FOSETYL-ALUMINIUM (302)
PHOSPHONIC ACID (301)

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EXPLANATION

Fosetyl (and its aluminium salt) and phosphonic acid (formulated as the potassium or sodium salts) are systemic fungicides with protectant action against a number of oomycete and ascomycete fungi and some plant pathogenic bacteria in a range of fruit, vegetables and ornamental crops. They are rapidly absorbed through both leaves and roots and exhibit both acropetal and basipetal translocation. Their mode of action is by inhibiting germination of spores and by blocking development of mycelium, competing with phosphate as allosteric regulator of several enzymes. In addition, they can induce direct or indirect production of phytoalexin and pathogenesis-related proteins leading to an induction of plant defence mechanisms against fungal or bacterial pathogens.

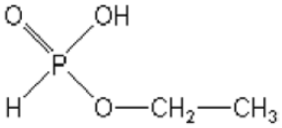
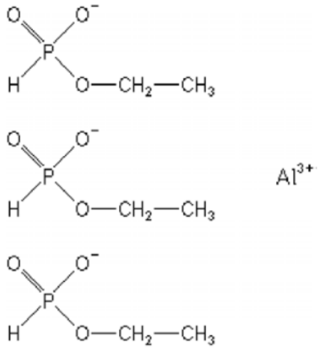
Authorisations exist in many countries for the use of fosetyl or its aluminium salt (fosetyl-Al) as a pre-plant dip, foliar, drench or drip-irrigation treatments and authorisations also exist for phosphonic acid (formulated as the monopotassium, dipotassium or sodium salts) in a number of countries for use as a trunk injection, pre-plant dip, foliar, soil and post-harvest treatments.

Fosetyl and phosphonic acid were scheduled by the 48th Session of the CCPR as a new compounds for consideration by the 2017 JMPR. Residue and analytical aspects were considered for the first time by the present meeting. The Meeting was provided with studies on metabolism, analytical methods, supervised field trials, processing, freezer storage stability and environmental fate in soil.

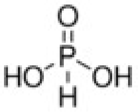
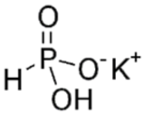
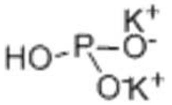
IDENTITIES

For fosetyl-aluminium, pesticide specifications have been established by the Joint FAO/WHO Meeting on Pesticide Specifications (JMPS) and published as FAO Specifications and Evaluations for Agricultural Pesticides (2013).

(http://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/jmps/en/).

	Fosetyl	**Fosetyl-aluminium**
ISO common names:	fosetyl (refers to the acid)	fosetyl-aluminium (derived name for the aluminium salt)
IUPAC name:	ethyl hydrogen phosphonate	aluminium tris-ethylphosphonate
Chemical Abstracts names:	ethyl hydrogen phosphonate	aluminium tris-O-ethylphosphonate
Synonyms	efosite phosphonic adid ethyl ester	efosite-Al
CAS number	15845-66-6	39148-24-8
Molecular mass:	110.0	354.1
Molecular formula	$C_2 H_7 O_3 P$	$C_6 H_{18} Al O_9 P_3$
Structural formula:		

Phosphonic acid (phosphorous acid) is the active constituent in authorised products containing either a mixture of mono- and di-potassium phosphonate ions (referred to as 'potassium phosphonates'), or the ammonium or dibasic sodium phosphonates. The Meeting was provided with information only on the potassium phosphonates compound.

	Phosphonic acid	Potassium phosphonates	
Common names:	phosphonic acid	potassium hydrogen phosphonate	dipotassium phosphonate
IUPAC name:	phosphonic acid	reaction mixture of potassium hydrogen phosphonate and dipotassium phosphonate	
Chemical Abstracts name:	phosphonic acid	reaction mixture of potassium hydrogen phosphonate and dipotassium phosphonate	
Synonyms	phosphorous acid	monopotassium phosphite	potassium dihydrogen phosphite
CAS number	13598-36-2	13977-65-6	13492-26-7
Molecular mass:	82	120.1	158.2
Molecular formula	H_3PO_3	KH_2PO_3	K_2HPO_3
Structural formula:			

Formulations of fosetyl and fosetyl-aluminium are available in a number of formulations, often mixed with one or more other fungicides.

Active ingredient	Formulation types	Other active ingredients
fosetyl	SL (Soluble concentrate)	propamocarb
fosetyl-aluminium	WG (Water dispersible granule)	- copper cymoxanil, folpet fenamidone fluopicolide folpet, iprovalicarb folpet iprovalicarb, mancozeb metiram-zinc
	WP (Wettable powder)	- captan copper cymoxanil, folpet fenamidone, iprovalicarb mancozeb trifloxystrobin
	WS (water dispersible powder for slurry seed)	thiabendazole, thiram

Phosphonic acid is available as ammonium, sodium or potassium salts, and for consistency, the active ingredient content is usually expressed as the acid equivalent. Formulations of potassium phosphonates manufactured from technical concentrates containing about 32% phosphonate ions and up to 20.0% potassium include:

Active ingredient	Formulation types	
Phosphonic acid (phosphorous acid)	SL (Soluble concentrate)	As potassium, sodium and/or amonium salts of phosphonic acid

PHYSICAL AND CHEMICAL PROPERTIES

Fosetyl-aluminium

Table 1 Physical and chemical data of fosetyl-aluminium (active ingredient and technical grade material)

Test or Study & Annex point	Test material purity and specification	Findings and comments	Reference
Melting point	Pure ai (99.1%) Technical (97.6%)	215 °C 207-210 °C	R009286 M-179033-01-1
Boiling point	Pure ai (99.1%) Technical (97.6%)	Not measured- decomposition at >190 °C Not measured- decomposition at >190 °C	R009286 M-179033-01-1
Relative density	Pure ai (99.1%) Technical (97.6%)	1.529 (20 °C) 1.54 (20 °C)	R009286 M-179033-01-1
Vapour pressure	Pure ai (98%)	$< 10^{-7}$ Pa at 25 °C (extrapolated)	R009300 M-179047-01-1
pH	Technical (97.6%)	3.1 in 1% aqueous suspension	R009295 M-179042-01-1
Henry's law constant	calculated	$K_H < 3.2$ Pa m³/mol (20 °C)	R009300 M-179047-01-1
Appearance	Pure ai (99.1%) Technical (97.6%)	white powder white powder	R009286 M-179033-01-1
Solubility in water (20 °C)	Pure ai (99.1%)	111.3 g/L in pure water at pH 6 111.4 g/L in buffer at pH 5.1 109.8 g/Lin buffer at pH 8.6	R009291 M-179038-01-1

Test or Study & Annex point	Test material purity and specification	Findings and comments	Reference
Solubility in organic solvents (mg/L, 20 °C)	Technical (97.6%)	Solvent Solubility (mg/L) Dichloromethane 4 Acetone 6 Acetonitrile: 1 Ethyl acetate: < 1 Methanol: 807 o-Xylene: 1 n-Octanol: 10 n-Heptane: < 1	R009291 M-179038-01-1
Octanol/water partition coefficient	Pure ai (99.1%)	Log P_{OW} -2.11 at 21-23 °C	R011712 M-184417-01-1
Hydrolysis (sterile water in the dark)	Pure ai (99.1%) Technical (97.6%)	Stable (< 10% degradation) for 1 month at pH 5-9, 22 °C DT_{50} 5 days at pH 3 and 22 °C Stable for 5 days at pH4-9, 50 °C	R000987 M-159693-01-1 C012596 M-159693-01-1

The JMPS evaluation of fosetyl-aluminium noted that when fosetyl-aluminium dissolves in sterile water it dissociates and the liberated aluminium (Al^{3+}) ions tend to form aluminium hydroxide (which may precipitate or flocculate in the spray tank), while the liberated acidic fosetyl ions tend to be hydrolysed (more rapidly in biological systems), with the formation of phosphonic/phosphorous acid and ethanol. This complex behaviour in water has important implications for the product specifications and the data relating to water solubility, octanol/water partition coefficient and hydrolysis.

Potassium phosphonates

Table 2 Physical and chemical data of potassium phosphonates (technical grade material)

Test or Study & Annex point	Test material purity and specification	Findings and comments	Reference
Melting point	Technical concentrate	73 °C (acid)	PPDB
Boiling point	Technical concentrate	Decomposes before boiling	PPDB
Relative density	Technical concentrate	1.651 (20 °C)	PManual
pH	Technical concentrate	5.9-6.4	EFSA
Appearance	Technical concentrate	Hygroscopic, delequescent white crystals	PManual
Solubility in water (20 °C)	Technical concentrate	425 g/litre 500 g/litre	PManual PPDB
Dissociation constant	Phosphonic acid	pK1 = 2.0 , pK2 = 6.59	EFSA
UV absorption	Technical concentrate	λmax = 198 nm - absorbance = 1.7859 No absorption after 200 nm	EFSA
Octanol/water partition coefficient	Technical concentrate	Not applicable (insoluble in n-octanol)	PMRA

EFSA: Conclusion on the peer review of the pesticide risk assessment of the active substance potassium phosphonates. EFSA Journal 2012;10(12):2963

PPDB: Pesticide Properties Database (http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm)

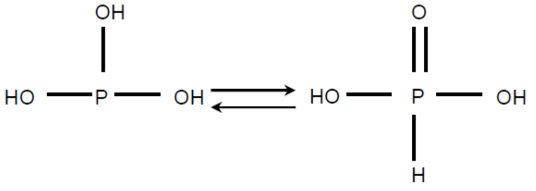
PManual: The Pesticide Manual, 15th Edition. BCPC

METABOLISM AND ENVIRONMENTAL FATE

The Meeting received metabolism studies for fosetyl-Al on plants (citrus, apples, grapes, pineapple and tomato) and animals (rats, lactating goats) and also received environmental fate and rotational crop studies for fosetyl-Al and phosphonic acid.

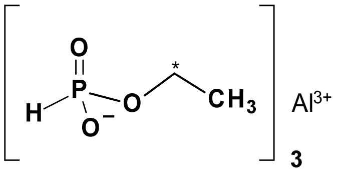
In this evaluation, information relating to "phosphonic (phosphorous) acid" formed as a major metabolite is reported as the free acid. After application, aluminium tris-O-ethyl phosphonate (i.e. fosetyl-Al) dissociates into the O-ethyl phosphonate and aluminium ions. Any phosphonate formed from O-ethyl phosphonate in biological systems would never be present in the form of the free acid (i.e. phosphonic acid) under physiological and environmental conditions (pH 4 to 9). This conclusion is supported by the molecular structure and by the dissociation constant observed (dissociation constant for the first step of deprotonation: pKa = 2.0). Consequently, phosphonates in their fully protonated form are strong acids that spontaneously form salts in contact with soil or natural water with any suitable counter ion present (i.e. sodium, potassium, magnesium, calcium). With the ability to readily form salts in the environment, in terms of their acidic or alkaline character, phosphonates are similar to the salts of phosphoric acid (i.e. phosphates) in their environmental behaviour.

In solution, phosphonic acid is in equilibrium with phosphorous acid, such that essentially all of the molecules are present as phosphonic acid

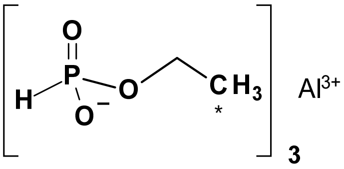


Phosphorous acid (H_3PO_3) **Phosphonic acid (H_3PO_3)**

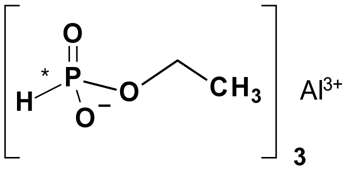
The studies investigating the environmental fate of fosetyl-aluminium were performed with the following positions of ^{14}C- and ^{32}P-radiolabel:



[1-^{14}C]fosetyl-aluminium



[2-^{14}C]fosetyl-aluminium

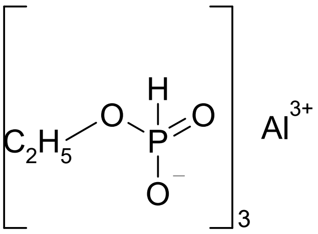
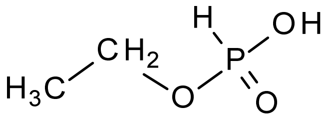


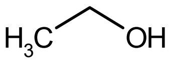
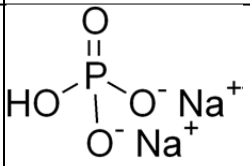
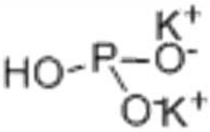
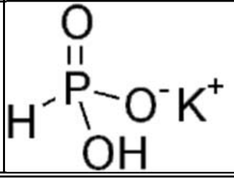
[^{32}P]fosetyl-aluminium

In addition, and for the metabolite phosphonic acid, some tests were performed with ^{33}P-radiolabelled test item. The short ^{32}P and ^{33}P half-lives of 14.3 and 25.3 days limits their use for long-term tests.

Relevant compounds used and metabolites identified in these studies and discussed in this Evaluation are listed below.

Table 3 Relevant compounds used or identified in plant, animal and soil matrices

Compound/Code	Name and Matrix	Structure
Fosetyl-Al	Fosetyl-aluminium (Aluminium tris-O-ethylphosphonate) MW: 354.1	
Fosetyl	O-ethyl phosphonic acid MW: 110.0	

Compound/Code	Name and Matrix	Structure
Ethanol	Ethyl alcohol (ethanol) MW 46.07 Rat, goat, Plants (transient followed by incorporation into natural products, e.g. glucose, starch, cellulose, lignin, lipids)	
Acetic acid	Acetic acid MW: 60.05 Rat, goat (transient followed by incorporation into natural products, e.g. lipids, fatty acids, amino acids, glycosides)	
Carbon dioxide	Carbon dioxide MW: 16.04 Rat, goat (in expired air), soil	CO_2
Phosphonic acid	Phosphonic acid (Phosphorous acid) MW: 81.99 Rat, goat, plants, soil, water/sediment	
Disodium phosphonate	Disodium dioxido-oxophosphanium (Phosphonic acid, sodium salt (1:2) (Disodium phosphite) MW:125.96	
Dipotassium phosphonate	Dipotassium dioxido-oxophosphanium (Phosphonic acid, potassium salt (1:2) (Dipotassium phosphite) MW : 158.17	
Monopotassium phosphonate	Potassium hydrogen phosphonate MW: 120.1	

Plant metabolism

The Meeting received plant metabolism studies on citrus, apple, grape leaves, pineapple and tomato following foliar applications of labelled and unlabelled fosetyl-Al and on pineapple (pre-plant dip) and tomato (hydroponic) treatments of fosetyl-Al.

Fosetyl-Al

Citrus – foliar applications (fosetyl-Al)

In a study reported by Bausher, 1982 [Ref: R002057; M-161888-01-1], tangerine and orange trees (grown outdoors, in pots) were treated with three (tangerine) or four (orange) applications of 0.066 g ai ^{14}C-fosetyl-Al/tree. Applications were made to all aerial parts of the trees using paint brush at 1–2 month intervals between the end of flowering and two months before harvest. Total application rates were 0.2 g ai/tree (tangerines) and 0.26 g ai/tree (oranges).

Samples of whole fruit were taken and either stored at -100 °C until analysis or washed and stored at 0 °C until processed into peel, flesh, seeds, oil, juice and press cake (remainder of pulp and seeds as well as hexane washed peel). Subsamples of peel were also triple-extracted with hexane.

Table 4 Distribution of radioactivity in matrices of orange and tangerine after combustion and liquid scintillation counting

Sample	Oranges		Tangerines	
	dpm/g	Fosetyl-Al mg equiv/kg	dpm/g	Fosetyl-Al mg equiv/kg
Whole fruit	8969 ± 2440	1.43	3314 ± 1316	0.52
Juice	1543 ± 508	0.24	247 ± 26	0.039
Juice sacs (flesh)	4790 ± 1520	0.76	793 ± 167	0.125
Seeds	28433 ± 12627	4.55	3330 ± 633	0.52
Peel	17088 ± 10040	2.73	12366 ± 2675	1.95
Hexane-washed peel (dried)	148493 ± 34227	23.8	50130 ± 10351	7.92
Press cake	35288 ± 3653	5.65	7367 ± 1420	1.16
Citrus oil	not available		20550 ± 2100*	3.29

* dpm/mL

Residues in these samples were further investigated in a study reported by Laurent *et al*., 1982 [Ref: R000861; M-159448-01-1], where fosetyl-Al and its metabolites were extracted from the whole fruit or the peel by two successive fractions of water, followed by acetone and finally, methanol containing 1% hydrochloric acid. The aqueous extracts of the whole fruits and the filtered juices were buffered to pH 3 to reduce hydrolytic cleavage of ethanol. The radioactivity contained in the different fractions was determined by liquid scintillation counting (LSC) and analysed by HPLC.

Table 5 Distribution of radioactive residue in matrices of orange and tangerine

Sample	Oranges		Tangerines	
	nCi/g	Fosetyl mg equiv/kg	nCi/g	Fosetyl mg equiv/kg
Whole fruit	8.5	2.8	3.5	1.2
Juice	2.2	0.7	0.7	0.25
Peel, hexane washed	164.1	54.7	66.1	22.0
Press cake	38.3	12.7	9.5	3.2
Citrus oil	0.5	0.2	0.6	0.2

Most of radioactivity, 66–68% TRR in whole fruit and 90–93% TRR in juice, was found in the aqueous extracts, predominantly as radioactive glucose. Fosetyl-Al was largely degraded and did not exceed 0.1 mg eq/kg in whole fruit and was < 0.1 mg eq/kg in juice.

Table 6 Distribution and identification of radioactive residue in matrices of orange and tangerine

Sample	Oranges			Tangerines		
	Whole Fruit	Peel	Juice	Whole Fruit	Peel	Juice
	% TRR [mg/kg(a)]	% TRR [mg/kg(a)]	% TRR [mg/kg(a)]	% TRR [mg/kg(a)]	% TRR [mg/kg(a)]	% TRR [mg/kg(a)]
Aqueous extract	68.3 [1.9]	50.2 [27.5]	89.5 [0.7]	66.3 [0.8]	44.8 [9.8]	92.8 [0.25]
Fosetyl	4.7 [0.1]		8.1 [< 0.1]	11.6 [0.1]		17.5 [< 0.1]
Glucose	50.3 [1.4]		74.7 [0.6]	46.5 [0.6]		70.2 [0.2]
Fosetyl + Glucose	55.0 [1.5]		82.8 [0.6]	58.1 [0.7]		87.7 [0.25]
Acetone extract	2.6 [0.1]	20.9 [11.4]		4.4 [< 0.1]	11.8 [2.6]	
Methanol/HCl extract	8.8 [0.2]	7.4 [4.0]		10.5 [0.1]	8.8 [1.9]	
Post extraction solids	20.3 [0.6]	21.4 [11.8]		18.8 [0.2]	34.6 [7.6]	
Accountability, TRR	100 [2.8]	100 [54.7]		100 [1.2]	100 [22.0]	

[a] mg/kg expressed as fosetyl equivalents

Radioactive residues of fosetyl-Al in citrus fruit and juice were low (≤ 0.1 mg eq/kg). The ^{14}C-label of fosetyl-Al is largely integrated into the normal plant metabolism (glycolytic cycle) resulting in the formation of sugars and lipids. As a result, the main ^{14}C-conversion product (^{14}C-D-glucose) accounted for 50% of the radioactivity in fruit and about 75% in the juice.

Citrus – foliar application (fosetyl-Al)

In a paper published in Pesticide Science, Pelegri *et al*, 1993 [Ref: C015326; M-200275-01-1] reported the metabolism of fosetyl-Al into phosphonic acid in oranges and tangerines following treatments with fosetyl-Al (WP formulations) at a rate of 30 g ai/tree.

Whole fruit, peel and pulp samples were taken at intervals from 0 to 49 days after treatment, blended with distilled water and Celite-545, filtered and diluted with acetone. Propionic acid was added to prevent hydrolytic cleavage between phosphonic acid and ethanol. Extracts were analysed by GC-FPD or GC-NPD after derivatisation with diazomethane. Methylated fosetyl-Al and phosphonic acid were used as reference standards.

Fosetyl-Al was very rapidly metabolised to phosphonic acid, since the parent substance could not be detected in any of the citrus sample, even directly after treatment. This conversion already occurred within few hours (12 to 24 hours) after addition of fosetyl-Al to untreated chopped orange peels at room temperature.

Phosphonic acid was detected in whole fruit, peel and pulp of orange or tangerine fruit treated with fosetyl-Al. Residues in whole fruit and pulp increased over the 49-day study period with levels in peel declining after 21 days. Since no fosetyl could be detected on/in the fruits the increase of phosphonic acid was attributed to translocation from the leaves to the fruits.

Table 7 Phosphonic acid residues in citrus fruit, peel and pulp following a single treatment of 30 g ai fosetyl-Al/tree.

	Phosphonic acid residues (mg/kg)					
Days after treatment	Oranges (cv. *Navelinas*)			Tangerines (cv. *Clemenules*)		
	Whole fruit	Peel	Pulp	Whole fruit	Peel	Pulp
0	1.32	3.55	0.66	3.38	11.27	1.12
7	1.93	4.45	1.19	4.18	33.37	2.19
14	2.65	4.20	2.21	4.49	15.17	2.80
21	3.21	5.28	2.63	7.40	16.12	4.68
28	3.36	3.35	3.82	9.44	14.2	7.73
49	3.38	1.43	4.03	-	-	-

Whole fruit: mean of three replicate fruits; peel and pulp: mean of three plots, total of 9 replicates

Apples – foliar applications (fosetyl-Al)

The distribution and composition of the radioactive residues of ^{14}C-fosetyl-Al in apples was investigated in a study reported by White, 1988 [Ref: C012424; M-202680-01-1]. One branch of an outdoor apple tree (fruit and leaves) was treated with two sprays of 0.2 g ai/branch, 7 days apart and fruit and leaves were sampled before and after each application and again 7 and 14 days after the second treatment.

Leaves and fruits were frozen within two hours and stored frozen for up to about 8 months before extraction and analysis. Leaves and fruits were washed with deionised water and aliquots of washed samples and washes were radioassayed by liquid scintillation counting (LSC). Washed fruit were separated into peel, pulp, juice and core.

Apple peels and leaves were washed with deionised water up to 5 times. Peel samples were extracted once and chopped pulp and leaves samples extracted twice by refluxing for 30 minutes in acetonitrile/water (1/1) acidified with conc. HCl to pH 3.0. An aliquot of the resulting extracts was partitioned three times with dichloromethane. The remaining residues of apple pulp and leaves (filter cake) were extracted by refluxing for 30 minutes twice with acetone and twice with 1N HCl methanol solution.

The washes, extractions and residual plant material were combusted and radioassayed by LSC. Extracts were chromatographically analysed against radioactive standards (^{14}C-fosetyl-Al, ^{14}C-glucose) by TLC on silica gel plates developed with acetone/2-propanol/ammonium hydroxide/water. Further solvent systems for development were chloroform/methanol/water/formic acid, ethyl acetate/2-propanol/water/formic acid and 2-propanol/ethyl acetate/formic acid.

HPLC separation of ^{14}C-fosetyl-Al, ^{14}C-glucose and ^{14}C-ethanol was also conducted on a RP (C18) column. The eluted radioactivity was collected in different fractions and quantified by radioassay. For determination of ^{14}C-D-glucose an isocratic eluent was used (40% tetrabutyl ammonium hydroxide and acetic acid or diluted phosphoric acid). For determination of ^{14}C-fosetyl-Al a different RP column was operated with diluted phosphoric acid.

Most of the radioactive residues in leaves were present as washable surface residues. Surface residues of the apple fruits predominated during the first 7 days, but subsequently penetrated into the fruit (53–58% TRR), mostly in the peel (39% TRR 14 days after the 2nd application).

Fosetyl-Al was the predominant residue in the fruit surface washes, initially 93% of TRR, decreasing to 41% TRR 14 days after the second application. Very small amounts of fosetyl-Al were detectable in peel and pulp (≤ 1.7% of TRR).

The major metabolite identified in both apple fruit and leaves was ^{14}C-ethanol, present as a surface residue from day 0, indicating that the metabolism of fosetyl-Al already started on the plant surface. The presence of ^{14}C-ethanol in the apple peel and leaves indicates either direct translocation of ^{14}C-ethanol or ^{14}C-fosetyl-Al penetration followed by metabolic transformation into ^{14}C-ethanol. The detection of ^{14}C-D-glucose in the apple juice indicates that ^{14}C-ethanol is subsequently metabolised and the radiocarbon incorporated into natural products.

Table 8 Distribution and identification of fosetyl-Al and its metabolites in washed apple fruits and fractions following 2 applications of ^{14}C-fosetyl-Al

Plant part	Day	Spray No	^{14}C-fosetyl-Al	^{14}C-ethanol	^{14}C-glucose	Total
			% TRR	% TRR	% TRR	% TRR
Water wash	0	1	93.07	4.40	ND	97.47
	7	1	74.80	17.56	ND	89.20
	7	1 & 2	75.15	18.82	ND	91.57**
	14	1 & 2	34.65	7.43	ND	42.08
	21	1 & 2	40.90	5.73	ND	46.63
Rinsed fruit	0	1	-	-	-	2.53
	7	1	-	-	-	10.80
	7	1 & 2	-	-	-	8.43
	14	1 & 2	-	-	-	57.92
	21	1 & 2	-	-	-	53.37
Peel	0	1	0.13	1.25	ND	1.38
	7	1	0.12	6.58	ND	6.70
	7	1 & 2	0.41	1.91	ND	2.32
	14	1 & 2	1.44	36.36	ND	37.80
	21	1 & 2	1.72	37.28	ND	39.00
Pulp	0	1	ND	ND	ND	0.29
	7	1	ND	ND	ND	1.61
	7	1 & 2	0.32	3.59	ND	3.91
	14	1 & 2	1.69	5.20	ND	6.89
	21	1 & 2	0.09	2.61	ND	2.70
Core	0	1	ND	ND	ND	0.21
	7	1	ND	ND	ND	0.52
	7	1 & 2	ND	ND	ND	1.14
	14	1 & 2	ND	ND	ND	7.11

Plant part	Day	Spray No	^{14}C-fosetyl-Al	^{14}C-ethanol	^{14}C-glucose	Total
			% TRR	% TRR	% TRR	% TRR
	21	1 & 2	ND	ND	ND	3.93
Juice	0	1	ND	0.39	0.25	0.64
	7	1	ND	0.84	1.12	1.96
	7	1 & 2	ND	0.68	0.37	1.05
	14	1 & 2	ND	4.42	1.70	6.12
	21	1 & 2	ND	2.80	4.95	7.75
Fruit total	0	1	93.20	6.04	0.25	99.49 (a)
	7	1	74.92	24.98	1.12	101.02 (a)
	7	1 & 2	75.88	25.00	0.37	101.25 (a)
	14	1 & 2	37.58	53.41	1.70	92.69 (a)
	21	1 & 2	42.71	48.42	4.95	96.08 (a)

ND: not determined, radioactivity < 10 dpm per sample aliquot

[a] radioactivity representing the sum of ^{14}C-fosetyl-Al, ^{14}C-ethanol and ^{14}C-glucose

Table 9 Distribution of radioactive residues and identification of fosetyl-Al and its metabolites in washed apple leaves following 2 applications with ^{14}C-fosetyl-Al

Plant part	Day	Spray No	^{14}C-fosetyl-Al	^{14}C-ethanol	^{14}C-glucose	Total
			% TRR	% TRR	% TRR	% TRR
Water wash	0	1	67.94	28.47	ND	96.41
	7	1	71.58	15.81	ND	86.07
	7	1 & 2	75.31	13.87	ND	88.48
	14	1 & 2	61.97	5.93	ND	67.90
	21	1 & 2	60.75	4.90	ND	65.65
Leaf tissue	0	1	0.33	3.26	ND	3.59
	7	1	2.21	11.72	ND	13.93
	7	1 & 2	2.97	3.51	ND	11.52
	14	1 & 2	1.00	13.05	ND	32.10
	21	1 & 2	3.53	21.38	ND	34.35
Total	0	1	68.27	31.73	ND	100.00
	7	1	73.79	27.53	ND	101.32
	7	1 & 2	78.28	17.38	ND	95.66
	14	1 & 2	62.97	18.98	ND	81.95
	21	1 & 2	64.28	26.28	ND	90.56

ND: not determined, radioactivity < 10 dpm per sample aliquot

Grape leaves – foliar applications (fosetyl-Al)

The translocation and metabolism of the radioactive residues of ^{14}C-fosetyl-Al in grape leaves was investigated in a study reported by Brockelsby *et al.*, 1977 [Ref: R001855; M-161435-01-1]. Individual leaves from one grape vine (pruned to a single 0.85–1.2 metre shoot) grown in a glasshouse were treated with 756 µg of ^{14}C-fosetyl-Al for autoradiography. Leaves from a different vine (pruned to a single 0.7–1 metre shoot) grown in a glasshouse were treated with 60 drops of 2.1 µL to give a dose of 3024 µg per plant for studying metabolism.

For autoradiography, leaves were harvested 5.5 hours, 1, 2, 5, 7 or 14 days after treatment, washed and the radioactive residues in the washings was determined by liquid scintillation counting (LSC) with quench correction. Autoradiographs were made by pressing parts of the plants and exposing them to X-ray film for two weeks.

Uptake of ^{14}C-fosetyl-Al did not exceed 3% except at 5.5 hours after treatment. This result is probably due to initial difficulties in washing the deposit from the leaf surface. The movement of radioactive residues from the treated leaves to the shoot apex (upper border of the leaves) was shown in the autoradiographs of treated vines. Uptake was shown to be greater at higher humidity: up to 4% uptake at 60% RH, up to 1% at 90% RH and up to 19% at 95% RH. The maximum uptake was assumed to be due to different ages of the leaves.

For the metabolism study, leaves were harvested 7, 14 or 21 days after treatment and either washed in an aqueous solution (0.01%, w/v) of a non-ionic surfactant (ethoxylated octyl phenol) or soaked in the surfactant solution for 15 minutes. Vines were sectioned into plant parts present at application (untreated leaves and stem above treated area; treated leaves (washed and soaked), untreated leaves (below treated area) and new grown plant parts after application. Leaf samples were broken up at -70 °C with a spatula, macerated with a minimum amount of water and filtered through cellulose. The solid plant remnants were again macerated with water and filtered as before. The washings were thereafter processed separately. Plant fibres were combusted. Leaf washings, plant macerates and absorbed carbon dioxide from combustion of fibre were radio-assayed by liquid scintillation counting.

Leaf washings and plant macerates were diluted with methoxyethanol, concentrated and mixed with acetonitrile and residues were derivatised using diazomethane and analysed by gas chromatography to measure residues of fosetyl and phosphonic acid. Leaf washings and plant macerates were also investigated by thin layer chromatography using isotopically-labelled reference compounds.

Most of radiolabelled fosetyl-Al applied to vine leaves remained on the leaf surface as it could be recovered by vigorous washing. Translocation to untreated parts of the plant or to new growth was observed, but only to a limited extent. The major metabolic product found in treated and untreated plant parts was identified as phosphonic acid.

Table 10 Recovery (%) of ^{14}C from grape leaves treated with ^{14}C-fosetyl-Al

Sample material	Leaves washed (rinsed)			Leaves soaked	
µg applied (as ^{14}C-fosetyl)	9072	4536		4536	
Days after treatment	7	14	21	14	21
% Recovery by surface washing	36.0	26.3	18.5	86.0	87.7
% Recovery by extraction	59.0	75.4	79.8	1.0	9.6
% in fibres (non extractable)	0.2	0.6	1.2	0.1	0.3
% Total	95.2	102.3	99.5	87.1	97.6

24 leaves treated on three plants; 4 leaves from each plant were washed or soaked

Table 11 Distribution of radioactivity in mg eq/kg of fosetyl and phosphonic acid in treated and untreated grape leaves

Days after treatment	Day 7			Day 14			Day 21		
Compound	Fosetyl		Phosphonic acid	Fosetyl		Phosphonic acid	Fosetyl		Phosphonic acid
Analysis method	Radio	GC	GC	Radio	GC	GC	Radio	GC	GC
Plant parts present at application									
Untreated leaves and stem (above treated area)	0.1	0	1.1	0.04	0	0.6	0.01	0	1.2
Treated leaves (wash)	252	190	5.0	372	297	4.8	345	272	5.2
Treated leaves (soaked)	n.a.	n.a	n.a.	4.0	3.0	1.8	24.1	23.2	1.5
Untreated leaves (below treated area)	0.01	< 0.3	< 0.6	2.5	2.1	1.1	0.03	0	1.6
New grown plant parts after application									
At top of plant	0.15	< 0.1	< 0.2	0.02	0	< 0.4	0.03	0	0.2
Within treated area	0.1	< 0.1	0.7	0.01	0	1.3	0.2	0.1	1.3
Below treated area	0.1	0	0.8	0.01	0	0.3	0.4	0.3	0

Radio: LSC/TLC; GLC: Gas liquid chromatography

n.a.: not analysed

Table 12 Translocation of ^{14}C-residues into untreated parts of the vine after "point" application of ^{14}C-fosetyl-Al

	Radioactive residues (mg fosetyl equiv./kg fresh weight)		
Days after treatment (3024 µg ^{14}C-fosetyl-Al per plant)	Day 7	Day 14	Day 21
Plant parts present at application			
Untreated leaves and stem (above treated area)	0.25	0.13	0.09
Treated leaves (washed) (soaked)	 1.01 -	 2.91 0.58	 5.07 0.91
Untreated leaves (below treated area)	0.03	0.07	0.36
New grown plant parts after application			
At top of plant	0.14	0.11	0.08
Within treated area	0.08	0.05	0.14
Below treated area	0.13	0.14	0.09

Pineapple – pre-plant dip/foliar applications (fosetyl-Al)

In a two-part study reported by Laurent et al, 1982, 1983 [Ref: R000790 (M-161435-01-1) and R000879 (M-229587-01-2)], ^{14}C-fosetyl-Al was applied to pineapples as a pre-plant crown dip (immediately after a dip treatment with unlabelled fosetyl-Al had dried), followed a year later by foliar application of ^{14}C-fosetyl-Al (after a foliar spray of unlabelled fosetyl-Al).

Pineapple crowns were dipped in a solution of 2.4 g ai/L fosetyl-Al (with wetting agent) and once dry, 100 µCi of ^{14}C-fosetyl-Al were applied to each crown (half on the leaves and half on the abscission area). The treated crowns were subsequently planted in individual pots and were grown in a greenhouse.

One year after planting, some of the dip-treated plants were sprayed with 2.4 g ai/L unlabelled fosetyl-Al followed by microdroplet deposition of 100 µCi/plant of ^{14}C-fosetyl-Al.

Whole plants were sampled at intervals up to 480 days after the dip treatment and samples from the combined dip+spray treatment were also sampled immediately after the spray treatment (day 365) and 122 days later (487 days after the dip treatment).

Samples of Day 0, 7, 14 and 365 were analysed as whole plant, all other samples were separated into crown, fruit and roots. Soil adhering to these roots was removed. Roots were examined separately. The fruit and crowns were separated from the plants at harvest and were analysed separately.

Whole plant, fruit or crown samples were macerated in the presence of solid carbon dioxide and 0.1N HCl was added to prevent the hydrolysis of fosetyl-Al residues. (Fosetyl-Al was not stable in a neutral water/acetonitrile extract, with 35% of the initial amount hydrolysing within 3 days at room temperature). In 0.1N HCl/acetonitrile extracts, 97% of the initial fosetyl could be recovered after 15 days storage at ambient temperature). After adding acetonitrile, extracts (at pH 3) were filtered, evaporated and the lipophilic products were separated by partitioning three times with water/dichloromethane. The filtration cake was extracted with acetone and then continuously extracted for 12 hours with methanol/1% HCl and the remaining solids were combusted. Samples of roots were homogenised and extracted with acetone followed by partitioning with methanol/HCl.

The radioactivity of all fractions was determined with liquid scintillation counting. The extracts from different samplings were recombined and the unknown components were isolated by TLC, identified by spectroscopic methods and if appropriate by GLC comparison with reference standards.

The acidified water/acetonitrile extracts were analysed by ion-exchange HPLC (with radiomonitoring) and confirmation of ethanol and fosetyl was by reversed-phase (C18) HPLC, also with radiomonitoring. The lipid fractions from the dichloromethane and acetone extractions were also separated by TLC and the ^{14}C-components identified by their IR and mass spectra as well as by GLC comparison with reference compounds.

Total radioactivity in the aerial parts of the dip-treated plants decreased considerably over the study period, declining from an initial 45.4 µCi to 10 µCi after about 11 months and to 1.9 µCi at harvest (Day 480). Levels of unextracted radioactivity increased steadily in the aerial plant parts until Day 342 (up to 6.3 µCi) then decreased to 1.1 µCi at harvest. At the same time, total radioactivity in the roots increased from 1.4 to 6.8 µCi (78% TRR in the whole plant).

Mature fruit at harvest contained negligible quantities of radioactive residues, 0.38% AR following the dip treatment and 1.1% AR following the combined dip+spray treatment. Natural by-products of the degradation cycle of ethanol made up at least 50% of these residues. The authors of the original report recognized a low recovery of the applied radioactivity. They assumed that this loss is due to volatilization of the primary metabolite ^{14}C-ethanol.

The metabolism of ^{14}C-fosetyl-Al was very fast and started directly after application with formation of ^{14}C-ethanol. The major radioactive residue components identified were the parent substance fosetyl-Al and ethanol. On the day of dipping, radioactive residues of fosetyl-Al and ethanol were both 19 µCi. After dipping and spray application the radioactive residues of fosetyl-Al immediately after the spray treatment were 14.8 µCi and the ethanol radioactivity was 30.4 µCi. These residues decreased steadily and could no longer be detected at harvest on Day 480 and 487.

In addition to ethanol, several radiolabelled substances were detected and identified as natural lipids consisting of long chain aliphatic acids, e.g. oleic acid and palmitic acid, and homologous primary alcohols, e.g. 1-docosanol and 1-tetracosanol. Other radiolabelled conversion products were characterised as long chain aliphatic acids or esters formed by incorporation of the ^{14}C-label into the natural synthesis of plant constituents.

Table 13 Distribution of radioactivity in pineapple plant after application of 100 µCi (dipping) or 100 µCi (dipping) + 100 µCi (spraying) ^{14}C-fosetyl-Al

	Radioactive residues (µCi)									
Nature of treatment	Dip treatment								Dip + spray treatment	
Treatment-sampling interval (days)	0	7	14	28	56	119-120	316-342	471-480	365	487
Whole plant/aerial plant parts $^{(a)}$										
Acidified water/acetonitrile extracts	41.9	25.5	18.6	7.1	5.2	2.1	0.8	0.5	48.9	2.9
Fosetyl Ethanol	19.0 19.1	19.3 4.4	10.5 6.2	4.3 1.8	3.9 0.5	1.4 0.2	≤ 0.5 ≤ 0.2	- -	14.8 30.4	- -
Aqueous phase after partitioning with DCM	21.2	20.2	11.0	3.7	3.2	1.3	0.4	0.3	17.5	2.0
Lipid fraction 1 after partitioning with DCM	1.0	1.4	1.6	1.0	0.9	0.4	0.2	≤ 0.05	1.0	0.2
Acetone extract	2.5	2.3	2.7	2.0	1.9	3.1	2.2	0.15	8.4	0.5
Lipid fraction 2 after acetone extraction	1.3	2.1	1.7	1.8	1.6	2.0	1.2	-	3.4	-
Methanol/HCl extract	0.4	3.0	1.7	1.8	2.1	2.5	1.0	0.15	4.2	0.9
Post extraction solids	0.6	3.2	4.5	3.9	5.2	5.8	6.3	1.1	8.8	3.2
Total radioactivity (whole / aerial plant)	45.4	34.0	27.5	14.8	14.4	13.5	10.3	1.9	70.3	7.5
Roots										
Acetone extract	-	-	-	2.2	0.5	0.1	≤ 0.05	2.0	-	0.9
Methanol/HCl extract	-	-	-	-	-	-	-	0.8	-	1.2
Post extraction solids, PES	-	-	-	1.5	1.6	1.3	1.4	4.0		3.4

	Radioactive residues (µCi)									
Nature of treatment	Dip treatment								Dip + spray treatment	
Treatment-sampling interval (days)	0	7	14	28	56	119-120	316-342	471-480	365	487
Total radioactivity (extracts + PES in roots)	-	-	-	3.6	2.1	1.4	1.4	6.8	-	5.5

DCM = dichloromethane

Since an application of an unknown amount of non-labelled fosetyl-Al was made prior to application of the defined amount of radiolabelled fosetyl-Al the specific radioactivity of the resulting blended radiolabelled test substance on the plant cannot be calculated

[a] At days 0, 7 and 14, samples were whole plants. On days 28, 56 and 119 samples were aerial parts and roots

Table 14 Distribution of radioactivity in pineapple plant fractions at harvest after application of 100 µCi (dipping) or 100 µCi (dipping) + 100 µCi (spraying) ^{14}C-fosetyl-Al

	Radioactive residues (µCi)							
Type of treatment	Dipping (day 480)				Dipping + spraying (day 487)			
Plant part	fruit	crown	leaves	roots	fruit	crown	leaves	roots
Acidified water/acetonitrile extracts	0.26	0.02	0.21	-	0.93	0.25	1.67	-
Aqueous phase after DCM partitioning	0.16	0.02	0.15	-	0.79	0.23	0.99	-
Lipid fraction 1 after DCM partitioning	< 0.005	< 0.005	0.02	-	0.003	0.01	0.16	-
Acetone extract	0.02	0.02	0.10	1.96	0.07	0.03	0.44	0.89
Lipid fraction 2 after acetone extraction	-	-	-	-	-	-	-	-
Methanol/HCl extract	0.03	< 0.005	0.14	0.81	0.18	0.05	0.66	1.24
Post extraction solids	0.07	0.04	1.02	3.96	0.99	0.48	1.76	3.36
Total radioactivity	0.38	0.05	1.47	6.8	2.17	0.81	4.53	5.5

DCM = dichloromethane

The metabolism of ^{14}C-fosetyl-Al in/on pineapples was very rapid and proceeded through the formation of ^{14}C-ethanol, which was subsequently incorporated into natural lipids or evaporated. Components of these lipids were identified as long-chain aliphatic acids, e.g. oleic acid and palmitic acid, and as long-chain primary alcohols, e.g. the homologous 1-docosanol and 1-tetracosanol. Other radiolabelled components were characterised as long-chain aliphatic acids or esters.

Tomato –foliar applications (fosetyl-Al)

In a study reported by Stewart & Xiao, 1991 [Ref: R000030; M-157723-01-1], two applications of ^{14}C-fosetyl-Al were made 14 days apart to fruit, leaves and stems of outdoor, sheltered tomato plants at a rate equivalent to 4.5 kg ai/ha, and samples of fruit were taken 2 hours and 14 hours after the first treatment and then 14 days (28 DAT-1) and 42 days (56 DAT-1) after the second treatment.

Fruit were washed, blended, and separated into juice and solids prior to freezing. All tomato wash and tomato liquid samples were centrifuged, filtered, and analysed directly by HPLC without solvent extraction. The tomato solid fractions were mixed with 0.1N sodium acetate, adjusted to pH 4.9 with HCl, enzymatically hydrolysed using β-glucosidase and then refluxed with CH$_3$CN/HCl. In addition, the solid fractions from the 56 DAT-1 samples were subjected to more extensive extraction techniques, involving triple acetone and HCl extractions; acid hydrolysis with 3.5N H$_2$SO$_4$; enzymatic hydrolysis with cellulase (at pH 5) and then amylase (pH 6.8); enzymatic hydrolysis with cellulase (at pH 5) and then β-glucosidase (pH 5); and refluxing with ethanol/water and ethanol/0.5N H$_2$SO$_4$.

In addition, tomato solids from the 56 DAT-1 samples were subjected to a range of solvent and reflux extractions to separate the ^{14}C-radioactivity into a lignin, cellulose and starch fractions.

Total radioactivity in the tomato wash and liquid fractions was determined by LSC and in the solid fractions by combustion followed by LSC. Selected tomato wash, tomato liquid and tomato solid fraction extractions were analysed directly by HPLC and by LSC. Retention times were compared to radiolabelled ^{14}C-standards. The identities of fosetyl-Al and its metabolites were confirmed using an alternative HPLC method or by derivatisation and GC-FPD analysis (fosetyl-Al only).

During the course of this study, all tomato fruit were washed and processed immediately after harvest (within 8 hours). The tomato wash, liquid, and solid fractions were stored in a freezer at approximately -20 °C. HPLC separation of the 2 hours tomato wash at the beginning and end of the analytical work resulted in similar portions of ^{14}C-fosetyl-Al (approx. 93 to 94%) and ^{14}C-ethanol (approx. 6%) and demonstrated a sufficient stability of the major residue components over at least 10 weeks at -20 °C for the entire course the study.

The ^{14}C-fosetyl-Al radioactive residue the fruit decreased from 1.51 mg ai eq/kg at 2 hours to 1.08 mg ai eq/kg after 14 days. Following the second treatment, TRR in fruit after 14 days (28 DAT-1) were 4.88 mg ai eq/kg, decreasing to 2.84 mg ai eq/kg after 28 days (56 DAT-1).

The amount of ^{14}C-residue in the tomato juice after the first application increased from 0.05 mg ai eq/kg at 2 hours to 0.27 mg ai eq/kg at 14 days but decreased after the second application, with TRR in the solid fraction steadily increasing over the study period.

Table 15 Distribution of radioactive residues of ^{14}C-fosetyl-Al residues in tomatoes after surface washing and maceration

Sampling interval	TRR in total tomato fruit	Tomato fruit washing		Tomato fruit liquid		Tomato fruit solid	
	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg
2 hours (0 DAT-1)	1.5101	93.3	1.41	3.2	0.05	3.6	0.05
14 days (14 DAT-1)	1.0797	49.1	0.53	24.8	0.27	26.1	0.28
28 days (14 DAT-2)	4.8813	47.0	2.29	25.8	1.26	27.2	1.33
56 days (42 DAT-2)	2.8402	12.2	0.34	37.6	1.07	50.2	1.43

The major portion of the total ^{14}C-residue at each sampling was the parent substance ^{14}C-fosetyl-Al and recovery decreased over time from 80% of TRR at 2 hours to 18% at 56 days. The majority of the ^{14}C-fosetyl-Al was recovered from the tomato wash with lower amounts recovered from the tomato liquid fraction and minimal amounts (< 0.2 mg ai eq/kg) recovered from the tomato solid fraction.

A major metabolite was ^{14}C-ethanol, making up 14.6% TRR after 2 hours and then decreasing to about 11.7% TRR after 14 days and in the later sampling intervals, found mostly in tomato solids fractions.

^{14}C-glucose was identified as a second major conversion product occurring in samples after the second application, making up 9.5% TRR in the 28-day samples and increasing to 16.4% TRR in 56-day samples.

Table 16 Identification of radioactive residues of fosetyl-Al and its metabolites in whole tomato fruit

Sampling interval	mg ai eq/kg	% TRR		
		Fosetyl-Al	Ethanol	D-glucose
2 hours (0 DAT-1)	1.3136	80.2	14.6	0
14 days (14 DAT-1)	1.1732	57.5	11.7	0
28 days (14 DAT-2)	5.0519	54.3	13.7	9.5
56 days (42 DAT-2)	2.8271	18.3	6.6	16.4

Table 17 Radioactive residues in wash and juice of tomatoes treated with ^{14}C-fosetyl-Al

Fraction	2 hours (0 DAT-1)		14 days (14 DAT-1)		28 days (14 DAT-2)		56 days (42 DAT-2)	
	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg
Tomato wash	87.87	1.1543	52.51	0.6160	39.23	1.9819	10.42	0.2946

Fraction	2 hours (0 DAT-1)		14 days (14 DAT-1)		28 days (14 DAT-2)		56 days (42 DAT-2)	
	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg
Fosetyl-Al	77.22	1.0144	43.68	0.5125	34.70	1.7528	8.28	0.2340
Ethanol	4.95	0.0650	3.15	0.0369	2.63	0.1330	1.33	0.0377
Glucose	0.00	0.0000	0.00	0.0000	0.98	0.0493	0.25	0.0070
Unknown	-	-	-	-	0.62	0.0315	0.28	0.0078
Unaccounted	5.70	0.0749	5.68	0.0666	0.30	0.0151	0.29	0.0081
Tomato juice [a]	6.90	0.0906	23.81	0.2793	30.55	1.5434	31.27	0.8840
Fosetyl-Al	2.97	0.0390	13.77	0.1615	15.70	0.7933	7.85	0.2220
Ethanol	1.43	0.0188	2.05	0.0241	0.77	0.0389	0.40	0.0112
Glucose	0.00	0.0000	0.00	0.0000	6.25	0.3159	9.48	0.2679
Unknown	-	-	-	-	0.72	0.0363	1.12	0.0316
Unaccounted	2.50	0.0328	7.98	0.0936	7.11	0.3590	12.43	0.3514
Tomato solid	5.23	0.0687	23.69	0.2779	30.21	1.5262	58.31	1.6485
Enzymatic hydrolysis with glucosidase	17.48	0.2296	37.92	0.4449	33.47	1.6910	49.45	1.3979
Aqueous	9.01	0.1183	18.40	0.2159	16.96	0.8568	23.47	0.6635
Fosetyl-Al	0.00	0.0000	0.00	0.0000	3.91	0.1974	2.20	0.0623
Ethanol	3.35	0.0440	6.50	0.0763	6.44	0.3252	4.82	0.1363
Glucose	0.00	0.0000	0.00	0.0000	2.24	0.1134	6.70	0.1893
Unaccounted	5.66	0.0743	11.90	0.1396	4.37	0.2208	9.76	0.2758
Unextracted	8.47	0.1112	19.52	0.2290	16.51	0.8342	25.98	0.7344
CH_3CN/HCl reflux			22.41	0.2629	20.13	1.0168	17.75	0.5019
Aqueous	6.78	0.0890	11.74	0.1377	7.62	0.3849	8.23	0.2327
Fosetyl-Al	0.00	0.000	NA	NA	0.00	0.0000	NA	NA
Ethanol	4.89	0.0643	NA	NA	3.83	0.1933	NA	NA
Glucose	0.00	0.0000	NA	NA	0.00	0.0000	NA	NA
Unaccounted	1.88	0.0247	NA	NA	3.79	0.1916	NA	NA
Unextracted	3.04	0.0399	10.67	0.1252	12.51	0.6319	9.52	0.2692

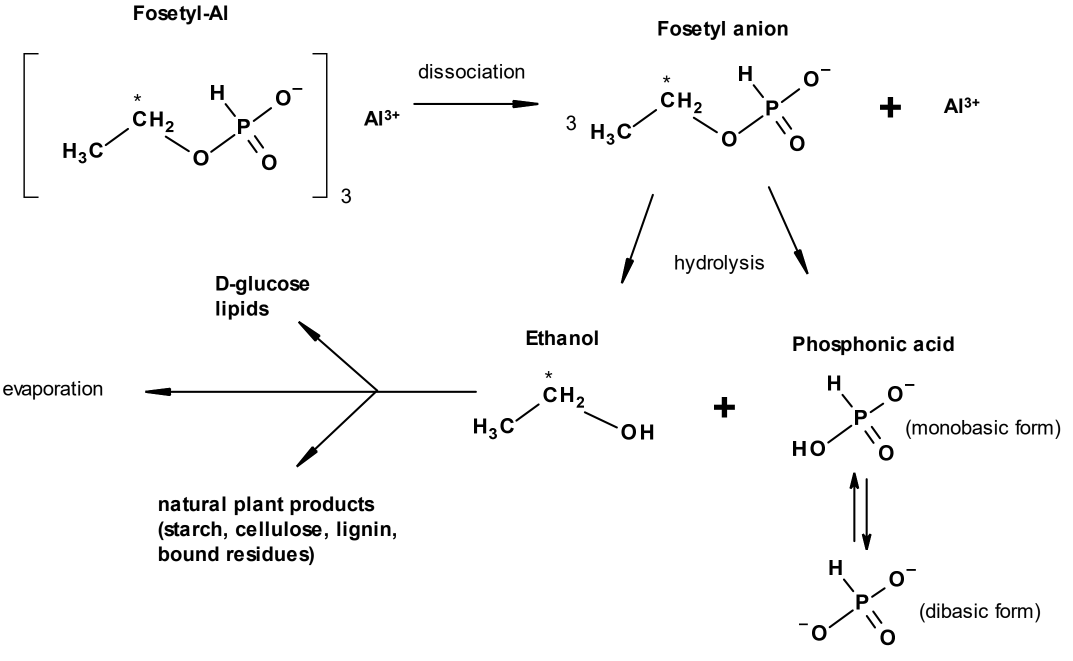
[a] Juice following surface wash, maceration and separation from tomato solids

In the tomato solids fraction from the 42 DAT-2 treatment, ^{14}C-cellulose was the major component accounting for 6.19% of TRR (0.175 mg ai eq/kg), while ^{14}C-lignin made up 1.72% TRR (0.049 mg ai eq/kg) and ^{14}C-starch accounted for 0.39% TRR (0.011 mg ai eq/kg). The amount of ^{14}C-cellulose, ^{14}C-lignin and ^{14}C-starch recovered represented 10.61, 2.95, and 0.66% of the ^{14}C-residue in the tomato solid fraction.

Table 18 Distribution of radioactive residues in the solid fraction of fruit from tomatoes treated with ^{14}C-fosetyl-Al

Extract	56 days (42 DAT-2)	
	% TRR	mg ai eq/kg
Total	34.55	0.9769
MeOH	10.81	0.3056
MeOH/HCl	3.60	0.1019
HCl	6.12	0.1731
Remainder	14.02	0.3963
DMSO	4.58	0.1294
Remainder (unextracted)	9.08	0.2568
Starch	0.39	0.0109
DMSO/Ethanol	4.11	0.1162
Total	13.58	0.3839
NaOH	8.45	0.2389
Cellulose	6.19	0.1750
Lignin	1.72	0.0486
Aqueous	6.39	0.1806
Total	14.30	0.4042

The metabolism of ^{14}C-fosetyl-Al in tomato involves the hydrolytic cleavage of the ethyl ester moiety yielding ^{14}C-ethanol and phosphonic acid. This metabolic step starts immediately after application at the surface of tomatoes as ^{14}C-ethanol could be detected in the surface wash already two hours after application. The further fate of ^{14}C-ethanol proceeds via integration into the glyoxylate cycle of plants resulting in radiolabelled natural plant constitutes, such as D-glucose, cellulose, lignin and starch.



* denotes ^{14}C-label

Figure 1 Proposed metabolic pathway of fosetyl-Al in tomatoes

Tomato - supplementary study (fosetyl-Al)

In a study reported by Luttringer & de Cormis, 1985 [Ref: R003858; M-165516-01-1], the absorption, degradation and migration of unlabelled fosetyl-Al was investigated in tomato following soil watering, petiole absorption and partial foliar treatments and analysis for fosetyl-Al and phosphonic acid by GC-NPD after acetone/acetic acid extraction and derivatisation with diazomethane (LOQ 0.2 mg/kg).

In the soil watering experiment, Fosetyl-Al was applied to tomato plants at 0.16 or 0.32 g/plant by soil watering and samples leaves and stems/petioles were taken at different time intervals (1, 2, 4, 8, 24, 48 hours as well as 7 and 14 days) for analysis.

Residues of fosetyl-Al were < 0.2 mg/kg in the stem/petioles from the plants treated with 0.16 g ai/plant and were 0.8 mg/kg in the samples taken 1 and 2 hours after soil treatment with 0.32 g ai/plant. In leaves, fosetyl-Al residues above the LOQ were only found in the 1 hour and 2 hour samples (1.4–3.6 mg ai/kg), with no apparent dose relationship.

Residues of phosphonic acid increased rapidly, being found in leaves and stems/petioles within 1 hour of watering, reaching a plateau in stems/petioles after 7 days and continuing to increase in leaves at the end of the 14-day study period.

Table 19 Residues of fosetyl-Al and phosphonic acid in tomato plants after soil watering treatment with fosetyl-Al (results in mg/kg fresh weight)

Sampling interval	0.16 g/plant				0.32 g/plant			
	Stem and petioles		Leaves		Stem and petioles		Leaves	
	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid
1 hour	< 0.2	1.5	1.4	1.4	0.8	2.2	3.5	1.5
2 hours	< 0.2	3.0	3.6	2.3	0.8	1.2	1.3	1.4
4 hours	< 0.2	2.9	< 0.2	1.8	< 0.2	2.7	< 0.2	2.5
8 hours	< 0.2	7.8	< 0.2	6.7	< 0.2	11.9	< 0.2	8.5
24 hours	< 0.2	19.0	< 0.2	7.1	< 0.2	24.1	< 0.2	9.1
48 hours	< 0.2	27.6	< 0.2	18.2	< 0.2	30.1	< 0.2	16.3
7 days	< 0.2	101.0	< 0.2	43.2	< 0.2	156.2	< 0.2	51.7
14 days	< 0.2	100.0	< 0.2	93.0	< 0.2	149.1	< 0.2	132.8

In the petiole absorption experiment, tomato plants were treated with 7200 µg fosetyl-Al or 5000 µg phosphonic acid per plant on the 5th petiole and samples of stem, petiole and leaves from the central plant part as well as from the upper plant part were taken 8 and 15 days after treatment for analysis.

In the fosetyl-Al treated plants, residues of parent remained in stem and petiole as well as in leaves of lower and upper plant part by Day 8 and 15, with no trend of degradation. Residues of both fosetyl-Al and phosphonic acid were similar in both the lower and upper plant parts.

In contrast, in the phosphonic acid treated plants, higher residues were found in upper plant parts (in stem, petioles and leaves) as well as in the lower leaves, indicating translocation in both directions, but preferentially migration towards the apex (acropetal).

Table 20 Residues of fosetyl-Al and phosphonic acid in various parts of tomato plants eight and fifteen days after petiole treatment with fosetyl-Al or phosphonic acid

Treatment	Analyte	Residues (mg/kg fresh weight) Lower plant part				Residues (mg/kg fresh weight) Upper plant part			
		Stem and petioles		Leaves		Stem and petioles		Leaves	
		8 days	15 days	8 days	15 days	8 days	15 days	8 days	15 days
Fosetyl-Al (7200 µg/plant)	Fosetyl-Al	0.2	0.5	0.5	0.5	0.2	0.7	0.4	0.3
	Phosphonic acid	3.8	4.8	3.1	3.4	3.4	4.5	3.4	3.3
Phosphonic acid (5000 µg/plant)	Phosphonic acid	3.2	3.8	10.2	5.4	10.8	5.4	12.9	9.0

In the foliar treatment experiment, tomato plants were treated with solution of 0.4 g ai/litre, spraying on the upper plant part, or the central plant part (with the untreated plant parts being covered with a plastic bag). Samples of stem and petiole as well as leaves were taken at 4, 8 and 24 hours after treatment.

Residues of fosetyl-Al and phosphonic acid were similar the lower and the upper plant parts (stem and petioles as well as leaves) but there was a high increase in residues of phosphonic acid after 8 hours in leaves from both the upper and lower parts of the plant, these decreasing after 24 hours.

Table 21 Residues of fosetyl-Al and phosphonic acid after partial spray treatment of tomato plants with a solution containing 0.4 g/L fosetyl-Al (results in mg/kg fresh weight)

Sampling interval	Treatment (0.4 g ai/L)of the upper plant part Recovered residues in the lower plant parts				Treatment (0.4 g ai/L) of the lower plant part Recovered residues in the upper plant parts			
	Stem and petioles		Leaves		Stem and petioles		Leaves	
	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid
4 Hours	1.4	4.8	3.3	3.1	1.6	3.6	3.2	3.3
8 Hours	1.1	2.8	2.7	9.8	1.2	5.4	2.8	6.3

Sampling interval	Treatment (0.4 g ai/L)of the upper plant part Recovered residues in the lower plant parts				Treatment (0.4 g ai/L) of the lower plant part Recovered residues in the upper plant parts			
	Stem and petioles		Leaves		Stem and petioles		Leaves	
	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid	Fosetyl-Al	Phosphonic acid
24 Hours	1.0	2.9	1.6	3.1	1.4	3.1	1.9	5.6

Tomato – root absorbtion (fosetyl-Al)

In a study reported by Leconte et al, 1988 [Ref: R001125; M-159938-01-1], hydroponically grown tomato plants (with 5 mature leaves) were treated by dipping the root systems in solution of 2.26 mM fosetyl-Al for either 1 hour or 3 hours. Samples of roots, mature leaves, mature internodes, young leaves and buds, and young internodes were taken at the end of the 1-hour dipping period and 3, 24 and 72 hours after the start of the 3-hour dipping period for analysis of fosetyl and phosphonic acid using gas chromatography (after derivatisation with diazomethane).

Fosetyl-Al uptake by the root system of tomato plants was accompanied by rapid hydrolytic split of ethanol to form phosphonic acid. Further hydrolysis occurred more slowly since minor amounts of fosetyl-Al could still be detected in roots after 24 hours.

Three days after the root absorption period the level of phosphonic acid in the roots and aerial organs was nearly equal, indicating migration of phosphonic acid to the growing organs (young leaves and buds as well as young internodes). Both fosetyl-Al and phosphonic acid were shown to be systemic as both compounds were transported into all parts of the plant shortly after beginning of the experiment.

Table 22 Residues of fosetyl and phosphonic acid (nmol/g fresh weight) at different time intervals after incubation of tomato plants in a hydroponic solution of fosetyl-Al

Dip exposure to fosetyl-Al	1 hour (2.26 mM)		3 hours (2.26 mM)		3 hours (2.26 mM)		3 hours (2.26 mM)	
Sampling time	1 hour		3 hours		24 hours		72 hours	
Analyte	Fosetyl	Phosphonic acid	Fosetyl	Phosphonic acid	Fosetyl	Phosphonic acid	Fosetyl	Phosphonic acid
Young leaves and buds	19.3±5.3	35.4±13.4	30.3±6.4	63.4±12.2	10.1±1.8	107.3±12.2	ND	163.4±28.1
Young internodes	traces	45.1±9.8	101.8±75.2	125.6±28.5	ND	120.7±17.1	ND	101.2±12.2
Mature leaves	7.7±1.6	14.6±4.9	11.0±1.8	39.0±6.1	4.6±0.9	58.5±15.9	traces	50.0±11.0
Mature internodes	6.4±0.9	26.8±8.5	12.8±3.7	43.9±8.5	6.4±0.9	108.5±20.7	traces	131.7±42.7
Roots	89.9±22.0	156.1±18.3	174.3±33.9	410.9±78.1	100.0±32.1	224.4±17.1	30.3±6.4	201.2±26.8

ND = not detected

Phosphonic acid

A summary review of published papers on the behaviour of phosphonic acid in plants was provided in a paper by Morgan et al, 2005 [Ref AWR 04/01]. General conclusions from this review are:

- Potassium phosphonates readily penetrates both bark and cuticle of *Betula pendula* trees (Garrec & Barrios, 1992).
- Phosphonates are absorbed rapidly by the plant leaves or roots and are translocated in both the xylem and phloem (Luttringer and Cormis 1985, Guest and Grant 1991).
- Phosphonate applied to the tomato roots was translocated to the leaves within a few minutes of treatment. Once in the leaf, the fungicide becomes phloem mobile and moves to sinks with the greatest demand for photoassimilate (D'Arcy-Lameta and Bompeix, 1991).

- Following trunk injection (avocados), phosphonate was first detected in the leaves 24 hours after application, and then detected in the bark and roots a few days later, supporting the notion of downward phloem transport of phosphonate from the leaves (Whiley *et al*., 1995).
- Following foliar application, phosphonate is detected in plant roots, confirming the mobility of phosphonate in the plant phloem (Ouimette & Coffey, 1989, 1990).
- In avocado seedlings, soil applications of potassium phosphonate led to higher residues of phosphonate in all tissues compared to foliar application. Residues in roots were relatively constant while residues in leaves and stems increased initially and then declined significantly by the end of the study period (Ouimette & Coffey, 1989).
- Distribution of phosphonate to both roots and leaves is more rapid after foliar application than after trunk injection (Schutte *et al*., 1991).
- Phosphonate can be actively taken up into the symplast of castor bean plants and sugar beet leaf discs, and transported through the phloem. The involvement of an active transport system is evidenced by the effect of metabolic inhibitors (Ouimette & Coffey, 1990).

Environmental fate

The Meeting received information on the environmental fate and behaviour of fosetyl-Al and phosphonic acid, including hydrolytic stability, photochemical degradation in soils and aerobic metabolism studies.

Hydrolysis – fosetyl-Al

Study 1

In a study reported by Buys et al., 1981 [Ref: R000987, M-159693-01-1], aqueous test solutions of 200 mg ai fosetyl-Al/litre were prepared using aqueous 0.1 N sulfuric acid (pH 1.2), 0.1 N sodium hydroxide (pH 13) citrate buffers (pH 3, 5, 6) and borate buffers (pH 8, 9) and were incubated in the dark at 70 ± 1 °C or at 22 ± 3 °C for intervals up to 33 days (48 hours for the pH 1, 2 and 13 samples). A further series of test solutions of 10 g ai/litre at pH 3, 6 and 9 were also incubated in the dark for intervals up to 32 days. Samples were analysed for both fosetyl-Al and phosphonic acid by GC-FPD.

Table 23 Recovery of fosetyl-Al after incubation in aqueous test solutions at pH 1.2 and 13 at 70 °C and 22 °C in the dark

pH	70 °C							22 °C						
	Incubation time (hours)							Incubation time (days)						
	0	2	4	6	8	24	48	0	1	2	7	14	21	30
1.2	106	82	65	50	38.5	< 2	< 2	106	97.5	100.5	85	69.5	55	43.5
13	103.5	93.5	79.5	73	63	19.5	< 2	103.5	101.5	93.5	72	49.5	33	23

Results are reported as percentage of nominal initial concentration of 200 mg/L

Table 24 Recovery of fosetyl-Al after incubation at 70° C and 22° C in aqueous buffer solutions at pH 3, 5, 6, 8 and 9 in the dark

pH	Incubation time (days)									
	0		5		8		20		33	
	70° C	22° C	70° C	22° C	70° C	22° C	70° C	22° C	70° C	22° C
3	91.5	103.5	59	-	38.5	97.5	5.5	104	< 2	101
5	98	96.5	96	-	91	87.5	95.5	89	81.5	84.5
6	100.5	98.5	101	-	94	93	106	99.5	101.5	94
8	108	103.5	106	-	102	99	116	108	107	106
9	108	105	103.5	-	100.5	98.5	111.5	106.5	102	104.5

Results are reported as percentage of nominal initial concentration of 200 mg/L

Table 25 Recovery of fosetyl-Al after incubation at 70 °C in aqueous buffer solutions at pH 3, 6 and 9 in the dark

pH	Incubation time (days)											
	0		2		4		7-8		14-16		28-32	
	70 °C	22 °C	70 °C	22 °C	70 °C	22 °C	70 °C	22 °C	70 °C	22 °C	70 °C	22 °C
3	100	100	59	-	46	-	12.5	42.5	< 2	12	< 2	< 2
6	113	113	104	-	103	-	100	112	103	101	100	92
9	100	100	94.5	-	107	-	103	85	107	110	103	125

Results are reported as percentage of nominal initial concentration of 10 mg/litre

Fosetyl-Al was found to be stable to hydrolysis in aqueous buffer solutions at pH 5, 6, 8 and 9 following 33 days of incubation at 70 or 22 °C but was degraded hydrolytically under conditions not representative for the environment in terms of pH and temperature. Phosphonic acid was the major transformation product.

Study 2

In a further study reported by Crowe, 2001 [Ref: C012596, M-203000-01-1], aqueous test solutions of 100 mg ai fosetyl-Al/litre were prepared using potassium biphthalate (pH 4) or boric acid (pH 7, 9) and incubated in the dark at 50 °C for 5 days. Samples were taken after 0, 2 and 5 days for analysis of fosetyl-Al, phosphonic acid and phosphoric acid by direct injection into an ion chromatographic system and conductimetric detection. The limit of quantification (LOQ) was 3 mg/litre each for fosetyl-Al and phosphonic acid. The LOQ for phosphoric acid was 8 mg/litre.

Table 26 Recovery of fosetyl-Al after incubation in sterile aqueous buffer solutions at pH 4, 7 and 9 at 50 °C in the dark

pH	Incubation time (days)					
	0		2		5	
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
4	82.4	100	83.7	101.6	83.7	101.6
7	100.3	100	102.1	101.8	102.0	101.7
9	88.5	100	90.0	101.7	90.9	102.7

Fosetyl-Al was found to be stable to hydrolysis in aqueous buffer solutions at pH 4, 7 and 9 following 5 days of incubation at 50 °C.

Hydrolysis – phosphonic acid

Study 1

In a study reported by Shepler, 1997 [Ref: R009302, M-179049-01-1], aqueous solutions of 200 mg ai phosphonic acid/litre were prepared using citrate (pH 4), acetate (pH 5), TRIS (pH 7) or borate (pH 9) buffers and were incubated in the dark at 25 °C for intervals up to 31 days. Samples were analysed for phosphonic acid and its potential transformation product phosphoric acid by anion exchange HPLC and by comparison with authentic reference material. The identity of phosphonic acid was confirmed by nuclear magnetic resonance (NMR) using a ^{31}Phosphorus probe.

Table 27 Recovery of phosphonic acid after incubation in sterile aqueous buffer solutions at pH 4, 5, 7 and 9 at 25 °C in the dark

pH	Compound	Incubation time (days)					
		0	3	7	12	20	31
4	Phosphonic acid	94.9	92.4	94.2	91.8	98.6	99.2
	Phosphoric acid	2.1	2.9	3.8	5.5	4.4	3.1
	Total	97.0	95.3	98.0	97.3	103.0	102.3

pH	Compound	Incubation time (days)					
		0	3	7	12	20	31
5	Phosphonic acid	94.7	94.5	99.9	93.2	98.3	98.3
	Phosphoric acid	0.0	2.6	0.0	0.0	0.0	1.1
	Total	94.7	97.1	99.9	93.2	98.3	99.4
7	Phosphonic acid	99.9	95.0	99.2	99.4	100.6	102.2
	Phosphoric acid	2.3	1.4	1.4	2.8	3.5	3.1
	Total	102.2	96.4	100.6	102.2	104.1	105.3
9	Phosphonic acid	95.7	92.0	94.8	93.4	98.5	97.1
	Phosphoric acid	1.7	0.0	0.0	0.0	1.4	1.2
	Total	97.4	92.0	94.8	93.4	99.8	98.3

Results are reported as percentage of nominal initial concentration of 200 mg ai/litre

Phosphonic acid was found to be stable under conditions of sterile aqueous buffer hydrolysis at pH 4, 5, 7 and 9 following 31 days of incubation at 25 °C. Phosphoric acid levels ranged from 0–5.5% with no clear trend with time.

Study 2

A study on the potential of phosphonic acid to undergo oxidation in sterile aqueous buffer solutions was reported by Corgier *et al*., 2000 [Ref: R014225, M-189210-01-1]. Aqueous buffer solutions of 1 g ai phosphonic acid/litre were prepared using citric acid (pH 4), imidazole (pH 7) or boric acid (pH 9) buffers and incubated under sterilised air or nitrogen (control) flow-through conditions for up to 30 days at 22 °C. Samples were analysed by ^{31}Phosphorus-NMR.

Values for phosphate were low to very low for all samples, with phosphate detected in one of the two pH 4 samples, present at 1.4% of the phosphonic acid concentration in the day-16 sample and 1.2% in the day 30 sample. No transformation was observed for samples of pH 7 and 9.

Photochemical degradation in soil – phosphonic acid

Study 1

A study on the photolytic transformation of phosphonic acid in soil was reported by Corgier, 2000 [Ref: R009319, M-179065-01-1]. An aqueous solution of phosphonic acid was applied drop-wise to the soil surface to achieve a concentration of 4 mg ai phosphonic acid/kg and the soils were exposed to simulating natural sunlight (602 W/m^2) at 30 °C for intervals up to 21 days.

Soil samples were extracted with aqueous ammonia buffer solution and then twice with isopropanol and the combined extracts were derivatised with trimethylsilyl diazomethane and analysed for the phosphonic acid dimethyl ester derivative by GC-FPD.

Table 28 Photo-transformation of phosphonic acid on soil

Compound	Treatment	Phosphonic acid residues in soil (mg/kg)					
		0 DAT	1 DAT	3 DAT	7 DAT	15 DAT	21 DAT
Phosphonic acid	irradiated	4.6	3.9	3.6	3.5	2.6	2.2
	dark	4.6	-	3.7	3.6	3.1	3.3

Extractable residues of phosphonic acid (phosphonate) decreased slowly in both the irradiated and non-irradiated samples, from 4.6 mg/kg to 2.2 mg.kg (irradiated samples) and 3.3 mg/kg (dark controls) by day 21.

Study 2

A further phototransformation study conducted at a lower test temperature (22 °C) and prolonged time of irradiation (45 days) was reported by Cavaille, 2001 [Ref: C011841, M-201629-01-1]. An aqueous solution of phosphonic acid was applied drop-wise to the surface of a loam soil (pH 6.6, 9.9% OM, 6.4 meq/100g CEC) to achieve a concentration of 4 mg ai phosphonic acid/kg and the soils were exposed to simulating natural sunlight (490 W/m^2) at 22 °C for intervals up to 45 days.

Soil samples were extracted with aqueous ammonia buffer solution and then twice with isopropanol and the combined extracts were derivatised with trimethylsilyl diazomethane and analysed for the phosphonic acid dimethyl ester derivative by GC-FPD. The LOQ of the method was 01 mg phosphonic acid/kg.

Table 29 Photo-transformation of phosphonic acid on soil

Compound	Treatment	Phosphonic acid residues in soil (mg/kg)					
		0 DAT	7 DAT	15 DAT	21 DAT	30 DAT	45 DAT
Phosphonic acid	irradiated	4.7	3.4	3.0	2.3	1.6	1.0
	dark	4.7	3.9	3.6	2.7	2.1	2.6

Extractable residues of phosphonic acid (phosphonate) decreased slowly in both the irradiated and non-irradiated samples, from 4.7 mg/kg to 1.0 mg.kg (irradiated samples) and 2.6 mg/kg (dark controls) by day 45.

In summary, following irradiation at soil surfaces, residues of phosphonate extractable from soil were found to decrease with time, possibly a result of a general decrease of extractability from soil, the influence of irradiation and/or possible microbial transformation. Overall, phosphonic acid could be subject to slow photo-degradation at soil surfaces caused by indirect photolytic processes influenced by soil components.

While photo-transformation in soil is a potential degradation mechanism, this is likely to be limited because of the slow photolysis process and the migration of residues to deeper soil layers after rainfall under field conditions.

Since the potential for direct absorption of light by phosphonic acid or the active substance fosetyl-Al is very limited (i.e. no significant absorption at wavelengths of more than 290 nm), the actual degradation observed is explained by indirect photolytic effects, i.e. the reaction of singlet oxygen, hydroxyl radicals and peroxy radicals as oxidative species formed in the top 2 mm of soil from irradiation.

Aerobic soil metabolism – fosetyl-Al

Study 1

A study investigating the biotransformation of fosetyl-Al in aerobic soils was reported by Hascoet et al. 1978 [Ref: R002963, M-163672-01-1]. Aqueous solutions of [1-ethyl-^{14}C]-fosetyl-Al or [^{32}P]-fosetyl-Al were applied drop-wise onto the soil surface to achieve a treatment rate of about 500 mg/kg dry weight of soil (equivalent to 80 kg ai/ha). Soil samples were incubated at 20 °C under aerobic conditions in the dark for intervals up to 32 days or at 12 °C for intervals up to 64 days.

Table 30 Characteristics of the soils used in the aerobic soil metabolism study

Parameter		Soil		
Soil Designation		Versailles (‘A’)	German 2.2 (‘B’)	German 2.3 (‘C’)
Sand [> 200 μm]	(%)	2.7	55.0	40.8
Fine Sand[20 – 200 μm]	(%)	55.2	28.4	37.6
Silt[2 – 20 μm]	(%)	21.1	10.0	12.4
Clay[< 2 μm]	(%)	20.5	6.6	9.2
pH		6.4	6.9	6.1
Organic Matter (%)		1.94	4.71	1.72
Organic carbon (%) [(a)]		1.13	4.17	1.00
Cation Exchange Capacity (meq/100 g)		10.0	13.2	5.0

Calculated by dividing organic matter content by 1.72

The tests were performed in flow through systems consisting of glass flasks each containing 50 g soil and attached to a trap for volatile radioactivity (mixture of methanol and phenethylamine, 2:1, *v/v*), i.e. ^{14}C-carbon dioxide. Soil moisture was maintained during incubation by passing humidified air through the samples.

Soil samples were triple-extracted with distilled water and radioactivity measured by liquid scintillation counting (LSC). Radioactivity present as ^{32}P in extracts was measured and confirmed by applying the Cherenkov effect. Soil extracts were concentrated and analysed by TLC/radio-detection and the identity of test item and degradation products (i.e. phosphonic acid) was confirmed by TLC co-chromatography with reference items. Volatile radioactivity in traps (methanol/phenethylamine mixture) was determined by LSC and the identity of ^{14}C-carbon dioxide formed and trapped as volatile radioactivity was confirmed by co-precipitation with aqueous barium chloride solution (barite water). Unextracted residues were determined by combustion/LSC and selected samples were subject to an additional harsh extraction step using aqueous hydrochloric acid.

Material balances reported for the samples incubated at 20 °C, these ranging from 93 to 110% AR except for the day-4 German 2.2 soil (118% AR) and the day-1 and day-2 German 2.3 soil 2.3 (81% and 85% AR, respectively).

Following incubation at 20 °C the total extractable radioactivity decreased from 48.1% AR to 1.3% AR (soil Versailles at day 4), from 11.3% AR to 0.5% AR (German 2.2 soil at day 16) and from 53% AR to 2.9% AR (German 2.3 soil at day 2).

Following incubation at 12 °C the total extractable radioactivity decreased from 82.9% AR to 0.5% AR (soil Versailles at day 32), from 64.9% AR to 0.4% AR (German 2.2 soil at day 32) and from 75.1% AR to 0.7% AR (German 2.3 soil at day 16).

No values for extractability of residues at the various time points were reported for samples following application of [^{32}P]-fosetyl-Al.

Degradation of [^{14}C]-fosetyl-Al was predominantly by rapid formation of carbon dioxide, reaching a maximum of 72–83% of the applied radioactivity at the end of the study periods (32 days for the 20 °C incubations and 64 days for the 12 °C incubations). For [^{32}P]-fosetyl-Al no volatile radioactivity was observed.

For samples incubated at 20 °C unextracted residues decreased from 28.4% AR by day one to 23.9% AR by day 32 (soil Versailles) and from 50.2% AR by day one to 20.4% AR by day 32 (German soil 2.2). Values of NER increased for German soil 2.3 from 14.1% AR by day one to 20.8% AR by day 32.

No values for unextracted residues at the various time points were reported for samples following application of [^{32}P]-fosetyl-Al at 20 °C and for samples incubated with [^{14}C]-fosetyl-Al at 12 °C.

Table 31 Aerobic degradation of [^{14}C]-fosetyl-Al at 20 °C in three European soils under aerobic conditions

Component		% Applied radioactivity (rounded)																	
		Day 1			Day 2			Day 4			Day 8			Day 16			Day 32		
Soil		A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Ambient extract	1st	42		44	3.0		2.9	1.3			-						-		
	2nd	6.2		9.1	1.1			-			-			-			-		
Total in ambient extracts		48	11	53	4.1	2.5	2.9	1.3	1.6		-			0.5	0.5		-		
Harsh extracts (aqueous HCl)	1st	1.3	6.1		1.1	4.2		1.0	4.5			4.3		1.6	1.6		-		
	2nd	0.5	4.4			3.4			4.7			3.9		-			-		
Total in harsh extracts		1.8	11		1.1	7.6		1.0	9.2			8.2		1.6	1.6		-		
Unextracted from combustion		27	40		39	41		38	37		30	27		27	22		24	20	
Total unextracted		28	50	14	40	49	23	40	46	34	30	35	27	27	23	21	24	20	21

Component	% Applied radioactivity (rounded)																	
	Day 1			Day 2			Day 4			Day 8			Day 16			Day 32		
Soil	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Volatiles (^{14}C-Carbon dioxide)	19	39	14	55	59	59	67	71	73	68	70	77	70	71	78	75	78	83
Total radioactivity	95	100	81	99	110	85	107	118	106	97	105	104	97	94	99	99	98	93

Total unextracted includes radioactivity in harsh extracts and radioactivity determined after combustion

Table 32 Aerobic degradation of [^{14}C]-fosetyl-Al at 12 °C in three European soils under aerobic conditions

ss		% Applied radioactivity (rounded)																	
		Day 1			Day 2			Day 4			Day 8			Day 16			Day 32		
Soil		A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Ambient extract	1st	69	48	64	51	37	58	5.2	5.2	7.5		1.1	1.4	1.1	0.6	0.7	0.5	0.4	
	2nd	12	17	11		5	6.3		0.7			0.1			0.1			0.0	
	3rd	1.3		0.9															
Total extracted		83	65	75	51	42	65	5.2	5.9	7.5		1.1	1.4	1.1	0.6	0.7	0.5	0.4	
Total unextracted		na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Volatiles (^{14}C-Carbon dioxide)		5	5.3	5.9	16	17	17	59	59	58	68	61	66	69	65	71	75	69	75
Total radioactivity		90	70	81	67	59	81	64	65	65	68	62	67	70	66	72	75	69	75

na Unextracted radioactivity not determined

Volatiles (^{14}C-Carbon dioxide) measured on day 64 at 75% AR, 72% AR and 84% AR in the three soils

[^{14}C]-fosetyl-Al was the only ^{14}C-containing compound detected by TLC/^{14}C-radiodetection in soil extracts of samples incubated up to four days after application. A volatile component observed in traps of the rotary evaporator after concentration of soil extracts was presumed to be ^{14}C-ethanol.

Analysis of soil extracts was performed by thin-layer chromatography (TLC) starting on day two. Besides the presence of [^{32}P]-fosetyl-Al, analysis revealed the formation of one ^{32}P-containing degradation product, i.e. phosphonate, formed from biotically induced hydrolysis of [^{32}P]-fosetyl-Al.

In summary, following application of [^{32}P]- or [^{14}C]-labelled fosetyl-Al to soil, residues were readily degraded to form [^{32}P]-phosphonate (phosphonic acid), ^{14}C-carbon dioxide and ethanol as degradation products of fosetyl-Al in aerobic soil.

Study 2

A further study on the biotransformation of fosetyl-Al and ethanol in four aerobic soils was reported by Buys & Bertrand, 1982 [Ref: R000825, M-159391-01-1]. Aqueous solutions of [1-ethyl-^{14}C]-fosetyl-Al or [1-^{14}C]-ethanol were applied drop-wise onto the soil surface to achieve a fosetyl-Al treatment rate of about 100 mg/kg dry weight of soil (equivalent to 80 kg ai/ha mixed to a depth of 6 cm) and an ethanol treatment rate of 39 mg/kg. Soil samples were incubated at 20 °C under aerobic conditions in the dark for intervals up to 16 hours.

Table 33 Characteristics of the soils used in the aerobic soil metabolism study

Parameter		Soil			
Soil Designation		Sandy loam	Clay loam	Loamy sand	Silt loam
Sand[50 – 2000 µm]	(%)	62.3	34.0	81.2	15.2
Silt[2 – 20 µm]	(%)	20.2	27.6	13.8	55.3
Clay[< 2 µm]	(%)	13.6	37.5	3.1	23.0
pH		5.3	7.6	6.6	6.6
Organic Matter (%)		3.6	2.6	1.3	2.3
Organic carbon (%) [(a)]		2.1	1.5	0.8	1.3

Parameter	Soil			
Soil Designation	Sandy loam	Clay loam	Loamy sand	Silt loam
Cation Exchange Capacity (meq/100 g)	13	21	5	14

Calculated by dividing organic matter content by 1.72

The tests were performed in flow-through systems consisting of glass flasks each containing 2.5 g of soil and attached to two successive traps for volatile radioactivity (0.1N aqueous sodium hydroxide solution). For the two soils Sandy loam and Clay loam and late sampling intervals of seven hours and 15 hours, an additional trap containing concentrated sulfuric acid was also included. Soil moisture during incubation was maintained by passing humidified air through the test samples.

Volatile radioactivity collected in traps was determined by liquid scintillation counting (LSC) and following precipitation as barium carbonate, ^{14}C-carbon dioxide was quantified by determination of the difference between total radioactivity and the radioactivity that remained in solution. The radioactivity remaining in solution after precipitation was ethanol (confirmed by reversed phase HPLC analysis combined with ^{14}C-radio-detection).

Soil samples were sequentially extracted with aqueous sulphuric acid, ammonium hydroxide, methanol and ethyl acetate. Maximum radioactivity in organic solvent extracts was below 1–3% AR and were not considered further. Total radioactivity in soil extracts was determined by LSC. Dependent on total radioactivity, extracts were analysed by HPLC combined with ^{14}C-radio-detection and unextracted residues were quantitated by combustion followed by LSC.

Material balances reported for the radio-labelled fosetyl-Al samples ranged from 95.1% to 99.5% AR and ranged from 96.4% to 106.3% AR for the radiolabelled ethanol samples.

Following application of fosetyl-Al, initial extraction efficiency ranged from 98.5 to 99.5% AR, decreasing to 10.9 to 12.6% AR after incubation for 15 to 16 hours (with unextracted residues increasing to 37–47% AR at the end of the incubation period.

Following application of ethanol, initial extraction efficiency ranged from 96.5 to 99.5% AR, decreasing to 7.8 to 10.6% AR after 15 to 16 hours incubation (when unextracted residues were 33.6 to 35.3% AR).

Volatile residues recovered from the soils treated with ^{14}C-fosetyl-Al were 37–46% AR after 15 and 16 hours of incubation, with ethanol accounting for 17.6–36.6% AR and carbon dioxide making up 9.4%–19.6% AR.

Following application of ^{14}C-ethanol, 54% AR was recovered in traps after 15–16 hours in two soils, with ethanol accounting for 40–47% AR and carbon dioxide making up 7.7–14% AR.

Table 34 Degradation of [^{14}C]-fosetyl-Al at 20 °C in four soils under aerobic conditions

Component	% Applied radioactivity						
	Soil	0 hours	0.75-1 hour	1.5 hours	3 hours	7 hours	15-16 hours
Fosetyl-Al	sandy loam	97	17	1.2	n.d.	n.d.	-
	clay loam	95	64		21	4	-
	loamy sand	97	63	41	17		
	silt loam	98	60	36	5		
Ethanol (extracted)	sandy loam	<1	73	78	48	5	-
	clay loam	1	27		43	6	-
	loamy sand	nd	30	39	44		
	silt loam	nd	25	44	46		
Ethanol (volatile)	sandy loam	-	2.4	6.7	27.9	36.5	36.6
	clay loam	-	1.8		12.9	29.3	17.6
	loamy sand	-	na	na	na		
	silt loam	-	na	na	na		

Component	% Applied radioactivity						
	Soil	0 hours	0.75-1 hour	1.5 hours	3 hours	7 hours	15-16 hours
Total ethanol	sandy loam	<1	75.4	84.7	75.9	41.5	36.6
	clay loam	1	28.8		55.9	29.3	17.6
	loamy sand	-	-	-	-		
	silt loam	-	-	-	-		
Unknown RRT 0.65 (alkaline extract)	sandy loam	2.2[a]	1.8[a]	2.5[a]	3.4[a]	5	5
	clay loam	-			-	trace[b]	-
	loamy sand	-	-	-	-		
	silt loam	-	-	-	-		
Others (alkaline extract)	sandy loam	n.d.	n.d.	n.d.	n.d.	3.9	4.5
	clay loam	1.7	1.8		2.6	6.3	5
	loamy sand	-	-	-	-		
	silt loam	-	-	-	-		
^{14}C-Carbon dioxide	sandy loam	-	0.4	1	2.2	6.3	9.4
	clay loam	-	0.7		3.2	12.1	19.6
	loamy sand	-	-	-	-		
	silt loam	-	-	-	-		
Total extracted	sandy loam	99.5	91.8	81	51.8	15.3	12.6
	clay loam	96.5	91.7		67.2	20.1	10.9
	loamy sand	98.8	92.9	81.7	64.8		
	silt loam	98.5	89.7	95.8	96.8		
Unextracted	sandy loam	0.1	3.7	7.8	14.8	38.4	37
	clay loam	0.1	3.5		17.4	40	47
	loamy sand	0.7	1.8	3.1	5.2		
	silt loam	1.5	5.1	6.5	21.4		
Total volatile radioactivity (CO_2 + ethanol)	sandy loam	-	2.8	7.7	30.1	42.8	46
	clay loam	-	2.5		16.1	35.4	37.2
	loamy sand	-	4	12	26.7		
	silt loam	-	2.9	8	23.1		
Total radioactivity	sandy loam	99.6	98.3	96.5	96.6	96.5	95.6
	clay loam	96.6	97.7		98	95.5	95.1
	loamy sand	99.5	98.7	96.8	96.7		
	silt loam	100	97.7	95.8	96.8		

n.d. = not detected

na = not determined

RRT = relative retention time derived from HPLC analysis

[a] Includes other compounds in alkaline extract (ammonium hydroxide extract). Attributed to microbial degradation of ethanol

[b] Presence of Unknown RRT reported in extract, but not quantified

Table 35 Degradation of [^{14}C]-ethanol at 20 °C in two soils under aerobic conditions

Component	% Applied radioactivity						
	Soil	0 hours	0.75-1 hour	1.5 hours	3 hours	7 hours	15-16 hours
Ethanol (extracted)	sandy loam	99.1	81	67	44	2	1.4
	clay loam	96	72		38	2.9	1.8
Ethanol (volatile)	sandy loam	-	10	17.5	29.4	44.6	46.7
	clay loam	-	16.2		32.8	41.7	40.2
Total ethanol	sandy loam	99.1	91	84.5	73.4	46.6	48.1
	clay loam	96	88.2		70.8	44.6	42
Unknown RRT 0.65 (alkaline extract)	sandy loam	0.4[a]	1.2[a]	2.4[a]	3.5[a]	5	5
	clay loam	-	-		-	trace	-
Others (alkaline extract)	sandy loam	-	-	-	-	2.4	3.3
	clay loam	0.5	1.2		2.4	4.4	3.8
^{14}C-Carbon dioxide	sandy loam	-	1	1.8	2.9	6.8	7.7
	clay loam	-	1.3		3.5	10.5	14.1
Total extracted	sandy loam	99.5	80.9	69.9	48.6	10.5	10.6
	clay loam	96.5	73.4		42.2	9.4	7.8
Unextracted	sandy loam	0.1	3.5	9.8	16.1	32.5	33.6
	clay loam	0.2	5.2		17.7	34.4	35.3

Component	% Applied radioactivity						
	Soil	0 hours	0.75-1 hour	1.5 hours	3 hours	7 hours	15-16 hours
Total volatile radioactivity (CO_2 + ethanol)	sandy loam	-	11	19.2	32.3	51.4	54.4
	clay loam	-	17.5		36.3	52.2	54.3
Total radioactivity	sandy loam	99.6	96.4	100.7	99.9	101.2	106.3
	clay loam	96.7	97.4		99.7	106.5	111.5

na = not determined

RRT = relative retention time derived from HPLC analysis

[a] Includes other compounds in alkaline extract (ammonium hydroxide extract). Attributed to microbial degradation of ethanol

In summary, following application of ^{14}C-fosetyl-Al to aerobic soil, the active substance was extensively and rapidly transformed to ethanol (max 85% AR after 1.5 hours), unextracted (bound) residues (max 47% AR after 16 hours) which were not converted further during the short runtime of the study and attributed to soil biological activity, and mineralisation to carbon dioxide (max 20% AR after 16 hours). Estimated half-lives for fosetyl-Al were 0.33–1.5 hours and 2.5 hours for ethanol.

Study 3

The degradation of fosetyl-Al in three UK soils was reported by Mackie & Phillips, 1999 [Ref: R011664, M-184329-01-1]. Aqueous solutions of [1-ethyl-^{14}C]-fosetyl-Al were applied drop-wise onto the soil surface to achieve a fosetyl-Al treatment rate of about 19 mg/kg dry weight of soil (equivalent to 20 kg ai/ha mixed to a depth of 6 cm). Soil samples were incubated at 20 °C under aerobic conditions in the dark for intervals up to 120 days.

Table 36 Characteristics of the soils used in the aerobic soil metabolism study

Parameter				
Soil Designation		Clay loam	Sand/Loamy sand	Sandy loam
Sand [63–2000 µm]	(%)	34.3	86.8	65.4
Silt [2 – 63 µm]	(%)	35	7	22.5
Clay [< 2 µm]	(%)	30.7	6.2	12.1
pH (water)		6.9	5.4	6.6
Organic Matter (%)		4.3	2.8	3.1
Organic carbon (%) (a)		2.5	1.6	1.8
Cation Exchange Capacity (meq/100 g)		20.6	9.3	18.1

Calculated by dividing organic matter content by 1.72

The tests were performed in flow-through systems consisting of glass flasks each containing 50 g of soil and attached to two successive traps for volatile radioactivity (ethanediol for non-specific volatiles and ethanolamine for carbon dioxide). Soil moisture during incubation was maintained by passing humidified air through the test samples.

Soil samples were extracted twice with aqueous formic acid, Radioactivity was determined by LSC and extracts were analysed by HPLC combined with ^{14}C-radio-detection and identified by comparison with authentic reference material. For determination of phosphonic acid/phosphonates, extracted soil samples were further extracted twice with ammonia buffer and following a derivatisation step (diazomethane) were analysed by gas chromatography (GC). Volatile radioactivity was collected in traps but not investigated further.

Initial extraction efficiency ranged from 98.5–99.5% AR, decreasing to 6.8–10.2% after 1 day and to 1.5–4.2% AR after incubation for 120 days.

Table 37 Degradation of [^{14}C]-fosetyl-Al at 20 °C in four soils under aerobic conditions

Component	% Applied radioactivity												
	Soil	0 hours	0.25 hours	0.5 hours	1 hour	2 hours	4 hours	8 hours	1 day	2 days	7 days	14 days	120 days
Fosetyl-Al	clay loam	28.9	15	10	6.3	2	0.5						
	sand/loamy sand	36.2	9.2	13.2	10.6	11	n.d.						
	sandy loam	39.7	15.4	7	n.d.	n.d.	n.d.						
Ethanol	clay loam	59.4	60.3	57.5	51.3	20.1	1.7						
	sand/loamy sand	54.3	75.8	70.1	68.6	67.7	62.4						
	sandy loam	51.4	65	69.8	69.1	53.6	21.9						
Unknown 2	clay loam	7.1	7.6	7.3	5.1	2.9	1.1						
	sand/loamy sand	8.6	11.7	11.6	12.8	11.5	6.3						
	sandy loam	9.7	17.2	16.1	14.6	15.3	3.3						
Unknown 5	clay loam	n.d.	n.d.	n.d.	n.d.	4.2	7.1						
	sand/loamy sand	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.						
	sandy loam	n.d.	n.d.	n.d.	n.d.	n.d.	6.1						
Total other unknown[a]	clay loam	3.8	4.5	3.5	6.9	7.8	7.6						
	sand/loamy sand	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.						
	sandy loam	n.d.-	n.d.	n.d.	n.d.	n.d.	n.d.						
Total extracted	clay loam	99.2	87.4	78.3	69.7	37.1	17.8	13.9	10.2	10.4	7.5	6.8	4.2
	sand/loamy sand	99.1	96.7	94.8	92	84.7	68.8	50.2	10	11.6	2.7	4	1.5
	sandy loam	100.8	97.6	92.9	83.6	68.9	31.3	12.4	6.8	7.5	4.9	4.6	2.4

n.d. = not detected

[a] Three unknown components, each less than 5% AR

Degradation of fosetyl-Al in soil was rapid, decreasing from 29–40% AR to 0.5% AR or less within 4 hours, with ethanol extracted from soil peaking at 58–76% AR after 15-30 minutes.

A total of five unknown components were observed in soil extracts in the course of incubation. Three components (reported as Unknowns 1, 3 and 4) showed a maximum occurrence below 5% AR for all soils at any sampling interval in the course of the tests.

Unknown 5 was detected in two soils at up to 7.1 and 6.1% AR and Unknown 2 was detected at maximum levels of 13–17% AR after 15-60 minutes, declining to less than 6% AR after 4 hours.

Analysis of extracted soils for phosphonic acid/phosphonates by GC did not result in a clear trend for values determined with time but did demonstrate that the degradation of fosetyl-Al had resulted in the presence of substantial amounts of phosphonic acid/phosphonates.

Degradation rates of fosetyl-Al in aerobic soil were calculated using the Timme-Frehse approach, the software KIM and linear regression analysis. Depending on method of calculation, the DT_{50} values ranged from 1 to 60 minutes.

Table 38 Rate of degradation of fosetyl-Al in three soils under aerobic conditions

	Method	DT_{50}	DT_{90}	Kinetic model
Soil		(minutes)	(minutes)	
Clay loam	TF	29	96	SFO
	KIM	17	104	SFO
	Linear	37	122	SFO
Sand/Sandy loam	TF	21	69	SFO
	KIM	5	369	SFO
	Linear	60	200	SFO
Sandy loam	TF	1	13	SFO
	KIM	11	37	SFO
	Linear	12	40	SFO

TFM: Timme-Frehse approach

KIM: software Kinetic Modelling (Thomae)

Linear: Linear regression analysis

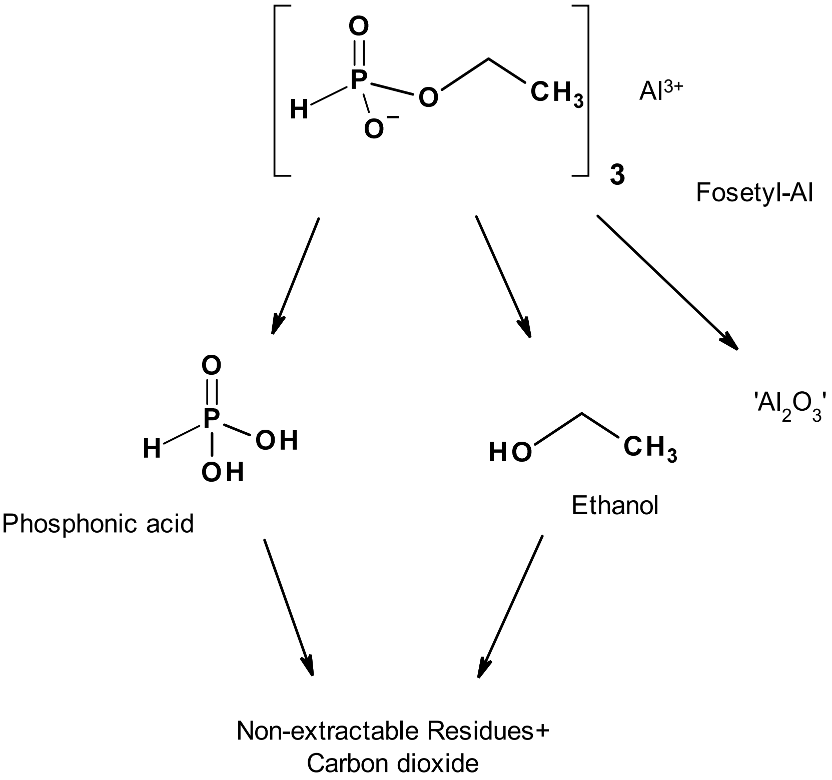


Figure 2 Fosetyl-Al degradation pathway in aerobic soil

Aerobic soil metabolism – phosphonic acid

Study 1

The soil degradation pathway of phosphonic acid was investigated under aerobic conditions of the laboratory in a clay loam by Adams & Conrad, 1953 [Ref: C034353, M-234773-01-1]. Soils were treated with 100 mg disodium phosphonate (pentahydrate)/kg soil (dry weight), and 400 g samples incubated in the dark at 28 °C and soil moisture at field capacity for intervals up to 16 weeks. The influence of toluene (as a fumigating-type agent) on microbial activity in soil was investigated in parallel.

Soil samples (25 g) were extracted by boiling gently with 2 N hydrochloric acid and passed through an ion exchange column. Analysis for phosphonate (phosphite) was performed indirectly by measuring the amount of phosphate in soil extracts prior to and the total phosphate after oxidation of phosphonates by iodine for the same soil sample using a modification of the method of Deniges (i.e. colorimetric method). Oxidation of phosphonates was performed by adding saturated aqueous sodium hydrogen carbonate. Aqueous 0.01 N iodine solution was added, and following acidification (2 N sulphuric acid), the excess of iodine was back-titrated with aqueous sodium thiosulfate (disappearance of brown iodine colour). Residues of phosphonates in soil were reported as phosphorus trioxide (P2O3) equivalents recovered/25 g subsample of soil in order to allow a comparison of the results.

Phosphonic acid residues (expressed as phosphorous trioxide equivalents/25 g soil) decreased from 1.95 mg at week 4 to 0.97 mg at week 16 while phosphate residues (also expressed as phosphorous trioxide equivalents/25 g soil) increased from 9.5 mg at week 4 to 10.4 mg at week 16.

In soils containing toluene, phosphonic acid and phosphate residues both remained constant over the study period suggesting that phosphonate transformation to phosphate in soil was related to microbial activity.

Table 39 Dissipation of disodium phosphonate and determination of phosphate in soil incubated at 28 °C under aerobic conditions

Treatment	Component	Residues (P2O3 equivalents/25 g soil)			
		4 weeks	8 weeks	12 weeks	16 weeks
Na_2HPO_3	Phosphonate	1.95	1.51	1.15	0.97
Na_2HPO_3	Phosphate	9.5	9.8	10.2	10.4
Na_2HPO_3 / toluene	Phosphonate	1.95	2.04	1.95	1.95
Na_2HPO_3 / toluene	Phosphate	9.3	9.2	9.4	9.4

Values given as mg ‘phosphorus trioxide’ (P_2O_3) eq/25 g subsample of soil treated with 2.04 mg Na_2HPO_3 (nominal)

Results are mean values from four 25 g subsamples

Study 2

The degradation of phosphonic acid in two UK soils was reported by Lowden & Oddy, 1999 [Ref: R011658, M-184316-01-1]. Aqueous solutions of [^{33}P]-phosphonic acid were applied drop-wise onto the soil surface to achieve a treatment rate of 15 mg/kg dry weight of soil. Soil samples were incubated at 20 °C under aerobic conditions in the dark for intervals up to 117 days.

Table 40 Characteristics of the soils used in the aerobic soil metabolism study

Parameter			
Soil Designation		Loam	Sandy loam
Sand [63 – 2000 μm]	(%)	24	57
Silt [2 – 63 μm]	(%)	52	36
Clay [< 2 μm]	(%)	24	7
pH (water)		7.3	6.0
Organic Matter (%)		3.6	2.2
Organic carbon (%)[a]		2.1	1.3
Cation Exchange Capacity (meq/100 g)		13.8	4.4
Biomass, initial (μg C /g soil)		566	377
Biomass, study end (μg C /g soil)		199	201

[a] Calculated by dividing organic matter content by 1.72

Soil samples were extracted four times with aqueous ammonia buffer (pH 9.3) with the day zero samples also being extracted with aqueous tartaric acid solution (pH 1.9). Radioactivity was determined by LSC and extracts were analysed by HPLC combined with ^{14}C-radio-detection and identified by comparison with authentic reference material.

Mean material balances (after correction for isotope half-life of 25.34 days) ranged from 91–107% AR except in the day 3 samples where material balances were 87–88% AR.

Total extracted radioactivity decreased from 62–77% AR to 31–47% AR after incubation for 117 days with unextracted residues increasing from 19–34% AR to 49–68% AR at the end of the study period and extracted radioactivity attributed to phosphonic acid decreased from 62–77% AR to 26–31% AR after 117 days incubation.

Table 41 Degradation of [^{33}P]-phosphonic acid at 20 °C in two soils under aerobic conditions

Component	% Applied radioactivity							
	Soil	0 days	3 days	7 days	14 days	28 days	56 days	87 days	117 days
Phosphonic acid	loam	62.1	39.4	26.5	35.3	41.3	40.6	28.8	25.7
	sandy loam	77.2	55.4	55.9	54.8	55.1	54.1	37.9	30.9

Component	% Applied radioactivity								
	Soil	0 days	3 days	7 days	14 days	28 days	56 days	87 days	117 days
Unknowns[a]	loam sandy loam							4.2 12.1	5.5 15.7
Total extracted	loam sandy loam	62.1 77.2	39.4 55.5	26.5 56	35.3 54.8	41.3 55.1	40.6 54.1	33.1 49.8	31.3 46.6
Unextracted	loam sandy loam	34.4 19.3	47.6 33.1	64.3 38.6	62.9 41.7	56.6 42.9	56 38.5	74.2 44.8	68.5 49.4
Total radioactivity	loam sandy loam	96.5 96.4	86.9 88.4	90.8 94.8	98.2 96.4	97.8 98	96.6 92.6	107.2 94.6	99.8 96

Values given as percentage of total applied radioactivity, corrected for isotope half-life of 25.34 days

[a] Sum of up to 8 unknown components/regions with relative retention times of 0.45, 0.5, 0.64, 0.74, 0.87, 1.45, 1.75, 1.96, each less than 10% AR

Degradation rates of phosphonic acid in aerobic soil were calculated using the Timme-Frehse approach, the software KIM and linear regression analysis. Because of the initial rapid decline of phosphonic acid and the slower decline at later sampling intervals, calculated half-lives ranged from 109 to 137 days when calculations were based on the data from the late sampling intervals.

Table 42 Rate of degradation of phosphonic acid in two soils under aerobic conditions

Soil	Approach	DT_{50} (days)	Quality of fit[a]	Kinetic model
UK clay loam	Excel/all sampling intervals	120.9	0.327	SFO
	KIM/all sampling intervals	8.7	0.906	SFO
	Timme Frehse/all sampling intervals	89.2	0.388	SFO
	Excel/late sampling intervals	116.8	0.906	SFO
	KIM/late sampling intervals	108.5	0.996	SFO
	Timme Frehse/ late sampling intervals	116.8	0.880	SFO
US sandy loam	Excel/all sampling intervals	102.8	0.730	SFO
	KIM/all sampling intervals	70.6	0.960	SFO
	Timme Frehse/all sampling intervals	37.4	0.759	SFO
	Excel/late sampling intervals	136.5	0.864	SFO
	KIM/late sampling intervals	133.3	0.985	SFO
	Timme Frehse/late sampling intervals	124.7	0.617	SFO

[a] r squared for Excel, 'modified r squared' for Timme-Frehse and 'fit criterion' (modification of r squared) for KIM (kinetic modelling).

Study 3

The degradation rate of phosphonic acid was investigated in four European soils under aerobic conditions at 20 °C and moisture of 50% of the maximum water holding capacity in the dark (Voelkel, 2015 [Ref: 20140225, M-53231-01-1].

Soil samples (100 g dry weight) were treated with 1.5 mg phosphonic acid/kg soil (equivalent to a field rate of 11.25 kg ai/ha. Following application, the samples were attached to ‘flow through’ systems and incubated at 20 °C and a moisture content of 50% of MWHC in the dark for intervals up to 117 days.

Duplicate samples were extracted four times successively with aqueous ammonium hydrogen carbonate (pH 9.2), concentrated to dryness, re-constituted in 0.1 M aqueous tartaric acid solution (pH 2) and analysed for phosphonic acid by HPLC-MS/MS.

Table 43 Characteristics of the soils used in the aerobic soil degradation study

	Soil			
Soil description	Hoefchen Am Hohenseh 4a	Dollendorf II	Wurmwiese	Laacher Hof AXXa
Textural class[a]	silt loam	clay loam	sandy loam	sandy loam
Sand (%)	25	29	53	77

	Soil			
Soil description	Hoefchen Am Hohenseh 4a	Dollendorf II	Wurmwiese	Laacher Hof AXXa
Silt (%)	61	39	31	15
Clay (%)	14	32	16	8
pH (water)	6.4	7.3	5.3	6.5
Organic matter [%][b]	2.8	7.4	2.8	2.1
Organic carbon [%]	1.6	4.3	1.6	1.2
Microbial biomass (mg C / 100 g soil)				
DAT-0	450	1250	537	382
DAT-117	497	892	436	405
Cation exchange capacity (meq/100 g)	10.3	17.5	9.1	7.1

[a] USDA classification

[b] % organic matter = % organic carbon × 1.724

Mean values of recoveries of phosphonic acid in soil extracts at day zero ranged from 94–99% of the applied doses in three of the soil types but were 64% of the applied dose in the clay loam soil (attributed to the higher calcareous content and the potential for phosphonic acid to form, in contact with soil, insoluble residues spontaneously). Concurrent recoveries from fresh spiked soil samples ranged from 79% to 102%.

Phosphonic acid residues declined to 50% (silt loam), 7.2% (clay loam), 66% (sandy loam) and 2% (sandy loam–Laacher Hof AXXa) of the applied doses after 117 days of incubation.

Table 44 Degradation of phosphonic acid in four European soils under aerobic conditions

Soil type		Phosphonic acid residues (% of the applied dose)							
		0 days	3 days	7 days	14 days	30 days	61 days	90 days	117 days
Hoefchen am Hohenseh 4a	silt loam	99.4	100.9	93.9	82.6	79.7	66.2	58.0	49.6
Dollendorf II	clay loam	63.5	56.0	48.5	40.4	32.1	23.4	13.3	7.2
Wurmwiese	sandy loam	96.0	84.3	90.0	79.4	73.9	64.0	67.3	66.4
Laacher Hof AXXa	sandy loam	93.6	81.1	86.6	82.2	48.7	13.8	3.3	2.0

Residues of phosphonic acid in aerobic soil were found to degrade with SFO fit half-lives ranging from 27.5 to 219 days under the conditions of the laboratory. The corresponding DT_{90}-values ranged from 91.4 to 726 days.

Table 45 Half-lives and DT_{90}-values of phosphonic acid in aerobic soil according to SFO kinetics

Soil	Kinetic Model	DT_{50} (days)	DT_{90} (days)	Chi² error (%)	r^2
Hoefchen (silt loam)	SFO	114	380	3.34	0.9497
Dollendorf II (clay loam)	SFO	38.9	129	7.17	0.9628
Wurmwiese (sandy loam)	SFO	219	726	5.75	0.7240
Laacher Hof AXXa (sandy loam)	SFO	27.5	91.4	11.3	0.9551

Published information suggests that there is some oxidation of phosphonate into phosphate through biologically induced process by soil microbes.

Rotational crop studies

Fosetyl-aluminium (fosetyl-Al) degrades very rapidly in soil with a half-life of ≤ 1 day, with the only relevant metabolite in soil being phosphonic acid. Due to the difficulties in radio-labelling of this metabolite and the short nuclear half-lives of suitable radiolabelled P (^{32}P: $t_{1/2}$ = 14.3 days; ^{33}P: $t_{1/2}$ = 25.3 days) no confined rotational crop studies were conducted.

The Meeting received information on the metabolism of fosetyl and phosphonic acid in a range of representative field crops grown in treated soil.

Field rotational crop studies – fosetyl

In four field trials conducted in Europe and reported by Melrose & Portet, 2009, 2010 [Refs: 08-2504 (M-349882-02-1); 08-2505 (M-349137-02-1); 08-2506 (M-361470-01-1) and 08-2507 (M-349147-02-1)], lettuce plants were treated with three foliar sprays of 0.71–0.775 kg ai fosetyl/ha (SL formulation) at 7–13 day intervals, a total of 2.26–2.33 kg ai/ha. The lettuce plants were harvested 7 days after the last application and lettuce, carrots and winter wheat or barley crops were planted as follow-crops 26–46 days later and sampled at maturity.

Samples were stored frozen for up to 444 days before analysis. Freezer storage stability studies indicate that the fosetyl-Al residues are not stable in high water content commodities after frozen storage above 12 months and not stable in high starch content after frozen storage for 5 months. Therefore the results for fosetyl in the rotational crop studies cannot be considered accurate. However the total residues which take into account the degradation of fosetyl to phosphonic acid during sample storage have been shown to be stable for at least 24 and 25 months in high water content and high starch content commodities, respectively.

Residues of fosetyl and phosphonic acid were measured using the LC-MS/MS method 00861/M001. Overall mean recovery values for fosetyl in all matrices ranged from 75–104% in samples spiked with 0.01–0.5 mg/kg. Except for carrot leafs, the overall mean recovery rates for phosphonic acid ranged from 70–104% in samples spiked with 0.1–5 mg/kg. In carrot leafs, overall mean recovery rates for phosphonic acid were 57, 64, 78 and 157%. The LOQs for fosetyl were 0.0093 mg/kg (0.047 mg/kg in wheat/barley forage and straw) and for phosphonic acid, were 0.1 mg/kg (0.5 mg/kg in wheat/barley forage and straw).

Fosetyl residues were < 0.0093 mg/kg in lettuce (head), carrots (root and leaf) and cereal (grain) and < 0.047 mg/kg in wheat/barley forage and straw. Residues of phosphonic acid were < 0.5 mg/kg in wheat forage and straw and were < 0.1 mg/kg in lettuce (head), carrots (root and leaf) and cereal grain (except at one site where residues of 0.21 mg/kg phosphonic acid were reported in the grain sample.

Table 46 Residues of fosetyl (expressed as fosetyl-Al) and phosphonic acid in carrots, lettuce and cereals grown as rotational crops in Europe following 3 applications of 0.71–0.775 kg ai fosetyl/ha to lettuce (total 2.3 kg ai/ha)

Crop commodity	PBI (days)	DALT	Residue	Individual results from 4 sites (mg/kg)	Average (mg/kg)
Carrot, root	27–38	103–212	Fosetyl	< 0.0093, < 0.0093, < 0.0093, < 0.0093	< 0.0093
			Phosphonic acid	< 0.10, < 0.10, < 0.10, < 0.10	< 0.1
			Total residue (as phosphonic acid)	< 0.11, < 0.11, < 0.11, < 0.11	< 0.11
Carrot, leaf	27–38	103–212	Fosetyl	< 0.0093, < 0.0093, < 0.0093, < 0.0093	< 0.0093
			Phosphonic acid	< 0.10, < 0.10, < 0.10, < 0.10	< 0.1
			Total residue (as phosphonic acid)	< 0.11, < 0.11, < 0.11, < 0.11	< 0.11
Lettuce head	26–46	54–141	Fosetyl	< 0.0093, < 0.0093, < 0.0093, < 0.0093	< 0.0093
			Phosphonic acid	< 0.10, < 0.10, < 0.10, < 0.10	< 0.1
			Total residue (as phosphonic acid)	< 0.11, < 0.11, < 0.11, < 0.11	< 0.11
Wheat/barley (grain)	30–38	106–309	Fosetyl	< 0.0093, < 0.0093, < 0.0093, < 0.0093	< 0.0093
			Phosphonic acid	< 0.10, < 0.10, **0.21**, < 0.10	0.1
			Total residue (as phosphonic acid)	< 0.11, < 0.11, **0.22**, < 0.11	0.11
Wheat/barley (forage)	30–38	106–309	Fosetyl	< 0.047, < 0.047, < 0.047, < 0.047	< 0.047
			Phosphonic acid	< 0.50, < 0.50, < 0.50, < 0.50	< 0.5
			Total residue (as phosphonic acid)	< 0.54, < 0.54, < 0.54, < 0.54	< 0.54
Wheat/barley (straw)	30–38	106–309	Fosetyl	< 0.047, < 0.047, < 0.047, < 0.047	< 0.047
			Phosphonic acid	< 0.50, < 0.50, < 0.50, < 0.50	< 0.5
			Total residue (as phosphonic acid)	< 0.54, < 0.54, < 0.54, < 0.54	< 0.54

DALT: Days after last treatment

PBI: Interval between the last application on the primary crop (lettuce) and the sowing/planting of the secondary crop (carrot/lettuce/winter barley)

Field rotational crop studies – Phosphonic acid

In a rotational crop study reported by Diot et al., 2001 [Ref: C012853; M-203498-01-1], a root crop (radish), a leafy crop (lettuce) and a cereal/grain crop (barley) were grown in soil treated with phosphonic acid at a target concentration of 4.9 mg/kg (equivalent to the concentration in a 15 cm soil layer resulting from the application of 10 kg ai phosphonic acid/ha).

A loamy sand soil (pH 6.5, organic matter 1.9%) was sprayed with phosphonic acid/potassium hydroxide, mixed and distributed in 20-cm pots. The potted soils were aged outdoors (sheltered from rain) for 32 days before being planted with barley and radish seeds and lettuce seedlings, with a further sowing of radish in pots aged for 182 days. The pots were maintained under a plastic tunnel (or in a greenhouse for barley towards the end of the growth period).

Samples of mature plants were analysed for phosphonic acid using the GC-FPD method AR 154–97 (LOQ of 0.5 mg/kg) with average recovery rates of 64% (radish leaves), 93% (radish roots), 91% (lettuce leaves), 93% (barley grain) and 71% (barley straw) in samples fortified with 0.1–2.0 mg/kg phosphonic acid.

Soil samples taken immediately after treatment and when the crops were planted and harvested were analysed for phosphonic acid using the GC-FPD method AR 214-99 (LOQs of 0.1–0.2 mg/kg), with an average recovery rate of 102% in samples fortified with 0.1–4.0 mg/kg phosphonic acid.

In the soil, no appreciable decline of phosphonic acid was observed during the 32-day ageing period but significant degradation (or irreversible binding) was observed afterwards, with depletion occurring faster in cropped soil, possibly a result of increased microbial activity.

In radish (roots and leaves) and in lettuce (leaves) sown/planted one month after treatment, residues of up to 1.0 mg/kg phosphonic acid were observed, while in barley (grain and straw) sown one month after treatment, and for radish (roots and leaves) sown 6 months after treatment of the soil, noting the relatively high LOQ of 0.5 mg/kg, differences between treated and untreated samples were not significant, all below the LOQ.

Table 47 Phosphonic acid residues in soil treated with the equivalent of 10 kg ai phosphonic acid/ha and in radish, lettuce and barley grown as rotational crops

Crop commodity	PBI (days)	Harvest (days after planting)	DALT	Phosphonic acid ((mg/kg)	
				Individual values	Mean
Radish, roots	32	40	69	0.58, 1.1, 0.69, 0.8 c=0.1	0.8 c=0.1
	182	40	222	< 0.10(0.04), < 0.10(0.02) c= n.a.	< 0.10(0.03) c= n.a.
Radish, leaves	32	40	69	0.45, 0.3, 0.34, 0.31 c=< 0.10(0.04)	0.35 c=< 0.10(0.04)
	182	40	222	0.13, < 0.10(0.05) c=n.a.	< 0.10(0.09) c=n.a.
Lettuce, leaves	32	37	69	0.67, 0.92, 1.0, 0.45 c=< 0.10(0.04)	0.76 c=< 0.10(0.04)
Barley, grain	32	150	182	0.11, 0.24, 0.1, 0.12 c=0.10	0.14 c=0.10
Barley, straw	32	150	182	0.80, 0.48, < 0.25(0.18), < 0.25(0.23) c=< 0.25(0.19)	0.42 c=< 0.25(0.19)
Bare soil					
At treatment			0	3.4, 3.7,	3.5
At sowing			32	3.7, 4.1	3.9

Crop commodity	PBI (days)	Harvest (days after planting)	DALT	Phosphonic acid ((mg/kg)	
				Individual values	Mean
At harvest (radish, lettuce)			69	1.89, 0.62	1.25
At harvest (barley)			182	0.13, < 0.01	< 0.01
Cropped soil					
Radish soil			69	0.12, 0.1, < 0.01, < 0.01, < 0.01	< 0.01
Lettuce soil			69	0.34, 0.18, 0.6, 0.27	0.35
Barley soil			189	< 0.01, < 0.01, < 0.01, < 0.01	< 0.01

PBI = plant back interval (interval between soil treatment and sowing/planting of the succeeding crop)

n.a. : not available

c: control sample

Values in brackets are estimated (below LOQ).

Animal metabolism

The Meeting received animal metabolism studies on rats and lactating goats where animals were dosed with fosetyl-Al radiolabelled in the 1-C position.

Fosetyl-aluminium

Rats

The metabolism of fosetyl-Al in rats was reviewed in the framework of the toxicological evaluation by the WHO Core Assessment Group of the 2017 JMPR.

Following oral administration, ^{14}C-fosetyl-Al was almost completely absorbed and almost completely eliminated in exhaled air, urine, and faeces within 24 hours. Fosetyl-Al undergoes extensive hydrolysis in vivo to give ethanol and phosphonate. The phosphonate is excreted predominately in the urine (equivalent to 73% of the administered compound) together with unchanged material (26–28% of the administered compound).

Lactating goats

Study 1

In a study reported by Predmore & Stumpner, 1987 [Ref: R001413; M-160479-01-1], two lactating goats (#29 and #31) were dosed orally by capsule for 7 consecutive days with ^{14}C-fosetyl-Al at doses equivalent to 10.5 ppm in the diet (21 mg/goat/day based on an average feed consumption of 2 kg/day and body weights of 49–50 kg). In a separate experiment an additional goat (#30) was also dosed for three days with 10.5 ppm in the diet and used in the CO_2 trapping chamber.

The goats were milked twice daily and urine and faeces from each goat were also collected each morning. In the CO_2 trapping experiment, expired CO_2 was drawn through a valve in a plexiglass chamber fitted over the head and neck of the goat and the upper corner and passed through an aqueous 2.5N potassium hydroxide trapping solution. All goats were sacrificed 24 hours after the 7th daily dose and various tissue samples were taken for analysis (blood (heparinized), fat, muscle, kidney, liver, heart and gall bladder contents).

Individual muscle, fat, kidney, liver and heart samples were homogenised and radioassayed by liquid scintillation counting (LSC) with quench control. Liquid samples (urine and homogenised milk) were directly measured after addition to a scintillation cocktail. Faeces and tissue samples were combusted in a sample oxidizer. Trapping solutions for exhaled CO_2 were mixed with water and scintillation cocktail before LSC analysis. Average LOQs for the different sample types were 0.0014 mg ai eq/kg in milk and 0.0026 to 0.0032 mg ai eq/kg in all tissues.

The majority of the dose was excreted with urine (12 and 14% of the total dose) and faeces (5.4 and 4.8% of the total dose). In expired air,$^{14}CO_2$ was not detected within the first 30 minutes but increased over the 3-day study period to 24% of the daily dose and in total, made up 17.5% of the administered dose.

In milk, residues reached a plateau after 3 days and in total made up 17% of the administered radioactivity.

Table 48 Radioactive residues (mg ai eq/kg) in milk of goats following daily dosing of ^{14}C-fosetyl-Al

Day of collection	Goat #29 7 daily doses of 10.5 ppm	Goat #31 7 daily doses of 10.5 ppm	Goat #30 3 daily doses of 10.5 ppm
-1	-	-	-
1	0.39	0.25	
2	2.2	1.4	
3	2.2	1.6	
4	2.2	1.6	
5	2.2	1.6	
6	2.2	1.6	
7	2.2	1.7	
13[a]			0.44
14[a]			1.4
15[a]			1.7

Values are means of duplicate analyses

[a] mean residues for Day 1 to 3 of a separate goat for determination of exhaled $^{14}CO_2$

In tissues, less than 1.0% of the administered dose was found in liver and kidney, up to 2.2% AD in fat and up to 1% AD in muscle. Highest concentrations of radioactive residues were in liver (0.49–0.57 mg ai eq/kg), kidney (0.28–0.32 mg ai eq/kg), heart (0.2–0.23 mg ai eq/kg) and muscle (0.11–0.15 mg ai eq/kg). Radioactive residues in fat were 0.086–0.096 mg ai eq/kg in one animal and 0.24–0.61 mg ai eq/kg in the second goat.

Table 49 Radioactive residues in tissues of lactating goats following 7 consecutive daily doses of 10.5 ppm ^{14}C-fosetyl-Al in the diet

Matrix	Goat #29 7 daily doses of 10.5 ppm	Goat #31 7 daily doses of 10.5 ppm
	[mg ai eq/kg]	[mg ai eq/kg]
Muscle		
Triceps	0.13	0.14
Semimembranosus	0.11	0.11
Longissimus dorsi	0.11	0.15
Fat		
Perirenal	0.086	0.61
Omental	0.096	0.24
Kidney	0.28	0.32
Heart	0.20	0.23
Liver	0.49	0.57
Gall bladder contents	0.52	0.30
Blood	0.11	0.12

Results are mean values of duplicate analyses

Total administered dose was 147 mg ^{14}C-fosetyl-Al/animal

Table 50 Radioactive residues in expired air ($^{14}CO_2$) from goats following 3 consecutive daily doses of 10.5 ppm ^{14}C-fosetyl-Al in the diet (daily dose of 21 mg ai/animal)

Hours after administration	Collection Day 1		Collection Day 2		Collection Day 3	
	mg ai equiv.	% daily dose	mg ai equiv.	% daily dose	mg ai equiv.	% daily dose
0.0	-	-	-	-	-	-
0.5	-	-	0.00868	0.0413	0.0110	0.0524
1.0	0.0150	0.0714	0.0245	0.117	0.0386	0.184

Hours after administration	Collection Day 1		Collection Day 2		Collection Day 3	
	mg ai equiv.	% daily dose	mg ai equiv.	% daily dose	mg ai equiv.	% daily dose
2.0	0.183	0.871	0.122	0.581	0.210	1.00
4.0	0.486	2.31	0.598	2.85	1.04	4.95
8.0	1.28	6.10	1.78	8.48	2.96	14.1
12.0	1.96	9.33	2.43	11.6	3.54	16.9
16.0	2.30	11.0	2.86	13.6	4.27	20.3
24.0	2.53	12.0	3.42	16.3	5.05	24.0

Table 51 Distribution of radioactive residues following 7 consecutive daily doses of 10.5 ppm ^{14}C-fosetyl-Al in the diet (Total administered dose of 140 mg ai/animal)

Matrix	Goat #29	Goat #31	Goat #30
	% of total administered dose		
Milk	17	11	5.0
Excreta			
Urine	12	14	10
Faeces	5.4	4.8	8.4
CO_2 (AD = 63 mg ai)			17
Tissues			
Fat	<1.0	2.2	-
Muscle	<1.0	1.0	-
Liver	<1.0	<1.0	-
Kidney	<1.0	<1.0	-
Heart	<1.0	<1.0	-
Gall bladder contents	<1.0	<1.0	-
Blood	<1.0	<1.0	-

Residues in milk were characterised in a supplementary study reported by Shaffer, 1987 [Ref: R003992; M-165774-01-1], where duplicate milk samples (containing 2.2 mg ai eq/kg fosetyl-Al) were taken from goat #29 on day 7, mixed with methanol to precipitate casein (milk proteins) and the methanolic suspensions containing precipitated casein were extracted with petroleum ether and separated in three fractions: 1) petroleum ether, 2) aqueous and 3) protein.

Radioactive residues in the petroleum ether fraction were 82% TRR with 10% TRR in the aqueous fraction and 9.3% in the protein fraction, and chromatographic analysis, although limited, was sufficient to conclude that the radioactivity in the milk does not represent the parent fosetyl-Al.

Study 2

A supplementary study to further investigate metabolic fate of ^{14}C-fosetyl-Al in lactating goats following oral administration, especially the formation of exhaled $^{14}CO_2$ was reported by Stumpner & Predmore, 1987 [Ref: R003993; M-160479-01-1].

One lactating goat was dosed orally by capsule for 7 consecutive days with ^{14}C-fosetyl-Al at rate equivalent to 10 ppm in the diet (20 mg/goat/day, equivalent to 0.513 mg ai/kg bw/day based on an average feed consumption of 2 kg/day and a body weight of 39 kg).

The goat was milked twice daily and urine and faeces from each goat were also collected each morning. Respired air was collected by using a mask which covered the goat's mouth and nostrils, with three minute collections taken every 30 minutes for the first 8 hours after dosing, then at 9, 10, 11, 12, 16 and 24 hours after dosing. Expired CO_2 was trapped in a 2 N potassium hydroxide trapping solution.

Milk and excreta samples were radioassayed by liquid scintillation counting (LSC) with quench control. Liquid samples (urine and homogenised milk) were directly measured after addition to a scintillation cocktail. Trapping solutions for exhaled CO_2 were mixed with water and scintillation cocktail before LSC analysis. Average LOQs for the different sample types were 0.0018 mg ai eq/kg in milk and 0.0024 mg ai eq/kg in urine, 0.0036 mg ai eq/kg in faeces and 0.0025–0.0043 mg ai eq/kg in CO_2 trapping solutions.

Table 52 Distribution of radioactive residues following 7 consecutive daily doses of 10 ppm ^{14}C-fosetyl-Al in the diet (0.513 mg/kg bw/day)

Matrix	% of administered dose (140 mg ^{14}C-fosetyl-Al)
Milk	2.06
Excreta	
Urine	7.09
Faeces	71.3
Air	5.71
Total	86.2

In milk, there was a gradual increase in residue levels, reaching a plateau after 3 days (0.27–0.3 mg ai eq/kg) with total residues making up about 2% of the administered dose.

Exhaled $^{14}CO_2$ was not detected during the first 30 minutes of the study, but were measured at all other sampling times, reaching a maximum between 1.5 and 2 hours after each dosing (mean values over all 7 days) and slowly declined to near background by 24 hours after each dosing. Over the 7-day study period, $^{14}CO_2$ residues peaked on Day 4, with total residues being about 5.7% of the administered dose.

Table 53 Radioactive residues (mg ai eq/kg) in milk of a goat following daily dosing of ^{14}C-fosetyl-Al at 10 ppm in the diet for 7 consecutive days (0.513 mg ai/kg bw/day)

Day of collection	mg ai eq/kg
-1	< 0.0018
1	0.1050
2	0.2447
3	0.2546
4	0.2703
5	0.2485
6	0.2688
7	0.3009

Results are mean values of duplicate analyses

Total administered dose was 140 mg ^{14}C-fosetyl-Al/animal

Table 54 Radioactive residues recovered in expired air of a goat—measured in 30 minutes increments—following daily dosing of ^{14}C-fosetyl-Al at a level 10 ppm in the diet for 7 consecutive days (0.513 mg/kg bw/day)

Time period after administration (hours)	$^{14}CO_2$ residues (μg ai eq)[a]
24.0-0.5[b]	35.12
0.5-1.0	71.95
1.0-1.5	99.13
1.5-2.0	109.1
2.0-2.5	97.94
2.5-3.0	76.95
3.0-3.5	69.41
3.5-4.0	55.00
4.0-4.5	48.48
4.5-5.0	43.14
5.0-5.5	34.14
5.5-6.0	27.14
6.0-6.5	28.82
6.5-7.0	26.08
7.0-7.5	23.14
7.5-8.0	23.89
8.0-9.0	45.97

Time period after administration (hours)	$^{14}CO_2$ residues (µg ai eq)[a]
9.0-10.0	33.79
10.0-11.0	26.32
11.0-12.0	20.24
12.0-16.0	59.40
16.0-24.0	73.84
Total to 9 hours	915.4
Total for 24 hours period	1129.0

[a] Means of all seven days (exception 24.0-0.5 and 0.5 to 1.0 hours: mean of 6 days only)

[b] 24 sample for the previous day, for day 1 it would be 0.0

Table 55 Daily amounts of radioactive residues recovered in expired air of a goat following daily dosing of ^{14}C-fosetyl-Al at a level 10 ppm in the diet for 7 consecutive days (0.513 mg/kg bw/day)

Study day	mg ai equivalent.
1	0.8035
2	0.9857
3	1.346
4	1.860
5	1.252
6	1.013
7	0.7372
Total	7.997 (5.71% Administered dose)

Study 3

In a further study reported by Norris et al, 1992 [Ref: C012432; M-202696-01-1], two lactating goats (#10 and #13) were dosed orally by capsule, morning and evening for 7 consecutive days with ^{14}C-fosetyl-Al at doses equivalent to 27.8 ppm and 30 ppm in the diet (1.46–1.5 mg/kg bw/day based on an average feed consumptions of 2.63 and 2.43 kg/day and body weights of 48.5–50 kg). After the first dose on the sixth day, each goat was placed in a respiration chamber for 10 hours to monitor for expired $^{14}CO_2$.

The goats were milked twice daily and urine and faeces from each goat were also collected each evening and in the morning before slaughter. Exhaled $^{14}CO_2$ was collected in a trapping solution. The total radioactive volatiles ($^{14}CO_2$) expired during the whole treatment period were calculated based on the dpm/hour values and the length of the total treatment period (approx. 171 hours). All goats were sacrificed 14–16 hours after the 7th daily dose and various tissue samples were taken for analysis. All samples were frozen immediately after slaughter and stored at about -20 °C for 8 days before extraction and analysis.

Tissue samples (liver, kidney, muscle) were homogenized and extracted initially with HCl/acetonitrile and partitioning three times into chloroform. The remainder and the supernatant layers were centrifuged and the supernatants were taken and diluted in HCl/acetonitrile (1/1). The chloroform extracts from liver and kidney were partitioned between acetonitrile and hexane. Glycogen was extracted from liver by mixing with 10% NaOH and precipitated by adding ethanol to the supernatant. Fat was extracted three times with hexane. Milk and blood were extracted twice with acetonitrile and centrifuged to separate the lipids and proteins. The combined supernatant and the remaining pellet were extracted separately with hexane to extract the lipids.

All samples were radioassayed by liquid scintillation counting (LSC) with automatic quench control. Volatiles collection solutions were radioassayed directly and faeces, tissue samples, gut contents and fat were combusted in a sample oxidizer. The trapped $^{14}CO_2$ was quantitated by LSC.

Sample extracts were analysed by HPLC/UV (254 nm) using different separation systems to analyse ethanol, fosetyl-Al, sugars, amino acids and other fractions. Thin layer chromatography was used to analyse fatty acids, esters and triglycerides and ion-exchange chromatography was used to fractionate aqueous samples into neutrals, acids, weak bases, ampholytes and bases. GC-FPD analysis was used for analysis of the parent substance fosetyl-Al (after methylation with diazomethane**)**.

The majority of the administered dose was excreted with urine (10.4–12.4%) and faeces (5.5–8.4%). In milk, there was a gradual increase of the radioactivity levels, reaching a plateau after 3 days, with total residues making up about 14–16% of the total administered dose. In tissues and gut contents, radioactive residues were <5% of the administered dose, measured in liver at about 2.4 mg ai eq/kg and in kidney at 1.0–1.43 mg ai eq/kg. In fat radioactive residues were 0.76–1.47 mg ai eq/kg and in muscle were 0.45-0.53 mg ai eq/kg. The total recovery of radioactive residues in expired air (CO_2) during a 10-hour collection starting just after the morning dose on the 6th day resulted in a calculated percent of total dose of 15.0% (goat #10) and 14.1% (goat #13).

Table 56 Radioactive residues in milk of goats following daily dosing of ^{14}C-fosetyl-Al in the diet for 7 consecutive days (1.46 to 1.50 mg/kg bw/day)

Day of collection (a.m./p.m.)	Goat #10 (27.8 ppm ^{14}C-fosetyl-Al)		Goat #13 (30 ppm ^{14}C-fosetyl-Al)	
	mg ai eq/kg	% admin. dose	mg ai eq/kg	% admin. dose
1 (p.m.)	1.67	0.62	1.10	0.27
2 (a.m.)	2.58	0.96	3.99	0.98
2 (p.m.)	2.98	1.07	4.28	1.02
3 (a.m.)	3.97	1.52	4.73	1.15
3 (p.m.)	3.52	1.28	4.77	1.10
4 (a.m.)	2.93	0.93	3.97	0.97
4 (p.m.)	3.24	1.03	4.16	0.94
5 (a.m.)	3.62	1.34	4.78	1.12
5 (p.m.)	4.12	1.37	5.36	1.04
6 (a.m.)	3.53	1.32	4.61	0.99
6 (p.m.)	3.73	1.29	5.43	1.07
7 (a.m.)	3.44	1.12	4.96	1.23
7 (p.m.)	3.73	1.28	5.37	1.11
8 (a.m.)	3.29	1.22	5.25	1.04
Total		16.3		14.0

Table 57 Distribution of radioactive residues after administration of ^{14}C-fosetyl-Al following daily dosing of ^{14}C-fosetyl-Al for 7 consecutive days

Matrix	Goat #10 (27.8 ppm ^{14}C-fosetyl-Al)		Goat #13 (30 ppm ^{14}C-fosetyl-Al)	
	mg ai eq/kg	% admin. dose	mg ai eq/kg	% admin. dose
Excreta				
Urine		10.4		12.4
Faeces		8.41		5.54
Milk		16.3		14.0
CO_2		15.0[a]		14.1[a]
Tissues				
Fat	1.47	0.37[b]	0.76	0.18[b]
Muscle	0.45	1.79[b]	0.53	2.02[b]
Liver	2.38	0.45	2.37	0.37
Kidney	1.04	0.03	1.43	0.05
Blood	0.35	0.28[b]	0.35	0.27[b]
Stomach contents	0.55	0.93	0.61	0.59
Small Intestine (contents)	1.06	0.22	1.22	0.20
Large Intestine	3.06	0.84	3.48	0.97
Total tissues		4.91		4.65
Total		55.0		50.7

[a] Recalculated from the 10-hour CO_2 collection period (CO_2/hour) and adjusted to the total dosing period

[b] For tissues not collected completely, body weight percentages used were: blood 8%, muscle 40%, and fat 2.5%

Total administered dose: 510.3 mg ^{14}C-fosetyl-Al

The radioactivity released from liver was assigned to ^{14}C-glucose and ^{14}C-glycogen, ^{14}C-amino acids and saponifiable fatty acids (e.g. ^{14}C-oleic and ^{14}C-palmitic acid) and lipids. Radioactivity in kidney was assigned to saponifiable fatty acids and lipids.

Radioactivity in muscle was assigned to the ampholyte fraction (representing amino acids) with minor fractions being "neutral" (representing carbohydrates) and "weak bases" (representing urea).

The majority of radioactivity in milk was assigned to saponifiable fatty acids (e.g. ^{14}C-palmitic acid 26.0% of TRR and ^{14}C-myristic acid 16.2% of TRR) and lipids as well as ^{14}C-lactose (10.6% of TRR) and amino acids, small peptides and urea. The radioactivity in fat was assigned predominantly to saponifiable fatty acids and lipids.

^{14}C-fosetyl-Al residues and ^{14}C-ethanol were found in the urine and stomach contents only. In milk and edible tissues all ^{14}C-residues were characterised as natural products (carbohydrates and carboxylic acids, glycogen, saponifiable fatty acids and lipids, as well as amino acids and peptides).

Table 58 Extraction profiles of radioactive residues in liver, kidney and muscle

Fraction	Liver		Kidney		Muscle		Fat		Milk	
	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg	% TRR	mg ai eq/kg
Chloroform	23.5	0.56	13.9	0.17	7.4	0.04				
Hexane	14.8	0.35	10.9	0.14	-	-	85.3	0.95	67.2	
Acetonitrile	8.2	0.19	3.0	0.04	-	-			10.6	
Aqueous extract	25.3	0.60	26.5	0.33	18.1	0.09				
Neutrals					3.1	0.02				
Acids					1.9	0.01				
Weak bases					3.5	0.02				
Ampholytes					7.0	0.03				
Bases					0.1	0.00				
Exhaustive extraction of the remainder										
Pronase E	34.6	0.82	44.3	0.55	49.2	0.24			6.2	
Neutrals	1.4	0.03	3.3	0.04	3.5	0.02			0.8	0.03
Acids										
Weak bases	3.2	0.08	4.0	0.05	11	0.05			4.3	0.18
Ampholytes	20.2	0.48	28.7	0.35	29.7	0.15				
Bases	0.6	0.01	1.0	0.01	0.8	0.00			0.4	0.02
1N HCl	0.8	0.02	2.1	0.03	2.4	0.01				
6N HCl	8.8	0.21	6.3	0.08	-	-				
Remainder	-	-	-	-	6.9	0.03	14.7			
Total	93.0	2.21	93.1	1.16	84.0	0.41	100		84	

Neutrals: fraction which composes carbohydrates, such as glucose, lactose and other sugars

Acids: fraction which composes carboxylic acids, such as fumaric, succinic, glycolic, citric and acetic acid

Weak bases: fraction which composes compounds such as urea

Ampholytes: fraction which composes amino acids (alanine, serine, methionine, leucine, glycine etc.)

Bases: fraction which composes primary, secondary and tertiary amines, such as triethylamine

In summary, when ^{14}C-fosetyl-Al is administered orally to goats, radioactivity is rapidly absorbed, extensively metabolized and rapidly eliminated *via* the expired air ($^{14}CO_2$), urine and faeces.

Radioactive residues in edible tissues accounted for less than 5% of the administered dose (AD), with up to 14% eliminated in urine, up to 71% in faeces, up to 17.5% in expired air ($^{14}CO_2$) and 11–17% AD in milk. Residues in milk reached a plateau after about 3 days. No fosetyl-Al or related metabolites were found in the edible tissues or in milk, with radioactivity being incorporated into endogenous fats, carbohydrates and proteins.. However fosetyl and ethanol were identified in stomach contents and fosetyl was the major component (over 90%) of the radioactivity in urine.

The proposed metabolic pathway involves dissociation and conversion of fosetyl-Al via O-ethyl phosphonic acid to ethanol and phosphonic acid. The ethanol is oxidized to acetic acid, which is then incorporated into natural products or exhaled as CO_2.

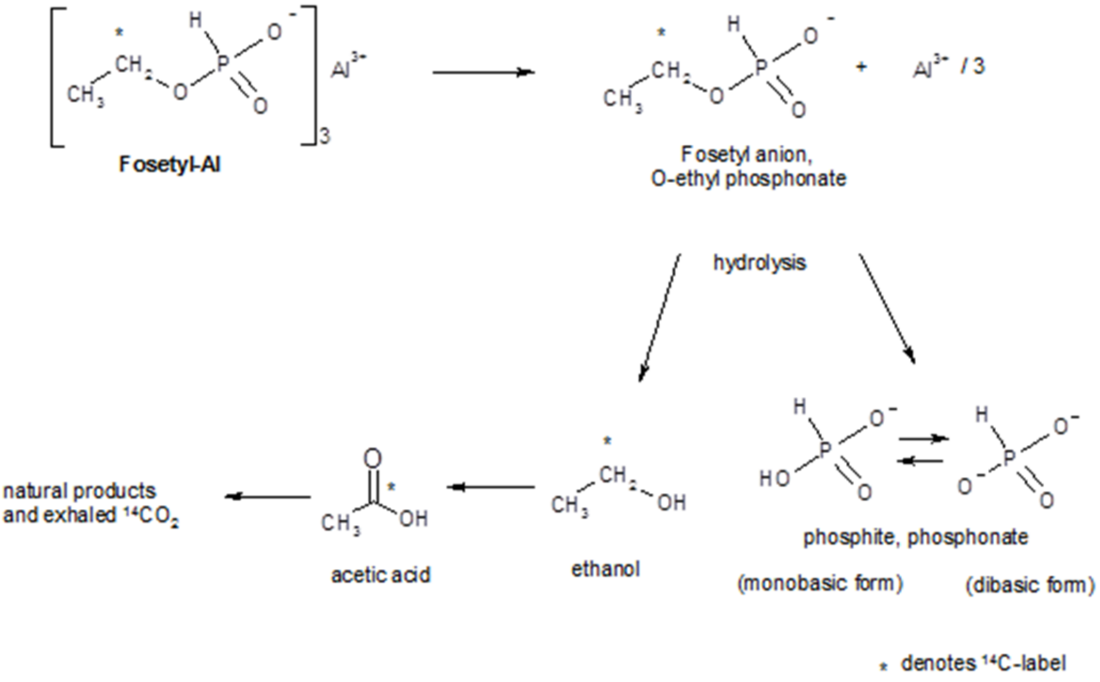


Figure 3 Proposed metabolic pathway of fosetyl-Al in the goat

Phosphonic acid

No information was available on the metabolism of phosphonic acid in animals, but the Meeting noted that inorganic phosphites are generally considered to be biologically inert in animals and are rapidly excreted. In a rat study using ^{32}P-phosphonate, around 30% of labelled material was excreted in faeces in the form of phosphonate or phosphate. Overall, conversion of phosphonate to phosphate was around 10% of the administered dose.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The meeting received analytical method descriptions and validation data for fosetyl-Al and phosphonic acid in plant and animal matrices. These methods can be divided into those involving GC analysis after derivatisation step (methylation to form the methyl ethylphosphonate and the dimethylphosphonate) and those involving HPLC-MS/MS analysis. The commonly used methods are summarised below:

Table 59 Summary of analytical methods for fosetyl-Al and phosphonic acid, developed for plant and animal matrices

Method No.	Matrix	Analyte	LOQ (mg/kg)	Method principle	References[a]
Plant matrices					
DFG 522	strawberries hops lettuce grapes, wine water	Fosetyl-Al Phosph acid	0.10 to 1.0	Sulphuric acid extraction Centrifugation/Filtration Dilution with isopropanol Derivatization with diazomethane GC-FPD analysis	R009308 (M-163761-01-2)

Method No.	Matrix	Analyte	LOQ (mg/kg)	Method principle	References[a]
AR155-97	citrus grapes (fresh & processed) strawberries, jam cucumber/courgette melons peppers lettuce potato tobacco apple hops, beer green beans	Fosetyl-Al Phosph acid	0.2 0.2	Sulphuric acid extraction Filtration Dilution with isopropanol Derivatization with diazomethane GC-FPD analysis	AR155-97 (M-165822-01-1) C024254 (M-216569-01-1) RA-2711/03 (M-255122-01-1)
20003024/02-RVP	cucumber lettuce melons tomato sweet pepper	Fosetyl-Al Phosph acid	0.2 0.2	Sulphuric acid extraction Filtration Dilution with isopropanol Derivatization with diazomethane GC-NPD analysis	C011966 (M-201858-01-1) 20003024/02-RVP (M-201858-01-1)
RE 21.82	pineapple	Fosetyl-Al Phosph acid	0.1 0.1	Water extraction Centrifugation/Filtration Dilution with isopropanol Derivatization with diazomethane GC-FPD analysis	R000843 (M-159422-01-1) R000844 (M-159423-01-1)
AR/1345	hops, beer	Fosetyl-Al Phosph acid	5.0 5.0	Water extraction Centrifugation/Filtration Dilution with isopropanol Derivatization with diazomethane GC-phosphorus specific flame-thermionic detector analysis	R011668 (M-184338-01-1)
MP-RE-03-78 RE 12-79	hops, beer	Fosetyl-Al Phosph acid	4.0	Water extraction Centrifugation/Filtration Dilution with isopropanol Derivatization with diazomethane GC-FPD analysis	C041516 (M-230875-01-2) R009283 (M-231761-01-2)
45205	oranges grapefruit lemons	Fosetyl-Al	0.1	Water extraction Centrifugation/Filtration Addition of sulphuric acid and isopropanol Filtration Derivatization with diazomethane GC-FPD analysis	B004224 (M-241182-01-1)
RPAC 44788	grapes	Fosetyl-Al	0.1	Sulphuric acid extraction Filtration Dilution with isopropanol Derivatization with TMSD GC-FPD analysis	R002649 (M-163082-01-1) R000070 (M-157829-01-1)
AR154-97	grapes oranges bananas avocados	Fosetyl-Al Phosph acid	0.5 0.5	Water/ACN extraction Octadecyl cartridge clean-up Derivatization with TMSD in isopropanol+sulphuric acid GC-FPD analysis	R003461 (M-164749-01-1) R004565 (M-166296-01-1)
	hops	Fosetyl-Al Phosph acid	2.0 20		
	lettuce	Fosetyl-Al Phosph acid	0.2 0.2		
AR 171-98	wine orange juice beer apple juice	Fosetyl-Al Phosph acid	0.5 0.5	Water/ACN extraction (Octadecyl cartridge clean-up) Derivatization with TMSD in isopropanol+sulphuric acid GC-FPD analysis	R004559 (M-166292-01-1) R014226 (M-189211-01-1)

Method No.	Matrix	Analyte	LOQ (mg/kg)	Method principle	References[a]
163	grapefruit, juice oranges, juice	Fosetyl-Al	0.05	Hydrochloric acid and ACN extraction Alumina Column Chromatography clean-up Derivatization with diazomethane in acetic acid GC-FPD analysis	C013813 (M-205315-01-1)
SOP-90113	avocados pineapples	Fosetyl-Al	0.05	Hydrochloric acid and ACN extraction Alumina Column Chromatography clean-up Derivatization with diazomethane GC-FPD analysis	C039814 (M-227242-01-1)
00861/M001	grapes oranges lettuce cucumbers avocados wheat grain	Fosetyl-Al Phosph acid	0.01 0.1	Water/ACN extraction Centrifugation Dilution HPLC-MS/MS analysis Fosetyl-Al: m/z 109→81 and 109→63 Phosphonic acid: m/z 81→63 and 81→79	00861/M001 (M-247699-01-1) RA-2524/05 (M-280250-01-1) 08-2092 (M-349106-01-1) 10-2061 (M-414163-01-1) VR-097/14 (M-519340-01-1) VR-020/15 (M-559769-01-1) MR-174/04 (M-252812-02-1)
	apples pears strawberries courgettes melons tomatoes (fresh & processed) sweet peppers non-bell peppers spinach	Fosetyl-Al Phosph acid	0.01 0.2		
	pineapple	Fosetyl-Al Phosph acid	0.05 0.5		
	hops	Fosetyl-Al Phosph acid	1.0 20		
	apple grape coffee	Fosetyl-Al Phosph acid	0.01 0.1		
QuPPe (Method 01501)	lettuce (head) bean (dried seed) barley (grain) grapes (berries)	Fosetyl-Al Phosph acid	0.01 0.1	Water/methanol (acidified) extraction Centrifugation Dilution HPLC-MS/MS analysis Fosetyl-Al: m/z 109→81 and 109→63 Phosphonic acid: m/z 81→63 and 81→79	MR-15/054 (M-523992-01-1) IR4-10687 TRC15-138 TRC15-139 IR4-11529 IR4-11530 IR4-11504
	avocado (fruit) cumin (seeds)	Fosetyl-Al Phosph acid	0.01 0.5		
	orange tree nuts	Phosph acid	1.0 0.5		
TRC09	orange mandarin	Phosph acid	0.186	Sulphuric acid extraction Filtration Dilution with isopropanol Derivatization with diazomethane HPLC-MS/MS analysis m/z 111→79 and 111→47	TRC09-02
	grape	Phosph acid	1.0		
AATM-R-127	grape	Phosph acid	1.0	Water/ACN extraction Centrifugation Mix with ion pairing reagent (tetrabutylammonium acetate) Filtration UPLC-MS/MS analysis m/z 81→63 and 81→79	NUF1104
Animal matrices					
Rhone-Poulenc Analytical Method No. 171	bovine meat bovine kidney bovine liver bovine heart bovine fat	Fosetyl-Al	0.05	Hydrochloric acid and ACN extraction (milk: C-18 Sep-Pak® clean-up, aluminium sulphate precipitation and propanol-2 precipitation)	R000918 (M-159551-01-1)

Method No.	Matrix	Analyte	LOQ (mg/kg)	Method principle	References[a]
	milk	Fosetyl-Al	0.02 mg/L	Alumina Column Chromatography clean-up Derivatization with diazomethane in acetic acid GC-FPD analysis	
AR 172-98	milk	Fosetyl-Al Phosph acid	0.1 mg/L 0.1 mg/L	Water/ACN extraction Octadecyl cartridge clean-up Derivatization with TMSD in isopropanol+sulphuric acid GC-FPD analysis (GC-NPD and GC-PFPD in the method modification)	R004563 (M-166294-01-1) C044136 (M-235827-01-1) C016012 (M-201568-01-1)
	bovine meat bovine kidney bovine liver egg hen muscle hen liver hen fat	Fosetyl-Al Phosph acid	0.5 0.5		
01005/M001	milk	Fosetyl-Al Phosph acid	0.01 0.01	Water/ACN extraction Centrifugation Dilution HPLC-MS/MS analysis Fosetyl-Al: m/z 109→81 and 109→63 Phosphonic acid: m/z 81→79 and 81→63	MR-06/212 (M-286555-01-1) 2011/0058/01 (M-412199-01-1)
	bovine meat bovine kidney bovine liver egg poultry muscle	Fosetyl-Al Phosph acid	0.05 0.05		

[a] References are to the original method development study and subsequent validation studies discussed below

Data collection methods

Methods DFG 522, AR 155-97 - fresh and processed plant matrices

The DFG 522 gas chromatography method was the initial method used to measure residues of fosetyl-Al and phosphonic acid in plant matrices, with minor modifications in method AR155-97 and method 20003024/02-RVP.

In this method, residues were extracted from crop samples by macerating with diluted sulphuric acid solution (except water and wine which were extracted with concentrated sulphuric acid). After centrifugation and filtration (except wine and water), the extract was diluted with isopropanol, residues methylated with diazomethane resulting in the formation of the methyl ethyl phosphonate (from fosetyl) and the dimethylphosphonate (from phosphonic acid). The final extract was measured by Gas Chromatography with a flame photometric detector (FPD) or NPD detector in the case of method 20003024/02-RVP. The quantification was carried out by external standardisation.

Specificity is assured by the sample preparation (derivatization step with diazomethane) and the possibility of using a second detector for confirmation (FDP or NPD for high water content commodities).

Good linearity was observed in the range of 10 to 2000 µg/L using an FPD detector (10–500 µg/L using an NPD detector). Correlation coefficients of 1/× weighted linear regression were calculated and were found above 0.99 for standards in solvent.

For most plant matrices tested, the method LOQ for fosetyl-Al and phosphonic acid is 0.20 mg/kg. For some matrices the lowest fortification level was 0.5 mg/kg for fosetyl-Al and phosphonic acid and in hops, the lowest fortification levels were 1.0 and 10 mg/kg for fosetyl-Al as well as 20 and 40 mg/kg for phosphonic acid in green cones and dry cones, respectively.

Repeatability of the method was shown by the relative standard deviations (RSDs) for each individual fortification level per sample material and overall mean RSDs per commodity being less than 20% for fosetyl-Al and for phosphonic acid. The overall mean RSDs per sample material and validation set were also below 20%, except for phosphonic acid in lettuce head (in one validation set the overall RSD was 21.5%).

Method validation studies were conducted prior to the analysis of the field trial samples, with untreated samples were fortified with fosetyl-Al and phosphonic acid at the LOQ and at 5-10 time the LOQ, with mean recovery rates for both analytes in each sample material calculated per fortification level were in the range of 70 to 110%, except for one mean recovery for fosetyl-Al in grape wine (FL 1.0 mg/kg 111%) and for phosphonic acid in single cases (in two validation sets for grape fruit, in one set for grape juice, in one for grape wine and in one validation set for cucumber the mean recovery was up to 123%). The overall mean recoveries per sample material and validation set were in the range of 70 to 110%, except for two phosphonic acid validation sets in grape fruit, one in grape juice and one in grape wine (up to 123%). The overall mean recoveries per commodity were all in the range of 70 to 110% for both analytes, except for phosphonic acid in grape juice (115%).

Residue field trial concurrent recovery rates where this method was used are summarised in the discussions on the individual crop field trials. These concurrent recoveries produced similar results to the fortification data obtained during method validation. The average recoveries ranged from 70–120%, with a standard deviation of ≤20%. Therefore, the recovery of this method is adequate for the purposes of residue data collection.

Table 60 Recovery results for fosetyl-Al and phosphonic acid (method AR 155-97)

Sample material	Fosetyl-Al					Phosphonic acid				
	Fortified [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]
Orange, mandarin	0.2–5.0	18	72–109	88	12.6	0.2–5.0	18	73–108	92	12.7
Orange, mandarin pulp	0.2–5.0	8	72–86	80	5.7	0.2–5.0	8	89–108	98	6.4
Orange, mandarin peel	0.2–5.0	8	72–107	89	15.5	0.2–5.0	8	75–108	93	13.7
Orange pomace	0.2–2.0	10	70–90	76	8.4	0.2–2.0	10	69–94	76	12
Apple	0.2–2.0	6	87–98	92	4.8	0.2–2.0	6	78–94	85	6.8
Grape	0.2–2.0	16	71–108	88	13.7	0.2–5.0	15	84–125	106	12.6
Grape juice	0.20	2	88–100	94	-	0.2	2	114–116	115	-
Grape wine	0.2–2.0	21	70–113	93	11.4	0.2–5.0	21	88–123	95	12.4
Grape must	0.2–2.0	4	73–105	93	14.9	0.2–5.0	4	89–110	99	11.2
Grape lees	0.2–2.0	5	78–104	92	12.4	0.5–5.0	5	72–96	81	13.1
Grape pomace	0.2–2.0	2	78–81	77	-	0.5–5.0	2	86–109	98	-
Strawberry	0.2–2.0	14	70–90	82	6.9	0.2–2.0	14	71–109	88	11.9
Strawberry jam	0.2–2.0	6	72–82	76	5.2	0.2–2.0	6	78–109	91	13.9
Strawberry, canned	0.2–2.0	6	70–88	77	8.9	0.2–2.0	6	87–108	96	9.4
Cucumber, courgette	0.2–2.0	29	70–110	86	14.7	0.2–2.0	29	72–129	93	16.2
Melon	0.2–2.0	14	70–101	82	13.0	0.2–2.0	14	75–120	97	14.5
Melon pulp	0.2–2.0	10	78–92	86	7.9	0.2–2.0	10	80–109	102	10.8
Melon peel	0.2–2.0	10	70–108	82	14.3	0.2–2.0	10	83–110	97	9.7
Pepper	0.2–2.0	6	89–94	88	8.8	0.2–2.0	6	89–109	102	7.1
Lettuce	0.2–2.0	18	71–105	86	12.4	0.2–2.0	18	70–117	91	18.3
Potato	0.2–2.0	4	83–100	89	8.9	0.2–2.0	4	75–111	103	18.2
Tobacco	0.2–2.0	4	70–97	83	13.4	0.2–2.0	4	72–116	97	19
Hops green	1.0	1	100	-	-	20	1	105		
Hops dry	10.0	1	87	-	-	40	1	72		
Beer	0.2-1.0	6	71-109	88	18.7	0.2-10	6	80-108	91	10.8
Green bean	0.2-2.0	6	71-83	76	6.0	0.2-2.0	6	70-90	78	10.9

Table 61 Recovery results for fosetyl-Al and phosphonic acid (method 20003024/02-RVP)

Sample material	Fosetyl-Al					Phosphonic acid				
	Fortified [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]

Sample material	Fosetyl-Al					Phosphonic acid				
	Fortified [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]
Cucumber	0.2–2.0	10	69–102	88	12.7	0.2–2.0	11	64–107	88	15.9
Lettuce	0.2–10	8	71–101	87	13	0.2–10	8	68–105	84	18
Melon	0.2–2.0	8	70–94	83	9.2	0.2–2.0	8	70–98	81	12
Melon pulp	0.2–2.0	6	77–99	87	10.3	0.2–2.0	6	80–104	91	13
Melon peel	0.2–2.0	6	69–92	83	12.2	0.2–2.0	6	70–108	87	17
Sweet pepper	0.2–3.0	20	72–99	87	8.4	0.2–3.0	13	69–115	92	13.4
Tomato	0.2–2.0	11	71–105	90	12.9	0.2–2.0	11	72–113	94	14.2

Methods RE 21.82, AR 1345, 45205 – pineapple, hops and citrus

In method RE 21.82, the original DFG 522 method was modified (and validated) for the analysis of fosetyl-Al and phosphonic acid in pineapple, using water extraction instead of diluted sulphuric acid and propionic acid was added before derivatization and detection was by AFID (LOQ in pineapple of 0.1 mg/kg for both analytes).

Modifications in method AR/1345 were that isopropanol was added after homogenization, a slightly different methylation procedure was used and a phosphorous specific flame-thermionic detector was used (LOQ in hops of 5.0 mg/kg for both analytes). In methods MP-RE-03-78 and RE 12–79, modifications to method RE 21.82 were that extracts were diluted with methylglycol and acetonitrile (rather than isopropanol) before methylation (LOQ in hops of 4.0 mg/kg for both analytes).

In method 45205, a modification of AR/1345, citrus fruit samples were extracted in water and then acidified with sulfuric acid (instead of propionic acid) before dilution with isopropanol and methylation. In this method, only fosetyl-Al residues were measured (LOQ in citrus fruit of 0.1 mg/kg).

For method RE 21.82, the overall mean recovery rates in pineapple were 110% for fosetyl-Al and 101% for phosphonic acid. In hops, the mean overall recovery rates for method AR/1345 were 75% (fosetyl-Al) and 64% (phosphonic acid).

Table 62 Recovery results for fosetyl-Al and phosphonic acid (methods RE 21.82, AR/1345, 45205)

Sample material	Fosetyl-Al					Phosphonic acid				
	Fortified [mg/kg]	n	% Recoveries – range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries – range	Mean [%]	RSD [%]
Pineapple (RE 21.82)	0.1–1.0	n.r	99–120	110	n.r	0.1–1.0	n.r	88–112	101	n.r
Hops (AR/1345)	5.0–80	4	66–81	75	8.6	5.0–500	4	55–70	64	10.2
Orange (45205)	0.1–0.5	8	66–83	73	7.7					
Grapefruit (45205)	0.1–0.5	4	78–99	89	10.2					
Lemon (45205)	0.1–0.5	4	74–86	78	6.9					

n.r = only the range of recoveries was given in the report.

Method RPAC File No. 44788

Residues of fosetyl-aluminium (fosetyl-Al) are extracted from sample material by macerating the chopped fruit with 1% aqueous sulfuric acid. After the mixture is centrifuged and filtered, an aliquot of the extract is diluted to a specified volume with isopropanol, and the diluted extract is filtered. A small portion of the filtrate is treated with diazomethane, converting fosetyl-Al to methyl ethyl phosphonate. The methyl ethyl phosphonate is determined by GC with phosphorus-specific flame phototmetric detection. The quantification was done using external standardization with fosetyl-Me standards, expressed as fosetyl-Al.

The calibration curve for derivatized fosetyl-Al standards showed a good linearity (correlation coefficient was ≥ 0.99) within the range of 0.005 to 0.10 µg/mL (calculated as fosetyl-Al equivalent).

The LOQ for fosetyl-Al in grapes was 0.10 mg/kg. Method LOQ for fosetyl-Al was 0.10 mg/kg. The mean recovery rates (per fortification level and overall) for fosetyl-Al in grapes were in the range of 70 to 110%, RSDs were always below 20%.

Table 63 Recovery results for fosetyl-Al (method RPAC File No. 44788)

Sample material	Fosetyl-Al				
	Fortified [mg/kg]	n	% Recoveries–range	Mean [%]	RSD [%]
Grape	0.10–50	12	84–118	95	10.3

Methods AR154-97, AR 171-98 – fresh and processed plant matrices

Methods AR154-97 and AR 171-98, were developed to replace diazomethane as the derivatising agent and were validated for a range of fruits, for lettuce and hops and also for liquid processed commodities (AR 171-98).

Residues of fosetyl-Al and phosphonic acid were extracted by macerating with a mixture of water and acetonitrile (50:50, v/v). The extracts were cleaned up using an octadecyl (C18) cartridge. After dilution with isopropanol acidified with 1% sulphuric acid, the extracts were derivatized with trimethylsilyldiazomethane reagent (TMSD). Quantification was by gas chromatography on a semicapillary column, using a flame photometric detector (phosphorus mode). Quantification was carried out by external standardization using derivatized solutions of fosetyl-Al and phosphonic acid.

Specificity is assured by the sample preparation (derivatization step with TMSD) and the analysis (specific column (DB WAX) column and detector (flame photometric detector).

Linear correlation between injected amount and detector response was obtained in the range of 20 to 2000 µg/L at five different concentrations (0.02–2.0 µg/L in liquid matrices for method AR 171–98). Correlation coefficients of 1/× weighted linear regression were calculated and were found above 0.99 for standards in solvent.

Method LOQs ranged from 0.5 mg/kg for grapes, oranges, avocados and bananas, 0.2 mg/kg for lettuce for both fosetyl-Al and phosphonic acid, while for hops (dried cones) the LOQs were 2.0 mg/kg for fosetyl-Al and 20 mg/kg for phosphonic acid.

Repeatability of the method was shown by the relative standard deviations (RSDs) per fortification level and overall being below 20%, except for phosphonic acid in avocado peel (22.5%) and the mean recovery rates per fortification level and overall for both analytes in each matrix were in the range of 70 to 110% except for one mean recovery rate of 112% (at 0.5 mg/kg) for fosetyl-Al in wine.

Table 64 Recovery results for fosetyl-Al and phosphonic acid (methods AR154-97, AR 171-98)

Sample material	Fosetyl-Al					Phosphonic acid				
	Fortified [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]
Grape	0.5–5.0	9	75–95	84	9.4	0.5–50	9	71–99	85	11.9
Grape[a]	0.5–5.0	7	89–122	103	12.9	0.5–5.0	7	70–104	85	15.6
Grape[b]	0.5–5.0	10	66–97	83	13,4	0.5–50	10	76–102	91	8.4
Wine	0.5–5.0	10	95–118	105	7.9	0.5–5.0	10	71–102	87	13.7
Wine	0.5–5.0	10	66–96	83	14	0.5–5.0	10	72–109	91	16
Orange	0.5–5.0	9	75–86	79	4.9	0.5–50	9	75–93	84	7.3
Orange juice	0.52–5.2	10	90–101	96	4.6	0.52–5.2	10	74–94	84	8.1

Sample material	Fosetyl-Al					Phosphonic acid				
	Fortified [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]
Orange juice[a,b]	0.52–5.2	10	62–99	82	16	0.52–5.2	10	61–97	79	13
	0.5–5.0	6	79–91	84	7.1	0.5–5.0	6	81–102	92	11.8
		4	75–87	84	6.9		4	76–84	79	4.3
Banana	0.5–2.0	9	71–83	79	4.9	0.5–20	9	74–82	79	3.5
Banana[b]	0.5–5.0	10	79–99	87	7.6	0.5–50	10	71–110	87	18.1
Avocado[a]	0.5–5.0	7	76–104	91	11	0.5–5.0	4	100–108	103	3.5
							3	76–102	85	17
Avocado pulp[a]	0.5–5.0	3	83–109	97	13.5	0.5–5.0	3	76–107	91	17.1
Avocado peel[a]	0.5–5.0	3	76–90	83	8.4	0.5–5.0	3	75–101	81	22.5
Lettuce[a]	0.2–2.0	6	80–105	92	11.9	0.2–2.0	6	105–109	107	1.7
Lettuce[b]	0.2–5.0	13	75–112	91	16.4	0.2–50	13	71–110	85	14.3
Hops (dry cone)	2.0–100	9	81–104	94	8.6	20–1000	9	66–101	85	14.8
Hops (dry cone)[b]	2.0–120	11	87–118	101	11.1	20–1000	11	73–95	85	10.4
Beer	0.5–5.0	10	82–114	104	9.5	0.5–5.0	10	75–117	98	12.9
Beer[b]	0.5–5.0	10	75–104	89	11	0.5–5.0	10	76–99	88	9
Apple juice	0.5–5.0	4	82–96	89	6.7	0.5–5.0	4	81–94	89	7.8

[a] Recovery rates in the method validation studies

[b] Recovery rates in the Independent Laboratory Validation study

Methods 163, SOP-90113 – avocado, pineapple, citrus fruit and juice

Methods based on DFG 522 were developed for measuring only fosetyl-Al residues in avocado, pineapple, citrus fruit and citrus juices. In these methods, residues were extracted using a 50:50 mixture of 0.1N HCl and acetonitrile (instead of sulfuric acid) and cleaned-up by alumina column chromatography (rather than centrifugation and filtration) before dilution with acetic acid and methylation with diazomethane to obtain methyl ethyl phosphonate. In method SOP-90113, the acetic acid dilution step was omitted. Measurement was by GC-FPD and gas chromatography using external derivatised fosetyl-Al standard.

The calibration curve for methyl ethyl phosphonate showed good linearity within the range of 0.05 to 1.0 µg/L (calculated as fosetyl-Al), and the LOQ was 0.05 mg/kg. Repeatability of the method was shown by the relative standard deviations (RSDs) per fortification level and overall being below 20% and the mean recovery rates per fortification level and overall for both analytes in each matrix were in the range of 70 to 110%.

Table 65 Recovery results for fosetyl-Al (methods 163, SOP-90113)

Sample material	Fosetyl-Al				
	Fortification levels [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]
Orange, grapefruit	0.05–8.0	13	84–97	90	5.0
Orange, grapefruit peel	0.05–80	9	80–96	90	6.4
Orange, grapefruit juice	0.05–8.0	10	77–98	90	8.6
Avocado	0.05–1.0	13	64–106	89	15.4
Pineapple[a]	0.05–0.1	8	85–100	91	6.5

[a] Recovery rates in the method validation studies

Method 00861/M001 –plant matrices

This method, developed to replace AR 154-97, uses a simpler extraction procedure and LC-MS/MS analysis and has been validated for a range of fruit and vegetable fresh and processed matrices, hops and wheat grain. Residues of fosetyl-Al and its metabolite phosphonic acid were extracted from the plant matrices with a mixture of acetonitrile/water (50/50). After centrifugation and dilution of the extracts, the residues were quantified by HPLC using PGC or C18 columns and tandem mass spectrometry (MS/MS) with electrospray ionisation. The quantification was carried out by external standardisation using matrix matched standards. The monitored mass transitions are:

Analyte	Quantitation	Confirmation
Fosetyl-Al	109→81	109→63
Phosphonic acid	81→63	81→79

Apparent residues for all control samples in the validation studies were below 30% of the LOQ for each analyte except in one study where residues of phosphonic acid were 40% LOQ in one control lettuce sample.

Linear correlation between the injected amount of both standards prepared in solvent or matrix matched standards and the detector responses of HPLC/MS/MS was observed within the range of 0.1–5 µg/L (0.31–8.3 µg/L for wheat) for fosetyl-Al and 1–50 µg/L (3.1 83 µg/L for wheat) for phosphonic acid, with correlation coefficients of the 1/× weighted linear regression of between 0.9942 to 1.0000.

For all the tested sample materials, a matrix effect was observed for phosphonic acid and therefore the quantitation of both compounds was established using matrix matched standards.

Fosetyl-Al limits of quantification were 0.01 mg/kg except for pineapple (0.05 mg/kg) and hops (1.0 mg/kg) and the phosphonic acid LOQ s were 0.1 or 0.2 mg/kg except for pineapple (0.5 mg/kg) and hops (20 mg/kg).

Repeatability of the method was shown by the relative standard deviations (RSDs) per fortification level and overall being below 20% and the mean recovery rates per fortification level and overall for both analytes in each matrix were in the range of 70 to 110% except for phosphonic acid in apple (mean recovery of 112% at 100xLOQ), non-bell pepper (111% at 100xLOQ) and dry hop cones (118% at the LOQ).

Table 66 Recovery results for fosetyl-Al (method 00861/M001)

Sample material	1st MRM: m/z 109→81					2nd MRM: m/z 109→63				
	Fortified [mg/kg]	N	% Recoveries – range	Mean [%]	RSD [%]	Fortified [mg/kg]	n	% Recoveries – range	Mean [%]	RSD [%]
Grape	0.01–0.1	10	95–102	101	2.1	0.1–1.0	10	85–107	99	6.7
Grape[a]	0.01–10	15	88–98	93	3.2	0.01–10	15	82–103	94	7.7
Orange	0.01–0.1	10	86–102	95	5.6	0.1–1.0	10	85–121	102	12.2
Orange (pulp)[c]	0.01–0.1	10	85–94	90	3.3					
Lettuce	0.01–0.1	10	98–114	106	4.5	0.1–1.0	10	87–113	97	7.4
Cucumber	0.01–0.1	10	95–106	99	3.4	0.1–1.0	10	98–117	105	6.6
Cucumber[c]	0.01–0.1	10	86–94	92	2.4					
Avocado	0.01–0.1	10	85–104	91	6.2	0.1–1.0	10	84–97	89	5.4
Wheat	0.01–0.1	10	69–93	80	10.9	0.1–1.0	9	72–98	81	10.8
Wheat (grain)[c]	0.01–0.1	10	76–93	86	7.6					
Apple[a]	0.01–10	15	71–96	85	10.3	0.01–10	15	77–120	93	12.5
Coffee bean[a]	0.01–1.0	10	71–90	79	7.7	0.01–1.0	10	71–98	83	11.5
Apple[b]	0.01–0.1	6	98–112	107	4.7					
Pear[b]	0.01–0.1	6	90–108	98	7.2					
Strawberry[b]	0.01–0.1	6	82–108	93	11.1					
Pineapple[b]	0.05–0.5	13	84–97	92	4.5					
Pineapple peel[b]	0.05	7	89–95	93	2.5					
Pineapple pulp [b]	0.05	7	75–91	83	6.8					
Courgette[b]	0.01–0.1	6	89–104	94	5.6					
Melon[b]	0.01–0.1	6	83–124	100	14.8					
Melon peel[b]	0.01–0.1	6	84–107	95	9.2					
Melon pulp[b]	0.01–0.1	6	97–106	103	3.4					
Tomato[b]	0.01–0.1	6	88–100	95	4.9					
Tomato (cherry)[b]	0.01–0.1	6	96–113	104	6.0					
Tomato juice[b]	0.01–0.1	6	94–101	97	3.2					
Tomato puree[b]	0.01–0.1	6	95–100	97	1.7					

Sample material	1st MRM: m/z 109→81					2nd MRM: m/z 109→63				
	Fortified [mg/kg]	N	% Recoveries – range	Mean [%]	RSD [%]	Fortified [mg/kg]	n	% Recoveries – range	Mean [%]	RSD [%]
Tomato peel[b]	0.01–0.1	6	85–92	88	3.3					
Pepper, sweet[b]	0.01–0.1	6	82–100	92	8.7					
Non-bell pepper[b]	0.01–1.0	10	78–103	93	9.2					
Spinach[b]	0.01–0.1	6	87–107	99	6.8					
Hops, green[b]	1.0–10	11	81–95	86	4.4					
Hops, dry[b]	1.0–10	11	72–79	76	3.8					

[a] Recovery rates in the method validation studies

[b] Recovery rates from method validation in the supervised residue field trials

[c] Recovery rates in the Independent Laboratory Validation study

Table 67 Recovery results for phosphonic acid (method 00861/M001)

Sample material	1st MRM: m/z 81→63					2nd MRM: m/z 81→79				
	Fortified [mg/kg]	N	% Recoveries – range	Mean [%]	RSD [%]	Fortified [mg/kg]	n	% Recoveries – range	Mean [%]	RSD [%]
Grape	0.1–1.0	10	92–113	101	6.0	0.1–1.0	10	86–119	98	9.6
Grape[a]	0.1–100	15	80–116	91	10.9	0.1–100	15	77–117	87	12.0
Orange	0.1–1.0	10	65–101	87	17.3	0.1–1.0	10	68–108	89	19.8
Orange (pulp)[c]	0.1–1.0	10	89–108	98	6.1					
Lettuce	0.1–1.0	10	74–108	93	14.7	0.1–1.0	10	69–105	91	14.9
Cucumber	0.1–1.0	10	82–102	93	8.9	0.1–1.0	10	77–101	93	9.8
Cucumber[c]	0.1–1.0	10	98–119	105	7.0					
Avocado	0.1–1.0	10	68–110	87	17.8	0.1–1.0	10	70–113	90	17.5
Wheat	0.1–1.0	10	77–103	89	12.2	0.1–1.0	10	71–83	77	5.1
Wheat (grain)[c]	0.1–1.0	10	80–90	83	5.3					
Apple[a]	0.1–100	15	74–118	99	15.6	0.1–100	15	82–109	95	9.1
Coffee bean[a]	0.1–10	10	77–108	93	10	0.1–10	10	79–102	91	8.2
Apple[b]	0.2–2.0	6	98–116	107	5.6					
Pear[b]	0.2–2.0	6	93–121	100	10.5					
Strawberry[b]	0.2–2.0	6	82–90	88	4.2					
Pineapple[b]	0.5–5.0	10	98–105	102	1.9					
Pineapple peel[b]	0.5	7	103–115	106	4.0					
Pineapple pulp[b]	0.5	7	87–103	96	6.7					
Courgette[b]	0.2–2.0	6	88–96	91	3.4					
Melon[b]	0.2–2.0	6	83–104	95	10.2					
Melon peel[b]	0.2–2.0	6	95–122	103	9.4					
Melon pulp[b]	0.2–2.0	6	101–109	105	3.4					
Tomato[b]	0.2–2.0	6	96–116	103	12.1					
Tomato (cherry)[b]	0.2–2.0	6	102–111	106	3.1					
Tomato juice[b]	0.2–2.0	6	91–98	95	3.3					
Tomato puree[b]	0.2–2.0	6	94–98	96	1.8					
Tomato peel[b]	0.2–2.0	6	87–94	92	2.9					
Pepper, sweet[b]	0.2–2.0	6	83–96	88	5.5					
Non-bell pepper[b]	0.1–10	10	86–114	100	8.9					
Spinach[b]	0.2–2.0	6	88–99	93	4.9					
Hops, green[b]	20–200	11	97–114	106	4.1					
Hops, dry[b]	20–200	11	98–126	113	7.7					

[a] Recovery rates in the method validation studies

[b] Recovery rates from method validation in the supervised residue field trials

[c] Recovery rates in the Independent Laboratory Validation study

Method TRC09 – citrus

Martos, 2011 [Ref TRC09-02] has reported a method using the extraction technique described in method DFG 522 and analysis by LC-MS/MS to measure residues of phosphonic acid in citrus.

Residues were extracted from crop samples by macerating with diluted sulphuric acid solution. After centrifugation and filtration, the extract was diluted with isopropanol and residues were methylated with diazomethane to form dimethylphosphonate. Residues were quantified by HPLC using tandem mass spectrometry (MS/MS) with electrospray ionisation. The quantification was carried out by external standardisation using matrix matched standards. The monitored mass transitions were m/z 111→79 (quantification) and m/z 111→47 (confirmation).

Linear correlation between the matrix matched standards and the detector responses of HPLC/MS/MS was observed within the range of 0.5–100 ng/ml, with correlation coefficients >0.99 and the LOQ was 0.186 mg/kg.

Repeatability of the method was shown by the relative standard deviations (RSDs) per fortification level and overall being below 20% and the mean recovery rates per fortification level and overall for both analytes in each matrix were in the range of 71 to 113%.

Table 68 Recovery results for phosphonic acid (method TRC09)

Sample material	1st MRM: m/z 111→79					2nd MRM: m/z 111→47				
	Fortified [mg/kg]	N	% Recoveries – range	Mean [%]	RSD [%]	Fortified [mg/kg]	n	% Recoveries – range	Mean [%]	RSD [%]
Mandarin (fruit)	0.19–37	10	79–113	95	9	0.19–37	11	80–111	94	9
Mandarin (flesh)	0.19–15	3	84–100	91	8	0.19–15	3	85–100	90	6
Mandarin (peel)	0.19–45	10	73–103	87	11	0.19–192	10	71–104	87	12
Orange (fruit)	0.19–194	9	62–103	85	19	0.19–194	9	62–101	85	15
Orange (flesh)	0.19–194	3	76–100	91	11	0.19–194	3	73–101	91	12
Orange (peel)	0.19–37	10	70–95	80	11	0.19–37	10	64–94	79	11

Method AR 172-98 – eggs, milk, animal tissues

A modification of method AR 171-98 was developed (and validated) for measuring residues of fosetyl-Al and phosphonic acid in animal matrices. Residues are extracted twice from the samples by macerating with a 50/50 water/acetonitrile mixture (20/80 for milk). An aliquot of the extract is then purified using an octadecyl (C18) cartridge (not for milk). After the addition of acidified isopropanol (1% sulphuric acid), the extracts are derivatized with the trimethylsilyldiazomethane reagent (TMSD) and residues analysed by GC-FPD. In the poultry feeding study, GC-NPD was used to detect residues in eggs and GC-PFPD was used for analysis of hen tissues. Quantification was done using external standardization with methylated fosetyl-Al and phosphonic acid standards.

In the method development study, residues of fosetyl-Al and phosphonic acid were found above the LOQ at the higher fortification levels, but all control samples in the validation studies were below 30% of the LOQ for each analyte.

The calibration curve for derivatized fosetyl-Al and phosphonic acid standards showed a good linearity (correlation coefficient was ≥ 0.99, n=7) within the range of 0.01–2.0 µg/mL in the original method. The response of the GC-NPD system to fosetyl-Al and phosphonic acid was shown to have a quadratic relationship with concentration over the range from 0.01 µg/mL to 2.0 µg/mL. Coefficients of determination (r^2) for the derived calibration lines were >0.980 in all cases. In practice the quadratic equations approximate closely to a linear relationship for all concentration values below 0.5 µg/mL. The response of the GC-PFPD system in the method modification to fosetyl-Al and phosphonic acid was shown to be linear over the concentration range from 10 µg/L to 500 µg/L. Coefficients of determination (r^2) for the derived calibration lines were >0.990 in all cases.

Limits of quantification for fosetyl-Al and phosphonic acid were 0.5 mg/kg in all matrices except milk, where the LOQs were both 0.1 mg/kg.

Repeatability of the method was shown by the relative standard deviations (RSDs) per fortification level and overall being below 20% and the mean recovery rates per fortification level and overall for both analytes in each matrix were in the range of 70 to 110%.

Table 69 Recovery results for fosetyl-Al and phosphonic acid (method AR 172-98)

Sample material	Fosetyl-Al					Phosphonic acid				
	Fortified [mg/kg]	n	% Recoveries–range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]
Milk	0.1–1.0	11	79–93	87	5.7	0.1–1.0	11	71–110	87	15.7
Milk[b]	0.1–1.0	10	88–122	101	11	0.1–1.0	10	71–99	82	13
Bovine muscle	0.5–5.0	10	94–112	104	5.6	0.5–5.0	10	74–101	85	9.8
Bovine muscle[b]	0.5–5.0	10	68–96	77	11	0.5–5.0	10	71–111	85	14
Bovine kidney	0.5–5.0	10	71–84	79	5.5	0.5–5.0	10	77–113	99	10.8
Bovine kidney[b]	0.5–5.0	10	66–103	83	12	0.5–5.0	10	76–104	86	12
Bovine liver	0.5–5.0	10	86–107	97	8.1	0.5–5.0	10	73–101	86	10.9
Bovine liver[b]	0.5–5.0	10	67–108	85	16	0.5–5.0	10	71–111	90	16
Egg	0.05–5.0	10	80–110	95	10.3	0.5–5.0	10	71–104	83	14.2
Egg[a]	0.5–2.5	10	73–94	85	8.6	0.5–2.5	10	84–120	98	12.6
Egg[b]	0.5–5.0	10	71–101	82	12	0.5–5.0	10	77–100	87	11
Hen muscle[a]	0.5–2.5	10	88–120	102	9.1	0.5–2.5	10	78–111	90	12.4
Hen liver[a]	0.5–2.5	10	81–106	93	7.4	0.5–2.5	10	67–101	83	11.7
Hen fat[a]	0.5–2.5	10	89–102	93	4.7	0.5–2.5	10	77–117	93	15.4

a Recovery rates in the method validation studies

b Recovery rates in the Independent Laboratory Validation study

Method 171 –milk, bovine tissues

A modification of method 163, with more extensive clean-up procedures was developed for measuring residues of fosetyl-Al in animal matrices. In this method, fosetyl-Al residues were extracted from the bovine tissues using 25% 0.02N hydrochloric acid in acetonitrile. The extract was cleaned up by alumina column chromatography. The eluate was evaporated and acetic acid added. The liberated O-ethyl phosphonic acid was esterified with diazomethane to obtain the corresponding methyl ester which was detected by phosphorus specific flame photometric gas chromatography. Milk samples were first passed through a C-18 column to remove fats. An aluminum sulfate precipitation step was used to remove proteins and a propanol-2 precipitation step to remove sugars. Additional clean-up was obtained by Alumina column chromatography. The eluate was esterified in the same manner as for the tissues. Quantification was based on the GC/FPD detection of the methyl ester derivative of fosetyl-Al.

The calibration curve for derivatized fosetyl-Al showed a good linearity within the range of 0.05–0.5 µg/mL and the LOQs were 0.05 mg/kg in tissues and 0.02 mg/L in milk. Repeatability of the method was shown by the relative standard deviations (RSDs) being below 20% and the mean recovery rates were in the range of 70 to 110%.

Table 70 Recovery results for fosetyl-Al (method 171)

Sample material	Fosetyl-Al				
	Fortification levels [mg/kg or mg/L]	n	% Recoveries - range	Mean [%]	RSD [%]
Bovine kidney	0.05–0.5	5	75–93	84	8.0
Bovine liver	0.05–2.0	7	79–96	86	8.7
Bovine muscle	0.05–0.5	6	70–93	82	13.7
Bovine fat	0.05–0.5	6	79–93	88	6.5
Bovine heart	0.05–0.5	5	71–80	76	4.5
Milk	0.02–0.4	10	72–98	84	8.1

Method 01005/M001 –milk, bovine tissues

The plant method 00861/M001 was adapted for animal matrices. Residues of fosetyl-Al and phosphonic acid were extracted with a 50:50 mixture of acetonitrile/water and after centrifugation and dilution (except for milk samples), residues were quantified by HPLC (tandem mass spectrometry with electrospray ionization in negative ion mode) without further clean-up and using external matrixmatched standards (since a matrix effect was observed for fosetyl-Al). Two MRM transitions were monitored for fosetyl-Al (m/z 109→81 and 109→63) and phosphonic acid (m/z 81→79 and 81→63).

Residues above 30% of the LOQ were found only in the phosphonic acid confirmation transition in meat, and the recoveries at the LOQ and 10xLOQ were corrected for interferences. Linear correlations were all >0.99 over the range of 0.5 to 50 µg/L (for both mass transitions) and LOQs for both fosetyl-Al and phosphonic acid were 0.01 mg/kg (milk) and 0.05 mg/kg (other matrices).

Table 71 Recovery results for fosetyl-Al (method 01005/M001)

Sample material	Fosetyl-Al (1st MRM m/z 109>81)					Fosetyl-Al (2nd MRM m/z 109>63)				
	Fortified [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]
Milk	0.01–0.1	10	83-95	89	4.6	0.01-0.1	10	87-95	91	2.8
Milk[a]	0.01–0.1	10	77-100	87	10.2	0.01-0.1	10	78-100	87	10
Bovine muscle	0.05–0.5	10	73-89	83	6.5	0.05-0.5	10	69-88	80	9.0
Bovine muscle[a]	0.05–0.5	10	93-103	97	3.3	0.05-0.5	10	93-101	97	3
Bovine kidney	0.05–0.5	10	85-94	90	3.1	0.05-0.5	10	86-97	91	3.7
Bovine kidney[a]	0.05–0.5	10	71-101	86	13.8	0.05-0.5	10	70-98	84	13
Bovine liver	0.05–0.5	10	75-92	84	7.3	0.05-0.5	10	73-93	84	8.0
Bovine liver[a]	0.05–0.5	10	89-107	97	6.2	0.05-0.5	10	87-107	97	7
Egg	0.05–0.5	10	91-99	94	3.0	0.05-0.5	10	89-98	93	4.0
Egg[a]	0.05–0.5	10	83-100	91	7.2	0.05-0.5	10	79-86	84	3
Hen muscle	0.05–0.5	10	93-100	95	2.5	0.05-0.5	10	92-97	94	1.9
Hen muscle[a]	0.05–0.5	10	87-92	90	2.3	0.05-0.5	9	87-92	90	2

[a] Recovery rates in the independent method validation study

Table 72 Recovery results for phosphonic acid (method 01005/M001)

Sample material	Phosphonic acid (1st MRM m/z 81>79)					Phosphonic acid (2nd MRM m/z 81>63)				
	Fortified [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]	FL [mg/kg]	n	% Recoveries - range	Mean [%]	RSD [%]
Milk	0.01–0.1	10	80–100	88	7.1	0.01–0.1	10	78–99	88	7.1
Milk[a]	0.01–0.1	10	78–95	88	6.6	0.01–0.1	10	79–96	88	8
Bovine muscle	0.05–0.5	10	87–95	92	2.9	0.05–0.5	10	63–103[b]	84	13.8
Bovine muscle[a]	0.05–0.5	10	71–88	80	8.4	0.05–0.5	10	77–92	87	5
Bovine kidney	0.05–0.5	10	66–91	79	11.0	0.05–0.5	10	77–91	83	5.3
Bovine kidney[a]	0.05–0.5	10	84–106	96	7.6	0.05–0.5	10	86–105	96	7
Bovine liver	0.05–0.5	10	76–93	87	6.1	0.05–0.5	10	82–95	91	4.9
Bovine liver[a]	0.05–0.5	10	69–94	80	9.9	0.05–0.5	10	71–88	80	8
Egg	0.05–0.5	10	71–93	80	7.2	0.05–0.5	10	72–89	79	6.4
Egg[a]	0.05–0.5	10	72–76	74	2.1	0.05–0.5	10	71–75	73	2
Hen muscle	0.05–0.5	10	87–93	90	2.1	0.05–0.5	10	86–97	91	3.6
Hen muscle[a]	0.05–0.5	10	78–90	85	4.6	0.05–0.5	10	77–99	86	8

[a] Recovery rates in the independent method validation study

[b] Due to the presence of an interfering peak in the control sample, the quantification was established using standards prepared in solvents; recoveries are corrected by subtraction of the interfering peak concentration found in the control sample

Enforcement methods

Method 00861/M001 (01005/M001)

This LC-MS/MS method, validated for a range of plant and animal commodities and used for data generation is suitable as an enforcement method for fosetyl-Al, with an LOQ of 0.01 mg/kg for plant commodities and milk and with an LOQ of 0.05 mg/kg for other animal commodities. The methods are also suitable for phosphonic acid, with an LOQ of 0.01 mg/kg for milk, 0.1 mg/kg for plant commodities and 0.05 mg/kg for other animal matrices.

Multi-residue QuPPe Method (version 7.1)

This multi-residue method, developed for the analysis of highly polar pesticides in foods of plant origin, using simultaneous extraction with methanol and HPLC-MS/MS determination has been validated by a number of analytical laboratories, and reported in the EURL database (www.eurl-pesticides-datapool.eu).

In the QuPPe (quick polar pesticide) method, residues of fosetyl-Al and phosphonic acid were extracted from the plant material following water adjustment and the addition of acidified (formic acid) methanol. After centrifugation and dilution, extracts were subjected to HPLC-MS/MS analysis and the residues were quantified using matrix matched standards. Two MRM transitions were monitored for fosetyl-Al (m/z 109→81 and 109→63) and phosphonic acid (m/z 81→63 and 81→79).

Based on the published EURL data, method QuPPe has been shown to be suitable for the determination of fosetyl-aluminium (fosetyl-Al) and phosphonic acid in commodities with high water content and high acid content and also for the determination of fosetyl-Al in dry commodities with high starch content.

Table 73 Representative validation data for fosetyl-Al in different crop groups from routine on-going validation of the QuPPe (quick polar pesticide) method (EURL Datapool)

Matrix type	n	Fortification levels (mg/kg)		Recoveries (%)		RSD [%]	% of recoveries in the range of 70-120%	No of labs involved
		Min	Max	Median	Mean			
High water	27	0.01	0.30	99	100	7	100	2
High acid	13	0.05	0.10	96	96	6	100	2
Dry (high starch)	10	0.02	0.10	106	107	5	100	1
Overall	50	0.01	0.30	100	100	7	100	2

Table 74 Representative validation data for phosphonic acid in different crop groups from routine on-going validation of the QuPPe (quick polar pesticide) method (EURL Datapool)

Matrix type	n	Fortification levels (mg/kg)		Recoveries (%)		RSD [%]	% of recoveries in the range of 70-120%	No of labs involved
		Min	Max	Median	Mean			
High water	43	0.10	33	110	107	9	95	1
High acid	34	0.10	40	105	104	9	100	1
Dry (high starch)	3	2.0	4.0	99	97	12	100	1
Dry (high fat)	1	19	19	-	109	-	100	1
Other	4	0.1	0.5	105	103	10	100	1
High sugar	1	4.0	4.0	-	92	-	100	1
High water (extract rich)	2	1	300	-	100	1	100	1
Overall	88	0.10	300	108	105	9	98	1

A validation study reported by Meklat & Venet, 2015 [Ref: MR-15/054] was conducted using a range of representative commodities from the crop categories. Modifications to the original method included the use of matrix matched standards (since instability was observed when using isotopically labelled internal standards) and the addition of a further formic acid/methanol adjustment after centrifugation. For oily matrices (avocado), improved recovery rates were obtained by using a double extraction procedure.

For each sample material tested, and both MRM transitions used, apparent residues in control samples were found to be below 30% of the LOQ. The lower margin of the linearity test was below 30% of the LOQ and the higher margin was 20% above the highest fortification level. The correlation between the injected amount of fosetyl-Al and phosphonic acid, for their both MRM transitions and the detector response in matrix matched standards were always above 0.99. The linearity range depended on compound, matrix and MRM transition, at least 0.006–0.4 mg/kg for fosetyl-Al and at least 0.06–12.5 mg/kg, except for cumin (0.1–50 mg/kg) for phosphonic acid.

The LOQ for fosetyl-Al was validated at 0.01 mg/kg in all matrices and calculated detection limits (LOD) ranged from 0.0008 to 0.0053 mg/kg. The LOQ for phosphonic acid was validated at 0.1 mg/kg in all matrices except in avocado and cumin (0.5 mg/kg) and calculated LODs ranged from 0.0218 to 0.111 mg/kg.

The RSD values per fortification level and across all validated sample materials were well below 20% for both MRM transitions at all fortification levels and mean recoveries for each fortification level and the overall mean recovery were within the 70 to 110% range for fosetyl-Al and its metabolite phosphonic acid for all tested matrices and for both MRM transitions used except for fosetyl-Al in cumin at LOQ level (112%) and in dried bean seed at 10xLOQ level (115%).

Table 75 Recovery results for fosetyl-Al (QuPPe method - BCS 01501)

Sample material			1st MRM: m/z 109→80.9			2nd MRM: m/z 109→63		
	Fortified [mg/kg]	N	% Recoveries – range	Mean [%]	RSD [%]	% Recoveries – range	Mean [%]	RSD [%]
Lettuce (high water)	0.01–1.0	15	71–105	89	9.3	64–102	88	9.9
Avocado (high oil)	0.01–1.0	15	89–96	93	2.2	85–96	92	2.7
Dry bean (high protein)	0.01–0.1	10	79–111	95	13	81–122	102	14.7
Barley (high starch)	0.01–0.1	10	83–104	97	8.5	78–113	96	11.5
Grape (high acid)	0.01–10	15	80–87	83	2.3	77–91	85	5.3
Cumin (other)[a]	0.01–5.0	15	79–120	93	15.8	84–93	87	3.2

[a] Considered difficult to analyse

Table 76 Recovery results for phosphonic acid (QuPPe method - BCS 01501)

Sample material			1st MRM: m/z 80.9→62.9			2nd MRM: m/z 81→79		
	Fortified [mg/kg]	N	% Recoveries– range	Mean [%]	RSD [%]	% Recoveries– range	Mean [%]	RSD [%]
Lettuce (high water)	0.1–100	15	72–94	81	7.0	72–102	86	8.3
Avocado (high oil)	0.5–20	15	88–95	91	2.5	88–98	92	2.9
Dry bean (high protein)	0.1–1.0	10	79–103	94	9.0	79–105	96	9.5
Barley (high starch)	0.1–1.0	10	89–107	96	6.8	90–106	98	4.8
Grape (high acid)	0.1–50	15	77–95	85	7.2	79–98	86	7.6
Cumin (other)[a]	0.5–250	15	83–94	89	3.2	87–96	92	2.8

[a] Considered difficult to analyse

Extraction efficiency

A cross-validation study to compare the extraction efficiencies of the LC-MS/MS methods (method 00861/M001 and the QuPPe-method) with the initial GC-MS method AR 155-97/DFG 522 was reported by Meklat, 2016 [Ref: MR-14-18]. In this study, incurred residues in samples of lettuce, strawberry and zucchini from supervised field trials were analysed five times using the extraction procedures for each of the three analytical methods. Extraction efficiency was calculated as the ratio (expressed as percentage) between the average residues measured using the extraction procedures from method 00861/M001 or method 01501 and the average residues measured using the extraction procedure of the method DFG 522.

Residues in control samples were all below 30% of the LOQ (0.01 mg/kg) for fosetyl-Al, with phosphonic acid residues in control samples measured at up to 38% of LOQ (0.2 mg/kg). The RSD values were < 20% for fosetyl-Al, but occasionally above 20% for phosphonic acid.

In strawberry and zucchini, extraction efficiency ratio of the LC-MS/MS methods were between 70% and 130% (fosetyl-Al) and 68–113% (phosphonic acid) of the efficiency of the GC-MS methods.

Table 77 A comparison of residue levels determined by Method DFG 522, Method 00861/M001 and the QuPPe-Method

		Fosetyl-Al			Phosphonic acid		
Sample material	Method used	Mean value[a] (mg/kg)	RSD (%)	Ratio[b] (%)	Mean value[a] (mg/kg)	RSD (%)	Ratio[b] (%)
Lettuce-1	DFG 522	0.056	6.2	-	13	7.3	-
	00861/M001	0.033	22.5	59	24	1.5	185
	QuPPe	0.019	21.0	34	19	6.1	146
Lettuce-2	DFG 522	0.20	9.0	-	10	5.0	-
	00861/M001	0.12	4.6	60	21	1.9	210
	QuPPe	0.08	4.1	40	17	5.0	170
Strawberry-1	DFG 522	2.1	5.4	-	35	7.4	-
	00861/M001	2.7	14.0	129	41	8.8	117
	QuPPe	1.9	16.5	90	27	19.5	77
Strawberry-2	DFG 522	0.23	3.8	-	31	2.7	-
	00861/M001	0.30	5.2	130	34	5.3	110
	QuPPe	0.20	6.4	87	21	8.7	68
Zucchini-1	DFG 522	0.054	11.6	-	9.9	8.0	-
	00861/M001	0.059	3.3	109	11	2.5	111
	QuPPe	0.052	7.5	96	9.5	3.3	96
Zucchini-2	DFG 522	0.052	3.3	-	16	3.4	-
	00861/M001	0.061	6.7	117	18	3.4	113
	QuPPe	0.054	3.5	104	15	3.8	94

[a] Mean value of 5 independent analyses of each treated sample.

[b] Ratio (percentage) between the average residues measured using these extraction procedures and the average residues measured using the extraction procedure of the method DFG 522.

A follow-up study comparing the two LC-MS/MS methods (Method 00861/M001 and the QuPPe-Method) was reported by Meklat & Meilland-Berthier, 2015 [Ref: MR-15/055]. In this study, lettuce, strawberry and zucchini field trial samples were analysed in parallel using the two methods.

In this study, residues in control samples were all < 30% LOQ, the linearity correlation coefficients were above 0.99 over the range 0.05–20 mg/kg (fosetyl-Al) and 0.5–200 mg/kg (phosphonic acid) and the individual concurrent recovery rates were 75–101% for fosetyl-Al and 70–99% for phosphonic acid (RSDs < 5%).

The method 00861/M001 used as data generation method and the multi-residue QuPPe-Method version 7.1 showed similar results on lettuce and zucchini for phosphonic acid. For strawberry the method 00861/M001 showed higher results for phosphonic acid with higher concurrent recoveries.

For fosetyl-Al, method 00861/M001 showed higher residues than the QuPPe method (ratio ≤ 75%) for lettuce, strawberry and zucchini except for one result (zucchini ratio: 115%).

The RSD obtained for each triplicate analysis was < 10% demonstrating the good repeatability for both methods. Highest RSDs were for strawberry (QuPPE method) with RSDs of 14% for fosetyl-Al and 13% for phosphonic acid.

Table 78 Comparison of residue levels obtained with the two LC-MS/MS analytical methods for fosetyl-Al and phosphonic acid

		Fosetyl-Al				Phosphonic acid			
Sample material	Method used	Range (mg/kg)	Mean[a] (mg/kg)	RSD (%)	Ratio[b]	Range (mg/kg)	Mean[a] (mg/kg)	RSD (%)	Ratio[b]
Lettuce-1	00861/M001	0.62–0.68	0.65	4.6	69%	44–45	44	1.3	109%
	QuPPe (01501)	0.44–0.46	0.45	2.5		47–49	48	2.1	
Lettuce-2	00861/M001	1.1–1.2	1.1	5.1	70%	67–78	73	7.8	100%
	QuPPe (01501)	0.72–0.82	0.77	6.5		70–75	73	3.9	
Strawberry-1	00861/M001	0.39–0.41	0.40	2.5	58%	31–33	32	3.1	69%
	QuPPe (01501)	0.21–0.27	0.23	13.8		19–24	22	12.9	
Strawberry-2	00861/M001	8.7, 8,7	8.7	-	75%	25–28	27	5.7	70%
	QuPPe (01501)	6.2–6.8	6.5	4.7		19–20	19	3.0	
Zucchini-1	00861/M001	0.57–0.62	0.59	4.2	115%	15–16	16	3.7	113%
	QuPPe (01501)	0.64–0.72	0.68	5.9		18–18	18	0.0	
Zucchini-2	00861/M001	0.12–0.13	0.13	4.6	64%	16–19	18	8.6	94%
	QuPPe (01501)	0.082–0.086	0.083	2.8		16–18	17	5.9	

[a] Mean value of 3 independent analyses of each sample

[b] The ratio (percentage) between the average residues of fosetyl-AL and phosphonic acid measured using the method QuPPe (01501) and the residues measured using the method 00861/M001

Analytical (concurrent) recoveries in supervised crop trials

Analytical recovery rates were measured in all the supervised crop field trials, with control samples being fortified with fosetyl-Al, fosetyl or phosphonic acid (as appropriate) at the LOQs of the methods and at higher levels that generally reflected the range of expected residues in the commodities tested. For each study, average recoveries per fortification level generally fell within the 70–120% range, with a relative standard deviation of 20% or less. Mean recovery rates for each analyte are reported in the individual crop residue supervised trials evaluations.

Stability of residues in stored analytical samples

The Meeting received information on the stability of residues of fosetyl-Al and phosphonic acid in a range of representative commodities.

Fosetyl-Al residue stability

In storage stability studies conducted in Europe, the stability of residues of fosetyl-Al and its metabolite phosphonic acid in frozen stored samples was investigated in vegetables (cucumber, cabbage, potato, tomato, lettuce), dry beans and in fruit (grapes, avocado, orange, pineapple) stored for up to 12 or 24 months. Diot & Kieken, 2001 [Ref: C013256 (M-204268-01-1)], Rosati & Venet, 2007 [Ref: MR-07/364 (M-296649-01-1)], Meklat, 2016 [Ref: 13-02 (M-529397-02-1)] and Anon, 1979 [Ref: R003861 (M-165522-01-1)]. Results of these studies are summarised below.

Table 79 Residue stability of fosetyl-Al and produced phosphonic acid in a range of plant matrices spiked at 2.0 mg/kg fosetyl-Al and stored at -18 °C to -20 °C for up to 24 months

Matrix	Storage period (days)	Fosetyl-Al			Phosphonic acid (as fosetyl-Al)			Total (as fosetyl-Al)	
		Residues remaining (mg/kg)	Residues remaining %	Procedural Recovery %	Residues remaining (mg/kg)	Residues remaining %	Procedural recovery %	Residues remaining (mg/kg)	Residues remaining %
C013256 (M-204268-01-1)									
Grape	0	1.9, 2.2	103	-	0.6, 0.5	28	-	2.8, 2.4	130
	105	1.4, 1.5	73	123	0.4, 0.4	20	77	1.9, 1.8	93
	180	1.4, 1.4	70	118	0.4, 0.4	20	98	1.8, 1.8	90
	270	1.4, 1.6	75	100	0.4, 0.4	20	100	1.8, 2.0	95
	365	1.5, 1.3	70	106	0.4, 0.4	20	72	1.9, 1.7	90
Cucumber	0	1.5, 1.5	75	-	0.5, 0.5	25	-	2.0, 2.0	100

Matrix	Storage period (days)	Fosetyl-Al			Phosphonic acid (as fosetyl-Al)			Total (as fosetyl-Al)	
		Residues remaining (mg/kg)	Residues remaining %	Procedural Recovery %	Residues remaining (mg/kg)	Residues remaining %	Procedural recovery %	Residues remaining (mg/kg)	Residues remaining %
	105	1.1, 0.9	50	109	0.5, 0.3	20	100	1.6, 1.2	70
	180	1.0, 1.0	50	85	0.4, 0.7	28	93	1.4, 1.7	78
	270	0.9, 1.0	48	101	0.7, 0.7	35	97	1.6, 1.7	83
	365	0.6, 0.7	33	108	1.0, 0.8	45	105	1.6, 1.5	78
Potato	0	1.7, 1.7	85	-	0.5, 0.6	28	-	2.2, 2.3	113
	120	0.5, 0.6	28	77	0.9, 1.3	55	88	1.4, 1.9	83
	180	0.3, 0.4	18	105	1.8, 1.5	83	106	2.1, 1.9	100
Lettuce	0	1.5, 1.5	75	-	0.5, 0.5	25	-	2.0, 2.0	100
	105	0.9, 0.9	45	95	0.8, 0.8	40	78	1.7, 1.7	85
	180	0.4, 0.6	25	106	1.2, 1.1	58	107	1.6, 1.7	83
MR-07/364 (M-296649-01-1)									
Cucumber	0	2.04, 2.03	102	106	0.18, 0.16	9	104	2.22, 2.19	110
	64	1.68, 1.74	86	95	0.35, 0.30	16	112	2.03, 2.04	102
	162	1.65, 1.64	82	99	0.38, 0.39	19	108	2.03, 2.03	102
	244	1.50, 1.46	74	94	0.43, 0.47	23	101	1.93, 1.93	97
	371	1.26, 1.48	69	90	0.75, 0.54	32	94	2.01, 2.02	101
	587	1.47, 1.39	72	92	0.62, 0.62	31	100	2.09, 2.01	102
	761	1.18, 1.31	62	93	0.93, 0.82	44	102	2.11, 2.13	106
Cabbage	0	2.10, 2.12	106	103	0.06, 0.09	4	100	2.16, 2.21	109
	25	1.70, 1.69	85	91	0.17, 0.21	9	110	1.87, 1.90	94
	125	1.33, 1.32	66	101	0.66, 0.69	34	83	1.99, 2.01	100
	202	1.41, 1.35, 1.4	69	98	0.58, 0.73, 0.65	33	103	1.99, 2.08, 2.1	102
	330	1.02, 1.02	51	88	1.02, 0.99	50	89	2.04, 2.01	101
	550	0.85, 0.81	42	83	1.11, 1.14	56	92	1.96, 1.95	98
	734	0.67, 0.63	32	92	1.29, 1.34	66	100	1.96, 1.97	98
Potato	0	2.06, 2.06	103	112	0.14, 0.14	7	105	2.20, 2.20	110
	65	1.45, 1.54	75	92	0.58, 0.47	26	96	2.03, 2.01	101
	164	1.48, 1.54	76	108	0.55, 0.60	29	120	2.03, 2.14	104
	241	1.50, 1.24	69	109	0.66, 0.72	34	104	2.16, 1.96	103
	371	1.35, 1.40	69	90	0.74, 0.81	39	89	2.09, 2.21	108
	589	0.90, 1.05	49	99	1.19, 1.06	56	99	2.09, 2.11	105
	758	1.03, 0.91	48	98	1.07, 1.16	56	102	2.10, 2.07	104
Grapes	0	2.04, 2.08	103	101	0.16, 0.15	8	103	2.20, 2.23	111
	63	1.93, 1.92	96	97	0.19, 0.16	9	104	2.12, 2.08	105
	162	1.89, 1.92	95	103	0.28, 0.22	13	105	2.17, 2.14	108
	244	1.89, 1.92	95	101	0.23, 0.25	12	105	2.12, 2.17	107
	371	1.83, 1.83	92	93	0.24, 0.24	12	92	2.07, 2.07	104
	587	1.94, 1.87	95	99	0.24, 0.25	12	101	2.18, 2.12	107
	761	1.91, 1.90	95	94	0.26, 0.27	13	99	2.17, 2.17	109
13-02 (M-529397-02-1)									
Lettuce	0	1.8, 1.8, 1.7	88	102	0.15, 0.15, 0.15	11	100	1.96, 1.9, 1.86	99
	70	0.04, 0.05, 0.03	2	90	1.46, 1.3, 1.3	98	97	1.5, 1.36, 1.35	100
	148	0.00, 0.00, 0.00	0	95	1.36, 1.4, 1.45	101	102	1.96, 2.0, 2.09	101
Tomato	0	1.8, 1.9, 1.8	91	95	0.11, 0.17, 0.13	7	101	1.9, 2.05, 1.92	98
	78	1.2, 1.2, 1.2	61	90	0.75, 0.79, 0.75	38	101	1.99, 2.0, 1.94	99
	162	0.98, 1.1, 0.96	50	100	1.0, 0.99, 0.97	50	100	2.0, 2.06, 1.93	100
	261	0.25, 0.32, 0.35	15	98	1.77, 1.76, 1.67	87	100	2.0, 2.08, 2.02	102
Avocado	0	1.7, 1.7, 1.7	85	94	0.24, 0.25, 0.24	12	97	1.9, 1.95, 1.95	97
	67	0.58, 0.8, 0.56	32	87	1.25, 1.06, 1.3	60	94	1.8, 1.86, 1.86	92

Matrix	Storage period (days)	Fosetyl-Al			Phosphonic acid (as fosetyl-Al)			Total (as fosetyl-Al)	
		Residues remaining (mg/kg)	Residues remaining %	Procedural Recovery %	Residues remaining (mg/kg)	Residues remaining %	Procedural recovery %	Residues remaining (mg/kg)	Residues remaining %
	151	0.63, 0.58, 0.42	27	93	1.27, 1.4, 1.4	67	95	1.9, 1.97, 1.81	95
	251	0.23, 0.23, 0.36	14	93	1.67, 1.61, 1.5	80	95	1.9, 1.84, 1.87	93
	876	0.08, 0.12, 0.06	4	100	1.76, 1.8, 1.77	89	98	1.84, 1.93, 1.8	, 93,
Dry bean (seed)	0	1.6, 1.6, 1.6	81	81	0.17, 0.17, 0.17	9	76	1.73, 1.8, 1.8	89
	81	1.4, 1.3, 1.4	68	82	0.40, 0.32, 0.40	19	84	1.8, 1.65, 1.78	87
	169	1.5, 1.5, 1.5	73	94	0.37, 0.39, 0.40	19	85	1.8, 1.86, 1.85	92
	271	1.5, 1.5, 1.5	75	93	0.48, 0.46, 0.51	24	92	1.98, 1.9, 1.98	99
	343	1.4, 1.4, 1.4	69	95	0.47, 0.43, 0.44	22	87	1.83, 1.8, 1.83	91
	447	1.3, 1.3, 1.3	66	85	0.4, 0.41, 0.42	21	81	1.74, 1.74, 1.7	86
	587	1.5, 1.5, 1.5	76	106	0.37, 0.42, 0.33	19	88	1.9, 1.89, 1.85	94
	748	1.3, 1.2, 1.3	63	93	0.46, 0.45, 0.45	23	82	1.7, 1.69, 1.73	86
Orange	0	1.8, 1.75, 1.7	88	90	0.1, 0.12, 0.1	5	95	1.87, 1.87, 1.8	93
	78	1.7, 1.5, 1.5	77	95	0.33, 0.33, 0.32	16	95	2.0, 1.82, 1.78	93
	175	1.35, 1.3, 1.4	68	94	0.64, 0.7, 0.53	31	98	2.0, 1.98, 1.97	99
	266	1.1, 1.15, 1.15	56	99	0.90, 0.85, 0.86	44	94	1.96, 2.0, 2.01	99
	343	0.75, 0.97, 1.0	46	95	1.08, 0.97, 0.83	48	95	1.8, 1.94, 1.85	94
	442	0.85, 0.83, 0.6	38	95	0.95, 0.99, 1.22	53	92	1.8, 1.82, 1.82	91
	582	0.67, 0.73, 0.61	34	115	1.51, 1.30, 1.39	70	113	2.18, 2.03, 2.0	104
	745	0.48, 0.3, 0.38	19	94	1.43, 1.63, 1.51	76	96	1.91, 1.93, 1.9	95
R003861 (M-165522-01-1)									
Pineapple	0	1.78	89		0.25	13		2.03	102
	45	1.74	87		< 0.20	-		1.74	87
	75	1.10	55		0.80	40		1.90	95
	135	1.26	63		0.62	31		1.88	94
	240	< 0.20	-		1.05	53		1.05	53
Pineapple (20 mg/kg)	0	17.7	89		0.85	4.3		18.6	93
	45	14.9	75		3.20	16		18.1	91
	75	11.0	55		2.70	14		13.7	69
	135	11.2	56		3.19	16		14.4	72
	240	10.1	51		6.0	30		16.1	81

In studies conducted in USA, the stability of fosetyl-Al residues in frozen stored samples was investigated in peas (pods and seeds) avocado, dry ginseng root, pineapple and citrus for intervals up to 8 months. In addition, in supervised field trials conducted on lettuce, tomato, summer squash, apple (processing study), grape, strawberry and raspberry, the stability of fosetyl-Al residues in frozen stored samples was also investigated during storage intervals up to 12 months. Results of these studies are summarised below.

Table 80 Residue stability of fosetyl-Al in a range of plant matrices fortified with fosetyl-Al and stored at -18 °C to -20 °C for up to 12 months

Matrix	Fortification (mg/kg)	Storage period (days)	Residues remaining (mg/kg)	%Residues remaining	Procedural %Recovery	Reference
Succulent peas	0.5	0	0.43, 0.40	83	-	B004134 M-241104-01-1
		30	0.32, 0.34	66	82	
		59	0.32, 0.31	63	102	
		90	0.25, 0.22	47	79	
Pea pod	0.5	0	0.38, 0.35	73	-	
		30	n.d., n.d.	0	93	
		59	n.d., n.d.	0	72	
Avocado	1.0	0	0.71, 0.78	75	76	R000027 M-157712-01-1
		14	0.83, 0.78	81	95	
		30	0.46, 0.45	46	101	
		60	0.28, 0.34	31	106	
Dried ginseng root	1.0	14	0.82, 0.78	80	86	R000005 M-157663-01-1
		28	0.82, 0.91	87	85	
		56	0.85, 0.85	85	100	
		84	1.02, 1.02	102	103	
		154	0.84, 0.85	85	108	
Pineapple-1	1.0	0	1.0, 0.8	90	-	B004623 M-240106-01-2
		30	< 0.1, < 0.1	<10	-	
		60	< 0.1, < 0.1	<10	-	
Pineapple-2	1.0	0	0.72, 0.9	81	-	
		60	0.17, 0.32	23	72	
Pineapple, canned	1.0	0	0.84, 0.96, 1.07	96	-	
		30	0.85, 0.97	91	103	
		60	1.01, 1.08	105	98	
		90	0.88, 0.9	89	89	
		120	0.84, 0.85	85	62	
Orange	1.0	0	0.98, 0.76, 0.75	83	83	B004624 M-240107-01-2
		30	0.76, 0.73	75	97	
		60	0.93, 0.69	81	115	
		90	0.62, 0.51	57	88	
		120	0.51, 0.44	48	61	
Orange	1.0	0	0.787, 0.779	79	78	B004225 M-241183-01-1
		60	0.665, 0.726	70	71	
		120	0.631, 0.649	64	66	
		180	0.714, 0.674	69	67	
		300	0.641, 0.529	59	68	
		365	0.546, 0.538	55	73	
Lettuce	1.0	9	0.52	52	55	R009240 M-178971-01-1
		14	0.86	86	90	
		35	0.59	59	84	
		70	0.51, 0.54	53	95	
		133	0.89, 0.89	89	92	
		189	0.92, 0.92	92	102	
Tomato	1.0	14	0.63	63	76	C016048 M-201634-02-1
		30	0.81	81	107	
		60	0.76	76	95	
		120	0.66, 0.66	66	89	
Squash	1.0	14	0.99	99	100	R000018 M-157686-01-1
		30	0.41, 0.46	44	73	
		45	0.86	86	96	
		120	0.57, 0.55	56	90	
		180	0.68, 0.54	61	97	
Strawberry	1.0	7	1.00, 0.90	95	96	R000021 M-157696-01-1
		14	0.96, 0.99	98	91	
		30	0.85, 0.89	87	90	
		60	0.96, 1.02	99	99	
		90	0.97, 0.98	98	96	

Matrix	Fortification (mg/kg)	Storage period (days)	Residues remaining (mg/kg)	%Residues remaining	Procedural %Recovery	Reference
		120	0.81, 0.69	75	86	
Raspberry	1.0	7	1.28	128	-	781R10 M-157664-01-2
		14	0.93	93	-	
		28	0.73	73	-	
		70	0.99, 0.61	80	103	
Apple whole fruit	incurred[a]	0	0.27, 0.22, 0.29	-	-	R009270 M-179019-01-1
		192	0.31, 0.18, 0.16	96	-	
Apple wet pomace		0	0.06, < 0.05, < 0.05	-	-	
		192	0.16, 0.14	250	-	
Apple dry pomace		0	0.14 (mean)	79	-	
		192	0.11, 0.11		-	
Apple juice		0	0.39, 0.26	-	-	
		192	0.51, 0.51	159		
Grape	Incurred[b]	0	6.8, 13.2, 7.54	-		R000049 M-157771-01-1
		365	10.5, 14.5, 9.49	125		
Grape	Incurred[c]	0	150, 69, 166	-		R000047 M-157764-01-1
		365	121, 74, 177	97		

[a] First analysis for storage stability investigation using samples already stored frozen for 109 days.

[b] First analysis for storage stability investigation using samples already stored frozen for 15 days.

[c] First analysis for storage stability investigation using samples already stored frozen for 25 days.

In two short-term residue stability studies reported by Lakaschus & Gizler, 2013 [Ref: S13-02757, M-474379-01-1] and Schoening & Billian, 2010 [Ref: MR-10/009, M-388450-02-1], residue stability of fosetyl-Al was investigated in lettuce samples stored for 5 days at -5 °C and tomato samples stored for 4 hours at 1°C and then 7 days at -11°C. Results of these studies are summarised below.

Table 81 Residue stability of fosetyl-Al in lettuce and tomato matrices fortified with fosetyl-Al and cold-stored for 5–7 days

Matrix	Fortification (mg/kg)	Storage period (days)	Residues remaining (mg/kg)	%Residues remaining	Procedural %Recovery	Reference
Tomato	1.0	0	0.85, 0.94, 0.94, 0.94, 0.87	91	-	S13-02757 M-474379-01-1
		4 hrs @ 1°C+ 7 days @ -11°C	0.82, 0.81, 0.81, 0.83, 0.78	81	82	
Lettuce	0.439	0	0.46, 0.49, 0.46, 0.43, 0.37	100	-	MR-10/009 M-388450-02-1
		5 days @ -5 °C	0.28, 0.35, 0.36, 0.27, 0.31	72	99	

In summary, a rapid degradation of fosetyl-Al was often observed in high water content commodities, in some cases within weeks but in most cases the degradation started after 1–2 months. Longer stability was reported in one cucumber study (8 months) and apple matrices (at least 6 months). In green peas, significant degradation occurred within 1 month (50% remaining after 3 months storage

A rapid degradation was also observed in high oil content commodities, with less than 50% of initial fosetyl-Al residues remaining after 2–8 weeks. In high starch matrices, fosetyl-Al were stable for up to about 5 months.

In high acid matrices, residue stability was variable, fosetyl-Al being stable for at least 2 months in raspberries, at least 4 months strawberries and canned pineapple and up to 1–2 years in grapes. However in fresh pineapple, fosetyl-Al residues were more rapidly degraded (after about 6 weeks, attributed to enzymatic degradation. In orange, residue stability was not more than about 6 months.

In general, fosetyl-Al residues were not stable (with residues hydrolysing to phosphonic acid) in high water content and high oil commodities and residue stability was variable in high acid commodities. For the commodities tested, residues of fosetyl-Al were stable (i.e. more than 70% of residues remaining) for the following storage intervals:

Table 82 Summary of storage stability of fosetyl-Al in plant matrices

Category	Commodity group	Commodity	Stability period
High water content	Pome fruit	Apple, juice	at least 27 weeks
	Fruiting vegetables	Tomato Cucumber Summer squash	up to 9 weeks[a] up to 35 weeks up to 6 weeks[b]
	Brassica vegetables	Cabbage	up to 4 weeks
	Leafy vegetables	Lettuce	up to 2 weeks[c]
	Legume vegetables	Succulent pea seed Fresh pea pod	less than 4 weeks
High acid/high water content	Citrus	Orange	up to 25 weeks
	Small fruit and berries	Grape Strawberries Raspberry	at least 109 weeks at least 17 weeks up to 10 weeks
	Other fruit	Pineapple	up to 6 weeks
High oil/intermediate water content	Oily fruit	Avocado	up to 2 weeks
High starch/protein content	Pulses	Dry bean seed	up to 39 weeks
	Root and tuber vegetables	Potato	up to 23 weeks
Others		Ginseng (dried)	at least 22 weeks

[a] A significant residue decline (more than 30%) was observed after 2 weeks and 4 months of storage, but not after 1 and 2 months storage.

[b] Residue decline was already observed after 1 month storage, but there was no decline after 2.5 months storage. Residue decline was again observed after 4 and 6 months storage.

[c] A significant residue decline (more than 30%) was observed after 9 days, 5 and 10 weeks, but not after 2, 19 and 27 weeks.

Phosphonic acid residue stability

In the studies conducted in Europe on the stability of residues of fosetyl-Al in frozen stored samples, separate samples cucumber, cabbage, potato, tomato, lettuce, dry beans, grapes, avocado, orange, and pineapple were fortified with 2.0 mg/kg phosphonic acid and residue stability was investigated at intervals up to 12 months. Results of these studies are summarised below.

In addition, the stability of phosphonic acid residues in tree nuts was investigated in parallel with supervised field trials in USA. Control samples were spiked with 1 mg/kg phosphonic acid soon after arrival at the laboratory, held in freezer storage and analysed at the same time as the field trial samples. The results of these studies are included in the following Table.

Table 83 Residue stability of phosphonic acid in a range of plant matrices spiked at 2.0 mg/kg phosphonic acid and stored at -18 °C to -20 °C for up to 24 months

Matrix	Storage period (days)	Phosphonic acid			Reference
		Residues remaining (mg/kg)	Residues remaining %	Procedural Recovery %	
Grape	0	2.3, 2.0	108	104	C013256 M-204268-01-1
	105	1.8, 1.8	90	77	
	180	1.9, 2.0	98	98	
	270	2.1, 2.0	103	100	
	365	2.1, 2.1	105	72	
Cucumber	0	2.1, 1.7	95	114	
	105	1.6, 1.8	85	100	
	180	1.6, 1.6	80	93	
	270	2.1, 2.0	103	97	
	365	2.0, 1.9	98	105	
Potato	0	2.0, 2.0	100	90	

Matrix	Storage period (days)	Phosphonic acid			Reference
		Residues remaining (mg/kg)	Residues remaining %	Procedural Recovery %	
	120	1.7, 2.2	98	88	
	180	2.5, 1.7	105	106	
	270	1.7, 1.8	88	93	
	365	2.0, 2.0	100	103	
Lettuce	0	1.9, 1.8	93	101	
	105	1.8, 1.7	88	78	
	180	1.8, 1.5	83	107	
	270	1.6, 1.7	83	100	
	365	2.2, 2.1	108	103	
Cucumber	0	1.89, 1.93	96	104	MR-07/364 M-296649-01-1
	64	2.10, 1.68	95	112	
	162	2.10, 2.24	109	108	
	244	2.00, 2.04	101	101	
	371	2.07, 2.04	103	95	
	587	1.94, 1.99	98	101	
	761	2.13, 2.15	107	102	
Cabbage	0	1.94, 1.90	96	100	
	25	1.99, 1.98	99	111	
	125	2.07, 2.10	104	83	
	202	1.92, 1.94	97	104	
	330	2.00, 1.95	99	90	
	550	2.01, 1.96	99	100	
	734	1.97, 1.93	98	92	
Potato	0	1.99, 2.07	102	106	
	65	2.05, 2.03	102	97	
	164	2.01, 1.96	99	120	
	241	2.14, 2.07	105	104	
	371	2.01, 2.01	101	90	
	589	2.06, 2.05	103	100	
	758	2.03, 2.06	102	103	
Grapes	0	1.95, 1.85	95	103	
	63	2.08, 2.10	105	104	
	162	2.19, 2.19	110	105	
	244	2.09, 2.10	105	105	
	371	2.13, 2.09	106	92	
	587	2.03, 1.97	100	101	
	761	2.00, 2.05	101	99	
Lettuce (head)	0	1.85, 1.90, 1.89	94	100	13-02 M-296649-01-1
	70	1.87, 2.03, 1.96	97	97	
	148	1.97, 1.95, 1.96	98	102	
	256	1.87, 1.82, 1.81	91	98	
	326	1.89, 1.89, 1.94	96	103	
	424	1.73, 1.68, 1.86	88	96	
	567	1.89, 1.84, 1.84	93	109	
	729	1.79, 1.72, 1.76	88	96	
Cherry tomato (fruit)	0	1.93, 1.93, 1.96	97	101	
	78	1.92, 2.01, 1.95	98	101	
	162	1.87, 1.82, 1.92	93	100	
	261	1.86, 1.88, 1.90	94	100	
	342	1.85, 1.81, 1.81	91	98	
	435	1.84, 1.96, 2.06	98	107	
	576	1.78, 1.98, 2.13	98	106	
	741	1.80, 1.84, 1.78	90	94	
Avocado (fruit)	0	2.05, 1.82, 1.76	94	97	
	67	1.80, 1.99, 1.98	96	94	
	151	1.87, 1.85, 1.82	93	95	
	251	1.81, 1.81, 1.81	90	95	
	328	1.79, 1.72, 1.82	89	97	
	421	1.52, 1.78, 1.52	80	98	

Matrix	Storage period (days)	Phosphonic acid			Reference
		Residues remaining (mg/kg)	Residues remaining %	Procedural Recovery %	
	567	1.79, 1.83, 1.81	90	103	
	732	1.78, 1.85, 1.76	90	92	
White dry bean (seed)	0	1.47, 1.51, 1.52	75	76	
	81	1.60, 1.62, 1.55	79	84	
	169	1.67, 1.56, 1.55	80	85	
	271	1.73, 1.71, 1.72	86	92	
	343	1.56, 1.54, 1.53	77	87	
	447	1.58, 1.60, 1.67	81	81	
	587	1.79, 1.60, 1.62	84	88	
	748	1.56, 1.50, 1.53	77	82	
Orange (fruit)	0	1.79, 1.81, 1.79	90	95	
	78	1.76, 1.78, 1.75	88	95	
	175	1.87, 1.91, 1.88	94	98	
	266	1.80, 1.80, 1.78	90	94	
	343	1.70, 1.68, 1.70	85	95	
	442	1.89, 1.83, 1.67	90	92	
	582	1.94, 1.86, 1.84	94	113	
	745	1.79, 1.90, 1.88	93	96	
Pistachio nutmeat (1.0 mg/kg)	0	0.919, 0.893	91	-	IR4-11530
	221	0.809, 0.806, 0.858	83	90	
Almond nutmeat (1.0 mg/kg)	0	0.872, 0.92	90	-	IR4-11529
	218	0.705, 0.763, 0.737	74	87	
Walnut nutmeat (1.0 mg/kg)	0	0.781, 0.809, 0.849	81	-	IR4-11504
	146	0.691, 0.749, 0.749	73	87	

In the two short-term fosetyl-Al residue stability studies reported by Lakaschus & Gizler, 2013 [Ref: S13-02757, M-474379-01-1] and Schoening & Billian, 2010 [Ref: MR-10/009, M-388450-02-1], residue stability of phosphonic acid was also investigated in lettuce samples stored for 5 days at -5 °C and tomato samples stored for 4 hours at 1 °C and then 7 days at -11 °C. Results of these studies are summarised below.

Table 84 Residue stability of phosphonic acid in lettuce and tomato matrices fortified with phosphonic acid and cold-stored for 5–7 days

Matrix	Fortification (mg/kg)	Storage period (days)	Residues remaining (mg/kg)	%Residues remaining	Procedural %Recovery	Reference
Tomato	1.0	0	0.89, 0.96, 1.05, 1.03, 0.92	96	-	S13-02757 M-474379-01-1
		4 hrs @ 1°C+ 7 days @ -11°C	1.03, 1.02, 1.0, 0.99, 1.04	102	104	
Lettuce	0.776	0	0.73, 0.76, 0.76, 0.77, 0.81	100	-	MR-10/009 M-388450-02-1
		5 days @ -5 °C	0.77, 0.58, 0.8, 0.83, 0.86	100	112	

In summary, residues of phosphonic acid residue in frozen stored analytical samples show no significant degradation over the 12–25 month storage intervals. Similarly, total residues of fosetyl-Al and phosphonic acid (calculated as fosetyl-Al) were also stable over the 12–25 month study periods.

Table 85 Summary of storage stability of phosphonic acid in plant matrices

Category	Commodity	Months[a]
High water	Cucumber	12, 25
	Cabbage	24
	Lettuce	12, 24
	Tomato	24
High oil	Avocado	24
High protein	Bean	25
High starch	Potato	12, 25
High acid	Grape	12, 25

Category	Commodity	Months[a]
	Orange	25

[a] Maximum investigated times

USE PATTERNS

Summary information on GAP for fosetyl-Al and fosetyl in over 90 countries and over 30 crops was available, with authorised labels provided for representative countries in Europe and the Americas. GAP information (and authorised labels) for phosphonic acid (as potassium salts) were also available from Australia, Europe and USA.

The following tables summarise the representative critical GAPs for fosetyl-Al, fosetyl and phosphonic acid for crops relevant to the available residue field trials.

Table 86 Representative registered uses of fosetyl-Al

Crop	Country	Application						PHI (days)	Remarks
		type	method	no	kg ai/hL (max)	water L/ha	kg ai/ha (max)		
Citrus fruits									
Citrus	Brazil	F	Foliar	4	0.2	1000 - 2000		25	
Citrus	Brazil	N	Foliar	3	0.2			Seedlings	
Citrus	Central Americas	F	Foliar		0.48		1.6	15	
Citrus	Costa Rica	F	Foliar	2			4.0	15	
Citrus	Cyprus	F	Foliar	4	0.2		5.6	14	
Citrus	Cyprus	F	PH dip	1	0.4			PH	
Citrus	France	F	Foliar	3		1000	2.0	15	
Citrus	Greece	F	Foliar	4	0.24	2000 - 4000	9.6	3	
Citrus	Nicaragua	F	Foliar				3.6	30	
Citrus	Spain	F	Foliar	3	0.24		7.2	14	
Citrus	Spain	F	Drip	2			8.0	14	20 g ai/tree
Citrus	United States	F	Trunk spray		9.6			30	
Citrus	United States	F	Foliar	4	0.096	4670 max	4.48	12 hours	18 kg ai/ha/year
Pome fruits									
Apple	Belgium	F	Foliar	3			1×3.0 2×2.0	28	
Apple	Brazil	F	Foliar	3	0.2	1000 min		35	
Apple	Cyprus	F	Foliar	4	0.2		4.0	14	
Apple	Greece	F	Foliar	4	0.2	1000–2000	4.0	3	
Pear	Belgium	F	Foliar	3			1×3.0 2×2.0	28	
Pear	Cyprus	F	Foliar	4	0.2		2.0	14	
Pome fruit	France	F	Foliar	4			2.0	28	
Pome fruit	France	F	Foliar	3			3.0	28	
Pome fruit	Hungary	F	Foliar	4		500–700	3.2	30	
Pome fruit	Spain	F	Foliar	3	0.24			28	
Pome fruit	United States	F	Foliar		0.096	4670 max	4.48	14	except persimmons
Berries and other small fruits									
Grape	Brazil	F	Foliar		0.2	1000 min		15	
Grape	Central Americas	F	Foliar		0.48		1.6	30	
Grape	Cyprus	F	Foliar		0.2			14	
Grape	Czech Republic	F	Foliar	3		200–500	1.0	Pre-flower	
Grape	Czech Republic	F	Foliar	3		200–1000	2.0	21	
Grape	Denmark	F	Foliar	6	0.2	200–1000	2.0	35	
Grape	Greece	F	Foliar	4	0.2	500–1500	3.6	14	
Grape	United States	F	Foliar	7		93 min	4.48	15	
Strawberry	Central Americas	F	Foliar		0.48		1.6	15	
Strawberry	Costa Rica	F	Foliar				2.0	15	

Crop	Country	Application						PHI (days)	Remarks
		type	method	no	kg ai/hL (max)	water L/ha	kg ai/ha (max)		
Strawberry	Cyprus	F,G	Root dip		0.16			Pre-plant	
Strawberry	Cyprus	F,G	Foliar		0.32			14	
Strawberry	Denmark	F,G	Foliar	3		800–1000	3.2	14	
Strawberry	Denmark	F,G	Root dip	1			0.2	Pre-plant	
Strawberry	Finland	F	Foliar	3		800–1000	3.2		
Strawberry	Finland	F,G	Root dip	1	-0.24			Pre-plant	
Strawberry	France	F,G	Foliar	3			4.0	14	
Strawberry	Germany	F	Foliar	1		5 000	40	Late Sept	
Strawberry	Germany	F	Root dip	1	0.4			Pre-plant	
Strawberry	Greece	F,G	Foliar	1	0.32	500–700	2.24	Seedlings	
Strawberry	Greece	F,G	Foliar	4	0.32	500–700	2.24	14	
Strawberry	Netherlands	F	Root dip	1	0.2			Pre-plant	
Strawberry	Netherlands	F	Inter-row	3	0.6	1 000	6.0	14	
Strawberry	Spain	F,G	Foliar	3	0.24		2.4	14	
Strawberry	Sweden	F,G	Foliar	3	0.32	800–1000	3.2	42	
Strawberry	Sweden	F,G	Root dip	1	0.24			Pre-plant	
Strawberry	United States	F	Foliar				4.48	12 hours	27 kg ai/ha/season
Strawberry	United States	F	Root dip		0.24			Pre-plant	
Assorted tropical and sub-tropical fruit – inedible peel									
Avocado	Central Americas	F	Foliar		0.48		1.6	15	
Avocado	Cyprus	F	Foliar		0.3			7	
Avocado	Spain	F	Foliar	3	0.24			14	
Avocado	United States	F	Trunk spray		9.6			12 hours	
Avocado	United States	F	Foliar		0.096	4670 max	4.48	12 hours	18 kg ai/ha/year
Pineapple	Brazil	F	Foliar	3	0.2	60–1000		20	
Pineapple	Brazil	F	Seedling dip	1	0.08			Pre-plant	
Pineapple	Central Americas	F	Foliar		0.48		2.4	90	
Pineapple	Costa Rica	F	Foliar				3.6	90	
Pineapple	France	F	Seedling dip	1			6.0	Pre-plant	
Pineapple	Nicaragua	F	Foliar				3.6	90	
Pineapple	United States	F	Seedling dip		0.24			Pre-plant	
Pineapple	United States	F	Foliar	6	0.36	3740 max		90	
Fruiting vegetables, Cucurbits									
Cucurbits	United States	F	Foliar	7		93 min	4.48	12 hours	
Cucumber	Central Americas	F	Foliar		0.48		1.6	30	
Cucumber	Costa Rica	F	Foliar	7			4.24	30	
Cucumber	Cyprus	F	Drench		0.16		4.8	Seedlings	
Cucumber	Cyprus	F	Foliar		0.16			1	
Cucumber	Denmark	F,G	Foliar	4		1000	3.2	3	
Cucumber	Finland	F	Foliar	4	0.24	500–1000	2.4	3	
Cucumber	Germany	F	Foliar	4		600	2.4	3	
Cucumber	Germany	G	Foliar	3	0.4	600–1200	4.8	3	
Cucumber	Greece	F,G	Foliar	4	0.24	500–2000	4.8	1	
Cucumber	Hungary	F,G	Foliar			300–700	1.2	3	
Cucumber	Sweden	F	Foliar	4		800–1000	3.2	3	
Cucumber	Sweden	G	Foliar	4	0.32	1000	3.2	3	
Melon	Central Americas	F	Foliar		0.48		1.6	7	
Melon	Costa Rica	F	Foliar	7			4.24	7	
Melon	Cyprus	F	Drench		0.16		4.8	Seedlings	
Melon	Cyprus	F	Foliar		0.16			3	
Melon	Denmark	F,G	Foliar	2		1000	3.2	3	
Melon	France	F,G	Foliar	2			3.2	3	
Melon	Greece	F,G	Foliar	3	0.24	500–1000	4.8	3	
Melon	Nicaragua	F	Foliar				3.6	7	
Pumpkin/squash	Denmark	F,G	Foliar	2		1000	3.2	3	

Crop	Country	Application						PHI (days)	Remarks
		type	method	no	kg ai/hL (max)	water L/ha	kg ai/ha (max)		
Squash, summer	Central Americas	F	Foliar		0.48		1.6	30	
Squash, summer	Cyprus	F,G	Foliar		0.16			3	
Squash, summer	Cyprus	F	Drench		0.16		4.8	Seedlings	
Squash, summer	Denmark	F,G	Foliar	4		1000	3.2	3	
Squash, summer	Germany	F	Foliar	4		600	2.4	4	
Squash, summer	Greece	F,G	Foliar	4	0.24	500–2000	4.8	3	
Squash, winter	Cyprus	F	Foliar		0.16			3	
Squash, winter	Cyprus	F	Drench		0.16		4.8	Seedlings	
Watermelon	Central Americas	F	Foliar		0.48		1.6	7	
Watermelon	Costa Rica	F	Foliar	7			4.24	7	
Watermelon	Cyprus	F	Foliar		0.16			3	
Watermelon	Cyprus	F	Drench		0.16		4.8	Seedlings	
Watermelon	Greece	F,G	Foliar	3	0.24	500–1000	4.8	3	
Watermelon	Nicaragua	F	Foliar				3.6	7	
Winter squash	Central Americas	F	Foliar		0.48		1.6	30	
Winter squash	Greece	F,G	Foliar	3	0.24	500–1000	4.8	3	
Fruiting vegetables, other than Cucurbits									
Pepper, sweet	Cyprus	F	Drench		0.16		4.8	Seedlings	
Pepper, sweet	Cyprus	F	Foliar		0.3			14	
Tomato	Central Americas	F	Foliar		0.48		1.6	3	
Tomato	Cyprus	G	Foliar				3.2	3	
Tomato	Cyprus	F	Foliar				2.4	3	
Tomato	Greece	G	Foliar	3	0.32	500–2000	6.4	3	
Tomato	Greece	F	Foliar	3	0.24	500–1000	2.4	3	
Tomato	Nicaragua	F	Foliar				3.6	3	
Tomato	United States	F	Foliar			93 min	4.48	14	18 kg ai/ha/season
Leafy vegetables									
Leafy vegetables	United States	F	Foliar	7		93 min	4.48	3	
Lettuce	Central Americas	F	Foliar		0.48		1.6	30	
Lettuce	Costa Rica	F	Foliar	5			2.0	30	
Lettuce	Cyprus	F	Drench		0.16		4.8	Seedlings	
Lettuce	Cyprus	F	Foliar		0.3			3	
Lettuce	Finland	F,G	Foliar			400–600	2.4	14	
Lettuce	Germany	F	Foliar	3		600	2.4	14	
Lettuce	Germany	G	Foliar	2		1 000	2.4	14	
Lettuce	Greece	F	Drench	2			480	Seedlings	
Lettuce	Hungary	F,G	Foliar		0.12	600–1000	1.2	14	
Lettuce	Sweden	F	Foliar	4		400–600	2.4	14	
Lettuce	Sweden	G	Soil incorp	1			0.7 kg/m^3	Pre-plant	
Lettuce, leaf	Germany	F	Foliar	3		600	2.4	14	
Spinach	Central Americas	F	Foliar		0.48		1.6	30	
Spinach	Cyprus	F	Drench		0.16		4.8	Seedlings	
Spinach	Cyprus	F	Foliar		0.3			3	
Spinach	Greece	F,G	Foliar	3	0.24	500–1000	2.4	15	
Dried herbs									
Hops	Belgium	F	Foliar	3			2.24	14	for 3 m high rows
Hops	France	F	Foliar	8			5	14	
Hops	Germany	F	Foliar	2		1 000	2	Seedlings	
Hops	Germany	F	Foliar	8			8.0	14	
Hops	Greece	F	Foliar	2	0.24	500–1000	2.4	3	
Hops	United States	F	Foliar				2.24	24	9 kg ai/ha/season

Note: Central American countries are Belize, El Salvador, Dominican Republic, Guatemala, Honduras and Panama.

F = field use, G = glasshouse/indoor use, N = nursery use/seedling treatments

Table 87 Representative registered uses of fosetyl (co-formulated with propamocarb)

Crop	Country	Application						PHI (days)	Remarks
		type	method	no	kg ai/hL (max)	water L/ha	kg ai/ha (max)		
Fruiting vegetables, Cucurbits									
Cucumber	Belgium	G	Drip	4			0.93	3	
Cucumber	Denmark	G	Drench	2		20000–40000	0.001	Seedlings	
Cucumber	Denmark	G	Drip	4			0.93	3	
Cucumber	Denmark	F	Drip	2			0.93	3	
Cucumber	France	G	Drip	4			0.93	3	
Cucumber	France	F	Drip	2			0.93	3	
Cucumber	France	N	Drench	2			9.3	3	
Cucumber	Hungary	G	Drench	2		20 000	9.3	Seedlings	
Cucumber	Hungary	G	Drip	4			0.93	3	
Cucumber	Portugal	N	Drench	2			9.3	Seedlings	
Cucumber	Portugal	F,G	Drip	1			0.62-0.93	Seedlings	
Cucumber	Sweden	G	Drench	2		20000–40000	9.3	Seedlings	
Cucumber	Sweden	G	Drip	4			0.93	3	
Melon	France	G	Drip	4			0.93	3	
Melon	France	F	Drip	2			0.93	3	
Melon	France	N	Drench	2			9.3	3	
Melon	Portugal	N	Drench	2			9.3	Seedlings	
Melon	Portugal	F,G	Drip	1			0.62-0.93	Seedlings	
Pumpkin/squash	Portugal	N	Drench	2			9.3	Seedlings	
Pumpkin/squash	Portugal	F,G	Drip	1			0.62-0.93	Seedlings	
Squash, summer	Belgium	G	Drip	4			0.93	3	
Squash, summer	France	N	Drench	2			9.3	3	
Squash, summer	France	G	Drip	4			0.93	3	
Squash, summer	France	F	Drip	2			0.93	3	
Squash, summer	Portugal	N	Drench	2			9.3	Seedlings	
Squash, summer	Portugal	F,G	Drip	1			0.62-0.93	Seedlings	
Watermelon	Hungary	G	Drench	2		20 000	9.3	Seedlings	
Watermelon	Hungary	G	Drip	4			0.93	14	
Watermelon	Portugal	N	Drench	2			9.3	Seedlings	
Watermelon	Portugal	F,G	Drip	1			0.62-0.93	Seedlings	
Fruiting vegetables, other than Cucurbits									
Eggplant	Belgium	G	Drip	4			0.93	3	
Eggplant	France	G	Drip	4			0.93	3	
Eggplant	France	F	Drip	2			0.93	3	
Eggplant	France	N	Drench	2			9.3	3	
Eggplant	Portugal	N	Drench	2			9.3	Seedlings	
Eggplant	Portugal	F,G	Drip	1			0.62-0.93	Seedlings	
Pepper, sweet	Belgium	G	Drip	4			0.93	3	
Pepper, sweet	France	G	Drip	4			0.93	3	
Pepper, sweet	France	N F	Drench Drip	2 2			18.6, 9.3 0.93	Seedlings 3	
Peppers	Hungary	G G	Drench Drip	2 4		20 000	18.6, 9.3 0.31-0.93	Seedlings 3	
Peppers	Portugal	N	Drench	2			9.3	Seedlings	
Peppers	Portugal	F,G	Drip	1			0.62-0.93	Seedlings	
Tomato	Belgium	G	Drip	4			0.93	3	
Tomato	Denmark	G	Drench Drip	2 4		20000–40000	0.001 0.93	Seedlings 3	
Tomato	Denmark	F	Drip	2			0.93	3	
Tomato	France	N G	Drench Drip	2 4			0.93	Seedlings 3	
Tomato	France	N F	Drench Drip	2 2			9.3 0.93	Seedlings 3	
Tomato	Hungary	N G	Drench Drip	2 4		20 000	9.3 0.93	Seedlings 3	
Tomato	Portugal	N	Drench	2			9.3	Seedlings	
Tomato	Portugal	F,G	Drip	1			0.62-0.93	Seedlings	

Crop	Country	Application						PHI (days)	Remarks
		type	method	no	kg ai/hL (max)	water L/ha	kg ai/ha (max)		
Tomato	Sweden	N G	Drench Drip	2 4		20000–40000	9.3 0.93	Seedlings 3	
Leafy vegetables									
Endive	Belgium	G	Foliar	1			0.775	21	
Lettuce	Denmark	F,G	Drench	2		20000–40000	0.001	Seedlings	
Lettuce	Denmark	F,G	Foliar	2		250–1000	0.775	21	
Lettuce	France	F	Foliar	2		400–1000	0.775	14	
Lettuce	France	G	Foliar	2			0.775	21	
Lettuce	Hungary	F	Foliar	2		400–800	0.775	14	
Lettuce	Hungary	G	Drench	2		20000	9.3	seedlings	
Lettuce	Hungary	G	Foliar	4		400–800	0.775	14	
Lettuce	Portugal	F	Foliar	2			0.775	14	
Lettuce	Portugal	N	Drench	2			9.3	Seedlings	
Lettuce	Portugal	G	Foliar	2			0.775	21	
Lettuce	Sweden	G	Drench	2			9.3	Seedlings	
Lettuce	Sweden	F,G	Foliar	2		250–1000	0.775	21	
Lettuce, head	Belgium	G	Foliar	2			0.775	21	
Lettuce, leaf	Belgium	G	Foliar	2			0.775	21	
Rucola	Belgium	G	Foliar	1			0.775	21	
Spinach	Belgium	F	Foliar	1			0.775	14	
Spinach	Belgium	G	Foliar	1			0.775	21	
Spinach	Portugal	F	Foliar	1			0.775	14	

F = field, G = glasshouse, N = nursery

Table 88 Representative registered uses of phosphonic acid (as mono- and di-potassium salts or a mixture of mono- and di-ammonium, potassium and sodium salts)

Crop	Country	Application[a]						PHI (days)	Remarks
		type	method	no	kg ai/hL (max)	water L/ha	kg ai/ha (max)		
Citrus fruits									
Citrus	Australia	F	Foliar			2000–5000	8.0	Not required	32 g ai/12 L/tree
Citrus	USA	F	Foliar	2–4		935–2300	6.76	Not required	Apply in spring, summer, autumn, 2-4 weeks before harvest
Citrus	USA	I	Post-harvest		1.8			PH	dip, drench, in-line spray
Berries and other small fruit									
Grapes	Australia	F	Foliar			500–2000	2.4	Not required	
Grapes	USA	F	Foliar	6		470 min 140 min (air)	1.9		7-10 day RTI
Tree nuts									
Tree nuts	USA	F	Foliar	6		930 min 190 min (air)	1.9	Not stated	Chemigation: max 3.8 kg ai/ha
Tree nuts	USA	F	Trunk	3	0.41				

[a] Application rates expressed as phosphorous acid equivalents.

Tree nuts: almond, beech nut, Brazil nut, butternut, cashew, chestnut, chinquapin, filbert, hazelnuts, hickory nut, macadamia nut, pecan, pistachio, and walnut

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials involving soil or foliar treatments of fosetyl, fosetyl-Al and phosphonic acid to the following crops.

Group	Crop	Active ingredient	Region/Country	Table no

Group	Crop	Active ingredient	Region/Country	Table no
Citrus fruits	Lemon	Fosetyl-Al	USA	89
	Mandarin	Fosetyl-Al	Europe	90
	Orange	Fosetyl-Al	Europe, USA, Brazil	91–93
	Grapefruit	Fosetyl-Al	USA	94
	Orange	Phosphonic acid	Europe	95
	Mandarin	Phosphonic acid	Europe	96
	Citrus (PH Dip)	Phosphonic acid	USA	97
Pome fruits	Apple	Fosetyl-Al	Europe, USA, Brazil	98–100
	Pear	Fosetyl-Al	Europe, USA	101–102
Berries and other small fruits	Grape	Fosetyl-Al	Europe, USA, Brazil	103–105
	Grape	Phosphonic acid	Australia	106
	Strawberry	Fosetyl-Al	Europe, USA	107–109|
Assorted tropical and sub-tropical fruits – Inedible peel	Avocado	Fosetyl-Al	Europe, USA	110–111
	Pineapple	Fosetyl-Al	Central America, Hawaii	112–113
Fruiting vegetables, Cucurbits	Cucumber	Fosetyl-Al	Europe, USA	114–115
	Summer squash	Fosetyl-Al	USA	116–117
	Melons	Fosetyl-Al	Europe, USA	118–120
Fruiting vegetables, other than Cucurbits	Peppers	Fosetyl	Europe	121–122
	Tomato	Fosetyl	Europe	123–124
	Tomato	Fosetyl-Al	USA	125
Leafy vegetables	Lettuce	Fosetyl-Al	Europe, USA	126–128
	Spinach	Fosetyl	Europe	129
	Spinach	Fosetyl-AL	USA	130
Tree nuts	Almond	Phosphonic acid	USA	131
	Pistachio	Phosphonic acid	USA	132
	Walnut	Phosphonic acid	USA	133
Dried herbs	Hops	Fosetyl-Al	Europe, USA	134–135

The supervised trials were well documented with laboratory and field reports. Laboratory reports included procedural recoveries with spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables unless residues in control samples exceeded the LOQ. In such cases, the residues found are noted as “c=nn mg/kg” and where these are greater than 20% of the residue in the corresponding samples from treated plots, the results are not considered suitable for estimating maximum residue levels. Residue data are recorded unadjusted for recovery unless noted.

Results from replicated field plots are presented as individual values. Residues and application rates have been reported as provided in the study reports except for finite values below the LOQ, where these have been reported as <LOQ mg/kg. The results from trials used for the estimation of maximum residue levels (underlined) have been rounded to two significant digits (or if close to the LOQ, rounded to one significant digit) in the Appraisal.

When multiple applications were made to a crop, the application rate, spray concentration and spray volume were not always identical from one application to the next. In most trials, the actual treatment rates were within 10% of the listed ‘target’ application rates, but if not, the actual treatment rates are listed.

In this Evaluation, the term ‘Total residues’ is used to report the sum of the phosphonic acid residues and the fosetyl/fosetyl-Al residues (expressed as phosphonic acid), using the following formulae:

$$\text{Total residue (as phosphonic acid) [mg/kg]} = \frac{\text{fosetyl-Al [mg/kg] x MW}_{\text{phosphonic acid}} \times 3}{\text{M}_{\text{fosetyl-Al}}} + \text{phosphonic acid [mg/kg]}$$

$\text{MW}_{\text{fosetyl-Al}}$: Molecular weight of fosetyl-Al = 354.1 g/mol

$\text{MW}_{\text{phosphonic acid}}$: Molecular weight of phosphonic acid = 82 g/mol

And

$$\text{Total residue (as phosphonic acid) [mg/kg]} = \frac{\text{fosetyl [mg/kg] x MW}_{\text{phosphonic acid}}}{\text{MW}_{\text{fosetyl}}} + \text{phosphonic acid [mg/kg]}$$

$\text{MW}_{\text{phosphonic acid}}$: Molecular weight of phosphonic acid = 82 g/mol

$\text{MW}_{\text{fosetyl}}$: Molecular weight of fosetyl = 110 g/mol

The conversion factors are 0.695 (fosetyl-Al to phosphonic acid) and 0.745 (fosetyl to phosphonic acid).

Citrus fruits

Lemons – fosetyl-Al

In supervised trials from USA four foliar sprays of fosetyl-Al (80 WDG) were applied to lemon trees at 27 to 42 day intervals and duplicate whole fruit samples were stored frozen for up to 194 days (except for trials in trials 10379-22 and 10379-23, where samples were stored for longer intervals of 253–257 days) before extraction and analysis using GC-FPD method 45205 to measure residues of fosetyl-Al. The overall mean concurrent recovery rate was 79% and the LOQ was 0.1 mg/kg.

Table 89 Residues in lemons from supervised trials in USA involving foliar applications of fosetyl-Al (80 WDG formulations)

LEMON Country, year Location (variety) References	Application				DALA	Fosetyl-Al residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	values	mean
GAP: USA	4	4.5		1000–3000	0	Max 18 kg ai/ha/season		
USA 1996 Hendry, FL (Bearss) B004224 10379-12	4	4.53–4.68	0.48	945–982	0	fruit	1.13, 1.01	1.1
USA, 1996 Tulare, CA (Lisbon) B004224 10379-18	4	4.44–4.53	0.24	1852–1880	0	fruit	1.24, 1.5	1.4
USA, 1996 Tulare, CA (Lisbon) B004224 10379-19	4	4.47–4.52	0.24	1861–1880	0	fruit	1.63, 2.71	2.2

LEMON	Application				DALA	Fosetyl-Al residues (mg/kg)		
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	values	mean
USA, 1996 Yuma, AR (Lisbon) B004224 10379-22	4	4.41–4.81	0.29–0.34	1403–1571	0	fruit	1.25, 1.57	1.4
USA, 1996 Calipatria, CA (Lisbon 8A) B004224 10379-23	4	4.27–4.59	0.26–0.39	1104–1749	0	fruit	1.24, 1.67	1.5

Mandarin – fosetyl-Al

In supervised trials conducted in Europe, four foliar sprays of fosetyl-Al (WG) were applied to mandarin trees, the first between growth stages BBCH 19 and 72, the second about 30 days later and the last applications were 35 and 15 days before harvest. Samples of whole fruit and sub-samples of flesh and peel were stored frozen for up to 187 days before extraction and analysis using GC method DFG 522 or AR 155-97 to measure residues of fosetyl-Al and phosphonic acid. Average concurrent recovery rates were 75–97% for fosetyl-Al and 81–109% for phosphonic acid (fortification levels of 0.2–50 mg/kg) and LOQs were 0.2–0.5 mg/kg. In many of the 2000 trials, control samples were found to contain residues of up to 0.72 mg/kg fosetyl-Al and up to 1.75 mg/kg phosphonic acid.

Table 90 Residues in mandarins from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

MANDARIN	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: USA	4	4.48			0				
GAP: Cyprus	4	5.6	0.2		14				
Spain, 2000 Valencia (Clementina de Nules) C013214 ESP0101	4	7.0	0.28	2500	0	fruit	9.2 c=0.52	28 c=1.8	34 c=2.1
					3		8.2 c=0.56	33 c=1.6	39 c=2
					7		5.0 c=0.58	28 c=1.2	31 c=1.6
					14		3.7 c=0.72	29 c=1.4	32 c=1.9
					14	flesh	< 0.5	29 c=1.6	29 c=1.9
					14	peel	6.0	45 c=1.7	49 c=2.1
Spain, 2000 Alicante (Marisol) C013214 ESP0102	4	7.0	0.35	2000	0	fruit	5.9	8.1	12
					3		7.4	8.1	13
					7		6.5	9.7	14
					16		1.4	9.1	10
					16	flesh	< 0.5 c=0.5	9.4 c=0.95	10 c=1.3
					16	peel	6.1	27	31

MANDARIN	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Spain, 2000 Sevilla (Clemenules) C013214 ESP0201	4	7.0	0.35	2000	0	fruit	9.7	32	39
						fruit[a]	c=0.58	c=1.2	c=0.85
					15		< 0.5	34	34
					15	flesh	< 0.5	26	26
					15	peel	< 0.5	61	61
Greece, 2000 Shinohori-Argolida (Klimentines) C013214 GRC0201	4	7.0	0.234	3000	0	fruit	3.9	20	23
							c=0.61		c=0.92
					3		1.2	18	19
							c=0.58		c=0.90
					7		0.61	12	12
							c=0.6	5	c=0.92
					14		0.52	12	12
							c=0.59		c=0.91
					14	flesh	< 0.5	5.9	6.2
					14	peel	< 0.5	13	13
Greece, 2000 Ireon-Argolida (Tirinthas) C013214 GRC0202	4	7.0	0.234	3000	0	fruit	1.1	20	21
							c=0.57		c=0.9
					14	fruit[a]	< 0.5	7.3	7.6
					14	flesh	< 0.5	7.5	7.8
					14	peel	< 0.5	7.0	7.3
Italy, 2000 Marconia MT (Clementino comune) C013214 ITA0201	4	7.0	0.466	1500	0	fruit	6.9	16	21
							c=0.53		c=0.87
					3		4.6	18	21
							c=0.5		c=0.85
					6		4.5	18	21
							c=0.53		c=0.87
					14		3.0	19	21
					14	flesh	0.96	10	11
					14	peel	2.3	30	32
Italy, 2000 Tursi MT (Clementino comune) C013214 ITA0202	4	7.0	0.466	1500	0	fruit	4.6	25	28
					16	fruit[a]	< 0.5	24	24
					16	flesh	< 0.5	19	19
					16	peel	< 0.5	33	33
Italy, 2001 Marconia di Pisticci (Clementino Comune) C025700 01R104-1	4	7.0	0.7	1000	0	fruit	2.6	19	21
					15	fruit[a]	0.4	19	19
					15	flesh	0.23	15	15
					15	peel	0.96	32	33
Greece, 2001 Sxinoxori - Argolidos (Climentines) C025700 01R104-2	4	7.0	0.234	3000	0	fruit	0.63	7.2	7.6
					14	fruit[a]	< 0.2	7.7	7.8
					14	flesh	< 0.2	4.4	4.5
					14	peel	0.43	16	16

[a] Calculated whole fruit residues [(peel weight × peel residues) + (flesh weight × flesh residues)] /total fruit weight

Orange – fosetyl-Al

In supervised trials conducted in Europe, four foliar sprays of fosetyl-Al (WG) were applied to orange trees, the first between BBCH 15 and 72, the second about 30 days later and the two last applications 35 and 15 days before harvest. Samples of whole fruit and sub-samples of flesh and peel were stored frozen for up to 186 days before extraction and analysis using GC method AR 155-97 to measure residues of fosetyl-Al and phosphonic acid. Average concurrent recovery rates were 74–93% for fosetyl-Al (fortification levels of 0.2–5 mg/kg) and 74–102% for phosphonic acid (fortification levels of 0.2–25 mg/kg) and the LOQs were 0.2 mg/kg.

Table 91 Residues in oranges from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

ORANGE Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: USA	4	4.48			0				
GAP: Cyprus	4	5.6	0.2		14				
Spain, 2000	4	7.0	0.28	2500	0	fruit	1.7	5.7	6.9
Valencia					3		1.2	8.1	8.9
(Navelina)					7		0.5	6.1	6.4
					14		0.44	7.8	8.1
C013213									
ESP0101					14	flesh	0.3	6.4	6.6
					14	peel	1.6	6.8	7.9
Spain, 2000	4	7.0	0.234	3000	0	fruit	1.6	5.2	6.3
Sevilla					14	fruit[a]	0.24	6.7	6.9
(Newhall)									
					14	flesh	< 0.2	6.7	6.8
C013213					14	peel	0.38	6.8	7.1
ESP0201								c=0.35	c=0.49
Spain, 2000	4	7.0	0.234	3000	0	fruit	2.8	3.7	5.6
Cordoba					3		1.2	7.0	7.8
(Navelina)								c=0.32	c=0.46
					7		0.41	7.3	7.6
C013213					15		0.22	6.1	6.3
ESP0202									
					15	flesh	< 0.2	7.7	7.8
					15	peel	0.25	4.8	5.0
Greece, 2000	4	7.0	0.234	3000	0	fruit	0.89	5.5	6.1
Shinohori-Argolida								c=0.41	c=0.55
(Novelines)					3		0.36	7.2	7.5
					7		0.61	5.4	5.8
C013213					14		< 0.2	1.7	1.8
GRC0201									
					14	flesh	< 0.2	6.4	6.5
					14	peel	< 0.2	4.2	4.3
Greece, 2000	4	7.0	0.234	3000	0	fruit	0.23	1.5	1.7
Ireon-Argolida					14	fruit[a]	< 0.2	6.8	6.9
(San Loutsiana)									
					14	flesh	< 0.2	7.9	8.0
C013213					14	peel	< 0.2	4.8	4.9
GRC0202									
Italy, 2000	4	7.0	0.466	1500	0	fruit	5.4	6.2	10
Marconia MT					3		4.1	7.4	10
(Navelina)					7		3.3	7.3	9.6
					14		1.7	7.8	9.0
C013213									
ITA0201					14	flesh	0.33	3.9	4.1
					14	peel	0.76	7.7	8.2
Italy, 2000	4	7.0	0.466	1500	0	fruit	5.1	10	14
Tursi MT					16	fruit[a]	0.3	7.6	7.8
(Navelina)									
					16	flesh	0.23	8.7	8.9
C013213					16	peel	0.44	5.5	5.8
ITA0202									

ORANGE Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Italy, 2001 Marconia di Pisticci (Navelina V.C) C025616 01R102-1	4	7.0	0.7	1000	0 15 15 15	fruit fruit[(a)] flesh peel	2.0 0.22 < 0.2 0.63	5.3 3.9 3.1 5.5	6.7 4.1 3.2 5.9
Greece, 2001 Sxinoxori - Argolidos (Merlin) C025616 01R102-2	4	7.0	0.7	3000	0 14 14 14	fruit fruit[a] flesh peel	0.6 0.21 < 0.2 0.22	5.2 3.3 3.6 2.8	5.6 3.4 3.7 3.0

[a] Calculated whole fruit residues [(peel weight × peel residues) + (flesh weight × flesh residues)] /total fruit weight

In supervised trials conducted in USA, four foliar sprays of fosetyl-Al (80 WDG) were applied to orange trees at 28 to 44 day intervals. Replicate whole fruit samples were stored frozen for up to 185 days (except in trials 10379-07, 10397-08, 10397-09, 10397-10, 10397-21 and 10397-24 where samples were stored for longer intervals of 202-280 days) before extraction and analysis using GC-FPD method 45205 to measure residues of fosetyl-Al. The overall mean concurrent recovery rate was 84% and the LOQ was 0.1 mg/kg.

Table 1292 Residues in oranges from supervised trials in USA involving foliar applications of fosetyl-Al (80 WDG formulations)

ORANGE Country, year Location (variety) References	Application				DALA	Fosetyl-Al residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	values	mean
GAP: USA	4	4.48		1000–3000	0			
USA 1996 Seminole, FL (Navel) B004224 10379-01	4	4.48–4.58	0.2–0.26	1749–2264	0	fruit	1.14, 0.51	0.83
USA 1996 Seminole, FL (Hamlin) B004224 10379-02	4	4.49–4.57	0.25–0.33	1394–1805	0	fruit	2.33, 1.47	1.9
USA 1996 Seminole, FL (Hamlin) B004224 10379-03	4	4.36–4.5	0.27–0.36	1244–1628	0	fruit	1.64, 2.2	1.9
USA 1996 Brevard, FL (Ambersweet) B004224 10379-04	4	4.45–4.63	0.24–0.31	1431–1880	0	fruit	0.9, 1.03	0.97
USA 1996 Orange, FL (Ambersweet) B004224 10379-07	4	4.49–4.68	0.48	935–973	0	fruit	1.49, 0.89	1.2

ORANGE Country, year Location (variety) References	Application				DALA	Fosetyl-Al residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	values	mean
USA, 1996 Orange, FL (Parson Brown) B004224 10379-08	4	4.44–4.5	0.47–0.48	926–954	0	fruit	1.25, 1.06	1.2
USA, 1996 St Lucie, FL (Pineapple) B004224 10379-09	4	4.41–4.57	0.48	926–954	0	fruit	0.48, 0.28	0.38
USA, 1996 Indian River, FL (Pineapple) B004224 10379-10	4	4.49–4.76	0.48	935–991	0	fruit	1.36, 0.63	1.0
USA, 1996 Willacy, TX (Everhard Navel) B004224 10379-13	4	4.40–4.71	0.31–0.33	1384–1459	0	fruit	2.23, 1.36	1.8
USA, 1996 Tulare, CA (Washington Navel) B004224 10379-16	4	4.47–4.50	0.24	1861–1880	0	fruit	0.86, 1.24	1.1
USA, 1996 Hemet, CA (Valencia) B004224 10379-21	4	4.15–5.51	0.14–0.2	2647–3367	0	fruit	1.23, 1.03	1.1
USA, 1996 Kern, CA (Olinda Valencia) B004224 10379-24	4	4.41–4.49	0.24	1833–1880	0	fruit	1.86, 2.92	2.4

Value in square brackets is the mean residue of two duplicate samples

In supervised trials conducted in Brazil, four foliar sprays of fosetyl-Al (WP) were applied to orange trees between BBCH 72 and 85 at about 60-day intervals. Samples of whole fruit were stored frozen for between 179 and 223 days before fosetyl-Al analysis and up to 252 days before phosphonic acid analysis. The analytical method was the LC-MS/MS method 00861/M001 with LOQs of 0.01 mg/kg (fosetyl-Al) and 0.1 mg/kg (phosphonic acid). Overall average concurrent recovery rates were 102% for fosetyl-Al (fortification levels of 0.1–10 mg/kg) and 96% for phosphonic acid (fortification levels of 0.1–100 mg/kg).

Table 93 Residues in oranges from supervised trials in Brazil involving foliar applications of fosetyl-Al (800 WP formulations)

ORANGE Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Brazil	4		0.2	2000	25				
Brazil, 2014 Holambra (Folha Murcha) F13-058/F15-015 F13-058-01	4	4.0	0.2	2000	0 14 24 34 42	fruit	1.6 0.14 0.094 0.076 0.099	6.1 c=1.5 5.7 c=1.5 7.3 c=1.8 8.3 c=4.9 8.9 c=2.6	7.2 c=1.5 5.8 c=1.5 7.4 c=1.8 8.3 c=4.9 9.0 c=2.6
Brazil, 2014 Piracicaba (Folha Murcha) F13-058/F15-015 F13-058-02	4	4.0 4.1	0.2	2000	0 14 24 34 42	fruit	1.2 0.27 0.31 0.18 0.12	11 c=0.40 8.7 c=0.53 11 c=0.63 10 c=0.49 12 c=0.59	11 c=0.41 8.9 c=0.54 12 c=0.64 11 c=0.50 12 c=0.60
Brazil, 2014 Aguai (Valencia) F13-058/F15-015 F13-058-03	4	4.0	0.2	2000	0 15 25 35 43	fruit	1.7 0.053 0.054 0.033 0.032	9.2 c=1.8 11 c=2.1 12 c=1.8 11 c=2.2 12 c=2.1	10 c=1.8 11 c=2.1 12 c=1.8 11 c=2.2 12 c=2.1
Brazil, 2014 Arthur Nogueira (Valencia) F13-058/F15-015 F13-058-04	4	4.0	0.2	2000	25	fruit	0.073	4.0	4.1
Brazil, 2014 Aguai Mogi Mirim (Valencia) F13-058/F15-015 F13-058-05	4	4.0	0.2	2000	25	fruit	0.048	7.8	7.8

Grapefruit – fosetyl-Al

In supervised trials conducted in USA, four foliar sprays of fosetyl-Al (80 WDG) were applied to grapefruit trees at 28 to 46 day intervals. Replicate whole fruit samples were stored frozen for up to 190 days (except in trials 10379-11 and 10397-20 where samples were stored for longer intervals of 204–274 days) before extraction and analysis using GC-FPD method 45205 to measure residues of fosetyl-Al. The overall average concurrent recovery rate was 76% and the LOQ was 0.1 mg/kg.

Table 94 Residues in grapefruit from supervised trials in USA involving foliar applications of fosetyl-Al (80 WDG formulations)

GRAPEFRUIT	Application				DALA	Fosetyl-Al residues (mg/kg)		
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	values	mean
GAP: USA	4	4.5		1000-3000	0			
USA, 1996 Seminole, FL (Flame) B004224 10379-05	4	4.50–4.61	0.2–0.27	1721–2264	0	fruit	0.57, 0.69	0.63
USA, 1996 Brevard, FL (Flame) B004224 10379-06	4	4.62–4.75	0.2–0.28	1656–2338	0	fruit	0.7, 1.31	1.0
USA, 1996 Lake, FL (Ruby Red) B004224 10379-11	4	4.44–4.52	0.48	926–945	0	fruit	1.66, 1.46	1.6
USA, 1996 Willacy, TX (Ruby Red) B004224 10379-14	4	4.36–4.69	0.31–0.32	1384–1450	0	fruit	1.12, 1.03	1.1
USA, 1996 Tulare, CA (Mellogold) B004224 10379-17	4	4.45–4.49	0.24	1852–1871	0	fruit	0.72, 0.85	0.79
USA, 1996 Hemet, CA (Marsh Ruby) B004224 10379-20	4	4.40–5.68	0.13–0.19	2993–3601	0	fruit	0.59, 0.26	0.43

Orange, Mandarin – phosphonic acid

In supervised trials on mandarins and oranges conducted in Europe, foliar sprays of phosphonic acid (as the mono- and di-potassium salts) were applied before flowering, early ripening and at maturity. Samples of whole fruit, and in some trials peel and flesh were stored frozen for up to 237 days before extraction based on method AR155-97 (sulphuric acid extraction, isopropanol dilution and diazomethane methylation, but residues were analysed by LC-MS/MS (as described in method 00861/M001). The LOQ of the method was 0.186 mg/kg (the lowest fortification level) and average concurrent recovery rates were 79–86% in fruit, flesh and peel fortified at 0.186–22 mg/kg.

In a further set of trials conducted in Europe, three foliar sprays of phosphonic acid (as the mono- and di-potassium salts) were applied at about 30 day intervals from about BBCH 72–74 and samples taken for subsequent analysis and also for post-harvest drench or in-line spray treatments with phosphonic acid. Unwashed fruit were either drenched continuously (in crates) for 30 seconds before being air-dried or were subjected to an in-line treatment of dry brushing, spraying with a 1 kg ai/hL solution of phosphonic acid (approx. 0.5 kg ai/tonne for fruit) and passing through a drying tunnel. The treated fruit were cool-stored for intervals up to 28 days before being sub-sampled and stored frozen for up to 128 days before analysis using the multi-residue QuPPe method to measure residues of phosphonic acid. The LOQ of the method was 1.0 mg/kg and average concurrent recovery rates were 90–97% in fruit, flesh and peel fortified at 1–20 mg/kg.

Table 95 Residues in oranges from supervised trials in Europe involving post-harvest and/or preharvest foliar applications of phosphonic acid (SL formulations of the mono- and di-potassium salts)

ORANGE	Application				DALA	Phosphonic acid residues (mg/kg)		
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		whole fruit	flesh	peel
GAP:								
Spain, 2010 Denia, Alicante (Navel Lane Late) TRC09-03R1	3	5.75–6.03	0.29–0.3	1942–2042	0	14.0		
					3	12.0		
					7	11.0		
					14	15.0		
					21	7.0		
Spain, 2010 Turis, Valencia (Navelate) TRC09-03R2	3	5.82–6.27	0.3	1971–2117	0	8.6		
					3	9.2		
					7	7.1		
					14	10.0		
					21	7.8		
Spain, 2010 Villareal, Castellón (Valencia, Late) TRC09-03R3	3	5.82–6.15	0.29	1992–2125	0	14		
					3	7.3		
					7	8.0		
					14	9.0	8.2	11.0
					21	7.1		
Spain, 2009 Alberic, Valencia (Navelina) TRC09-03R4	3	5.64–5.98	0.29–0.3	1905–2019	0	20.0		
					3	15.0		
					7	15.0		
					14	26.0	27.0	21.0
					21	15.0		
Spain, 2010 Pobla Llarga, Valencia (Navelina) TRC09-03R5	3	5.87–6.33	0.29	2025–2182	0	10.0		
					14	8.4		
Spain, 2010 Montesa, Valencia (Lane Late) TRC09-03R6	3	5.83–5.96	0.29	2011–2055	0	16.0		
					14	21.0		
Spain, 2010 Benifaio, Valencia (Navel Powell) TRC09-03R7	3	5.41–5.81	0.29	1866–2003	0	20.0		
					14	22.0	20.0	28.0
Spin, 2010 Albalat de la Ribera, Valencia (Lane Late) TRC09-03R8	3	5.33–5.97	0.29	1840–2058	0	22.0		
					14	22.0	23.0	17.0
Spain, 2015 Torrent, Valencia (Navelina) TRC15-138 R1	3 foliar+ 1 drench	4.0	0.2 0.5	2000	-0	10.0		
					0	28.7	13.4	72
					5	23.8		
					14	31.6		
					28	28	17.5	54.5
Spain, 2015 Torrent, Valencia (Navelina) TRC15-138 R1	3 foliar+ 1 in-line spray	4.0	0.2 1.0	1980–2010	-0	10.0		
					0	13.6	8.3	29.1
					5	20.6		
					14	17.8		
					28	15.0	10.7	26.3

ORANGE Country, year Location (variety) References	Application				DALA	Phosphonic acid residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		whole fruit	flesh	peel
Spain, 2015	3 foliar+	3.9–4.0	0.2	2000	-0	12.6		
Tortosa, Tarragona	1 drench		0.5		0	33.0	16.3	88
(Washington Navel)					5	38.6		
					14	38.2		
TRC15-138 R2					28	33.3	17.5	76
Spain, 2015	3 foliar+	3.9–4.0	0.2	1950–1990	-0	12.6		
Tortosa, Tarragona	1 in-line		1.0		0	23.3	19.4	33
(Washington Navel)	spray				5	28.4		
					14	21.4		
TRC15-138 R2					28	20.5	15.5	36.3
Spain, 2015	3 foliar+	4.0–4.1	0.2	2000	-0	8.2		
Benicarlo, Castellon, Spain	1 drench		0.5		0	23.2	10.3	66
(Newhall)					5	17.5		
					14	20.6		
TRC15-138 R3					28	20.1	9.8	51
Spain, 2015	3 foliar+	4.0–4.1	0.2	200–2030	-0	8.2		
Benicarlo, Castellon	1 in-line		1.0		0	18.4	11.2	43
(Newhall)	spray				5	12.5		
					14	16.5		
TRC15-138 R3					28	15.9	9.6	32.5
Spain, 2015	3 foliar+	4.0	0.2	2000	-0	16.8		
Algemesi, Valencia	1 drench		0.5		0	34.7	24.9	68
(Navelina)					5	31.0		
					14	26.7		
TRC15-138 R4					28	30.8	20.6	59
Spain, 2015	3 foliar+	4.0	0.2	2000	-0	16.8		
Algemesi, Valencia	1 in-line		1.0		0	25.3	20.0	42.5
(Navelina)	spray				5	17.8		
					14	20.6		
TRC15-138 R4					28	22.7	16.6	38.7

Table 96 Residues in mandarins from supervised trials in Europe involving post-harvest and/or pre-harvest foliar applications of phosphonic acid (SL formulations of the mono- and di-potassium salts)

MANDARIN Country, year Location (variety) References	Application				DALA	Phosphonic acid residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		whole fruit	flesh	peel
GAP:								
Spain, 2010	3	6.02–	0.29–0.3	2058–2083	0	13		
Denia, Alicante		6.17			3	11		
(Ortanique)					7	12		
					14	8.6		
TRC09-02-02R1					21	10		
Spain, 2009	3	5.76–	0.29–0.3	1971–1999	0	28		
Alberic, Valencia		5.92			3	38		
(Orogrande)					7	32		
					14	15		
TRC09-02-02R2					21	26		
Spain,2009	3	5.72–	0.29	1967–2042	0	7.8		
Almarossa, Castellón		5.97			3	17		
(Clemenules)					7	13		
					14	11	9.7	14
TRC09-02-02R3					21	10		
Spain, 2009	3	5.73–	0.29	1958–2083	0	17		
Villareal, Castellón		5.92			3	24		
(Mioro)					7	18		
					14	18	18	18
TRC09-02R4					21	21		

MANDARIN Country, year Location (variety) References	Application				DALA	Phosphonic acid residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		whole fruit	flesh	peel
Spain, 2009 Pobla Llarga, Valencia (Afourer) TRC09-02R5	3	5.79–5.93	0.29	1981–2032	0	34		
					14	39		
Spain, 2010 Benissanó, Valencia (Clemenules) TRC09-02R6	3	5.34–5.9	0.29	1827–2022	0	33		
					14	33		
Spain, 2010 Moncofar, Castellón (Clementina tomatera) TRC09-02R7	3	5.37–5.84	0.29	1839–2001	0	31		
					14	27	23	39
Spain, 2010 Montesa, Valencia (Clemenvilla) TRC09-02R8	3	5.69–5.95	0.29	1950–2038	0	29		
					14	23	25	17
Spain 2015 Chella, Valencia (Marisol) TRC15-139 R1	3 foliar+ 1 drench	4.0	0.2 0.5	2000	-0	18.6		
					0	20.7	10.2	54.5
					5	35.0		
					14	23.6		
					28	27.8	10.7	87
Spain 2015 Chella, Valencia (Marisol) TRC15-139 R1	3 foliar+ 1 in-line spray	4.0	0.2 1.0	200–2020	-0	18.6		
					0	33.9	20.4	75
					5	35.2		
					14	43.3		
					28	43.4	29.9	93
Spain 2015 Tortosa, Tarragona (Clemenpons TRC15-139 R2	3 foliar+ 1 drench	4.0	0.2 0.5	1990–2010	-0	19.8		
					0	27.9	14.2	73
					5	26.6		
					14	40.4		
					28	35.6	18.3	99
Spain 2015 Tortosa, Tarragona, Spain (Clemenpons) TRC15-139 R2	3 foliar+ 1 in-line spray	4.0	0.2 1.0	2000	-0	19.8		
					0	27.7	18.3	54
					5	33.0		
					14	28.3		
					28	29.7	20.3	63
TRC15-139 Torrent, Valencia (Marisol) TRC15-139 R3	3 foliar+ 1 drench	3.8–4.1	0.2 0.5	1930–2030	-0	17.4		
					0	30.1	20.8	57
					5	29.5		
					14	26.1		
					28	36	27.7	64
Spain 2015 Torrent, Valencia (Marisol) TRC15-139 R3	3 foliar+ 1 in-line spray	3.9–4.1	0.2 1.0	1930–2030	-0	17.4		
					0	24.3	15.7	50
					5	26.5		
					14	24.8		
					28	35.9	27.8	63
Spain 2015 Algemesi, Valencia (Satsuma) TRC15-139 R4	3 foliar+ 1 drench	4.0	0.2 0.5	1990–2020	-0	11.7		
					0	19.4	15.9	30.2
					5	32.2		
					14	25.5		
					28	25.8	14.5	70

MANDARIN Country, year Location (variety) References	Application				DALA	Phosphonic acid residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		whole fruit	flesh	peel
Spain 2015	3 foliar+	4.0	0.2	1990–2020	-0	11.7		
Algemesi, Valencia	1 in-line spray		1.0		0	24.3	17.9	44.9
(Satsuma)					5	25.1		
					14	21.9		
TRC15-139 R4					28	28	19.4	59

Citrus (post harvest) – phosphonic acid

In post-harvest trials conducted in USA with oranges, mandarins, lemons and grapefruit, mature washed fruit were treated with phosphonic acid (potassium salts) as a dip, drench or an in-line spray. In the dip treatments, fruit were placed in crates and dipped in the treatment solution for 30 seconds. Drench treatments were applied by rolling the fruit over PVC pipes while the test solution was poured through holes in the drench tank. The in-line sprays were applied using a single flat fan nozzle to spray the fruit while rolling over PVC pipes. The treated fruit was allowed to dry and then samples were taken and stored frozen for up to 397 days before analysis for phosphonic acid using the multi-residue QuPPe method. The LOQ of the method was 1.0 mg/kg (the lowest level of method validation) and average concurrent recovery rates were 53–80% in fruit fortified at 1–20 mg/kg.

Table 97 Residues in citrus from supervised trials in USA involving post-harvest dip, drench or in-line spray applications of phosphonic acid (as the mono- and di-potassium salts)

CITRUS Country, year Location (variety) References	Application		DALA	matrix	Phosphonic acid residues (mg/kg)	Notes
	method	kg ai/hL				
GAP: USA	Dip, drench, in-line	1.8	-			
Orange						
USA, 2012 Parlier, CA (Cutter)	Dip	0.6	0	Whole fruit	8.8	Dip with drencher reservoir tank and plastic fruit crate
	Drench	0.6	0	Whole fruit	7.4	Drench with drencher treater
IR4-10687 12-CA84	In-line spray	0.6	0	Whole fruit	3.0	Packing line spray, PVC rollers, High Volume Applicator
USA, 2012 Parlier, CA (Old Line)	Dip	0.6	0	Whole fruit	7.0	Dip with drencher reservoir tank and plastic fruit crate
	Drench	0.6	0	Whole fruit	6.1	Drench with drencher treater
IR4-10687 11-CA125	In-line spray	0.6	0	Whole fruit	1.9	Packing line spray, PVC rollers, High Volume Applicator
Mandarin						
USA, 2012 Parlier, CA (Pixie)	Dip	0.6	0	Whole fruit	14	Dip with drencher reservoir tank and plastic fruit crate
	Drench	0.6	0	Whole fruit	12	Drench with drencher treater
IR4-10687 12-CA85	In-line spray	0.6	0	Whole fruit	2.9	Packing line spray, PVC rollers, High Volume Applicator
USA, 2012 Parlier, CA (W Murcott)	Dip	0.6	0	Whole fruit	12	Dip with drencher reservoir tank and plastic fruit crate
	Drench	0.6	0	Whole fruit	7.6	Drench with drencher treater
IR4-10687 11-CA126	In-line spray	0.6	0	Whole fruit	3.4	Packing line spray, PVC rollers, High Volume Applicator
Lemon						
USA, 2012 Parlier, CA	Dip	0.6	0	Whole fruit	14	Dip with drencher reservoir tank and plastic fruit crate
(Allen Eureka)	Drench	0.6	0	Whole fruit	9.7	Drench with drencher treater

CITRUS Country, year Location (variety) References	Application		DALA	matrix	Phosphonic acid residues (mg/kg)	Notes
	method	kg ai/hL				
IR4-10687 12-CA83	In-line spray	0.6	0	Whole fruit	3.4	Packing line spray, PVC rollers, High Volume Applicator
USA, 2012 Parlier, CA (Lisbon) IR4-10687 11-CA127	Dip	0.6	0	Whole fruit	18	Dip with drencher reservoir tank and plastic fruit crate
	Drench	0.6	0	Whole fruit	16	Drench with drencher treater
	In-line spray	0.6	0	Whole fruit	5.2	Packing line spray, PVC rollers, High Volume Applicator
Grapefruit						
USA, 2012 Parlier, CA (Melogold) IR4-10687 12-CA82	Dip	0.6	0	Whole fruit	7.1	Dip with drencher reservoir tank and plastic fruit crate
	Drench	0.6	0	Whole fruit	3.6	Drench with drencher treater
	In-line spray	0.6	0	Whole fruit	2.8	Packing line spray, PVC rollers, High Volume Applicator
USA, 2012 Parlier, CA (Rio Red) IR4-10687 11-CA128	Dip	0.6	0	Whole fruit	8.9	Dip with drencher reservoir tank and plastic fruit crate
	Drench	0.6	0	Whole fruit	7.1	Drench with drencher treater
	In-line spray	0.6	0	Whole fruit	3.5	Packing line spray, PVC rollers, High Volume Applicator

Pome fruits

Apples – fosetyl-Al

In supervised trials conducted in Europe, three foliar sprays of fosetyl-Al (WG) were applied to apple trees between BBCH 75 and 85 with a retreatment interval of about 10 days. Samples of whole fruit were stored frozen for 383 to 475 days before extraction and analysis using the LC-MS/MS method 00861/M001to measure residues of fosetyl-Al and phosphonic acid. Average concurrent recovery rates were 88–91% for fosetyl-Al (fortification levels of 0.01–2.0 mg/kg) and 86–99% for phosphonic acid (fortification levels of 0.2–21 mg/kg) and the LOQs were 0.1 (fosetyl-Al) and 0.2 mg/kg (phosphonic acid).

Table 98 Residues in apples from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

APPLES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: France	3	3.0			28				
Germany.2010 Zaschwitz (Jonagold) 10-2058 10-2058-01	3	3.6	0.72	500	-0	fruit	0.68	6.8	7.3
					0		0.12	6.5	6.6
					7		0.14	8.8	8.9
					14		0.11	9.5	9.6
					28		0.03	7.6	7.6
France (N), 2010 Lignières de Touraine (Golden) 10-2058 10-2058-02	3	3.6	0.24	1500	-0	fruit	0.09	14 c=4.9	14 c=4.9
					0		0.61	14	14
					7		0.28	15	15
					14		0.14	14	14
					28		0.06	16 c=3.8	16 c=3.8

APPLES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Belgium, 2010 Fleurus (Reinettes de Flandres) 10-2058 10-2058-03	3	3.6	0.29	1250	-0	fruit	0.02	6.3	6.3
					0		0.52	10	10
					7		0.02	9.7	9.7
					14		0.02	12	12
					28		< 0.01	11	11
UK, 2010 Royston (Jonathan) 10-2058 10-2058-04	3	3.6	0.36	1000	-0	fruit	< 0.01	3.6	3.6
					0		0.15	5.9	6.0
					8		0.03	11	11
					15		0.03	8.8	8.8
					28		< 0.01	8.2	8.2
Spain, 2010 Bellmunt d'Urgell (Golden) 10-2064 10-2064-01	3	3.6	0.26	1400	-0	fruit	0.77	7.5	8.0
					0		2.1	8.2	9.7
					6		1.3	13	14
					15		0.78	15	16
					28		0.33	17	17
Italy, 2010 Dodici Morelli (Golden Delicious) 10-2064 10-2064-02	3	3.6	0.36	1000	-0	fruit	0.03	13	13
					0		1.4	14	15
					7		0.73	17	18
					14		0.72	19	20
					28		0.01	22 c=4.1	22 c=4.1
France (S), 2010 Reynies (Gala) 10-2064 10-2064-03	3	3.6	0.36	1000	-0	fruit	0.30	9.6	9.8
					0		2.1	9.9	11
					7		0.39	12	12
					14		0.28	12	12
					28		0.03	12	12
Portugal, 2010 Cadaval (Mondial Gala) 10-2064 10-2064-04	3	3.6	0.36	1000	-0	fruit	0.69	9.2	9.7
					0		1.7	11	12
					7		1.4	17	18
					14		0.88	17	18
					28		0.89	15	16

In supervised trials conducted in USA, four foliar sprays of fosetyl-Al (80 WDG) were applied to apple trees at 27 to 72 day intervals. Duplicate whole fruit samples were stored frozen for up to 109 days before extraction and analysis using GC-FPD method 163 to measure residues of fosetyl-Al. The average concurrent recovery rate was 89% fosetyl-Al in samples fortified with 0.5–10 mg/kg and the LOQ was 0.05 mg/kg.

Table 1399 Residues in apples from supervised trials in USA involving foliar applications of fosetyl-Al (80 WDG formulations)

APPLES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)	
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al
GAP: USA	4	4.5		1000–3000	14		
USA, 1986 Wooster, OH (Red Delicious) R009270 253486-023-T3	4	4.5	0.12	3742	14	fruit	< 0.05

APPLES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)	
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al
USA, 1986 Wavseon, OH (Viking) R009270 253486-049-T3	4	4.5	0.12	3742	14	fruit	0.05
USA, 1986 Geneva, NY (Golden Delicious) R009270 453186-116-T3	4	4.5	1.1 0.6 0.5 0.45	421–991	14	fruit	2.9
USA, 1986 Geneva, NY (Red Delicious) R009270 453186-124-T3	4	4.5	1.1 0.68 049 0.45	421–991	14	fruit	4.3
USA, 1986 Biglerville, PA (Various) R009270 453786-115-T3	4	4.5	0.72 0.48 0.26 0.26	627–1702	14	fruit	0.14
USA, 1986 Philo, CA (Jonathan) R009270 530486-119-T3	4	4.5	0.19	2338	14	fruit	2.3
USA, 1986 Moravian Falls, NC (Golden Delicious) R009270 903286-100-T3	4	4.5	0.24 0.16	1871–2806	14	fruit	< 0.05
USA, 1986 Boomer, NC (Red Delicious) R009270 903286-101-T3	4	4.5	0.24 0.16	1871–2806	14	fruit	0.12
USA, 1986 Harrisonburg, VA (Rome Beauty) R009270 904586-104-T3	4	4.5	0.32	1403	14	fruit	1.9
USA, 1986 Berkley Springs, WV (Various) R009270 904786-102-T3	4	4.5	0.32	1403	14	fruit	0.18 c=0.08
USA, 1986 Mattawa, WA (Red Delicious) R009270 984686-104-T3	4	4.5	0.48	935	14	fruit	0.94

APPLES	Application				DALA	Residues (mg/kg)	
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al
USA, 1986 Moxee, WA (Granspur) R009270 984686-112-T3	4	4.5	0.48	935	14	fruit	0.26
USA, 1986 Paw Paw, MI (Jonathan) R009270 992186-014-T3	4	4.5	0.27	1684	14	fruit	0.07

In supervised trials conducted in Brazil, three foliar sprays of fosetyl-Al (WP) were applied to apple trees between BBCH 61 and 81 with a retreatment interval of 64 days. Samples of whole fruit were stored frozen for up to 180 days before analysis for fosetyl-Al analysis and up to 398 days before analysis for phosphonic acid. The analytical method was the LC-MS/MS method 00861/M001 with LOQs of 0.01 (fosetyl-Al) and 0.1 mg/kg (phosphonic acid). Average concurrent recovery rates were 89% for fosetyl-Al (fortification levels of 0.1–10 mg/kg) and 84% for phosphonic acid (fortification levels of 0.1–10 mg/kg).

Table 100 Residues in apples from supervised trials in Brazil involving foliar applications of fosetyl-Al (800 WP formulations)

APPLE	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Brazil	3	2.0		1000	35				
Brazil, 2013	3	2.1	0.2	1014–1060	0	fruit	2.8	1.5	3.4
Antonio Prado								c=0.20	c=0.21
(Fuji)					14		< 0.01	4.4	4.4
					28		< 0.01	4.0	4.0
F13-034/F15-015								c=0.23	c=0.24
F13-034-01					35		< 0.01	9.2	9.2
								c=0.43	c=0.44
					42		< 0.01	3.6	3.6
Brazil, 2013	3	2.1–2.2	0.1	1029–2093	0	fruit	0.76	3.6	4.1
Flores da Cunha			0.2					c=6.9	c=6.9
(Fuji)			0.2		14		< 0.01	16	16
								c=5.1	c=5.1
F13-034/F15-015					28		< 0.01	3.1	3.1
F13-034-02					35		< 0.01	20	20
								c=13	c=13
					42		< 0.01	3.6	3.6
								c=9.2	c=9.2
Brazil, 2013	3	2.0–2.1	0.2	1022–1062	0	fruit	0.93	12	13
Farroupilha								c=13	c=13
(Fuji)					14		< 0.01	25	25
					28		< 0.01	24	24
F13-034/F15-015								c=24	c=24
F13-034-03					35		< 0.01	19	19
								c=18	c=18
					42		< 0.01	21	21
								c=21	c=21

APPLE Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Brazil, 2013	3	2.0–2.1	0.2	1015–1072	0	fruit	0.5	0.69	1.0
Bento Goncalves					14		< 0.01	4.1	4.1
(Fuji)								c=22	c=22
					28		< 0.01	4.1	4.1
F13-034/F15-015					35		< 0.01	5.0	5.0
F13-034-04					42		< 0.01	4.2	4.2

Pears

In supervised trials conducted in Europe, three foliar sprays of fosetyl-Al (WG) were applied to pear trees between BBCH 74 and 85 with a retreatment interval of about 10 days. Samples of whole fruit were stored frozen for 330 to 413 days before extraction and analysis using the LC-MS/MS method 00861/M001 to measure residues of fosetyl-Al and phosphonic acid. Average concurrent recovery rates were 87–94% for fosetyl-Al (fortification levels of 0.01–2.0 mg/kg) and 98–99% for phosphonic acid (fortification levels of 0.2–21 mg/kg) and the LOQs were 0.1 (fosetyl-Al) and 0.2 mg/kg (phosphonic acid).

Table 101 Residues in pears from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

PEARS Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: France	3	3.0			28				
France, 2009	3	3.6	0.36	1000–1500	-0	fruit	0.03	9.5	9.5
Ecquevilly			0.24		0		1.4	13	14
(Beurré hardy)			0.36		7		0.24	13	13
					14		0.21	12	12
09-2039					28		0.06	12	12
09-2039-01									
Germany. 2009	3	3.6	0.72	500	-0	fruit	0.01	21	21
Burscheid					0		0.62	18	18
(Williams Christ)					7		0.04	17	17
					14		0.02	17	17
09-2039					28		0.01	15	15
09-2039-02									
Belgium, 2009	3	3.6	0.36	1000	-0	fruit	0.03	11	11
Nodebais								c=1.1	c=1.1
(Conference)					0		1.1	16	17
					7		0.25	20	20
09-2039					14		0.05	19	19
09-2039-03					28		0.01	17	17
								c=0.88	c=0.89
Netherlands, 2009	3	3.6	0.36	1000	-0	fruit	0.10	15	15
Blokker					0		1.7	17	18
(Conference)					7		0.08	20	20
					14		0.01	14	14
09-2039					28		0.01	14	14
09-2039-04									
France (S), 2009	3	3.6	0.24	1500	-0	fruit	0.02	17	17
Reynies					0		0.61	17	17
(Williams)					7		0.01	20	20
					14		< 0.01	20	20
09-2252					28		< 0.01	15	15
09-2252-01									

PEARS Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
France, 2009	3	3.6	0.36	1000	-0	fruit	0.1	12	12
Les Cheres							c=0.03	c=3.1	c=3.1
(William)					0		1.5	19	20
					7		0.09	27	27
09-2252					14		0.03	18	18
09-2252-02									
Spain, 2009	3	3.6	0.24	1500	-0	fruit	0.01	9.4	9.4
Lleida					0		1.5	10	11
(Conference)					6		0.91	17	18
					14		0.78	16	17
09-2252					28		< 0.01	17	17
09-2252-03									
Italy, 2009	3	3.6	0.24	1500	-0	fruit	0.01	19	19
Ostellato (Ferrara)								c=1.8	c=1.8
(William)					0		1.4	20	21
					7		< 0.01	21	21
09-2252					14		< 0.01	21	21
09-2252-04					28		< 0.01	15	15
								c=1.4	c=1.4
Spain, 2009	3	3.6	0.28	1300–1500	-0	fruit	0.01	9.7	9.7
Bellmunt d´Urgell			0.26		0		1.5	12	13
(Leida)			0.24		6		0.67	14	14
(Conference)					14		0.42	13	13
					28		< 0.01	13	13
09-2252									
09-2252-05									

In supervised trials conducted in USA, four foliar sprays of fosetyl-Al (80 WDG) were applied to pear trees at 27 to 75 day intervals. Duplicate whole fruit samples were stored frozen for up to 103 days before extraction and analysis using GC-FPD method 163 to measure residues of fosetyl-Al. The overall average concurrent recovery rate was 86% fosetyl-Al in samples fortified with 0.5–5 mg/kg and the LOQ was 0.05 mg/kg. Results were corrected for recovery.

Table 102 Residues in pears from supervised trials in USA involving foliar applications of fosetyl-Al (80 WDG formulations)

PEARS Country, year Location (variety) References	Application				DALA	Residues (mg/kg)	
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al
GAP: USA	4	4.5			14		
USA, 1986 Cornvallis, OR (Bartlett) R009270 353686-103-T3	4	4.5	0.48	935	14	fruit	6.5
USA, 1986 Hood River, OR (Anjou) R009270 353686-104-T3	4	4.5	0.48	935	14	fruit	9.5
USA, 1986 North Rose, NY (Clapps Favorite) R009270 353686-118-T3	4	4.5	0.22 0.18 0.18 0.18	2039–2554	14	fruit	0.2

PEARS Country, year Location (variety) References	Application				DALA	Residues (mg/kg)	
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al
USA, 1986 North Rose, NY (Bartlett) R009270 353686-119-T3	4	4.5	0.22 0.18 0.18 0.18	2039–2554	15	fruit	0.1
USA, 1986 Ukiah, CA (Bartlett) R009270 530486-120-T3	4	4.5	0.19	2338	14	fruit	1.1
USA, 1986 Templeton, CA (Bartlett) R009270 353686-121-T3	4	4.5	0.14	3274	14	fruit	0.52
USA, 1986 Mattawa, WA (Bartlett) R009270 353686-105-T3	4	4.5	0.48 0.24 0.24 0.24	935–1871	14	fruit	1.9
USA, 1986 Zillah, WA (Bartlett) R009270 353686-125-T3	4	4.5	0.48 0.24 0.24 0.24	935–1871	14	fruit	1.2

Berries and other small fruit

Grapes – fosetyl-Al

In supervised trials conducted in Europe, three foliar sprays of fosetyl-Al (as a WG co-formulated with fluopicolide) were applied to grape vines between BBCH 75 and 83 at either 6-8 day intervals (2007/2008 trials) or 13–15 day intervals. Samples of grapes (bunches) were stored frozen for up to 679 days before extraction and analysis using either the GC-FPD methods AR 155-97 or AR 154-97 or in the more recent trials, the LC-MS/MS method 00861/M001 to measure residues of fosetyl-Al and phosphonic acid. Average concurrent recovery rates were 77–102% for fosetyl-Al (fortification levels of 0.01–10 mg/kg) and 80-107% for phosphonic acid (fortification levels of 0.2–40 mg/kg) and the LOQs were 0.2–0.5 mg/kg in the early studies and 0.01 mg/kg (fosetyl-Al) and 0.2 mg/kg (phosphonic acid) in the more recent trials.

Table 103 Residues in grapes from supervised trials in Europe involving foliar applications of fosetyl-Al (WG formulations)

GRAPE	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Czech Republic	3	2.0		200-1000	21				
Germany, 2001 Neustadt Mußbach (Riesling) 01R284-1	3	1.878	0.376	500	0	grape bunch	5.2 c=0.48	13 c=10	17 c=10
					7		3.2 c=0.39	11 c=9.2	13 c=10
					14		2.2 c=0.43	19 c=12	21 c=12
					21		1.6 c=0.29	15 c=12	16 c=12
					29		3.1 c=0.32	23 c=11	25 c=11
Germany, 2001 Ihringen (Silvaner) 01R284-2	3	1.878	0.376	500	0	grape bunch	4.3	13	16
					7		5.2	18	22
					14		3.4	21	23
					21		1.3	21	22
					29		2.2	22	24
France, 2001 Doue la Fontaine (Cabernet Franc) 01R284-3	3	1.878	0.754	250	0	grape bunch	2.1	9.4 c=2.1	11 c=2.2
					7		1.5	12 c=2.3	13 c=2.4
					14		1.3	11 c=2.4	12 c=2.5
					21[a]		0.70	13 c=3.3	14 c=3.4
					28		0.39	16 c=3.4	16 c=3.5
France, 2001 Vernou Sur Brenne (Chenin) 01R284-4	3	1.878	0.854	220	0	grape bunch	1.5	7.7	8.7
					7		1.3	12	13
					14		0.93	9.7	10
					21		0.85	14	15
					28		0.62	16	16
France, 2001 Brouillet (Pinot Meunier) 01R284-5	3	1.878	0.188	1000	0	grape bunch	2.0	7.1 c=0.29	8.5 c=0.43
					7		0.62	9.6 c=0.29	10 c=0.43
					14		0.47	12 c=0.36	12 c=0.50
					21		0.25	11 c=0.40	11 c=0.54
					28		< 0.20	11 c=0.49	11 c=0.63
France, 2001 Mazeres (Cabernet Sauvignon) 01R285-1	3	1.878	1.25	150	0	grape bunch	3.9	20 c=6.8	23 c=6.9
					7		3.8	28 c=5.1	31 c=5.2
					12		3.8	27 c=5.8	30 c=5.9
					21		1.4	21 c=5.3	22 c=5.4
					28		1.1	31 c=6.1	32 c=6.2

GRAPE Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
France, 2001 Chazay D'Azergues (Chardonnay) 01R285-2	3	1.878–2.078	0.94	200–222	0	grape bunch	1.7	6.6 c=1.1	7.8 c=1.2
					7		1.0	8.6 c=1.2	9.3 c=1.3
					14		0.93	8.6 c=1.3	9.2 c=1.4
					21		0.97	8.6 c=1.1	9.3 c=1.2
					28		0.94	11 c=1.3	12 c=1.4
Italy, 2001 San Prospero (Lambrusco Di Sorbara) 01R285-3	3	1.878	0.188	1000	0	grape bunch	5.2	7.0 c=0.38	11 c=0.52
					7		2.7	6.4 c=0.27	8.3 c=0.41
					14		0.81	11 c=0.37	12 c=0.51
					20		0.42	7.7 c=0.39	8.0 c=0.53
					28		0.23	7.7 c=0.40	7.9 c=0.54
Spain, 2001 Godelleta (Moscatel, table) 01R285-4	3	1.878	0.188	1000	0	grape bunch	1.6	11 c=0.63	12 c=0.77
					7		1.3	11 c=0.85	12 c=0.99
					14		1.2	13 c=0.88	14 c=1.0
					22	grape bunch	0.20	12 c=0.94	12 c=1.1
					28		0.28	12 c=0.58	12 c=0.72
Greece, 2001 Goumenisa – Kilkis (Xinomavro) 01R285-5	3	1.878	0.235	800	0	grape bunch	2.3	2.2	3.8
					7		2.8	4.7	6.7
					14		1.4	4.2	5.2
					22		< 0.20	3.1	3.2
					28		< 0.20	4.6	4.7
Germany, 2002 Neustadt-Mußbach (Müller-Thurgau) 02R288-1	3	1.878	0.235	500	0	grape bunch	2.2	8.4 c=0.93	9.9 c=1.3
					21		1.9	13 c=1.8	14 c=2.1
Germany, 2002 Mühlhausen (Spätburgunder) 02R288-2	3	1.878	0.235	500	0	grape bunch	9.5	24	31
					21		4.3	37	40
France, 2002 Gueux (Pinot Meunier) 02R288-3	3	1.878–2.086	0.376	500–556	0	grape bunch	3.8	13 c=0.79	16 c=1.1
					21		1.2	14 c=0.61	15 c=0.96
France, 2002 Epernay (Chardonnay) 02R288-4	3	1.878	0.235	500	0	grape bunch	4.3 c=0.57	14 c=5.0	17 c=5.4
					21		< 0.50	19 c=2.3	19 c=2.7
France, 2002 Chazay D'Azergues (Gamay) 022R289-1	3	1.878	0.626	300	0	grape bunch	2.2	36 c=1.8	38 c=2.2
					21		8.1	26 c=1.0	32 c=1.4

GRAPE Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
France, 2002 Graveson (Carignan) 02R289-2	3	1.878	0.626	300	0	grape bunch	2.5	22	24
								c=0.86	c=1.2
					21		0.97	23	24
Italy, 2002 Andria (Malvasia Leccese) 02R289-3	3	1.878	0.188	1000	0	grape bunch	10	11	18
					21		1.4	11	12
							c=1.5	c=5.5	c=6.5
Spain, 2002 Campo Arcís-Requena (Macabeo) 02R289-4	3	1.878	0.25	750	0	grape bunch	1.1	12	13
					21		< 0.50	12	12
France, 2007 Graveson (Carignan) RA-2671/07 R 2007 0816/5	3	2.00	1.0	200	-0	berries	6.0	11	15
							c=0.01	c=1.8	c=1.8
					0		9.8	10	17
					21		7.1	29	34
					28		6.4	33	37
								c=2.5	c=2.5
Spain, 2007 La Fortesa (Maccabeo) RA-2671/07 R 2007 0817/3	3	2.00	0.2	1000	-0	berries	6.5	8.6	13
					0		12	6.5	15
					21		0.84	13	14
					28		0.56	10	10
Italy, 2007 Barletta (Sangiovese) RA-2671/07 R 2007 0818/1	3	2.00	0.2	1000	-0	berries	5.4	7.7	12
					0		8.7	8.8	15
					21		1.8	11	12
					28		1.6	12	13
France, 2008 Athee sur Cher (Cot) 08-2040 08-2040-01	3	2.0	1.0	200	-0	grape bunch	1.8	4.1	5.4
								c=1.7	c=1.7
					0		6.6	4.6	9.2
					21		1.4	9.2	10
					28		1.5	8.5	9.5
								c=2.0	c=2.0
France, 2008 St Nicolas de Bourgueil (Cabernet franc) 08-2040 08-2040-02	3	2.0	1.0	200	-0	grape bunch	3.9	10	13
								c=2.6	c=2.6
					0		7.7	9.9	15
					21		1.9	26	27
					28		1.8	24	25
								c=2.5	c=2.5
Germany, 2008 Maikammer (Dornfelder) 08-2040 08-2040-03	3	2.0	0.25	800	-0	grape bunch	4.9	12	15
								c=0.35	c=0.36
					0		12	13	21
					21		5.2	24	28
					28		4.5	24	27
								c=0.36	c=0.37
Germany, 2008 Kressbronn (Mueller-Thurgau) 08-2040 08-2040-04	3	2.0	0.27	750	-0	grape bunch	1.8	13	14
								c=7.4	c=7.4
					0		5.2	11	15
					22		1.8	19	20
					28		2.2	21	23
								c=7.5	c=7.5

[a] A potential mislabelling of untreated sample and treated sample. Highest values have been selected for treated sample

In supervised trials conducted in USA, seven foliar sprays of fosetyl-Al (WDG or WP) were applied to grape vines at 7 to 28 day intervals. Samples of grape bunches (2 or 3 replicates) were stored frozen for up to 115 days before extraction and analysis using GC-FPD method SOP-90113 or AR 155-97 to measure residues of fosetyl-Al. The average concurrent recovery rates were 75–95% fosetyl-Al in samples fortified with 0.5–5 mg/kg and the LOQs were 0.5 mg/kg and 0.5 mg/kg in the 1996 trials.

Table 104 Residues in grapes from supervised trials in USA involving foliar applications of fosetyl-Al (WDG or WP formulations)

GRAPES Country, year Location (variety) References	Application				DALA	Fosetyl-Al residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	values	mean
GAP: USA	7	4.5			15			
USA, 1992 Stanislaus Cty, CA (Carrignane) R000049 92-102	7	4.37–4.93	0.39–0.73	679– 1151	15	grape bunch	6.81, 13.2, 7.54	9.2
USA, 1992 Allegan Cty, MI (Concord) R000049 92-103	7	4.5	0.96	468	15	grape bunch	0.52, < 0.50, 0.69	0.57
USA, 1992 Ontario Cty, NY (Catawba) R000049 92-104	7	4.5	0.47–0.48	925–963	15	grape bunch	0.52, 0.71, 0.64	0.62
USA, 1992 Grant County, WA (Concord) R000049 92-105	7	4.5	0.48	935	14	grape bunch	2.74, 1.74, 2.34	2.3
USA, 1992 Monterey Cty, CA (Pinot Noir/ Chardonay) R000049 92-106	7	4.38–4.5	1.0–1.1	421	16	grape bunch	10.6, 10.6, 8.34	9.8]
USA, 1992 Yolo County, CA (Symphony) R000049 92-107	7	4.22–4.78	0.9–1.0	449–468	15	grape bunch	5.82, 5.6, 7.1	6.2
USA, 1992 Fresno County, CA (Thompson) R000049 92-109	7	4.08–6.10	0.19–0.24	2020–2544	15	grape bunch	13.9, 16.2, 17.8	16
USA, 1996 Orefield, PA (Concord) R000070 11733-01	7	4.48–4.52	0.58–0.62	734– 772	15	grape bunch	1.18, 1.38	1.3

GRAPES Country, year Location (variety) References	Application				DALA	Fosetyl-Al residues (mg/kg)		
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	values	mean
USA, 1996 Dundee, NY (DeChaunac) R000070 11733-02	7	4.44–4.71	0.8	555–588	14	grape bunch	2.45, 2.41	2.3

Value in square brackets is the mean residue of two or three replicate samples

In supervised trials conducted in Brazil, three foliar sprays of fosetyl-Al (WP) were applied to grape vines between BBCH 75 and 81 at about 15-day intervals. Samples of grapes (bunches) were stored frozen for up to 449 days before analysis for fosetyl-Al and phosphonic acid. The analytical method was the LC-MS/MS method 00861/M001 with LOQs of 0.01 (fosetyl-Al) and 0.1 mg/kg (phosphonic acid). Average concurrent recovery rates were 102% for fosetyl-Al (fortification levels of 0.1–10 mg/kg) and 98% for phosphonic acid (fortification levels of 0.1–10 mg/kg).

Table 105 Residues in grapes from supervised trials in Brazil involving foliar applications of fosetyl-Al (WP formulations)

GRAPES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residue
GAP: Brazil	3		0.2		15				
Brazil, 2013 Santa Cruz do Sul (Bordô) F13-035-01/F15-015	3	2.0–2.1	0.2	1027–1061	0 7 15 21 28	grape bunch	6.9 5.7 2.6 1.7 0.90	35 45 39 38 24	40 49 41 39 24
Brazil, 2013 Passo do Sobrado (Francesa) F13-035-02/F15-015	3	2.1	0.2	1038–1052	0 7 15 21 28	grape bunch	4.7 3.3 0.72 0.22 1.5	16 c=0.42 30 c=0.66 24 c=0.83 18 c=0.41 55 c=0.58	19 c=0.43 32 c=0.67 24 c=0.84 18 c=0.42 56 c=0.59
Brazil, 2013 Fazenda Vilanova (Moscato) F13-035-03/F15-015	3	2.0–2.1	0.2	1019–1039	0 7 15 21 28	grape bunch	4.5 2.5 0.44 0.60 0.31	67 c=77 52 c=94 87 c=57 82 c=52 90 c=71	70 c=77 54 c=94 88 c=57 83 c=52 91 c=71
Brazil, 2013 Vera Cruz (Bordô) F13-035-04/F15-015	3	2.1	0.2	1042–1052	15	grape bunch	3.2	15	17
Brazil, 2013 Antonio Prado (Bordô) F13-035-05/F15-015	3	2.1	0.2	1042–1050	15	grape bunch	1.2	45 c=35	46 c=35

Grapes – phosphonic acid

In supervised wine grape trials conducted in Australia, up to six foliar applications of phosphonic acid (as potassium salts) were applied at various stages of growth, from flowering through to pre-bunch closure and pre-harvest. In one study, grapes from commercial vineyards known to have applied phosphonic acid were sampled at maturity for analysis. In the 2004 trials, samples of grapes from the 2005 vintage (1 year after treatment) were also analysed to estimate the potential carry-over of residues from season to season.

In a number of these trials, treated grapes were also processed into wine, using a microvinification process that involved crushing and destemming the bunches, the addition of sulphur dioxide and pH adjustment, fermentation (with skins), the addition of diammonium phosphate (DAP), pressing and further fermentation prior to racking (settling and decanting to remove lees) and bottling.

Samples of grapes (berries) were stored frozen for up to about 180 days before analysis for phosphonic acid. The analytical methods used in the 2004 and 2005 trials was based on the GC-FPD method AR155-97 (LOQ of 1.0 mg/kg) and an LC-MS/MS method based on method 00861/M001 was used for the 2011 grower samples (LOQ 0.1 mg/kg). In the 2013 trials, a modification of method 00861/M001 was used (i.e. the addition of an ion-pairing reagent tetrabutylammonium acetate prior to filtration and analysis). The LOQ, at the lowest fortification level, was 1.0 mg/kg and concurrent recoveries were 101–106% (fortification levels of 1.0–52 mg/kg).

In a study reported by Odell et al, 2010 [Ref: AWRI-2010], phosphonic acid residues were measured in wines that had been treated during the wine-making process with 300 mg/litre diammonium phosphate (DAP) containing levels of phosphonic acid up to 3.9 g/kg. Residues of phosphonic acid in the treated wine were up to about 1.0 mg/kg.

Table 106 Residues in grapes from supervised trials in Australia involving foliar applications of phosphonic acid (as mono- and di-potassium salts)

GRAPES	Application					DALA	Phosphonic acid residues (mg/kg)	
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)	total kg ai/ha		Grape	Wine
GAP: Australia		2.4				not required		
Australia 2004 Riverland, SA (Cabernet Sauvignon) AWR 04/01	1	2.4	0.5	475	2.4	8+ 1 year	6.6 <1.0	4.5
	3	2.4	0.5	475	7.2	73 + 1 year	31.5 <1.0	21
	4	2.4	0.5	475	9.6	8 + 1 year	46.5 2.0	41
	6	2.4	0.5	475	14.4	8 + 1 year	45.5 2.5	87
Australia 2005 Riverland, SA (Cabernet Sauvignon) AWR 04/01	1	2.4	0.54	443	2.4	44	7.1	21.0
	1	2.4	0.54	443	2.4	98	2.3	3.4
	1	1.2	0.27	443	1.2	119	<1.0	1.5
	2	2.4	0.54	443	4.8	51	5.8	12.0
	2	1.2–1.8	0.27–0.41	443	3.0	113	2.6	3.9
	3	2.4	0.54	443	7.2	44	6.8	16.0
	3	1.2–2.4	0.27–0.54	443	5.4	98	4.1	9.7
	4	1.2–2.4	0.27–54	443	7.8	51	9.2	12.0
	5	1.2–2.4	0.27–	443	10.2	44	13.0	18.0
Australia, 2011 Hunter Valley, NSW (Verdelho) AC77220 AWRI 2016	2	1.4–1.6			3.0	55	11	10

GRAPES Country, year Location (variety) References	Application					DALA	Phosphonic acid residues (mg/kg)	
	no	kg ai/ha	kg ai/hL	water (L/ha)	total kg ai/ha		Grape	Wine
Australia, 2011 Hunter Valley, NSW (Chardonnay) AC77222 AWRI 2016	2	1.6–1.8			3.4	60	19	16
Australia, 2011 Hunter Valley, NSW (Semillion) AC77219 AWRI 2016	2	1.4–1.8			3.2	57	14	
Australia, 2011 Hunter Valley, NSW (Chardonnay) AC77221 AWRI 2016	2	1.4–1.8			3.2	57	16	
Australia, 2011 Hunter Valley, NSW (Shiraz) AC77225 AWRI 2016	2	1.4–1.8			3.2	65	26	
Australia, 2011 Hunter Valley, NSW (Shiraz) AC77226 AWRI 2016	2	1.4–1.8			3.2	65	21	
Australia, 2011 Hunter Valley, NSW (Tempranillo) AC77224 AWRI 2016	3	2.4			7.2	85	33	32
Australia, 2011 Eden Valley, SA (Shiraz) AC77210 AWRI 2016	2	2.4			4.8	114	25	21
Australia, 2011 Eden Valley, SA (Cabernet Sauvignon) AC77209 AWRI 2016	2	2.4			4.8	114	22	
Australia, 2011 Barossa Valley, SA (Cabernet Sauvignon) AC77229 AWRI 2016	3	2.4–3.0			8.4	78	32	30
Australia, 2011 Barossa Valley, SA (Shiraz) AC77227 AWRI 2016	3	2.4–3.0			8.4	63	52	

GRAPES	Application					DALA	Phosphonic acid residues (mg/kg)	
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)	total kg ai/ha		Grape	Wine
Australia, 2011 Barossa Valley, SA (Semillion) AC77228 AWRI 2016	3	2.4–3.0			8.4	42	9.0	
Australia, 2011 Barossa Valley, SA (Sauvignon Blanc) AC77230 AWRI 2016	3	2.4–3.0			8.4	29	27	
Australia, 2011 Adelaide Hills, SA (Riesling) AC77217 AWRI 2016	4	2.4			9.6	27	77	42
Australia, 2011 Adelaide Hills, SA (Chardonnay) AC77213 AWRI 2016	4	2.4			9.6	6	102	
Australia, 2011 Adelaide Hills, SA (Chardonnay) AC77214 AWRI 2016	4	2.4			9.6	8	67	
Australia, 2011 Adelaide Hills, SA (Pinot Noir) AC77215 AWRI 2016	4	2.4			9.6	14	88	
Australia, 2011 Adelaide Hills, SA (Pinot Noir) AC77216 AWRI 2016	4	2.4			9.6	5	67	
Australia, 2011 Adelaide Hills, SA (Merlot) AC77217 AWRI 2016	4	2.4			9.6	48	106	
Australia, 2013 Tamar Valley, TAS Sauvignon Blanc) NUF-1104 S1	3	0.97–1.0		675-690	3.0	61	19	
	3	2.0		690	6.0	61	39	
Australia, 2013 Yarra Valley, VIC (Shiraz) NUF-1104 S2	3	0.88–1.1		1880-2010	2.9	49	16	
	3	2.0		2140-2180	3.0	49	26	
Australia, 2013	3	0.92–1.2		730-939	3.1	89	27	

GRAPES	Application					DALA	Phosphonic acid residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)	total kg ai/ha		Grape		Wine	
McLaren Vale, SA (Chardonnay) NUF-1104 S3	3	2.0–2.3		800-900	6.4	89	75			
Australia, 2013 Barossa Valley, SA (Shiraz) NUF-1104 S4	3	0.98–1.0		580-690	3.0	84	9.9			
	3	2.0		590-690	6.0	84	27			
Australia 2004 Griffith, NSW (Chardonnay) AWR 04/01							values	mean	values	mean
	1	2.4	0.48	500	2.4	35	7.7, 2.6	5.2	23, 15	19
	1	2.4	0.48	500	2.4	93	1.9, 1.6	1.8	25, 6.5	15.8
	1	2.4	0.48	500	2.4	124	<1.0, <1.0	<1.0	<1.0, 1.2	1.1
	2	2.4	0.48	500	4.8	50	7.2, 4.7	6.0	22, 14	18
	2	1.2	0.24	500	2.4	113	1.0, 1.7	1.4	2.3, 4.0	3.2
	3	2.4	0.48	500	7.2	35	24, 9.5	16.8	44, 48 26, 24	46 25[a]
	3	1.2–1.8	0.24–0.36	500	4.2	111	4.0, 1.4	2.7	7.2, 6.0	6.6
	4	1.2–2.4	0.24–0.48	500	6.6	93	17, 6.0	11.5	13, 17 21, 12	15 16.5[a]
	5	1.2–2.4	0.24–0.48	500	9.0	50	14, 9.2	11.6	35, 43 40, 33	39 36.5[a]
	6	1.2–2.4	0.24–0.48	500	11.4	35	12, 11	11.5	43, 46 48, 38	44.5 43[a]

[a] Wine fermentation was 'off-skin'

Strawberries - fosetyl-Al

In supervised trials conducted in Europe, three foliar sprays of fosetyl-Al (WG) were applied to indoor and outdoor strawberries between BBCH 49 and 87 with a retreatment interval of about 20 days. In the 2000 and 2001 trials, samples of whole fruit were stored frozen for up to 383 days before extraction and analysis using the GC-FPD or GC-NPD methods DFG 522 or AR 155-97 to measure residues of fosetyl-Al and phosphonic acid (LOQs of 0.2 mg/kg for each analyte). In the 2013 trials, the LC-MS/MS method 00861/M001 was used, with LOQs of 0.01 mg/kg (fosetyl-Al) and 0.2 mg/kg (phosphonic acid). Average concurrent recovery rates were 75–117% for fosetyl-Al (fortification levels of 0.2–10 mg/kg) and 77–114% for phosphonic acid (fortification levels of 0.2–100 mg/kg).

Table 107 Residues in protected strawberries from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

STRAWBERRIES	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: France	3	4.0			14				
France, 2000 Pernes les Fontaines (Pajero) C012378 00-539-AV1-A	3	4.0		1000	14	fruit	0.59	9.1	9.5
France, 2000 Pernes les Fontaines (Pajero) C012378 00-539-AV1-B	3	4.0		1000	7	fruit	0.52	10	10

STRAWBERRIES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
France, 2000 Pernes les Fontaines (Pajero) C012378 00-539-AV1-C	3	4.0		1000	4	fruit	0.70	14	14
France, 2000 Pernes les Fontaines (Pajero) C012378 00-539-AV1-D	3	4.0		1000	-0 0	fruit	< 0.20 1.4	7.0 7.4	7.1 8.4
France, 2000 Janze (Elsanta) C012378 00-539-RN1-A	3	4.0		1000	14	fruit	0.96	10	11
France, 2000 Janze (Elsanta) C012378 00-539-RN1-B	3	4.0		1000	7	fruit	1.4	16	17
France, 2000 Janze (Elsanta) C012378 00539RN1-C	3	4.0		1000	3	fruit	1.1	11	12
France, 2000 Janze (Elsanta) C012378 00-539-RN1-D	3	4.0		1000	-0 0	fruit	0.64 2.2	6.8 8.9	7.2 10
France, 2000 Pernes les Fontaines (Pajero) C012376 00-540-AV1	3	3.975		1000	12	fruit	1.4	33	34
France, 2000 Saint Meloir des Ondes (Garriguette) C012376 00540RN1	3	3.617–3.983		909-1000	16	fruit	1.1	25	26
France, 2001 Allonnes (Diamante) C023520 01R110-1	3	4.0		250	0 5 9 14 19	fruit	4.7 2.3 2.0 1.4 0.44	5.1 7.9 11 8.5 6.9	8.4 9.5 12 9.5 7.2
France, 2001 Port Foucault Fondettes (Mara Des Bois) C023520 01R110-2	3	4.0		250	0 4 10 14 18	fruit	3.5 1.5 0.83 0.46 0.44	7.9 8.0 11 18 16	10 9.0 12 18 16

STRAWBERRIES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
France, 2001 Cremery (Darselect) C023520 01R110-3	3	4.0		250	0 5 10 14 20	fruit	2.5 1.3 1.4 0.90 0.75	11 9.3 8.9 9.6 9.4	13 10 9.9 10 9.9
France, 2001 Mondescourt (Elsanta) C023520 01R110-4	3	4.0		250	0 7 10 14 23	fruit	0.99 0.58 0.49 0.26 0.65	11 9.1 7.2 7.0 10	12 9.5 7.5 7.2 10

Table 108 Residues in outdoor strawberries from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

STRAWBERRIES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: France	3	4.0			14				
France, 2000 Pernes les Fontaines (Pajero) C012374 00-538-AV1	3	4.0		1000	13	fruit	< 0.20	4.2	4.3
France, 2000 Coutens (Majoral) C012374 00-538-TL1	3	4.0		1000	14	fruit	< 0.20	11	11
Germany, 2000 Meckenheim (Elsanta) C017215 DEU0201	3	6.0		600	0 14	fruit	1.4 < 0.20	5.4 7.2	6.4 7.3
Germany, 2000 Wurzen -Roitzsch (Korona) C017215 DEU0601	3	6.0		600	0 14	fruit	2.4 < 0.20	6.4 4.9	8.1 5.0
UK, 2000 Norwich (Elsanta) C017215 GBR0101-P2	3	6.0		600	0 14	fruit	10 < 0.20	14 11	21 11
UK, 2000 Norwich (Elsanta) C017215 GBR0101-P3	3	6.0		600	0 21	fruit	11 0.24	13 12	21 12

STRAWBERRIES Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
UK, 2000 Norwich (Elsanta) C017215 GBR0101-P4	3	6.0		600	0 7	fruit	4.6 4.0	9.3 16	12 19
UK, 2000 Norwich (Elsanta) C017215 GBR0101-P5	3	5.3-6.0		530-600	0	fruit	4.1	8.2	11
UK, 2000 Fulbourn (Symphony) C017215 GBR0103-P2	3	6.0		695	0 14	fruit	0.28 < 0.20	5.3 9.3	5.5 9.4
UK, 2000 Fulbourn (Symphony) C017215 GBR0103-P3	3	6.0		695	0 21	fruit	0.60 < 0.20	8.1 18	8.5 18
UK, 2000 Fulbourn (Symphony) C017215 GBR0103-P4	3	6.0		695	0 8	fruit	1.2 0.33	9.8 14	11 14
UK, 2000 Fulbourn (Symphony) C017215 GBR0103-P5	3	6.0		695	0	fruit	0.94	15 c=3.6	16 c=3.7
Spain, 2000 Paterna (Huelva (Tudla) C017306 ESP0201-P2	3	4.0		300–500	0 20	fruit	1.7 < 0.20	1.8 11	3.0 11
Spain, 2000 Paterna (Huelva) (Tudla) C017306 ESP0201-P3	3	4.0		300–500	0 13	fruit	1.5 < 0.20	0.75 6.6	1.8 <u>6.7</u>
Spain, 2000 Paterna (Huelva) (Tudla) C017306 ESP0201-P4	3	4.0		300–500	0 7	fruit	1.5 < 0.20	3.3 1.9	4.3 2.0
Spain, 2000 Paterna (Huelva) (Tudla) C017306 ESP0201-P5	3	4.0		300–500	0	fruit	1.8	5.3	6.6

STRAWBERRIES	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Italy, 2000 San Martino (Ferrara) (Marmolada) C017306 ITA0101-P2	3	4.0		600	0 20	fruit	0.93 < 0.20	1.8 2.9	2.4 3.0
Italy, 2000 San Martino (Ferrara) (Marmolada) C017306 ITA0101-P3	3	4.0		600	0 14	fruit	0.83 < 0.20	7.4 5.0	8.0 5.1
Italy, 2000 San Martino (Ferrara) (Marmolada) C017306 ITA0101-P4	3	4.0		600	0 7	fruit	4.7 0.37	4.5 6.9	7.8 7.2
Italy, 2000 San Martino (Ferrara) (Marmolada) C017306 ITA0101-P5	3	4.0		600	0	fruit	0.65	4.4	4.9
Italy, 2000 Sala (FO) (Marmolada) C017306 DR-00-EUS154 ITA0102-P2	3	4.0		600	0 21	fruit	3.0 0.26	8.2 4.9	10 5.1
Italy, 2000 Sala (FO) (Marmolada) C017306 ITA0102-P3	3	4.0		600	0 14	fruit	5.1 < 0.20	14 44	18 44
Italy, 2000 Sala (FO) (Marmolada) C017306 ITA0102-P4	3	4.0		600	0 7	fruit	4.1 0.28	7.8 18	11 18
Italy, 2000 Sala (FO) (Marmolada) C017306 ITA0102-P5	3	4.0		600	0	fruit	4.3	2.9	5.9
France, 2001 Soings En Sologne (Valeta) C023522 01R113-1	3	6.0		250	0 5 9 14 20	fruit	5.9 < 0.20 < 0.20 < 0.20 < 0.20	12 8.7 8.0 8.1 7.6	16 8.8 8.1 8.2 7.7
France, 2001 Cremery (Elsanta) C023522 01R113-2	3	6.0		250	0 5 10 15 21	fruit	0.79 1.0* 0.31 0.23 < 0.20	2.0 9.8* 11 10 7.8	2.5 10 11 10 7.9

STRAWBERRIES	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
UK, 2001 Tunstead (Elsanta) C023522 01R113-3	3	6.0		250	0 5 10 14 21	fruit	3.6 0.43 0.26 0.24 < 0.20	18 c=0.35 23 c=0.56 22 19 c=0.36 11 c=0.20	21 c=0.49 23 c=0.70 22 19 c=0.50 11 c=0.34
UK, 2001 Cambridge (Bolero) C023522 01R113-4	3	6.0		250	0 4 9 15 21	fruit	1.2 2.0 1.7 1.4 1.3	21 29 28 43 38	22 30 29 44 39
France, 2013 Carpentras (Clery) 13-2038-01	3	4.0		1000	-0 0 7 14 21	fruit	< 0.01 0.78 0.44 0.51 0.16	4.8 4.5 11 11 9.3	4.8 5.0 11 11 9.4
Spain, 2013 Gava (Albion) 13-2038-02	3	4.0		400	-0 0 6 14 21	fruit	0.045 9.6 1.9 0.22 0.018	26 21 26 24 18	26 28 27 24 18
Italy, 2013 Maletto (CT) (Elsinore) 13-2038-03	3	4.0		500–700	-0 0 7 14 21	fruit	0.44 5.0 2.0 0.69 0.21	39 c=7.8 37 44 c=6.1 36 c=4.5 26 c=3.6	39 c=7.8 40 45 c=6.1 36 c=4.5 26 c=3.6

In supervised trials conducted in USA, combination treatments of a pre-plant root dip and six foliar sprays of fosetyl-Al (WP) applied about 7 days apart in the subsequent spring/summer, 360–389 days after the root dip treatment and planting. In two trials, the foliar sprays were applied the same season, 44–113 days after the root dip treatment. Samples of strawberry fruit (2 or 3 replicates) were stored frozen for up to 138 days before extraction and analysis using GC-FPD method 163 or SOP-90113 to measure residues of fosetyl-Al. The overall mean concurrent recovery rate was 88% fosetyl-Al in samples fortified with 1–20 mg/kg and the LOQ was 0.05 mg/kg.

Table 109 Residues in strawberries from supervised trials in USA involving pre-plant root dip and foliar applications of fosetyl-Al (WP formulations)

STRAWBERRIES Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) (corrected for recovery
	no	kg ai/ha	Water (L/ha)	RTI (days)			Fosetyl-Al
GAP: USA	1 dip + 6 foliar	0.24 4.5			0		
USA, 1987 Watsonville, CA (Silva) R000021 530487-101	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 1403	75 7	0	fruit	4.0

STRAWBERRIES Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) (corrected for recovery
	no	kg ai/ha	Water (L/ha)	RTI (days)			Fosetyl-Al
USA, 1987 Salinas, CA (Silva) R000021 530487-102	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 1403	75 7	0	fruit	9.3
USA, 1987 Dover, FL (Dover) R000021 560987-115	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	44 6–8	0	fruit	5.9
USA, 1987 Dover, FL (Dover) R000021 560987-136	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	93 7	0 7 14 21 28 35	fruit	7.2 c=0.19 4.0 5.0 3.1 4.1 8.3
USA, 1987 Irvine, CA (Douglas "Mac Doel") R000021/B004619 920487-110	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	113 7-10	0 10 17 24 31 38	fruit	39 c=0.1 0.08 22 19 72 38
USA, 1987 Quincy, FL (Silva) R000021 960987-162	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 500-561	52 6-8	0 8 15 21	fruit	2.0 0.71 4.3 0.5
USA, 1987 Quincy, FL (Silva) R000021 960987-163	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 234	49 7	0 7 14	fruit	7.4 11 7.1
USA, 1987 Vermillion, OH (Guardian) R000021 JEM88-045	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	378 5–9	0	fruit	3.5
USA, 1987 Onondaga, MI (Red Chief) R000021 JOJ88-105	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	356 6–7	0	fruit	10 c=0.05
USA, 1987 Ephrata, WA (Shuckson) R000021 JRM 89-155	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	389 6-7	0 7	fruit	6.6 6.1
USA, 1987 Moses Lake, WA (Strawberry) R000021 JRM88-131	9 foliar	4.5	941	6-8	0 7	fruit	18 19

STRAWBERRIES Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) (corrected for recovery
	no	kg ai/ha	Water (L/ha)	RTI (days)			Fosetyl-Al
USA, 1987 Sublimity, OR (Benton) R000021 RJB88-001	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 767	372 7	0 7 14	fruit	11 c=0.05 5.8 6.2
USA, 1987 Sublimity, OR (Hood) R000021 RJB88-002	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 767	360 7	0 7 14	fruit	12 8.4 4.0
USA, 1987 Clifty, IN (Earliglow) R000021 TRS88-001	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	365 7	0	fruit	1.0
USA, 1987 Owen, IN (Earliglow) R000021 TRS88-248	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	365 7	0	fruit	3.2
USA, 1987 Iola, WI (Dunlap) R000021 VHL88-034	1 dip + 6 foliar	0.48 kg ai/hL 4.5	- 935	380 7	0 7	fruit	4.1 16

Assorted tropical and sub-tropical fruits – inedible peel

Avocado – fosetyl-Al

In supervised trials conducted in Europe, three foliar sprays of fosetyl-Al (WG formulations) were applied to avocado trees, the first at BBCH 61-67 and then at 14 days intervals. Samples of whole fruit were separated into peel and flesh and stored frozen for 108–237 days before extraction and analysis using the GC-FPD method AR 155-97 to measure residues of fosetyl-Al and phosphonic acid. Average concurrent recovery rates in flesh were 84% (fosetyl-Al) and 95% (phosphonic acid) and in peel were 88% and 71% respectively. Fortification levels were 0.5 and 5.0 mg/kg and also 50 mg/kg in peel (phosphonic acid). LOQs were 0.5 mg/kg for both analytes.

Table 110 Residues in avocado from supervised trials in Europe involving foliar applications of fosetyl-Al (WG formulations)

AVOCADO Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Spain	3		0.24		14				
Spain, 2000 Coin (Malaga) (Fuerte) C015422 ESP0201	3	4.8	0.24	2000	0 3 7 14 14 14	fruit fruit[a] flesh peel	< 0.50 < 0.50 < 0.50 < 0.50 < 0.50 < 0.50	3.6 3.7 3.7 2.9 3.1 4.1	3.9 4.0 4.0 3.2 3.4 4.4

AVOCADO	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Spain, 2000 Almuñecar (Hass) C015422 ESP0301	3	4.8	0.4 0.34 0.34	1200–1400	0	fruit	< 0.50	5.4	5.7
					13	fruit[a]	< 0.50	3.5	3.8
					13	flesh	< 0.50	2.5	2.8
					13	peel	0.58	7.2	7.6
Spain, 2000 Bayeniza-Velez (Hass) C015422 ESP0302	3	4.8	0.4 0.34 0.34	1200–1400	0	fruit	0.63	5.5	5.9
					3		0.56	5.0	5.4
					7		< 0.50	3.8	4.1
					13	fruit[a]	0.72	4.3	4.8
					13	flesh	< 0.50	3.7	4.0
					13	peel	1.4	7.0	8.0
Spain, 2001 Andújar (Jaén) (Hass) C024339 01R109-1	3	4.8	0.46	1050	0	fruit	2.2	48	49
					14	fruit[a]	< 0.50	20	20
					14	flesh	< 0.50	35	35
					14	peel	< 0.50	14	14
Spain, 2001 Velez Málaga (Fuerte) C024339 01R109-2	3	4.8	0.32 0.31 0.31	1500–1550	0	fruit	< 0.50	3.3	3.6
					14	fruit[a]	< 0.50	3.2	3.5
					14	flesh	< 0.50	7.5	7.8
					14	peel	< 0.50	2.3	2.6

[a] Calculated whole fruit residues [(peel weight × peel residues) + (flesh weight × flesh residues)] /total fruit weight

In supervised trials from USA four foliar sprays of fosetyl-Al (80 WDG) were applied to avocado trees at 26 to 127 day intervals and duplicate whole fruit samples were stored frozen for up to 51 days before extraction and analysis using GC-FPD method 163 to measure residues of fosetyl-Al. The overall average concurrent recovery rate was 78% and the LOQ was 0.0.05 mg/kg.

Table 111 Residues in avocados from supervised trials in USA involving foliar applications of fosetyl-Al (80 WDG formulations)

AVOCADO	Application				DALA	Residues (mg/kg) corrected for recovery	
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al
GAP: USA	4	4.5		1000-3000	0		
USA, 1984 Goleta, CA (Hass/Duke 7) R003869 0920484-111-A	4	4.5	0.24	1871	0	fruit	7.1
USA, 1984 Homestead, FL (Lisa) R003869 0930984-105-A	4	4.5	0.48	935	0	fruit	1.4
USA, 1984 Fallbrook, CA (Hass/Topa Topa) R003869 0920485-108-A	4	4.5	0.086	5238	0	fruit	1.5

AVOCADO Country, year Location (variety) References	Application				DALA	Residues (mg/kg) corrected for recovery	
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al
USA, 1984 Homestead, FL (Miguel) R003869 0930984-118-A	4	4.5	0.48	935	0	fruit	0.72
USA, 1985 Fallbrook, CA (Hass/Topa Topa) R003869 0920485-127-A	4	4.5	0.086	5238	0	fruit	2.6

Pineapple – fosetyl-Al

In supervised trials conducted in Central America and Hawaii, pineapple slips or suckers (ratoons) were dipped in solutions of 2.4–6.2 g ai/litre fosetyl-Al (WDG formulations immediately before planting and treated with 3–10 foliar sprays of fosetyl-Al (WG) from the 9-leaf, root hair formation, start of flowering or fruit formation.

In the central American trials, samples of fruit (without crowns) and sub-samples of flesh and peel were stored frozen for 170–333 days before extraction and analysis and in the Hawaiian trials conducted in 1982 and 1983, samples of fruit, leaves and bran (animal feed) were stored for up to 50 days between extraction and analysis. No information was available on the frozen storage intervals in the 1990 Hawaiian trials.

Analytical methods used in these trials were the LC-MS/MS method 00861/M001 (Central American trials) and the GC-FPD method RE 21.82 (Hawaii 1980–83 trials) to measure residues of fosetyl-Al and phosphonic acid and the GC-FPD method SOP-90113 was used in the Hawaii 1990 trials to measure residues of fosetyl-Al. Average concurrent recovery rates were 68–111% for fosetyl-Al (fortification levels of 0.05–1.5 mg/kg) and 68–140% for phosphonic acid (fortification levels of 0.05–25 mg/kg) and LOQs were 0.05 mg/kg (fosetyl-Al) and 0.5 mg/kg (phosphonic acid).

Table 112 Residues in pineapples from supervised trials in Central America and Hawaii involving pre-plant dip and foliar applications of fosetyl-Al (WDG formulations)

PINEAPPLE Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) corrected for recovery		
	no	kg ai/hL	Water (L/ha)	RTI (days)			Fosetyl-Al	Phos-acid	Total residues
GAP: USA	1 dip 6 foliar	0.24 0.36			90				
Costa Rica, 2005 Del Monte-Pindeco (MD2) RAFYX078 FY001-04H-TRTD1	1 dip+ 3 foliar	0.24 0.13	- 2732–2745	139 121 78	84	flesh peel	< 0.05 < 0.05	< 0.5 1.6	< 0.53 1.6
Costa Rica, 2005 Guacimo, Limon (MD2) RAFYX078 FY002-04D-TRTD1	1 dip+ 3 foliar	0.24 0.13-0.14	- 2700–2736	189 70 76	30 60 92 120 92 92	fruit fruit fruit fruit flesh peel	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	2.5 1.9 2.4 2.8 2.0 2.8	2.5 1.9 2.4 2.8 2.0 2.8

PINEAPPLE Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) corrected for recovery		
	no	kg ai/hL	Water (L/ha)	RTI (days)			Fosetyl-Al	Phos-acid	Total residues
Guadeloupe, 2005	1 dip +	0.3	-	166	84	flesh	< 0.05	3.1	3.1
Sainte Marie	3 foliar	0.14	2500–2546	171		peel	< 0.05	5.8	5.8
(Cayenne)				48					
RAFYX078									
FY005-04H-TRTD1									
Martinique, 2005	1 dip +	0.3	-	167	27	fruit	< 0.05	3.2	3.2
Basse Pointe	3 foliar	0.06	2494–6294	181	55	fruit	< 0.05	4.7	4.7
(Cayenne)		0.06		65	88	fruit	< 0.05	1.0	1.0
		0.14			111	fruit	< 0.05	3.8	3.8
RAFYX078									
FY008-04D-TRTD1					88	flesh	< 0.05	4.2	4.2
						peel	< 0.05	7.0	7.0
Costa Rica, 2014	1 dip +	0.24	-	125	90	fruit	< 0.05	2.2	2.2
La Virgen de	3 foliar	0.14	2501–2503	148					
Sarapiquí Heredia				90	90	flesh	< 0.05	1.7	1.7
(MD-2)						peel	< 0.05	2.6	2.6
RAFYN023									
FY001-13HA-TRTD1									
Costa Rica	1 dip +	0.24	-	128	30	fruit	< 0.05	1.7	1.7
Puerto Viejo Heredia	3 foliar	0.14	2501–2503	138	60	fruit	< 0.05	2.8	2.8
America, Middle				118	89	fruit	< 0.05	3.6	3.6
2014									
Pineapple MD-2					89	flesh	< 0.05	2.7	2.7
(Golden)						peel	< 0.05	2.6	2.6
RAFYN023									
FY002-13DA-TRTD1									
Costa Rica	1 dip +	0.24	-	118	30	fruit	< 0.05	9.5	9.5
Muelle Alajuela	3 foliar	0.14	2501–2511	100	60	fruit	< 0.05	5.7	5.7
America, Middle				88	84	fruit	< 0.05	5.9	5.9
2014								c=2.8	c=2.8
Pineapple MD-2					120	fruit	< 0.05	6.9	6.9
(Golden)									
					84	flesh	< 0.05	3.9	3.9
RAFYN023								c=2.1	c=2.1
FY003-13DA-TRTD1					84	peel	< 0.05	7.0	7.0
								c=3.9	c=3.9
Guatemala	1 dip +	0.24	-	170	89	fruit	< 0.05	6.4	6.4
Bolivar Tiquisate	3 foliar	0.13	2867–4455	152				c=4.6	c=4.6
America, Middle				47					
2014					89	flesh	< 0.05	4.5	4.5
Pineapple MD-2								c=2.4	c=2.4
(Golden)					89	peel	< 0.05	2.6	2.6
								c=5.1	c=5.1
RAFYN023									
FY004-13HA-TRTD1									
USA, 1980	1 dip	0.24	-		harvest	fruit	< 0.05	0.17	0.20
Honolua Plantation,								c=0.17	c=0.20
Hawaii									
(unspecified)					harvest	leaf	< 0.05	0.22	0.25
								c=0.15	c=0.18
R000990									
185080-001-B1					harvest	dry bran	< 0.10	0.42	0.49
								c=0.57	c=0.64

PINEAPPLE Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) corrected for recovery		
	no	kg ai/hL	Water (L/ha)	RTI (days)			Fosetyl-Al	Phos-acid	Total residues
USA, 1980 Honolua Plantation, Hawaii (unspecified) R000990 185080-001-B3	4 foliar	0.08	2806		harvest	fruit	< 0.05	1.0 c=0.17	1.1 c=0.20
					harvest	leaf	< 0.05	0.64 c=0.18	0.67 c=0.21
					harvest	dry bran	< 0.10	3.0 c=0.57	3.1 c=0.64
USA, 1980 Honolua Plantation, Hawaii (unspecified) R000990 185080-001-C1	1 dip	0.48	-		harvest	fruit	< 0.05	0.16 c=0.17	0.19 c=0.20
					harvest	leaf	< 0.05	0.41 c=0.15	0.44 c=0.18
					harvest	dry bran	< 0.10	0.42 c=0.57	0.49 c=0.64
USA, 1980 Honolua Plantation, Hawaii (unspecified) R000990 185080-001-C3	4 foliar	0.16	2806		harvest	fruit	< 0.05	1.8 c=0.20	1.8 c=0.23
					harvest	leaf	< 0.05	0.99 c=0.15	1.0 c=0.18
					harvest	dry bran	< 0.10	5.7 c=0.57	5.8 c=0.64
USA, 1980 Dole Lanai Plantation (unspecified) R000990 185080-002-M	1 dip	0.24	-		559	fruit	< 0.05	0.22 c=0.09	0.25 c=0.12
					559	leaf	< 0.05	0.20 c=0.16	0.23 c=0.19
					559	dry bran	< 0.10	1.5 c=0.42	1.6 c=0.49
USA, 1980 Dole Lanai Plantation (unspecified) R000990 185080-002-N	1 dip	0.48	-		559	fruit	< 0.05	0.26 c=0.09	0.29 c=0.12
					559	leaf	< 0.05	0.16 c=0.16	0.19 c=0.19
					559	dry bran	< 0.10	2.5 c=0.42	2.6 c=0.49
USA, 1980 Dole Lanai Plantation (unspecified) R000990 185080-002-PC	1 dip + 2 foliar	0.24 0.08	- 2806	60 61	438	fruit	< 0.05	0.32 c=0.09	0.35 c=0.12
					438	leaf	< 0.05	0.25 c=0.16	0.28 c=0.19
					438	dry bran	< 0.10	1.8 c=0.42	1.9 c=0.49
USA, 1980 Kunia Plantation (unspecified) R000990 185080-003-B	1 dip	0.31	-		9 mo	fruit	< 0.05	0.33	0.36
					9 mo	leaf	< 0.05	0.31	0.34
					9 mo	dry bran	< 0.10	0.91 c=0.55	0.97 c=0.62
USA, 1980 Kunia Plantation (unspecified) R000990 185080-003-C	1 dip	0.62	-		9 mo	fruit	< 0.05	0.83	0.86
					9 mo	leaf	< 0.05	0.28	0.31
					9 mo	dry bran	< 0.10	1.7 c=0.55	1.8 c=0.62

PINEAPPLE Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) corrected for recovery		
	no	kg ai/hL	Water (L/ha)	RTI (days)			Fosetyl-Al	Phos-acid	Total residues
USA, 1980 Kunia Plantation (unspecified)	1 dip + 1 foliar	0.31 0.1	- 2806	92	9 mo	fruit	< 0.05	0.56	0.59
					9 mo	leaf	< 0.05	0.44	0.47
R000990 185080-003-E2					9 mo	dry bran	< 0.10	1.7 c=0.55	1.7 c=0.62
USA, 1980 Kunia Plantation (unspecified)	1 dip + 1 foliar	0.62 0.21	- 2806	92	9 mo	fruit	< 0.05	0.98	1.0
					9 mo	leaf	< 0.05	0.50	0.53
R000990 185080-003-F2					9 mo	dry bran	< 0.10	2.6	2.7 c=0.62
USA, 1980 Kunia Plantation (unspecified)	1 dip	0.24	-		9 mo	fruit	< 0.05	0.13	0.16 c=0.14
R000990 185080-004-B1					9 mo	leaf	< 0.05	0.14 c=0.14	0.17 c=0.17
					9 mo	dry bran	< 0.10	0.56 c=0.39	0.63 c=0.46
USA, 1980 Kunia Plantation (unspecified)	1 dip + 4 foliar	0.24 0.24	- 2806	88 108 51 91	9 mo	fruit	< 0.05	0.43	0.46 c=0.14
R000990 185080-004-B3					9 mo	leaf	< 0.05	0.52 c=0.14	0.55 c=0.17
					9 mo	dry bran	< 0.10	5.0 c=0.39	5.1 c=0.46
USA, 1980 Kunia Plantation (unspecified)	1 dip	0.48	-		9 mo	fruit	< 0.05	0.20	0.23 c=0.14
R000990 185080-004-C1					9 mo	leaf	< 0.05	0.26 c=0.17	0.29 c=0.20
					9 mo	dry bran	< 0.10	1.4 c=0.31	1.5 c=0.38
USA, 1980 Kunia Plantation (unspecified)	1 dip + 4 foliar	0.48 0.48	- 2806	88 108 51 91	9 mo	fruit	< 0.05	1.1	1.1 c=0.14
R000990 185080-004-C3					9 mo	leaf	< 0.05	1.4 c=0.17	1.4 c=0.20
					9 mo	dry bran	< 0.10	6.6 c=0.31	6.7 c=0.38
USA, 1980 Haliimaile Plantation Hawai (unspecified)	1 dip + 6 foliar	0.24 0.24	- 2806	91 90–92	90	fruit	< 0.05	3.1	3.1
					90	leaf	< 0.05	1.6	1.6
R001845 185080-005-B3					90	dry bran	< 0.10	12 c=1.7	12 c=1.8
USA, 1980 Haliimaile Plantation Hawai (unspecified)	1 dip + 6 foliar	0.48 0.48	- 2806	91 90–92	90	fruit	< 0.05	5.3	5.3
					90	leaf	< 0.05	3.0	3.0
R001845 185080-005-C3					90	dry bran	< 0.05	15 c=1.7	15 c=1.8

PINEAPPLE Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) corrected for recovery		
	no	kg ai/hL	Water (L/ha)	RTI (days)			Fosetyl-Al	Phos-acid	Total residues
USA, 1982 Honolua Plantation Hawai (unspecified) R003880 UH8.3P37-3-A	1 dip	0.24	-		634	fruit	< 0.05	< 0.05	< 0.085
					634	leaf	< 0.05	< 0.05 c=0.078	< 0.085 c=0.11
					634	dry bran	< 0.05	0.18 c=0.11	0.21 c=0.14
					634	peel	< 0.05	0.081 c=0.15	0.12 c=0.18
USA, 1982 Honolua Plantation Hawai (unspecified) R003880 UH8.3P37-3-D	1 dip + 6 foliar	0.24 0.12	- 2806	96 78–97	90	fruit	< 0.05	0.71	0.74
					90	leaf	< 0.05	0.11 c=0.078	0.15 c=0.11
					90	dry bran	< 0.05	2.2	2.2 c=0.14
					90	peel	< 0.05	0.51 c=0.15	0.54 c=0.18
USA, 1982 Honolua Plantation Hawai (unspecified) R003880 UH8.3P37-3-E	1 dip + 6 foliar	0.24 0.24	- 2806	95 78–97	90	fruit	< 0.05	1.0	1.0
					90	leaf	< 0.05	0.16 c=0.078	0.19 c=0.11
					90	dry bran	< 0.05	3.2 c=0.11	3.2 c=0.14
					90	peel	< 0.05	1.2 c=0.15	1.2 c=0.18
USA, 1983 Kunia Plantation Hawai (unspecified) R003880 UH8.3P37-4-A	1 dip	0.24	-		602	fruit	< 0.05	0.067	0.10
					602	leaf	< 0.05	0.067	0.10
					602	dry bran	< 0.05	0.084	0.12
					602	peel	< 0.05	< 0.05	< 0.085
USA, 1983 Kunia Plantation Hawai (unspecified) R003880 UH8.3P37-4-D	1 dip + 6 foliar	0.24 0.12	- 2806	90 84–93 64	82	fruit	< 0.05	4.1	4.1
					82	leaf	< 0.05	3.1	3.1
					82	dry bran	< 0.05	15	15
					82	peel	< 0.05	2.8	2.8
USA, 1983 Kunia Plantation Hawai (unspecified) R003880 UH8.3P37-4-E	1 dip + 6 foliar	0.24 0.24	- 2806	90 84–93 64	82	fruit	< 0.05	8.2	8.2
					82	leaf	< 0.05	7.8	7.8
					82	dry bran	< 0.05	26	26
					82	peel	< 0.05	6.5	6.5
USA, 1983 Kunia Plantation Hawai (unspecified) R003881 UH8.3P37-4-D	1 dip + 10 foliar	0.24 0.12	- 2806	90 84–122 86	92	fruit	< 0.05	4.0 c=0.05	4.0 c=0.085
					92	leaf	< 0.05	2.2 c=0.14	2.2 c=0.17
					92	dry bran	< 0.05	8.8 c=0.38	8.8 c=0.42
					92	peel	< 0.05	3.5 c=0.13	3.5 c=0.16

PINEAPPLE Country, year Location (variety) References	Application				DALA	matrix	mean residues (mg/kg) corrected for recovery		
	no	kg ai/hL	Water (L/ha)	RTI (days)			Fosetyl-Al	Phos-acid	Total residues
USA, 1983 Kunia Plantation Hawai (unspecified) R003881 UH8.3P37-4-E	1 dip + 10 foliar	0.24 0.24	- 2806	90 84– 122 86	92	fruit	< 0.05	5.0 c=0.05	5.0 c=0.085
					92	leaf	< 0.05	4.1 c=0.14	4.1 c=0.17
					92	dry bran	< 0.05	12 c=0.38	12 c=0.42
					92	peel	< 0.05	5.6 c=0.13	5.7 c=0.16
USA, 1990 Poamoho, Hawai (Smooth cayenne) B003960 90-155	1 dip + 6 foliar	0.24 0.18	- 1871	74 74–76	88	fruit	< 0.05	n.a.	
USA, 1990 Makawao, Hawai (Smooth cayenne) B003960 90-156	1 dip + 6 foliar	0.24 0.18	- 1871	91 87–92	89	fruit	< 0.05	n.a.	

In supervised trials conducted in Brazil, three foliar sprays of fosetyl-Al (WP formulations) were applied to pineapples at 15 day intervals between BBCH73 and BBCH 85. Whole fruit samples (without crowns) were stored frozen for 131–277 days up to 51 days before extraction and analysis using the LC-MS/MS method 00861/M001 to measure residues of fosetyl-Al (LOQ of 0.01 mg/kg) and phosphonic acid (LOQ of 0.1 mg/kg). The overall average concurrent recovery rates were 83–85% for fosetyl-Al (fortification levels of 0.01 mg/kg and 1.0 mg/kg) and were 88–106% for phosphonic acid (fortification levels of 0. 1 mg/kg and 100 mg/kg).

Table 113 Residues in pineapples from supervised trials in Brazil involving foliar applications of fosetyl-Al (WP formulations)

PINEAPPLE Country, year Location (variety) References	Application			DALA	Residues (mg/kg) corrected for recovery			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid[a]	Total residues
GAP: Brazil	1 3	0.08 kg ai/hL dip 0.2 kg ai/hL foliar		20				
Brazil, 2014 Colombia (Pérola) F14-023-01/F15-150	3	2.00–2.06	1004–1031	0	fruit	0.24	4.0 c=0.43	4.1 c=0.44
				7		0.13	5.6 c=0.62	5.7 c=0.63
				14		0.084	5.8 c=0.59	5.9 c=0.60
				20		0.06	7.0 c=0.57	7.0 c=0.58
				28		0.043	5.5	5.5
Brazil, 2014 Fronteira(Pérola) F14-023-02/F15-150	3	1.96–1.99	979–997	0	fruit	0.34	4.8	5.0
				7		0.34	4.5	4.7
				13		0.040	3.8	3.8
				19		< 0.01	4.9	4.9
				28		< 0.01	4.3	4.3

PINEAPPLE	Application			DALA	Residues (mg/kg) corrected for recovery			
Country, year Location (variety) References	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid[a]	Total residues
Brazil, 2014 Frutal (Pérola) F14-023-03/F15-150	3	2.02–2.1	1007–1051	0	fruit	0.038	10 c=3.3	10 c=3.3
				7		< 0.01	11 c=3.9	11 c=3.9
				14		< 0.01	9.9 c=3.7	9.9 c=3.7
				20		< 0.01	8.8 c=3.3	8.8 c=3.3
				27		< 0.01	12 c=2.7	12 c=2.7
Brazil, 2014 Araraquara (Pérola) F14-023-04/F15-150	3	2.06–2.10	1034–1053	19	fruit	0.035	5.3	5.3
Brazil, 2014 Motuca (Pérola) F14-023-05/F15-150	3	1.99–2.12	996–1055	20	fruit	0.013	3.6 c=2.4	3.6 c=2.4

[a] Mean of two residues values

Fruiting vegetables, Cucurbits

The Meeting received trials with fosetyl-Al on cucumber, courgette (summer squash), winter squash and melon (cantaloupe) for Europe and North America.

Cucumber – fosetyl-Al

In supervised trials conducted in Europe, four foliar sprays of fosetyl-Al (WG) were applied to greenhouse cucumbers at 8–14 day intervals. Samples of whole fruit were stored frozen for up to 118 days (except for trials DR 00 EUI 162 and 02R340, where the samples were stored for up to 205–284 days. Extraction and analysis was by GC-FPD methods DFG 522 or AR 155-97, measuring residues of fosetyl-Al and phosphonic acid (LOQs of 0.2 mg/kg for each analyte). Overall average concurrent recovery rates were 87–96% for fosetyl-Al (fortification levels of 0.2–10 mg/kg) and 71–92% for phosphonic acid.

Table 114 Residues in protected cucumbers from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

CUCUMBER	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Greece	4	4.8			1				
France, 1996 Lucenay (Pyralis) R002924 96-517-LY1	4	3.2	0.48–0.34	667–933	3	fruit	0.52	8.4	8.7
France, 1996 Ouvrouer les champs (Serami) R002924 96-517-OR1	4	2.8–3.1	0.72–0.4	394–742	3	fruit	1.2	11	12

CUCUMBER	Application				DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
France, 2000 Ouvrouer les champs (Avalon) C012372 00-541-OR1	4	3.2	0.32	1000	0 1 3 7	fruit	1.0 1.1 1.2 < 0.20	11 12 11 11	12 13 12 11
France, 2000 Jargeau (Avalon) C011722 00-542-OR1	4	3.2	0.32	1000	3	fruit	0.87	12	12
Spain, 2000 Los Palacios (Sevilla) (Darina) C012595 DR 00 EUI 162-ESP0201	4	3.63–4.2	0.32	1000–1300	0 3 7	fruit	0.21 0.44 0.34	12 13 14	12 13 14
Spain, 2000 El Alquián- Almería (Crispina) C012595 DR 00 EUI 162-ESP0301	4	3.2	0.38–0.32	850–1000	0 3	fruit	1.6 3.5	25 25	26 27
Italy, 2000 Pontegradella (Fe) (Jazzer) C012595 DR 00 EUI 162-ITA0101	4	3.2	0.32	1000	0 3 7	fruit	0.77 0.94 0.38	19 32 26	20 33 26
Italy, 2000 Molfetta Puglia (Locale di Polignano) C012595 DR 00 EUI 162-ITA0201	4	3.2	0.32	1000	0 3	fruit	1.3 1.4	10 14	11 15
Germany, 2000 Haidlfing Bayern (Melody) C012409 DR 00 EUN 161-DEU0301	4	4.5	0.75	600	0 4 8	fruit	0.77 c=0.46 0.29 < 0.20	5.5 c=1.9 7.3 c=2.2 4.3 c=1.3	6.0 c=2.2 7.5 c=2.3 4.4 c=1.4
Germany, 2000 Mettenhausen (Melody) C012409 DR 00 EUN 161-DEU0302	4	4.5	0.75	600	0 4 8	fruit	0.79 0.28 < 0.20	6.1 c=2.8 11 c=3.4 11 c=1.1	6.6 c=2.9 11 c=3.5 11 c=1.2
Germany, 2000 Erftstadt - Friesheim (Otello) C012409 DR 00 EUN 161-DEU0501	1+ 3	4.5+ 4.5	1.5 0.75	300 600	0 4	fruit	0.34 0.21	2.9 13	3.1 13

CUCUMBER Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Germany, 2002 Brandis Sachsen (Eva) C033448 02R340-1	4	4.5	1.5	300	0	fruit	< 0.20	9.2	9.3
					4		0.25	9.9	10
					7		0.35	11	11
Germany, 2002 Düren – Echtz (Kapra) C033448 02R340-2	4	4.5		300	0	fruit	< 0.20	4.3	4.4
					4		0.68	30	30
								c=0.35	c=0.49
					7		0.95	37	38
								c=0.24	c=0.38
Germany, 2002 Haidlfing (Carine) C033448 02R340-3	4	4.5		300	0	fruit	0.21	6.9	7.0
					4		0.32	6.6	6.8
					7		< 0.20	4.8	4.9
Germany, 2002 Neusling(Adam) C033448 02R340-4	4	4.5		300	0	fruit	0.43	17	17
					4		0.20	21	21
					7		< 0.20	12	12
Germany, 2002 Mettenhausen (Melody) C033448 02R340-5	4	4.5		300	0	fruit	0.98	11	12
					4		0.41	14	14
					7		0.33	9.3	9.5

In supervised trials conducted in USA, fosetyl-Al was applied to cucumbers as a pre-plant soil incorporation, a subsequent foliar spray of seedlings prior to transplanting and 5–6 foliar sprays in the field, with retreatment intervals ranging from 3 to 97 days. Samples of whole fruit (2 or 3 replicates) were stored frozen for up to 92 days, except in trials GGB88-65, -66 and -67, where samples were stored for up to 244 to 251 days. Extraction and analysis was by GC-FPD method SOP-90113 to measure residues of fosetyl-Al. The overall average concurrent recovery rate was 87% fosetyl-Al in samples fortified with 0.5–5 mg/kg and the LOQ was 0.05 mg/kg.

Table 115 Residues in cucumbers from supervised trials in USA involving pre-plant soil incorporation and foliar applications of fosetyl-Al (WP formulations)

CUCUMBER Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) – corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
GAP: USA	7 foliar	2.2-5.6			0			
USA, 1988 Belle Glade, FL (Market More) R000018 560988-113	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 94	22 24, 7–5	0	fruit	1.9, 1.8, 1.5	1.7 c=0.08
USA, 1988 Quincy FL (XPN 1473) R000018 960987-165	6 foliar	4.5	49	3–5	0	fruit	0.13, 0.17	0.15

CUCUMBER Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) – corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
USA, 1988 El Centro, CA (SMR 58 Ferry Morse) R000018 BDD88-008	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47	5 37, 7–8	0	fruit	0.50, 0.36, < 0.05	0.3
USA, 1988 Columbus, OH (Marketmore 76) R000018 DPV88-039	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 99	7 19, 7–8	0	fruit	0.40, 0.22, 0.23	0.28 c=0.07
USA, 1988 Columbus, OH Cucumber (Pickles) Calypso) R000018 DPV88-040	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 99	7 19, 7–8	0	fruit	1.5, 0.52, 0.49	0.84 c=0.05
USA, 1988 Erie County OH (Marketmore 76) R000018 DPV88-041	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 99	7 19, 7–7	0	fruit	0.22, 0.41, 0.24	0.29 c=0.07
USA, 1988 Danevang, TX (Improved Long Green) R000018 GGB88-065	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 94	12 28, 3–7	0	fruit	0.21, 0.22, 0.16	0.2
USA, 1988 Danevang, TX (Poinsett) R000018 GGB88-066	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 94	13 35, 3–7	0	fruit	1.1, 2.1, 0.46	1.2
USA, 1988 Danevang, TX (Chicago Pickling) R000018 GGB88-067	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 94	8 32, 3–7	0	fruit	0.23, 0.21, 0.24	0.23
USA, 1988 Florida Cucumber) R000018 HSY88-073	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- -	14 21, 6–11	0	fruit	0.70, 0.27, 0.11	0.36
USA, 1988 Anderson County, SC (Poinsett 76) R000018 JDH88-081	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 93	18 24, 7–8	0	fruit	1.7, 2.9, 1.1	1.9

CUCUMBER Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) – corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
USA, 1988 Williamsburg County, SC (Scab Mosaic Resistant 58) R000018 JDH88-082	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 93	16 24, 6–7	0	fruit	1.4, 1.3, 1.4	1.4 c=0.05
USA, 1988 Ingham County, MI (Marketmore 76) R000018 JOJ88-089	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 187	16 21, 6–7	0	fruit	2.5, 1.2, 1.9	1.9
USA, 1988 Clinton County MI (Marketmore 76) R000018 JOJ88-091	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 187	24 12, 2–6	0	fruit	0.47, 1.2, 1.5	1.1
USA, 1988 Phelps, NY (Wisconsin) R000018 JPC88-108	7 foliar	4.5	-	22 37, 7–8	0	fruit	1.6, 1.9, 2.0	1.8
USA, 1988 Salinas, CA (Raider) R000018 KWD88-142	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47		0	fruit	5.0, 3.7, 2.9	3.9 c=0.13
USA, 1988 Apex, Wake County, NC (Early) R000018 LCM88-152	7 foliar	4.5	-	50, 2–7, 1, 1	0	fruit	1.0, 1.4, 1.8	1.4
USA, 1988 Lubbock County TX (Straight Eight) R000018 MLC88-194	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 80	16 30, 1-7	0	fruit	1.0, 3.7, 1.2	2.0
USA, 1988 Porterville, CA (Burpless) R000018 RLD88-226	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47	15 30, 3-7	0	fruit	0.38, 0.87, 0.91	0.72

Summer squash – fosetyl-Al

In supervised trials conducted in Europe, three or four foliar sprays of fosetyl-Al (WG) were applied to outdoor courgettes/zucchini at 9–13 day intervals. Samples of whole fruit were stored frozen for up to 247 days (except for trials 01R326 and 01R327, where the samples were stored for up to 245–318 days. In the trials conducted in 2000 and 2001, extraction and analysis was by GC-FPD, methods DFG 522 or AR 155–97, measuring residues of fosetyl-Al and phosphonic acid (LOQs of 0.2 mg/kg for each analyte). Average concurrent recovery rates were 72–96% for fosetyl-Al (fortification levels of 0.01–1.0 mg/kg) and 83–94% for phosphonic acid (fortification levels of 0.2–20 mg/kg). In the more recent studies (2013), the LC-MS/MS method 00861/M001 was used, with a lower LOQ of 0.01 mg/kg for fosetyl-Al.

Table 116 Residues in summer squash from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

SUMMER SQUASH Country, year Location (variety) References	Application				DALA	Residues (mg/kg)			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Greece	4	4.8			3				
France, 2000 Noves (Cora) C012331 00-544A-V1	4	3.2	0.32	1000	0.08 1 3 7	fruit	0.32 0.34 0.54 1.4	7.8 13 19 12 c=0.31	8.0 13 19 13 c=0.45
France, 2000 Mauremount (Tosca) C012331 00-544-TL1	4	3.2	0.32	1000	0.08 1 3 7	fruit	0.38 0.54 0.67 0.37	4.9 3.9 7.6 4.0 c=0.49	5.2 4.3 8.1 4.3 c=0.63
Italy, 2001 Boara (FE) (Storr'S Green F1) C025407 01-R326-1	4	3.2	0.64	500	0 7	fruit	< 0.20 < 0.20	10 13	10 13
Spain, 2001 Brenes (Sevilla) (Clarita) C025407 01R326-2	4	3.2	0.64	500	0 7	fruit	0.26 < 0.20	10 14	10 14
Portugal, 2001 Salvaterra de Magos (Cora) C025407 01R326-3	4	3.2	1.0	300	0 7	fruit	0.59 < 0.20	5.0 6.0	5.4 6.1
Spain, 2001 Alginet (Valencia) (Lola F-1) C025568 01R327-1	4	3.2	0.42	750	0 3 4 7 10	fruit	< 0.20 < 0.20 < 0.20 < 0.20 < 0.20	3.9 11 11 5.7 6.2	4.0 11 11 5.8 6.3
Greece, 2001 Valtohori Chalkidonas (John Jendida) C025568 01R327-2	4	3.2	0.64	500	0 3 5 7 10	fruit	< 0.20 < 0.20 < 0.20 < 0.20 < 0.20	13 15 15 16 12	13 15 15 16 12
Spain, 2013 Alginet (Diamand) 13-2037-01	4	3.2	0.21-0.32	1000-1500	-0 0 3 7 14	fruit	< 0.01 0.16 0.035 < 0.01 < 0.01	9.2 11 18 14 6.9	9.2 11 18 14 6.9
Italy, 2013 Bitonto (President) 13-2037-02	4	3.2	0.32	1000	-0 0 3 7 14	fruit	< 0.01 0.20 0.12 0.029 < 0.01.	9.8 12 18 19 11	9.8 12 18 19 11

In supervised trials conducted in USA, fosetyl-Al was applied to summer squash as a pre-plant soil incorporation, a subsequent foliar spray of seedlings prior to transplanting and/or 6–7 foliar sprays in the field, with retreatment intervals ranging from 3 to 33 days. Samples of whole fruit (3 replicates) were stored frozen for up to 89 days, except in trials 960987-169 and RLD88-227, where samples were stored for up to 97–114 days. Extraction and analysis was by GC-FPD method SOP-90113 to measure residues of fosetyl-Al. The overall average concurrent recovery rate was 92% fosetyl-Al in samples fortified with 0.05–5 mg/kg and the LOQ was 0.05 mg/kg.

Table 117 Residues in summer squash from supervised trials in USA involving pre-plant soil incorporation and foliar applications of fosetyl-Al (WP formulations)

SUMMER SQUASH Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
GAP: USA	7 foliar	2.2-5.6			0			
USA, 1987 El Campo, TX (Pavo) R000018 434287-116	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47	7 25, 7–7	0	fruit	0.68, 0.84, 0.68	0.73
USA, 1987 El Campo, TX (Senator) R000018 434287-117	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	47	7 25, 7–7	0	fruit	0.83, 0.47, 0.33	0.54 c=0.06
USA, 1987 Belle Glade, FL (Zucchini Elite) R000018 560988-114	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 94	22 24, 5–7	0	fruit	0.32, 0.31, 0.43	0.35
USA, 1987 Quincy,FL (Dixie) R000018 960987-165	6 foliar	4.5	49	3–5	0	fruit	< 0.05, < 0.05	< 0.05
USA, 1987 Quincy, FL (Dixie - Yellow Crook Neck) R000018 960987-169	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 49	11 16, 5-9	0	fruit	0.08, < 0.05, < 0.05	0.06
El Centro, CA (Squash, summer) R000018 BDD88-009	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47	24 33, 6–9	0	fruit	1.5, 3.3, 2.5	2.4 c=0.05
USA, 1988 Florida (Dixie) R000018 HSY88-010	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 49	21 25, 5–7	0	fruit	0.49, 0.34, 0.33	0.39

SUMMER SQUASH Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
USA, 1988 Haslett, MI (Elite Hybrid) R000018 JOJ88-092	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 187	28 3–12	0	fruit	1.4, 1.6, 1.6	1.5
USA, 1988 Charlotte, MI (Elite Hybrid) R000018 JOJ88-093	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 187	28 9, 3–12	0	fruit	2.5, 2.6, 2.4	2.5
USA, 1988 Grand Ledge, MI (Elite Hybrid) R000018 JOJ88-094	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 187	28 9, 6–12	0	fruit	0.68, 0.59, 0.89	0.72
USA, 1988 Ontario County, NY (Sundance president) R000018 JPC88-109	7 foliar	4.5	94	24, 2–6	0	fruit	0.66, 0.78, 1.2	0.88 c=0.05
USA, 1988 Salinas, CA (Zuccini) R000018 KWD88-143	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47	22 31, 4–4	0	fruit	3.5, 6.9, 7.8	6.1 c=0.17
USA, 1988 Clackamas Cty, OR (Summer Crookneck) R000018 RJB88-010	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- n.a.	21 33, 5–7	0	fruit	0.31, 0.31, 0.55	0.39
USA, 1988 Benton County, OR (Black Beauty) R000018 RJB88-011	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- n.a.	21 33, 6–7	0	fruit	0.69, 0.78, 0.75	0.74
USA, 1988 Benton County, OR (Bennings Greentint) R000018 RJB88-012	1 soil + 7 foliar	4.5	- n.a.	21 33, 6–7	0	fruit	0.49, 0.64, 0.41	0.51
USA, 1988 Porterville, CA (Italian Zuccini) R000018 RLD88-227	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47	15 30, 3–7	0	fruit	0.07, 0.05, 0.19	0.1
USA, 1987 Lubbock County, TX (Straightneck Early) R000018 MLC88-195	1 soil + 7 foliar	4.5	- n.a.	n.a.	0	fruit	1.2, 0.7, 0.54	0.81

Melons – fosetyl-Al

In supervised outdoor and greenhouse trials conducted in Europe, two or three foliar sprays of fosetyl-Al (WG) were applied to melons at 7–13 day intervals. Melon samples were stored frozen for up to 195 days (except for trials 02R384, 08-2105 and 11-2005, where the samples were stored for up to 173–533 days. In the trials conducted before 2003, extraction and analysis was by GC-FPD methods DFG 522 or AR 155-97 (LOQs of 0.2 mg/kg) and in the more recent studies the LC-MS/MS method 00861/M001, measuring residues of fosetyl-Al (LOQ of 0.01 mg/kg) and phosphonic acid (LOQ of 0.2 mg/kg). Average concurrent recovery rates were 85–118% for fosetyl-Al (fortification levels of 0.01–4.1 mg/kg) and 79–105% for phosphonic acid (fortification levels of 0.2–40 mg/kg).

Table 118 Residues in protected melons from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

MELONS	Application				DALA	Residues (mg/kg)[a]			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Greece	4	4.8			3				
GAP: France	2	3.2			3				
France, 2001	2	3.2	1.3	250	0	fruit	0.86	14	15
Virazeil					3		0.26	5.6	5.8
(Cyrano)								c=0.29	c=0.43
C022016					3	flesh	0.92	20	21
01R383-1					3	peel	1.5	11	12
France, 2001	2	3.2	1.3	250	0	fruit	< 0.20	21	21
Isle Sur La Sorgue					3		0.41	21	21
(Lunastar)									
					3	flesh	0.59	12	12
C022016					3	peel	< 0.20	22	22
01R383-2									
France, 2001	2	3.2	1.3	250	0	fruit	0.52	8.9	9.3
47200 Virazeil								c=2.6	c=2.7
(Cyrano)					1		0.46	9.1	9.4
					2		0.44	9.4	9.7
C021275					3		1.2	27	28
01R384-1									
					3	flesh	0.63	18	18
					3	peel	1.9	13	14
France, 2001	2	3.2	1.3	250	0	fruit	0.33	6.0	6.2
Pernes les Fontaines					1		0.40	5.3	5.6
(Luna Star)					2		0.42	11	11
					3		0.81	18	19
C021275									
01R384-2					3	flesh	0.50	11	11
					3	peel	1.1	14	15
Spain, 2002	2	3.2	0.27	1200	0	fruit	0.68	9.0	9.5
Puebla de Vicar					1		2.3	13	15
(Vulcano)					2		2.1	12	14
					3		2.2	15	17
C031635									
02R384-1					3	flesh	2.4	17	19
					3	peel	1.2	11	12
Spain, 2002	2	3.2	0.29	1100	0	fruit	0.77	7.3	7.8
Almeria					1		1.7	7.8	9.0
(Vulcano)					2		3.0	7.9	10
					3		3.1	10	12
C031635									
02R384-2					3	flesh	5.4	14	18
					3	peel	1.1	4.8	5.6

MELONS Country, year Location (variety) References	Application				DALA	Residues (mg/kg)[a]			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Italy, 2002 Terlizzi (Bari) (Proteo)	2	3.2	0.4	800	0	fruit	0.48	10 c=0.25	10 c=0.39
					1		1.2	6.6 c=0.38	7.4 c=0.52
C031635 02R384-4					2		0.38	8.8 c=0.25	9.1 c=0.39
					3		0.53	14 c=0.29	14 c=0.43
					3	flesh	0.38	14 c=0.26	14 c=0.4
					3	peel	< 0.20	7.8 c=0.28	7.9 c=0.42
Italy, 2002 Giovinazzo (Bari) (Proteo)	2	3.2	0.32	1000	0	fruit	1.2	5.3 c=0.22	6.1 c=0.36
					1		0.67	15 c=0.21	16 c=0.35
C031635 02R384-5					2		< 0.20	16 c=0.29	16 c=0.43
					3		0.34	14 c=0.28	14 c=0.42
					3	flesh	0.27	14 c=0.24	14 c=0.38
					3	peel	< 0.20	10 c=0.22	10 c=0.36

[a] Mean of two residues values for fosetyl-Al and phosphonic acid

Table 119 Residues in outdoor melons from supervised trials in Europe involving foliar applications of fosetyl-Al (80 WG formulations)

MELONS Country, year Location (variety) References	Application				DALA	Residues (mg/kg)[a]			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Greece	4	4.8			3				
GAP: France	2	3.2			3				
France, 1995 Sainte Lheurine (Fiesta)	3	3.2	1.2	260	0	fruit	0.21	11 c=0.46	11 c=0.6
					2		0.27	20 c=0.38	20 c=0.52
R011709 95-668BX1[a]					5		0.32	17 c=0.28	18 c=0.42
					9		0.26	21 c=0.35	21 c=0.49
France, 1995 Robion (Manta)	3	3.2	1.1-1.2	270-290	0	fruit	0.29	15 c=0.22	15 c=0.36
					2		0.44	16	17
R011709 95-668AV1[a]					4		0.49	19 c=0.47	19 c=0.61
					7		0.38	23 c=0.22	23 c=0.36
France, 2008 Monteux (Maltese)	2	3.2	0.53	600	-0	fruit	0.55	14	14
					0		0.70	12	12
					1		1.3	16	17
					2		1.3	21	22
08-2105-01					3		0.89	28	29
					3	flesh	0.60	24	24
					3	peel	1.2	26	27

MELONS	Application				DALA	Residues (mg/kg)^a			
Country, year Location (variety) References	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Spain, 2008	2	3.2	0.32	1000	-0	fruit	0.19	13	13
Gavä								c=3.6	c=3.6
(Sancho)					0		0.26	13	13
					1		0.52	20	20
08-2105-02					2		0.51	20	20
					3		0.52	17	17
								c=4.2	c=4.2
					3	flesh	0.58	19	19
								c=5.0	c=5.0
					3	peel	0.28	14	19
								c=3.3	c=3.3
Italy, 2008	2	3.2	0.4	800	-0	fruit	0.09	7.4	7.5
Palgonia (CT)					0		0.27	8.3	8.5
(Helios)					1		0.21	7.0	7.2
					2		0.31	11	11
08-2105-03					3		0.28	12	12
					3	flesh	0.17	9.1	9.2
					3	peel	0.34	11	11
France, 2008	2	3.2	0.64	500	-0	fruit	0.09	3.4	3.5
Scorbe- Clairvaux					0		0.33	4.5	4.7
(Hugo)					1		0.57	5.1	5.5
					2		0.87	5.8	6.4
08-2105-04					3		1.3	11	12
					3	flesh	1.1	11	12
					3	peel	1.1	12	13
Greece, 2011	2	3.2	0.64	500	-8	fruit	< 0.01	0.39	0.40
Aron as, Katerini					-0		0.22	11	11
(Lavigal)								c=1.5	c=1.5
					0		1.1	9.6	10
11-2005-01					1		0.74	10	11
					2		0.68	11	11
					3		0.42	10	10
								c=2.1	c=2.1
					7		0.63	14	14
					14		0.080	14	14
					3	flesh	0.16	13	13
								c=3.3	c=3.3
					3	peel	0.68	7.8	8.3
								c=1.8	c=1.8
Spain, 2011	2	3.0	0.32	800-944	-8	fruit	< 0.01	< 0.20	< 0.21
Vilanova i la Geltru		3.2	0.4		-0		0.29	9.6	9.8
(Sancho Piel de sapo)					0		0.63	10	10
					1		0.77	11	12
11-2005-02					2		0.66	11	11
					3		0.61	14	14
					7		0.36	22	22
					14		0.21	14	14
					3	flesh	0.60	14	14
					3	peel	0.62	11	11

MELONS Country, year Location (variety) References	Application				DALA	Residues (mg/kg)[a]			
	no	kg ai/ha	kg ai/hL	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Portugal, 2011 Vilafranca de Xira (Leusiada) 11-2005-03	2	3.2	0.64	500	-7	fruit	< 0.01	< 0.20	< 0.21
					-0		0.84	5.9	6.5
					0		1.1	5.8	6.6
					1		1.7	7.6	8.8
					2		1.6	8.3	9.4
					3		1.3	10	11
					7		0.92	14	15
					13		0.53	20	20
					3	flesh	0.69	9.2	9.7
					3	peel	1.7	9.8	11
France, 2011 Monteux (Arapaho) 11-2005-04	2	3.2	0.53	600	-8	fruit	< 0.01	< 0.20	< 0.21
					-0		0.11	9.6	9.7
					0		0.19	9.4	9.5
					1		1.0	12	13
					2		0.79	13	14
					3		0.44	17	17
					7		0.35	19	19
					14		0.20	25	25
					3	flesh	0.30	16	16
					3	peel	0.89	16	17

[a] Mean of two residues values for fosetyl-Al and phosphonic acid

In supervised trials conducted in USA, fosetyl-Al was applied to cantaloupes (melons) as a pre-plant soil incorporation, a subsequent foliar spray of seedlings prior to transplanting and 5–6 foliar sprays in the field, with retreatment intervals ranging from 2 to 77 days. Samples of fruit (3 replicates) were stored frozen for up to 96 days, except in trials 434287-133 and 960987-166, where samples were stored for up to 293–414 days. Extraction and analysis was by GC-FPD method SOP-90113 to measure residues of fosetyl-Al. The overall average concurrent recovery rate was 95% fosetyl-Al in samples fortified with 0.1–10 mg/kg and the LOQ was 0.05 mg/kg.

Table 120 Residues in cantaloupes from supervised trials in USA involving pre-plant soil incorporation and foliar applications of fosetyl-Al (WP formulations)

MELONS Country, year	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) corrected for recovery	
Location (variety) References	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
GAP: USA	7 foliar	5.6			0			
USA, 1987 Donna, TX (Perlita) R000018 434287-133	6 foliar	4.5	47	7–8	0	fruit	1.0, 0.64, 1.2	0.95
USA, 1988 Belle Glade, FL (Magnum 45) R000018 560988-129	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 94	22 51, 4–6	0	fruit	0.48, 0.45, 0.43	0.45
USA, 1988 El Centro, CA (Easy Rider) R000018 BDD88-007	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47	5 37, 7–7	0	fruit	0.61, 1.3, 0.6	0.84

MELONS Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
USA, 1988 Danevang, TX (Magnum 45) R000018 GGB88-069	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 94	12 35, 3–11	0	fruit	0.40, 0.27, 0.3	0.32
USA, 1988 Quincy, FL (Nova) R000018 HSY88-071	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 49	21 56, 2–7	0	fruit	6.1, 11, 4.5	7.2 c=0.06
USA, 1988 Quincy, FL (Cantaloupe) R000018 HSY88-072	1 soil + 6 foliar	0.95 kg ai/m^3 4.5	- 49	28 77, 3–10	0	fruit	1.4, 5.6, 5.2	4.1
USA, 1988 Williamsburg Cty, SC (Hales Best Jumbo) R000018 JDH88-080	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 93	15 17, 48–7	0	fruit	2.7, 1.3, 2.5	2.2
USA, 1988 Haslett, MI (Summet WGP 100) R000018 JOJ88-086	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 187	16 76, 3–4	0	fruit	1.3, 1.9, 2.8	2.0
USA, 1988 Charlotte, MI (Summet WGP 100) R000018 JOJ88-087	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 187	16 76, 3–4	0	fruit	4.3, 4.7, 5.8	4.9
USA, 1988 Grand Ledge, MI (Summet WGP 100) R000018 JOJ88-088	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 187	16 76, 3–4	0	fruit	3.3, 2.6, 2.0	2.6
USA, 1988 Salinas, CA (All Star) R000018 KWD88-141	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- n.a.	22 44, 7–7	0	fruit	3.8, 5.7, 3.8	4.4 c=0.06
USA, 1988 Porterville, CA (Imperial) R000018 RLD88-225	1 soil + 7 foliar	0.95 kg ai/m^3 4.5	- 47	19 56, 7–7	0	fruit	3.6, 3.8, 5.7	4.4
USA, 1988 Wayne, Owen County, IN (Cantaloupe) R000018 TRS88-245	6	4.5	n.a.	7	0	fruit	0.88, 0.24, 0.49	0.54

MELONS Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
USA, 1988 Vincennes, IN (All Star) R000018 TRS88-246	6	4.5	n.a.	7–14	0	fruit	1.6, 2.0, 2.4	2.0
USA, 1988 Lafayette, IN (All Star) R000018 TRS88-247	1 soil + 7 foliar	4.5	- 538	13 7, 7–12	0	fruit	< 0.05, < 0.05, < 0.05	< 0.05
USA, 1987 Quincy, FL (Cantaloupe) R000018 960987-166	6	4.5	49	5–21	0	fruit	0.3	0.3
USA, 1988 Lubbock County, TX (Cantaloupe) R000018 MLC88-193	1 soil + 7 foliar	4.5	- n.a.	n.a.	0	fruit	1.7, 1.4, 1.5	1.5

Fruiting vegetables, other than Cucurbits

The Meeting received trials with fosetyl on tomatoes and peppers from Europe and with fosetyl-Al on tomatoes from North America.

Peppers – fosetyl

In supervised trials on peppers conducted in Europe, two drench applications of fosetyl (SL co-formulated with propamocarb) were applied between seeding and transplanting. A further two simulated drip irrigation treatments were applied to field peppers 0–2 days after transplanting and 3 days before harvest and a further four simulated drip irrigation or drench treatments were made to greenhouse peppers directly after transplanting, 10–21 days later, 7–72 days later and 3 days before harvest. Samples of fruit were stored frozen for 84–342 days. Extraction and analysis for fosetyl and phosphonic acid was by GC-NPD method 20003024/02-RVP (LOQs of 0.2 mg/kg for both analytes) in the 2001 trials, by the GC-FPD method AR 155-97 in the 2003 trials (LOQs of 0.2 mg/kg for both analytes) and in the later trials (2004–2014), the LC-MS/MS method 00861/M001 (LOQs of 0.01 mg/kg for fosetyl and 0.2 mg/kg for phosphonic acid. Average concurrent recovery rates were 73–104% for fosetyl-Al (fortification levels of 0.01–5.0 mg/kg) and 71–107% for phosphonic acid (fortification levels of 0.2–100 mg/kg).

Table 121 Residues in protected peppers from supervised trials in Europe involving drench/drip irrigation applications of fosetyl (SL formulations)

PEPPERS	Application			DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
GAP: Hungary	1+1 drench 4 drip	18.6+9.3^{a} 0.93	20000^{a} -	3				
Germany, 2001 Hamburg Pepper, sweet (Bell Boy F1) C024482 01R013-1	1 drench 1 drench 4 drip	18.7 9.19 1.11-1.12	20058 19714 1786-1807	0 3	fruit	< 0.19 < 0.19	0.3 0.4	0.44 0.54
Italy, 2001 Imola Emilia - Romagna Pepper, sweet (F1 Magnigold) C024482 01R013-2	1 drench 1 drench 4 drip	18.6 9.32 1.88	20000 20000 3030	0 3	fruit	< 0.19 < 0.19	< 0.20 0.2	< 0.34 0.34
Germany, 2001 Hamburg Pepper, sweet (Mazurka RZ) C024482 01R013-3	1 drench 1 drench 4 drip	18.7 8.99 1.09-1.45	20058 19286 1741-1852	0 3	fruit	< 0.19 < 0.19	0.2 0.2	0.34 0.34
Greece, 2001 55102 Thessaloniki Pepper, sweet (Florina) C024482 01R013-4	1 drench 1 drench 4 drip	18.4 9.22 1.94	20000 20000 3125	0 3	fruit	< 0.19 < 0.19	0.7 2.0	0.84 2.1
Greece, 2003 Agia Marina Pepper, sweet (Raiko RZ) C048490 R 2003 0685 7	1 drench 1 drench 4 drip	9.3 9.3 0.93	5000 10000 1267	0 3	fruit	< 0.19 < 0.19	0.54 0.62	0.68 0.76
Italy, 2003 Andria (BA) Pepper, sweet (Valdor) C048490 R 2003 0683 0	2 drench 4 drip	9.3 0.93	20000 -	0 3	fruit	< 0.19 < 0.19	< 0.20 < 0.20	< 0.34 < 0.34
Netherlands, 2003 Zwaagdijk Ost Pepper, sweet (Zerto) C048490 R 2003 0650 4	1 drench 1 drench 4 drip	9.3 9.3 0.93	- - -	0 3	fruit	< 0.19 < 0.19	0.23 0.28	0.37 0.42
Spain, 2003 La Mojonera Pepper, sweet (Flamenco) C048490 R 2003 0684 9	2 drench 4 drip	9.3 0.93	20000 20000	0 3	fruit	< 0.19 < 0.19	0.23 0.28	0.37 0.42

PEPPERS Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
Belgium, 2004 Saint Amand (Rapido) RA-2559/04 R 2004 0755 6	1 drench 1 drench 4 drip	18.6 9.3 0.93	20000 20000 250 (mL/plant)	0 1 3	fruit	< 0.0093 < 0.0093 < 0.0093	2.6 2.5 2.4	2.6 2.5 2.4
Netherlands, 2004 Zwaagdijk-Oost (Festivo) RA-2559/04 R 2004 0754 8	1 drench 1 drench 4 drip	18.6 9.3 0.93	20000 20000 250 (mL/plant)	0 1 3	fruit	< 0.0093 < 0.0093 < 0.0093	5.1 c=0.20 4.3 c=0.20 3.5	5.1 c=0.21 4.3 c=0.21 3.5
Italy, 2004 Scanzano Jonico (Adina) RA-2559/04 R 2004 0752 1	1 drench 1 drench 4 drip	18.6 9.3 0.93	20000 20000 100 (mL/plant)	0 1 3	fruit	< 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21
Spain, 2004 Roquetas de Mar (Olmo) RA-2559/04 R 2004 0680 0	1 drench 1 drench 4 drip	18.6 9.3 0.93	20000 20000 100 (mL/plant)	0 1 3	fruit	< 0.0093 < 0.0093 < 0.0093	4.0 c=0.44 3.4 c=0.35 3.1 c=0.42	4.0 c=0.45 3.4 c=0.36 3.1 c=0.43
Netherlands, 2012 Zwaagdijk Pepper, sweet (Maranello) 12-2057 12-2057-01	1 drench 1 drench 4 drip	18.6 9.3 0.93	20000 20000 1500	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.24 0.26 0.30 0.23 0.21	0.25 0.27 0.31 0.24 0.22
Italy, 2012 Terlizzi Pepper, sweet (Nestor F1) 12-2057 12-2057-02	1 drench 1 drench 4 drip	18.6 9.3 0.93	20000 20000 1071	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.30 0.38 0.30 0.35 0.20	0.31 0.39 0.31 0.36 0.21
Netherlands, 2012 Honselersdijk Pepper, sweet (Maranello) 12-2057 12-2057-03	1 drench 1 drench 4 drip	18.6 9.3 0.93	20000 20000 1500	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.38 0.34 0.21 < 0.20 0.21	0.39 0.35 0.22 < 0.21 0.22
Italy, 2012 Palidoro Fiumicino Pepper, sweet (Lido) 12-2057 12-2057-04	1 drench 1 drench 4 drip	18.6 9.3 0.93	20000 20000 2000	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20 < 0.20 0.20	< 0.21 < 0.21 < 0.21 < 0.21 0.21

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[a] Drench rates equivalent to 1.86 g ai/square metre and 0.93 g ai/square metre, drip irrigation rate based on 15000 plants/ha

Table 122 Residues in outdoor peppers from supervised trials in Europe involving drench/drip irrigation applications of fosetyl (SL formulations)

PEPPERS	Application			DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
GAP: France	1+1 drench 2 drip	18.6+9.3[a] 0.93	20000[a] -	3				
Germany, 2001 Hamburg Pepper, sweet (Bell Boy F1) C024482 01R013-1	1 drench 1 drench 4 drip	18.7 9.19 1.11–1.12	20058 19714 1786–1807	0 3	fruit	< 0.19 < 0.19	0.3 0.4	0.44 0.54
Italy, 2001 Imola Emilia - Romagna Pepper, sweet (F1 Magnigold) C024482 01R013-2	1 drench 1 drench 4 drip	18.6 9.32 1.88	20000 20000 3030	0 3	fruit	< 0.19 < 0.19	< 0.20 0.2	< 0.34 0.34
Germany, 2001 Hamburg Pepper, sweet (Mazurka RZ) C024482 01R013-3	1 drench 1 drench 4 drip	18.7 8.99 1.09–1.45	20058 19286 1741–1852	0 3	fruit	< 0.19 < 0.19	0.2 0.2	0.34 0.34
Greece, 2001 55102 Thessaloniki Pepper, sweet (Florina) C024482 01R013-4	1 drench 1 drench 4 drip	18.4 9.22 1.94	20000 20000 3125	0 3	fruit	< 0.19 < 0.19	0.7 2.0	0.84 2.1
Greece, 2003 Agia Marina Pepper, sweet (Raiko RZ) C048490 R 2003 0685 7	1 drench 1 drench 4 drip	9.3 9.3 0.93	5000 10000 1267	0 3	fruit	< 0.19 < 0.19	0.54 0.62	0.68 0.76
Italy, 2003 Andria (BA) Pepper, sweet (Valdor) C048490 R 2003 0683 0	2 drench 4 drip	9.3 0.93	20000 -	0 3	fruit	< 0.19 < 0.19	< 0.20 < 0.20	< 0.34 < 0.34
Netherlands, 2003 Zwaagdijk Ost Pepper, sweet (Zerto) C048490 R 2003 0650 4	1 drench 1 drench 4 drip	9.3 9.3 0.93	- - -	0 3	fruit	< 0.19 < 0.19	0.23 0.28	0.37 0.42
Spain, 2003 La Mojonera Pepper, sweet (Flamenco) C048490 R 2003 0684 9	2 drench 4 drip	9.3 0.93	20000 20000	0 3	fruit	< 0.19 < 0.19	0.23 0.28	0.37 0.42

PEPPERS	Application			DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
Belgium, 2004	1 drench	18.6	20000	0	fruit	< 0.0093	2.6	2.6
Saint Amand	1 drench	9.3	20000	1		< 0.0093	2.5	2.5
(Rapido)	4 drip	0.93	250 (mL/plant)	3		< 0.0093	2.4	2.4
RA-2559/04								
R 2004 0755 6								
Netherlands, 2004	1 drench	18.6	20000	0	fruit	< 0.0093	5.1	5.1
Zwaagdijk-Oost	1 drench	9.3	20000				c=0.20	c=0.21
(Festivo)	4 drip	0.93	250 (mL/plant)	1		< 0.0093	4.3	4.3
							c=0.20	c=0.21
RA-2559/04				3		< 0.0093	3.5	3.5
R 2004 0754 8								
Italy, 2004	1 drench	18.6	20000	0	fruit	< 0.0093	< 0.20	< 0.21
Scanzano Jonico	1 drench	9.3	20000	1		< 0.0093	< 0.20	< 0.21
(Adina)	4 drip	0.93	100 (mL/plant)	3		< 0.0093	< 0.20	< 0.21
RA-2559/04								
R 2004 0752 1								
Spain, 2004	1 drench	18.6	20000	0	fruit	< 0.0093	4.0	4.0
Roquetas de Mar	1 drench	9.3	20000				c=0.44	c=0.45
(Olmo)	4 drip	0.93	100 (mL/plant)	1		< 0.0093	3.4	3.4
							c=0.35	c=0.36
RA-2559/04				3		< 0.0093	3.1	3.1
R 2004 0680 0							c=0.42	c=0.43
Netherlands, 2012	1 drench	18.6	20000	-0	fruit	< 0.0093	0.24	0.25
Zwaagdijk	1 drench	9.3	20000	1		< 0.0093	0.26	0.27
Pepper, sweet	4 drip	0.93	1500	3		< 0.0093	0.30	0.31
(Maranello)				7		< 0.0093	0.23	0.24
				14		< 0.0093	0.21	0.22
12-2057								
12-2057-01								
Italy, 2012	1 drench	18.6	20000	-0	fruit	< 0.0093	0.30	0.31
Terlizzi	1 drench	9.3	20000	1		< 0.0093	0.38	0.39
Pepper, sweet	4 drip	0.93	1071	3		< 0.0093	0.30	0.31
(Nestor F1)				7		< 0.0093	0.35	0.36
				14		< 0.0093	0.20	0.21
12-2057								
12-2057-02								
Netherlands, 2012	1 drench	18.6	20000	-0	fruit	< 0.0093	0.38	0.39
Honselersdijk	1 drench	9.3	20000	1		< 0.0093	0.34	0.35
Pepper, sweet	4 drip	0.93	1500	3		< 0.0093	0.21	0.22
(Maranello)				7		< 0.0093	< 0.20	< 0.21
				14		< 0.0093	0.21	0.22
12-2057								
12-2057-03								
Italy, 2012	1 drench	18.6	20000	-0	fruit	< 0.0093	< 0.20	< 0.21
Palidoro Fiumicino	1 drench	9.3	20000	1		< 0.0093	< 0.20	< 0.21
Pepper, sweet	4 drip	0.93	2000	3		< 0.0093	< 0.20	< 0.21
(Lido)				7		< 0.0093	< 0.20	< 0.21
				14		< 0.0093	0.20	0.21
12-2057								
12-2057-04								
Spain, 2014	1 drench	18.6	20000	-0	fruit	< 0.0093	< 0.20	< 0.21
Alginet	1 drench	9.30	20000	0		< 0.0093	< 0.20	< 0.21
Pepper, sweet	2 drip	0.93	1000	1		< 0.0093	< 0.20	< 0.21
(Lipari)				3		< 0.0093	< 0.20	< 0.21
				7		< 0.0093	< 0.20	< 0.21
14-2080				14		< 0.0093	< 0.20	< 0.21
14-2080-01								

PEPPERS Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
France, 2014 Le Burgaud Pepper, sweet (Lamuyo) 14-2080 14-2080-02	1 drench 1 drench 2 drip	18.6 9.30 0.93	20000 20000 1000	-0 3	fruit	< 0.0093 < 0.0093	0.78 0.71	0.79 0.72
Italy, 2014 Catania Pepper, sweet (Macio) 14-2080 14-2080-03	1 drench 1 drench 2 drip	18.6 9.30 0.93	20000 20000 1500	-0 0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20 < 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21 < 0.21 < 0.21 < 0.21
Portugal, 2014 Vila-Franca Pepper, sweet (Torpedo) 14-2080 14-2080-04	1 drench 1 drench 2 drip	18.6 9.30 0.93	20000 20000 1500	-0 3	fruit	< 0.0093 < 0.0093	< 0.20 < 0.20	< 0.21 < 0.21
France, 2014 Mont Pouillan Bonnefon Pepper, sweet (Mariner) 14-2177 14-2177-01 (1)	1 drench 1 drench 2 drip	18.6 9.30 0.93	20000 20000 700	-0 0 1 3 8 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 0.20 0.20 < 0.20 < 0.20	< 0.21 < 0.21 0.21 0.21 < 0.21 < 0.21
Spain, 2014 Pedroche Cordoba Pepper, sweet (Heracles) 14-2177 14-2177-02	1 drench 1 drench 2 drip	18.6 9.30 0.93	20000 20000 1000	-0 3	fruit	< 0.0093 < 0.0093	< 0.20 0.20	< 0.21 0.21
Spain, 2014 Velez Malaga Pepper, sweet (Alicum) 14-2177 14-2177-03	1 drench 1 drench 2 drip	18.6 9.30 0.93	20000 20000 1000	-0 0 1 3 8 15	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20 < 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21 < 0.21 < 0.21 < 0.21
Italy, 2014 Moilno dei Giusi Pepper, sweet (Quadrato giallo) 14-2177 14-2177-04	1 drench 1 drench 2 drip	18.6 9.30 0.93	20000 20000 1000	-0 3	fruit	< 0.0093 < 0.0093	< 0.20 0.74	< 0.21 0.75
Italy, 2014 Papiano Marsciano Pepper, sweet (Rosso Tosca F1) 14-2177 14-2177-05	1 drench 1 drench 2 drip	18.6 9.30 0.93	20000 20000 1000	-0 0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.20 < 0.20 < 0.20 0.28 < 0.20 0.22	0.21 < 0.21 < 0.21 0.29 < 0.21 0.23

[a] Drench rates equivalent to 1.86 g ai/square metre and 0.93 g ai/square metre, drip irrigation rate based on 15000 plants/ha

Tomato - fosetyl

In supervised trials on tomatoes conducted in Europe, two seedling drench applications of fosetyl (SL co-formulated with propamocarb) were applied 0–40 days after seeding and again 7–54 days before transplanting, a further two simulated drip irrigation treatments were applied to field tomatoes 0–2 days after transplanting and 3 days before harvest and a further four simulated drip irrigation treatments were made to greenhouse tomatoes directly after transplanting, 10–23 days later, 12–50 days later and 3 days before harvest. Samples of fruit were stored frozen for 73–400 days. Extraction and analysis for fosetyl and phosphonic acid was by GC-NPD method 20003024/02-RVP (LOQs of 0.2 mg/kg for both analytes) in the 2001 trials or LC-MS/MS method 00861/M001 (LOQs of 0.01 mg/kg for fosetyl and 0.2 mg/kg for phosphonic acid. Average concurrent recovery rates were 79–102% for fosetyl-Al (fortification levels of 0.01–5.0 mg/kg) and 82–104% for phosphonic acid (fortification levels of 0.2–100 mg/kg).

Table 123 Residues in protected tomatoes from supervised trials in Europe involving drench/drip irrigation applications of fosetyl (SL formulations)

TOMATOES Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
GAP: Hungary	2 drench 4 drip	9.3[a] 0.93	2000–4000[a] 3000	3				
Spain, 2001 Beniganim (Salvador) C021852 01R015-1	2 drench 4 drip	9.3 1.15–1.16	20074 1875–2343	0 3	fruit	< 0.19 < 0.19	0.2 0.2	0.34 0.34
Germany, 2001 Hamburg (Rougella RZ F1) C021852 01R015-2	2 drench 4 drip	9.2–9.3 1.09–1.19	19876–20026 1763–1914	0 3	fruit	< 0.19 < 0.19	0.2 < 0.20	0.34 < 0.34
Netherlands, 2001 Zwaagdijk (Fergie F6197) C021852 01R015-3	2 drench 4 drip	9.20–9.23 1.55–1.56	19790–19860 2499–2507	0 3	fruit	< 0.19 < 0.19	1.1 0.9	1.2 1.0
Netherlands, 2001 Zwaagdijk (Rapsodie) C021852 01R015-4	2 drench 4 drip	9.14–9.30 1.55–1.56	19658–20000 2502–2512	0 3	fruit	< 0.19 < 0.19	0.6 0.5	0.74 0.64
Belgium , 2004 Saint Amand (Clotilde) RA-2560/04 0712-04	2 drench 4 drip	9.30 0.93	20000 250 (mL/plant)	0 1 3 7 14	fruit	< 0.0093 < 0.0093 0.019 0.019 < 0.0093	4.8 5.4 5.1 5.2 4.1	4.8 5.4 5.1 5.2 4.1
Germany, 2004 Moers-Kapellen (Culina F1) RA-2560/04 0681-04	2 drench 4 drip	9.30 0.93	20000 100 (mL/plant)	0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.33 0.39 0.46 0.42 0.36	0.34 0.40 0.47 0.43 0.37

TOMATOES Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
Italy, 2004 Scanzano (Conchita) RA-2560/04 0682-04	2 drench 4 drip	9.30 0.93	20000 100 (mL/plant)	0 3	fruit	< 0.0093 < 0.0093	< 0.20 0.20	< 0.21 0.21
Spain, 2004 Roquetas de Mar (Pitenza) RA-2560/04 0713-04	2 drench 4 drip	9.30 0.93	20000 100 (mL/plant)	0 3	fruit	< 0.0093 < 0.0093	1.4 c=0.48 1.3 c=0.59	1.4 c=0.49 1.3 c=0.6
Netherlands, 2011 Zwaagdijk (Favorita F1) (cherry) 11-2012-01	2 drench 4 drip	9.30 0.93	20000 2300	-0 1 3	fruit	< 0.0093 < 0.0093 < 0.0093	0.24 0.25 0.23	0.25 0.26 0.24
Spain, 2011 El Ejido, Gualchos (Guindo) (cherry) 11-2012-02	2 drench 4 drip	9.30 0.93	20000 2000	-0 1 3	fruit	< 0.0093 < 0.0093 < 0.0093	0.48 0.35 0.35	0.49 0.36 0.36
Germany, 2011 Bornheim-Merten (Super Sweet 100) (cherry) 11-2012-03	2 drench 4 drip	9.30 0.93	20000 2000	-0 1 3	fruit	< 0.0093 0.025 0.031	< 0.20 0.26 0.32	< 0.21 0.28 0.34

[a] Drench rates equivalent to 0.93 g ai/square metre, drip irrigation rate based on 15000 plants/ha

Table 124 Residues in outdoor tomatoes from supervised trials in Europe involving drench/drip irrigation applications of fosetyl (SL formulations)

TOMATOES Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
GAP: France	2 drench 2 drip	9.3[a] 0.93	2000–4000[a] 3000	3				
France, 2009 Chazay d' Azergues (Roma) 09-2043-01	2 drench 2 drip	9.30 0.93	18700–20000 1225–1248	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.25 0.24 0.26 0.23 < 0.20	0.26 0.25 0.27 0.24 < 0.21
Spain, 2009 Brenes, Sevilla (Juncal) 09-2043-02	2 drench 2 drip	9.30 0.93	20000 2000	-0 1 3 7 13	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21 < 0.21 < 0.21
Italy, 2009 Andria (NUN 6005 TP) 09-2043-03	2 drench 2 drip	9.30 0.93	20000 2000	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21 < 0.21 < 0.21
Portugal, 2009 Vale de Cavalos (Gades) 09-2043-04	2 drench 2 drip	9.30 0.93	20000 1000–2000	-0 1 3 7 13	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21 < 0.21 < 0.21

TOMATOES	Application			DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
France, 2009 St. Ouen L'Aumone (Coeur de bœuf) 09-2043-05	2 drench 2 drip	9.30 0.93	20000 2000	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21 < 0.21 < 0.21
Germany, 2009 Leichlingen (Philona F1) 09-2043-07	2 drench 2 drip	9.30 0.93	20000 1000	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.72 0.75 0.95 0.60 0.69	0.73 0.76 1.0 0.61 0.70
Belgium, 2009 Villers-Perwin (Brodena F1) 09-2043-08	2 drench 2 drip	9.30 0.93	20000 1500	-0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.60 0.53 0.39 0.50 0.34	0.61 0.54 0.40 0.51 0.35
Poland, 2013 Mazowieckie (Polonais F1) 13-2043-01	2 drench 2 drip	9.30 0.93	20000 2000	0 1 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093 < 0.0093	0.35 0.49 0.43 0.37 0.41	0.36 0.50 0.44 0.38 0.42
Hungary, 2013 Kecskemet (Mano H-X/2110) 13-2043-03	2 drench 2 drip	9.30 0.93	20000 1500	-0 1 3	fruit	< 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21
Italy, 2013 Imperia (Marglobe) 13-2044-02	2 drench 2 drip	9.30 0.93	20000 2000	-0 3	fruit	< 0.0093 < 0.0093	0.70 1.0	0.71 1.0
Spain, 2013 Velez Malaga, (Anairis) 13-2044-03	2 drench 2 drip	9.30 0.93	20000 1500	-0 3	fruit	< 0.0093 < 0.0093	< 0.20 < 0.20	< 0.21 < 0.21
Spain, 2013 Velez Malaga (Birloque) 13-2044-05	2 drench 2 drip	9.30 0.93	20000 1500	-0 3	fruit	< 0.0093 < 0.0093	< 0.20 < 0.20	< 0.21 < 0.21
Spain, 2013 Torrox (Birloque) 13-2044-06	2 drench 2 drip	9.30 0.93	20000 1500	-0 3	fruit	< 0.0093 < 0.0093	< 0.20 < 0.20	< 0.21 < 0.21
Poland, 2014 Plochocin (Kmicic) 14-2079-02	2 drench 2 drip	9.30 0.93	20000 1487–1522	-0 3	fruit	< 0.0093 < 0.0093	< 0.20 < 0.20	< 0.21 < 0.21
UK, 2014 Branbury (Ferline) 14-2079-03	2 drench 2 drip	9.30 0.93	20000 1493	0 3 7 14	fruit	< 0.0093 < 0.0093 < 0.0093 < 0.0093	< 0.20 < 0.20 < 0.20 < 0.20	< 0.21 < 0.21 < 0.21 < 0.21
France, 2014 Allonnes (Pépite HF1) 14-2079-04	2 drench 2 drip	9.30 0.93	20000 1194–1201	-0 3	fruit	< 0.0093 < 0.0093	< 0.20 < 0.20	< 0.21 < 0.21

[a] Drench rates equivalent to 0.93 g ai/square metre, drip irrigation rate based on 15000 plants/ha

Tomato – fosetyl-Al

In supervised trials conducted in USA, four foliar sprays of fosetyl-Al (WDG formulations) were applied to field tomatoes at about 14 day intervals and duplicate samples of whole fruit were stored frozen for 26–123 days before analysis. Extraction and analysis was by GC-FPD method 163 to measure residues of fosetyl-Al. The average concurrent recovery rate was 83% fosetyl-Al in samples fortified with 0.2–12 mg/kg and the LOQ was 0.05 mg/kg.

Table 125 Residues in tomatoes from supervised trials in USA involving foliar applications of fosetyl-Al (WDG formulations)

TOMATO Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
GAP: USA	4	4.5	94 min		14			
USA, 1986 Perrysville, OH (FM.6203) C016048 253486-007	4	4.5	94	7–9	14	fruit	< 0.05	< 0.05
USA , 1986 Ohio (Heinz 7145) C016048 253486-051	4	4.5	94	6–15	14	fruit	< 0.05	< 0.05
USA, 1986 King City, CA (Peto 19) C016048 550486-105	4	4.5	702	14	12	fruit	0.1	0.1
08022 Columbus New Jersey USA, 1986 Tomato Campbells) C016048 575186-015	4	4.5	94	14	16	fruit	0.05	0.05
USA, 1986 El Centro, CA (Superior F1 hybrid) C016048 920486-103	4	4.5	468	14–15	14	fruit	1.9	1.9
USA, 1986 Quincy, FL (Sunny) C016048 960986-107	4	4.5	94	13–14	14	fruit	< 0.05	< 0.05
USA, 1987 Marcellus, MI (Pik Red) C016048 992187-006	4	4.5	94	9–20	14	fruit	0.1	0.1

TOMATO Country, year Location (variety) References	Application				DALA	matrix	Fosetyl-Al residues (mg/kg) corrected for recovery	
	no	kg ai/ha	Water (L/ha)	RTI (days)			values	mean
USA, 1988 Columbus, OH (OH 7870) C016048 DPV 88-037	4	4.5	99	14	14	fruit	< 0.05, 0.08, 0.08	0.07
USA, 1988 Huron, OH (Jet Star) C016048 DPV 88-038	4	4.5	99	14	14	fruit	< 0.05, < 0.05, < 0.05	< 0.05
USA, 1988 Gadsden County, FL (Sunny) C016048 HSY 88-007	4	4.5	94	14	14	fruit	0.19, 0.18, 0.3	0.22
USA, 1989 Solano County, CA (Diego 3075) C016048 LWB 89-089	4	2.7	187	14	14	fruit	1.5, 1.3, 1.7	1.5
USA, 1989 Fresno County, CA (UC 82) C016048 RLD 89-019	4	4.5	187	14	14	fruit	1.1, 1.3, 1.5	1.3
USA, 1989 Fresno County, CA (Castle Rock) C016048 RLD 89-090	4	4.5	187	14	14	fruit	0.21, 0.26, 0.16	0.21
USA, 1988 Wayne, IN (OH 7814) C016048 TRS 88-243	4	4.5	94	14	14	fruit	< 0.05, 0.06, < 0.05	0.06
USA, 1988 Wayne, IN (OH 7814) C016048 TRS 88-244	4	4.5	-	14	14	fruit	0.06, 0.05, 0.06	0.06

Leafy vegetables

Lettuce – fosetyl-Al

In supervised trials on greenhouse and outdoor lettuce conducted in Europe, three or four foliar applications of fosetyl-Al (WG formulations) between BBCH 12 and 48, at about 10 day intervals, up to 14 days before harvest. Lettuce samples were stored frozen for 70–333 days. Extraction and analysis for fosetyl and phosphonic acid was by the GC-FPD methods 522 or AR 155-97 (LOQs of 0.2 mg/kg for both analytes) in the earlier and the LC-MS/MS method 00861/M001 (LOQs of 0.01 mg/kg for fosetyl and 0.2 mg/kg for phosphonic acid) in the more recent trials. Average concurrent recovery rates were 80–103% for fosetyl-Al (fortification levels of 0.01–100 mg/kg) and 71–108% for phosphonic acid (fortification levels of 0.2–200 mg/kg).

Table 126 Residues in protected lettuce from supervised trials in Europe involving foliar applications of fosetyl-Al (WG formulations)

LETTUCE	Application			DALA	Residues (mg/kg)			
Country, year Location (variety) References	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Finland		2.4	400–600	14				
Germany 2000 Weingarten lettuce, head (Sensai) C015381 DEU0201	4	2.4	600	0	head	0.73	90	91
				0	head	0.49	86	86
				7		0.21	73	73
				0	head	0.20	77	77
				14		0.21	66	66
				0	head	0.20	11	110
				21		< 0.2	49	49
Germany, 2000 Bornheim lettuce, head (Lollo Bianca) C015381 DEU0501	4	2.1–2.4	533–600	0	head	0.25	180	180
				0	head	0.31	190	190
				7		0.38	180	180
				0	head	< 0.20	110	110
				14		< 0.20	41	41
				0	head	0.2	20	200
				21		< 0.2	24	24
United Kingdom, 2000 Algarkirk/ Boston lettuce, head (Beverley) C015381 GBR0101	4	2.4	600	0	head	1.8	100	101
				14		< 0.2	36	36
Germany, 2003 Bornheim Sechtem lettuce, butterhead (Roderick) RA-2607/03 0127-03	4	2.4	600	0	head	1.1	80	81
				3		0.38	70	70
				7		0.29	59	59
							c=0.41	c=0.55
				14		0.72	56	57
				21		0.6	56	56
France, 2003 St. Jory lettuce, butterhead (Sensai) RA-2607/03 1049-03	4	2.4	600	0	head	1.8	57	58
				3		0.67	55	55
				7		0.38	34	34
				14		0.27	19	19
				21		< 0.2	14	14
Netherlands, 2003 Wervershoof lettuce, butterhead (Flandria) RA-2607/03 1047-03	4	2.4	600	0	head	7.3	89	94
							c=5.7	c=5.8
				3		0.79	35	36
							c=3.9	c=4.0
				7		0.39	15	15
							c=3.7	c=3.8
				14		< 0.2	9.0	9.1
							c=2.0	c=2.1
				21		< 0.2	6.1	6.2
							c=2.4	c=2.5
Germany, 2004 Bornheim Sechtem lettuce, butterhead (Roderick) RA 2518/04 0295-04	4	2.4	600	0	head	0.66	75	75
				3		0.78	110	111
				6		0.64	98	98
				13		0.65	92	92
				20		0.45	120	120

LETTUCE Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Germany, 2004 Langenfeld lettuce, butterhead (Alexandria) RA 2518/04 R 2004 0296 1	4	2.4	600	0	head	1.1	63	64
				3		0.06	21	21
				7		< 0.010	17	17
				14		< 0.010	12	12
				20		< 0.010	8.7	8.7
France 2004 Montfavet lettuce, butterhead (Arcadia) RA 2518/04 R 2004 0298 8	4	2.40	600	0	head	1.4 c=0.02	110 c=14	111 c=14
				3		0.20	49 c=9.9	49 c=9.9
				7		0.090	39 c=8.3	39 c=8.3
				14		0.030	23 c=5.5	23 c=5.5
				21		0.020	18 c=4.4	18 c=4.4
Germany, 2013 Leichlingen lettuce, leaf (Kirinia RZ) 13-2039 13-2039-01	4	2.4	600	-0	leaves	0.82	15	16
				0		4.7	48	51
				7		2.6	19	21
				14		0.073	7.7	7.8
				21		0.010	2.9	2.9
Greece, 2013 Aronas – Katerini Lettuce, leaf (Manchester) 13-2039 13-2039-02	4	2.4	600	0	leaves	5.3	61	65
				14		0.28	27	27
France, 2013 Toulouse lettuce, leaf (Fogo) 13-2039 13-2039-03	4	2.4	800	-0	leaves	0.022	7.3	7.3
				0		4.2	61	64
				7		0.12	14	14
				14		0.037	9.2	9.2
				21		0.050	5.9	5.9
Belgium, 2013 Saint-Amand lettuce, leaf (Sansula) 13-2039 13-2039-04	4	2.4	600	-0	leaves	< 0.010	12	12
				0		0.079	36	36
				7		< 0.010	19	19
				14		< 0.010	13	13
				21		< 0.010	9.1	9.1
Spain, 2013 Bigues i Riells lettuce, leaf (Rouxaï RZ) 13-2039 13-2039-05	4	2.4-2.69	500	-0	leaves	2.1	39	40
				0		4.6	63	66
				7		2.2	34	36
				14		1.9	30	31
				21		0.20	15	15
Portugal, 2013 Malaqueijo lettuce, leaf (Invicta) 13-2039 13-2039-06	4	2.4-2.56	320-500	0	leaves	4.1	37	40
				14		0.048	15	15

LETTUCE Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Netherlands, 2013 DA Ridderkerk lettuce, leaf (Satine) 13-2039 13-2039-07	4	2.2-2.78	275-347	0 14	leaves	9.5 0.024	97 7.7	104 <u>7.7</u>
Italy, 2013 Acate (RG) lettuce, leaf (Nauplus canasta) 13-2039 13-2039-08	4	2.4	500-600	0 14	leaves	1.7 0.23	48 17	49 <u>17</u>

Table 127 Residues in outdoor lettuce from supervised trials in Europe involving foliar applications of fosetyl-Al (WG formulations)

LETTUCE Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Finland	4	2.4		14				
Germany , 1995 Werl Westönnen lettuce, leaf (Ralf) C024353 WTA 31-P3	3	2.3–2.5	300	0 14 21	leaves	61 < 0.2 < 0.2	72 1.9 2.5	114 2.0 2.6
Germany 1995 Werl Oberbergstrasse lettuce, leaf (Ralf) C024353 WTA 32-P3	3	2.322–2.387	300	0 14 21	leaves	21 < 0.2 < 0.2	102 3.5 0.75	117 3.6 0.89
Germany, 1995 Fussgonheim lettuce, leaf (Thirza) C024353 WTA 50-P3	3	2.36–2.59	300	0 14 21	leaves	17 < 0.2 < 0.2	35 1.7 c=0.21 0.81	47 1.8 c=0.35 0.95
Germany, 1995 Werl Westönnen lettuce, leaf (Ralf) C024353 WTA 31-P2	3	2.4–2.5	300	0 14 21	leaves	58 < 0.2 < 0.2	75 2.3 2.4	115 2.4 2.5
Germany, 1995 Werl Oberbergstrasse lettuce, leaf (Ralf) C024353 WTA 32-P2	3	2.387–2.452	300	0 14 21	leaves	16 < 0.2 < 0.2	119 2.3 2.2	130 2.4 2.3

LETTUCE Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Germany, 1995 Fussgonheim lettuce, leaf (Thirza) C024353 WTA 50-P2	3	2.19–2.7	300	0	leaves	13	23	32
				14		< 0.2	1.4	1.5
							c=0.21	c=0.35
				21		< 0.2	0.54	0.68
Greece, 2000 Nea Chalkidona lettuce, leaf (Paris Island Cosh) C016903 GRC0101	4	2.4	500	0	leaves	9.2	19	25
				0	leaves	1.2	14	15
				7		< 0.2	7.8	7.9
				0	leaves	2.3	53	55
				14		< 0.2	5.3	5.4
				0	leaves	4.0	7	73
				21		0.59	7.8	8.2
Greece, 2000 Korifi – Imathia lettuce, leaf (Atraxion) C016903 GRC0102	4	2.4	500	0	leaves	2.9	9	92
				0	leaves	1.4	34	35
				7		0.3	43	43
				0	leaves	0.55	26	26
				14		< 0.2	16	16
				0	leaves	1.2	23	24
				21		< 0.2	7.1	7.2
Italy, 2000 Sala Di Cesenatico lettuce, leaf (Gentilina) C016903 ITA0101	4	2.4	500	0	leaves	0.49	37	38
				14		0.42	4.5	4.8
Italy, 2000 Bologna lettuce, leaf (Aramy) C016903 ITA0102	4	2.4	300	0	leaves	3.5	23	25
				14		< 0.2	6.8	6.9
Italy, 2000 Andria (Bari) lettuce, leaf (Calgary) C016903 ITA0201	4	2.4	600	0	leaves	3.0	30	32
				14		< 0.2	15	15
Portugal, 2000 Salvaterra de Magos lettuce, leaf (Sequeira) C016903 PRT0101	4	2.4	350	0	leaves	4.3	19	22
				0	leaves	4.5	22	25
				7		< 0.2	5.9	6.0
				0	leaves	3.4	30	32
				14		0.2	8.9	9.0
				0	leaves	2.8	22	24
				21		< 0.2	3.3	3.4
Portugal, 2000 Caldas da Rainha lettuce, leaf (Vanity) C016903 PRT0102	4	2.4	350	0	leaves	2.5	30	32
				0	leaves	3.6	27	30
				7		0.63	20	20
				0	leaves	6.6	71	76
				14		0.3	11	11
				0	leaves	2.4	46	48
				21		0.56	15	15

LETTUCE Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Netherlands, 2013 DA Ridderkerk lettuce, leaf (Satine) 13-2082 13-2082-01	4	2.4	300	-0 0 7 14 21	leaves	< 0.010 4.1 0.12 0.051 0.011	14 63 13 8.1 6.6	14 66 13 8.1 6.6
Germany, 2013 Leichlingen lettuce, butterhead (Mafalda) 13-2082 13-2082-02	4	2.4	600	-0 0 7 14 21	head	< 0.010 1.3 0.15 < 0.010 < 0.010	1.2 28 10 4.7 4.1	1.2 29 10 4.7 4.1
France, 2013 St Etienne du Gres lettuce, leaf (Kiribati, Lollo Rosso) 13-2040 13-2040-01	4	2.4	300	-0 0 8 14 21	leaves	< 0.010 0.70 < 0.010 < 0.010 < 0.010	15 57 13 8.5 6.9	15 57 13 8.5 6.9
Italy, 2013 Lusia Rovigo lettuce, leaf (Soupirai, Lollo rossa) 13-2040 13-2040-02	4	2.4	600	-0 0 7 14 21	leaves	0.018 8.7 0.19 0.031 < 0.010	13 43 11 7.1 2.8	13 49 11 7.1 2.8

In supervised trials on leaf and head lettuce conducted in USA, two foliar sprays of fosetyl-Al (WP formulations) were applied to seedlings just emergence and 5-9 days before transplanting into soil that had been mixed with fosetyl-Al at a rate equivalent to 0.95 kg ai/m^3 and a further 3–7 foliar sprays were applied at 5–19 day intervals.

Samples of lettuce leaves or heads (without wrapper leaves) were stored frozen for up to 218 days. Extraction and analysis for fosetyl-Al was by GC-FPD method SPO-90113 with an LOQ of 0.05 mg/kg. Concurrent recovery rates were 71–122% at fortification levels of 0.05-30 mg/kg.

Table 128 Residues in lettuce from supervised trials in USA involving soil incorporated and foliar applications fosetyl-Al (WP formulations)

LETTUCE Country, year Location (variety) References	Application			RTA (days)	DALA	Fosetyl-Al residues (mg/kg) corrected for recovery		
	no	kg ai/ha	water (L/ha)			matrix	values	mean
GAP: USA	7 foliar	4.48	94 (min)		3			
USA, 1988 Castroville, CA Lettuce, head (Salinas Ice Berg) R009240 KWD88-049	4 foliar	4.5	350	9, 15, 5	3	head	0.09, 0.05, < 0.05	0.063

LETTUCE Country, year Location (variety) References	Application			RTA (days)	DALA	Fosetyl-Al residues (mg/kg) corrected for recovery		
	no	kg ai/ha	water (L/ha)			matrix	values	mean
USA, 1988 Monterey, CA Lettuce, head (Salinas Harris Moren) R009240 KWD88-148	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	42, 14 7–7	3	head	3.2, 1.3, 2.6	2.4
USA, 1988 Belle Glade, FL Lettuce, head (Ithaca) R009240 560988-117	1 soil inc 4 foliar	0.95 kg ai/m^3 4.5	- 94	22, 24 7–7	3	head	1.4, 0.56, 1.4	1.1 c=0.05
USA, 1988 Sorrento, FL Lettuce, head (Raleigh) R009240 MLK88-202	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	43, 24 12, 7–7	3	head	1.9, 1.1, 1.1	1.4
USA, 1988 Zellwood, FL Lettuce, head (Ithaca) R009240 MLK88-203	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	26, 38 2–7	3	head	0.10, 0.23, 0.17	0.17
USA, 1988 Monte Vista, CO Lettuce, head (Fame) R009240 CPH88-023	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	-	3	head	0.05, < 0.05, < 0.05	0.05
USA, 1988 Monte Vista, CO Lettuce, head (Fame) R009240 CPH88-024	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	21, 21 7–7	3	head	0.14, 0.43, 0.56	0.38
USA, 1988 Monte Vista, CO Lettuce, head (Fame) R009240 CPH88-025	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	-	3	head	0.63, 0.31, 0.85	0.6
USA, 1988 Ingham, MI Lettuce, head (Ithaca) R009240 JOJ88-099	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 187	14, 30 7–19	3	head	0.05, < 0.05, < 0.05	0.05

LETTUCE Country, year Location (variety) References	Application			RTA (days)	DALA	Fosetyl-Al residues (mg/kg) corrected for recovery		
	no	kg ai/ha	water (L/ha)			matrix	values	mean
USA, 1988 Eaton, MI Lettuce, head (Ithaca) R009240 JOJ88-100	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 187	14, 30 7–19	3	head	< 0.05, 0.05, 0.05	0.05
USA, 1988 Clinton County, MI Lettuce, head (Ithaca) R009240 JOJ88-101	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 187	16, 28 6–19	3	head	0.14, 0.15	0.15
USA, 1988 Wrightstown, NJ Lettuce, head (Ithaca) R009240 MDP88-170	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	13, 29 7–18	3	head	1.4, 1.3, 1.2	1.3
USA, 1988 Wrightstown, NJ Lettuce, head (Ithaca) R009240 MDP88-171	1 soil inc 8 foliar	0.95 kg ai/m^3 4.5	- 94	13, 29 7–18	3	head	0.20, 0.10, 0.09	0.13
USA, 1988 Pennsgrove, NJ Lettuce, head (Ithaca) R009240 MDP88-172	1 soil inc 8 foliar	0.95 kg ai/m^3 4.5	- 94	13, 29 5–13	3	head	3.5, 4.6, 5.1	4.4
USA, 1988 El Campo, TX Lettuce, head (Golden State) R009240 GGB88-030	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	12, 41 3–7	3	head	0.42, 0.06, < 0.05	0.18 c=0.06
USA, 1988 Garwood, TX Lettuce, head (Great Lakes 6238) R009240 GGB88-031	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	22, 31 3–8	3	head	0.15, 0.44, 0.3	0.3
USA, 1987 Donna, TX Lettuce, head (Great Lakes 6238) R009240 434287-139	1 soil inc 8 foliar	0.95 kg ai/m^3 4.5	- 47	25, 22 6–13	3	head	5.1, 4.9	5.0 c=0.05

LETTUCE Country, year Location (variety) References	Application			RTA (days)	DALA	Fosetyl-Al residues (mg/kg) corrected for recovery		
	no	kg ai/ha	water (L/ha)			matrix	values	mean
USA, 1988 California Lettuce, leaf Gennecorp leafy green) R009240 KWD88-019	3 foliar	4.5	-	7, 10	3	leaf	0.06, 0.06, 0.11	0.077
USA, 1988 California Lettuce, romaine (Perris Cross) R009240 KWD88-020	4 foliar	4.5	350	19, 7, 3	3	leaf	1.8, 2.2, 2.1	2.0 c=0.09
USA, 1988 Belle Glade, FL Lettuce, leaf (Waldman's Green) R009240 560988-118	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	22, 24 5–7	3	leaf	6.6, 5.1, 2.1	4.6 c=0.19
USA, 1988 Florida Lettuce, leaf (1589 Slobolt Harris-Moran) R009240 MLK88-204	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	45, 24 7–12	3	leaf	2.9, 4.9, 4.8	4.2
USA, 1988 Zellwood, FL Lettuce, leaf (Waldman`s Green) R009240 MLK88-205	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	26, 38 2–7	3	leaf	0.49, 0.72, 1.0	0.74 c=0.88
USA, 1988 El Campo, TX Lettuce, leaf (Waldmann`s Green Mit) R009240 GGB88-028	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 47–94	10, 43 3–7	3	leaf	0.95, 0.40, 0.42	0.59 c=0.06
USA, 1988 Garwood, TX Lettuce, leaf (Red Sail) R009240 GGB88-029	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 47–94	15, 32 3–7	3	leaf	2.7, 1.4, 2.6	2.2 c=0.07
USA, 1988 Uvalde, TX Lettuce, leaf (Black Seeded Simpson) R009240 AMW88-004	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	99, 7 7–7	3	leaf	< 0.05, 0.49, < 0.05	0.2

LETTUCE Country, year Location (variety) References	Application			RTA (days)	DALA	Fosetyl-Al residues (mg/kg) corrected for recovery		
	no	kg ai/ha	water (L/ha)			matrix	values	mean
USA, 1988 Ingham County, MI Lettuce, leaf (Black Seeded Simpson) R009240 JOJ88-102	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 187	16, 28 5-7	3	leaf	17, 25, 14	19
USA, 1988 Eaton County, MI Lettuce, leaf (Black Seeded Simpson) R009240 JOJ88-103	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 187	16, 28 5–7	3	leaf	14, 15, 32	20
USA, 1988 Clinton County, MI Lettuce, leaf (Black Seeded Simpson) R009240 JOJ88-104	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 187	16, 28 6–19	3	leaf	0.47, 1.1, 0.77	0.78
USA, 1988 Monte Vista, CO Lettuce, leaf (Grand Rapids) R009240 CPH88-026	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	21, 14 7–7	3	leaf	< 0.05, 0.07, < 0.05	0.057
USA, 1988 Monte Vista, CO Lettuce, leaf (Grand Rapids) R009240 CPH88-027	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	21, 14 7–7	3	leaf	0.97, 1.4, 0.9	1.1
USA, 1988 Monte Vista, CO Lettuce, leaf (Grand Rapids) R009240 CPH88-028	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	21, 14 7–7	3	leaf	0.29, 0.41, 0.55	0.42
USA, 1988 Wrightstown, NJ Lettuce, leaf (Black Seeded Simpson) R009240 MDP88-173	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	13, 29 5–7	3	leaf	33, 12, 13	19
USA, 1988 Wrightstown, NJ Lettuce, leaf (Black Seeded Simpson) R009240 MDP88-174	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	13, 29 5–7	3	leaf	31, 28, 24	28

LETTUCE Country, year Location (variety) References	Application			RTA (days)	DALA	Fosetyl-Al residues (mg/kg) corrected for recovery		
	no	kg ai/ha	water (L/ha)			matrix	values	mean
USA, 1988 Pennsgrove, NJ Lettuce, leaf (Black Seeded Simpson) R009240 MDP88-175	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	13, 29 5–7	3	leaf	20, 22, 27	23 c=0.06
USA, 1988 California Lettuce, leaf (unspecified) B004617 BBD88	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	n.a	0	leaf	104, 182, 69	118 c=0.32
					3		68, 22, 61	50

Spinach - fosetyl

In supervised trials on spinach conducted in Europe, one foliar application of fosetyl (SL coformulations with propamocarb) was applied between BBCH 11 and 19 and leaf samples were stored frozen for 46–76 days in trial 13-2019-04 and 146–338 days in the other trials. Extraction and analysis for fosetyl and phosphonic acid was by the GC-FPD methods 522 or AR 155-97 (LOQs of 0.2 mg/kg for both analytes) in the earlier and the LC-MS/MS method 00861/M001 (LOQs of 0.01 mg/kg for fosetyl and 0.2 mg/kg for phosphonic acid). Average concurrent recovery rates were 86–102% for fosetyl (fortification levels of 0.01–1.0 mg/kg) and 103–110% for phosphonic acid (fortification levels of 0.2–100 mg/kg).

Table 129 Residues in spinach from supervised trials in Europe involving foliar applications of fosetyl (SL formulations)

SPINACH Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
GAP: Belgium	1	0.775		14				
Netherlands, 2012 Wervershoof (Celesta) early baby leaf 12-2056 12-2056-01	1	0.775	300	0 3 7 14 21	leaf	0.05 < 0.0093 < 0.0093 < 0.0093 < 0.0093	23 4.4 1.2 0.52 0.32	23 4.4 1.2 0.53 0.33
Germany , 2012 Calveslage (Ballet F1) summer variety 12-2056 12-2056-02	1	0.775	300	0 2 7 14 21	leaf	0.67 0.084 < 0.0093 < 0.0093 < 0.0093	57 18 5.1 2.4 1.4	57 18 5.1 2.4 1.4
Italy, 2012 Manfredonia (America - Royal Sluis) curly leaf 12-2056 12-2056-03	1	0.775	750	0 3 7 14 21	leaf	0.82 0.025 < 0.0093 < 0.0093 < 0.0093	28 7.0 8.8 5.3 4.2	29 7.0 8.8 5.3 4.2

SPINACH Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl	Phos-acid	Total residues
Spain , 2012 Almodovar del Rio (Solomon) winter spinach 12-2056 12-2056-04	1	0.775	300	0	leaf	0.16	35	35
				3		0.13	16	16
				7		0.026	4.2	4.2
				14		< 0.0093	4.2	4.2
				22		< 0.0093	3.0	3.0
Netherlands , 2013 Wervershoof (Monza) flat leaf, slow growing 13-2019 13-2019-01	1	0.775	400	0	leaf	0.44	78	78
				3		0.011	10	10
				7		< 0.0093	1.9	1.9
				14		< 0.0093	0.78	0.79
				21		< 0.0093	0.42	0.43
Belgium , 2013 Saint-Amand (SV3523VC) hybrid spinach 13-2019 13-2019-02	1	0.775	427	0	leaf	0.15	32	32
				3		< 0.0093	12	12
				7		< 0.0093	5.4	5.4
				14		< 0.0093	4.0	4.0
				21		< 0.0093	2.4	2.4
Spain , 2013 La Albuera (Novico) 13-2019 13-2019-03	1	0.775	400	0	leaf	0.93	47	48
				4		0.014	19	19
				7		0.012	18	18
				13		< 0.0093	6.5	6.5
				21		< 0.0093	4.4	4.4
Italy, 2013 Bitonto (America - Royal Sluis) Curly leaf 13-2019 13-2019-04	1	0.775	800	0	leaf	0.68	25	25
				3		0.014	26	26
				7		< 0.0093	14	14
				14		< 0.0093	11	11
				21		< 0.0093	9.7	9.7

Spinach – fosetyl-Al

In supervised trials on spinach conducted in USA, two foliar sprays of fosetyl-Al (WP formulations) were applied to seedlings just emergence and 2–9 days before transplanting into soil that had been mixed with fosetyl-Al at a rate equivalent to 0.95 kg ai/m^3 and a further 6 foliar sprays were applied at 3–7 day intervals.

Samples of spinach leaves were stored frozen for up to 116–348 days. Extraction and analysis for fosetyl-Al was by GC-FPD method SPO-90113 with an LOQ of 0.05 mg/kg. Average concurrent recovery rates were 75–125% at fortification levels of 0.05–25 mg/kg.

Table 130 Residues in spinach from supervised trials in USA involving soil incorporated and foliar applications fosetyl-Al (WP formulations)

SPINACH Country, year Location (variety) References	no	kg ai/ha	water (L/ha)	DALA	Fosetyl-Al residues (mg/kg) – corrected for recovery		
					matrix	values	mean
GAP: USA	7 foliar	4.48	94 (min)	3			
USA , 1988 Porterville, CA (Thick leaf) R009240 RLD88-234	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 47	3	leaf	< 0.05, < 0.05, < 0.05	< 0.05
USA , 1988 Salinas, CA (Baker/Harris Moran) R009240 KWD88-150	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 56	3	leaf	0.18, 0.17, 0.15	0.17 c=0.15
USA , 1988 Zellwood, FL (America) R009240 MLK88-207	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	0	leaf	0.08, 0.07, 0.06	0.07
USA , 1988 Shoffner, AK (Bloomsdale Long Standing) R009240 SDL88-241	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	3	leaf	0.43, 0.39, 0.41	0.41
USA , 1988 Lonoke, AK (Tyee) R009240 SDL88-242	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 62	3	leaf	< 0.05, < 0.05, < 0.05	< 0.05
USA , 1988 Rio Grande, CO (Melody) R009240 CPH88-029	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- 94	2	leaf	0.06, < 0.05, 0.2	0.1 c=0.5
USA , 1988 Maryland (Agway hybrid 30) R009240 LJW88-176	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	3	leaf	< 0.05, < 0.05, 0.3	0.13
USA , 1988 Virginia (Agway hybrid 30) R009240 LJW88-154	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	3	leaf	0.09, < 0.05, < 0.05	0.06
USA , 1988 Virginia (Agway hybrid 30) R009240 LJW88-155	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	3	leaf	0.81, 0.98, 0.93	0.91

SPINACH Country, year Location (variety) References	no	kg ai/ha	water (L/ha)	DALA	Fosetyl-Al residues (mg/kg) – corrected for recovery		
					matrix	values	mean
USA , 1988 New Jersey (Early hybrid 30) R009240 MDP88-177	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	3	leaf	0.54, 0.06, 0.54	0.38 c=0.25
USA , 1988 Wrightstown, NJ (Spinach) R009240 MDP88-178	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	3	leaf	0.68, 0.24, 0.25	0.39 c=0.15
USA , 1988 Penns Grove, NJ New Jersey (Spinach) R009240 MDP88-179	1 soil inc 7 foliar	0.95 kg ai/m^3 4.5	- -	3	leaf	0.24, 0.29, 0.19	0.24

Value in square brackets is the mean residue of two duplicate samples

Tree nuts

Almonds – phosphonic acid

In supervised trials on almonds conducted in USA, 5–6 foliar sprays of phosphorous acid (as the mono- and di-potassium salts) were applied at 6–8 day intervals. Nuts were shaken from the trees, allowed to dry on the ground (5–6 days) before duplicate samples were shelled and frozen for 238 days before extraction and analysis for phosphonic acid using the LC-MS/MS method QuPPE Version 7.1 (LOQ of 0.5 mg/kg for phosphonic acid. Average concurrent recovery rates were 81–87% at fortification levels of 0.5–200 mg/kg). Parallel method validation recoveries ranged from 75–89% at fortification levels from 0.5–10 mg/kg.

Table 131 Residues in almonds from supervised trials in USA involving foliar sprays of phosphonic acid (as the mono- and di-potassium salts - WP formulations)

ALMOND Country, year Location (variety) References	no	kg ai/ha	water (L/ha)	total kg ai/ha	DALA	matrix	Phosphonic acid residues (mg/kg)	
							values	mean
GAP: USA	6	1.9			not stated			
USA , 2015 Hanford, CA (Nonpareil) IR4-11529 CA117	6	1.9	1020–1060	11.3	2+ 6 drying	nutmeat	< 0.5, 0.51	0.505
USA , 2015 Parlier, CA (Padre) IR4-11529 CA118	6	1.9	1540–1590	11.3	2+ 5 drying	nutmeat	< 0.5,< 0.5	< 0.5

ALMOND Country, year Location (variety) References	no	kg ai/ha	water (L/ha)	total kg ai/ha	DALA	matrix	Phosphonic acid residues (mg/kg)	
							values	mean
USA , 2015 Arbuckle, CA (Nonpareil) IR4-11529 CA119	5	1.9	925–1090	9.4	1+ 6 drying	nutmeat	< 0.5,< 0.5	< 0.5
USA , 2015 Winters, CA (Padre) IR4-11529 CA120	6	1.9	1310–1330	11.4	4+ 6 drying	nutmeat	91, 108	99.5
USA, 2015 Hamilton City, CA (Nonpareil) IR4-11529 CA121	6	1.9	1170	11.4	3	nutmeat	6.0, 5.1	5.55

Pistachio – phosphonic acid

In supervised trials on pistachio conducted in USA, 6 foliar sprays of phosphorous acid (as the mono- and di-potassium salts) were applied at 6–9 day intervals. Nuts were shaken onto sheets, collected and duplicate samples were hulled, the shells were removed and the nutmeat samples were taken in the field and frozen for 234 days before extraction and analysis for phosphonic acid using the LC-MS/MS method QuPPE Version 7.1 (LOQ of 0.5 mg/kg for phosphonic acid. Average concurrent recovery rates were 86–96% at fortification levels of 0.5–400 mg/kg). Parallel method validation recoveries ranged from 74–97% at fortification levels from 0.5–10 mg/kg.

Table 132 Residues in pistachio from supervised trials in USA involving foliar sprays of phosphonic acid (as the mono- and di-potassium salts - WP formulations)

PISTACHIO Country, year Location (variety) References	no	kg ai/ha	water (L/ha)	total kg ai/ha	DALA	matrix	Phosphonic acid residues (mg/kg)	
							values	mean
GAP: USA	6	1.9			not stated			
USA , 2015 Winters, CA (Kerman) IR4-11530 CA122	6	1.9	940–1000	11.3	4	nutmeat	63, 66	64.5
USA , 2015 Hanford, CA (Golden Hills) IR4-11530 CA123	6	1.9	1300–1340	11.3	4	nutmeat	151, 182	166.5
USA , 2015 Parlier, CA (Kerman) IR4-11530 CA124	5	1.9	940–970	11.4	3	nutmeat	186, 152	169

PISTACHIO Country, year Location (variety) References	no	kg ai/ha	water (L/ha)	total kg ai/ha	DALA	matrix	Phosphonic acid residues (mg/kg)	
							values	mean
USA , 2015 Arbuckle, CA (Kerman) IR4-11530 CA125	6	1.9	1300–1330	11.5	3	nutmeat	218, 176	197
USA , 2015 Chico, CA (Kerman) IR4-11530 CA126	6	1.9	1170	11.4	3	nutmeat	1.8, 1.8	1.8

Walnut – phosphonic acid

In supervised trials on walnuts conducted in USA, 6–8 foliar sprays of phosphorous acid (as the mono- and di-potassium salts) with added non-ionic surfactant were applied at 6–8 day intervals. Nuts were shaken onto sheets, collected and duplicate samples were hulled, the shells were removed and the nutmeat samples taken in the field and frozen for 154 days before extraction and analysis for phosphonic acid using the LC-MS/MS method QuPPE Version 7.1 (LOQ of 0.5 mg/kg for phosphonic acid. Average concurrent recovery rates were 80–119% at fortification levels of 0.5–200 mg/kg). Parallel method validation recoveries ranged from 80–82% at fortification levels from 0.5–10 mg/kg.

Table 133 Residues in walnuts from supervised trials in USA involving foliar sprays of phosphonic acid (as the mono- and di-potassium salts - WP formulations)

WALNUT Country, year Location (variety) References	no	kg ai/ha	water (L/ha)	total kg ai/ha	DALA	matrix	Phosphonic acid residues (mg/kg)	
							values	mean
GAP: USA	6	1.9			not stated			
USA , 2015 Arbuckle, CA (Chandler) IR4-11504 CA127	6	1.9	990–1080	11.4	3	nutmeat	58, 49	53.5
USA , 2015 Hanford, CA (Chandler) IR4-11504 CA128	7	1.9	1040–1080	15.1	3	nutmeat	37, 38	37.5
USA , 2015 Hamilton City, CA (Chandler) IR4-11504 CA129	5	1.9	1170	11.3	3+ 2 d drying	nutmeat	4.2, 3.3	3.75
USA , 2015 Arbuckle, CA (Howard) IR4-11504 CA130	6	1.9-2.0	1100–1160	11.4	3	nutmeat	169, 174	171.5

WALNUT Country, year Location (variety) References	no	kg ai/ha	water (L/ha)	total kg ai/ha	DALA	matrix	Phosphonic acid residues (mg/kg)	
							values	mean
USA , 2015 Woodland, CA (Howard) IR4-11504 CA131 [applications 1 month later than in CA127]	6	1.9	1130–1330	11.5	4	nutmeat	65, 69	67

Dried herbs

Hops – fosetyl-Al

In supervised trials on hops conducted in Europe, eight foliar applications of fosetyl-Al (WG formulations) were applied between BBCH 30 and 85 at about 12 day intervals using water rates of 600 L/ha increasing to 3000 L/ha as leaf area increased. Fresh hop cone samples were kiln-dried at 16–63 °C for 1.45–20 hours and both fresh and dried cones were stored frozen for 287–428 days. Extraction and analysis for fosetyl-Al and phosphonic acid was by the LC-MS/MS method 00861/M001 (LOQs of 0.1 mg/kg for fosetyl-Al and 20 mg/kg for phosphonic acid). Average concurrent recovery rates were 72–75% for fosetyl-Al (fortification levels of 1–40 mg/kg) and 86–106% for phosphonic acid (fortification levels of 21–420 mg/kg).

Table 134 Residues in hop cones from supervised trials in Europe involving foliar applications of fosetyl-Al (WG formulations)

HOPS Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
GAP: Germany	8	8.0	800–5000	14				
France, 2009	8	7.4–8.0	1200–2200	0	cone, green	7.2	181	186
Schleithal				15		3.0	174	176
(Strisselspalt)								
				15	cone, dried	11	317	325
09-2038							c=34	c=35
09-2038-01								
UK, 2009	8	8.0–8.6	1000–1071	0	cone, green	12	406	414
Bishops Frome				14		8.0	387	393
(Target)							c=56	c=57
09-2038				14	cone, dried	73	816	867
09-2038-02						c=1.3	c=189	c=190
Germany, 2009	8	8.0	600–2100	0	cone, green	8.5	358	364
Tettnang				14		4.7	275	278
(Hallertauer Mittelfrueh)								
				14	cone, dried	12	396	404
09-2038								
09-2038-03								
Germany, 2009	8	8.0	600–2400	0	cone, green	1.4	172	173
Wolznach				14		<1.0	157	158
(Perle)								
				14	cone, dried	2.6	320	322
09-2038								
09-2038-04								

HOPS Country, year Location (variety) References	Application			DALA	Residues (mg/kg)			
	no	kg ai/ha	water (L/ha)		matrix	Fosetyl-Al	Phos-acid	Total residues
Germany, 2010 Ellingen (Hallertauer Gold) 10-2062 10-2062-01	8	8.0	1000–3000	-0	cone, green	<1.0	73	74
				0		7.0	150	155
				7		<1.0	110	111
				14		<1.0	120	121
				21		<1.0	160	161
				14	cone, dried	8.3	370	376
Germany, 2010 Luetzensoemmern (Magnum) 10-2062 10-2062-02	8	8.0	1000–2000	0	cone, green	<1.0	150	151
				12		<1.0	160	161
				12	cone, dried	15	650 c=34	660 c=35
Germany, 2010 Muegeln (Hallertauer Magnum) 10-2062 10-2062-03	8	8.0	800–1500	-0	cone, green	<1.0	130	131
				0		1.3	160	161
				7		1.9	210 c=25	211 c=26
				14		<1.0	200 c=21	201 c=22
				21		<1.0	100	101
				14	cone, dried	<1.0	42 c=55	43 c=56
Germany, 2010 Tettnang (Hallertauer Tradition) 10-2062 10-2062-04	8	8.0	600–1000	0	cone, green	1.8	38	39
				13		2.1	110	111
				13	cone, dried	28	290	309

In supervised trials on hops conducted in USA, foliar applications of fosetyl-AL (WP formulations) were applied when shoots were 15–36 cm high, at training, 2–3 weeks later and during bloom. Retreatment intervals were 27–55 days. Fresh hop cone samples were kiln-dried (hot air) for 8–12 hours and both fresh and dried cones were stored frozen for 21–40 days. Extraction and analysis for fosetyl-Al was by the GC-FPD method 163 (LOQ of 0.05 mg/kg). Average concurrent recovery rates were 79–105% for fosetyl-Al (fortification levels of 0.1–40 mg/kg).

Table 135 Residues in hop cones from supervised trials in USA involving foliar applications of fosetyl-Al (WP formulations)

HOPS Country, year Location (variety) References	Application			DALA	Fosetyl-Al residues (mg/kg) corrected for recovery	
	no	kg ai/ha	water (L/ha)		matrix	values
GAP: USA		2.24		24		max 9 kg ai/ha/season
USA, 1984 Newberg, OR (Cascade) B004621 353684-014	4	2.2	468	24	cone, green	1.5 c=0.07
					cone, dried	16 c=0.15
USA, 1984 Newberg, OR (Cascade) B004621 353684-014	4	4.5	468	24	cone, green	1.5 c=0.07
					cone, dried	19 c=0.15

HOPS Country, year Location (variety) References	Application			DALA	Fosetyl-Al residues (mg/kg) corrected for recovery	
	no	kg ai/ha	water (L/ha)		matrix	values
USA, 1984 Oregon (Hop) B004621 353684-023	4	2.2	-	28	cone, green cone, dried	4.8 9.9 c=0.06
USA, 1984 Oregon (Hop) B004621 353684-023	4	4.5	-	28	cone, green cone, dried	9.7 19 c=0.06
USA, 1985 Salem, OR (Nugget) B004621 353685-006	4	2.2	468	24	cone, green cone, dried spent hops wort sludge	0.54 11 0.08, 0.08, < 0.05, 0.25 0.12 0.11
USA, 1985 Salem, OR Oregon (Willamette) B004621 353685-008	4	2.2	468	24	cone, green cone, dried spent hops wort sludge	2.7 41 0.25, 0.23, 2.2 0.2 0.12
USA, 1985 Weedburn, OR (Nugget) B004621 353685-010	4	2.2	281	24	cone, green cone, dried	< 0.05 0.44

FATE OF RESIDUES IN STORAGE AND PROCESSING

Nature of the residue during processing

High-temperature hydrolysis

High-temperature hydrolysis of fosetyl-Al and its metabolite phosphonic acid was investigated by Crowe, 2001 [Ref: C013568]. In the study, 100 mg/L solutions of either fosetyl-Al or phosphonic acid were prepared in 1 M boric acid or 1 M sodium hydroxide as appropiate to adjust the pH to 4, 5 or 6 and incubated in the dark, simulating pasteurisation (90 °C, pH 4, 30 min.); baking, brewing, boiling (100 °C, pH 5, 60 min); and sterilisation (120 °C, pH 6, 20 min.).

Samples were analysed at zero time and at the end of each incubation period by ion chromatography to measure residues of fosetyl-Al, phosphonic acid and phosphoric acid. The LOQs of the method were 3 mgL and 8 mg/L for phosphoric acid. Recovery rates in fortified buffer solutions (3.3–110 mg/L were 82–103% for fosetyl-Al, 108–110% for phosphonic acid and 93–102% for phosphoric acid.

Concentrations of both fosetylAl and phosphonic acid were essentially unchanged and both compounds can be considered hydrolytically stable under conditions simulating pasteurisation, baking, brewing, boiling and sterilisation.

Table 136 Residues of fosetyl-Al and phosphonic acid in buffer solutions (100 mg/L) incubated under high temperature hydrolysis conditions

Component	Residues detected (mg/L					
	pH 4 (90 °C)		pH 5 (100 °C)		pH 6 (120 C)	
	Time 0	30 minute	Time 0	60 minutes	Time 0	20 minute
Fosetyl-Al	97.6	97.4	98.6	99.9	96.7	96.2
Phosphonic acid	95.9	97.6	95.9	98.4	98	99.9

Peel and flesh residue distribution

In the supervised trials on citrus, avocado, pineapple and melons, whole fruit, peel and flesh samples were analysed for fosetyl-Al and phosphonic acid, and these results are reported in the supervised trials tables (see above).

Household washing, trimming and cooking

Lettuce – fosetyl

In a study reported by Billian & Reineke, 2009 [Ref: 08-3137], greenhouse head lettuce samples were taken from supervised field trials conducted in Europe to investigate the distribution of residues in the outer leaves, heads and washed and unwashed inner leaves. Lettuce samples were taken 14 days after the last of 4 foliar applications of 0.775 kg ai/ha fosetyl (SL co-formulations with propamocarb) and were sub-sampled into outer leaves, the remaining heads and inner leaves (i.e. head leaves without the stems). Samples of the inner leaves were also washed in luke-warm water for about 5 minutes and drained (to reflect household practice).

Samples were frozen and stored for up to 243 days before analysis for fosetyl and phosphonic acid using the LC-MS/MS method 00861/M001. For fosetyl, the LOQ of the analytical method was 0.0093 mg/kg (equivalent to 0.01 mg/kg fosetyl-Al) and the mean concurrent recovery rate was 113% (fortification levels of 0.01–0.1 mg/kg fosetyl-Al). For phosphonic acid, the LOQ was 0.2 mg/kg with a mean concurrent recovery rate of 105% (fortification levels of 0.2–100 mg/kg).

Table 137 Residues of fosetyl and phosphonic acid in inner and outer lettuce leaves (washed and unwashed) following the use of fosetyl (foliar sprays) in Europe

Country, Year Location, (variety) References	Application	matrix	Residues (mg/kg			Processing factors
			Fosetyl	Phos-acid	Total residues	
Netherlands, 2008 Wervershoof (Legenda) 08-3137-01	4 x 0.775 kg ai/ha 14 day PHI	Lettuce, head (RAC)	< 0.0093	5.8	5.8	
		Outer leaves	< 0.0093	5.8	5.8	1.0
		Heads	< 0.0093	5.9	5.9	1.0
		Inner leaves	< 0.0093	5.2	5.2	0.9
		Washings	< 0.0093	< 0.2	< 0.22	
		Inner leaves, washed	< 0.0093	4.0	4.0	0.69
Germany, 2008 Meckenbeuren (Lucia) 08-3137-02	4 x 0.775 kg ai/ha 13 day PHI	Lettuce, head (RAC)	< 0.0093	4.2	4.2	
		Outer leaves	< 0.0093	3.1	3.1	0.74
		Heads	< 0.0093	3.0	3.0	0.71
		Inner leaves	< 0.0093	3.8	3.8	0.9
		Washings	< 0.0093	< 0.20	< 0.22	
		Inner leaves, washed	< 0.0093	2.2	2.2	0.52

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

Spinach – fosetyl

In a study reported by Billian & Krusell, 2010 [Ref: 09-3401], spinach samples were taken from supervised field trials conducted in Europe at exaggerated application rates to investigate the effects of washing and cooking on residues of fosetyl and phosphonic acid. Spinach samples were taken 14–15 days after the last of 4 foliar applications of 2.33 kg ai/ha fosetyl (SL co-formulations with propamocarb) and were washed in luke-warm water for 2–5 minutes and drained. Washed leaves were also cooked in a sieve in boiling water (2 litres/kg of leaf) for about 8–10 minutes (to reflect household practice).

Samples were frozen and stored for up to 420 days before analysis for fosetyl and phosphonic acid using the LC-MS/MS method 00861/M001. For fosetyl, the LOQ of the analytical method was 0.0093 mg/kg (equivalent to 0.01 mg/kg fosetyl-Al) and the mean concurrent recovery rates were 84–113% (fortification levels of 0.01–50 mg/kg fosetyl-Al). For phosphonic acid, the LOQ was 0.2 mg/kg with mean concurrent recovery rates of 97–102% (fortification levels of 0.2–500 mg/kg).

Table 138 Residues of fosetyl and phosphonic acid in washed and cooked spinach following the use of fosetyl (foliar sprays) in Europe

Country, Year Location, (variety) References	Application	matrix	Residues (mg/kg			Processing factors
			Fosetyl	Phos-acid	Total residues	
Germany, 2009 Bornheim (Cheetah) 09-3401-01	4 x 2.2-2.3 kg ai/ha 15 day PHI	Spinach leaves (RAC)	< 0.0093	11	11	
		Washed leaves	< 0.0093	13	13	1.2
		Washing water	< 0.0093	< 0.2	< 0.21	
		Cooking water	0.01	3.5	3.5	
		Cooked leaves	0.02	10	10	0.91
France, 2009 Champien (Emilia) 09-3401-02	4 x 2.3 kg ai/ha 15 day PHI	Spinach leaves (RAC)	< 0.0093	17	17	
		Washed leaves	< 0.0093	20	20	1.2
		Washing water	< 0.0093	< 0.2	< 0.21	
		Cooking water	< 0.0093	5.0	5.0	
		Cooked leaves	< 0.0093	17	17	1.0
Belgium, 2009 Villers-Perwin (El Forte) 09-3401-03	4 x 2.3 kg ai/ha 14 day PHI	Spinach leaves (RAC)	< 0.0093	15	15	
		Washed leaves	< 0.0093	11	11	0.73
		Washing water	< 0.0093	< 0.2	< 0.21	
		Cooking water	< 0.0093	0.92	0.93	
		Cooked leaves	< 0.0093	9.9	10	0.66
Netherlands, 2009 Andijk (spinach) 09-3401-04	4 x 2.3 kg ai/ha 14 day PHI	Spinach leaves (RAC)	< 0.0093	22	22	
		Washed leaves	< 0.0093	19	19	0.86
		Washing water	< 0.0093	< 0.2	< 0.21	
		Cooking water	< 0.0093	12	12	
		Cooked leaves	< 0.0093	21	21	0.95

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

Green beans – fosetyl-Al

In a study reported by Simonin, 2006 [Ref: 02-08], green beans samples were taken from supervised field trials conducted in Europe to investigate the effects of washing and cooking on residues of fosetyl-Al and phosphonic acid. Green bean samples were taken 16–18 days after the last of 2 foliar applications of 1.43 kg ai/ha fosetyl-Al and were trimmed, cooked in boiling water (2 litres/kg of beans) for about 15 minutes and were vacuum-packed and sterilised (2 minutes and 85 °C) before frozen for analysis. Canned beans were prepared by blanching the beans for 1 minute and placing them in jars until two thirds full. The jars were then topped up with a brine solution (30 g salt/litre of water) and citric acid was added to obtain a pH of about 3.5 and the jars were sealed and sterilised (10 minutes at 115–120 °C) before being frozen for analysis.

Samples were frozen and stored for up to 120 days before analysis for fosetyl and phosphonic acid using the GC-FPD method AR 155-97. For fosetyl-Al, the LOQ of the analytical method was 0.2 mg/kg and the mean concurrent recovery rates were 75–95% (fortification levels of 0.2–0.4 mg/kg). For phosphonic acid, the LOQ was 0.2 mg/kg with mean concurrent recovery rates of 77–100% (fortification levels of 0.2–5.0 mg/kg).

Table 139 Residues of fosetyl and phosphonic acid in cooked and canned green beans following the use of fosetyl (foliar sprays) in Europe

Country, Year Location, (variety) References	Application	matrix	Residues (mg/kg			Processing factors
			Fosetyl	Phos-acid	Total residues	
France, 2002 Fresnoy Les Roye (Mention) 02-08 FR1	2 x 1.43 kg ai/ha 16 day PHI	Green beans (RAC)	< 0.19	7.8	7.9	
		Trimming waste	< 0.19	7.1	7.2	0.91
		Blanching water	< 0.19	0.13	0.14	
		Canned beans	< 0.19	3.7	3.8	0.48
		Brine	< 0.093	3.8	3.9	
		Cooking water	< 0.19	0.67	0.68	
		Cooked beans	< 0.19	1.1	1.2	0.16
France, 2002 Rilly sur Vienne (Lausanne) 02-08 FR2	2 x 1.43 kg ai/ha 18 day PHI	Green beans (RAC)	< 0.19	3.4	3.5	
		Trimming waste	< 0.19	3.4	3.5	1.0
		Blanching water	< 0.19	0.07	0.084	
		Canned beans	< 0.19	1.8	1.9	0.55
		Brine	0.15	2.0	2.1	
		Cooking water	< 0.19	0.36	0.37	
		Cooked beans	< 0.19	2.6	2.7	0.77

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

Residues after processing

The Meeting received processing studies for fosetyl-Al and/or fosetyl on oranges, apples, grapes, strawberries, tomatoes, peppers, lettuce, spinach, beans and hops. Processing studies for phosphonic acid on citrus and grapes were also provided. Information on the residue distribution of fosetyl-Al in peel and flesh (citrus, avocado, pineapple and melons) is presented in the above summaries of the supervied field trials.

Orange – fosetyl-Al

In orange processing studies conducted in Europe, fruit treated with fosetyl-Al in supervised field trials, were washed and halved, the juice was extracted using a bench-top extractor and the wet pomace (peel and pulp) was ground and oven-dried (3 days at approx. +60 °C). The juice was pasteurised by heating to approx. 85 °C for at least one minute, bottled and sterilised in boiling water for 20 minutes and stored frozen for up 236 days in the first study (Ref: C0146449) and 75–146 days in the remaining studies.

Samples of washing water, juice and wet pomace were analysed for the parent compound fosetyl-Al and phosphonic acid using the GC-NPD methods 155-97 (for fruit and pomace), method AR 171-98 (for orange juice) and method AR 231-99 for washing water. LOQs for both analytes were 0.2 mg/kg in orange (fruit and pomace) and 0.5 mg/kg fin orange juice. The LOQs in washing water were 1 µg/L for fosetyl-Al and 20 µg/L for phosphonic acid.

Concurrent recovery rates for fosetyl-Al averaged 78–96% in all matrices fortified at levels of 0.02–2.0 mg/kg (fruit and pomace) and 0.2–5.0 mg/kg (juice) and 0.001–0.02 mg/L (washing water). For phosphonic acid, average concurrent recovery rates were 72–109% in matrices spiked with 0.2–10.0 mg/kg (fruit), 0.2–5.0 (pomace and juice) and 0.02–0.2 mg/L in washing water.

Table 140 Residues of fosetyl-Al and phosphonic acid in orange and processed commodities following the use of fosteyl-Al in supervised trials in Europe

Trial, Location, Year, Commodity, Variety	Application	matrix	Residues (mg/kg or mg/L)			Processing factors	
			Fosetyl-Al	Phos-acid	Total residues	fresh weight	dry weight
Spain, 2000 Brenes (Newhall) C014644 ESP0201	Foliar sprays 4 x 7.0 kg ai/ha 0.23 kg ai/hL 14 day PHI	Orange (RAC)	< 0.2	5.6 c=0.2	5.7 c=0.35		
		Washing water	0.091	0.039	0.10		
		Juice	< 0.2	5.3	5.4	0.94	
		Pomace	< 0.2	5.0	5.1	0.9	3.9
Italy, 2000 Marconia di Pisticci (Navelina V.C) 01-89 ITA1	Foliar sprays 4 x 7.0 kg ai/ha 0.7 kg ai/hL 15 day PHI	Orange (RAC)	< 0.2	4.4	4.5		
		Washing water	0.14	0.16	0.26		
		Juice	< 0.5	5.8	6.1	1.35	
		Pomace	< 0.2	0.62	0.8	0.17	0.77
Greece, 2001 Argolidos (Merlin) 01-89 GRC1	Foliar sprays 4 x 7.0 kg ai/ha 0.23 kg ai/hL 14 day PHI	Orange (RAC)	< 0.2	3.8	3.9		
		Washing water	0.35	0.058	0.3		
		Juice	< 0.5	4.0	4.3	1.1	
		Pomace	< 0.2	0.28	0.40	0.11	0.45
Italy, 2000 Marconia - Basilicata (Navelina) 02-219 ITA0201	PH Dip 0.4 kg ai/hL 0 day PHI	Orange (RAC)	< 0.2	3.2	3.3		
		Washing water	0.034	0.094	0.12		
		Juice	0.85	0.59	1.2	0.35	
		Pomace	< 0.2	2.5	2.6	0.79	3.4
Italy, 2000 Tursi - Basilicata (Navelina) 02-219 ITA0202	PH Dip 0.4 kg ai/hL 0 day PHI	Orange (RAC)	< 0.2	1.9	2.0		
		Washing water	0.025	0.098	0.12		
		Juice	0.83	0.58	1.2	0.57	
		Pomace	0.46	1.8	2.1	1.0	4.6

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

Pomace dry weight approx 23%

In a processing study conducted in USA, oranges treated with fosetyl-Al at an exaggerated rate of 44.8 kg ai/ha were collected as soon as the last application had dried and were processed into juice, pulp, peel, molasses and oil.

In the simulated commercial practices, oranges were washed and scrubbed prior to going to a commercial in-line extractor. The raw juice was filtered to obtain finisher pulp and orange juice. Citrus oil was obtained from this step, too, as were peel frits. The refuse from the extractor (peel, pulp and seeds) was chopped and filtered to obtain pressed liquor and expressed peel. The wet chopped peel went through a triple pass forced air furnace, to yield dried citrus peel (peel, seeds and pulp). Under vacuum and heat, molasses was obtained from a portion of the pressed liquor.

Samples of the processed fractions were stored for up to 41 days before analysis for fosetyl-Al using method 163, with the dried peel being pre-soaked in extracting solution, the aqueous samples were diluted and filtered; the oil sample was extracted directly. The LOQ was 0.05 mg/kg for fruit and juice, 0.1mg/kg for oil, 0.5 mg/kg for pulp and molasses and 1.0 mg/kg for peel. Mean concurrent recovery rates in all matrices were 72–105%, except for molasses with only one recovery value of 124%.

Table 141 Residues of fosetyl-Al in/on orange and processed commodities following foliar applications of fosetyl-Al in USA

Trial, Location, Year, Commodity, Variety	Application	matrix	Fosetyl-Al	
			Residues (mg/kg)	Processing factors

Trial, Location, Year, Commodity, Variety	Application	matrix	Fosetyl-Al	
			Residues (mg/kg)	Processing factors
USA, 1985 Lebelle, FL (Valencia) R003863 930984-110	Foliar sprays 2 x 44.8 kg ai/ha 1.9 kg ai/hL 0 day PHI	orange, unwashed (RAC)	1.8	
		orange, washed	0.4	0.22
		chopped peel	0.12	
		peel frits	0.12	
		finisher pulp	< 0.05	< 0.03
		dried peel	0.61	0.34
		pressed liquor	0.16	
		fruit juice	< 0.05	< 0.03
		molasses	0.38	0.21
		oil	< 0.05	< 0.03

Processing factor: Ratio of fosetyl-Al residue in the processed item divided by the fosetyl-Al residue in the RAC

Orange – phosphonic acid

In a supervised field trials conducted in Europe, three foliar sprays of phosphonic acid (as the mono- and di-potassium salts) were applied to oranges at about 30 day intervals from about BBCH 72-74 and after harvest, the fruit were subsequently drenched continuously (in crates) for 30 seconds before being air-dried and sampled for further processing into juice, dry pomace, marmalade, canned fruit and essential oil.

The fruit were first washed with water and allowed to drain before being halved and the juice extracted using a benchtop citrus squeezer. The juice was then pasteurized at about 80 °C for 1 minute and stored for analysis. The remaining pulp was blended to obtain wet pomace, which was dried at about 60ºC until constant weight and stored for analysis.

For marmalade, the washed oranges were finely peeled, the albedo was discarded and the peel cut into thin strips and blanched in water for about 10 minutes. The peeled oranges were finely chopped, combined with the blanched peels and the mixture was brought to a boil and then simmered for about 10 minutes with sugar added to achieve a Brix level of 65–68º. Once cooked, the finished marmalade was bottled and sterilized at 115–120 ºC.

For the canned fruit processing, the washed oranges were peeled, sectioned and the membranes, core and fibre strands were removed. The fruit segments were dipped in boiling water for 30–60 seconds and the segment walls were removed before placing the segments in jars with syrup. After sealing, the jars were sterilized at 90–100 °C for 1 minute.

Orange oil was obtained by steam distillation of the orange peel at low temperature. Washed oranges were finely peeled with a citrus peeler and the peel was steamed on a rack to release and vaporise the oil from the oil sacs. The vapour and water (hydrosol) was condensed into a glass container and the oil decanted.

The storage period between sampling and extraction was 15–128 days and samples were analysed within 6 days after the extraction for phosphonic acid using the QuPPe method for highly polar pesticides. The method involved methanol/formic acid extraction, phase separation by centrifuging, dilution with methanol/millipore water acidified with formic acid and analysed by LC-MS/MS. The LOQ of the method was 1.0 mg/kg and average concurrent recovery rates were 79–106% in all matrices fortified at 1–0 mg/kg.

Table 142 Residues of phosphonic acid in processed orange commodities from supervised trials in Europe involving post-harvest and/or preharvest foliar applications of phosphonic acid

ORANGE Country, year Location (variety) References	Application				DALA	matrix	Phosphonic acid	
	no	kg ai/ha	kg ai/hL	water (L/ha)			Residue (mg/kg)	Processing factor

ORANGE Country, year Location (variety) References	Application				DALA	matrix	Phosphonic acid	
	no	kg ai/ha	kg ai/hL	water (L/ha)			Residue (mg/kg)	Processing factor
Spain, 2015 Torrent, Valencia (Navelina) TRC15-138 R1	3 foliar+ 1 drench	4.0	0.2 0.5	2000	0	orange (RAC)	26.4	
						washed fruit	12.3	0.47
						juice (pasteurised)	7.6	0.29
						pomace (dry)	54	2.0
						marmalade	8.7	0.33
						canned fruit	9.0	0.34
						oil	<1.0	< 0.04
Spain, 2015 Tortosa, Tarragona (Washington Navel) TRC15-138 R2	3 foliar+ 1 drench	3.9–4.0	0.2 0.5	2000	0	orange (RAC)	40	
						washed fruit	24	0.59
						juice (pasteurised)	13.8	0.34
						pomace (dry)	138	3.4
						marmalade	12.0	0.29
						canned fruit	15.4	0.39
						oil	<1.0	< 0.02
Spain, 2015 Benicarlo, Castellon, Spain (Newhall) TRC15-138 R3	3 foliar+ 1 drench	4.0–4.1	0.2 0.5	2000	0	orange (RAC)	22.7	
						washed fruit	11.9	0.52
						juice (pasteurised)	6.1	0.27
						pomace (dry)	60	2.7
						marmalade	8.3	0.37
						canned fruit	4.9	0.22
						oil	<1.0	< 0.04

Processing factor: Ratio of phosphonic acid residue in the processed item divided by the phosphonic acid residue in the RAC

Apple – fosetyl-Al

In apple processing studies conducted in Europe, fruit treated with fosetyl-Al in supervised field trials were collected at harvest, 28 days after the last application and were processed into apple juice and puree.

For juice, samples were washed, crushed with an electric crusher and then pressed. The apple juice was collected and the wet pomace was oven-dried (60 °C for 2–3 days). Pectolytic enzymes were added to the apple juice which was left to settle for at least 12 hours before decanting. The clear juice was filtered under nitrogen pressure, pasteurised (approx. 85 °C for at least one minute) and subsequently bottled and sterilised in boiling water for 20 minutes.

For puree, washed apples were blanched in boiling water for 2 minutes, crushed with an electric crusher and sieved to obtain puree. After the addition of sugar, the puree was reduced by heating to achieve 24° Brix, bottled and sterilised (115–120 °C for 10 minutes).

Samples of fruit and processed fractions were stored for up to 229 days before analysis for fosetyl-Al and phosphonic acid using the GC-FPD methods AR 155-97 (for apples, pomace, puree, lees and waste puree), AR 171-98 for juice and AR 231-99 for washing water and blanching water. LOQs for both analytes were 0.5 mg/kg for juice and 0.2 mg/kg for the other processed fractions. In the washing and blanching water, the LOQs were 1 µg/L for fosetyl-Al and 20 µg/L for phosphonic acid.

For fosetyl-Al, mean concurrent recoveries in all matrices ranged from 73–103% in samples fortified with 0.2–20 mg/kg (apples, pomace, puree), 0.5–5.0 mg/kg (juice) and 0.001–0.01 mg/L in water. For phosphonic acid, mean concurrent recoveries in all matrices ranged from 74–99% in samples fortified with 0.2–20 mg/kg (apples, pomace, puree), 0.5–5.0 mg/kg (juice) and 0.02–0.2 mg/L in water.

Table 143 Residues of fosetyl-Al and phosphonic acid in apples and processed commodities following the use of fosteyl-Al in supervised trials in Europe

Trial,	Application	Commodity	Residues (mg/kg or mg/L)	Processing

Location, Year, Commodity, Variety			Fosetyl-Al	Phos-acid	Total residues	factors
UK 2001 Royston (Bramley) 01-90 0190GBR1	Foliar sprays 3 x 3.6 kg ai/ha 0.72 kg ai/hL 28 day PHI	Apple (RAC)	1.5	4.2	5.2	
		Washing water	< 0.001	< 0.02	< 0.021	
		Blanching water	< 0.001	< 0.02	< 0.021	
		Wet pomace	< 0.20	4.3	4.4	n.c[a]
		Lees	0.28	5.5	5.7	
		Apple juice	< 0.50	15	15	n.c[a]
		Apple puree	0.35	3.5	3.7	0.71
UK 2001 Cambridge (Cox) 01-90 0190GBR2	Foliar sprays 3 x 3.6 kg ai/ha 0.72 kg ai/hL 28 day PHI	Apple (RAC)	2.1	4.7	6.2	
		Washing water	0.002	0.038	0.039	
		Blanching water	< 0.001	< 0.02	< 0.021	
		Wet pomace	0.40	9.3	9.6	1.6
		Lees	0.32	6.6	6.8	
		Apple juice	< 0.5	7.1	7.4	1.2
		Apple puree	0.39	9.5	9.8	n.c[a]
France, 2001 Picardie (Jonagored) 01-90 0190FRA1	Foliar sprays 3 x 3.6 kg ai/ha 0.72 kg ai/hL 28 day PHI	Apple (RAC)	0.5	9.3	10	
		Washing water	0.001	0.029	0.03	
		Blanching water	< 0.001	< 0.02	< 0.021	
		Wet pomace	< 0.20	4.6	4.7	0.49
		Lees	0.26	4.1	4.3	
		Apple juice	< 0.50	5.7	6.0	0.63
		Apple puree	0.2	4.1	4.2	0.44
France, 2001 Soucelles (Golden Delicious) 01-90 0190FRA2	Foliar sprays 3 x 3.6 kg ai/ha 0.72 kg ai/hL 28 day PHI	Apple (RAC)	0.70	3.0	3.5	
		Washing water	< 0.001	< 0.02	< 0.021	
		Blanching water	< 0.001	< 0.02	< 0.021	
		Wet pomace	0.20	5.4	5.5	n.c[a]
		Lees	0.24	4.7	4.9	
		Apple juice	< 0.50	8.3	8.6	n.c[a]
		Apple puree	1.1	3.0	3.8	1.1

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

[a] Processing factors not calculated – reported mass balances of 188-215%

Grapes – fosetyl-Al

In grape processing studies conducted in Europe, fruit treated with fosetyl-Al in supervised field trials involving up to 8 foliar applications of 1.3–2.3 kg ai/ha fosetyl-Al were collected at harvest, 24–81 days after the last application and were processed into juice and wine using simulated commercial practices.

For juice, grape bunches were stemmed and crushed. Pectolytic enzyme (0.06%) was added to the must. The must was transferred into glass jars which were sterilised (50–65 °C for 2 hours), cooled and then pressed, bottled, sterilised (85–88 °C for five minutes) and allowed to settle for at least twelve hours in a cold room. The clear juice was filtered, packaged, sterilised and stored frozen for up to 295 days before analysis.

Red wine was produced by crushing and stemming the grape bunches and adding potassium metabisulphite (0.06 g/L) and dry yeast to initiate fermentation. When alcoholic fermentation was completed (the wine density had stabilised below 1000) the must was pressed to obtain the AF (after alcoholic fermentation) wine. Malolactic fermentation (MF) was accelerated by inoculation with lactic bacteria and once completed, 0.1 g/L potassium metabisulphate was added to the wine. After racking for about 8–9 days, the wine was decanted from the lees and further clarified by racking and filtration after the addition of dry gelatine (0.1 g/L) and potassium metabisulphate (0.04 g/L). After bottling, the wine samples were stored frozen for up to 295 days before analysis.

The same process was used to produce white wine, but with the crushed grapes being first pressed, the must treated with pectolytic enzymes (0.02 g/L) and potassium metabisulphite (0.12 g/L), allowed to settle for 24 hours before decanting and the addition of the yeast.

Samples were analysed for fosetyl-Al and phosphonic acid using the GC-FPD method DFG 522 (AR 155-97). The LOQs for fosetyl-Al were 0.2 mg/kg for all matrices and ranged from 0.2–0.5 mg/kg for phosphonic acid.

For fosetyl-Al, mean concurrent recoveries in all matrices ranged from 70–112% in samples fortified with 0.02–5.0 mg/kg (grapes), 0.02–1.0 mg/kg (juice) and 0.2–2.0 mg/kg (wine). For phosphonic acid, mean concurrent recoveries in all matrices ranged from 70–123% in samples fortified with 0.2–30 mg/kg (grapes), 0.2–40.0 mg/kg (juice and wine).

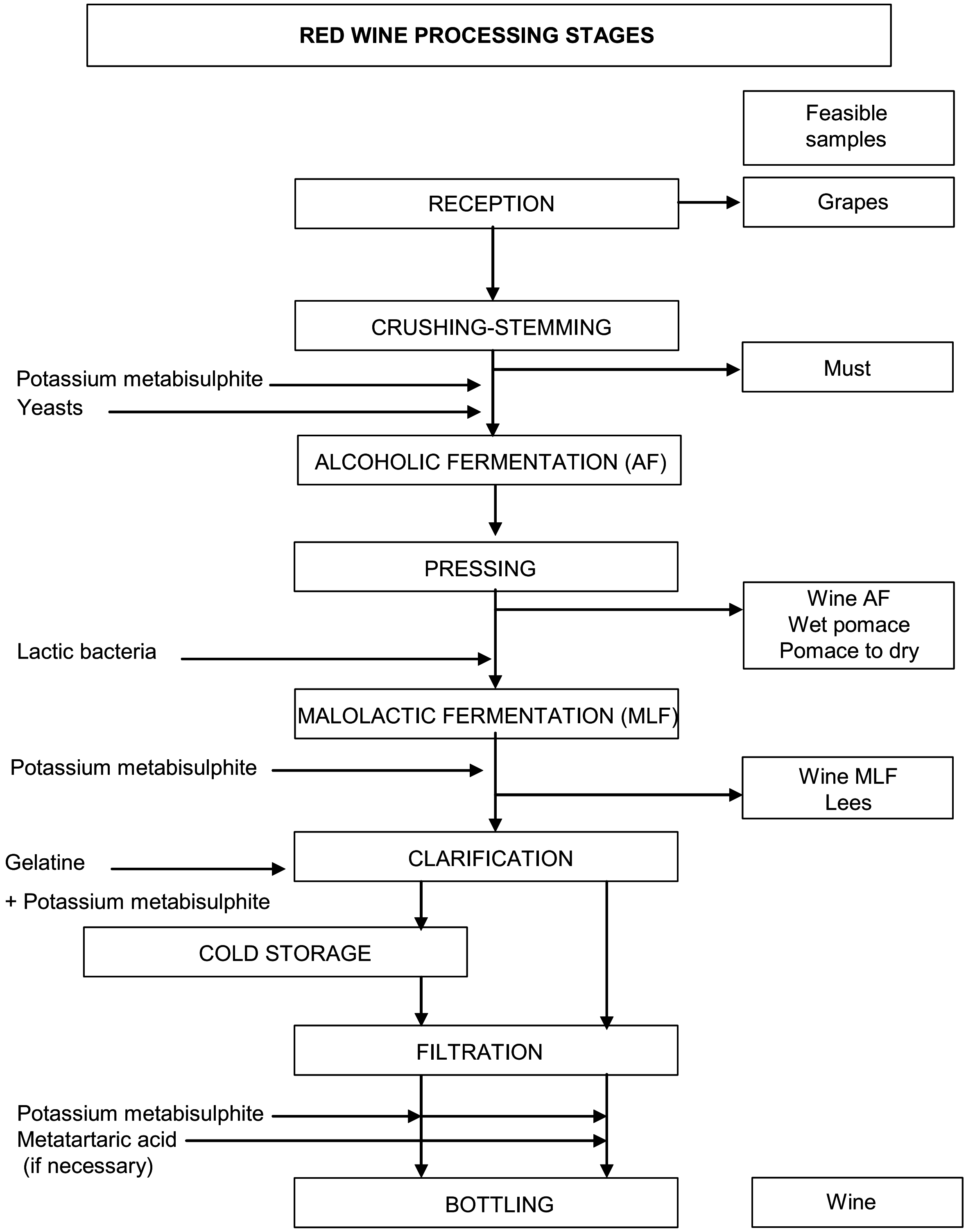


Figure 4 Flow chart for the preparation of grapes into red wine.

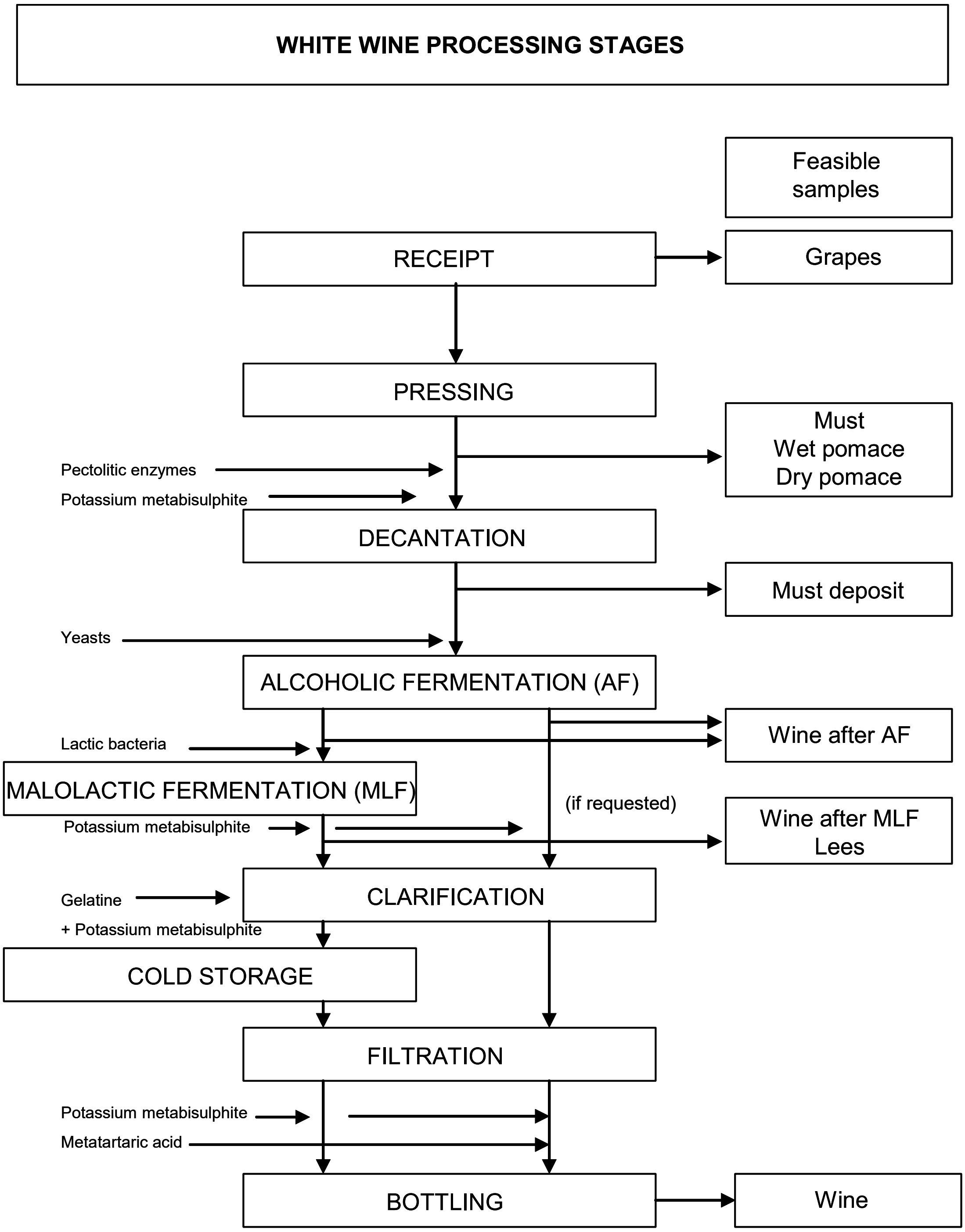


Figure 5 Flow chart for the preparation of grapes into white wine

Table 144 Residues of fosetyl-Al and phosphonic acid in grapes and processed grape commodities following the use of fosteyl-Al (foliar sprays) in supervised trials in Europe

Trial, Location, Year, Commodity, Variety	Application	Commodity	Residues (mg/kg or mg/L)			Processing factors
			Fosetyl-Al	Phos-acid	Total residues	
France 1996 Brachon (Pinot Noir) R003431 96598DJ1	8 × 1.4-1.6 kg ai/ha 32 day PHI	Grapes (RAC)	1.9	14	15	
		Grape juice	1.3	15	16	1.2
		Wine	0.89	21	22	1.4
France 1996 Bouloc (Cabernet) R003431 96598TJ1	8 × 1.4-1.6 kg ai/ha 32 day PHI	Grapes (RAC)	1.9	13	14	
		Grape juice	0.51	17	17	1.2
		Wine	0.43	25	25	1.8
France 1998 Vallet (Cabernet) R005031 98562RN1	7 × 1.8 kg ai/ha 24 day PHI	Grapes (RAC)	0.33	25	25	
		Grape juice	0.35	24	24	0.96
		Must	0.68	19	19	0.77
		Wine	0.23	21	21	0.84
France 1998 Seguret (Grenache) R005031 98562AV1	7 × 1.8 kg ai/ha 25 day PHI	Grapes (RAC)	0.39	15	15	
		Grape juice	0.43	14	14	0.94
		Must	1.2	12	13	0.84
		Wine	0.34	17	17	1.1
France 1998 Montady (Cinsault) R005031 98721BO1-2	7 × 1.8 kg ai/ha 28 day PHI	Grapes (RAC)	0.38	17	17	
		Grape juice	1.0	19	20	1.1
		Must	1.1	24	25	1.4
		Wine	0.52	22	22	1.3
Italy 1998 Bologna (Malvasia) R005058 98721BO1-2	7 × 1.8 kg ai/ha 41 day PHI	Grapes (RAC)	0.58	22	22	
		Wine	0.38	14	14	0.64
Italy 1998 Bologna (Malvasia) R005058 98721BO1-3	7 × 1.8 kg ai/ha 41 day PHI	Grapes (RAC)	0.53	14	14	
		Wine	0.38	16	16	1.1
Italy 1998 Bologna (Moscato) R004791 98736BO1	5 × 1.3 kg ai/ha 40 day PHI	Grapes (RAC)	0.24	6.7	6.9	
		Wine	0.39	9.8	10	1.5
Italy 1998 Tebano (Pinot Bianco) R005056 98738BO1	5 × 1.3 kg ai/ha 40 day PHI	Grapes (RAC)	0.68	17	17	
		Wine	1.1	6.8	7.6	0.43
France, 1999 Sercy et Prin (Chardonnay) 99-531 99531RS1-01	4 × 2.1–2.3 kg ai/ha 74 day PHI	Grapes (RAC)	< 0.2	9.0	9.1	
		Wine	< 0.2	4.9	5.0	0.55

Trial, Location, Year, Commodity, Variety	Application	Commodity	Residues (mg/kg or mg/L)			Processing factors
			Fosetyl-Al	Phos-acid	Total residues	
France, 1999 Sercy et Prin (Chardonnay) 99-531 99531RS1-02	4 × 2.0–2.3 kg ai/ha 74 day PHI	Grapes (RAC)	< 0.2	6.8	6.9	
		Wine	< 0.2	3.4	3.5	0.51
France, 1999 Brochon (Pinot Noir) 99-531 99531DJ1-01	4 × 2.1 kg ai/ha 81 day PHI	Grapes (RAC)	< 0.2	9.7	10	
		Wine	< 0.2	6.7	6.8	0.7
France, 1999 Brochon (Pinot Noir) 99-531 99531DJ1-02	4 × 2.1 kg ai/ha 81 day PHI	Grapes (RAC)	< 0.2	11	11	
		Wine	0.24	6.8	7.0	0.63
France, 1999 Oger (Chardonnay) 99-629 99629RS1	4 × 2.1 kg ai/ha 30 day PHI	Grapes (RAC)	0.34	7.2	7.4	
		Grape juice	< 0.2	3.6	3.7	0.5
		Must	0.37	4.1	4.4	0.59
		Wine	0.34	2.4	2.6	0.35
France, 1999 Camont-Durance (Grenache) 99-629 99629AV1	4 × 2.1 kg ai/ha 28 day PHI	Grapes (RAC)	0.94	12	13	
		Grape juice	1.1	8.0	8.8	0.69
		Must	< 0.2	0.56	0.7	0.06
		Wine	0.48	9.4	10	0.77
France, 2000 Limas (Gamay) VCE0001AVN 00-2006 AVE/01-040 002006-2R	1 × 2.0 kg ai/ha 78 day PHI	Grapes (RAC)	< 0.2	4.0	4.1	
		Must	< 0.2	0.58	0.7	0.17
		Pomace (wet)	< 0.2	2.3	2.4	0.59
		Wine	< 0.2	10	10	2.4
France, 2000 Limas (Gamay) VCE0001AVN 00-2006 AVE/01-040 002006-3R	3 × 2.0 kg ai/ha 64 day PHI	Grapes (RAC)	< 0.2	9.6	9.7	
		Must	< 0.2	3.2	3.3	0.34
		Pomace (wet)	< 0.2	12	12	1.3
		Wine	< 0.2	4.9	5.0	0.52
France, 2000 Limas (Gamay) VCE0001AVN 00-2006 AVE/01-040 002006-4R	5 × 2.0 kg ai/ha 50 day PHI	Grapes (RAC)	< 0.2	16	16	
		Must	0.35	5.8	6.0	0.39
		Pomace (wet)	< 0.2	22	22	1.4
		Wine	< 0.2	1.6	1.7	0.11
France, 2000 Limas (Gamay) VCE0001AVN 00-2006 AVE/01-040 002006-5R	6 × 2.0 kg ai/ha 35 day PHI	Grapes (RAC)	< 0.2	8.9	9.0	
		Must	0.22	5.5	5.6	0.62
		Pomace (wet)	< 0.2	22	22	2.4
		Wine	< 0.2	11	11	1.2

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

In a grape processing study conducted in USA, Replicate samples of fruit treated with 7 foliar applications of fosetyl-Al at an exaggerated rate of 41–61 kg ai/ha were collected 7 days after the last application and processed into juice and raisins.

For juice, grape bunches were stemmed and crushed. Pectolytic enzyme (0.06%) was added to the must. The must was then pressed to obtain unclarified juice and wet pomace. The juice was allowed to settle before being filtered, packaged, sterilised and stored frozen for analysis. Raisins were prepared by sun-drying in trays for 15–21 days and after the stems were removed, the grapes were washed and stored frozen for analysis.

Samples of the processed fractions were stored for up to 139 days before analysis for fosetyl-Al using the GC-FPD method SOP-90113. The LOQs were 0.5 mg/kg for fruit, 2.0 mg/kg in wet pomace, 5.0 mg/kg for raisins, 10 mg/kg for juice and dry pomace and 50 mg/kg in raisin waste. Mean concurrent recovery rates in all matrices were 73–92%, except for wet and dry pomace, where the recovery rates were 67% and 61% respectively.

Table 145 Residue of fosetyl-Al in grapes and processed grape commodities following foliar applications of fosetyl-Al in USA

Trial, Location, Year, Commodity, Variety	Application	Commodity	Fosetyl-Al		
			Residue values (mg/kg)	mean (mg/kg)	Processing factors
USA, 1992 Fresno, CA (Thompson) R000047 92-109	Foliar sprays 7 x 41–61 kg ai/ha 7 day PHI	grapes, unwashed (RAC)	150, 69, 166	128	
		raisins	7.2, 6.5, 12	8.5	0.066
		wet pomace	131, 128, 130	130	1.0
		dry pomace	212, 316, 164	231	1.8
		raisin waste	1007, 1076, 729	937	7.3
		grape juice	166, 150, 172	163	1.3

Processing factor: Ratio of fosetyl-Al residue in the processed item divided by the fosetyl-Al residue in the RAC

Grapes – phosphonic acid

In a number of supervised wine grape trials and commercial vineyard trials conducted in Australia, where up to six foliar applications of phosphonic acid (as potassium salts) were applied at various stages of growth, from flowering through to pre-bunch closure and pre-harvest, treated grapes were processed into wine, using a microvinification process that involved crushing and destemming the bunches, the addition of sulphur dioxide and pH adjustment, fermentation (with skins), the addition of diammonium phosphate (DAP), pressing and further fermentation prior to racking (settling and decanting to remove lees) and bottling.

Samples of grapes (berries) and wine were stored frozen for up to about 180 days before analysis for phosphonic acid. The analytical methods used in the 2004 and 2005 trials was based on the GC-FPD method AR155-97 (LOQ of 1.0 mg/kg) and an LC-MS/MS method based on method 00861/M001 was used for the 2011 grower samples (LOQ 0.1 mg/kg). In the 2013 trials, a modification of method 00861/M001 was used (i.e. the addition of an ion-pairing reagent tetrabutylammonium acetate prior to filtration and analysis). The LOQ, at the lowest fortification level, was 1.0 mg/kg and concurrent recoveries were 101-106% (fortification levels of 1.0–52 mg/kg).

In a study reported by Odell *et al.*, 2010 [Ref: AWRI-2010], phosphonic acid residues were measured in wines that had been treated during the wine-making process with 300 mg/litre diammonium phosphate (DAP) containing levels of phosphonic acid up to 3.9 g/kg. Residues of phosphonic acid in the treated wine were up to about 1.0 mg/kg.

Table 146 Residues in grapes and wine from supervised trials in Australia involving foliar applications of phosphonic acid (as mono- and di-potassium salts)

GRAPES Country, year Location (variety) References	Application					DALA	Phosphonic acid residues (mg/kg)			Processing factors
	no	kg ai/ha	kg ai/hL	water (L/ha)	total kg ai/ha		Grape	Wine		
GAP: Australia		2.4				nr				
Australia 2004 (Cabernet Sauvignon) AWR 04/01	1	2.4	0.5	475	2.4	8	6.6	4.5		0.7
	3	2.4	0.5	475	7.2	73	31.5	21		0.7
	4	2.4	0.5	475	9.6	8	46.5	41		0.9
	6	2.4	0.5	475	14.4	8	45.5	87		1.9
Australia 2005 (Cabernet Sauvignon) AWR 04/01	1	2.4	0.54	443	2.4	44	7.1	21.0		3.0
	1	2.4	0.54	443	2.4	98	2.3	3.4		1.5
	1	1.2	0.27	443	1.2	119	<1.0	1.5		>1.5
	2	2.4	0.54	443	4.8	51	5.8	12.0		2.1
	2	1.2-1.8	0.27-0.41	443	3.0	113	2.6	3.9		1.5
	3	2.4	0.54	443	7.2	44	6.8	16		2.4
	3	1.2-2.4	0.27-0.54	443	5.4	98	4.1	9.7		2.4
	4	1.2-2.4	0.27-54	443	7.8	51	9.2	12		1.3
	5	1.2-2.4	0.27-	443	10.2	44	13	18		1.4
Australia, 2011 (Verdelho) AWRI 2016 AC77220	2	1.4-1.6			3.0	55	11	10		0.9
Australia, 2011 (Chardonnay) AWRI 2016 AC77222	2	1.6-1.8			3.4	60	19	16		0.8
Australia, 2011 (Tempranillo) AWRI 2016 AC77224	3	2.4			7.2	85	33	32		1.0
Australia, 2011 (Shiraz) AWRI 2016 AC77210	2	2.4			4.8	114	25	21		0.8
Australia, 2011 (Cabernet Sauvignon) AWRI 2016 AC77229	3	2.4-3.0			8.4	78	32	30		0.9
Australia, 2011 (Riesling) AWRI 2016 AC77217	4	2.4			9.6	27	77	42		0.5
Australia 2004 (Chardonnay) AWR 04/01							mean	values	mean	
	1	2.4	0.48	500	2.4	35	5.2	23, 15	19	3.6
	1	2.4	0.48	500	2.4	93	1.8	25, 6.5	15.8	8.8
	1	2.4	0.48	500	2.4	124	<1.0	<1.0, 1.2	1.1	>1.1
	2	2.4	0.48	500	4.8	50	6.0	22, 14	18	3.0
	2	1.2	0.24	500	2.4	113	1.4	2.3, 4.0	3.2	2.3
	3	2.4	0.48	500	7.2	35	16.8	44, 48 26, 24	46 25[a]	2.7 1.5
	3	1.2-1.8	0.24-0.36	500	4.2	111	2.7	7.2, 6.0	6.6	2.4
	4	1.2-2.4	0.24-0.48	500	6.6	93	11.5	13, 17 21, 12	15 16.5[a]	1.3 1.4
	5	1.2-2.4	0.24-0.48	500	9.0	50	11.6	35, 43 40, 33	39 36.5[a]	3.4 3.1
	6	1.2-2.4	0.24-0.48	500	11.4	35	11.5	43, 46 48, 38	44.5 43[a]	3.9 3.7

Processing factor: Ratio of phosphonic acid residue in the processed item divided by the phosphonic acid residue in the RAC

[a] Wine fermentation was ‘off-skin’

Strawberry – fosetyl-Al

In strawberry processing studies conducted in Europe and reported by Simonin & Ratajczak, 2006 [Ref: 01-71], fruit (without sepals) from supervised field trials involving 3 foliar applications of 6.0 kg ai/ha fosetyl-Al were collected at harvest, 14 days after the last application and were processed into jam and canned fruit.

For jam, unwashed strawberries were crushed, sugar was added and the puree was reduced to achieve 62°Brix if necessary the pH was corrected with citric acid to obtain approx. 3.5. The puree was sealed in glass jars and sterilised at 115 °C for 10 minutes before cooling and stored frozen for analysis.

The canning process involved blanching the unwashed strawberries in boiling water for 1 minute and placed into glass jars. A sugar syrup (200 g of sugar + 800 g of water) was added to the jars, the pH was corrected to about 3.5 with citric acid and the jars were sealed, pasteurised (90–95 °C for 1 minute), cooled and stored frozen for analysis.

Samples were stored for up to 348 days before analysis for fosetyl-Al and phosphonic acid using the GC-FPD method AR 155-97 with LOQs of 0.2 mg/kg for both analytes in the processed fractions (canned strawberries and jam). Average concurrent recovery rates for fosetyl-Al were 72–98% (fortification levels of 0.2–0.5 mg/kg) and were 74–106% for phosphonic acid (fortification levels of 0.2–10 mg/kg).

Table 147 Residues of fosetyl-Al and phosphonic acid in strawberries and processed commodities following the use of fosteyl-Al (foliar sprays) in supervised trials in Europe

Trial, Location, Year, Commodity, Variety	Application	Commodity	Residues (mg/kg or mg/L)			Processing factors
			Fosetyl-Al	Phos-acid	Total residues	
France 2001 Soings (Valeta) 01-71FR1	3 x 6.0 kg ai/ha 14 day PHI	Strawberry (RAC)	0.25	10	10	
		Washing water	0.001	0.047	0.048	
		Washed fruit	< 0.2	8.9	9.0	0.89
		Jam	< 0.2	5.2	5.3	0.52
		Blanching water	< 0.02	< 0.02	< 0.34	
		Canned fruit	< 0.2	6.2	6.3	0.62
UK 2001 Tunstead (Elsanta) 01-71UK1	3 x 6.0 kg ai/ha 14 day PHI	Strawberry (RAC)	0.26	15 c=0.35	15 c=0.49	
		Washing water	0.004	0.023	0.026	
		Washed fruit	0.32	15 c=0.4	15 c=0.54	1.0
		Jam	< 0.20	7.4 c=0.29	7.5 c=0.43	0.5
		Blanching water	< 0.02	1.7 c=0.025	1.7 c=0.16	
		Canned fruit	< 0.2	6.0 c=0.23	6.1 c=0.37	0.4

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

Tomato – fosetyl

In tomato processing studies conducted in Europe and reported by Freitag & Czaja, 2014 [Ref: 13-3047], mature tomatoes from supervised glasshouse trials involving two seedling drench applications equivalent to 9.3 kg ai/ha fosetyl (SL co-formulated with propamocarb) applied before transplanting and four drip irrigation treatments of 4.7 kg ai/ha fosetyl after transplanting, were sampled 3 days after the last application and were processed into juice, preserve and puree using simulated commercial practices.

For juice, fruit were hand washed in luke-warm water, chopped and simmered in water for about 20 minutes. The pulp was sieved to obtain raw juice and strain rest. The sample of raw juice was combined with salt (0.5–0.7%), canned and pasteurized in an autoclave. Aliquots were retained for use in preparing tomato preserve.

To obtain tomato preserve, washed fruit were peeled by hand, canned with the retained raw tomato juice and pasteurized in an autoclave. The obtained sample of "preserve" was pureed using a mixer and then sampled for analysis.

For puree, washed fruit were chopped and simmered in water for about 20 minutes and the pulp was passed through a sieve to obtain raw juice and pomace. After the addition of salt (0.5–0.7%), the raw juice was concentrated at about 62 °C under vacuum for 13–20 hours to produce raw puree with a dry weight of about 10%. This raw puree was canned and pasteurized in an autoclave to produce puree.

Samples were stored for up to 194 days before analysis for fosetyl-Al and phosphonic acid using the LC-MS/MS method 00861/M001 with LOQs of 0.0093 mg/kg for fosetyl and 0.2 mg/kg for phosphonic acid. Average concurrent recovery rates for fosetyl-Al were 87–98% (fortification levels of 0.01–10 mg/kg as fosetyl-Al) and were 91–112% for phosphonic acid (fortification levels of 0.2–100 mg/kg).

Table 148 Residues of fosetyl and phosphonic acid in tomatoes and processed commodities following the use of fosteyl (foliar sprays) in supervised trials in Europe

Trial, Location, Year, Commodity, Variety	Application	Commodity	Residues (mg/kg or mg/L)			Processing factors
			Fosetyl	Phos-acid	Total residues	
Netherlands, 2013 Zwaagdijk (Ingar) 13-3407-01	2 x dip 9.3 kg ai/ha 4 x drip 4.7 kg ai/ha 3 day PHI	Tomato (RAC)	0.01	0.79	0.79	
		Washed fruit	< 0.0093	0.8	0.81	1.0
		Washings	< 0.0093	< 0.2	< 0.21	
		Raw juice	0.009	0.66	0.67	
		Juice	0.01	0.58	0.59	0.75
		Washed peel	< 0.0093	0.62	0.63	
		Peeled fruit	< 0.0093	0.82	0.83	
		Peeling water	< 0.0093	< 0.2	< 0.21	
		Preserve	0.01	0.71	0.72	0.91
		Pomace	< 0.0093	0.9	0.91	1.1
		Raw puree	0.019	1.3	1.3	
		Puree	0.014	1.0	1.0	1.3
Spain, 2013 Lora del Rio (Motril) 13-3407-02	2 x dip 9.3 kg ai/ha 4 x drip 4.7 kg ai/ha 3 day PHI	Tomato (RAC)	0.01	0.79	0.79	
		Washed fruit	< 0.0093	0.6	0.61	0.75
		Washings	< 0.0093	< 0.2	< 0.21	
		Raw juice	< 0.0093	0.71	0.72	
		Juice	< 0.0093	0.67	0.68	0.83
		Washed peel	< 0.0093	0.46	0.47	
		Peeled fruit	< 0.0093	0.83	0.84	
		Peeling water	< 0.0093	< 0.2	< 0.21	
		Preserve	< 0.0093	0.71	0.72	0.87
		Pomace	< 0.0093	0.9	0.91	1.1
		Raw puree	0.012	1.2	1.2	
		Puree	0.014	1.3	1.3	1.5

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

In a tomato processing study conducted in USA and reported by Chow & Rives, 1990 [Ref: C016048], replicate samples of fruit treated with 4 foliar applications of fosetyl-Al at an exaggerated rate of 22.4 kg ai/ha were collected 14 days after the last application and processed into juice, puree and paste.

Washed tomatoes were soaked in a dilute solution of chlorine 10 minutes at 25 °C and rinsed in warm water before being crushed and rapidly heated to 107 °C for 50–60 seconds and pressed to separate the hot-break juice and pomace, with the hot-break juice being vacuum evaporated to obtain puree (10% solids) and paste (31.7% solids). Juice was prepared by diluting the paste to achieve 5.5% solids.

The puree, paste, hot break juice and reconstituted juice were then heated to 85–93 °C, canned, sterilized in a boiling water bath for about 15 minutes and cooled before freezing for subsequent analysis.

Samples of the processed fractions were stored for an unknown interval before analysis for fosetyl-Al using the GC-FPD method 163. The LOQ for all matrices was 0.05 mg/kg. Mean concurrent recovery rates in all tomato matrices were 79–98% (98–130% in the wash water).

Table 149 Residue of fosetyl-Al in tomatoes and processed commodities following foliar applications of fosetyl-Al in USA

Trial, Location, Year, Commodity, Variety	Application	Commodity	Fosetyl-Al	
			Residues (mg/kg)	Processing factors
USA, 1989 Fresno, CA (Castle Rock) C016048	Foliar sprays 4 x 22.4 kg ai/ha 14 day PHI	Tomato (RAC)	3.0	
		Tomato, washed	0.24	0.08
		Wet pomace	0.31	0.1
		Dry pomace	0.76	0.25
		Canned juice	0.26	0.09
		Canned juice from concentrate	0.38	0.13
		Canned puree	0.15	0.05
		Canned paste	0.49	0.16
		Wash soak water	2.7	
		Wash rinse water	0.13	

Processing factor: Ratio of fosetyl-Al residue in the processed item divided by the fosetyl-Al residue in the RAC

Chili pepper – fosetyl

In a study reported by Hoag & Harbin, 2013 [Ref: RAFYL023-2], chili pepper samples were taken from supervised field trials conducted in Mexico, Peru and USA and processed into dried chili pepper. Fosetyl (SL co-formulations with propamocarb) treatments were applied 3 times to seedlings before transplanting and 3 further chemigation or foliar drench treatments at about 10 day intervals up to 4–5 days before harvest.

Duplicate samples of fresh chili peppers and samples that had been allowed to dry under field conditions or in drying ovens for 7–20 days were frozen and stored for up to 409 days before analysis. The fresh chili peppers were analysed for fosetyl and phosphonic acid using the LC-MS/MS method 00861/M001.

Because the method could not be validated for dried chili pepper, the % dry matter of both the fresh and dried samples were measured to derive a concentration factor based on the ratio between the dry matter content of the fresh and the dried chili peppers. The residue results from the analysis of the fresh samples were used to calculate potential residues in the dried chili peppers.

For fosetyl, the LOQ of the analytical method was 0.0093 mg/kg (equivalent to 0.01 mg/kg fosetyl-Al) and the concurrent recovery rates were 82–93% (fortification level of 0.01 mg/kg fosetyl-Al). For phosphonic acid, the LOQ was 0.1 mg/kg with concurrent recovery rates of 94–104% (fortification level of 0.1 mg/kg).

Table 150 Residues of fosetyl-Al and phosphonic acid in dried chili pepper following foliar applications of fosetyl

Trial, Location, Year, Commodity, Variety	Application	DALA	Commodity	% dry matter	Residues (mg/kg)			Concentration factors
					Fosetyl-Al	Phos- acid	Total residue	
USA, 2011 Sanger, CA (Numex Joe E. Parker) RAFYL023-2 FY011-11DA	3 foliar drenches 9.2-9.5 kg ai/ha 3 chemigations 0.93 kg ai/ha	0	Chili pepper (RAC)	10.51 32.47	< 0.01 < 0.01 [< 0.01]	0.17 0.14 [0.16]	0.17 0.15 [0.16]	
			Dried chili pepper	10.09 34.17	< 0.01 < 0.01 [< 0.01]	0.52 0.49 [0.5]	0.53 0.50 [0.51]	3.1 3.4
		2	Chili pepper (RAC)	10.29 35.44	< 0.01 < 0.01 [< 0.01]	0.15 0.22 [0.19]	0.16 0.23 [0.2]	
			Dried chili pepper	10.72 32.80	< 0.01 < 0.01 [< 0.01]	0.52 0.69 [0.61]	0.53 0.70 [0.61]	3.4 3.1
		5	Chili pepper (RAC)	10.51 75.12	< 0.01 < 0.01 [< 0.01]	0.17 0.25 [0.21]	0.18 0.26 [0.22]	
			Dried chili pepper	10.92 77.45	< 0.01 < 0.01 [< 0.01]	1.2 1.8 [1.5]	1.2 1.8 [1.5]	7.1 7.1
		7	Chili pepper (RAC)	10.39 78.30	< 0.01 < 0.01 [< 0.01]	0.26 0.32 [0.29]	0.27 0.33 [0.3]	
			Dried chili pepper	10.72 75.30	< 0.01 < 0.01 [< 0.01]	2.0 2.3 [2.1]	2.0 2.3 [2.1]	7.5 7.0
		9	Chili pepper (RAC)	10.78 74.25	< 0.01 < 0.01 [< 0.01]	0.31 0.45 [0.38]	0.31 0.45 [0.38]	
			Dried chili pepper	10.42 24.00	< 0.01 < 0.01 [< 0.01]	2.1 3.0 [2.5]	2.1 3.0 [2.6]	6.9 6.7
Mexico, 2011 Los Mochis (Tuxtlas) RAFYL023-2 FY012-11HA	3 foliar drenches 9.2-9.3 kg ai/ha 3 field drenches 0.93 kg ai/ha	5	Chili pepper (RAC)	12.30 85.63	< 0.01 < 0.01 [< 0.01]	0.13 0.17 [0.15]	0.14 0.18 [0.16]	
			Dried chili pepper	12.93 85.59	< 0.01 < 0.01 [< 0.01]	0.93 1.1 [1.0]	0.93 1.2 [1.0]	7.0 6.6
Mexico, 2011 Guasave (Tuxtlas) RAFYL023-2 FY013-11HA	3 foliar drenches 9.1-9.3 kg ai/ha 3 chemigations 0.94 kg ai/ha	5	Chili pepper (RAC)	12.59 76.98	< 0.01 < 0.01 [< 0.01]	0.12 0.17 [0.14]	0.13 0.17 [0.15]	
			Dried chili pepper	11.08 84.36	< 0.01 < 0.01 [< 0.01]	0.73 1.3 [0.99]	0.77 1.3 [1.0]	6.1 7.6
Peru, 2011 Chincha (Queen) RAFYL023-2 FY014-11HA	3 foliar drenches 9.3-9.4 kg ai/ha 3 chemigations 0.93 kg ai/ha	4	Chili pepper (RAC)	21.12 78.70	< 0.01 < 0.01 [< 0.01]	< 0.1 < 0.1 [< 0.1]	< 0.107 < 0.107 [< 0.107]	
			Dried chili pepper	18.94 85.00	< 0.01 < 0.01 [< 0.01]	0.13 0.17 [0.15]	0.14 0.17 [0.16]	3.7 4.5
Peru, 2011 Chincha (King) RAFYL023-2 FY015-11DA	3 foliar drenches 9.2-9.3 kg ai/ha 3 field drenches 0.93 kg ai/ha	0	Chili pepper (RAC)	16.63 82.15	< 0.01 < 0.01 [< 0.01]	0.20 0.17 [0.18]	0.21 0.18 [0.19]	
			Dried chili pepper	17.43 82.04	< 0.01 < 0.01 [< 0.01]	0.97 0.80 [0.89]	0.98 0.81 [0.89]	4.9 4.7
		2	Chili pepper (RAC)	20.10 84.58	< 0.01 < 0.01 [< 0.01]	0.14 0.34 [0.24]	0.14 0.35 [0.25]	

Trial, Location, Year, Commodity, Variety	Application	DALA	Commodity	% dry matter	Residues (mg/kg)			Concentration factors
					Fosetyl-Al	Phos- acid	Total residue	
			Dried chili pepper	17.78 84.82	< 0.01 < 0.01 [< 0.01]	0.58 1.6 [1.1]	0.58 1.7 [1.1]	4.2 4.8
		4	Chili pepper (RAC)	18.54 86.92	< 0.01 < 0.01 [< 0.01]	0.12 0.23 [0.17]	0.12 0.24 [0.18]	
			Dried chili pepper	17.30 80.72	< 0.01 < 0.01 [< 0.01]	0.55 1.1 [0.81]	0.56 1.1 [0.82]	4.7 4.7
		7	Chili pepper (RAC)	18.94 79.60	< 0.01 < 0.01 [< 0.01]	0.13 0.44 [0.28]	0.14 0.44 [0.29]	
			Dried chili pepper	20.24 79.50	< 0.01 < 0.01 [< 0.01]	0.56 1.7 [1.1]	0.57 1.7 [1.1]	4.2 3.9
		9	Chili pepper (RAC)	21.64 80.14	< 0.01 < 0.01 [< 0.01]	0.13 0.26 [0.2]	0.14 0.27 [0.2]	
			Dried chili pepper	22.75 80.40	< 0.01 < 0.01 [< 0.01]	0.48 0.92 [0.7]	0.48 0.92 [0.7]	3.7 3.5

Residue values in italics are indicative – analytical method not validated for dried chili peppers.

Concentration factor = Total residue in RAC × (% dm in dried fruit / % dm in fresh fruit).

Value in square brackets is the mean residue of two independent samples

Hops – fosetyl-Al

In a number of hop processing studies conducted in Europe, hops from vines treated with 5-9 foliar or drench applications of 0.7–8.0 kg ai/ha fosetyl-Al were sampled 7–47 days after the last application, dried and used to produce beer. While no details were available on the processing methods, dried cones are usually milled and added to the separated wort and after boiling for about 90 minutes, the flocs (hops draff) are separated and yeast is added to the brew to initiate fermentation. Primary fermentation proceeds for 9–11 days at about 9 °C and secondary (cask) fermentation continues for a further 2 days at 20 °C and under pressure for a further 24 days at 2 °C before being filtered and sampled for subsequent analysis.

Samples of the dried cones and beer were stored for up to 63–540 days in the four studies before analysis for fosetyl-Al and phosphonic acid using the GC-FPD methods AR/1345, MP-RE-03-78 (RE 12-79) or DFG 522. The LOQs for these methods ranged from 0.2–5.0 for beer and dried hops (both analytes) and mean recovery rates ranged from 66–105% in hop samples fortified with 5.0–500 mg/kg and beer samples fortified with 0.2–10 mg/kg.

Table 151 Residues of fosetyl-Al and phosphonic acid in hops (dry cones) and beer following the use of fosetyl-Al (foliar sprays) in Europe

Country, Year Location, (variety) References	Application	matrix	Residues (mg/kg)			Processing factors
			Fosetyl-Al	Phos-acid	Total residue	
Germany, 1979 Meckenbeuren (Hallertauer Mittelfrueher) R003364 24896	8 foliar 1.4-5.6 kg ai/ha 14 day PHI	Dried cones (RAC)	19	182	195	
		Beer	< 0.2	0.3	0.4	0.0022
Germany 1979 Bucherhof	7 foliar 0.7-2.8 kg ai/ha	Dried cones (RAC)	13	271	280	

Country, Year Location, (variety) References	Application	matrix	Residues (mg/kg)			Processing factors
			Fosetyl-Al	Phos-acid	Total residue	
Hallertauer Mittelfrueher) R003364 24898	14 day PHI	Beer	< 0.2	1.2	1.3	0.0048
Germany, 1979 Huell (Brewers Gold) R003364 24902	8 foliar 2.2-8.0 kg ai/ha 14 day PHI	Dried cones (RAC)	20	222	236	
		Beer	< 0.2	0.6	0.7	0.0031
Germany, 1979 Huell (8069) (Hallertauer) R003364 24904	2 drench + 3 foliar 4.6 kg ai/ha 7 day PHI	Dried cones (RAC)	61	411	453	
		Beer	< 0.2	2.1	2.2	0.0049
UK 1980 Ongar (Northern Brewer) R000758 0895	7 foliar 0.2 kg ai/hL 29 day PHI	Dried cones (RAC)	20	404 c=0.55	418 c=4.0	
		Beer	< 1.0	1.2 c=0.48	1.9 c=1.2	0.0045
UK, 1979 Castle Frome (Early Bird) R000758 0898	7 foliar 0.2 kg ai/hL 47 day PHI	Dried cones (RAC)	6.0 c=0.20	133 c=0.24	137 c=3.7	
		Beer	< 1.0	< 1.0 c=0.14	< 1.7 c=0.8	< 0.012
UK, 1980 Rosenmaund (Bullion) R000758 0920	7 foliar 0.16 kg ai/hL 21 day PHI	Dried cones (RAC)	< 5.0 c=0.28	< 5.0 c=0.38	< 8.0 c=3.9	
		Beer	<1.0	<1.0	<1.7	
Germany 1980 Tettnang (Hallertauer Mittelfrueher) 444058 14939	1 drench 5.3 kg ai/ha 6 foliar 2.6-7.9 kg ai/ha 14 day PHI	Dried cones (RAC))	18	249	262	
		Beer	< 0.2	1.3	1.4	0.0055
Germany, 1980 Huell (Brewers Gold) 444058 14957	7 foliar 4.0 kg ai/ha 14 day PHI	Dried cones (RAC)	4.4	166	169	
		Beer	< 0.2	1.0	1.1	0.0064
Germany, 1980 Geroldshausen (Brewers Gold) 444058 24845	1 drench 4.8 kg ai/ha 8 foliar 5.6 kg ai/ha 18 day PHI	Green cones	< 4.0	39	42	
		Dried cones (RAC)	8.0	87	93	
		Beer	< 0.2	0.6 c=0.30	0.74 c=0.40	0.008
Germany, 1980 Schaching (Hersbruecker Spaet) 444058 24868	1 drench 4.8 kg ai/ha 8 foliar 4.8-8.0 kg ai/ha 14 day PHI	Green cones	< 4.0	0.8	3.6	
		Dried cones (RAC)	30	370	391	
		Beer	< 0.2	2.0	2.1	0.0055
France, 1997 Schnersheim	9 foliar 2.4-5.0 kg ai/ha	Green cones	0.66	20 c=3.59	20 c=3.7	

Country, Year Location, (variety) References	Application	matrix	Residues (mg/kg)			Processing factors
			Fosetyl-Al	Phos-acid	Total residue	
(Strisselspalt)	13 day PHI	Dried cones (RAC)	19	102 c=1.83	114 c=2.0	
RBHOXX197/45 RE97098		Beer	0.21	1.9	2.0	0.018

Processing factor: Ratio of total residue in the processed item divided by the total residue in the RAC

Residues in must after boiling in 1 trial were 0.28 mg/kg (fosetyl-Al) and 3.5 mg/kg (phosphonic acid)

Summary of Processing Studies

In processing studies conducted on oranges, apples, grapes, tomatoes, strawberries and hops and simulating commercial practices, residues of fosetyl-Al/fosetyl increased in some dried or concentrated commodities (tomato puree, dried peppers). Phosphonic acid residues also concentrated in these dried or concentrated commodities but being highly water-soluble, also increased in a number of juices and wine.

Table 152 Summary of processing factors for fosetyl-Al

RAC	Matrix	Fosetyl-Al[a]	
		Calculated processing factors	P Factor
Orange	juice pomace	0.35, 0.57, 0.94, 1.1, 1.4 0.45, 0.77, 3.4, 3.9, 4.6	0.94 3.4
Apple	juice wet pomace puree	0.63, 1.2 0.49, 1.6 0.44, 0.71, 1.1	0.92 1.0 0.71
Grape	juice must wet pomace wine	0.5, 0.69, 0.94, 0.96, 1.1, 1.2, 1.2 0.06, 0.17, 0.34, 0.39, 0.59, 0.62, 0.77, 0.84, 1.4 0.59, 1.3, 1.4, 2.4 0.11, 0.35, 0.43, 0.51, 0.52, 0.55, 0.63, 0.64,0.7, 0.77, 0.84, 1.1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.8, 2.4	0.96 0.59 1.4 0.77
Strawberry	washed fruit jam canned fruit	0.89, 1.0 0.52, 0.5 0.62, 0.4	0.95 0.51 0.51
Spinach	washed cooked	0.73, 0.86, 1.2, 1.2 0.66, 0.91, 0.95, 1.0	1.0 0.93
Green bean	cooked canned	0.16, 0.77 0.48, 0.55	0.47 0.52
Hops	beer	0.0022, 0.0031, 0.0045, 0.0048, 0.0049, 0.0055, 0.0055, 0.0064, 0.018	0.0049

[a] Each value represents a separate study where residues were above the LOQ in the RAC. The factor is the ratio of total residues in the processed item divided by the total residue in the RAC.

Table 153 Summary of processing factors for fosetyl

RAC	Matrix	Fosetyl-Al[a]	
		Calculated processing factors	P Factor
Tomato	washed fruit juice (pasteurised) puree preserve wet pomace	0.75, 1.0 0.75, 0.83 1.3, 1.5 0.87, 0.91 1.1, 1.1	0.88 0.79 1.4 0.89 1.1
Lettuce	outer leaves heads inner leaves washed inner leaves	0.74, 1.0 0.71, 1.0 0.9, 0.9 0.52, 0.69	0.87 0.86 0.9 0.61
Spinach	washed cooked	0.73, 0.86, 1.2, 1.2 0.66, 0.91, 0.95, 1.0	1.0 0.93

[a] Each value represents a separate study where residues were above the LOQ in the RAC. The factor is the ratio of total residues in the processed item divided by the total residue in the RAC.

Table 154 Summary of processing factors for phosphonic acid

RAC	Matrix	Phosphonic acid[a]	
		Calculated processing factors	P Factor
Orange	washed fruit	0.47, 0.52, 0.59	0.52
	juice (pasteurised)	0.27, 0.29, 0.34	0.29
	pomace (dry)	2.0, 2.7, 3.4	2.7
	marmalade	0.29, 0.33, 0.37	0.33
	canned	0.22, 0.34, 0.39	0.34
	oil	< 0.02, < 0.04, < 0.04	< 0.04
Grape	wine	0.5, 0.7, 0.7, 0.8, 0.8, 0.9, 0.9, 0.9, 1.0, >1.1, 1.3, 1.3, 1.4, 1.4, 1.5, 1.5, 1.5, >1.5, 1.9, 2.1, 2.3, 2.4, 2.4, 2.4, 2.7, 3.0, 3.0, 3.1, 3.4, 3.6, 3.7, 3.9, 8.8	1.5

[a] Each value represents a separate study where residues were above the LOQ in the RAC. The factor is the ratio of phosphonic acid residues in the processed item divided by the residue of phosphonic acid in the RAC.

RESIDUES IN ANIMAL COMMODITIES

Livestock feeding studies

Lactating dairy cows – fosetyl-Al

In a lactating dairy cow feeding study reported by Somma *et al*., 1984 [Ref: R011762], three groups of 3 dairy cows (525-600 kg bw) were dosed orally each morning for 28 days with fosetyl-Al (in gelatine capsules) at rates equivalent to 3 ppm, 9 ppm and 30 ppm (0.086, 0.26 and 0.87 mg/kg fosetyl-Al/kg bodyweight/day).

The afternoon milk was composited with the following morning milk and subsamples were taken at intervals during the dosing period and all cows were sacrificed 20 hours after dosing on Day 28. Samples of liver, kidneys, heart, muscle (composite of leg and loin muscle), fat and blood (EDTA added) were taken from each cow and frozen for analysis. No information is available on the interval between sampling and analysis.

Tissue samples (liver, kidney, heart, muscle, and fat) and milk were analysed for fosetyl-Al using the GC-FPD method No. 171, involving acetonitrile/HCl extraction, alumina column clean-up, the addition of acetic acid and methylation with diazomethane. Additional steps for milk before the final alumina column clean-up included a C-18 column clean-up to remove fats, an aluminum sulfate precipitation step to remove proteins and a propanol-2 precipitation step to remove sugars. The LOQs were 0.05 mg/kg in tissues and 0.02 mg/kg in milk. Concurrent recovery rates ranged from 70–96% in control samples fortified with 0.02–2.0 mg/kg fosetyl-Al

No residues of fosetyl-Al were found above the LOQs in any milk or tissue sample at any dose rate.

Table 155 Residues of fosetyl-Al in milk and cow tissues following dietary administration of fosetyl-Al

Matrix	Fosetyl-Al feeding level (ppm dw)	Residues (mg/kg)
		Fosetyl-Al
Kidney	0	< 0.05
	9	< 0.05
	30	< 0.05
Liver	0	< 0.05
	9	< 0.05
	30	< 0.05
Muscle	0	< 0.05
	30	< 0.05
Heart	0	< 0.05
	30	< 0.05

Matrix	Fosetyl-Al feeding level (ppm dw)	Residues (mg/kg)
		Fosetyl-Al
Fat	0	< 0.05
	30	< 0.05
Milk	0	< 0.02
	30	< 0.02

Lactating dairy cows – fosetyl-Al + phosphonic acid

In a lactating dairy cow feeding study reported by van Dijk, 2000 [Ref: C010251], three groups of 3 dairy cows (500–755 kg bw) were dosed orally twice a day (after each milking) for 28 days with a mixture of fosetyl-Al and disodium phosphonate (in gelatine capsules) at dry weight dietary equivalents of 11 ppm, 32 ppm and 100 ppm (calculated as phosphonic acid). The dose rates were equivalent to feed concentrations of 1 ppm, 3 ppm and 10 ppm fosetyl-Al and 10 ppm, 30 ppm and 94 ppm phosphonic acid equivalents respectively. Based on a daily feed consumption of 19–22 kg feed per cow, the total dose rates were the equivalent of 0.25, 0.76 and 2.5 mg phosphonic acid equivalents/kg bodyweight/day.

The afternoon milk was composited with the following morning milk and subsamples were taken at intervals during the dosing period and all cows were sacrificed within 24 hours after the last dosing. Samples of liver, kidneys, trimmed muscle and fat were taken from each cow, homogenised and stored frozen for up to 30 days before analysis.

Samples were analysed for fosetyl-Al and phosphonic acid using the GC-FPD method AR 172-98, involving acetonitrile/water extraction, C18 cartridge clean-up (not milk), the addition of acidifies isopropanol and methylation with TMSD. The LOQs were 0.5 mg/kg in tissues and 0.1 mg/kg in milk. Concurrent recovery rates ranged from 70–118% in control samples fortified with fosetyl-Al or phosphonic acid at 0.1–1.0 mg/kg in milk and 0.5–5.0 mg/kg in tissues.

No fosetyl-Al equivalent residues were detected in any of the tissues or milk analysed except in one sample of liver from the 30 ppm dose group, where a residue of 0.081 mg/kg (<LOQ) was detected.

Phosphonic acid residues were detected at all three dose levels but were all below the respective LOQs in milk, muscle, liver, kidney and fat except in the 100 ppm dose group, where residues in kidney were about 0.5–0.6 mg/kg (reflecting the urinary route of elimination).

Table 156 Residues of fosetyl-Al and phosphonic acid in milk and bovine tissues following dietary administration of fosetyl-Al:disodium phosphonate (1:9 fosetyl-Al equivalents)

Matrix	Feeding level (ppm dw)			Residues (mg/kg)			
	Fosetyl-Al	Phos-acid[a]	Total[b]	Fosetyl-Al	Phos-acid (mean of 3 animals)	Total residues (as Phos-acid)	
						mean	max
Kidney	0	0	0	ND	0.08	0.08	0.14
	1	10	11	ND	0.16	0.16	0.22
	3	30	32	ND	0.29	0.29	0.3
	10	94	100	ND	0.55 (max = 0.6)	**0.55**	**0.6**
Liver	0	0	0	ND	0.04	0.04	0.069
	1	10	11	ND	ND	ND	ND
	3	30	32	ND – 0.081[c]	0.16	0.22	0.33
	10	94	100	ND	0.16	0.16	0.28
Muscle	0	0	0	ND	0.09	0.09	0.16
	1	10	11	ND	0.05	0.05	0.088
	3	30	32	ND	0.07	0.07	0.089
	10	94	100	ND	0.02	0.02	0.06
Fat	0	0	0	ND	0.02	0.02	0.067
	1	10	11	ND	0.13	0.13	0.16
	3	30	32	ND	0.12	0.12	0.18
	10	94	100	ND	0.2	0.2	0.22

Matrix	Feeding level (ppm dw)			Residues (mg/kg)			
				Fosetyl-Al	Phos-acid (mean of 3 animals)	Total residues (as Phos-acid)	
	Fosetyl-Al	Phos-acid[a]	Total[b]			mean	max
Milk	0	0	0	ND	ND	ND (mean)	
	1	10	11	ND	0.04	0.04 (mean)	
	3	30	32	ND	0.05	0.05 (mean)	
	10	94	100	ND	0.06	0.06 (mean)	

LOQs: 0.1 mg/kg (milk), 0.5 mg/kg (tissues)

[a] Sodium phosphite dibasic pentahydrate, expressed as phosphonic acid equivalents (conversion factor of 0.38)

[b] Expressed as phosphonic acid equivalents

[c] Residue detected in one sample

Poultry – fosetyl-Al + phosphonic acid

In a poultry feeding study reported by Heal, 2004 [Ref: C044136], three groups of hens (10 point-of-lay pullets, 1.9–2.0 kg bw) were acclimatised and once they had reached a steady rate-of-lay, were dosed for 28 days with a 1:9 mixture of fosetyl-Al:disodium phosphonate incorporated into their diet. Dose rates, expressed as phosphonic acid equivalents, were 14 ppm, 42 ppm and 142 ppm dry weight in the diet (1.1, 4.1 and 12.7 mg/kg phosphonic acid equivalents/kg bodyweight/day).

All eggs were collected and pooled to obtain a single sample from each dose group and pooled eggs from each dose group were also sampled at intervals throughout the dosing period. On day 28 the hens were sacrificed and breast and thigh muscle, liver and abdominal fat were sampled and stored frozen for less than 28 days before analysis.

Tissue and egg samples were analyzed for fosetyl-Al and phosphonic acid using method AR 172–98, involving water/acetonitrile extraction, C18 cartridge clean-up, the addition of acidified isopropanol and methylation using TMSD. Analysis was by GC-NPD (eggs) and GC-PFPD (tissues) with quantification using external methylated fosetyl-Al and phosphonic acid standards. The LOQ for this method was 0.5 mg/kg for both analytes in all matrices and mean concurrent recovery rates ranged from 86–100% (RSDs of 11.4–16) in control samples fortified with 0.5 mg/kg fosetyl-Al and 76–84% (RSDs 15.1–17.8) in control samples fortified with 0.5 mg/kg phosphonic acid.

No residues of either fosetyl-Al or phosphonic acid were found above the LOQ (0.5 mg/kg) in any egg or tissue sample, with only trace levels detected in egg samples.

Table 157 Residues of fosetyl-Al and phosphonic acid in eggs and poultry tissues following dietary administration of fosetyl-Al:disodium phosphonate (1:9)

Matrix	Feeding level (ppm dw)			Residues (mg/kg)			
				Fosetyl-Al	Phos-acid	Total residues (as Phos-acid)	
	Fosetyl-Al	Phos-acid[a]	Total[b]			mean	max
Muscle	0	0	0	ND - 0.155[c]	ND	ND	0.11
	2	13	14	ND	ND	ND	ND
	6	38	42	ND	ND	ND	ND
	20	128	142	ND	ND	ND	ND
Liver	0	0	0	ND - 0.129[c]	ND - 0.111[a]	ND	0.1
	2	13	14	ND	ND	ND	ND
	6	38	42	ND	ND	ND	ND
	20	128	142	ND	ND	ND	ND
Fat	0	0	0	ND	ND	ND	ND
	2	13	14	ND	ND	ND	ND
	6	38	42	ND	ND	ND	ND
	20	128	142	ND	ND	ND	ND
Egg	0	0	0	ND - 0.024[c]	< 0.5 (0.005 - 0.056)	0.028 (mean)	
	2	13	14	ND	ND – 0.176	0.039 (mean)	
	6	38	42	ND - 0.025[c]	ND - 0.196	0.041 (mean)	
	20	128	142	ND - 0.067	ND - 0.185	0.049 (mean)	

LOQ: 0.5 mg/kg (eggs and tissues)

[a] Sodium phosphite dibasic pentahydrate, expressed as phosphonic acid equivalents (0.38 conversion factor)

[b] Expressed as phosphonic acid equivalents

[c] Residue detected in one sample

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Wine – phosphonic acid

The Meeting received information on the results of a wine residue monitoring programme conducted in Australia on the presence of phosphonic acid in 163 samples of wines in the market place produced between 2000 and 2011. In this review, reported by Longbottom et al, 2012 [Ref: AWRI 2012], samples were analysed for phosphonic acid using an LC-MS/MS method based on method 00861/M001. The LOQ was 0.1 mg/kg and concurrent recovery rates were 81–100% in samples fortified with 0.5–10 mg/kg. REF:

Table 158 Phosphonic acid residues in commercially available wine [Ref: AWRI 2012]

Distribution of phosphonic acid residues in commercially available wine (2000–2011)									
<LOQ		0.1–1.0 mg/kg		1.1–5.0 mg/kg		5.1–10 mg/kg		>10 mg/kg	
no	%	no	%	no	%	no	%	no	%
60	37%	73	45%	17	10%	7	4%	6 [a]	4%

LOQ – 0.1 mg/kg

[a] Maximum residue of 15 mg/kg

NATIONAL RESIDUE DEFINITIONS

Table 159 Fosetyl/Fosetyl-Al: National residue definitions for MRL-compliance and dietary intake estimation

Country	MRL-compliance	Dietary intake estimation
Australia	Fosetyl or Fosetyl-Aluminium	
Brazil	Fosetyl	
Canada	Fosetyl-aluminium	Fosetyl-aluminium
Europe	Fosetyl-Al (sum of fosetyl, phosphonic acid and their salts, expressed as fosetyl	Fosetyl-Al (sum of fosetyl, phosphonic acid and their salts, expressed as fosetyl
Japan	Fosetyl (sum of fosetyl and phosphorous acid, calculated as fosetyl	
Korea	Fosetyl-aluminium	
Russian Federation	Fosetyl-Al (sum of fosetyl, phosphonic acid and their salts, expressed as fosetyl)	Fosetyl-Al (sum of fosetyl, phosphonic acid and their salts, expressed as fosetyl)
South Africa	Fosetyl-aluminium	Fosetyl-Al (sum of fosetyl, phosphonic acid and their salts, expressed as fosetyl)
USA	Fosetyl-aluminium	

Table 160 Phosphonic acid: National residue definitions for MRL-compliance and dietary intake estimation

Country	MRL-compliance	Dietary intake estimation
Canada	Exempt	-
USA	Exempt	-

APPRAISAL

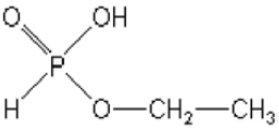
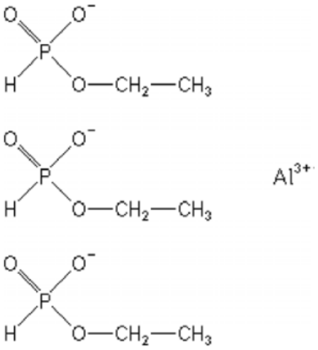
Fosetyl-aluminium (fosetyl-Al), fosetyl and phosphonic acid are systemic fungicides with protectant action against a number of oomycete and ascomycete fungi and some plant pathogenic bacteria in a range of fruit, vegetables and ornamental crops. They are rapidly absorbed through both leaves and roots and exhibit both acropetal and basipetal translocation. Their mode of action is by inhibiting germination of spores and by blocking development of mycelium, competing with phosphate as allosteric regulator of several enzymes.

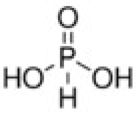
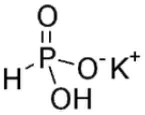
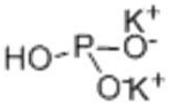
Fosetyl-Al and phosphonic acid were scheduled by the 48th Session of the CCPR as new compounds for consideration by the 2017 JMPR. The Meeting received information and studies on metabolism, analytical methods, supervised field trials, processing, freezer storage stability and environmental fate in soil for fosetyl, fosetyl-Al and phosphonic acid.

Authorisations exist in many countries for the use of fosetyl and fosetyl-Al as pre-plant dips, foliar, drench or drip-irrigation treatments and authorisations also exist for phosphonic acid (formulated as potassium, sodium and ammonium salts) in a number of countries for use as trunk injections, pre-plant dips, foliar, soil and post-harvest treatments.

In biological systems, since fosetyl, fosetyl-Al and the phosphonic acid are closely related, the Meeting agreed to evaluate the three compounds together and that the conclusions in this Appraisal would cover fosetyl and its salts as well as phosphonic acid and its salts.

Fosetyl-Al has been evaluated by the Joint FAO/WHO Meeting on Pesticide Specifications (JMPS). Specifications, published in 2013 and available at http://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/jmps/en/.

Fosetyl	Fosetyl-Al
	
MW 110	MW 354.1

Phosphonic acid	Potassium hydrogen phosphonate	Dipotassium phosphonate
		
MW 82	MW 120	MW 158

Plant metabolism

The Meeting received plant metabolism studies on citrus, apple, grape leaves, pineapple and tomato following foliar applications of labelled and unlabelled fosetyl-Al and on pineapple (pre-plant dip) and tomato (hydroponic) treatments of fosetyl-Al and phosphonic acid.

Fosetyl-Al

Citrus– foliar applications

In a study on outdoor pot-grown tangerine and orange trees, three (tangerine) or four (orange) ^{14}C-fosetyl-Al treatments of 0.066 g ai/tree were applied with a paint brush to all aerial parts of the trees at 1–2 month intervals between the end of flowering and two months before harvest. Total application rates were 0.2 g ai/tree (tangerines) and 0.26 g ai/tree (oranges).

Total radioactive residues were 2.8 mg ai/kg in oranges and 1.2 mg ai/kg in mandarins. Residues were extracted twice with water, then with acetone, and finally with acidified methanol. Most of the extracted residue was found in the aqueous extracts, 66–68% TRR in whole fruit and 90–93% TRR in juice. About 46–50% TRR in whole fruit was present as glucose, with fosetyl-Al accounting for about 5–12% TRR. In juice, fosetyl-Al residues were about 8–18% TRR with glucose being the predominant component (70–75% TRR).

Apples– foliar applications

In a study on the distribution and composition of ^{14}C-fosetyl-Al in apples, one branch of an outdoor apple tree (fruit and leaves) was treated with two sprays of 0.2 g ai/branch, 7 days apart and fruit and leaves were sampled before and after each application and again 7 and 14 days after the second treatment. Fruit and leaves were washed with deionised water and peel/flesh samples were extracted by refluxing in acidified acetonitrile/water.

Most of the radioactive residues in leaves were found in the surface wash, 96% TRR decreasing to 66% TRR at the end of the 21-day study period. Surface residues of the apple fruits predominated during the first 7 days (89% TRR), but subsequently penetrated into the fruit (53-58% TRR), mostly in the peel (39% TRR 14 days after the 2nd application).

Fosetyl-Al was the predominant residue in the fruit surface washes, initially 93% of TRR, decreasing to 41% TRR 14 days after the second application. Very small amounts of fosetyl-Al were detectable in peel and flesh (≤ 1.7% TRR).

The major radioactive metabolite identified in both apple fruit and leaves was ^{14}C-ethanol, present as a surface residue from day 0 (4.4% TRR in fruit and 28% TRR in leaves). ^{14}C-ethanol residues increased to about 50% TRR in fruit and 26% TRR in leaves.

Grape leaves – foliar treatment

Individual leaves from one grape vine (pruned to a single 1.2 metre shoot) grown in a glasshouse were treated with 0.76 mg of ^{14}C-fosetyl-Al for autoradiography. Leaves from a different vine (pruned to a single 1 metre shoot) grown in a glasshouse were treated with 4.5-9 mg of ^{14}C-fosetyl-Al for studying metabolism. Leaves were harvested at intervals up to 14 days after treatment, washed or soaked for 15 minutes in water (with added non-ionic surfactant) and the radioactive residues in the washings was determined by liquid scintillation counting (LSC). Autoradiography involved exposure to X-ray film for two weeks.

Autoradiography showed that radioactive residues moved from the treated leaves to the shoot apex (upper border of the leaves) with uptake being greater in younger leaves. Most of radiolabelled fosetyl-Al applied to vine leaves remained on the leaf surface (recovered in the wash), with limited translocation to untreated parts of the plant or to new growth. The major metabolic product found in treated and untreated plant parts was phosphonic acid.

Pineapple – dip/foliar treatments

In a two-part study on pineapple, ^{14}C-fosetyl-Al was applied as a pre-plant crown dip, followed a year later by foliar application of ^{14}C-fosetyl-Al. Whole plants were sampled at intervals up to harvest (480 days after the dip treatment) and samples from the combined pre-plant dip+foliar spray treatment were also sampled immediately after the spray treatment (day 365) and at harvest, 122 days later (487 days after the dip treatment).

Total radioactivity in the aerial parts of the pre-plant dip-treated plants decreased considerably over the study period, unextracted radioactivity increased steadily in the aerial plant parts and total radioactivity in the roots increased to 6.8% AR in the whole plant at harvest. Mature fruit at harvest contained negligible quantities of radioactive residues, 0.38% AR following the pre-plant dip treatment and 1.1% AR following the combined pre-plant dip+foliar spray treatment.

Tomato – foliar applications

In a study on tomato, two applications of ^{14}C-fosetyl-Al were made 14 days apart to fruit, leaves and stems of outdoor, sheltered tomato plants at a rate equivalent to 4.5 kg ai/ha, and samples of fruit were taken 2 hours and 14 hours after the first treatment and then 14 days and 42 days after the second treatment (42 DALA). Fruit were washed in water and subsequently blended and separated into juice and solids.

In whole tomatoes, about 98% TRR (1.4 mg ai eq/kg) was found in the 2-hour wash, with about 12% TRR (0.34 mg ai eq/kg) being removed in the 42 DALA fruit wash. Initial radioactivity in the liquid and solid fractions (3-4% TRR) increased to about 38% TRR (liquid fraction) and 50% TRR (tomato solids).

In the tomato wash, ^{14}C-fosetyl-Al initially accounted for about 77% TRR, decreasing to about 10% TRR in the 42 DALA samples. A similar pattern was observed in whole fruit, with parent decreasing from 80% TRR to about 3% TRR. Conversely, fosetyl-Al was a minor component of the radioactivity in tomato juice and extracted solids, increasing from about 3% TRR to 16% TRR in juice and from 0% TRR to 4% TRR in the solids.

Significant metabolites in whole fruit were ^{14}C-ethanol, making up about 15% TRR 2 hours after the first application, decreasing to about 12% TRR after 14 days. In the 14 DALA samples, ^{14}C-glucose was present at about 9.5% TRR, increasing to about 16% TRR in 48 DALA samples. Other radiolabelled components in the tomato solids fraction included ^{14}C-cellulose, ^{14}C-lignin and ^{14}C-starch.

Tomato – soil, petiole, leaf applications (supplementary study)

In a study using unlabelled fosetyl-Al or phosphonic acid, to investigate the distribution of residues in tomatoes, plants were treated with 0.16 or 0.32 g ai/plant by soil watering; with 7.2 mg ai fosetyl-Al/plant or 5 mg ai phosphonic acid per plant as a petiole application or with 0.4 g ai/L fosetyl-Al as a partial leaf spray. Treated and untreated stems, petioles and leaves were analysed for fosetyl-Al and phosphonic acid.

In the soil watering experiment, residues of fosetyl-Al were only found in stem/petioles 1–2 hours after treatment, with residues of phosphonic acid increasing rapidly in leaves and stems/petioles within 1 hour of watering, reaching a plateau in stems/petioles after 7 days and continuing to increase in leaves at the end of the 14-day study period.

In the petiole absorption experiment, residues of fosetyl-Al were found in stems, petioles and leaves above and below the treated petiole, with no trend of degradation. In contrast, in the phosphonic acid treated plants, higher residues were found in upper plant parts (in stem, petioles and leaves) as well as in the lower leaves, indicating translocation in both directions, but preferentially migration towards the apex (acropetal).

In the foliar treatment experiment, residues of fosetyl-Al were found at similar levels in the untreated plant parts (stems, petioles and leaves) above and below the treated leaves. Residues of phosphonic acid were also found in the untreated plant parts, peaking in the 8-hour leaf samples.

Tomato – hydroponic applications (supplementary study)

Hydroponically grown tomato plants (with 5 mature leaves) were treated with unlabelled fosetyl-Al by dipping the root systems in a solution of 2.26 mM fosetyl-Al for either 1 hour or 3 hours. Samples of roots, leaves, internodes and growing tips were analysed for fosetyl and phosphonic acid.

Fosetyl-Al was taken up by the roots and distributed through the plants within 1–3 hours and hydrolysed to phosphonic acid. After 3 days, residues of fosetyl were not found above trace levels in any aerial parts, with minor amounts found in roots. Phosphonic acid residues were found in all plant parts, increasing in young leaves and buds over the 3-day study period.

In summary, fosetyl-Al metabolism involves dissociation to fosetyl and conversion to O-ethyl phosphonate, the hydrolysis of the ethyl ester bond to form phosphonic acid and ethanol, the latter being either volatilised or incorporated into natural products. Fosetyl-Al and especially phosphonic acid are readily absorbed in plants and able to migrate in both directions, with phosphonic acid tending to migrate preferentially towards the growing tips.

Phosphonic acid

In addition to the studies conducted with fosetyl-Al (where the distribution and fate of phosphonic acid were investigated), a number of published papers were available on the behaviour of phosphonic acid in plants. Generally, phosphonic acid is rapidly (within minutes) absorbed by plant leaves or roots and translocated in both xylem and phloem, moving to sinks with the greatest demand for nutrients. Phosphonic acid is not readily oxidised to phosphate in plants.

Environmental fate

The Meeting received information on the environmental fate and behaviour of fosetyl-Al and phosphonic acid, including hydrolytic stability, photochemical degradation in soils and aerobic metabolism studies.

Hydrolysis

Fosetyl (and fosetyl-Al) dissociate in water to form O-ethyl phosphonate (and aluminium ions), with the O-ethyl phosphonate hydrolysing in biological systems to phosphonic acid by microbial activity. Phosphonic acid is not likely to occur in biological systems as the free acid under physiological and environmental conditions (pH 4 to 9), spontaneously forming salts in contact with soil or natural water with any suitable counter ion present (i.e. sodium, potassium, magnesium, calcium).

Both fosetyl-Al and phosphonic acid were stable for at least 30 days in sterile buffered solutions at pH levels reflecting those in biological systems (pH 5 to 9).

Aerobic soil metabolism

Fosetyl-Al

Aerobic degradation of fosetyl-Al was investigated in ten different soils (16 hours to 120 days in the dark at 20 °C or up to 64 days at 12 °C). Degradation was rapid, with DT_{50} values of 15–90 minutes. The proposed degradation pathway involves dissociation to O-ethyl phosphonate, the hydrolysis of the ethyl ester bond to form phosphonic acid (attributed to microbiological activity) and ethanol, the latter being either released as CO_2 or incorporated into soil organic matter as bound residues. Fosetyl-Al (and fosetyl) can be classified as non-persistent. The predominant degradate is phosphonic acid.

Phosphonic acid

Aerobic degradation of phosphonic acid was investigated in seven different soils (16–17 weeks in the dark at 20–28 °C). The studies generally reported a steady decline, attributed to soil reactions or to microbial transformation to phosphate. Calculated DT_{50} values ranged from 28–219 days. Phosphonic acid can be classified as moderately persistent to persistent.

Photochemical degradation in soil

Fosetyl-Al

No fosetyl-Al photolysis studies were conducted because of the rapid aerobic soil degradation and the lack of significant light absorption at wavelengths of more than 290 nm.

Phosphonic acid

The photolytic degradation of phosphonic acid in soil was investigated in two studies, involving treated soil surface irradiation for intervals up to 21 days and 45 days. Extractable residues of phosphonic acid decreased slowly over time, this being attributed to reactions with hydroxyl or peroxy radicals formed in irradiated soil components. The lack of significant light absorption at wavelengths of more than 200 nm provides support for this indirect photolytic effect. Residues degraded to about half the initial concentrations after about 21 days in the two studies.

Rotational crops

Fosetyl

In four rotational crop field trials involving total application rates equivalent to 2.3 kg ai fosetyl/ha to lettuce as the primary crop, carrots, lettuce and wheat or barley were planted as rotational crops, at plant-back intervals of 26–46 days. In mature carrot roots and tops, lettuce, wheat/barley forage, fodder and grain, total residues of fosetyl plus phosphonic acid were all below the phosphonic acid LOQs of 0.1 mg/kg (0.5 mg/kg for cereal forage and fodder). The one exception was a phosphonic acid residue of 0.21 mg/kg in one sample of grain.

Based on the results for the combined residues of fosetyl and phosphonic acid in these studies, and on the short soil half-life for fosetyl, residues of fosetyl (and fosetyl-Al) are not expected in rotational crops.

Phosphonic acid

In a rotational crop study involving a total (bare soil) application rate equivalent to 10 kg ai phosphonic acid/ha, residues of phosphonic acid were measured in radish roots and tops, lettuce and barley fodder and grain from crops planted 32 days after treatment and also in radish roots and tops from plants sown 182 days after treatment.

In the 32-day PBI crops, average phosphonic acid residues of 0.58–1.1 mg/kg were found in radish roots and 0.67–1.0 mg/kg in lettuce leaves. Residues below the LOQ of 0.5 mg/kg were detected in the 32-day PBI radish leaves, barley fodder and grain. Only low levels remained in the radish roots and leaves from plants sown 6 months after treatment, (estimated levels of 0.03 mg/kg and 0.09 mg/kg respectively).

Taking into account the results from the rotational crop studies for fosetyl and phosphonic acid, residues of phosphonic acid are not expected in rotational crops at levels above 0.5 mg/kg, especially at PBIs longer than 30 days.

Animal metabolism

Fosetyl-Al

The Meeting received animal metabolism studies on rats and lactating goats where animals were dosed with fosetyl-Al radiolabelled in the 1-C position.

In rats, the metabolism of fosetyl-Al and phosphonic acid was reviewed in the framework of the toxicological evaluation by the current Meeting

Following oral administration to rats, ^{14}C-fosetyl-Al was almost completely absorbed and almost completely eliminated in exhaled air, urine, and faeces within 24 hours. Fosetyl-Al undergoes extensive hydrolysis *in vivo* to give ethanol and phosphonate. The phosphonate is excreted predominately in the urine (equivalent to 73% of the administered compound) together with unchanged material (26–28% of the administered compound).

In a lactating goat study, two animals were orally dosed for 7 days with ^{14}C-fosetyl-Al at doses equivalent to 10.5 ppm in the diet (21 mg/goat/day) with an additional goat being dosed for three days with 10.5 ppm in the diet and used in the CO_2 trapping chamber. All goats were sacrificed 24 hours after the 7th daily dose and various tissue samples were taken for analysis. Average LOQs for the different sample types were 0.0014 mg ai eq/kg in milk and 0.0026 to 0.0032 mg ai eq/kg in all tissues.

About 13% of the total dose was excreted with urine and about 5% in faeces. In expired air, $^{14}CO_2$ was not detected within the first 30 minutes but increased over the 3-day study period to 24% of the daily dose and in total, made up 17.5% of the administered dose.

In milk, residues reached a plateau after 3 days (about 2 mg ai eq/kg–17% AD). In tissues, less than 1.0% of the administered dose was found in liver and kidney, up to 2.2% AD in fat and up to 1% AD in muscle. Highest concentrations of radioactive residues in the two goats were in liver (0.49-0.57 mg ai eq/kg), kidney (0.28–0.32 mg ai eq/kg), and muscle (0.11–0.15 mg ai eq/kg). Radioactive residues in perirenal and omental fat averaged 0.091-0.43 mg ai eq/kg in the two animals.

In a supplementary study, one lactating goat was orally dosed for 7 days with 10 ppm ^{14}C-fosetyl-Al in the diet (20 mg/day). Milk, urine and faeces were collected daily and respired air was collected using a mask covering the goat's mouth and nose, with 3-minute collections taken at 30–60 minute intervals.

In expired air, $^{14}CO_2$ was not detected within the first 30 minutes but reached a maximum about 1.5–2 hours after each dosing and slowly declined to near background within 24 hours, with total residues being about 5.7% of the administered dose

In milk, residues reached a plateau after 3 days (0.27–0.3 mg ai eq/kg) and in total, made up 2% of the administered dose. Milk samples (containing 2.2 mg ai eq/kg fosetyl-Al) were fractionated into casein (milk proteins) and extracted with petroleum ether. Radioactive residues in the petroleum ether fraction were 82% TRR with 10% TRR in the aqueous fraction and 9.3% in the precipitated protein fraction.

In a third study where lactating goats (2) were dosed orally by capsule, morning and evening for 7 consecutive days with ^{14}C-fosetyl-Al at doses equivalent to 27.8 ppm and 30 ppm in the diet, the animals were sacrificed 14–16 hours after the 7th daily dose and various tissue samples were taken for extraction and analysis.

About 11% of the administered dose was excreted in urine and 5.5–8.4% in faeces. In milk, there was a gradual increase of the radioactivity levels, reaching a plateau after 3–4 days, with total residues making up about 14–16% of the total administered dose.

In tissues, radioactive residues were < 5% of the administered dose, measured in liver at about 2.4 mg ai eq/kg) and in kidney at 1.0–1.4 mg ai eq/kg. Radioactive residues in fat were 0.76–1.5 mg ai eq/kg and in muscle were 0.45–0.53 mg ai eq/kg. The total recovery of radioactive residues in expired air (CO_2) during a 10-hour collection starting just after the morning dose on the 6th day was used to calculate a total contribution of 14–15% of the administered dose.

Residues of ^{14}C-fosetyl-Al and ^{14}C-ethanol were only found in the urine and stomach contents. In milk and edible tissues all ^{14}C-residues were characterised as natural products (carbohydrates and carboxylic acids, glycogen, saponifiable fatty acids (about 42% TRR in milk) and lipids, as well as amino acids and peptides).

The proposed fosetyl-Al metabolic pathway in animals involves dissociation and conversion of fosetyl via O-ethyl phosphonic acid to ethanol and phosphonic acid. The ethanol is oxidized to acetic acid, which is then incorporated into natural products or exhaled as CO_2.

Phosphonic acid

No information was available on the metabolism of phosphonic acid in animals, but the Meeting noted that inorganic phosphites are generally considered to be biologically inert in animals and are rapidly excreted. In a rat study using ^{32}P-phosphonate, around 30% of labelled material was excreted in faeces in the form of phosphonate or phosphate. Overall, conversion of phosphonate to phosphate was around 10% of the administered dose.

Methods of analysis

Analytical methods have been reported and validated for the analysis of fosetyl-Al (and fosetyl) and for phosphonic acid in plant and animal commodities. These methods are based on either those involving GC analysis after a derivatisation step (methylation) or those involving LC-MS/MS analysis.

Data generation methods for plant and animal commodities, based on the methylation of fosetyl-Al (and fosetyl) to methyl ethylphosphonate and phosphonic acid to dimethylphosphonate, generally involve extraction with either water, sulphuric acid or HCl/ACN, followed by either centrifugation and filtration or cartridge or column clean-up. Extracts are then diluted with isopropanol and residues are derivatised with diazomethane or TMSD. The methylated residues are then analysed by GC-FPD or GC-NPD with external standards. LOQs for fosetyl-Al range from 0.05–0.5 mg/kg (up to 5.0 mg/kg in hops). The LOQs for phosphonic acid ranged from 0.1–0.5 mg/kg (up to 20 mg/kg in hops).

The more recent LC-MS/MS methods for data generation (plant and animal commodities) also generally involve extraction with either water/ACN, sulphuric acid or HCl/ACN, followed by either centrifugation and filtration or cartridge or column clean-up, with analysis by LC-MS/MS. LOQs for fosetyl-Al were generally 0.01 mg/kg (0.05 mg/kg in pineapple and animal tissues, 1.0 mg/kg in hops). The LOQs for phosphonic acid ranged from 0.01 (milk) to 0.2 mg/kg (0.5 mg/kg in pineapple and up to 20 mg/kg in hops).

In addition to the above LC-MS/MS methods, the multi-residue QuPPe method is suitable for the analysis of fosetyl-Al and phosphonic acid in representative samples with a high water, high oil, high protein, high starch and high acid content. This method involves extraction in acidified methanol, centrifugation and dilution prior to LC-MS/MS analysis. LOQs are 0.01 mg/kg (fosetyl-Al) and 0.1 mg/kg (phosphonic acid).

The Meeting concluded that suitable data generation methods are available to measure fosetyl-Al, fosetyl and phosphonic acid in plant and animal commodities and the QuPPe multi-residue method is suitable for monitoring residues of these analytes in most plant commodities.

Stability of pesticide residues in stored analytical samples

The stability of fosetyl-Al and phosphonic acid residues in frozen stored analytical samples was investigated in a range of plant commodities with high water content, high acid content, high oil content and high starch/protein content.

While fosetyl-Al residues were not stable in high water content and high oil commodities and residue stability was variable in high acid commodities (with residues hydrolysing to phosphonic acid), in the storage stability studies where both fosetyl-Al and phosphonic acid residue degradation was measured, the total residues of fosetyl-Al and phosphonic acid were stable over the storage intervals in the studies (6–25 months for high water content, high starch/protein content, high acid content and 29 months for high oil content.

Definition of the residue

Plant commodities

Plant metabolism and environmental fate studies show that following the use of fosetyl and its aluminium salt (fosetyl-Al), residues are readily and rapidly hydrolysed to phosphonic acid and ethanol in plants and soil. Phosphonic acid is the predominant metabolite, generally making up more than 80% of the total residue, with fosetyl or fosetyl-Al also present in food commodities from treated crops. The ethanol metabolite is either volatilized or degraded and incorporated in natural constituents of plant and animal tissues.

Following the use of phosphonic acid (as the ammonium, potassium, sodium salts), residues are also rapidly absorbed and translocated, accumulating in sink organs.

Although analytical methods are available for measuring fosetyl/fosetyl-Al and phosphonic acid separately, as either the individual compounds or their methylated derivatives, storage stability studies show that in a number of commodities fosetyl/fosetyl-Al can degrade to phosphonic acid in frozen analytical samples.

The Meeting therefore considered that establishing separate residue definitions for fosetyl/fosetyl-Al and phosphonic acid (and it salts) would not be appropriate and agreed to consider a single residue definition based on the combined residues of fosetyl/fosetyl-Al and phosphonic acid, expressed as phosphonic acid.

Phosphonic acid, as the major metabolite of fosetyl-Al, and fosetyl are toxicologically similar to fosetyl-Al and are covered by the ADI for fosetyl-Al.

The proposed residue definition for plant commodities, for both MRL-compliance and for dietary exposure estimation is “Sum of fosetyl, phosphonic acid and their salts, expressed as phosphonic acid”.

Animal commodities

The animal metabolism studies indicate that the behaviour of fosetyl/fosetyl-Al in animals is similar to that in plants, with residues being rapidly metabolised to phosphonic acid and to ethanol which in turn is incorporated into natural products.

For fosetyl-Al, the results of the 7-day goat metabolism study and the 28-day dairy cow and poultry feeding studies show that residues of intact fosetyl-Al or fosetyl are not expected in milk, eggs or any tissues from animals dosed with 10 ppm (dairy cows), 20 ppm (poultry) and 30 ppm (goat) in the diet.

For phosphonic acid, the 28-day dairy cow feeding study indicates that measurable residues can be found in kidney (0.55 mg/kg) and detectable residues could be expected in fat and liver (about 0.2 mg/kg) and also in muscle (0.02 mg/kg) following dosing with 94 ppm in the diet. Residues were not detected in milk or in eggs and poultry tissues from hens exposed to 265 ppm phosphonic acid in the diet.

Based on the above, the Meeting considered that only phosphonic acid residues could be expected in tissues, milk or eggs from animals exposed to feed commodities from crops treated with fosetyl/fosetyl-Al or phosphonic acid or its salts.

The proposed residue definition for animal commodities is “phosphonic acid and its salts, expressed as phosphonic acid’, for both MRL-compliance and for dietary exposure estimation.

The Meeting noted that multi-residue methods exists to measure fosetyl-Al, fosetyl and phosphonic acid residues in plant and animal commodities and based on the chemical properties of phosphonic acid the Meeting concluded that the residue is not fat soluble.

Proposed definition of the residue for compliance with the MRL and for estimation of dietary exposure for plant commodities: *“Sum of fosetyl, phosphonic acid and their salts, expressed as phosphonic acid”*

Proposed definition of the residue for compliance with the MRL and for estimation of dietary exposure for animal commodities: *“Phosphonic acid”*

The residue is not fat-soluble.

Results of supervised residue trials on crops

The Meeting received GAP information and supporting residue information for fosetyl-Al on citrus, pome fruit, grapes, strawberries, avocado, pineapple, cucurbits, other fruiting vegetables, leafy vegetables and hops; for fosetyl on tomatoes, peppers and spinach and for phosphonic acid on citrus, grapes and tree nuts.

In this Appraisal, the term ‘total residues’ is used to describe the sum of the phosphonic acid residues and the fosetyl/fosetyl-Al residues (expressed as phosphonic acid) and the Meeting agreed to use the following formulae to calculate these total residues:

Fosety-Al

$$\text{Total residue [mg/kg]} = \frac{\text{fosetyl-Al [mg/kg]} \times \text{MW}_{\text{phosphonic acid}} \text{ x } 3}{\text{MW}_{\text{fosetyl-Al}}} + \text{phosphonic acid [mg/kg]}$$

Fosetyl

$$\text{Total residue [mg/kg]} = \frac{\text{fosetyl [mg/kg]} \times \text{MW}_{\text{phosphonic acid}}}{\text{MW}_{\text{fosetyl}}} + \text{phosphonic acid [mg/kg]}$$

$\text{MW}_{\text{fosetyl-Al}}$: Molecular weight of fosetyl-Al = 354.1 g/mol
$\text{MW}_{\text{phosphonic acid}}$: Molecular weight of phosphonic acid = 82 g/mol
$\text{MW}_{\text{fosetyl}}$: Molecular weight of fosetyl = 110 g/mol

Conversion factors are 0.695 (fosetyl-Al to phosphonic acid) and 0.745 (fosetyl to phosphonic acid).

In many trials, residues of phosphonic acid (and to a lesser extent fosetyl and fosetyl-Al) were measured in control samples. The Meeting agreed that where these residues were less than 20% of the concentrations reported in the treated samples, the values could be used for maximum residue level estimation.

Supervised residue trials from USA on citrus, pome fruit, grapes, strawberries, avocados, cucumber, summer squash, melons, tomatoes, lettuce, spinach and hops were provided to the Meeting. However, since these trials only reported residues of fosetyl-Al but not phosphonic acid, the Meeting was not able to use these data.

Citrus fruits

Mandarin - Fosetyl-Al

The GAP for fosetyl-Al on citrus in USA is for up to 4 foliar sprays of up to 4.48 kg ai/ha, with a PHI of 12 hours.

In trials conducted in Europe on mandarin, matching the GAP in USA but with a higher application rate of 7 kg ai/ha, total residues were (n=9): 7.8, 14, 21, 21, 21, 23, 28, 39 and 39 mg/kg.

When scaled to the USA GAP application rate (4.48/7.0), total residues are (n=9): 5.0, 9.0, 13, 13, 13, 15, 18, 25 and 25 mg/kg.

The Meeting estimated an STMR of 13 mg/kg and a maximum residue level of 50 mg/kg for the sub-group of mandarins

Orange - Fosetyl-Al

In trials in conducted in Europe on orange, matching the GAP in USA for citrus (4 foliar sprays of 4.48 kg ai/ha, PHI of 12 hours) but with a higher application rate of 7 kg ai/ha, total residues were: 5.6, 6.7, 6.9, 6.9, 7.5, 7.8, 8.9, 10 and 14 mg/kg.

When scaled to the USA GAP application rate (4.48/7.0), total residues are (n=9): 3.6, 4.3, 4.4, 4.4, 4.8, 5.0, 5.7, 6.4 and 9.0 mg/kg.

The Meeting estimated an STMR of 4.8 mg/kg and a maximum residue level of 20 mg/kg for the sub-group of oranges

Citrus fruit - Phosphonic acid

In USA, the post-harvest GAP for phosphonic acid on citrus is as a dip, drench or an in-line spray of 1.8 kg ai/hL. No trials matching this GAP were available and although trials involving application rates of 0.6 kg ai/hL were available, the Meeting noted that the proportionality approach was not yet validated for post-harvest treatments.

GAP in the USA for foliar applications is 6.76 kg ai/ha, usually applied in March/April, May/June and September/October, with an application made 2-4 weeks before harvest for post-harvest mould suppression, but with no defined PHI. No trials matching this GAP were available.

Pome fruits

Apples, pears - Fosetyl-Al

GAP for fosetyl-Al on apples and pears in Greece is for up to 4 foliar sprays of 0.2 kg ai/hL, up to 4.0 kg ai/ha, 3-day PHI. No supervised field trials were available matching this GAP.

The critical GAP in France for fosetyl-Al on pome fruit is 3 foliar applications of 3.0 kg ai/ha, 28-day PHI. In European trials matching this GAP, total residues in apples were (n=7): 7.6, 8.2, 11, 12, 16, 17, and 22 mg/kg and in pears, were (n=8): 12, 13, 14, 15, 15, 15, 17 and 17 mg/kg

Since the Mann-Whitney test indicated that the data sets for apples and pears were not statistically different, the Meeting agreed to combine them to estimate a group maximum residue level for pome fruit. The combined data set is (n=15): 7.6, 8.2, 11, 12, 12, 13, 14, 15, 15, 15, 16, 17, 17, 17 and 22 mg/kg.

The Meeting estimated an STMR of 15 mg/kg and a maximum residue level of 50 mg/kg for pome fruit.

Berries and small fruit

Grapes - Fosetyl-Al

GAP for fosetyl-Al on grapes in Denmark is for up to 6 foliar sprays of 0.2 kg ai/hL, 35-day PHI and the GAP in Greece is for up to 4 foliar applications of 0.2 kg ai/hL, 3.6 kg ai/ha, 14-day PHI. No supervised field trials were available matching these GAPs.

GAP for fosetyl-Al on grapes in Brazil is up to 3 foliar applications of 0.2 kg ai/hL, 15-day PHI. In Brazilian trials matching this GAP, total residues were: 17, 41 and 56 mg/kg.

The critical GAP in the Czech Republic for fosetyl-Al on grapes is for up to 3 foliar applications of 2.0 kg ai/ha, 21-day PHI. In European trials matching this GAP, total residues were (n=22): 4.7, 8.0, 10, 11, 12, 12, 12, 13, 14, 14, 15, 16, 19, 20, 24, 24, 27, 28, 32, 32, 37, 40 mg/kg.

The Meeting estimated an STMR of 15.5 mg/kg and a maximum residue level of 60 mg/kg for grapes.

Grapes - Phosphonic acid

GAP for phosphonic acid on grapes in Australia is 2.4 kg ai/ha, with no reference to a maximum number of applications or to a PHI.

In the residue trials from Australia, treatments ranged from 1–6 applications of 1.0–3.0 kg ai/ha, with intervals to harvest ranging from 5 days to about 18 weeks. In trials involving 4 applications of 2.4 kg ai/ha, phosphonic acid residues in grapes sampled 5–8 days after the last treatment were: 47, 67, 67 and 102 mg/kg. The Meeting agreed that these data were not sufficient to estimate a maximum residue level for phosphonic acid on grapes.

Strawberries - Fosetyl-Al

GAP for fosetyl-Al on strawberries in France is up to 3 foliar applications of 4.0 kg ai/ha, 14-day PHI. In European indoor strawberry trials matching this GAP, total residues were: 9.5, 9.5, 10, 10, 11, 18, 26, 34 mg/kg.

In European outdoor strawberry trials matching the GAP in France, total residues were: 4.3, 5.1, 6.7, 11, 11, 24, 36, 44 mg/kg

Since the Mann-Whitney test indicated that the data sets for indoor and outdoor strawberries were not statistically different, the Meeting agreed to combine these data sets to estimate a maximum residue level. The combined data set is (n=16): 4.3, 5.1, 6.7, 9.5, 9.5, 10, 10, <u>11, 11</u>, 11, 18, 24, 26, 34, 36, 44 mg/kg

The Meeting estimated an STMR of 11 mg/kg and a maximum residue level of 70 mg/kg for strawberries.

Assorted tropical and subtropical fruit – inedible peel

Avocado – fosetyl-Al

GAP for fosetyl-Al on avocados in Spain is for up to 3 foliar applications of 0.24 kg ai/hL, 14-day PHI and 5 trials conducted in Spain were available.

In one trial matching the GAP in Spain, total residues in whole fruit were 3.2 mg/kg and in flesh were 3.4 mg/kg

In three trials matching the GAP in Spain but with higher application rates of 0.31–0.34 kg ai/hL, total residues in whole fruit were 3.5, 3.8 and 4.8 mg/kg and in flesh were 2.8, 4.0 and 7.8 mg ai/kg.

In one trial matching the GAP in Spain but with a higher application rate of 0.46 kg ai/ha, total residues in whole fruit were 20 mg/kg and in flesh were 35 mg/kg

When proportionally adjusted to match the GAP in Spain, scaled total residues in whole fruit are (n=5): 2.7, 2.7, 3.2, 3.4 and 10 mg/kg and in flesh, are (n=5): 2.0, 2.8, <u>3.4</u>, 6.0 and 18 mg/kg in flesh.

The Meeting estimated an STMR of 3.4 mg/kg (in flesh) and a maximum residue level of 20 mg/kg for avocado.

Pineapple – fosetyl-Al

GAP for pineapples in USA is for a pre-plant dip (0.24 kg ai/hL) followed by up to 6 foliar applications of 0.36 kg ai/hL, 90-day PHI. In trials conducted in USA matching this GAP but with lower foliar application rates of 0.24 kg ai/hL, total residues were: 1.0, 3.1 and 8.2 mg/kg

When proportionally adjusted to match the USA GAP foliar application rate, scaled total residues are: 1.5, 4.7 and 12 mg/kg.

GAP for pineapples in Brazil is for a pre-plant dip (0.08 kg ai/hL) and up to 3 foliar applications of 0.2 kg ai/hL, 20-day PHI. No trials matching this GAP were available.

The Meeting concluded there were insufficient data to estimate a maximum residue level for pineapple.

Fruiting vegetables, Cucurbits

Cucumber – fosetyl-Al

The GAP for cucumbers in Greece is for up to 4 foliar applications of 4.8 kg ai/ha, 1-day PHI. In protected cucumber trials conducted in Europe matching this GAP, total residues were (n=7): 6.8, 11, 13, 14, 14, 21 and 38 mg/kg.

The Meeting estimated an STMR of 14 mg/kg and a maximum residue level of 60 mg/kg for cucumber.

Summer Squash – fosetyl-Al

The GAP for summer squash in Greece is for up to 4 foliar applications of 4.8 kg ai/ha, 3-day PHI. In summer squash trials conducted in Europe matching this GAP but involving lower application rates (3.2 kg ai/ha), residues were: 8.1, 11, 16, 18, 19 and 19 mg/kg.

When proportionally adjusted to match the GAP in Greece, scaled residues (4.8/3.2) are (n=6): 12, 17, 24, 27, 29 and 29 mg/kg.

The Meeting estimated an STMR of 25.5 mg/kg and a maximum residue level of 70 mg/kg for summer squash.

Melons – fosetyl-Al

The GAP for melons in Greece is for up to 4 foliar applications of 4.8 kg ai/ha, 3-day PHI. No supervised field trials were available matching this GAP.

The GAP for melons in France is for up to 2 foliar applications of 3.2 kg ai/ha, 3-day PHI. In protected melon trials conducted in Europe matching this GAP, total residues in whole fruit were (n=8): 5.8, 12, 14, 14, 17, 19, 21 and 28 mg/kg and in flesh, were (n=8): 11, 12, 14, 14, 18, 18, 19 and 21 mg/kg.

In outdoor melon trials conducted in Europe matching the GAP in France, total residues in whole fruit were (n=6): 12, 12, 20, 22, 25 and 29 mg/kg and in flesh, were (n=6): 9.2, 9.7, 12, 14, 16 and 24 mg/kg.

Since the Mann-Whitney test indicated that the data sets for indoor and outdoor melons were not statistically different, the Meeting agreed to combine these data sets to estimate a maximum residue level. For whole fruit, the combined data set is (n=14): 5.8, 12, 12, 12, 14, 14, 17, 19, 20, 21, 22, 25, 28 and 29 mg/kg. For flesh, the combined data set is (n=14): 9.2, 9.7, 11, 12, 12, 14, 14, 14, 16, 18, 18, 19, 21 and 24 mg/kg

The Meeting estimated an STMR of 14 mg/kg (in flesh) and a maximum residue level of 60 mg/kg for melons (except water melon).

Fruiting vegetables, other than Cucurbits

Peppers – fosetyl

The GAP for outdoor sweet peppers in France is for up to 2 seedling drench treatments prior to planting out, the first at the equivalent of 18.6 kg ai/ha and the second equivalent to 9.3 kg ai/ha, with these being followed by up to 2 drip irrigation treatments of 0.93 kg ai/ha, 3-day PHI. In outdoor sweet pepper trials conducted in Europe matching this GAP, total residues were (n=9): < 0.21 (4), 0.21, 0.21, 0.29, 0.72 and 0.75 mg/kg.

The GAP for indoor peppers in Hungary is for up to 2 seedling drench treatments prior to planting out, the first at the equivalent of 18.6 kg ai/ha and the second equivalent to 9.3 kg ai/ha, with these being followed by up to 4 drip irrigation treatments of 0.93 kg ai/ha, 3-day PHI. In indoor sweet pepper trials conducted in Europe matching this GAP, total residues were (n=9): < 0.21, 0.21, 0.22, 0.31, 0.36, 0.54, 2.4, 3.1 and 3.5 mg/kg.

Based on the data supporting the GAP for indoor peppers, the Meeting estimated an STMR of 0.36 mg/kg and a maximum residue level of 7 mg/kg for peppers, sweet.

Tomato - fosetyl

The GAP for outdoor tomatoes in France is for up to 2 seedling drench treatments (equivalent to 9.3 kg ai/ha) prior to planting out, followed by up to 2 drip irrigation treatments of 0.93 kg ai/ha, 3-day PHI. In outdoor tomato trials conducted in Europe matching this GAP, total residues were: < 0.21 (10), 0.27, 0.44, 0.51, 1.0 and 1.0 mg/kg.

The GAP for indoor tomatoes in Hungary is for up to 2 seedling drench treatments (equivalent to 9.3 kg ai/ha) prior to planting out, followed followed by up to 4 drip irrigation treatments of 0.93 kg ai/ha, 3-day PHI. In indoor tomato trials conducted in Europe matching this GAP, total residues were (n=8): 0.21, 0.24, < 0.34, 0.34, 0.34, 0.36, 0.47 and 5.2 mg/kg.

Based on the data supporting the GAP for indoor tomatoes, the Meeting estimated an STMR of 0.34 mg/kg and a maximum residue level of 8 mg/kg for tomato.

Leafy vegetables

Lettuce – fosetyl-Al

The GAP for lettuce in Finland is for foliar applications of 2.4 kg ai/ha, 14-day PHI.

In indoor leaf lettuce trials conducted in Europe matching this GAP, with 4 applications of fosetyl-Al, total residues were (n=8): 7.7, 7.8, 9.2, 13, 15, 17, 27 and 31 mg/kg.

In outdoor leaf lettuce trials conducted in Europe matching this GAP, with 4 applications of fosetyl-Al, total residues were (n=10): 4.8, 6.9, 7.1, 8.1, 8.2, 8.5, 9.0, 15, 15 and 16 mg/kg.

Since the Mann-Whitney test indicated that the data sets for indoor and outdoor leaf lettuce were not statistically different, the Meeting agreed to combine these data sets to estimate a maximum residue level. For leaf lettuce, the combined data set is (n=18): 4.8, 6.9, 7.1, 7.7, 7.8, 8.1, 8.2, 8.5, 9.0, 9.2, 13, 15, 15, 15, 16, 17, 27 and 31 mg/kg.

The Meeting estimated an STMR of 9.1 mg/kg and a maximum residue level of 40 mg/kg for leaf lettuce.

In indoor head lettuce trials conducted in Europe matching the GAP for lettuce in Finland (2.4 kg ai/ha, PHI of 14 days), with 4 applications of fosetyl-Al, total residues were (n=7): 12, 19, 36, 41, 57, 66 and 120 mg/kg.

Based on the data supporting the GAP for indoor head lettuce, the Meeting estimated an STMR of 41 mg/kg and a maximum residue level of 200 mg/kg for lettuce.

Spinach - fosetyl

The critical GAP for fosetyl on spinach in Belgium is on outdoor crops, one foliar application of 0.775 kg ai/ha, with a 14-day PHI on outdoor crops. In outdoor spinach trials conducted in Europe matching this GAP, total residues were (n=8): 0.53, 0.79, 2.4, 4.0, 4.2, 5.3, 6.5, 11 mg/kg.

The Meeting estimated an STMR of 4.1 mg/kg and a maximum residue level of 20 mg/kg for spinach.

Tree nuts

Almond, pistachio, walnut – phosphonic acid

The GAP for tree nuts in USA is for up to 6 foliar applications of 1.9 kg ai/ha, with no specified PHI.

In trials conducted in USA and matching this GAP (with PHI of 1-4 days), phosphonic acid residues in almond nutmeat were (n=5): < 0.5, < 0.5, 0.51, 5.6 and 100 mg/kg, in pistachio nutmeat, residues were (n=5) 1.8, 65, 167, 169 and 197 mg/kg and in walnut nutmeat, were (n=5): 3.8, 38, 54, 67 and 172 mg/kg.

Since the Kruskall-Wallis test indicated that the data sets for almonds, pistachios and walnuts were not statistically different, the Meeting agreed to combine these data sets to estimate a maximum residue level for tree nuts. The combined data set is (n=15): < 0.5, < 0.5, 0.51, 1.8, 3.8, 5.6, 38, 54, 65, 67, 100, 167, 169, 172 and 197 mg/kg.

The Meeting estimated an STMR of 54 mg/kg and a maximum residue level of 400 mg/kg for tree nuts.

Dried herbs

Hops (dry) – fosetyl-Al

The GAP for fosetyl-Al in Germany is for up to 8 foliar applications of 8.0 kg ai/ha, 14-day PHI. In trials conducted in Europe matching this GAP, total residues in dried cones were (n=6): 309, 322, 325, 376, 404 and 660 mg/kg.

The Meeting estimated an STMR of 350 mg/kg and a maximum residue level of 1500 mg/kg for hops (dry).

Fate of residues during processing

Both fosetyl-Al and phosphonic acid are stable to hydrolysis under conditions simulating pasteurisation, baking, brewing, boiling and sterilization.

The fate of fosetyl-Al, fosetyl and phosphonic acid residues has been examined in a number of studies simulating household processing involving peeling (citrus, avocado, pineapple and melon), washing (lettuce), cooking (spinach, green beans) and commercial processing of oranges, apples, grapes, strawberries, tomatoes, peppers, lettuce, spinach, beans and hops.

Following the use of fosetyl/fosetyl-Al, total residues increased in tomato puree and in grape pomace and dry citrus pomace. Following the use of phosphonic acid, residues increased in wine and citrus pomace.

For the commodities considered at the Meeting, estimated processing factors and STMR-Ps for their processed food or feed commodities are summarised below.

RAC [STMR]	Matrix	Calculated processing factors	PF (median or best fit)	STMR-P (mg/kg)
Fosetyl-Al[a]				
Orange [4.8 mg/kg]	juice	0.35, 0.57, 0.94, 1.1, 1.4	0.94	4.5
	pomace (dry)	0.45, 0.77, 3.4, 3.9, 4.6	3.4	16
Apple [15 mg/kg]	juice	0.63, 1.2	0.92	14
	wet pomace	0.49, 1.6	1.0	15
	puree	0.44, 0.71, 1.1	0.71	11
Grapes [15.5 mg/kg]	juice	0.5, 0.69, 0.94, 0.96, 1.1, 1.2, 1.2	0.96	15
	must	0.06, 0.17, 0.34, 0.39, 0.59, 0.62, 0.77, 0.84, 1.4	0.59	9.1
	wet pomace	0.59, 1.3, 1.4, 2.4	1.4	22
	wine	0.11, 0.35, 0.43, 0.51, 0.52, 0.55, 0.63, 0.64,0.7, 0.77, 0.84, 1.1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.8, 2.4	0.77	12
Strawberry [11 mg/kg]	washed	0.89, 1.0	0.95	11
	jam	0.52, 0.5	0.51	5.6
	canned	0.62, 0.4	0.51	5.6
Hops [350 mg/kg]	Beer	0.0022, 0.0031, 0.0045, 0.0048, 0.0049, 0.0055, 0.0055, 0.0064, 0.018	0.0049	1.7
Fosetyl[a]				

RAC [STMR]	Matrix	Calculated processing factors	PF (median or best fit)	STMR-P (mg/kg)
Tomato [0.34 mg/kg]	washed	0.75, 1.0	0.88	0.3
	juice	0.75, 0.83	0.79	0.27
	puree	1.3, 1.5	1.4	0.48
	preserve	0.87, 0.91	0.89	0.3
	wet pomace	1.1, 1.1	1.1	0.37
Spinach [4.1 mg/kg]	washed	0.73, 0.86, 1.2, 1.2	1.0	4.1
	cooked	0.66, 0.91, 0.95, 1.0	0.93	3.8

[a] The processing factor is the ratio of total residues in the processed item divided by the total residue in the RAC.

Residues in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of fosetyl, phosphonic acid and their salts (expressed as phosphonic acid) in farm animals on the basis of the diets (US/CAN, EU, Australia and Japan) listed in OECD Feed Table 2013.

	Animal dietary burden, ppm of dry matter diet							
	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	1.8	1.8	7.5	7.5	31[a]	31[c]	-	-
Dairy cattle	3.8	3.8	5.5	5.5	31[b]	31[d]	-	-
Poultry – broiler	-	-	-	-	-	-	-	-
Poultry – layer	-	-	-	-	-	-	-	-

[a] Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian tissues

[b] Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk

[c] Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian tissues.

[d] Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

Farm animal feeding studies

Lactating dairy cows – fosetyl-Al + phosphonic acid

In a lactating dairy cow feeding study, groups of 3 cows were dosed orally twice a day (after each milking) for 28 days with a 1:10 mixture of fosetyl-Al and disodium phosphonate (in gelatine capsules) at rates equivalent to 11 ppm, 32 ppm and 100 ppm phosphonic acid equivalents respectively.

No intact fosetyl-Al or fosetyl residues were detected in any of the tissues or milk analysed except in one sample of liver from the 32 ppm dose group, where a residue of 0.081 mg/kg (<LOQ) was detected. Phosphonic acid residues were detected at all three dose levels, estimated at up to 0.16 mg/kg in liver, 0.2 mg/kg in fat, 0.06 mg/kg in milk in the 100 ppm dose group and 0.02–0.09 mg/kg in muscle. Highest residues were in kidney (up to 0.6 mg/kg), reflecting the urinary route of elimination. In the 32 ppm dose group, estimated mean total residues were 0.29 mg/kg (kidney), 0.22 mg/kg (liver), 0.12 mg/kg (fat), 0.07 mg/kg (muscle) and 0.05 mg/kg in milk, with maximum residues in individual animals being 0.3 mg/kg (kidney), 0.33 mg/kg (liver), 0.18 mg/kg (fat) and 0.086 mg/kg (muscle).

Poultry – fosetyl-Al + phosphonic acid

In a poultry feeding study, three groups of ten hens were dosed for 28 days with a 1:9 mixture of fosetyl-Al:disodium phosphonate incorporated into their diet. Dose rates were equivalent 14 ppm, 42 ppm and 142 ppm phosphonic acid equivalents.

All eggs were collected and pooled to obtain a single sample from each dose group and pooled eggs from each dose group were also sampled at intervals throughout the dosing period. On day 28 the hens were sacrificed and breast and thigh muscle, liver and abdominal fat were sampled and stored frozen for less than 28 days before analysis.

No residues of either intact fosetyl-Al, intact fosetyl or phosphonic acid were detected in any tissue samples with trace levels of phosphonic acid (estimated at up to 0.2 mg/kg phosphonic acid) found in eggs from some hens in all dose groups.

Animal commodity maximum residue levels

Cattle

The Meeting noted that the maximum and mean cattle dietary burden of 31 ppm was approximately the same as the 32 ppm dose group in the second dairy cow feeding study where mean estimated phosphonic acid equivalent residues were 0.29 mg/kg (kidney), 0.22 mg/kg (liver), 0.12 mg/kg (fat), 0.07 mg/kg (muscle) and 0.05 mg/kg in milk.

The Meeting estimated maximum residue levels of 0.15 mg/kg for meat (from mammals other than marine mammals), 0.5 mg/kg for edible offal (mammalian) and 0.2 mg/kg for mammalian fat and a maximum residue level of 0.1 mg/kg for milks.

Estimated STMRs are 0.29 mg/kg (kidney), 0.22 mg/kg (liver), 0.12 mg/kg (fat), 0.07 mg/kg (muscle) and 0.05 mg/kg for milks.

Poultry

As there were no poultry feed commodities from the treated crops, the Meeting agreed not to estimate maximum residue levels for poultry commodities.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue (for compliance with the MRL and for the estimation of dietary exposure) for plant commodities: *Sum of fosetyl, phosphonic acid and their salts, expressed as phosphonic acid*.

Definition of the residue (for compliance with the MRL and for the estimation of dietary exposure) for animal commodities: *Phosphonic acid*.

The residue is not fat soluble.

2010	Commodity	MRL	mg/kg	STMR or	HR or	Source
CCN	Name	New	Prev	STMR-P	HR-P	
FI 0236	Avocado	20		3.4		Fosetyl-Al
VC 0424	Cucumber	60		14		Fosetyl-Al
MM 0105	Edible offal (mammalian)	0.5		kidney: 0.29 liver: 0.22		
FB 0269	Grapes	60		15.5		Fosetyl-Al
FP 0009	Group of Pome fruits	50		15		Fosetyl-Al
DH 1100	Hops (dry)	1500		350		Fosetyl-Al

2010	Commodity	MRL	mg/kg	STMR or	HR or	Source
CCN	Name	New	Prev	STMR-P	HR-P	
VL 0482	Lettuce, Head	200		41		Fosetyl-Al
VL 0483	Lettuce, Leaf	40		9.1		Fosetyl-Al
MF 0100	Mammalian fat (except milk fats)	0.2		0.12		
MM 0095	Meat (from mammals other than marine mammals)	0.15		fat: 0.12 muscle: 0.07		
VC 0046	Melon (except water melon)	60		14		Fosetyl-Al
MM 0106	Milks	0.1		0.05		
VO 0445	Peppers, Sweet	7		0.36		Fosetyl
VL 0502	Spinach	20		4.1		Fosetyl
FB 0275	Strawberries	70		11		Fosetyl-Al
FC 003	Subgroup of Mandarins	50		13		Fosetyl-Al
FC 0004	Subgroup of Oranges, Sweet, Sour	20		4.8		Fosetyl-Al
VC 0431	Summer squash	70		25.5		Fosetyl-Al
VO 0448	Tomato	8		0.34		Fosetyl
TN 0085	Tree nuts	400		54		Phos Acid
JF 0226	Apple juice			14		Fosetyl-Al
AB 1230	Apple pomace (wet)			15		Fosetyl-Al
	Apple puree (sauce)			11		Fosetyl-Al
	Beer (hops)			1.7		Fosetyl-Al
	Canned strawberries			5.6		Fosetyl-Al
	Cooked spinach			3.8		Fosetyl
JF 0269	Grape juice			15		Fosetyl-Al
	Grape must			9.1		Fosetyl-Al
	Grape pomace (wet)			22		Fosetyl-Al
JF 0004	Orange juice			4.5		Fosetyl-Al
	Orange pulp (dry)			16		Fosetyl-Al
	Strawberry jam			5.6		Fosetyl-Al
JF 0448	Tomato juice			0.27		Fosetyl
	Tomato pomace (wet)			0.37		Fosetyl
	Tomato preserve			0.3		Fosetyl
	Tomato puree			0.48		Fosetyl
	Wine			12		Fosetyl-Al

DIETARY RISK ASSESSMENT

Long-term exposure

The current Meeting established an ADI of 0–1 mg/kg bw for fosetyl-aluminium and noted that this ADI also applied to phosphonic acid.

The Meeting agreed that the International Estimated Daily Intakes (IEDIs) for fosetyl-aluminium, fosetyl and phosphonic acid could be calculated using STMRs estimated by the current Meeting for the total residues of fosetyl, phosphorous acid and their salts (expressed as phosphonic acid).

The International Estimated Daily Intakes (IEDIs) for fosetyl, phosphorous acid and their salts were calculated for the 17 GEMS/Food cluster diets using STMRs estimated by the current Meeting for raw and processed commodities in combination with consumption data for corresponding food commodities. The results are shown in Annex 3.

The calculated IEDIs were 1–30% of the maximum ADI of 1 mg/kg bw.

The Meeting concluded that the long-term dietary exposure to residues of fosetyl, phosphonic acid and their salts from uses considered by the current Meeting is unlikely to present a public health concern.

Short-term dietary exposure

The 2017 JMPR decided that an ARfD is unnecessary. The Meeting therefore concluded that the short-term dietary exposure of residues of fosetyl, phosphonic acid and their salts is unlikely to present a public health concern.

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