 4	Day 7
1	Standard fumigation	73.9	1892	1.84	<0.6	0.009	<0.008	NA
		73.6	1883	1.93		<0.008	<0.008	NA
2	Percent load 1%	62.5	1606	1.95	<0.6			
		54.9	1412	2.00				
	Percent load 50%	73.9	1802	1.78	<0.6			
		61.9	1510	1.85				
	Percent load 80%	73	1774	1.47	<0.6			
		67	1629	1.99				
3	CTP 250 mg hr/m^3	11.1	268	0.676	<0.6	<0.008	<0.008	NA
		10.9	264	0.651		<0.008	<0.008	NA
	CTP 1000 mg hr/m^3	59.2	1421	1.74	<0.6	0.008	<0.008	NA
		54.1	1299	1.52		<0.008	<0.008	NA
	CTP 2500 mg hr/m^3	129	3120	2.03	<0.6	0.035	<0.008	NA
		102	2457	1.85		0.021	<0.008	NA
4	Temperature 10 °C	65.2	1597	0.79	<0.6	0.033	0.043	0.021
		671.	1644	0.91		0.032	0.042	0.019
	Temperature 30 °C	76.8	1867	2.79	<0.6	0.014	<0.008	NA
		75.1	1825	2.96		0.013	<0.008	NA
5	Repeat fumigations #1	72.6	1845	3.1	<0.6	0.011	<0.008	NA
		78.3	1989	3.94		0.009	<0.008	NA
	Repeat fumigations #2	75.2	1827	5.02	<0.6	0.009	<0.008	NA
		70.2	1707	5.02		0.008	<0.008	NA
	Repeat fumigations #3	81.2	2045	6.15	<0.6	0.028	<0.008	NA
		81.1	2044	6.31		0.022	<0.008	NA
	Repeat fumigations #4	91.1	2223	7.95	<0.6	0.021	<0.008	NA
		92.7	2262	8.0		0.023	<0.008	NA
6	Vacuum 28 mmHg	547	2188	3.2	<0.6			
		548	2193	4.08				
7	Exposure time 4 hrs	426	1791	3.93	<0.6			
		413	1734	2.91				
	Exposure time 48 hrs	37.2	1792	2.22	<0.6			
		37	1782	2.36				

<u>Experiments 2 to 7</u>: Residues of SO_2F_2 and fluoride in wheat flour resulting from varying conditions of fumigation.

Expt. No.	Experimental design	Measured concentrations in the chamber		Fluoride concentration (mg/kg) Day 7 only		SO_2F_2 concentration (mg/kg)		
		SO_2F_2 (mg/L)	CTP (mg hr/L)	Treated	Control	Day 1	Day 4	Day 7
1	Standard fumigation	67.9	1719	32.2	<0.3	<0.008	<0.008	NA
		67.9	1718	33.5		<0.008	<0.008	NA
2	Percent load 1%	52.8	1356	33.5	<0.3			
		57.5	1477	37.8				
	Percent load 50%	47	1142	21.5	<0.3			
		45.5	1106	26.4				
	Percent load 80%	64.5	1562	25.9	<0.3			
		56.2	1359	25.7				
3	CTP 250 mg hr/m^3	10.2	247	6.88	<0.3	<0.008	<0.008	NA
		10	241	7.34		<0.008	<0.008	NA
	CTP 1000 mg hr/m^3	52.4	1257	19.3	<0.3	<0.008	<0.008	NA
		49.2	1181	21.1		<0.008	<0.008	NA
	CTP 2500 mg hr/m^3	106	2554	39.9	<0.3	0.008	<0.008	NA
		111	2677	42.8		<0.008	<0.008	NA
4	Temperature 10 °C	55.5	1360	15.7	<0.3	<0.008	<0.008	NA
		63.6	1559	14.6		<0.008	<0.008	NA
	Temperature 30 °C	65.5	1592	37.8	<0.3	<0.008	<0.008	NA
		57	1384	33.4		<0.008	<0.008	NA
5	Repeat fumigations #1	72.9	1831	44.7	<0.3	<0.008	<0.008	NA
		55.9	1404	34.2		<0.008	<0.008	NA
	Repeat fumigations #2	64.1	1557	62.5	<0.3	0.008	<0.008	NA
		80.3	1952	62.6		0.009	<0.008	NA
	Repeat fumigations #3	73.8	1846	101	<0.3	0.009	<0.008	NA
		67.5	1688	93.7		0.008	0.009	NA
	Repeat fumigations #4	84.6	2056	97.1	<0.3	0.012	0.008	<0.008
		78.6	1910	93.2		0.015	<0.008	<0.008
6	Vacuum 28 mmHg	448	1792	33.3	0.708			
		441	1764	31.6				
7	Exposure time 4 hrs	396	1665	43.4	<0.3			
		400	1678	39.9				
	Exposure time 48 hrs	25.8	1247	28.2	<0.3			
		33.5	1617	35.3				

Experiments 2 to 7: **Residues of SO_2F_2 and fluoride in wheat germ resulting from varying conditions of fumigation.**

Expt. No.	Experimental design	Measured concentrations in the chamber		Fluoride concentration (mg/kg) Day 7 only		SO_2F_2 concentration (mg/kg)		
		SO_2F_2 (mg/L)	CTP (mg hr/L)	Treated	Control	Day 1	Day 4	Day 7
1	Standard fumigation	59	1482	59	<0.8	<0.02	<0.02	NA
		56.9	1428	52		<0.02	<0.02	NA
2	Percent load 1%	55.7	1426	43.5	1.03			
		53.5	1369	41.6				
	Percent load 50%	59.5	1440	84.1	0.812			
		57.7	1396	83.9				
	Percent load 80%	65.5	1578	66.3	<0.8			
		60.5	1459	73.2				
3	CTP 250 mg hr/m^3	9.7	235	18.1	0.814	<0.02	<0.02	NA
		9.6	233	17.1		<0.02	<0.02	NA
	CTP 1000 mg hr/m^3	50.8	1215	58.6	<0.8	<0.02	<0.02	NA
		48.3	1154	55.3		<0.02	<0.02	NA
	CTP 2500 mg hr/m^3	101	2436	95.8	<0.8	<0.02	<0.02	NA
		99.8	2406	94.2		<0.02	<0.02	NA
4	Temperature 10 °C	59.8	1466	17.4	<0.8	<0.02	<0.02	NA
		69.8	1709	18.6		<0.02	<0.02	NA
	Temperature 30 °C	63.7	1548	72.3	<0.8	<0.02	<0.02	NA
		63.2	1536	82.6		<0.02	<0.02	NA
5	Repeat fumigations #1	53.1	1337	88.5	0.87	<0.02	<0.02	NA
		51.2	1290	81.9		<0.02	<0.02	NA
	Repeat fumigations #2	84.7	2050	158	<0.8	<0.02	<0.02	NA
		92.1	2230	121		<0.02	<0.02	NA
	Repeat fumigations #3	68.6	1701	218	0.87	<0.02	<0.02	NA
		76.7	1903	201		<0.02	<0.02	NA
	Repeat fumigations #4	79.7	1921	235	1.23	<0.02	<0.02	NA
		80.5	1939	222		<0.02	<0.02	NA
6	Vacuum 28 mmHg	504	2018	53.7	<0.8			
		467	1869	54.3				
7	Exposure time 4 hrs	388	1630	104	0.84			
		386	1621	90.3				
	Exposure time 48 hrs	24.5	1181	58.8	<0.8			
		22.4	1078	60.1				

In experiment 1, the CTP ranged from 1540 to 2295 or 1× to 1.5× the maximum CTP proposed on the product label. The results from experiment 1 show that sulfuryl fluoride residues are below the limits of quantitation at 24 hours after cessation of fumigation of whole grain commodities. The reported limits of quantitation were <0.008 mg/kg in whole grains. The fumigant was only detected in corn oil, corn grits and rice hulls at levels above the reported limits of quantitation. Of all the commodities fumigated, corn oil had the greatest ability to absorb sulfuryl fluoride.

The highest fluoride concentrations were found in fumigated processed fractions rather than fumigated whole commodity. For example, the fluoride levels in corn starch were approximately 9× higher than in whole corn and were approximately 3× and 4× higher in rice bran and rice hulls, respectively, compared to paddy rice. Similarly, fluoride levels in wheat bran, flour and germ were approximately 17×, 17× and 29×, respectively, the levels found in fumigated whole wheat.

Processing of fumigated whole grains (wheat and corn) generally resulted in low levels of fluoride. The processing factors derived from experiment 8 indicate that there is a concentration of fluoride in wheat bran, shorts and germ compared to whole wheat. By comparison, fluoride does not concentrate in corn fractions processed from fumigated whole corn.

Processing factors derived from Experiment 8

Commodity	Fluoride Concentration (mg/kg)		Processing factor
	Commodity	Control	
Wheat			
Whole fumigated grain	1.19, 1.30	<0.6	–
Flour	0.446	<0.3	0.36
Shorts	1.50	0.339	1.2
Bran	3.05	<0.8	2.45
Middlings	0.718	<0.3	0.57
Germ	5.74	<0.8	4.6
Corn (Maize)			
Whole fumigated grain	1.76, 1.89	<0.6	–
Flour	1.29	0.49	0.71
Meal	1.37	<0.3	0.75
Grits	0.826	<0.3	0.45
Oil	<0.3	<0.3	<<1
Oil (wet)	<0.3	<0.3	<<1
Starch	<0.3	0.4	<<1

Of the other experiments that were conducted, the repeat fumigation experiment (experiment 5) showed that with successive fumigations there is a cumulative effect on fluoride concentration in whole wheat, wheat flour and wheat germ. After 4 successive fumigations, the fluoride concentrations increase two-fold in whole wheat grain and wheat flour and three-fold in wheat germ. The data reflect the sorption properties of the processed fractions compared to the whole grain commodity.

In experiment 4, the increase in temperature (and hence pressure) results in an increase in concentrations of fluoride with higher temperature. This effect is seen in the whole commodity as well as in the processed commodities.

Fumigation under reduced pressure (experiment 6, vacuum) did not seem to have any effect on final fluoride concentrations, compared to fumigation under standard conditions. Similarly,

fumigation for prolonged periods (experiment 7) did not appear to have a significant effect on fluoride concentrations.

Mean reported recoveries of sulfuryl fluoride in corn, wheat and rice commodities were 93% (n = 60), 86% (n = 36) and 82% (n = 32), respectively in experiment 1. Mean reported recoveries for whole wheat, wheat flour and wheat germ in experiments #3 to #5 were 97% (n = 17), 88% (n = 18) and 84% (n = 16), respectively.

Mean reported recoveries of fluoride ion in corn, wheat and rice commodities were 114% (n = 27), 116% (n = 20) and 113% (n = 8), respectively in experiment 1. Mean reported recoveries for whole wheat, wheat flour and wheat germ in experiments #3 to #5 were 119% (n = 16), 105% (n = 16) and 104% (n = 16), respectively.

8.2. Magnitude Of The Terminal Fluoride Ion Level In Cereal Grain Commodities Fumigated With Sulfuryl Fluoride. Rick, D.L., Marty, G.T., Krieger, S.M., Byrne, S.L. and Barnekow, D.E. Dow AgroSciences LLC, Study ID 011057, 28 September 2001. (Ref. 2).

Whole grains and some processed commodities were fumigated with SO_2F_2 under controlled laboratory conditions and in milling facilities to determine the residues of fluoride ion generated under both sets of conditions. In the laboratory experiments, samples of 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 were fumigated at atmospheric pressure for 24 hours at 200 or 1500 mg hr/L CTP at 30° C followed by a 24 hour aeration period at the same temperature. Four replicate samples were fumigated and analysed for fluoride ion once the sulfuryl fluoride levels in the commodities had decreased to less than LOQ (<0.008 mg/kg).

In the trials conducted at three mills, the whole grains listed above, as well as selected processed fractions were placed in the mills at three locations (replicates) and fumigated at 200 to 2000 mg hr/L CTP for 24 to 36 hours. The mills were aerated for 4 to 5 hours before entry. Samples from the replicate locations were collected once the SO_2F_2 concentrations were below OH&S requirements (5 ppm). The mean fluoride ion residues in the laboratory and mill trials are tabulated below. All reported values are uncorrected for recovery.

Laboratory fumigations for whole cereal grains

Commodity	Experimental conditions	Measured concentrations in the chamber		Fluoride concentration (mg/kg)	
		SO_2F_2 (mg/L)	CTP (mg hr/L)	Treated	Control
Popcorn	200 mg hr/L CT	9.03 – 10.2	219 – 247	<0.5, <0.5, <0.5, <0.5	<0.5
	1500 mg hr/L CT	59.4 – 63.7	1449 – 1556	0.76, 1.41, 0.97, 0.88	<0.5
White corn	200 mg hr/L CT	7.96 – 9.79	193 – 238	<0.5, <0.5, <0.5, <0.5	<0.5
	1500 mg hr/L CT	51.6 – 65.7	1261 – 1603	1.42, 1.36, 1.31, 1.64	<0.5
Barley	200 mg hr/L CT	8 – 8.4	195 – 205	1.01, 1.03, 1.0, 0.85	<0.5
	1500 mg hr/L CT	67.3 – 69.7	1616 – 1672	2.79, 3.05, 2.76, 2.92	<0.5
Oats	200 mg hr/L CT	6.48 – 8.21	158 – 200	1.87, 1.76, 1.81, 1.85	<1.5*
	1500 mg hr/L CT	63.9 – 67.9	1533 – 1630	7.0, 7.39, 7.5, 8.27	<0.5
White rice	200 mg hr/L CT	7.39 – 9.27	179 – 224	<0.5, <0.5, <0.5, <0.5	<0.5
	1500 mg hr/L CT	62.2 – 70.8	1465 – 1706	2.01, 2.03, 1.96, 1.83	<0.5
Brown rice	200 mg hr/L CT	8.57 – 9.01	207 – 218	0.56, 0.61, 0.57, 0.56	<0.5
	1500 mg hr/L CT	62.7 – 71.8	1511 – 1728	2.23, 2.17, 2.16, 2.38	<0.5
SRWW	200 mg hr/L CT	9.35 – 10.3	227 – 250	0.72, 0.71, 0.89, 0.75	<0.5
	1500 mg hr/L CT	64 – 76.2	1553 – 1817	4.84, 3.38, 3.8, 4.2	<0.5
HRWW	200 mg hr/L CT	8.92 – 11.5	214 – 275	0.80, 0.87, 0.88, 0.86	<0.5
	1500 mg hr/L CT	64.7 – 88.3	1553 – 2119	2.64, 3.5, 3.3, 2.66	<0.5
Durum wheat	200 mg hr/L CT	9.45 – 10.3	242 – 248	0.85, 0.86, 0.90, 0.92	<0.5
	1500 mg hr/L CT	67.2 – 81.6	1619 – 1964	2.05, 2.24, 2.11, 1.93	<0.5

* 10 g samples analysed only for the control.

Fumigations of whole cereal grains in mills at replicate locations

Replicate & CTP	Site description	Durum wheat	HRWW	SRWW	Popcorn	White corn	Brown rice	White rice	Oats	Barley
Mill #1 West Milling Company										
1 974	warehouse	3.61	2.12	3.59	1.09	1.03	3.84	4.99	7.88	4.47
2 1146	1st floor	5	3.89	1.42	1.42	2.25	6.95	5.47	9.15	7.09
3 984	5th floor	23.6	6.54	2.05	2.05	5.31	11.8	16.10	15.25	9.25
Controls		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.61
Mill #2 Stafford County Flour Milling Company										
1 1803	1st floor	5.8	4.84	4.73	1.52	1.71	6.24	7.64	12.5	6.49
2 1793	2nd floor	4.79	5.65	6.06	1.19	1.86	7.29	10.7	14	7.96
3 943	4th floor	4.56	3.74	2.98	1.0	1.11	4.54	3.21	6.82	4.27
Controls		<0.5	0.76	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

Mill #3 American Rice Texas										
1 271	1st floor	2.76	2.06	2.50	1.06	2.07	3.84	2.23	7.78	3.48
2 288	4th floor	2.55	2.13	2.59	1.03	1.46	2.35	2.42	7.46	2.58
Controls		<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.52	<0.5

Fumigations of processed commodities in mills at replicate locations

Replicate & CTP	Site description	Durum germ	Durum semolina	Durum flour	HRWW flour	HRWW white flour	HRWW germ	SRWW flour	SRWW white flour	White corn meal	Yellow corn meal
Mill #1 West Milling Company											
1 974	warehouse	46.8	13.1	21.2	22.4	26.5	33.4	29.5	33.9	10.5	17.2
2 1146	1st floor	81.6	25.9	41.5	32.9	51.5	38.6	39.4	40.4	12.1	18
3 984	5th floor	89.7	27.3	49.7	27.2	49.1	41.4	82.3	57	21.0	24.1
Controls		1.03	<0.5	<0.5	0.59	<0.5	2	<0.5	<0.5	<0.5	<0.5
Mill #2 Stafford County Flour Milling Company											
1 1803	1st floor	78.7	25.5	46.4	40.4	40.4	55.9	48.2	45.3	26.4	22.7
2 1793	2nd floor	85.9	28.4	49.3	35.6	49.3	63.3	40.5	41.7	21.6	24.1
3 943	4th floor	41.4	20.2	33.5	24.8	22.9	39.3	28.1	26	15.7	18.1
Controls		<0.5	0.76	<0.5	<0.5	<0.5	0.78	0.54	<0.5	<0.5	<0.5
Mill #3 American Rice Texas											
1 271	1st floor	43.3	11.2	17.8	15.9	17.6	34.9	19	20	8.3	10.4
2 288	4th floor	49.5	12.4	15.2	15.4	16.2	42.1	19.3	14.7	6.6	12.2
Controls		<0.5	<0.5	<0.5	<0.5	<0.5	0.9	<0.5	<0.5	<0.5	<0.5

Mean recoveries of fluoride ion in fortified popcorn, white corn, barley, oats, white rice, brown rice, soft red winter wheat (SRWW), hard red winter wheat (HRWW) and durum wheat were 94, 93, 103, 94, 91, 94, 109, 115 and 98%, respectively; (n = 4) for all commodities.

Mean recoveries of sulfuryl fluoride in fortified popcorn, white corn, barley, oats, white rice, brown rice, soft red winter wheat (SRWW), hard red winter wheat (HRWW) and durum wheat were 97, 90, 98, 89, 104, 94, 97, 101 and 100%, respectively; (n = 8) for all commodities.

Recoveries in the processed commodities were not reported.

In the laboratory trials, fluoride concentrations in whole grains following fumigation at 1500 mg hr/L ranged from 0.76 mg/kg in popcorn to 8.3 mg/kg in oats. The levels in white corn, barley, white rice, brown rice, hard red winter wheat and durum wheat were comparable, with mean concentrations ranging 2 to 3 mg/kg. The fluoride concentrations in oats ranged from 7 to 8.3 mg/kg and were the highest observed for all of the whole grain commodities.

In the mill trials, fluoride concentrations in whole grains from two of the three mills were comparable where fumigations were conducted at similar CTP. The highest fluoride concentrations were found in oats at levels of 7.8 to 15 mg/kg and the lowest concentrations were in popcorn at 1 to 1.5 mg/kg. These results are similar to those observed in the laboratory trials. In one sample of durum wheat a high value of 23.6 mg/kg was observed. The mill experiments also demonstrated that the location of the commodity within the mill leads to some variation in terminal fluoride concentration. For example at the West Milling Company, fluoride concentrations were generally higher in commodities that were on the 5th floor rather than on the 1st floor; a similar trend was observed in the processed commodities.

As observed in the previous study, fluoride concentrations in processed commodities following fumigation with SO_2F_2 were higher than in whole grains.

In summary, the results confirm that the terminal fluoride concentrations are dependent on the sorption properties of the commodity.

8.3. Residues of Fluoride Ion In Cereals Following Fumigation Of A Flour Mill With Sulfuryl Fluoride – Germany 2000. Perkins, J.M. and Foster, D.R. Dow AgroSciences LLC, Report No. GHE-P-9349, Study ID 000319, 22 January 2002. (Ref. 3).

In this study, a flour mill in Germany was fumigated with SO_2F_2 at a CTP of 2016 g hr/m^3. The mill had 5 floors with an estimated volume of 10, 000 m^3. Prior to the fumigation, samples of cereals grains, namely wheat, barley, rice, wheat flour and maize flour weighing between 0.5 to 1 kg were placed in open bags on the 2nd floor of the mill. Fumigation occurred for 24 hours, followed by aeration for 12 hours. Samples were collected for analysis 12 hours after the aeration phase had been completed.

The results from the study are shown below and were reported as uncorrected for recovery:

Commodity	Mean Fluoride Ion (mg/kg)	Control (mg/kg)
Wheat grain	11.4, 14.3	ND
Wheat flour	55	<2
Barley grain	23.3	ND
Maize flour	38.5	ND
Rice grain	6.75	ND

LOQ = 2 mg/kg; ND = <20% of LOQ or <0.4 mg/kg.

Recoveries following fortification at 0.5 mg/kg in all commodities ranged 97 – 158%; recoveries were 127 and 118% following fortification at 2 mg/kg in rice grain and maize flour, respectively. A single recovery of 92% was reported in rice grain following fortification at 50 mg/kg.

The data show that the fluoride concentrations in whole grain are lower than those in fumigated processed commodities. Due to reported recoveries being above the acceptable limits of 70 – 110%, the data will not be considered for the establishment of MRLs.

8.4. Residues of Fluoride Ion In Cereals Following Fumigation Of A Flour Mill With Sulfuryl Fluoride – UK 2000. Perkins, J.M. and Foster, D.R. Dow AgroSciences LLC, Report No. GHE-P-9846, Study ID 000389, 14 June 2002. (Ref. 4).

A flour mill in the UK was fumigated with SO_2F_2 at a CTP of 1814 g hr/m^3. The mill was a 4-storey structure with an estimated volume of 2500 m^3. Prior to the fumigation, samples of cereals grains, namely wheat, barley, rice, wheat flour and maize flour weighing between 0.5 to 1 kg were placed in open bags on the 4th floor of the mill. Fumigation occurred for 38 hours, followed by aeration for 4 hours. The measured CTP near the commodities was 1585 CTP. Samples were collected for analysis immediately after the aeration phase had been completed.

The results from the study are shown below and were reported as uncorrected for recovery:

Commodity	Mean Fluoride Ion (mg/kg)	Control Samples(mg/kg)
Wheat grain (organic)	12.3	ND
Wheat grain (consort)	14.3	ND
Wheat flour	55	ND
Barley grain	21	<2
Maize flour	55.5	ND
Rice grain	14.6	ND

LOQ = 2 mg/kg; ND = <20% of LOQ or <0.4 mg/kg.

Recoveries following fortification at concentrations ranging 0.5 to 0.9 mg/kg in all commodities ranged 90 – 164%; recoveries were 106 and 109% following fortification at 2 mg/kg in maize flour and wheat grain, respectively. Recoveries of 58% and 76% were reported in wheat flour and barley grain, following fortification at 30 and 38 mg/kg, respectively.

The data show that the fluoride concentrations in whole grain are lower than those in fumigated processed commodities, as also found in the previous study. Due to reported recoveries being above the acceptable limits of 70 – 110%, the data will not be considered for the establishment of MRLs.

8.5. Residues of Fluoride Ion Following Fumigation Of A Mill With Sulfuryl Fluoride In Grain, Flour And Bran That May Be Retained In Machinery During Fumigation, In Flour and Bran Produced Immediately After Restart Of Production And In Commodities Placed In The Mill Prior To Fumigation, UK – 2002. Bostock, N and Foster, D.R. Dow AgroSciences LLC, Report No. 26367019-3, Study Plan No. AF/6270/DE, 11 July 2002. (Ref. 5).

A flour mill in the UK was fumigated with SO_2F_2 at a CTP of 1595 g hr/m^3. The mill consisted of 3 floors with a mezzanine floor with an estimated volume of 10,000 m^3. Prior to the fumigation, samples of cereals grains, namely wheat grain, barley grain, brown rice, organic wheat flour and maize flour weighing between 0.5 to 1 kg were placed in open bags on the 1st floor of the mill. Samples were taken approximately 3 hours after aeration had been completed. In addition, samples of wheat flour and bran were taken from their final production points in the mill prior to fumigation. Immediately after restart of production, samples were taken every 6 minutes and then regularly up to 90 minutes from the time that production had started. Control samples were taken prior to fumigation.

Similarly, samples of wheat grain, cracked wheat admixed with flour, semolina flour, and final production flour and bran were placed in bags close to the machinery from which they would be produced. The whole grain was placed on the 2nd floor, while the other commodities were placed on the 1st floor. The samples were fumigated and aerated and collected for analysis approximately 3 hours after aeration had been completed.

The results from the study are shown below and were reported as uncorrected for recovery:

Commodity	Fluoride Ion (mg/kg)	Control Samples (mg/kg)
Samples stored on 1st floor		
Wheat grain (organic)	9.21	<2
Wheat grain (mill blend)	14.28	<2
Wheat flour (organic)	51.09	<2
Barley grain	18.38	<2
Maize flour	70.09	<0.4
Brown rice	8.35	<2
Cracked wheat grain/flour	52.59	<2
Flour and bran mix	94.49	<2
Semolina flour	82.99	<2
Wheat flour final production	45.09	<2
Wheat bran final production	83.93	<2
Samples stored on 2nd floor		
Wheat grain (mill blend)	19.98	<0.4

LOQ = 2 mg/kg; ND = <0.4 mg/kg.

The results show that the fluoride ion concentrations in whole grain are lower than those in fumigated processed commodities, as found in other studies. The fluoride concentrations in whole grains ranged from 8.35 mg/kg for brown rice to 18.38 for barley grain, following a CTP of 1595 g hr/m^3 which is comparable to that proposed for fumigation in Australia. Fumigation of processed commodities, leads to terminal fluoride concentrations that are almost 5 times higher than those of the whole commodity, again demonstrating that the nature of the commodity to be fumigated has a large impact on the fluoride concentration.

Fluoride concentrations in the flour and bran prior to fumigation and post fumigation with time are tabulated below:

Description	Time (min.s)	Fluoride concentrations (mg/kg) Flour	Bran
Pre-fumigation		**<2**	**<4**
Post-fumigation	**0**	**83**	**33.23**
Pre-production	12	85.6	39.58
	60	25.1	–
	66	17.9	–
	72	15.5	–
Full production	0	12.6	15.23
	6	9.09	11.13
	12	7.37	10.03
	18	4.56	9.15
	24	3.83	8.81
	30	3.4	6.76
	36	2.85	4.5
	42	2.23	4.57
	48	2.25	4.52
	54	<2	4.24
	60	<2	<4
	66	<2	–
	72	<2	<4
Bulk sample from 1st hour		**4.55**	**11.03**

The results of this experiment demonstrate after approximately 75 minutes of production time, there is a marked decrease in fluoride concentrations in flour and bran produced following mill fumigation. There is a dilution of fluoride concentration with time that may allow millers to make decisions regarding what period of time is required for flour and bran that is retained within a mill at fumigation to be collected for disposal after mill restart. The data allow a time period of disposal to be specified for commercial production depending on the MRL that must be met.

Recoveries for wheat flour following fortification at concentrations of 2 mg/kg (n = 7), 5 mg/kg (n = 2), 50 mg/kg (n = 2) and 100 mg/kg (n = 3) were 109, 106, 99 and 100%, respectively. The mean recovery in wheat flour was 103%.

Recoveries for wheat bran following fortification at concentrations of 4 mg/kg (n = 5), 20 mg/kg (n = 5) and 100 mg/kg (n = 2) were 104, 92 and 89%, respectively. The mean recovery in wheat bran was 97%.

Recoveries for wheat and barley grain following fortification at concentrations of 2 mg/kg (n = 6), 5 mg/kg (n = 3), 50 mg/kg (n = 3) and 100 mg/kg (n = 3) were 108, 97, 88 and 90%, respectively. The mean recovery in wheat and barley grain was 98%.

8.6. Residues of Fluoride Ion Following Fumigation Of A Mill With Sulfuryl Fluoride In Flour And Bran Produced Immediately After Restart Of Production And In Commodities Placed In The Mill Prior To Fumigation Germany – 2002. Blaschke, U. Dow AgroSciences European Development Centre, Report No. GHE-P-9909, Study ID DOS 300/023403, 23 July 2002. (Ref. 6).

A flour mill in Germany was fumigated with SO_2F_2 at a CTP of 1484 g hr/m^3. The mill consisted of 4 floors; the estimated volume of the premises was not given. Prior to the fumigation, samples of cereals grains, namely wheat grain, barley grain, brown rice, wheat flour and maize flour weighing between 0.5 to 1.5 kg were placed in open bags on the 4th floor of the mill. Fumigation was conducted for 20 hours followed by 15.5 hours aeration time. Samples were taken approximately 1.5 hours after aeration had been completed and personnel were allowed to enter the mill.

In addition, samples of wheat flour and bran were taken from their final production points in the mill prior to fumigation. Immediately after restart of production, samples were taken every 6 minutes for up to 2 hours; a sample was bulked to represent a composite sample for the first hour of production. Control samples were taken prior to fumigation.

The results from the study are shown below and were reported as uncorrected for recovery; CTP near the commodities was measured at 1333 g hr/m^3:

Commodity	Mean Fluoride Ion (mg/kg)	Control Samples(mg/kg)
Wheat grain (organic)	2.92	<2
Wheat grain (mill blend)	5.9	<2
Wheat flour	28.66	ND
Barley grain	10	<2
Maize flour	14.06	ND
Rice grain	2.8	<2

LOQ = 2 mg/kg; ND = <20% of LOQ or <0.4 mg/kg.

The results show that fluoride concentrations are higher in the processed commodities such as wheat flour and maize flour compared to the whole cereal grains, following fumigation. Fluoride concentrations ranged from 2.8 mg/kg in rice to 10 mg/kg in barley.

Description	Flour		Bran	
	Time (min.s)	Fluoride concentrations (mg/kg)	Time (min.s)	Fluoride concentrations (mg/kg)
Pre-fumigation		**<2**		**<4**
Post-fumigation	**0**	**10.37**	**0**	**10.05**
	6	**11.27**	**6**	**1.58 <LOQ**
Full production	0	3.37		
	6	2.43	5	1.41 <LOQ
	12	4.88	11	1.46 <LOQ
	18	2.37	17	1.49 <LOQ
	24	1.76 <LOQ	23	1.41 <LOQ
	30	2.07	29	1.36 <LOQ
	36	1.64 <LOQ	35	1.53 <LOQ
	42	1.66 <LOQ	41	1.46 <LOQ
	48	1.22 <LOQ	47	1.44 <LOQ
	54	1.15 <LOQ	53	1.55 <LOQ
	60	1.32 <LOQ	59	1.81 <LOQ
	66	2.70	65	1.54 <LOQ
	72	1.17 <LOQ	71	1.60 <LOQ
	78	0.84 <LOQ	77	0.58 <LOQ
	84	0.85 <LOQ	83	1.22 <LOQ
	90	0.84 <LOQ	89	1.39 <LOQ
	96	0.75 <LOQ	95	1.26 <LOQ
	102	0.28 ND	101	1.98 <LOQ
	108	0.45 <LOQ	107	1.25 <LOQ
	114	0.19 ND	113	1.20 <LOQ
	120	0.18 ND	119	1.51 <LOQ
	126	0.16 ND		
Bulk sample from 1st hour		**4.55**		**1.21**

The results of this experiment demonstrate after approximately 36 minutes of production time, fluoride concentrations in flour are at or about the reported LOQ of 2 mg/kg. In bran, fluoride concentrations were below the LOQ of 4 mg/kg at the beginning of production.

There is a dilution of fluoride concentration with time that may allow millers to make decisions regarding what period of time is required for flour and bran that is retained within a mill at fumigation to be collected for disposal after mill restart. The data allow a time period of disposal to be specified for commercial production depending on the MRL that must be met.

The reported LOQ for flour and bran were 2 mg/kg and 4 mg/kg fluoride.

Recoveries for wheat flour following fortification at concentrations of 2 mg/kg (n = 7), 5 mg/kg (n = 3), 50 mg/kg (n = 3) and 100 mg/kg (n = 4) were 103, 104, 96 and 100%, respectively. The mean recovery in wheat flour was 101%.

Recoveries for wheat bran following fortification at concentrations of 4 mg/kg (n = 6), 20 mg/kg (n = 5) and 100 mg/kg (n = 3) were 87, 88 and 79%, respectively. The mean recovery in wheat bran was 86%.

Recoveries for wheat and barley grain following fortification at concentrations of 2 mg/kg (n = 5), 5 mg/kg (n = 3), 50 mg/kg (n = 3) and 100 mg/kg (n = 3) were 97, 95, 88 and 97%, respectively. The mean recovery in wheat and barley grain was 95%.

8.7. Residues of Fluoride Ion In Cereals Following Fumigation Of A Flour Mill With Sulfuryl Fluoride – Italy 2001. Perkins, J.M. and Foster, D.R. Dow AgroSciences LLC, Report No. GHE-P-9862, Study Plan No. 010093, 22 July 2002. (Ref. 7).

A flour mill in Italy was fumigated with SO_2F_2 at a CTP of 1387 g hr/m^3. The mill was a large structure with a basement, ground floor and seven additional floors; the estimated volume of the building was not provided. The mill was primarily for production of semolina for pasta. Prior to the fumigation, samples of cereals grains, namely wheat, barley, rice, wheat flour and maize flour weighing between 0.5 to 3 kg were placed in open bags on the 1st floor of the mill. Fumigation occurred for 17 hours, followed by aeration for 18 to 27 hours. The measured CTP near the commodities was 1380 CTP. Samples were collected for analysis approximately 18 hours into the aeration phase.

The results from the study are shown below and were reported as uncorrected for recovery:

Commodity	Mean Fluoride Ion (mg/kg)	Control Samples(mg/kg)
English wheat grain (organic)	4.5	ND
Canadian wheat grain	6.18	ND
Wheat flour	40.82	ND
English barley grain	11.75	ND
Maize flour	24.27	ND
Italian long grain rice	3.56	ND

LOQ = 2 mg/kg; ND = <33% of LOQ or <0.66 mg/kg.

Fluoride concentrations ranged from 3.56 mg/kg in Italian long grain rice to 11.75 in barley grain.

Recoveries of fluoride ion in wheat, barley and rice grain following fortification at concentrations of 2, 5, 50 and 100 mg/kg ranged 78 – 105%, with a mean recovery of 92% (n = 15). Recoveries in wheat and maize flour ranged 83 – 108%, with a mean recovery of 95% (n = 12), following fortification at concentrations of 2, 5, 50 and 100 mg/kg.

The data show that the fluoride concentrations in whole grain are lower than those in fumigated processed commodities, as also found in other studies.

8.8. Residues of Fluoride Ion In Flour Produced Immediately After Fumigation Of A Flour Mill With Sulfuryl Fluoride – Italy 2001. Perkins, J.M. and Foster, D.R. Dow AgroSciences LLC, Report No. GHE-P-9863, Study Plan No. 010094, 23 July 2002. (Ref. 8).

This study was conducted at the same mill as that described in the previous study (8.7), with the same CTP, fumigation time and aeration conditions. Samples of various grain fractions that were retained within the mill during fumigation were sampled and analysed. These were whole wheat grain, cracked wheat and flour from various stages of the milling process.

Samples of flour (0.4 to 1 kg) were taken at the end of the production process after restart of the mill. The mill was run dry for a few minuted while operators dislodged any flour remaining in the machinery during fumigation. Grain was then introduced and samples of flour were taken after 8 minutes of commercial production, 14 minutes then 20 minutes. Due

to technical difficulties, no samples after 20 minutes were taken therefore there was no bulked sample representing the first hour of production.

The results of the study are given below:

Commodity	Mean Fluoride Ion (mg/kg)	Control Samples(mg/kg)
Wheat grain (mill blend)	2.04	ND
Cracked wheat grain & fines	15.19	ND
Wheat flour	36.91	ND
Flour (shakers)	38.61	ND
Flour (end of transfer pipe)	15.91	ND
Flour (final product)	29.86	ND

LOQ = 2 mg/kg; ND = <33% of LOQ or <0.66 mg/kg.

Description	Time from start of machinery (minutes)	Time of commercial production (minutes)	Fluoride (mg/kg)
Retained flour dislodged from machinery and run dry	0 (1st flush of flour)	–	45.21
Start up of production	6	–	36.26
Flour from freshly milled grain	20	0	36.61
	28	8	17.91
	34	14	10.04
	40	20	5.44

Recoveries of fluoride ion in wheat grain following fortification at concentrations of 2, 5, 50 and 100 mg/kg ranged 72 – 107%, with a mean recovery of 90% (n = 12). Recoveries in wheat flour ranged 83 – 118%, with a mean recovery of 103% (n = 11), following fortification at concentrations of 2, 5, 50 and 100 mg/kg.

8.9. Residue Of Fluoride Ion Following Fumigation Of A Mill With Sulfuryl Fluoride in Grain, Flour And Bran Produced Immediately After Restart of Production And In Commodities Placed In The Mill Prior To Fumigation, North America – 2002.
Barnekow, D.E. and Foster, D.R. Dow AgroSciences LLC, Report No. 020046, 27 June 2002. (Ref. 9).

A flour mill in Indiana USA was fumigated with SO_2F_2 at a CTP of 1626 g hr/m^3. The mill consisted of 5 storeys with an estimated volume of 14,640 m^3. Prior to the fumigation, samples of cereals grains, namely wheat, barley and rice grain, wheat flour and maize flour weighing between 0.7 to 1.3 kg were placed in open bags on the 2nd floor of the mill. The fumigation phase was 14 hours followed by 12 hours aeration time. Samples were taken immediately after aeration had been completed and personnel were allowed to enter the mill.

In addition, samples of wheat flour and bran were taken from their final production points in the mill prior to fumigation. Immediately after restart of production, samples of flour and bran were taken every 3 minutes for up to 2 hours; samples were bulked to represent a composite sample for the first and second hour of commercial production. Control samples were taken prior to fumigation.

The results from the study are shown below and were reported as uncorrected for recovery; CTP near the commodities was measured at 1761 g hr/m^3:

Commodity	Mean Fluoride Ion (mg/kg)	Control Samples(mg/kg)

Wheat grain	9.09	<2
Wheat flour	42.94	<2
Barley grain	18.27	<2
Maize flour	37.34	ND
Rice grain	7.86	<2

LOQ = 2 mg/kg; ND = <20% of LOQ or <0.4 mg/kg.

As shown in other studies, fluoride concentrations are higher in fumigated processed commodities than whole grain commodities. Fluoride concentrations in whole cereals ranged from 7.86 mg/kg in rice to 18.27 mg/kg in barley.

Description	Time (min.s)	Fluoride Ion Concentration (mg/kg)	
		Wheat Bran	Wheat flour
At start of milling process	**0**	**90**	**61.32**
	6	2.45 <LOQ	11.02
	12	1.86 <LOQ	8.28
	18	2.42 <LOQ	3.17
	24	1.93 <LOQ	5.47
	30	1.83 <LOQ	3.0 <LOQ
	36	0.97 <LOQ	2.20 <LOQ
	42	1.51 <LOQ	1.93 <LOQ
	48	1.59 <LOQ	1.54 <LOQ
	54	1.80 <LOQ	1.32 <LOQ
	60	2.09 <LOQ	1.06 <LOQ
	66	0.43 <LOQ	1.03 <LOQ
	72	0.16 <LOQ	0.89 <LOQ
	78	0.21 <LOQ	0.94 <LOQ
	84	0.46 <LOQ	0.87 <LOQ
	90	1.04 <LOQ	1.36 <LOQ
	96	1.01 <LOQ	0.80 <LOQ
	102	0.79 <LOQ	0.74 <LOQ
	108	0.97 <LOQ	0.77 <LOQ
	114	1.12 <LOQ	0.87 <LOQ
	120	0.98 <LOQ	0.75 <LOQ
Bulk of 1st hour	**–**	**1.24** <LOQ	**3.60** <LOQ
Bulk of 2nd hour	**–**	**1.20** <LOQ	**0.96** <LOQ

LOQ = 4 mg/kg for bran and 2 mg/kg for flour.

The results of the milling study show that fluoride concentrations are below the reported LOQ in bran after 6 minutes of production and after 30 minutes of production for flour. The data allow a time period of disposal to be specified for commercial production of bran and flour depending on the MRL that must be met.

Recoveries for wheat flour following fortification at concentrations of 2 mg/kg (n = 6), 5 mg/kg (n = 3), 50 mg/kg (n = 3) and 100 mg/kg (n = 3) were 101, 101, 99 and 90%, respectively. The mean recovery in wheat flour was 98%.

Recoveries for wheat bran following fortification at concentrations of 4 mg/kg (n = 5), 20 mg/kg (n = 5) and 100 mg/kg (n = 2) were 83, 97 and 78%, respectively. The mean recovery in wheat bran was 88%.

Recoveries for wheat, barley and rice grain following fortification at concentrations of 2 mg/kg (n = 7), 5 mg/kg (n = 3), 50 mg/kg (n = 3) and 100 mg/kg (n = 4) were 92, 96, 92 and 89%, respectively. The mean recovery in wheat, barley and rice grain was 92%.

8.10 Determination Of Sulfuryl Fluoride and Fluoride Ion Residuals In Corn, Rice, Soyabean and Wheat Kernels Following Fumigation At A Targeted Dosage of 150 mg hr/L. Creasy, S.R., Hartsell, P.L. and Hurley, J.M. Dried Fruit Association of California, 10 December 2001. Non-GLP Study

In this laboratory study, wheat, rice, corn, and soya beans were fumigated twice at CTPs ranging 127 to 197 mg hr/L. These values are well below the CTP specified as the proposed Australian use pattern. The commodities were fumigated for 48 hours followed by a 2 hour aeration period and stored at 30 °C for residue analysis.

SO_2F_2 residues ranged <1 ppb in wheat, rice, and soya beans to 2 ppb in corn following two fumigations. By Day 4, SO_2F_2 residues in corn were <1 ppb.

SO_2F_2 concentrations were determined by head-space measurements using GC/ECD with a J & W GS-Q megabore column. The mean limit of detection for the commodities tested was determined as 1 ppb; corn 1.24 ppb, rice 1.15 ppb, soy beans 1 ppb and wheat 1.1 ppb. A mean recovery of 108% was reported for 30 fortifications at 1 ppb.

The fluoride ion concentrations are shown below for the four commodities, following two fumigations:

Commodity	Fumigation	Fluoride ion concentration (mg/kg)	
		Day 0	Day 4
Rice	#1	<2, <2	–
	#2	2.5, 2.6	–
Wheat	#1	<2, <2	–
	#2	<2, <2	–
Corn	#1	<2; 1.8	–
	#2	3.2, 3.8	3.2, 3.4
Soya beans	#1	2.5, 3.7	–
	#2	<2	–

The results above show that corn when fumigated twice leads to detectable SO_2F_2 residues as well as an increase in fluoride ion concentration with the second fumigation.

Fluoride concentrations were determined by fluoride selective electrode with a reported detection limit of 2 mg/kg; mean detection limits were 2.3 mg/kg for corn, 2 mg/kg for rice, 2.4mg.kg for soya beans and 2.8 mg/kg for wheat. Recoveries were conducted by fortification at concentrations of 59, 57, 62 and 52 mg/kg for corn, rice, soya beans and wheat, respectively. The mean recoveries were 115%, 146%, 98% and 116% for corn, rice, soya beans and wheat, respectively. Additional recoveries were as reported 112% at 2 mg/kg from 10 fortifications.

As the CTP was very low compared to the proposed fumigation CTP, fluoride ion recoveries were consistently high and the study was not GLP, the results will not be considered as part of the MRL determinations. The study is supportive in nature.

Dried Fruit and Nuts

8.11. To Determine and Evaluate the Significance of Sulfuryl Fluoride Residues in Dried Fruits and Tree Nuts Following Fumigation Treatments with Sulfuryl Fluoride at Different Temperatures, Sample Locations, Desorption Rates, Repeated Fumigations and A Comparison of Treatments Done Under Vacuum or Normal Atmospheric

Pressure – Phase I. Hartsell, P.L. Dow AgroSciences LLC, Protocol No. DFA SF-1, 1 June 2000.

In this study, raisins and walnuts were exposed to controlled fumigations of sulfuryl fluoride under laboratory conditions at the Dried Fruit Association of California. Experiments were conducted to determine the effect of different fumigation conditions on the rate of sulfuryl fluoride desorption and resulting fluoride levels in the two commodities. The experimental conditions included:

1. varying exposure temperature (CTP 2500 and 30% loading factor)
2. repeat fumigations (1 to 5 consecutive fumigations)
3. vacuum or pressure fumigations

For each experiment, fumigations were conducted in individual chambers with a control chamber for each commodity tested. In all of the experiments the commodities were loaded to occupy approximately 30% of the total fumigation chamber. Due to intrinsic differences in the densities of the raisins and walnuts, the equivalence in volumetric loading between commodities would not equate to equivalence in weight loading. Rates of fumigation (dosages) were adjusted to accommodate the displacement volume of the commodity.

For experiment 2, samples were analysed after 1, 3 and 5 fumigations only. Experiment 3 was only conducted in walnuts, with pressures ranging 240 – 270 mm Hg at 21 °C, CTP 2500 and 30% loading.

The results from the different treatments are tabulated below. Values of sulfuryl fluoride for each fumigated commodity are reported as corrected for recovery. Values of fluoride are reported as ‘net concentrations’, i.e. measured fluoride concentration in fumigated commodity — concentration in untreated control sample. As the fluoride concentrations in the control samples were <LOQ in most cases, the reported values were not adjusted. Samples were analysed on the day of sampling; no storage of samples was considered necessary.

Mean recoveries of sulfuryl fluoride in raisins were reported as 98% and in walnuts were 94%. For each experiment, a set of validated spike recoveries were reported and were within the acceptable limits of 70 – 110%.

Reported recoveries of fluoride ion in raisins were within the acceptable limits of 70 – 110%, as reported for each experiment. In walnuts however, recoveries of 120 and 124% were reported in some of the experiment 2 validation results. Overall however, the mean of reported recoveries were within acceptable limits. In an independent laboratory validation of fluoride ion in walnuts, acceptable recoveries were reported (section 9).

Residues of SO_2F_2 and fluoride in raisins resulting from varying conditions of fumigation.

Expt. No.	Experimental design	Measured concentrations in the chamber		SO_2F_2 concentration (µg/kg or ppb)		Fluoride concentration (mg/kg)		
		SO_2F_2 (mg/L)	CTP (mg hr/L)	Day 4	Day 7	Day 4	Day 7	Control
1	Temperature 10 °C	100	2511	<4.2	–	<2.2	<2.2	<0.75
			2534	<4.2	–	<2.2	<2.2	
	Temperature 21 °C	101	2529	<1	<1	<2.2	<0.75	<0.75
			2535	<1	<1	<2.2	<0.75	
	Temperature 32.2 °C	94	2464	<1	<1	<2.2	<2.2	<0.75
			2548	<1	<1	<2.2	<2.2	
2	Repeat fumigations #1	105	2520	<4.2	<1		<2.2	ND <0.75
	Repeat fumigations #2		2550					
	Repeat fumigations #3	110	2552	<4.2	<1		<2.2	ND <0.75
	Repeat fumigations #4		2502					
	Repeat fumigations #5	100	2521	<1	<1		<2.2	ND <0.75

Residues of SO_2F_2 and fluoride in walnuts resulting from varying conditions of fumigation.

Expt. No.	Experimental design	Measured concentrations in the chamber		SO_2F_2 concentration (µg/kg or ppb)		Fluoride concentration (mg/kg)		
		SO_2F_2 (mg/L)	CTP (mg hr/L)	Day 4	Day 7	Day 4	Day 7	Control
1	Temperature 10 °C	100	2494	277	<4.2	2.9		<0.75
		101	2514	243	<4.2	3.1		
	Temperature 21 °C	101	2548	44.1	5.6	7	5.7	<0.75
			2550	44.7	6.3	7.2	5.8	
	Temperature 32.2 °C	94	2495	208	67.6	7.9	9.8	<0.75
			2501	216	60	8.2	9.4	

Expt. No.	Experimental design	Measured concentrations in the chamber		SO_2F_2 concentration (µg/kg or ppb)			Fluoride concentration (mg/kg)	
		SO_2F_2 (mg/L)	CTP (mg hr/L)	Day 1	Day 4	Day 7	Day 7	Control
2	Repeat fumigations #1	100	2500	1534	123	7.4	2.3	<0.75
	Repeat fumigations #2							
	Repeat fumigations #3	100	2500	4794	829	211	14.3	<0.75
	Repeat fumigations #3B			3082	679	94	10.4	<0.75
	Repeat fumigations #4							
	Repeat fumigations #5	100	2500	4811	2069	665	25.8	<2.2
3	Vacuum 240 – 270 mm Hg	650 – 687	2500	1628	539		5.33	<0.75

8.12. Magnitude of the Sulfuryl Fluoride and Terminal Fluoride Ion Levels in Dried Fruit and Tree Nut Commodities Fumigated with Sulfuryl Fluoride. Byrne, S.L., Hartsell, J.M., Hurley, D.B., Allred, D.B., Carmona, L.M. and Bunnell, J. Dow AgroSciences LLC Report No. 010014.02, 2 October 2001.

Dried fruit and nuts (dates, figs, dried plums, raisins and walnuts, pistachios, pecans and almonds) were exposed to controlled fumigations of sulfuryl fluoride under laboratory conditions. A number of experiments were conducted involving varying conditions of fumigation for 24 hours followed by aeration for 24 hours. The experimental conditions included:

1..a single controlled fumigation at CTP 200 mg hr/L at normal T & P
2. repeat fumigations
3. vacuum fumigations

For each experiment, there were two replicate exposure chambers and one control chamber for each commodity tested. In all of the experiments the commodities were loaded to occupy approximately 30% of the total fumigation chamber. The commodity was allowed to equilibrate to the fumigation temperature overnight, typically 32° C prior to the chamber being sealed and fumigated.

The results of the controlled fumigations from experiment 1, 2 and 3 are tabulated below. Following fumigation, each of the commodities were samples as soon as possible to determine the day 1 or day 2 SO_2F_2 concentrations. Fluoride concentrations were only determined after the SO_2F_2 concentrations had become non-detectable. Following sampling, the boxes containing the commodities were maintained at 20° C.

Values of sulfuryl fluoride for each fumigated commodity are reported as uncorrected for recovery. Values of fluoride are reported as ‘net concentrations’, i.e. measured fluoride concentration in fumigated commodity — concentration in untreated control sample. As the fluoride concentrations in the control samples were <LOQ in most cases, the reported values were not adjusted.

<u>Experiment 1</u>: CT = 196 – 226 mg hr/L; exposure time 24 hours. Two replicate results and one control result is reported for each commodity tested at each time point. Fluoride ion concentrations were measured on the day indicated next to the value.

Commodity	CTP (mg hr/L)	SO_2F_2 concentration (ng/g)				Fluoride ion concentration (mg/kg)
		Day 2	Day 3	Day 6	Day 9	
Walnuts	219	74.1		<2.1	<2.1	<1.4 Day 10
		67.8		<4.2	<2.1	<1.4
	214	76		<4.2	<2.1	<1.4
		69.4		<4.2	<2.1	<1.4
Pistachios	226	<2.1				<2.4 Day 6
		<2.1				<2.4
	202	<2.1				<2.4
		<2.1				2.91
Pecans	200	43.1	25.3	4.8	<2.1	<1.4 Day 9
		32.2	23.3	7.4	<2.1	<1.4
		42.8				
	197	53.6	21.7	4.9	<2.1	<2.4
		60.3	17.3	5	<2.1	<2.4
Almonds	205	12.4	<2.1			3.25 Day 3
		10.9	<4.2			3.20
	201	11.9	<2.1			3.44
		8.9	<2.1			3.77
Dates	208	<2.1				<1.4 Day 7
		<2.1				<1.4
	206	<2.1				<1.4
		<2.1				<1.4
Figs	197	<2.1				<1.4 Day 2
		4.7				<1.4 Day 2
		7.2				<1.4 Day 8
	196	4.7				<1.4 Day 2
		4.4				<1.4 Day 2
Dried plums	219	<2.1				<1.4 Day 2
		<2.1				<1.4
	218	<2.1				<1.4
		<2.1				<1.4
Raisins	221	<2.1				<1.4 Day 6
		<2.1				<1.4 Day 6
						<1.4 Day 9
	221	<2.1				<1.4 Day 6
		<2.1				<1.4 Day 6

Experiment 2: Repeat fumigations at CTP 1500 mg hr/L.

Commodity	CTP (mg hr/L)	SO_2F_2 concentration (ng/g)					Fluoride ion concentration (mg/kg)
		Day 2	Day 3	Day 6	Day 9	Day 16	
Pistachios							
Fumigation #1	1515	252		18			3.95 Day 8
		287		29			4.29
	1519	267		24			3.58
		303		22			4.56
Fumigation #2	1503	63		<2.1			12.6 Day 7
		51		<2.1			10.7
	1510	69		<2.1			9.98
		70		<2.1			10.9
Fumigation #3	1516	36	8.1	<2.1			15 Day 6
		35	9.9	<2.1			16.7
	1496	56	16	<2.1			17.9
		52	15	<2.1			13.2
Pecans					Day 11		7.72 Day 14
Fumigation #1	1527	2224		104	15		8.28
		2323		99	16		9.59
	1539	2688		103	15		8.68
		2395		105	20		
Fumigation #2						Day 13	
	1461	5040				13	
						12	
	1443	5532				16	
		4146				14	
Fumigation #3	1512	4276	3157	240	68	<2.1	20.1 Day 17
		5209	3915	261	69	<2.1	21.8
	1508	6030	1880	214	57	<2.1	19.8
		4287	1304	199	57	<2.1	21.6
Figs							
Fumigation #1	1482	40					<2.4 Day 7
		41					<2.4
	1441	34					<2.4
		33					<2.4
Fumigation #2	1483	11	9.3	4.5			<1.4 Day 6
		13	8.8	5.6			<1.4
	1513	13	<4.2				<2.4
		15	<4.2				<2.4

Experiment 2: Repeat fumigations at CTP 1500 mg hr/L.

Commodity	CTP (mg hr/L)	SO_2F_2 concentration (ng/g)					Fluoride ion concentration (mg/kg)
		Day 2	Day 3	Day 6	Day 9	Day 16	
Almonds							
Fumigation #1	1520	33					4.07 Day 2
		40					4.48
	1558	33					5.96
		28					4.13
Fumigation #2	1538	75	34	8.1			7.94 Day 6
		61	55	7			6.93
			42				
	1537	50	23				6.65
		44	22				7.97
Fumigation #3	1485	125		14	<4.2	<2.1	9.71 Day 16
		107		18	<2.1	<2.1	9.9
	1491	128		14	<4.2	<2.1	9.07
		124		16	<4.2	<2.1	9.37
Dates							
Fumigation #1	1474	8.3					<1.4 Day 5
		6.1					<1.4
	1493	8.1					<1.4
		6.6					<1.4
Fumigation #2	1506	<2.1					<1.4 Day 6
		<2.1					<1.4
	1502	<4.2					<2.4
		<4.2					<2.4
Fumigation #3	1539	7.1					<2.4 Day 6
		5.9					<2.4
	1447	6.2					<2.4
		5.2					<2.4
Fumigation #4	1488	15		11 Day 5			2.74 Day 5
		12		8.8 Day 5			<1.4
	1518	8.6		7.5 Day 5			<2.4
		11		9.2 Day 5			<2.4
Fumigation #5	1503	15	7.5	7.9	<4.2	<2.1	<2.4 Day 16
		13	11	16	<2.1	<2.1	3.09
					8		
	1518	23	19	5.5	<4.2	<2.1	<2.4
		16	18	6	<4.2	<2.1	<2.4
					6.8		

Experiment 2: Repeat fumigations at CTP 1500 mg hr/L.

Commodity	CTP (mg hr/L)	SO_2F_2 concentration (ng/g)					Fluoride ion concentration (mg/kg)
		Day 2	Day 3	Day 6	Day 9	Day 16	
Dried plums							
Fumigation #1	1538	<2.1					<1.4 Day 3
		<2.1					<1.4
	1611	<2.1					<1.4
		<2.1					<1.4
Fumigation #2	1486	<2.1					<2.4 Day 3
		<2.1					<2.4
	1521	<2.1					<2.4
		<2.1					<1.4
Fumigation #3	1510	<4.2					<1.4 Day 5
		<2.1					<2.4
		<2.1					
	1521	<4.2					<2.4
		<2.1					2.56
		<2.1					
Fumigation #4	1519	<2.1					<2.4 Day 6
		<2.1					3.14
	1523	<2.1					<2.4
		<2.1					<2.4

Experiment 3: Four hour vacuum fumigation at CTP 200 mg hr/L.

Commodity	CTP (mg hr/L)	SO_2F_2 concentration (ng/g)					Fluoride ion concentration (mg/kg)
		Day 1	Day 2	Day 5	Day 8	Day 15	
Walnuts	183	591	349	92	25	<2.1	<2.4 Day 15
		569	290	90	24	<2.1	<1.4
	182	610	425	101	29	<2.1	<1.4
		640	384	95	29	<2.1	<1.4
Pistachios	208	17	<2.1				<1.4 Day 3
		26	<2.1				<1.4
	197	13	<2.1				<1.4
		14	<2.1				<2.4
Pecans	203	1190	369	51	4.5	<2.1	<2.4 Day 16
		1095	392	39	7.2	<2.1	<1.4
	209	1306	456	55	4.9	<2.1	<2.4
		1139	462	47	5.8	<2.1	<2.4
Almonds	195	18	6.3	<2.1			<1.4 Day 7
		20	8.8	<2.1			<1.4
	240	12	<2.1	<2.1			<1.4
		12	<4.2	<2.1			<1.4

In experiment 1, mean recoveries of sulfuryl fluoride in nuts were 76% and 101% with fortification at 4.2 and 21 ng/g, respectively. The mean recovery in dried fruit was 88% with fortification at 4.2 ng/g. In experiment 2, mean recoveries of sulfuryl fluoride in nuts in experiment 2 were 71%, 102% and 97% with fortification at 4, 21 and 105 ng/g, respectively. The mean recoveries of sulfuryl fluoride in dried fruit were 101%, 98% and 80% with fortification at 4.2, 8.4 and 21 ng/g, respectively. In experiment 3, the mean recoveries in nuts were 73%, 105% and 97% with fortification at 4, 21 and 105 ng/g, respectively. Overall, the mean recoveries of sulfuryl fluoride in dried fruit and nuts were within acceptable limits of 70 – 110%.

Mean recoveries of fluoride ion in experiment 1 for nuts and fruit were 80% and 86%, respectively with fortification at 5 mg/kg. In experiment 2, the mean recoveries were 101% and 89% in nuts and fruits respectively, with fortification at 5 mg/kg (4.8 – 5.2 mg/kg). In experiment 3, the mean fluoride ion recovery was 102% with fortification at 5 mg/kg (4.8 – 5.2 mg/kg). Overall the mean fluoride ion recoveries in dried fruit and nuts were within acceptable limits of 70 – 110%.

The results of experiment 1 show that following fumigation at CTPs approximating 200 mg hr/L, sulfuryl fluoride residues are highest in walnuts and pecans at 2 days after fumigation. By day 9 however, sulfuryl fluoride concentrations had decreased to below detectable limits. By 9 to 10 days after fumigation, the fluoride ion concentrations in walnuts and pecans were also below the limits of quantitation of fluoride ion.

In experiment 2, the highest sulfuryl fluoride concentrations were found in pecans on day 2 following fumigation at 1500 CTP. With each fumigation, the mean sulfuryl fluoride concentrations increased from 2407 ng/g with fumigation #1 to 4906 ng/g with fumigation #2 to 4950 ng/g with fumigation #3. As pecans appear to be the worst case in relation to sulfuryl fluoride residue potential, it will be considered as the representative commodity for the tree nut group. The highest mean residue in pecans was 4950 ng/g or 4.95 mg/kg sulfuryl fluoride.

Repeat fumigations of pecans, almonds and pistachios also lead to cumulative effects on fluoride concentration following. For example, in pecans, the mean fluoride ion concentrations increased from 8.56 mg/kg at 14 days following fumigation #1 to 20.8 mg/kg at 17 days after fumigation #3. Similarly in almonds, the mean fluoride ion concentrations increased from 4.66 mg/kg (day 2) to 7.37 mg/kg (day 6) to 9.51 mg/kg (day 16) following consecutive fumigations. With pistachios, the mean fluoride ion concentrations increased from 4.1 mg/kg to 11 mg/kg to 15.7 mg/kg following consecutive fumigations. The single highest fluoride ion concentration was reported for pecans at 21.8 mg/kg at 17 days after 3 fumigations.

The results of experiment 3 when compared to experiment 1 show that higher sulfuryl fluoride concentrations result in the fumigated commodity when under vacuum. This also corresponded to longer times for the SO_2F_2 to dissipate, i.e. up to 15 days compared to 9 days at atmospheric pressure (time includes fumigation and aeration period in experiment 1).

8.13. Post-Fumigation Fate of Sulfuryl Fluoride Desorption From Structural Commodities and Transient and Permanent Residues in Protected and Exposed Foodstuffs. Scheffrahn, R.H., Osbrink, W.L.A., Hsu, R-C. and Su, N-Y. Dow Chemical USA, Project ID GH-C 1939, 4 September 1987.

This study comprised four components including food and non-food uses. The subtitles are listed below:

- Desorption of Residual Sulfuryl Fluoride (SF) From Structural and Household Commodities
- Post-Fumigation Desorption of Sulfuryl Fluoride From Polystyrene Panels
- Sulfuryl Fluoride Residues of Fumigated Foods Protected by Polyethylene Film
- Ionic Fluoride and Sulfate Residues in Food Fumigated with Sulfuryl Fluoride

The first and second studies did not involve food uses and therefore they are not considered further in this report. In the third study, sulfuryl fluoride concentrations were measured by head-space analysis in eight food items that were either sealed or unsealed in polyethylene bags or film. The food commodities included flour, dog food, powdered milk, vegetable oil, dried beef (jerky), Tylenol, apples and twinkies snack cakes. The commodities were fumigated at 36 or 360 mg/L sulfuryl fluoride for 20 hours at 27° C. After fumigation, the chamber was aerated for 8 minutes with forced ventilation to reduce the SO_2F_2 concentration to below OH&S limits (5 ppm). SO_2F_2 concentrations were determined in the commodities at 2, 8, 26 hours and 5, 20 and 40 days.

The results of the study showed that vegetable oil contained the highest concentrations of SO_2F_2 compared to all the other commodities, at 20.5 mg/kg at 2 hours aeration and no polyethylene film following fumigation at 36 mg/L. The sample that was fumigated with 2 layers of film at 2mm thick contained SO_2F_2 concentrations of 0.65 mg/kg at the same sampling point. By 960 hours and 480 hours the SO_2F_2 concentrations had decreased to below detectable limits for the uncovered sample and the sample with 2 layers of film, respectively.

Following fumigation at 360 mg/L SO_2F_2 concentrations in vegetable oil were 221 mg/kg and 3.7 mg/kg at 2 hours with no film and 2 layer of film, respectively. The data show that use of polyethylene film to cover or protect the commodity to be fumigated can lead to decreases in the SO_2F_2 concentrations observed immediately after fumigation.

In the fourth study, the fluoride ion and sulfate ion concentrations were measured in the fumigated commodities described above. The highest fluoride ion concentrations were in beef jerky at 3404 mg/kg and 3569 mg./kg at 1 day after fumigation at 36 and 360 mg/L, respectively. Sulfate ion concentrations were higher in dog food however. The reported mean recoveries of fluoride and sulfate ions were within acceptable limits of 70 – 110%.

As the data in this study are not directly relevant to the proposed label directions, the study is considered supportive in nature.

8.14. Magnitude Of The Terminal Fluoride Ion Level In Finished Food Products Fumigated With Sulfuryl Fluoride. Rick, D.L., Krieger, S.M. and Mielke, M.S. Dow AgroSciences LLC, Report No. 021080, 26 March 2003.

In this study, 24 finished food products were fumigated for 24 hours under controlled conditions of 1500 mg hr/L and 30° C. The commodities included: spaghetti, egg noodles, dry chocolate cake mix, dry white pudding mix, soft corn tortillas, soft wheat tortillas, cheese crackers, tortilla chips, corn-based chips, peanut butter cookies, pecan shortbread cookies, chocolate cream cookies (Oreos), granola cereal, corn flakes, coconut flakes, beef jerky, cocoa beans, unroasted coffee beans, ground coffee, ham, two varieties of cat food and two varieties of dog food. Key food ingredients that were fumigated included: powdered eggs, powdered whole milk, powdered non-fat milk, powdered cheese, sugar, baking soda, baking powder, salt, onion powder, garlic powder, dried chilli peppers, peanuts in-shell, peppercorns, parsley flakes and basil.

Sulfuryl fluoride concentrations were below the reported LOQ of 4 μg/kg in 12 commodities (spaghetti, cheese crackers egg noodles, chocolate cake mix, peanut butter cookies, powdered non-fat milk, garlic powder, onion powder, baking soda, salt, sugar and ham. Concentrations above 1000 μg/kg were only present in the pet foods, whole powdered milk and corn flakes.

Thirty-five commodities contained quantifiable levels of fluoride ion ranging from 1.03 mg/kg in sugar to 754 mg/kg in powdered eggs; the two highest concentrations were 61 mg/kg in open fumigated peanut butter cookies and 754 mg/kg in powdered eggs.

As none of the commodities are directly relevant to the proposed use, the data will not be considered further for the purposes of MRL setting, although the study is supportive in nature and may be of use in the future for extension of uses and dietary exposure assessments.

Quality of cereal grains and processed fractions

The following studies (8.15 – 8.19) were provided in support of the current application. Although some of the studies contain data on fluoride ion concentrations in processed fractions, they are primarily concerned with quality and performance of the commodity during cooking or baking. As they do not relate directly to the purposes of MRL setting, they are considered as being supportive in nature.

8.15 Quality Characteristics of Wheat Kernels Treated With Profume® Gas Fumigant (Sulfuryl Fluoride). Prabhakaran, S.K. and Schneider, B. Protocol No. SM01G1A003. 29 December 2001.

8.16 Nutritional Analysis of Wheat and its Milled Fractions Exposed to Sulfuryl Fluoride. Prabhakaran, S.K. and Schneider, B. Protocol No. SM01G1A003. 29 December 2001.

8.17 Quality of Spaghetti Made From Durum Wheat Fumigated With Sulfuryl Fluoride. Prabhakaran, S.K. and Schneider, B. Protocol No. SM01G1A003. 29 December 2001.

8.18. Quality Characteristics Of Wheat Flour Fumigated With Profume® Gas Fumigant (Sulfuryl Fluoride). S.K. and Schneider, B. Protocol No. SM01G1A003. 28 April 2002.

8.19. Quality Characteristics of Rice Treated With Profume® Gas Fumigant (Sulfuryl Fluoride). Prabhakaran, S.K. Reference 240, 15 December 2003.

Animal Transfer Studies

8.20. Fluorine Concentration and Distribution in Hen's Eggs in Aspect of Selected Biological Parameters. Machalinski. B. *Ann. Acad. Med. Stetin.*, 1996, **42**, 25 – 38.

In this published article (written in Polish), the effect of NaF in drinking water and its effect on the distribution of fluorine in eggs and laying hens was investigated.

As the article is not in English, the details of the study cannot be accurately determined. Also the article does not appear to be relevant to the current application or proposed use of sulfuryl fluoride as a fumigant. Therefore the article is not considered further for the purposes of MRL setting.

9. ANALYTICAL METHODS AND STORAGE STABILITY

A number of reports were provided in which are described analytical methods and/or independent laboratory validations of methods used to determine residues of sulfuryl fluoride or inorganic fluoride ion in cereal grains and processed fractions, nuts, dried fruits and other commodities. The reports provided are listed below.

9.1. 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". Davis, B. Study ID 010115, Dow AgroSciences LLC, Lab Report Code GH-C 5382, 7 February 2002.

This report describes the independent laboratory validation of the Dow Chemical Company Method "Residue Method Validation for the Determination of Fluoride Anion in Corn, Wheat, Corn oil and Flour", Rick, D.L. and Marty, G.T. This method was used in all of the studies described in sections 8.1 to 8.10 and 8.14.

9.2. 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". Davis, B. Study ID 010114, Dow AgroSciences LLC, Lab Report Code GH-C 5398, 5 March 2002. Amended report date 5 March 2002.

This report describes the independent laboratory validation of the Dow Chemical Company Method "Determination of Residues of Sulfuryl Fluoride in Corn, Wheat and Rice Commodities by Gas Chromatography with Electron Capture Detection", Rick, D.L. and Marty, G.T. This method was used in all of the studies described in sections 8.1 and 8.10.

9.3. Determination of Residues of Sulfuryl Fluoride in Dried Fruit and Tree Nuts by Gas Chromatography with Electron Capture Detection. Creasy, S.R., Hartsell, P.L., Hurley, J.M., Carmona, L.M. and Byrne, S.L. Method GRM 01.12, 3 July 2001.

This method describes the determination of sulfuryl fluoride residues ion in dried fruit and tree nuts following fumigation with sulfuryl fluoride. Sulfuryl fluoride residues are extracted from a portion of a fumigated dried fruit or tree nut sample with water in an air-tight blender jar. An aliquot of the head-space is analysed by GC/ECD.

The validation concentration range was 4.2 to 63 ng/g for dried fruit and 4.2 to 105 ng/g for tree nuts, with mean recoveries 93% for both commodity types. The method limit of quantitation was 4.2 ng/g and the limit of detection was 2.1 ng/g. Detailed values of recoveries are reported in the table below.

9.4. Independent Laboratory Validation of Dow AgroSciences LLC Method GRM 01.12 – Determination of Residues of Sulfuryl Fluoride in Dried Fruit and Tree Nuts by Gas Chromatography with Electron Capture Detection. Davis, B. Study ID 010098, Dow AgroSciences LLC, Lab Report Code GH-C 5422, 26 March 2002.

This report describes the independent laboratory validation of the Dow Chemical Company Method "Determination of Residues of Sulfuryl Fluoride in Dried Fruit and Tree Nuts by Gas Chromatography with Electron Capture Detection", Creasy, S.R., Hartsell, P.L., Hurley, J.M., Carmona, L.M. and Byrne, S.L. This method was used in the studies described in sections 8.11 and 8.12.

9.5. Determination of Fluoride Anion in Corn, Wheat, Corn Oil and Flour with a Fluoride Selective Electrode. Rick, D.L., Marty, G.T. and Foster, D.R. Method GRM 01.17, 1 April 2002.

This method describes the determination of fluoride ion in corn, wheat, corn oil and flour following fumigation with sulfuryl fluoride. Fluoride ion is extracted from crop samples or

processed commodities using water and Total Ionic Strength Adjustment Buffer (TISAB). The extract is then centrifuged, decanted and analysed using a fluoride selective electrode with a known double addition technique. Typically an Orion fluoride electrode with an Orion 920A pH/ISE meter would be used.

The validation concentration range was 0.5 – 50 mg/kg for each commodity type and the mean recoveries were 84, 101, 99 and 109% for whole grain wheat, corn, wheat flour and corn oil, respectively. The calculated limit of quantitation was 0.5 mg/kg fluoride ion with a limit of detection of 0.2 mg/kg; both were calculated at 10× and 3× the standard deviation, respectively, from the results of the analyses of 7 replicate samples. The LOD and LOQ were based on sample sizes of 25 g of commodity. Where less dense commodities were tested with a smaller 10 g sample, the LOD and LOQ values would theoretically increase by a factor of 2.5, to give an LOD of 0.5 mg/kg and LOQ of 1.25 mg/kg. Detailed values of recoveries are reported in the table below.

9.6. 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. Lala, M. and Randolph, R. Study ID 020013, Dow AgroSciences LLC, Lab Report Code GH-C 5408, 12 March 2002.

This report describes the independent laboratory validation of the Dow AgroSciences Method GRM 01.17 “Determination of Fluoride Anion in Corn, Wheat, Corn Oil and Flour”, Rick, D.L., Marty, G.T. and Foster, D.R. This method was used in the studies described in sections 8.11 and 8.12.

9.7. Determination of Residues of Sulfuryl Fluoride as Fluoride in Dried Fruit and Tree Nuts Using a Fluoride Selective Electrode with a Known Double Addition Calibration Technique. Creasy, S.R., Hartsell, P.L., Hurley, J.M., Mukker, G.K., Bunnell, J. and Byrne, S.L. Method GRM 01.11, 29 June 2001.

This method describes the determination of fluoride ion in dried fruit (raisins, dried plums, figs and dates) and tree nuts (pistachios, almonds, pecans and walnuts) following fumigation with sulfuryl fluoride. Fluoride ion is extracted from the samples by shaking with deionised water and and Total Ionic Strength Adjustment Buffer (TISAB). The extract is then filtered to remove particles. The filtrate is then analysed using a fluoride selective electrode with a known double addition technique. Typically an Orion fluoride electrode with an Orion 920A pH/ISE meter would be used.

The validation concentration range was 2.4 to 47.7 mg/kg for the dried fruit and 2.4 to 36 mg/kg for the tree nuts, with mean recoveries of 101% and 102%, respectively. The calculated limit of quantitation ranged from 2.99 to 4.64 mg/kg for dried fruit and from 2.37 to 3.16 mg/kg for tree nuts. Recoveries for samples fortified at the proposed LOQ ranged from 68% to 127% for dried fruit and from 86% to 139% for tree nuts. However the majority of the reported results were within the acceptable range of 70 to 120% (23 from 28 dried fruit samples and 24 of 27 tree nuts samples). The overall acceptable method recovery was at the LOQ of 2.4 mg/kg. Similarly, the calculated LOD was <1.4 mg/kg.

9.8. Independent Laboratory Validation of Dow AgroSciences LLC Method GRM 01.11 – Determination of Residues of Sulfuryl Fluoride as Fluoride in Dried Fruit and Tree Nuts Using a Fluoride Selective Electrode with a Known Double Addition Calibration Technique. Davis, B. Study ID 010099R, Dow AgroSciences LLC, Lab Report Code GH-C 5434R, 5 April 2002. Amended report 30 July 2002.

This report describes the independent laboratory validation of the Dow AgroSciences Method GRM 01.11 "Determination of Residues of Sulfuryl Fluoride as Fluoride in Dried Fruit and Tree Nuts Using a Fluoride Selective Electrode with a Known Double Addition Calibration Technique. This method was used in the studies described in sections 8.11 and 8.12.

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Summary of methods: Details of limits of quantitation and detection, reported recoveries and an indication of instrumentation used are tabulated below for each of the methods provided above.

For the quantitation of sulfuryl fluoride in fumigated commodities, head-space determinations were generally used followed by gas chromatography with electron capture detection (GC-ECD). Minimal extraction work-up is generally required for head-space sampling techniques. For the quantitation of fluoride ion in commodities, determinations were generally conducted using fluoride selective electrodes. In one study, quantitation of fluoride ion was described using neutron activation analysis (NAA). As none of the quantitative analyses in the residue studies were reported as having used this technique, it is not described here in further detail.

Study reference; ID number	**Description of work-up**	**Reported LOD and LOQ**	**Method recoveries and fortifications**	**Comments**
GH-C 5382; ID 010115 (section 9.1) Fluoride analysis	To the fumigated commodity, water and TISAB are added. The sample is macerated and centrifuged as part of the extraction. The extract is decanted and analysed using a fluoride-selective electrode.	LOD = 0.2 mg/kg and LOQ = 0.5 mg/kg for original method. ILV LOQ = 2 mg/kg.	Wheat grain: mean recoveries were 103%, 96% and 103% with fortification at 2 (n = 5), 10 (n = 3) and 20 mg/kg (n = 5) respectively. Overall mean recovery 102%. Wheat flour: mean recoveries were 95%, 95% and 99% with fortification at 2 (n = 5), 10 (n = 3) and 20 mg/kg (n = 5), respectively.	Only whole wheat and wheat flour were chosen for the ILV; method sensitivities caused problems with attaining the manufacturers reported LOQ of 0.5 mg/kg, therefore ILV LOQ was 2 mg/kg.
GH-C 5398; ID 010114 (section 9.2) Sulfuryl fluoride analysis	A grain commodity is accurately weighed into an air-tight blender with 200 ml water. For most grains, 25 g of sample is extracted; with lighter commodities such as wheat germ 10g is extracted. The samples are blended with water and an aliquot of the headspace is sampled with a gas tight syringe and analysed via direct injection into a GC using ECD.	ILV LOQ = 8.3 µg/kg; original reported LOQ = 8 µg/kg and LOD = 4 µg/kg.	Wheat flour: mean recoveries were 93% and 95% with fortification at 8.3 (n = 5) and 78.9 µg/kg (n = 5), respectively. Overall mean recovery 94%. Wheat grain: mean recoveries were 112% and 95% with fortifcation at 8.3 (n = 5) and 78.9 µg/kg (n = 5), respectively. Overall mean recovery 104%.	
GRM 01.12 (9.3) Sulfuryl fluoride analysis	Residues of sulfuryl fluoride are extracted from a portion of a dried fruit or nut sample with water in an air-tight blender jar. The head-space is analysed by GC/ECD.	LOQ = 4.2 ng/g; LOD = 2.1 ng/g.	Raisins: mean recoveries were 80%, 66% and 78% with fortification at 4.2 ng/g (n = 10), 18.3 ng/g (n = 2) and 21.1 ng/g, respectively. Figs: mean recoveries were 100%, 96% and 95% with fortification at 4.2 ng/g (n = 7), 15.2 ng/g (n = 2) and 63.1 ng/g (n =	

			2). Prunes: mean recoveries were 93%, 97% and 93% with fortification at 4.2 ng/g (n = 7), 14.5 ng/g (n = 2) and 63.1 ng/g (n = 2). Dates: mean recoveries were 114%, 94.5% and 102.5% with fortification at 4.2 ng/g (n = 7), 12 ng/g (n = 2) and 20 ng/g (n = 2). Almonds: mean recovery was 83% with fortification at 4.2 ng/g (n = 7). Pecans: mean recovery was 85% with fortification at 4.2 ng/g (n = 7). Pistachios: mean recoveries were 91%, 91% and 95.5% with fortification at 4.2 ng/g (n = 7), 31.9 ng/g (n = 2) and 105 ng/g (n = 2). Walnuts: mean recoveries were 105%, 118% and 96% with fortification at 4.2 ng/g (n = 7), 24 ng/g (n = 2) and 103.6 ng/g (n = 2).	
GH-C 5422; ID 010098 (section 9.4). Sulfuryl fluoride analysis	Work-up is as described above.	ILV LOQ = 4.2 ng/g; original reported LOQ = 4.2 ng/g; LOD = 2.1 ng/g.	Raisins: mean recoveries were 97.5%, 103% and 99% with fortification at 4.2 ng/g (n = 5), 8.5 ng/g (n = 3) and 42 ng/g (n = 5). Walnuts: mean recoveries were 88%, 93% and 97% with fortification at 4.2 ng/g (n = 5), 8.5 ng/g (n = 3) and 42 ng/g (n = 5).	
GRM 01.17 (9.5) Fluoride ion analysis	Fluoride residues resulting from fumigation of sulfuryl fluoride are extracted from samples with water and TISAB. The extract is centrifuged, decanted and analysed using a fluoride selective electrode with a double addition technique.	LOQ = 0.5 mg/kg and LOD = 0.2 mg/kg for all matrices tested.	Wheat grain: mean recoveries were 79%, 97%, 90% and 76% with fortification at 0.5 mg/kg (n = 7), 2 mg/kg (n = 3), 5 mg/kg (n = 3) and 50 mg/kg (n = 3). Overall recovery 84%. Corn: mean recoveries were 102%, 102%, 102% and 98% with fortification at 0.5 mg/kg (n = 7), 2 mg/kg (n = 3), 5 mg/kg (n = 3) and 50 mg/kg (n = 3). Wheat flour: mean recoveries were 99%, 101%, 99% and 96% with fortification at 0.5 mg/kg (n = 7), 2 mg/kg (n = 3), 5 mg/kg (n = 3) and 50 mg/kg (n = 3). Corn oil: mean recoveries were 104%,	

			112%, 105% and 119% with fortification at 0.5 mg/kg (n = 7), 2 mg/kg (n = 6), 5 mg/kg (n = 6) and 50 mg/kg (n = 3).	
GH-C 5408; ID 020013 (section 9.6). Fluoride analysis	Work-up of samples as described above.	ILV LOQ = 2 mg/kg in corn oil and raisins. Original LOQ = 0.5 mg/kg and LOD = 0.2 mg/kg for all matrices tested.	Corn oil: mean recoveries were 98% and 100% with fortification at 2 mg/kg (n = 5) and 20 mg/kg (n = 5). Overall mean recovery 99.5%. Raisins: mean recoveries were 91% and 87% with fortification at 2 mg/kg (n = 5) and 20 mg/kg (n = 5). Overall recovery 89%.	
GRM 01.11 (9.7) Fluoride ion analysis	Fluoride ion residues are extracted from the commodity by shaking with deionised water and TISAB. The sample is filtered to remove particulates. The filtrate is analysed using a fluoride selective electrode with a double known addition technique.	LOQ = 2.4 mg/kg; LOD = 1.4 mg/kg.	Dates: mean recovery of 108% with fortification at 2.5 mg/kg. Figs: mean recovery of 93% with fortification at 2.5 mg/kg. Raisins: mean recovery of 109% with fortification at 2.4 mg/kg. Prunes: mean recovery of 116% with fortification at 2.6 mg/kg. Mean recoveries for fruit was 101%. Almonds: mean recovery of 109% with fortification at 2.4 mg/kg. Pecans: mean recovery of 96% with fortification at 2.4 mg/kg. Walnuts: mean recovery of 110% with fortification at 2.5 mg/kg. Pistachios: mean recovery of 116% with fortification at 2.5 mg/kg. Mean recovery for nuts was 102%.	
GH-C 5434R; ID 010099R (section 9.8) Fluoride analysis	Work up as described above.	ILV LOQ = 2.4 mg/kg for tree nuts.	Walnuts: mean recoveries were 85%, 76% and 93% wit fortification at 2.4 mg/kg (n = 5), 4.8 mg/kg (n = 3) and 24 mg/kg (n = 5), respectively.	

9.9. Storage Stability of Fluoride in Cereal Grain and Flour, Dried Fruit (Raisins), Nuts (Walnuts) and Corn Grain and Meal. Foster, D.R. Dow AgroSciences LLC, Study ID 010017, 21 September 2001. Amended report date 28 March 2002.

Samples of wheat grain and corn grain (which were control samples in studies described above) as well as purchased samples of raisins, walnuts, wheat flour and corn meal were fortified with 20 mg/kg fluoride ion and stored at room temperature for 35 days then placed in a freezer at –20° C. The samples were analysed on the day of fortification and then at 35, 75, 103 and 140 days of storage. The samples were analysed according to method GRM 01.11 described in section 9.7 above.

Concurrent recoveries were conducted at each of the sampling times. The results are tabulated below:

Storage (days)	% Fluoride remaining					
	Wheat grain	Wheat flour	Raisins	Walnuts	Corn grain	Corn meal
0	92	100	98	97	119	101
34 – 36	88	87	100	106	93	110
74 – 77	97	78	93	113	93	102
102 – 105	85	72	94	116	93	97
138 – 141	92	55 (55, 54)	98	110	91	98
Concurrent recoveries						
0	106, 104	103, 119	103, 100	90, 93	89, 104	109, 108
30	94, 104	107, 106	94, 101	86, 94	104, 105	106, 95
60	97, 97	109, 107	106, 102	90, 95	101, 103	102, 99
90	95, 95	101, 101	95, 95	86, 84	99, 103	102, 101
140	92, 93	97, 100	90, 95	87, 80	94, 100	97, 95

The data show that fluoride ion in the commodities tested is stable for at least 140 days of frozen storage, with the exception of wheat flour. The recovery of fluoride ion in wheat flour had decreased from 100% at day 0 to 55% by 140 days.

9.10. Interim Report – Storage Stability of Sulfuryl Fluoride on SKC 1g Anasorb Tubes at Ambient and Frozen Temperature Conditions. Barnekow, D.E. and Foster, D.R. Dow AgroSciences LLC, Study ID 990040.01, 27 June 2002.

The purpose of this study was to confirm the storage stability of sulfuryl fluoride residues on Anasorb CSC tubes[13] when stored under frozen conditions. Sample tubes were fortified with 104.5 µg sulfuryl fluoride/tube and stored at ambient temperature for 46 days or in a freezer (–20 °C) for 180 days. Samples were fortified while air was being drawn through the tube. Samples were analysed on days 0, 3, 7, 10, 15, 20, 29 and 46 days after fortification and storage at ambient temperature and on days 0, 29, 60, 75, 90, 105, 120 and 180 days after fortification and storage under freezer conditions. The method of analysis used[14] had a validated LOQ of 3.5 µg/tube; the reported LOQ of the study was 5.94 µg/tube sulfuryl fluoride and LOD was 1.78 µg/tube sulfuryl fluoride.

The results of the study are shown below, with mean results shown for each set of storage conditions, with three replicates; concurrent recoveries were conducted at each interval.

Ambient Conditions			Frozen Conditions		
Storage interval	% Recovery	Mean % Recovery	Storage interval	% Recovery	Mean % Recovery
Day 0	88, 101, 84	91	Day 0	106, 91, 96	98
Day 3	109, 109, 108	109	Day 29	83, 92, 98	91
Day 7	90, 95, 104	96	Day 60	124, 107, 103	111
Day 10	82, 92, 102	92	Day 75	123, 122, 204*	122
Day 15	95, 91, 97	94	Day 90	105, 89, 103	99
Day 20	99, 115, 99	104	Day 105	99, 96, 106	100
Day 29	97, 96, 106	100	Day 120	98, 117, 89	101
Day 46	88, 88, 88	88	Day 180	95, 94, 84	91

* value disregarded in calculating mean values.

The results show that no significant decline in sulfuryl fluoride residues was observed during storage on Anasorb tubes under conditions of either ambient temperature or freezer conditions.

[13] Charcoal sorbent sample tubes for air sampling.

[14] MVTL Method F45323, based on Dow AgroSciences laboratory report: Sulfuryl Fluoride: Development and Validation of an Air Monitoring method HEH2.12-38-26(6).

10. DIETARY EXPOSURE CALCULATIONS

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