

## PHOSMET (103)

### EXPLANATION

Phosmet has been evaluated at several Joint Meetings between 1976 and 1988 (FAO/WHO 1977, 1979, 1980, 1982, 1985, 1988a,b). Maximum residue limits (MRLs) were recommended for a number of commodities of plant and animal origin

Updated information on GAP and details of supervised trials, processing trials and studies of metabolism and the stability of residues during frozen storage have been made available for evaluation within the CCPR periodic review programme.

No data to support the direct use of phosmet to control ectoparasites on domestic animals have been submitted for review.

### IDENTITY

ISO common name: phosmet

Chemical name:

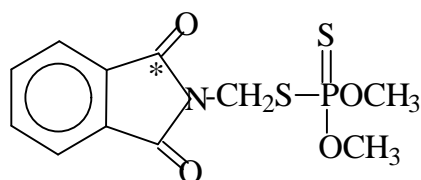
IUPAC: *O,O*-dimethyl *S*-phthalimidomethyl phosphorodithioate,  
*N*-(dimethoxyphosphinothioylthiomethyl)phthalimide

CA: *S*-[1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yl)methyl] *O,O*-dimethyl phosphorodithioate

CAS No.: 732-11-6

Molecular Formula:  $C_{11}H_{12}NO_4PS_2$

Structure:



Synonyms: R-1504, PMP

Trade names: 'Imidan'; 'Prolate'; 'Phthalophos'; 'Kenolate'; 'Appa'

Physical State: Colourless crystalline solid

Melting Point: 72°C

Vapour Pressure:  $4.9 \times 10^7$  mm Hg at 25°C

Log  $P_{ow}$ : 2.95 at 20°C

Formulations: Phosmet is formulated mainly as wettable powders (WP, up to 70%) and emulsion concentrates (EC).

## METABOLISM AND ENVIRONMENTAL FATE

Phosmet labelled at the carbonyl groups of the phthalimide moiety has been used in metabolism and other environmental fate studies. The designation of metabolites and their chemical structural formulae are shown in Table 1.

### Animal metabolism

The absorption, distribution, metabolism and excretion of  $^{14}\text{C}$ ]phosmet has been studied in rats, goats and hens. A study on cows from 1963 was also reported.

Groups of five male and five female rats were given a single oral dose of either 1 or 25 mg [ $^{14}\text{C}$ ]phosmet without prior exposure to the chemical, or 14 daily oral doses of 1 mg unlabelled phosmet/kg followed by a single dose of 1 mg of the labelled compound. Urine and faeces were collected at regular intervals, and selected tissues were collected when the animals were killed at 96 hours after dosing. By 24 hours after dosing, at least 70% of the dose had been excreted with the urine by all dose groups. By 96 hours, the single-dose and the repeated-dose animals had excreted mean urinary levels of 81-89% and 75-77% of the dose respectively. Faecal excretion amounted to 6-13% of the dose. Radioactive residues in tissues accounted for 1.2-2.1% of the dose in all dose groups (Fisher, 1989).

In the early study of Ford *et al.* (1966) in rats, it was observed that <1% of the label in the urine was in the form of phosmet oxon and less than 0.04% of the radioactivity was recovered in the expired air.

Radiolabelled phosmet was administered orally to two lactating goats for four days at dietary equivalent levels of 8.0-8.8 ppm. Radioactive material was quickly absorbed and excreted. Most of each day's dose was recovered in the urine within the following 24 hours. In total, urinary excretion accounted for 60% of the cumulative dose. Less than 6% remained in the edible tissues at slaughter, 13-14 hours after the final dose.

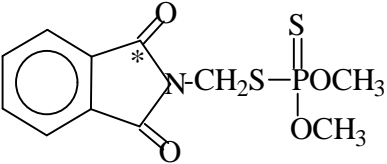
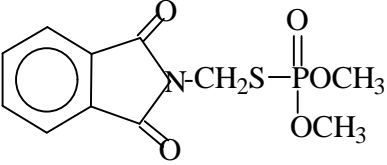
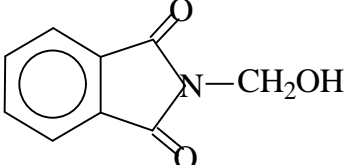
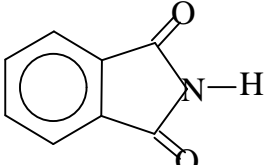
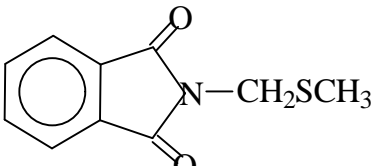
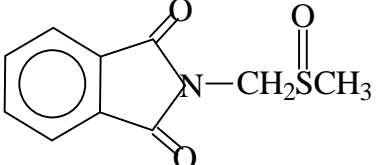
The levels of total radioactive residues (as phosmet equivalents) in the liver, muscle, kidneys, milk and fat ranged from 0.24 mg/kg in kidneys to 0.005-0.007 mg/kg in fat. In milk the highest residue levels were 0.014-0.017 mg/kg, found two to four days after the start of dosing; less than 3% of the  $^{14}\text{C}$  was associated with the fat.

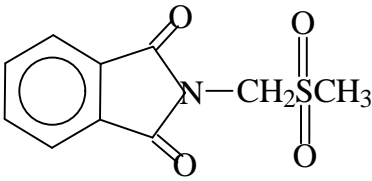
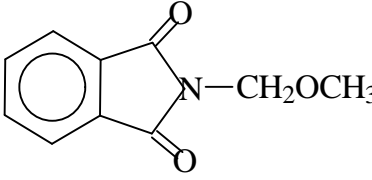
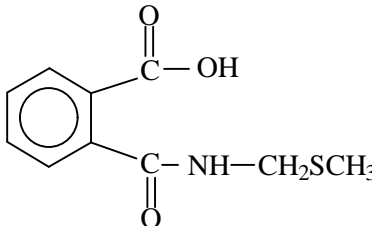
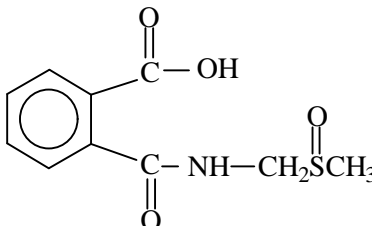
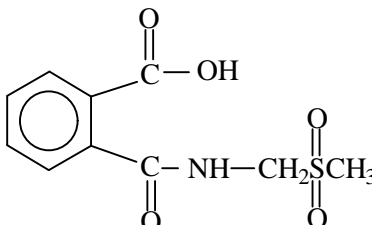
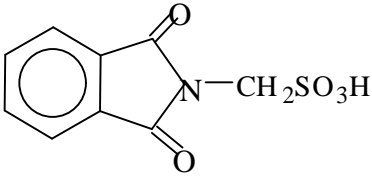
Nine identified metabolites (PiMSM, PiMS(O)M, PiMS(O<sub>2</sub>)M, PaAMS(O)M, PaAMS(O<sub>2</sub>)Me, Pi, PaAMOH, PaA and Pa, see Table 1) and two unidentified metabolites AQ1 (thought to be a derivative of phthalamic acid with an acidic *N*-substituent) and AQ2 were quantitatively determined in all samples, while one metabolite was tentatively identified as PaAMSM in liver samples. Neither phosmet nor phosmet oxon were detected in edible tissues (<0.002-0.003 mg/kg) or milk (<0.0004 mg/kg). Each of the samples contained the same metabolites but the relative amounts varied. The highest concentrations of individual metabolites found in each of the substrates were 0.035-0.036 mg/kg of AQ1 in kidneys, 0.007-0.009 mg/kg of PiMSM in liver, 0.018-0.022 mg/kg of PaAMS(O<sub>2</sub>)M in muscle and 0.004-0.005 mg/kg of PaAMS(O<sub>2</sub>)M in milk. These observations indicate that residues of phosmet are not retained in fat and do not accumulate in tissues or milk.

Bound residues accounted for about 70% of the total residues in liver and muscle, 40% in the kidneys and, associated with milk solids, 8-19% of the total residues in milk. A small proportion of the bound residues was released by mild acid hydrolysis and treatment of extracted samples with hydrazine solubilized more than half of the bound residues. The solubilized products of hydrazinolysis consisted mostly of phthalohydrazide. The results indicate that the bound residues in tissues and milk contain the phthalimide moiety, bound via *N*-substituents, with little or no chemical modification. The nature of the solvent-extractable residues, as well as other known chemical

properties of the metabolites and related compounds, suggested to the author that the residues that remained bound after hydrazinolysis were *N*-substituted derivatives of phthalamic acid.

Table 1 Common designations, chemical names and structural formulae of phosmet and its metabolites.

Common designation	Chemical name	Structure
1. Phosmet	O,O-dimethyl-S-phthalimidomethyl phosphorodithioate (Asterisk shows position of label)	
2. Phosmet oxon	O,O-dimethyl-S-phthalimidomethyl phosphorothioate	
3. PiMOH	N-hydroxymethylphthalimide	
4. Pi	Phthalimide	
5. PiMSM	N-methylthiomethylphthalimide	
6. PiMS(O)M	N-methylsulfinylmethylphthalimide	

Common designation	Chemical name	Structure
7. PiMS(O <sub>2</sub> )M	N-methylsulfonylmethylphthalimide	
8. PiMOM	N-methoxymethylphthalimide	
9. PaAMSM	N-methylthiomethylphthalamic acid	
10. PaAMSO(O)M	N-methylsulfinylmethylphthalamic acid	
11. PaAMS(O <sub>2</sub> )M	N-methylsulfonylmethylphthalamic acid	
12. PiMSO <sub>3</sub> H	N-sulfomethylphthalimide	

Common designation	Chemical name	Structure
13. PaAMSO <sub>3</sub> H	N-sulfomethylphthalamic acid	
14. PaAMOH	N-hydroxymethylphthalamic acid	
15. PaA	Phthalamic acid	
16. Pa	Phthalic acid	
17. 3-OHPA	3-hydroxyphthalic acid	
18. 4-OHPA	4-hydroxyphthalic acid	

Several groups of cows were treated with phosmet either in the diet at 100, 45 or 20 ppm or by spray application at 0.5% or 0.25%. Milk was sampled up to 21 days in the feeding study and 28 days in the spray study. Eleven tissues were analysed from cows slaughtered 1 and 6 days after the last phosmet feeding. The residues in all samples were below the limit of determination (0.05 mg/kg) of the colorimetric (phosphomolybdate) or enzyme-inhibition methods used (Batchelder and Patchett, 1966). Five cows were sprayed with 1 g ai/cow in a more recent supervised trial in The Netherlands. Phosmet residues in milk were 0.012, 0.002, 0.0009 and <0.0005 mg/kg at 0, 12, 24 and 36-72 hours after treatment (Ernst, 1983).

Radiolabelled phosmet was administered orally to laying hens for seven days at a dietary equivalent level of 10.5 ppm. Most of each day's dose was recovered in the excreta within the following 24 hours. In total the excreta accounted for 89.6% of the cumulative dose. Edible tissues collected at slaughter (15-18 hours after the final dose) and eggs accounted for only 0.3% of the cumulative dose.

In egg yolks and whites, the highest levels of  $^{14}\text{C}$  as phosmet equivalents were 0.040 mg/kg on day 7 and 0.007 mg/kg on day 4 respectively. At slaughter the levels of total radioactivity expressed as phosmet were 0.24 mg/kg in liver, 0.21 mg/kg in kidneys, 0.021 mg/kg in breast muscle, 0.015 mg/kg in thigh muscle, 0.005 mg/kg in fat and 0.068 mg/kg in blood.

Phosmet itself was not detected (<0.005 mg/kg) in any of the edible tissues, but 0.001 mg/kg was found in egg yolks. None of the metabolites exceeded 0.005 mg/kg in the edible tissues or eggs, where the identified metabolites were phthalimide and phthalic acid. These compounds are believed to reflect a sequence of hydrolytic degradation steps that can occur without enzymatic catalysis: loss of the phosphorus-containing moiety, hydrolysis of the phthalimide to yield phthalamic acid, and hydrolysis of the phthalamic acid to phthalic acid.

Hydrolysis of phosmet to *N*-mercaptomethylphthalimide may occur in tissues. An oxidation product of this compound, *N*-sulfomethylphthalamide (phthalimidomethylsulfonic acid), was identified in excreta but not in tissues.

Proposed metabolic pathways of phosmet in goats are shown in Figure 1 (Tarr, 1993a).



Extraction of tissues and egg yolks recovered only 30-50% of the total  $^{14}\text{C}$  in the samples. Unextractable  $^{14}\text{C}$  residues, which appear to be covalently bound, were solubilized to a small extent by mild acid hydrolysis. Treatment of extracted samples with hydrazine solubilized approximately a third to half of the bound  $^{14}\text{C}$ . The soluble products of hydrazinolysis consisted mainly of phthalohydrazide. Bound  $^{14}\text{C}$  residues therefore contain the *N*-substituted phthalimide moiety of phosmet, with little or no chemical modification. In liver, a substantial proportion of the extractable  $^{14}\text{C}$  was associated with material that was precipitated upon concentration. This fraction, perhaps bound to soluble proteins, did not react with hydrazine. According to the author, the nature of the characterized residues, as well as the known chemical properties of the metabolites and related compounds, suggested that the  $^{14}\text{C}$  residues that remained bound after hydrazinolysis were derivatives of phthalamic acid. The author believed that bound  $^{14}\text{C}$  residues were probably cleared from the tissues by hydrolysis to phthalic acid (Tarr, 1993b).

Although the rat liver microsomal NADPH<sub>2</sub> enzyme system readily converts phosmet to phosmet oxon (McBain *et al.*, 1968), neither phosmet nor its oxon could be detected in the tissues of goats or hens (Tarr, 1993a,b).

### Plant metabolism

Reports of studies on the metabolism of phosmet in sour cherries (Barnes and Goldsby, 1989), corn (Toia *et al.*, 1993b) and potatoes (Toia *et al.*, 1993c) were submitted for evaluation.

[ $^{14}\text{C}$ ]phosmet was applied to sour cherry trees in a greenhouse to determine the metabolic fate of phosmet in a representative orchard crop. A single high rate of application of 4.2 kg/1000 litres (equivalent to 13.7 kg/ha) was used for the study. Fruit samples were taken at 4 hours and 7 and 14 days after treatment.

Phosmet was absorbed rapidly (44% in 4 hours) to the interior of the fruit where most of the metabolism took place. While the parent compound was the major residue on the surface of the fruit (39.1 and 48.4% of the total radioactivity at 7 and 14 days respectively), as many as 16 or 17 different metabolites were found in the pulp.

Phthalic acid was the major metabolite identified and accounted for 17 to 21% of the total radioactivity. Several other metabolites accounting for a small fraction of the radioactivity were identified, including phosmet oxon, phthalimide, *N*-hydroxyphthalimide, phthalic anhydride, *N*-hydroxymethylphthalimide and derivatives of phthalamic acid. However conjugates dominated the metabolic picture. The key conjugate identified was *N*-glucosylphthalimide. Structures of three additional unknowns could be derived from this through either enzymatic hydrolysis or chemical breakdown.

The conjugates and some other metabolites were readily converted to phthalic acid (Pa) by acid hydrolysis. Pa accounted for 85-90% of the extractable radioactivity after hydrolysis. No benzoic acid or ring-hydroxylated products were detected.

Proposed pathways of metabolism in cherries are shown in Figure 2.

Maize plants were grown singly in pots in an outdoor screened location in California and sprayed with carbonyl-labelled phosmet in 50% aqueous acetone containing 0.5% Tween 20. Four plants were treated with 1 kg [ $^{14}\text{C}$ ]phosmet/ha at the onset of silk formation and one plant was harvested at the forage stage. The remaining three plants were treated with a further 1.12 kg [ $^{14}\text{C}$ ]phosmet/ha 14 days before harvest and grown to maturity. During the latter stages, these plants were protected from adverse weather conditions.



At maturity, the fodder, cobs and grain were collected and analysed separately. Two untreated plants served as controls.

The distribution of the total  $^{14}\text{C}$  expressed as phosmet in the plant fractions was as follows.

Forage (whole plant): 31 mg/kg  
 Fodder (husks, leaves and stalks): 267 mg/kg  
 Cobs: 5 mg/kg  
 Grain: 3 mg/kg

More than 95% of the radiocarbon was extractable from all four fractions. HPLC and TLC analyses of the extracts indicated a large number of metabolites, all more polar than phosmet, and a similar pattern of metabolites in all fractions. Details of the compounds found in the mature fodder and grain are given in Table 2 and a proposed scheme for the metabolism of phosmet in maize is shown in Figure 3.

Table 2. Radioactive compounds found in mature maize, fodder and grain from plants treated with  $^{14}\text{C}$  phosmet.

Compound	% of TRR	
	Fodder	Grain
Phosmet	53	0
Phosmet oxon	1.2	0
Phthalic acid (Pa)	5.5	61
PaAMOH	6.8	*
PaAMSM	0.56	*
PaAMSO <sub>3</sub> H	0.71	*
Phthalimide (Pi)	3.9	*
PiMOM	3.6	*
PiMSO <sub>2</sub> M	0.54	8
Unknowns	16.3 <sup>1</sup>	32.7 <sup>1</sup>
Unextracted (mainly hydrolysed to phthalates)	3.2	1.2

TRR = Total radioactive residue

<sup>1</sup>Not observed

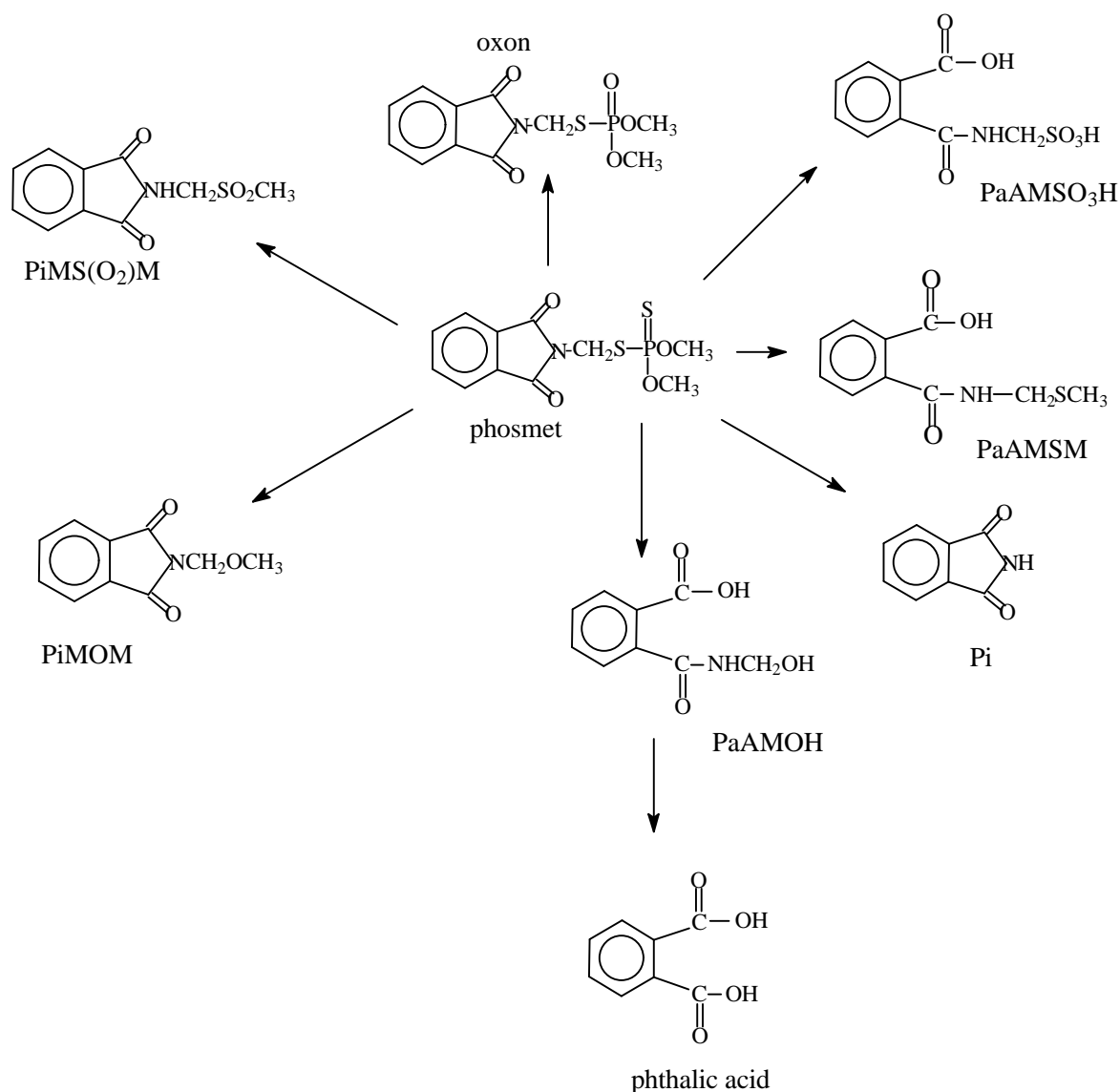
<sup>2</sup>At least 15 separate compounds (the highest 2.7% in fodder and 13.4% in grain, mainly converted to phthalic acid on acid hydrolysis)

Only traces (approximately 1% of the TRR) of phosmet oxon were found in the forage. Phosmet itself was the major residue (53% of the TRR) in the fodder, but was not found in the grain.

Four application of [ $^{14}\text{C}$ ]phosmet were made to potato plants (*Solanum tuberosum*) growing in a large box filled with a sandy loam soil in a field plot in California. The treatments (1.68 to 2.0 kg ai/ha) were by spray application of [ $^{14}\text{C}$ ]phosmet in 50% acetone/water (containing 0.5% Tween 20) to the plant foliage.



Figure 3. Metabolism of phosmet in maize



Applications were made at day 0 (to small immature plants), day 40, day 62 (7 days before the harvest of thin-skinned potatoes) and day 88, 7 days before the harvest of mature potatoes. The total amounts of phosmet applied were 5.6 kg ai/ha for thin-skinned potatoes and 6.8 kg ai/ha for mature potatoes. A control plot of the same size as the  $^{14}\text{C}$ -plot was treated by application of solvent only. Samples were collected before the second and third applications, at thin-skinned potato harvest, and at mature potato harvest.

The total radioactive residue in the potato foliage ranged from 14 to 109 mg/kg, increasing with each treatment. The TRR in the tubers was 1.4-2.1 mg/kg, indicating only a small degree of translocation into them. Solvent extraction removed more than 92% of the residue. Most of the unextracted remainder could be hydrolysed to phthalic acid.

HPLC and TLC analysis of the extracts showed that phthalic acid (Pa) and phthalamic acid (PaA) were the major metabolites, although the latter was readily hydrolysed to phthalic acid during attempts to characterize it. Phosmet, its oxygen analogue and hydroxylated phthalic acids were not found in any of the extracts. Pa and PaA constituted 88%, 35% and 77% of the TRR in the first, third and final samples of the tubers respectively. Most of the unidentified metabolites were hydrolysed to phthalic acid, showing them to be derivatives or conjugates of it.

### Environmental fate in soil

In early studies using unlabelled phosmet it was shown that its rate of degradation in soils was influenced more by soil pH than by the activity of micro-organisms. The half-life values for phosmet ranged from 3 days in a pH 7.2 loam to 12.2 days in a pH 5.1 sandy loam soil. Autoclaving increased the half-life only moderately (Menn *et al.*, 1965).

The metabolism of phosmet was studied by McBain (1986) who incorporated the carbonyl-labelled compound into moist loam soil (pH 7.1) at a rate of 4.77 mg/kg. The soil was kept under aerobic conditions for 3 days, then anaerobic conditions for 60 days. The evolved  $^{14}\text{CO}_2$  amounted to nearly 40% of the applied  $^{14}\text{C}$ . The extractable  $^{14}\text{C}$  and the  $^{14}\text{C}$  in flood water decreased with time. Under anaerobic conditions the metabolism of phosmet continued, but at a slower rate. In addition to unchanged phosmet, phosmet oxon, Pi, PaA, Pa, benzoic acid, PiMOM and PiMOH, were detected. Their concentration remained below 0.04 mg/kg during the study.

In another study with similar soil (pH 7.1) 5 mg/kg of the carbonyl-labelled compound was incorporated (McBain, 1990). After 4 days of aerobic conditions one test system was changed to anaerobic. The recovery of radioactivity was 92% of that applied. The radioactivity evolved as carbon dioxide from the aerobic and anaerobic soils was respectively 14.95 and 8.3%, and that remaining after extraction respectively 16.3% and 11.6% of the applied amount. About 11% of the radioactivity was found in the flood water.

The residue components and their percentages in the total residue, expressed as phosmet found in the aerobic soil were phosmet 36.6%, phosmet oxon 0.5%, Pi 1.53%, PaA <0.01%, Pa 0.88%, PiMOM 5.68%, PiMOH 0.41%, PaAMOH 2.44%, PiMSM 0.37%, PiMS(O)M 2.59%, PiMS(O<sub>2</sub>)M 0.34%, PiAMS(O)M 0.97%, PiAMS(O<sub>2</sub>)M 0.56%. Some unidentified intermediate products were also detected.

A proposed degradation pathway is shown in Figure 4.

Field dissipation studies indicated that phosmet would have an initial half-life of about 6 days in soils with a pH of about 8. Phosmet remained mainly in the top 10 cm soil layer, and no phosmet residue was detectable below 20-25 cm. Phthalimide, phosmet oxon and PiMOM were all undetectable (<0.02, <0.01 and <0.01 mg/kg respectively (Riggle *et al.*, 1990; Roper, 1990, McKay, 1988).

Phosmet did not undergo significant photo degradation when exposed on thin layer plates of soil to natural sunlight for a period of 30 days (Zeigler and Hallenbeck, 1988).

The adsorption and desorption of [ $^{14}\text{C}$ ]phosmet were examined in a sand, a sandy loam, a silty loam and a loam.  $K_d$  values were 1.17, 12.4, 15.8 and 13.6 respectively, giving  $K_{oc}$  values mainly in the range of 700-975. It was concluded that phosmet would be relatively immobile in all the soils studied except sand (Yeh, 1988).



### Uptake of residues from soil

[<sup>14</sup>C]carbonyl-labelled phosmet was sprayed at about 5.6 kg ai/ha (equivalent to 5 times the single application rate) on a sandy loam soil with an organic matter content of 1.6% and a pH of 6.5, confined in boxes in an outdoor location in California. Radishes, lettuce and wheat were subsequently planted in the soil 30, 120 and 365 days after the treatment. The total radioactive residues in the plants grown to maturity and the corresponding soil residues are shown in Table 3.

Neither phosmet nor its oxygen analogue were detected in the plant extracts. Analysis by HPLC showed a number of polar metabolites, most of which were characterized by chemical and enzymatic hydrolysis as esters or conjugates of phthalic acid (Toia *et al.*, 1993a).

Table 3. Total radioactive residues in plants grown to maturity in soils treated with labelled phosmet.

Sample	<sup>14</sup> C as phosmet, mg/kg, at (periods in days)		
Soil <sup>1</sup> after application	7.74 (0)		
Soil <sup>1</sup> at planting 0-7.5 cm	4.68 (30)	4.24 (120)	2.00 (365)
Soil <sup>1</sup> at radish harvest	2.91 (71)	3.81 (167)	1.55 (392)
Radish roots	0.46	0.10	0.03
Radish foliage	0.61	0.15	0.05
Soil <sup>1</sup> at lettuce harvest	3.72 (83)	2.82 (171)	0.43 (406)
Lettuce	0.29	0.19	0.042
Soil <sup>1</sup> at wheat forage harvest	2.87 (92)	1.71 (192)	2.12 (406)
Wheat forage	0.59	0.12	0.045
Soil <sup>1,2</sup> at wheat harvest	1.18 (169)	1.60 (290)	2.21 (516)
Wheat chaff	0.76	0.26	0.12
Wheat Straw	0.93	0.46	0.11
Wheat grain	0.54	0.21	0.10

<sup>1</sup>0-7.5 cm layer. The residues in the 7.5-15 cm layer were <0.08 mg/kg

<sup>2</sup>0-7.5 cm layer. The residues in the 7.5-15 cm layer were <0.15 mg/kg at days 290 and 516

### **Environmental fate in water**

Phosmet undergoes fairly rapid hydrolysis at ambient temperatures. The half-life values for phosmet in water at 25<sup>0</sup>C were 7.5-9.7 days at pH 5, 9.4 hours at pH 7 and 5.5 minutes at pH 9 (Chang, 1987; Robinson, 1992). Degradation is enhanced by light: in a separate study the half-life of phosmet at pH 5 and 25<sup>0</sup>C was reduced from 9.7 days in the dark to 2.42 days in the light (Robinson, 1992).

The major hydrolysis products formed at pH 5 in the dark were *O,O*-dimethyl hydrogen phosphorodithioate (79.4 mol %), *O*-methyl dihydrogen phosphorodithioate (4.1 mol %), PaA (34.4 mol %), Pi (10 mol %) and Pa (8.9 mol %). Following irradiation with a xenon lamp at pH 5 dimethyl hydrogen phosphate (72.3 mol %), phosphoric acid (33 mol %), methyl dihydrogen phosphate (7.3 mol %), Pi (62.5 mol %), PA (15.7 mol %) and PaA (12.7 mol %) were also detected. PiMOH was also detected in small amounts. Other minor products were detected but not identified.

The recovery of labelled compounds from the organic and water phases was between 96.2% and 98.9 %. Volatile compounds accounted for <0.05% of the total radioactivity (Robinson, 1992).

### **METHODS OF RESIDUE ANALYSIS**

Methods in current use rely on gas chromatography and determine the oxygen analogue of phosmet as well as phosmet itself, using a nitrogen-phosphorus selective thermionic detector. Variations used for the different types of sample are described below.

### Food crops

Methods used for the analysis of samples from supervised field trials are modifications of the official method of analysis as published in the Pesticide Analytical Manual.

Phosmet and its oxygen analogue are extracted from the crop with benzene. Oils, when present, are separated from the extracted residues by hexane-acetonitrile partition. A charcoal shake-out provides adequate clean-up for most crops; peas and pea forage require a charcoal column clean-up and interfering co-extractives may be separated by a silica column clean-up. A thermionic detector is used for quantification of phosmet and its oxygen analogue down to 0.05 mg/kg. Recoveries from a large number of crops with added levels of each compound at 0.05-1.0 mg/kg were 71-101% for phosmet and 70-100% for its oxygen analogue. Carbofenothion interferes with phosmet oxon on OV-1 and OV-17 liquid phases. They can be separated on QF-1 or columns of similar polarity (Adelson *et al.*, 1973).

Improvements to this method have involved the use of a more polar extraction solvent (acetone), evaporation and partitioning into dichloromethane, followed by hexane/acetonitrile partitioning. The hexane is discarded, the acetonitrile evaporated, and the residue re-dissolved in ethyl acetate. An aliquot is analysed on a gas chromatograph equipped with a fused silica capillary column with a cross-linked silicone stationary phase. Phosmet and its oxygen analogue are quantified with a phosphorus-selective detector (FPD). Recoveries were generally >80% and the limit of quantification for a 10 g sample was 0.05 mg/kg (Meyers, 1994a,b).

According to the official method in The Netherlands phosmet is extracted with ethyl acetate in the presence of sodium sulfate. The organic phase can be injected onto a GLC column without further clean-up or for some crops after clean-up on an SX-3 GPC column with cyclohexane/ethyl acetate as eluent. The LODs reported are between 0.01 and 0.05 mg/kg. Phosmet can also be detected on silica gel TLC plates, after oxidation to its oxon, by a cholinesterase-inhibition method (Netherlands, 1996).

### Milk, eggs and animal tissues

Phosmet and phosmet oxon are extracted from tissues with toluene and glacial acetic acid or, for milk and eggs, methylene chloride and glacial acetic acid. Fat is removed from the extract by acetonitrile-hexane partition. The acetonitrile, containing the analyte, is diluted with toluene and the solvents concentrated. An aliquot of the residual toluene solution is analysed by programmed-temperature gas chromatography on a fused silica capillary column, with a chemically bonded liquid phase of methyl silicone containing 6% cyanopropylphenyl groups. Phosmet and phosmet oxon are detected and quantified with a mass-selective detector. Mean recoveries from all samples were 84% for phosmet and 95% for phosmet oxon. With a few exceptions, neither phosmet nor phosmet oxon was detected in any control sample above 0.05 mg/kg, the limit of determination (Curry, 1989).

Phosmet can also be extracted from milk with ethyl acetate. The extract is dried over sodium sulfate, an aliquot is evaporated to dryness and the residue is dissolved in hexane. After partition with acetonitrile, the acetonitrile phase is evaporated to dryness and the residue re-dissolved in ethyl acetate. This solution is suitable for GLC or TLC analysis. The LOD is 0.01 mg/kg for whole milk (Netherlands, 1996a).

### Soil

Samples of soil (50 g) are extracted by shaking for one hour with water and toluene. The mixture is centrifuged to separate the toluene, water and soil phases and an aliquot of the toluene phase is removed and analysed by gas chromatography. A gas chromatograph equipped with a nitrogen/phosphorus selective thermionic detector and a fused silica capillary column

(polyphenylmethylsiloxane) is used with temperature programming for the determination of the residues. Recoveries of phosmet from control soil fortified in the range of 0.05-3.0 mg/kg were 103-120%, and of phosmet oxon at the same levels 68-100%. The limit of determination was given as 0.05 mg/kg (De Guzman and Iwata, 1986).

In an alternative method distilled water (10 ml) is mixed with the sub-sample of soil (50 g) which is then extracted for 30 minutes with ethyl acetate (100 ml). The ethyl acetate extract is dried and an aliquot analysed by gas chromatography as described above. Recoveries of phosmet and phosmet oxon at 0.02-2.0 mg/kg were 96-99% (California Department of Food and Agriculture, 1986a).

### Water

A 50 ml sample of water is shaken for two minutes with 5 ml toluene and a small aliquot of the toluene injected directly into a gas chromatograph equipped as described above (North Coast Laboratories, 1986).

### **Stability of residues in stored analytical samples**

#### Food crops

A storage stability study was carried out with phosmet on a variety of food crops stored at  $-20 \pm 10^{\circ}\text{C}$  for periods up to 2½ years (wheat grain and wheat straw), or 3 years (green alfalfa hay, almond nut meat, fresh apples, maize ears, fresh orange fruit, peppers, potato tubers and soya bean seed). The crops were chopped, blended or milled to produce homogeneous material and 25 g samples were fortified with phosmet (25 µg), i.e. at 1.0 mg/kg, and analysed at intervals of 0 days, 3 months, 8 months, 1 year, 2 years, 2½ years (wheat only) and 3 years.

The results showed that phosmet is stable at  $-20 \pm 10^{\circ}\text{C}$  in almonds, apples, soya beans, and wheat grain and straw for a minimum of 2½ years, and in alfalfa, maize, oranges, peppers and potatoes for a minimum of 2 years. The criterion for stability was that the mean residue level found in duplicate sample analyses should be not less than 75% of the value found on day 0 (McKay, 1989).

Apples and processed apple commodities (sauce, juice and dry pomace) were fortified at 0.5 mg/kg with either phosmet or phosmet oxon and stored at  $-20 \pm 10^{\circ}\text{C}$  for periods up to 39 months. The results indicated that phosmet and phosmet oxon were both stable in fresh apples, apple juice and dry pomace for 39 months. In apple sauce phosmet and its oxon were stable for 28 months, when the last samples were analysed.(Meyers, 1994a).

Fresh, dried and canned peaches were separately fortified at 0.5 mg/kg with phosmet or phosmet oxon and stored at  $-20 \pm 10^{\circ}\text{C}$  for more than 3 years. Triplicate samples were analysed at intervals. The results showed that phosmet and the oxon were stable in fresh and canned peaches for periods up to 28 months. In dried peaches, phosmet and phosmet oxon both decreased to about 50% of the initial value in 4 months. The drying process involves dipping peaches in bisulfite solution, which may have affected the results (Meyers, 1994b).

#### Commodities of animal origin

Samples of cow muscle, fat, kidneys, liver and milk, and chicken eggs were each fortified separately with phosmet and phosmet oxon at 0.5 mg/kg and analysed at 0 day, 1 month, 3 months, 6 months and 1 year after storage at  $-20^{\circ}\text{C}$ .

The results show that phosmet is stable in milk, liver and fat for a year when stored at  $-20^{\circ}\text{C}$ ; recoveries after a year of storage were within 10% of the initial values. In eggs phosmet was stable for six months, and its recovery was still above 70% after a year. In kidneys phosmet was stable with



recovery above 80% after six months and nearly 70% after a year, indicating reasonable stability. Phosmet was stable in muscle for one month, but even after a year recovery was nearly 70%.

Phosmet oxon, while generally less stable than phosmet, was stable for one year in fat, 6 months in milk and one month in muscle and eggs. The oxon was relatively stable in eggs for up to 3 months, as shown by a recovery of nearly 70%. Phosmet oxon is unstable in liver and kidneys; its recovery decreased to 18% of the initial level after one hour in liver and to 50% after 5 hours in kidneys. Because the compound is so unstable in these organs, it is unlikely that any residues of phosmet oxon would occur in the commercial product (Curry, 1989).

### Soil

A clay loam soil (pH 7.3, organic matter 4.1%, sand 28.9%, silt 45.8%, clay 21.2% and cation exchange capacity 1.5 m eq/100 g) was thoroughly mixed and 25 g samples were fortified with phosmet at 1 mg/kg. The samples were stored at  $-20 \pm 10^{\circ}\text{C}$  for up to three years and sub-samples taken periodically for analysis in duplicate. Phosmet was stable in the soil at  $-20^{\circ}\text{C}$  for at least two years (McKay, 1989).

### USE PATTERN

Phosmet is a broad-spectrum organophosphorus insecticide used to control a variety of insect and mite pests which attack pome, stone and citrus fruit. It is also used on field, pasture and forage crops. Phosmet is non-systemic and acts by contact and ingestion as a cholinesterase inhibitor.

Phosmet suppresses the two-spotted mite *Tetranychus urticae* and the European red mite *Paratetranychus ulmi* when used in spray programmes on deciduous fruit. A list of the major insects controlled is given in Table 4.

The registered or approved uses of phosmet on food crops are shown in Table 5. The direct use of phosmet in treating livestock for the control of warble fly, ticks and lice on cattle, resulting in residues in animal commodities, was not reported to the Meeting and is not included.

Table 4. Insects controlled by phosmet (a partial listing)

Anarsia lineatella	Peach twig borer
Anthonomus piri	Pear blossom weevil
Anthonomus pomorum	Apple blossom weevil
Anuraphis persicae	Black peach aphid
Aphis pomi	Green apple aphid
Argyresthia ephipella	Cherry fruit moth
Aspidiotus perniciosus	San José scale
Bruchus rufimamus	Broad bean weevil
Carpocapsa pomonella	Codling moth
Ceratitis capitata	Mediterranean fruit fly
Colaspidema atrum	Alfalfa beetle
Dacus oleae	Olive fruit fly
Eriosoma lanigerum	Woolly aphid
Hoplocampa testudinae	European apple sawfly
Polychrosis botrana/Clysia ambiguella	Grape-berry moth
Psylla mali	Apple-tree psylla
Psylla piri	Pear-tree psylla
Rhagoletis cerasi	Cherry fruit fly
Saissetia oleae	Olive scale
Sitona lineata	Pear weevil

Table 5. Main registered uses of phosmet on food crops.

Crop	Country	Form.	Application			PHI, days
			Rate, kg ai/ha	Spray Conc., g ai/l	Number	
Alfalfa	Argentina	50 WP	0.5	-	As required	7
	Australia	150 EC	0.04-0.05	0.38-1.1	1-3	2
	Canada	50 WP	1.13	2.25-5.6	1	7
	Mexico	50	0.5 -1			7
	Uruguay	50 WP	0.5	-	As required	7
	USA	70 WSB	0.8-1.0	-	1	14
Almonds	Chile	50 WP		0.5-0.6		
	USA	70 WSB	3.4	2.25-5.6	2	30
Apples	Argentina	50 W	-	0.6	Every 25-30 days	n <sup>1</sup>
	Australia	500 WP	-	0.75	Every 3 weeks	21
	Brazil	500 WP	-	1.0	Every 10 days	14
	Canada	50 WP	1.9	-	As required	1
	Chile	50 WP	1.0-1.5	0.5-0.75	As required	
	France	50 WP	-	0.5	As required	15
	Greece	50 WP		1.2-1.5	At 30 day intervals	30
	Italy	50 WP	-	0.75-1.0	As required	30
	Mexico	50	0.5-1			7
	Portugal	50 BT	-	0.5	As required	-
	Spain	20 LE	-	0.75-1.25	As required	30
	Tunisia	50 WP	-	0.5-0.6	As required	15
	Uruguay	50 WP	-	0.5-0.6	Every 18-20 days	7
	USA	70 WSB	1.7-4.1	1.2	As required (max 34 kg/ha)	7
Apricots	Greece	50 WP		1.2-1.4	At 20 days	30
	USA	70 WSB	1.75-3.4	1.0-1.2	As required	14
Blueberries	Canada	50 WP	1.13	1.13	1-2	15
	USA	70 WSB	1.0	-	1-2	3
Carrots	Canada	50 WP	1.13	-	1-2	40
Celery	Canada	50 WP	1.13	1.13	1-2	40
Cereals (forage crop)	Australia	150 EC	0.04-0.05	0.4-1.0	Every 3-5 weeks	7
Cherries (sour)	Canada	50 WP	1.9		As required	7
	Chile	50 WP	-	0.5-0.9	As required	-
	Greece	50 WP		1.2-1.4		30
	USA	70 WSB	1.7-2.0		As required	7
Citrus (orange, lemon, grapefruit)	Argentina	50 WP	-	0.6	As required	n <sup>2</sup>
	Brazil	500 WP	-	1.0	As required	14
	Chile	50 WP	-	0.5-0.75	As required	-
	Greece	50 WP	-	1.2-1.4		30
	Italy	50 WP	-	0.3-0.75	As required	30
	Spain	20 LE	-	1.5	As required	30
	Tunisia	50 WP	-	0.6-0.75	As required	15
	Uruguay	50 WP		0.5-0.75	As required	14
Clover	Greece	50 WP		1.2-1.4		30
Cotton	Argentina	50 WP	0.4-0.75	-	As required	15
	Brazil	500 WP	0.5	-	As required	14
	Cotton	50 WP		1.2-1.4		30
	Mexico	50 WP	0.5-1.0	1.25-5.0	As required <sup>3</sup>	-
	USA	70 WSB	0.4-0.6		Every 3-7 days (max 11 kg ai/ha)	21
Grapes	Chile	50 WP	1.0-1.5	0.75-0.9	As required	15
	Greece	50 WP		1.2-1.4		30
	Spain	20 LE	1.5	0.15	As required	30
	USA (west)	70 WSB	1.5-2.4	-	As required	7
	USA (east)	70 WSB		-	As required	14
Kiwi fruit	Chile	50 WP	1.0-1.5	0.75-0.9	As required	1
	New Zealand	50 WP	2.53	1.1	5 times	21
Maize	Greece	50 WP		1.2-1.4		30
Melons	Portugal	50 BT		0.5		

Crop	Country	Form.	Application			PHI, days
			Rate, kg ai/ha	Spray Conc., g ai/l	Number	
Nectarines	Chile	50 WP	-	0.5-0.6	As required	14
	Uruguay	50	-	1.0-1.2	At 18-20 days	14
	USA	70 WSB	1.7-3.3	-	As required	14
Oil palm	Malaysia	50 WP	0.5	0.75	As required	14
Olives	Greece	50 WP	-	1.2-1.4	-	30
	Italy	50 WP	-	0.75-1.5	As required	30
	Portugal	50 BT	-	0.5	As required	-
	Spain	50 WP	-	1.5	As required	30
	Tunisia	50 WP	-	0.5-1.0	As required	15
Pasture (forage)	Australia	150 EC	0.04-0.05	0.38-1.1	1-3	2
Peaches	Argentina	50 WP	-	0.6	Every 25-30 days	5
	Australia	500 WP	-	0.5	Every 3 weeks	21
	Brazil	500 WP	-	1.0	As required	14
	Canada	50 WP	1.9	-	-	1
	Chile	50 WP	-	0.5-0.6	As required	14
	Greece	50 WP	-	1.2-1.5	At 30 days	30
	Spain	20 LE	-	1.5	As required	30
	Portugal	50 BT	-	0.6	-	-
	Tunisia	50 WP	-	0.5-0.6	As required	15
	Uruguay	50 WP	-	0.5-0.6	Every 18-20 days	14
	USA	70 WSB	1.7-3.3	-	As required (max 13 kg ai/ha)	14
Pears	Argentina	50 WP	-	0.6	Every 25-30 days	5
	Australia	500 WP	-	0.75	Every 3 weeks	21
	Brazil	500 PM	-	1.0	Every 10 days	14
	Canada	50 WP	1.9	-	-	1
	Chile	50 WP	-	0.75-0.9	As required	7
	France	50 WP	-	0.5	As required	15
	Italy	50 WP	-	0.75-1.0	As required	30
	Portugal	50 BT	-	0.5	As required	-
	Tunisia	50 WT	-	0.5-0.75	As required	15
	Uruguay	50 WP	-	0.5-0.6	Every 18-20 days	7
	USA	70 WSB	1.7-5.6	-	As required	7
Peas (fresh and dry)	USA	70 WSB	0.75	-	As required	7
Pecans	USA	70 WSB	2.45	-	As required	14
Plums	Argentina	50 WP	-	0.6	Every 25-30 days	20
	Canada	50 WP	1.9	-	-	1
	Chile	50 WP	1.7 -3.3	0.75-0.9	As required	7
	USA	70 WSB	1.7-3.3	-	As required	7
Prunes	USA	70 WSB	1.7-3.3	-	As required	7
Potatoes	Canada	50 WP	1.2	-	-	7
	France	50 W	0.5	0.5-0.6	As required	15
	Italy	50 WP	-	0.75-1.0	As required	30
	Portugal	50 BT	-	0.6	As required	-
	Spain	50 WP	-	0.75-1.25	As required	30
	Tunisia	50 WP	0.5	0.5-0.6	As required	15
	Uruguay	50 WP	0.88	-	As required	7
	USA	70 WSB	-	-	As required	7
Quinces	Argentina	50 WP	-	0.5-0.6	As required	5
	Uruguay	50 WP	-	0.5-0.6	Every 18-20 days	7
Sweet potatoes	USA	5% Dust	125-250 g/tonne	-	Apply once post-harvest for storage	-
Walnuts	Argentina	50 WP	-	0.6	As required	5
	USA	50 WP	3.3-6.6	-	Max 5 application	14

<sup>1</sup> Red Delicious and Granny Smith 20 days, others 15 days

<sup>2</sup> Applied as a bait

<sup>3</sup> Not more than 11 kg ai/ha for every agricultural cycle

## RESIDUES RESULTING FROM SUPERVISED TRIALS

Citrus fruits (Table 6). Reports of recent supervised trials (1991) on oranges in Argentina and Brazil were submitted. In Argentina, 0.5 kg ai/ha as a 0.6 g ai/l solution was applied six times and the crop harvested 7 days after the last application. Residues of phosmet were found to be confined entirely to the peel (0.27-1.0 mg/kg). Phosmet residues in the whole fruit were in the range 0.07-0.32 mg/kg. Residues of phosmet oxon were below the limit of quantification (<0.05 mg/kg).

In Brazil, two different formulations were used in supervised residue trials at concentrations of 1.0 g ai/l (the recommended rate) and 2.0 g ai/l. Oranges were harvested 14 days after the last of 5 applications. Only the pulp was analysed for parent phosmet residues, which were below the limit of quantification (<0.05 mg/kg).

Pome fruit (Table 7). Supervised residue trials on apples and pears have been carried out in Australia, Brazil, Canada, Germany, The Netherlands, New Zealand, the UK and several States of the USA. Many of the trials were carried out at rates above those now recommended.

Table 6. Residues of phosmet from supervised trials on oranges.

Country Year	Application			PHI, days	Sample	Residue, mg/kg	Reference
	Form. Rate, kg ai/ha	Conc., g ai/l	No.				
Argentina 1991	50 WP 0.5	0.6	6	7	Whole fruit	<u>0.32</u>	Grant and Meyers, 1992a
					Peel	1.0	
					Pulp	<0.05	
			6	7	Whole fruit	<u>0.13</u>	
					Peel	0.60	
					Pulp	<0.05	
		6	7	Whole fruit	<u>0.07</u>		
				Peel	0.27		
				Pulp	<0.05		
Brazil 1991	500 WP-	1.0	5	14	Pulp	<0.05	Suchek, 1992
	450 SC	2.0	5	14	Pulp	<0.05	
	-	1.0	5	14	Pulp	<0.05	
	-450 SC	1.0	5	21	Pulp	<0.05	
		2.0	5	14	Pulp	<0.05	
		2.0	5	21	Pulp	<0.05	

Table 7. Residues of phosmet from supervised trials on pome fruits.

Commodity Country Year	Application			PHI, days	Sample	Residue <sup>1</sup> mg/kg	Reference/Remarks
	Form. Rate, kg ai/ha	Conc., g ai/l	No.				
Apples Brazil 1992	500 PM- 450 SC	1.0	7	14	Peeled fruit	<u>&lt;0.05</u>	Suchek, 1993a
		2.0	7	14		<0.05	
		1.0	7	14		<u>&lt;0.05</u>	
		1.0	7	21		<0.05	
		2.0	7	14		<0.05	
		2.0	7	21		<0.05	
Apples Canada 1965	50 WP 2.35	-	1	0	Whole fruit	2.16	A 1004
				7		1.4	
				14		1.3	
				21		0.87	
Apples Germany 1974	50 WP-	1.5	1	0	Whole fruit	1.4-2.9 <sup>2</sup>	Apple report R3/12 1974
				6		1.1-2.1	
				13		0.8-1.5	
				20		0.4-0.7	

Commodity Country Year	Application			PHI, days	Sample	Residue <sup>1</sup> mg/kg	Reference/Remarks
	Form. Rate, kg ai/ha	Conc., g ai/l	No.				
Apples Germany 1977	50 WP 1.125	2.25	6	0 8 15 22 29	Whole fruit	2.1 0.74 0.52 0.65 0.52	Apple report R3/13 1977
Apples Germany 1977	50 WP 1.5	0.75	7	0 7 14 21 28	Whole fruit	1.4 1.4 1.0 0.58 0.47	Apple report R3/14 1977
Apples Germany 1977	50 WP 1.125	0.75	6	0 7 14 21 28	Whole fruit	2.3 1.7 0.83 0.70 0.68	Apple report R3/15 1977
Apples Netherlands 1970	50 W  50 WP	1.5  1.5	1  1	0 7 14 21  0 7 14 21	Whole fruit  Whole fruit	1.3-2.1 <sup>3</sup> 0.7-1.3 0.34-0.95 0.13-0.65  1.5-3.4 1.7-2.3 0.6-2.0 0.24-0.59	Apple report R3/46 1970 Oxon <0.10 mg/kg  Apple report R3/45 1970 Oxon <0.1 mg/kg
Apples USA Washington 1965	50 WP 4.48	-	3	1 7 14 21	Whole fruit	4.9 <u>4.2</u> 2.7 2.6	A 906
Apples USA Washington 1965	50 WP 4.48	-	3	1 7 14 21	Whole fruit	3.8 <u>1.8</u> 1.3 <0.4	A 1660
Apples USA Oregon 1965	50 WP 4.48	-	1	1 7 14 21	Whole fruit	5.7 <u>3.4</u> 2.2 1.0	A 1563
Apples USA California 1965	50 WP 1.96	-	2	1 8 15 23	Whole fruit	1.67 1.68 <sup>4</sup> <u>1.2-1.8</u> 0.9-1.4 1.1-1.8	A 1751
Apples USA 1965	50 WP 1.7	-	9	1 7 14 21	Whole fruit	2.6-3.75 <sup>4</sup> <u>2.65-3.7</u> 0.46-0.66 0.74-0.78	A 1939
Apples USA Virginia 1965	50 WP 3.8	-	1	1 7 14 21	Whole Fruit	8.9-10.0 <sup>4</sup> <u>6.3-7.3</u> 3.2-4.5 2.9-3.2	A 1948
Apples USA Pennsylvania 1965	50 WP 4.2	-	6	0 7 14 21 28 0 7 14 21 28	Whole fruit	4.0-4.6 <sup>4</sup> <u>2.4-2.8</u> 1.4-1.6 0.9-1.1 0.51-0.75 6.1-6.5 <u>4.1-4.3</u> 2.6-3.3 2.1-2.1 1.0-1.3	A 1953
Apples USA N.Y.	50 WP 2.2	-	6	1 8 15	Whole fruit	5.4 <u>3.4</u> 2.8	A 1977

Commodity Country Year	Application			PHI, days	Sample	Residue <sup>1</sup> mg/kg	Reference/Remarks
	Form. Rate, kg ai/ha	Conc., g ai/l	No.				
1965	3.8	-	8	22		1.3	A 1962 A 1978
				7 14 21 <sup>5</sup>		0.69 0.68 0.32	
	6	-	9	1		1.7	A 1983
				7 14 21 <sup>5</sup>		1.4 0.38 0.26	
Apples <sup>6</sup> USA 1990	50 WP 4.48	-	9	7 7	Whole fruit	12.9 <u>3.3</u>	Meyers et al.,1991a
Pears Canada 1965	50 WP 3.36	-	3	1	Whole fruit	1.9	4515
				7 14 28		0.65 0.26 0.1	
Pears Canada 1965	50 WP 2.24	0.6	2	1	Whole fruit	2.3	Pear report R3/18 1965)
				7 14 21		<u>0.85</u> 0.70 0.52	
Pears USA 1965  1967	50 WP 5.6  50 WP 6.7-9.0	1.2  -	1-2  3	1	Whole fruit	2.4	Pear report R3/17 1965  oxon 0.18 mg/kg
				8 15 22 9		<u>1.7</u> 1.2 0.8 0.26	
Pears USA 1973	70 WP 6.3	0.84	3	0 7 14	Whole fruit	3.4 <u>1.3</u> 0.45	Pear report R3/44 1973
Pears UK 1970	50 WP 1.12 2.24	2 2		36	Whole fruit	0.22	Pear report R3/42 oxon 0.03, 0.04 mg/kg
				36		0.25	

<sup>1</sup>as phosmet

Netherlands (1970): phosmet oxon <0.01-0.06 mg/kg

USA (1990): phosmet oxon <0.05 mg/kg

Other countries except UK: oxon not detected or not analysed

<sup>2</sup>6 varieties grown at one site were sampled separately. The lowest and highest residues are reported

<sup>3</sup>Range in triplicate analyses

<sup>4</sup>Replicate samples taken from the same plot

<sup>5</sup>Sampling was continued until 47-49 days

<sup>6</sup>Used for a processing study

Even at higher than recommended rates, the residues of phosmet found after a PHI of 7 days were all below 5.0 mg/kg, except in the trial in Virginia in 1965 and the 1990 trial carried out as a processing study in the USA where a total of 40 kg ai/ha was applied (as 9 separate applications) and a residue of phosmet of 12.9 mg/kg was found in the whole unwashed apples 7 days after the last application (according to US GAP 33.6 kg ai/ha is the maximum total application).

Residues of phosmet in pears in supervised residue trials in Canada and the USA in 1964 and 1965 reviewed by the 1981 JMPR were all below 5 mg/kg following applications approximating GAP and a PHI up to 7 days.

**Stone fruit** (Table 8). Supervised residue trials were carried out on apricots (USA), nectarines (USA), peaches (Canada and USA), plums (Chile and USA) and prunes (USA). The results are shown in Table 8.

Two apricot trials in the USA (California) at an application rate of 4.2 kg ai /ha (1.25 times GAP) yielded residues of 1.19 and 2.76 mg/kg at 14 days PHI. The oxon residues were 0.01 and 0.02 mg/kg.

Residues of phosmet in peaches were generally below 5 mg/kg after a 7 or 14-day PHI, except in two trials in the USA. In the 1964-65 trials at rates within or close to those specified by GAP (4-8 applications at rates up to 2.24 kg ai/ha in most of the trials), residues of phosmet up to 11 mg/kg were found 5-10 days after the last application. The highest residue at about 14 days after application was 6.8 mg/kg. In the 1990 US trial phosmet was applied 10 times at 3.36 kg ai/ha (a total of 33.6 kg ai/ha, almost three times the maximum recommended total of 13 kg ai/ha, specifically for a processing study. The residue of phosmet in the peaches was about 13 mg/kg 14 days after the last application. This was the only trial in which finite residues of phosmet oxon were found, at a maximum of 0.08 mg/kg.

Four trials on nectarines were reported. In two of them (Table 8) the samples were taken from 0 to 25 days after application. In the other two trials, with application rates of about 4.2 kg ai/ha, the residues were 0.22 mg/kg and 0.35 mg/kg at days 31 and 29 following one and two applications respectively.

In one set of supervised residue trials on plums in Chile (1991) above the recommended spray concentration the residues were all below 0.55 mg/kg, even at a 0-day PHI.

Two trials in 1965 and 1967 in the USA (California) on plums at GAP rates or higher, produced maximum residues of 0.48 mg/kg at a 9-day PHI, and similar trials also in California on prunes in the same years gave residues of 0.53-2.6 mg/kg in the dried prunes after harvesting at 1-3 day PHIs.

More recent trials were carried out on plums and prunes in California in 1993. Five applications of Imidan 50 WP were made at the label recommended rate of 3.4 kg phosmet/ha, with intervals of about 14 days between applications. Fresh plums and prunes were harvested for analysis 7 days after the final application. Phosmet residues in the pitted whole fruit from the three separate sub-plots were 0.40-0.43 mg/kg in plums and 1.8-2.3 mg/kg in prunes. No residues of phosmet oxon (<0.05 mg/kg) were found in any sample of plums or fresh prunes (Dykeman, 1994a,b).

A separate trial was carried out on prunes for a processing study. The prunes were treated with four applications of Imidan 50 WP at the maximum recommended rate of 3.4 kg ai/ha followed by one application at 6.8 kg ai/ha. The fresh prunes were harvested 7 days after the final application for analysis and processing. The residues of phosmet in the fresh prunes were 2.6 mg/kg in both samples. No residues (<0.05 mg/kg) of phosmet oxon were found (Dykeman, 1994c).

Table 8. Residues of phosmet from supervised trials on stone fruits carried out with 50 WP formulations.

Commodity country Year	Application			PHI, days	Sample	Residue, mg/kg	Reference Remarks
	Rate, kg ai/ha	Conc., g ai/l	No.				
Apricots USA 1967 California	4.2	-	1	0	Whole fruit <sup>1</sup>	9.4 (0.21)	A 396
				7		4.7 (0.016)	
				14		<u>2.8</u> (0.018)	
Apricots USA 1967 California	4.2	-	1	0	Whole fruit <sup>1</sup>	11 (0.36)	A 397
				7		4.2 (0.08)	
				14		<u>1.2</u> (0.01)	
				21		1.6 (0.06)	
				28		0.09	

Commodity country Year	Application			PHI, days	Sample	Residue, mg/kg	Reference Remarks
	Rate, ai/ha	kg Conc., g ai/l	No.				
Nectarines USA 1967	4.2	-	1	0 7 14 21	Whole fruit <sup>1</sup>	4.0 (0.05) 2.2 (0.01) 0.55 0.05	B 1090
Nectarines USA 1965	2.24	-	1	3 9 16 25	Whole fruit	0.67 0.81 <u>0.45</u> <0.4	A 1734
Peaches Canada 1965	2.24	-	1	1 7 14 21	Whole fruit	10 3.4 <u>1.5</u> 1.7	A 1986
Peaches USA Pennsylvania 1965	2.8	-	4	0 7 14 21 28	Whole fruit <sup>2</sup>	10, 13 11, 11 3.1, <u>6.8</u> 1.9, 2.3 1.7, 2.1	A 1957
Peaches USA California 1965	2.24	-	1	1 7 14 21	Whole fruit <sup>2</sup>	2.6, 3.4 2.0, 2.8 1.2, <u>1.6</u> 0.51, 0.81	A 1416
Peaches USA Virginia 1965	2.24	-	5	1 7 14 21	Whole fruit <sup>2</sup>	3.0, 3.3 0.96, 1.2 0.59, <u>0.87</u> 0.43	A 1940
Peaches USA Georgia 1965	2.24	-	1	1 7 14	Whole fruit <sup>2</sup>	6.3, 13 4.7, 10 3.0, <u>6.4</u>	A 2403
Peaches USA California 1965	2.24	-	1	3 9 16 25	Whole fruit	3.8 1.8 <u>1.2</u> 0.77	A 1420
Peaches USA California 1965	2.24	-	5	2 9 15 23	Whole fruit <sup>2</sup>	1.6, 2.5 1.1, 1.9 0.68, <u>0.78</u> 0.44, 0.49	A 1726
Peaches USA 1963	5.6	-	1	0-3 5-10 11- 16	Whole fruit	6.2 5.2 -	FAO/WHO 1982
Peaches USA, Connecticut 1965	1.68	-	9	1 7 14	Whole fruit <sup>2</sup>	5.9, 6.3 3.3, 3.7 2.1, 2.9	A 1944
Peaches USA Michigan 1965	1.12	-	8	1 7 12 21	Whole fruit	1.9 0.87 0.28 <0.1	A 2027 A 2031
Peaches USA, Connecticut 1966	1.12	-	8	1 7 14	Whole fruit <sup>1</sup>	1.8 (0.1) 1.9 (0.14) 0.93 (0.06)	A 2093
Peaches USA 1990	3.36	-	10	14	Whole fruit	13	Meyers <i>et al.</i> , 1991b oxon max. 0.08 mg/kg
Plums Chile 1991	1.4	-	1	0 3 7 10	Whole <sup>3</sup> plums	0.16(0.46) 0.08(0.22) 0.12 ( <u>0.55</u> ) 0.07(0.28)	Grant and Meyers, 1992b
Plums (late Santa Rosa) USA (CA) 1965	2.24	0.6	1	3 9 16 25	Whole plums	0.55 <u>0.48</u> 0.28 <0.2	Plum report R3/32



Commodity country Year	Application			PHI, days	Sample	Residue, mg/kg	Reference Remarks
	Rate, kg ai/ha	Conc., g ai/l	No.				
Prunes (French) USA (CA) 1965	2.8	0.60	3	1 8 14 21	Dried prunes <sup>4</sup>	2.3 <u>2.2</u> 2 1.1	Prune report R3/37 1965
Plums USA (CA) 1967	4.2	0.9	1	27- 28	Whole plums	<0.1-0.12	Plum reports R3/33, 34, 41 oxon <0.10 mg/kg
Prunes <sup>5</sup> USA (CA) 1967	4.2	0.90	1	3 38 52	Dried prunes	0.53-1.8 0.07-0.45 <0.1(3)	Prune rep. R3/38, 39, 40, 1967 oxon <0.1 mg/kg
Plums Castleman USA (CA) 1974	3.5	0.63 <sup>6</sup>	1	35 65	Whole plums	0.09 <0.05-0.06	Plum reports R3/31, 35 Oxon <0.05 mg/kg
Plums <sup>7</sup> (Angeleno) USA (CA) 1993	3.4	-	5	7	Pitted whole plums	<u>0.41</u>	Dykeman, 1994b oxon <0.05 mg/kg
Fresh prunes USA (CA) 1993	3.4	-	5	7	Pitted whole prunes <sup>8</sup>	1.80 <u>2.3</u> 1.8	Dykeman, 1994a Oxon <0.05 mg/kg
Fresh prunes <sup>9</sup> USA (CA) 1993	4 x 3.4 + 1 x 6.8 <sup>10</sup>	-	5	7	Pitted whole prunes	2.6, 2.6	Dykeman, 1994c Oxon <0.05 mg/kg

<sup>1</sup>Oxon residues in parentheses

<sup>2</sup>Residues in duplicate samples from the same plot

<sup>3</sup>Total of 8 trials. Figures are average values of 6-15 determinations, with maximum values in parentheses. Phosmet oxon <0.05 mg/kg. Volume and concentration of spray were not reported

<sup>4</sup>Results are means of triplicate analyses by spectrophotometric method

<sup>5</sup>3 trials

<sup>6</sup>70 WP formulation

<sup>7</sup>Replicate analyses by spectrophotometric method described in FAO/WHO, 1977

<sup>8</sup>Results from three replicate sub-plots

<sup>9</sup>Trial was carried out to obtain treated fruits for processing

<sup>10</sup>Twice the recommended label rate

Grapes (Table 9). The results of supervised residue trials on grapes in Canada and the USA in the period 1963-69 were evaluated by the 1981 JMPR. No new trials have been submitted. The results of the trials are reported in more detail in Table 9.

Table 9. Residues of phosmet from supervised field trials on grapes with 50 WP formulations.

Country Year	Application			PHI, days	Sample	Residue, mg/kg	Reference Remarks
	Rate, kg ai/ha	Conc., g ai/l	No.				
Canada Orlando 1968	1.4	-	4	1 7 14 21	Whole fruit	11 7.2 6.0 2.9	B 0535
USA New York 1963	0.7, 0.7, 0.9	-	3	0 10 14 28	Whole fruit <sup>1</sup>	3.9, 4.3 1.1, 1.4 0.1, 2.5 0.3, 0.8	Cornell 1963
USA New York 1963	1.4, 1.4, 1.8	-	3	0 7 14 28	Whole fruit <sup>1</sup>	8.3 3.6, 4.2 4.0, <u>4.2</u> 2.2	Cornell 1963

Country Year	Application			PHI, days	Sample	Residue, mg/kg	Reference Remarks
	Rate, kg ai/ha	Conc., g ai/l	No.				
USA New York 1965	0.7, 0.7, 0.9	-	3	7 15 21 28 42	Whole fruit <sup>1</sup>	2.1 1.2, 1.4 0.7, 0.9 0.6, 0.76 0.28, 0.44	Cornell 1965a
USA New York 1965	1.4, 1.4, 1.8	-	3	7 15 21 28 42	Whole fruit <sup>1</sup>	3.8, 4.1 3.2, <u>3.3</u> 1.7, 2.1 1.1, 1.9 0.9, 1.1	Cornell 1965a
USA New York 1965	0.7, 0.7, 0.84	0.6	3	0 7 14 21 28	Whole fruit <sup>1</sup>	0.32, 1.76 0.36, 0.4 0.84, 0.96 0.32, 0.4 0.16, 0.2	Cornell 1965b
USA New York 1965	0.7, 0.7, 0.84	1.2	3	0 7 14 21 28	Whole fruit <sup>1</sup>	2.3, 2.4 1.36, 2.0 1.3, 1.4 0.96, 1.1 0.4, 0.56	Cornell 1965b
USA New York 1966	0.7, 0.7, 0.9	,	3	0 10 14 21 35	Whole fruit <sup>1</sup>	2.5, 2.6 1.5, 1.6 0.67, 0.75 0.7, 0.75 0.48, 0.55	Cornell 1966
USA New York 1966	1.4, 1.4, 1.8	,	3	0 7 14 21 35	Whole fruit <sup>1</sup>	5.9, 6.2 3.9, 4.8 1.4, <u>2.8</u> 1.6, 2.0 1.4, 1.5	Cornell 1966
USA New York 1967	1.4, 1.4, 1.8	,	3	0 7 14 21 24 42	Whole fruit <sup>1</sup>	8.2, 8.8 4.4, 5.0 <u>4.0</u> 4.0, 4.8 3.3 2.6, 3.7	Cornell 1967
USA New York 1967	2.1, 2.1, 2.8	-	3	0 7 14 21 28 35	Whole fruit <sup>1</sup>	11 15 8.5, 10 6.8, <u>9.2</u> 7.0, 7.6 6.2, 6.5 3.8, 6.2	Cornell 1967
USA, CA 1969	1.7 Imidan 5 Dust		2	0 7	Whole fruit	0.42 <u>0.24</u>	B-0665
USA, CA 1969	1.7 Imidan 5 Dust		1	0 7 14 21	Whole fruit <sup>2</sup>	1.6 <u>0.61</u> (oxon 0.16) <u>0.2</u> 0.43	B-0651
Grapes <sup>2</sup> USA, CA 1969	1.7 Imidan 5 Dust		1	4 7 31	Whole fruit	0.2-0.48 0.1- <u>0.17</u> 0.22	B-106, 107 B-1073,1075 B-0105

<sup>1</sup>Residues in duplicate samples taken from the same plot

<sup>2</sup>5 trials at different locations in California

Olives (Table 10). Supervised residue trials were carried out on olives in France, Italy and Spain in 1975 and 1976, and in Greece in 1965. At the maximum registered concentration of 1.5 g ai/l, the residues in the whole fruit one day after treatment were in the range of 1.1-2.5 mg/kg. Generally, the

residues declined, with a half-life of around 10 days or less, to <0.02-0.34 mg/kg after a PHI of 28-30 days.

Kiwifruit (Table 11). Supervised residue trials reported to the 1976 JMPR showed residues at a 21-day PHI mainly below 10 mg/kg, except for two high results (12 and 17 mg/kg) following seven applications at 1.5 times the GAP rate.

Residue data from trials in 1980 and 1986 were reviewed by the 1987 JMPR. The residues after a 21-day PHI were all well below 5 mg/kg (FAO/WHO, 1988a).

Table 10. Residues of phosmet from supervised trials on olives with 50 WP formulation.

Commodity Country Year	Application			PHI, days	Sample	Residue, mg/kg	Reference Remarks
	Rate, kg ai/ha	Conc., g ai/l	No.				
Olives (table)		1	1	1	Whole fruit	1.6 (2.4)	Mestres, 1976
France 1976				7	(pulp)	0.73 (1.1)	
				14		0.56 (0.80)	
				21		0.54 (0.77)	
				28		0.12 (0.18)	
				35		0.008 (0.012)	
		1.5	1	1	Whole fruit	2.3 (3.5)	
				7	(pulp)	1.6 (2.2)	
				14		1.4 (2.1)	
				21		0.43 (0.60)	
				35		0.24 (0.38)	
Olives (table)		-	1	1	Whole fruit	1.2 (1.5)	Mestres, 1975
France				7	(pulp)	0.62 (0.80)	
1975				14		0.15 (0.19)	
				20		0.08 (0.10)	
				29		0.02 (0.02)	
	1.5	-	1	1	"	1.1 (2.7)	
				7		0.39 (0.6)	
				14		0.06 (0.10)	
				20		<0.03	
				29		<0.03	
Olives		-	1	1	Whole fruit	1.4 (1.8)	Mestres, 1975
(for oil)				7	(pulp)	1.3 (1.8)	
France				14		0.44 (0.59)	
1975				21		0.25 (0.33)	
				30		0.11 (0.15)	
			1	1	Whole fruit	1.3 (1.9)	
				7	(pulp)	0.81 (1.1)	
Olives				14		0.11 (0.16)	
				21		0.04 (0.06) 0.07 (0.01)	
Olives (for oil)		1	1	1	Whole fruit	2.2 (3.50)	Mestres, 1976
France				7	(pulp)	0.75 (1.1)	
1976				14		0.6 (0.9)	
				20		0.27 (0.42)	
				28		0.13 (0.22)	
				35		0.23 (0.45)	
				42		0.07 (0.13)	
		1.5	1	1	Whole fruit	4.3 (6.6)	
				7	(pulp)	1.5 (2.2)	
				14		0.9 (1.4)	
				20		0.53 (0.9)	
				28		0.34 (0.56)	
				35		0.29 (0.57)	

Commodity Country Year	Application			PHI, days	Sample	Residue, mg/kg	Reference Remarks
	Rate, kg ai/ha	Conc., g ai/l	No.				
				42		0.21 (0.40)	
Olives <sup>1</sup> (for oil)	-	3.0		10	Whole fruit (oil)	0.77 (2.5) 0.44 (1.5)	Batchelder, 1966
Greece 1965				15		0.6 (2.1) 0.57 (2.4) 0.25 (1.4) 0.54 (2.1)	
Olives (for oil)	-	1.0	1	1	Whole fruit (pulp)	1.7 (3.0) 0.4 (0.73)	Mestres, 1977
Italy 1976				15		0.19 (0.31)	
				22		0.14 (0.24)	
				29		0.09 (0.15)	
	-	1.5	1	1		2.5 (4.5)	
				8		1.1 (1.9)	
				15		0.54 (0.93)	
				22		0.19 (0.31)	
				29		0.16 (0.25)	
	-	2.0	1	1		4.5 (7.6)	
				8		1.7 (3.1)	
				15		0.59 (0.96)	
				22		0.34 (0.55)	
				29		0.25 (0.40)	
	-	3.0	1	1		5.8 (9.7)	
				8		1.5 (2.7)	
				15		0.58 (0.95)	
				22		0.25 (0.40)	
				29		0.12 (0.19)	
Olives <sup>2</sup> (green)	-	1.25	4	6	Whole fruit	>20 (0.7)	Agallauel, 1977
Spain 1976				13		0.8 (0.04)	
				20		0.5 (<0.02)	
				27		<0.02 (<0.02)	

<sup>1</sup>Phosphomolybdate spectrophotometric method. Mean of three replicates

<sup>2</sup>Phosmet oxon residues were 0.3 and 0.7 mg/kg at 6 days PHI and in the range <0.02-0.07 mg/kg at other intervals

Table 11. Residues of phosmet from supervised field trials on kiwifruit in New Zealand.

Year	Application			PHI, days	Residues, mg/kg	
	Rate, kg ai/ha	Conc., g ai/l	No.		Whole fruit	Flash
1974-75 <sup>1</sup>	1.12		2	10	5.8-9.5	0.5-1
	1.12		7	10	7.2-25	0.8-2.5
1976	0.75		7	10	4.8-8.8	0.3-1.3
	1.6-1.7		6	1	5-11	
				7	4-8	
				14	3-8	
				24	5-7	
				35	3-4	
1976	3.7-3.8		6	1	14-27	
				7	14-18	
				14	18-36	
				24	10-12	
				35	10-18	

<sup>1</sup>Abbott and Hayward varieties

Peas (Table 12). Peas were grown in three separate sub-plots in the Washington and Oregon states, and treated three times with 'Imidan' 50 WP at a nominal rate of 1.12 kg phosmet/ha (about 1.5 times the recommended rate) with 7-8 days between applications. Peas, pods and forage were sampled 7 days and dry pea hay 10 days after the last application (Dykeman, 1994e). The samples were analysed for phosmet and phosmet oxon by a GLC with flame photometric detection.

Table 12. Residues of phosmet in peas from supervised trials. in the USA with 50 WP formulations, 1993 (Dykeman, 1994e).

Commodity	Application			PHI, days	Sample	Residue, mg/kg in replicate analytical samples
	Rate, kg ai/ha	Conc., g ai/l	No.			
Peas <sup>1</sup> (succulent)	1.12	-	3	7	Peas Pods Forage	<0.05 (3) 0.2, 0.51, 0.30 3.0, 2.7, 5.7
Peas <sup>2</sup> (succulent)	1.12	-	3	7	Peas Pods Forage	<0.05 (3) 0.26, 0.19, 0.15 3.5, 3.6, 3.1
Peas <sup>2</sup> (dried)	1.12	-	3	7 10	Peas <sup>1</sup> Hay <sup>3</sup>	0.068, 0.084, 0.063 17, 13.6, 10.9
Peas <sup>2</sup> (dried)	1.12	-	3	7 10	Peas <sup>1</sup> Hay <sup>4</sup>	<0.05 (3) 3.3, 2.5, 4.0

<sup>1</sup>Residues of phosmet oxon all <0.05 mg/kg

<sup>2</sup>See also Table 13 (Forage crops)

<sup>3</sup>Residues of phosmet oxon 0.16-0.28 mg/kg

<sup>4</sup>Phosmet oxon 0.06-0.08 mg/kg

Potatoes. Several trials were carried out in The Netherlands (1970), the USA (1970, 1973, 1974 and 1975) and Canada (1970). Some of the data were reported to the 1976 and 1978 Meetings. Only one residue (0.04 mg/kg) was above the limit of determination of either the parent compound or its oxygen analogue.

Supervised trials were carried out in five different States of the USA in 1993 on three varieties of potato. At each site there was an untreated plot and a treated plot divided into three sub-plots, samples from which were analysed separately. 'Imidan' 50 WP was applied one to five times at nominal rates ranging from 0.56 to 1.56 kg phosmet/ha, with 10-14 days interval between applications. Samples of tubers taken 7 to 85 days after the last application were analysed for phosmet and phosmet oxon by GLC. No residues of phosmet or its oxon (<0.05 mg/kg) were found in any of 71 samples from 24 sites (Dykeman, 1994g, 1995b; Potato summary report R3/49).

In a separate trial for a processing study (see below) potato plants were sprayed with 'Imidan' 50 WP four times at 1.12 kg ai/ha and once at 4.5 kg ai/ha and the tubers harvested 7 days after the final application. Residues of phosmet in tubers from the three treated sub-plots were 0.09-0.11 mg/kg and those of phosmet oxon were all <0.05 mg/kg (Dykeman, 1994f).

Two trials in 1994 in the States of Maine and Washington were to compare the residues resulting from the application of the 50 WP and 2.5 EC formulations. The formulations were applied five times at 1.12 kg phosmet/ha, with 10-14 days between applications. Samples of mature potato tubers harvested 7 days after the final application contained no quantifiable residues of phosmet or its oxon (Dykeman, 1995b).

Tree nuts. Data on trials on tree nuts were presented to the 1978 JMPR. It was reported that the residues in almonds, filberts, pecans and walnuts were all below 0.08 mg/kg in the nut meat, most being in the range 0.01-0.05 mg/kg. Residues in almond hulls ranged up to 5.6 mg/kg (FAO/WHO, 1979).

In a supervised residue trial in 1994 in California, walnut trees were treated five times with Imidan 70 WP at a nominal rate of 6.72 kg phosmet/ha with 18-21 day intervals between applications (three replicate plots of two trees with an untreated control plot). Samples of walnuts taken from the replicate plots 14 and 27 days after the final application were analysed for phosmet and phosmet oxon by GLC with flame photometric detection. No residues (<0.05 mg/kg) of phosmet or phosmet oxon were detected in five samples; the sixth, taken at day 14, contained 0.06 mg/kg phosmet (Dykeman, 1995a).

Cotton seed. Six supervised trials were carried out on cotton in Brazil in 1992 with five spray applications of PM and SC formulations at rates between 0.75 and 2.25 kg ai/ha (1.5-4.5 times the Brazilian GAP rate). Residues of phosmet in all the seed samples were <0.05 mg/kg at harvest 15 or 21 days after the last application (Suchek, 1993b).

Fodder crops (Table 13). Supervised residue trials have been reported on a variety of crops for animal consumption: alfalfa (USA), Bermuda grass (USA), lupins (Australia), maize (USA), peas (Australia and USA), rape (Australia) and soya beans (USA). A number of the trials were evaluated by the JMPR in 1976, 1978 and 1984.

Table 13. Residues of phosmet in fodder and forage crops from supervised trials.

Commodity Country or State Year	Application			PHI, days	Residue, mg/kg		Ref/Report no.
	Form. Rate, kg ai/ha	Conc., g ai/l	No.		Phosmet	Oxon <sup>1</sup>	
Alfalfa fresh plant							
	3EV, 0.56		1	1	8.9, 13.8		3157
1962				3	0.88, 1.0		
Alabama				7	0.27		
	1.12		1	1	93, 93		
				3	14, 24		
				7	0.42, 0.65		
				13	0.3		
Alabama	3 EV		1	1	148, 175		3724
1963	1.12			7	9.9, 10.6		
				14	1.8, <u>2.1</u>		
Alabama	3 EV		1	1	64, 105		3724
1963	1.12			7	4.4, 5.5		
				14	0.76, <u>0.84</u>		
Alabama	3 E		1	1	38, 45		3778
1963	1.12			7	3.2, 3.7		
				14	<0.2, <u>0.21</u>		
				21	<0.2, <0.2		
Alabama	3 E		1	1	7.2, 19		3778
1963	1.12			7	1.3, 1.5		
				14	<0.2, <u>0.24</u>		
				21	<0.2, <0.2		
Md. 1962	3 EV		1	1	64		3826
	1.12			7	16		
				14	<u>1.6</u>		
Md. 1963	3 E		1	1	64		3969
	1.12			7	12.3		
				14	<u>2.1</u>		
				21	2.43		
Md. 1963	3 EV		1	1	126		3827
	1.12			7	13		
				14	<u>2.2</u>		
N.Y. 1964	36% EC		1	1	46.7, 40.2		Alfalfa report R3/16 (A1904)
1965	1.12			8	2.5, 1.7		
				14	0.44, <u>0.84</u>		
				27	<0.4, <0.4		

Commodity Country or State Year	Application			PHI, days	Residue, mg/kg		Ref/Report no.
	Form. Rate, kg ai/ha	Conc., g ai/l	No.		Phosmet	Oxon <sup>1</sup>	
Nebraska	50 W		1	1	12, 18	0.05, 0.04 <sup>2</sup>	B-002
1967	0.56			7	<0.01, 0.33		B-0001
				14	0.12, 0.21		
				21	1.2, 0.22		
Nebraska	50 W		1	1	59, 110 <sup>2</sup>	0.27	B-002,
1967	1.12			7	0.5, 0.88		B-001
				14	0.19, 0.21		
				21	0.54, 0.05		
1967	50 W		1	1	50	0.12	A-0440
	1.12			7	1.4		
				14	0.26		
				21	0.15		
1967	50 W		1	0	58, 75	0.43, 0.52	A-02030
	2.24			7	5.7, 5.7	0.04, 0.04	
				14	0.8, 0.87		
				21	0.11, 0.11		
Pennsylvania	3 E		1	1	67		3972
1963	1.12			7	9.1		
				15	0.77		
Virginia	50 W		1	0	101	0.34	A-0447
1967	1.12			7	9.9	0.06	
				14	1.2		
				21	0.42		
New Jersey	3 E		1.	0	42	0.12	A-0405
1967	1.12			7	0.57		
				14	0.4		
				21	<0.01		
Florida	50 W		1	1	4.4, 4.5	0.1, 0.12	B-0102
1967	1.12			7	0.77, 14	0.04	B-0104
				14	3.0, 3.5	0.04, 0.07	B-0106
				21	0.38, 0.50	0.03	B-0108
1968	50 W	2.24	1	0	86	0.67	A-0479
				7	32	0.39	
				14	0.13		
				21	2.6	0.1	
				28	1.3		
Alfalfa hay							
	3 E		1	7	0.27, 6.6		3968
N.Y. 1963	1.12			15	<0.2, 0.59		
				33	<0.2, <0.2		
Pennsylvania	3 E		1	1	31, 80 <sup>1</sup>		3971, 3972
1963	1.12			7	11, 3.2		
				15-16	0.6, 1.1		
New Jersey	3 E		1.	3	61	1.53	A-0405
	1.12			10	0.77		
				17	0.15		
				24	0.2		
Iowa 1967	50 W		1	0	29.5	0.15	B-0003
	0.56			7	0.015		B-0012
				14	1.5		B-0013
	1.12		1	0	71	0.26	B-0003
				7	0.07		B-0012
				14	4.5		B-0013

Commodity Country or State Year	Application			PHI, days	Residue, mg/kg		Ref/Report no.
	Form. Rate, kg ai/ha	Conc., g ai/l	No.		Phosmet	Oxon <sup>1</sup>	
Lupins (whole plant analysed)							
Australia 1991	0.053	-	2	7	0.14		Marcus 1992a
	0.105	-		14	0.07		
	0.053	-	2	7	0.50		
	0.105	-		14	0.09		
Peas <sup>3</sup>							
Australia Whole plant	150 EC	-	2	7	1.1, 2.0		Markus, 1992b
1991	0.053			14	3.1		
Seeds and Pods	0.105	-	2	7	4.4		
				14	4.1		
	0.053	-	2	7	0.22, 0.18		
				14	0.10, 0.11		
	0.105	-	2	7	0.44		
				14	0.27		
Rape (whole plant analysed)							
Whole plant	0.053	-	2	3	0.39		Markus, 1991
Australia 1988				7	0.20		
				14	0.14		
				24	0.06		
	0.105	-	2	3	1.1, 1.2		
				7	0.38, 0.50		
				14	0.14, 0.12		
				24	0.07, 0.07		

<sup>1</sup>Oxon residues below the limit of detection are not reported

<sup>2</sup>Oxon max. 0.5 mg/kg at day 0

<sup>3</sup>See also US data in Table 12.

## FATE OF RESIDUES IN STORAGE AND PROCESSING

### In processing

Studies have been carried out to determine the effect of processing on phosmet residues in apples, apricots, peaches, prunes, grapes, olives and potatoes.

**Apricots.** Three field trials were reported in which apricot trees were treated once with 2.8 kg ai/ha and the fruits sampled 14 days later. The fruits were dried and analysed about a year later. The phosmet residues were 0.29, 0.63 and 1.63 mg/kg. Phosmet oxon (0.19 mg/kg) was detectable only in the last sample.

**Apples.** A field trial was conducted in the apple-growing region of Washington, USA. One plot of apple trees was treated with nine applications of 'Imidan' 50 WP at 4.48 kg ai/ha per application, giving a total of 40 kg ai/ha (1.2 times the maximum allowed amount). The last application was made seven days before harvest as required by the current US label. Apples were harvested and shipped fresh and chilled to a pilot-scale food processor which converted the whole unwashed raw apples into the processed products within 14 days.

Whole unwashed raw apples and apple products were stored frozen until analysis. Samples were analysed for phosmet and phosmet oxon by gas chromatography with a limit of determination of



0.05 mg/kg for each compound. The mean recoveries of phosmet and phosmet oxon from fortified samples were 92% and 100% respectively. The fortification range was from 50 to 0.05 mg/kg; all recoveries were above 70%. The results are shown in Table 14 (Meyers *et al.*, 1991a).

Table 14. Phosmet and phosmet oxon residues in processed apple products.

Sample	Residue, mg/kg	
	Phosmet	Oxon
Unwashed raw apples (duplicate samples)	14, 12	<0.05, <0.05
Washed apples	15.5	0.090
Peeled sliced apples	1.05	<0.05
Canned sliced apples	0.32	<0.05
Canned apple sauce	0.95	<0.05
Ground apple slurry	11	<0.05
Unclarified apple juice	5.35	<0.05
Canned unclarified apple juice	5.4	<0.05
Filter cake	16	0.055
Canned clarified apple juice	1.4	<0.05
Wet pomace	29	0.072
Dry pomace	89, 88	0.25, 0.25
Dried apples	1.2	<0.05
Peels and cores	43	0.068

Grapes. Four applications of Imidan 50 WP, an average of 7 days apart, were made at a nominal rate of 3.4 kg phosmet/ha (three times the maximum label rate for grapes in western USA) and samples were taken 7 days after the final application (Dykeman, 1994d).

Grapes were processed into raisins and raisin waste by sun-drying in California, and into wet and dry pomace. Samples were analysed for phosmet and phosmet oxon. The results are shown in Table 15.

Table 15. Residues of phosmet and phosmet oxon in processed fractions of grapes.

Sample	Compound	Residue, Range, mg/kg	Mean residue, mg/kg	Mean total toxic residue, mg/kg
Grapes	Phosmet	3.8-4.3	4.1	4.2
	Phosmet oxon	0.05-0.07	0.06	
Raisins	Phosmet	3.0-3.8	3.4	3.8
	Phosmet oxon	0.39-0.48	0.43	
Raisin waste	Phosmet	41-45	42	48
	Phosmet oxon	5.2-6.0	5.5	
Grapes (Engler) <sup>1</sup>	Phosmet	2.6-2.8	2.7	2.7
	Phosmet oxon	<0.05(3)	<0.05	
Wet pomace	Phosmet	7.6-8.7	8.2	8.3
	Phosmet oxon	0.10-0.11	0.10	
Dry pomace	Phosmet	15-17	16	15.9
	Phosmet oxon	0.11-0.13	0.12	

Separate grape samples from the field test facility and stored at the pomace processor.

Peaches. In a field trial in the peach-growing region of Oregon, USA, one plot of peach trees was treated with ten applications of Imidan 50 WP at 3.36 kg ai /ha per application, a total of 33.6 kg ai/ha (about 3 times the recommended maximum). The last application was made 14 days before harvest according to the current US label. Whole unwashed raw peaches were shipped fresh and chilled to a pilot-scale food processor and converted, within two days, into the processed products and wastes: washed peaches, peach pits, first rinse water and peels, peeled raw peaches before canning, canned peaches and dried peaches.

Whole unwashed peaches and their processed products were stored frozen until analysis for phosmet and phosmet oxon with a limit of determination of 0.05 mg/kg for each compound. The results are shown in Table 16.

The residue of phosmet oxon was only 1-2% of that of phosmet. The mean recoveries of phosmet and phosmet oxon from samples fortified in the range 0.05-5.0 mg/kg were 89-101% (Meyers *et al.*, 1991b).

Table 16. Phosmet and phosmet oxon residues in products of peach processing.

Sample	Residue, mg/kg	
	Phosmet	Oxon
Unwashed raw peaches	13, 10	0.082, 0.072
Washed peaches	11	0.20
Peach pits (stones)	<0.05	<0.05
First water rinse and peels	<0.05	<0.05
Peeled raw peaches before canning	0.18	<0.05
Canned peaches	0.08	<0.05
Dried peaches	0.39, 0.30	<0.05, <0.05

In dried peaches the phosmet residue was 11 mg/kg following two field treatments with 2.8 kg ai/ha, and a PHI of 7 days (Report No. B-0180).

Olives. In supervised trials in Greece in 1965 and Spain in 1976, olives received five treatments at 1.25 or 2.5 g ai/l corresponding to about 1.7 and 3.3 times the maximum application allowed by current Spanish GAP.

The harvested olives were washed with hot water and pressed. Water was separated from the pressed oil by decantation. For deodorization and decolorization, steam was bubbled through the crude oil and volatiles were removed under vacuum, the exact process depending on the quality category. Export quality refined oil, obtained by several steam treatments and a vacuum treatment, usually contains <0.1% "acid".

Olives and crude olive oil analysed for phosmet residues from trials in Greece in 1965 gave the results shown in Table 17 (Batchelder, 1966).

Table 17. Phosmet residues in olives and crude olive oil (Greece, 1965).

Treatment, g ai/l	PHI, days	Phosmet residues, mg/kg	
		Olives	Greek olive oil
1.25	10	0.77	2.5
		0.44	1.5
		0.60	2.1
1.25	15	0.57	2.4
		0.25	1.4
		0.54	2.1

The olives from the Spanish trials were harvested 9, 16, 23 and 30 days after the last of five spray applications at 1.25 or 2.5 g ai/l. The crude oil contained the residues of phosmet and phosmet oxon shown in Table 18. The residues in the olives before processing were not reported.

Table 18. Phosmet residues in olive oil after spraying with "midan 50W, 1976.

Application		PHI, days	Residues, mg/kg, in crude olive oil	
Rate, g ai/l	No.		Phosmet	Oxon
1.25	5	9	5.5	<0.1
		16	<0.4	<0.1
		23	7.6	1.0
		30	5.5	<0.1
2.5	5	9	7.6	<0.1
		16	10.0	0.4
		23	7.6	<0.1
		30	7.6	<0.1

Bulked samples of the oil from the 30-day PHI, together with other oils from olives treated at higher rates, were purified to obtain a "neutral" oil and analysed for phosmet residues with the results shown in Table 19 (Pereiro, 1978).

Table 19. Effect of "neutralizing" crude olive oil on residues of phosmet.

Rate, g ai/l	Phosmet, mg/kg	
	Not neutralized	Neutralized
2.5	6.3	<0.02
5.0	10.7	3.7
10	15.3	4.2

Potatoes. For a processing study on potatoes, Imidan 50 WP was applied to the foliage of growing potato plants four times at the maximum recommended rate of 1.12 kg ai/ha and once at four times that rate (4.5 kg ai/ha), with 11-13 days between applications. Potato tubers were harvested for analysis and processing 7 days after the final application. The trial took place in Washington State, USA, in 1993. Tubers were processed, simulating industrial operations as closely as possible, to yield potato chips, wet peel, dry peel and potato granules. Samples were analysed in triplicate. The residues of phosmet are shown in Table 20 (Dykeman, 1994f). The residues of phosmet oxon were below the limit of quantification (<0.05 mg/kg) in all the samples.

Table 20. Phosmet residues in fractions from processed potatoes.

Sample	Phosmet, mg/kg	Mean, mg/kg
Washed tubers	0.092	0.099
	0.095	
	0.11	
Chips	<0.05(3)	<0.05
Wet peel	0.10	0.095
	0.094	
	0.087	
Dry peel	0.36	0.323
	0.30	
	0.31	
Granules	<0.05(3)	<0.05

Oxon residues were all <0.05 mg/kg

Prunes. In a study in California in 1993 three replicate plots in a prune orchard were treated with "Imidan 50WP four times at the maximum recommended rate of 3.4 kg ai/ha, with an average of 14 days between applications.

Fresh prunes were processed to dried prunes and both commodities were analysed for phosmet and phosmet oxon. The residues of phosmet are shown in Table 21. Phosmet oxon was not detectable in any of the samples.

Table 21. Residues of phosmet in fresh and dried prunes.

Commodity	Phosmet, mg/kg	Mean, mg/kg
Fresh prunes	2.6	2.63
	2.7	
	2.6	
Dried prunes	0.72	0.82
	0.82	
	0.92	

Residues of phosmet oxon were in all cases <0.05 mg/kg

The lower residue in dried prunes is not surprising despite the loss of moisture since the prunes were dried at a temperature of 54-60°C for two days (typical commercial practice) which would be expected to contribute significantly to the breakdown of phosmet and phosmet oxon (Dykeman, 1994c).

## RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Information on residues found in food in commerce was submitted by The Netherlands for the period 1991-94. The results are shown in Table 22. Residues found in kiwifruit during monitoring in 1975-78 were tabulated in the 1979 Evaluations (FAO/WHO, 1980) and are repeated in Table 23.

Table 22. Phosmet residues detected in the Dutch monitoring programme during 1991-94.

Sample	Sample analysed	Number of samples with residues		
		<LOD	<MRL	>MRL
Oranges	1306	1289	17	0
Tangerines	738	724	14	0
Apples	2410	2390	20	0
Pears	663	654	9	0
Peaches	113	111	1	1
Nectarines	103	100	2	1
Plums	148	147	1	0
Grapes	999	997	1	1
Kiwi	309	304	5	0

Table 23. Phosmet residues in kiwifruit in commerce (FAO/WHO, 1980).

Year	No. of samples (different growers)	Residues, mg/kg	
		Mean	Range
1975	20	3.8	0.3-10
1977	28	4.8	0.0-23
1978	9	2.2	0.0-9

## NATIONAL MAXIMUM RESIDUES LIMITS

The following national MRLs have been reported to the Meeting.

Crop group	Commodity	Country	MRL	PHI
Citrus fruit	Citrus	Netherlands	5	-
		USA	5	-
Pome fruit	Apples and pears	Australia	1	-
		Canada	10	-
		Netherlands	1	21

Crop group	Commodity	Country	MRL	PHI
		Switzerland	1	15
		USA	10	7
Stone fruit	Stone fruit	Australia	1	-
	Stone fruit	New Zealand	10	14
	Apricots	USA	5	-
	Cherries	Canada	7	-
		USA	10	-
	Nectarines	USA	5	-
	Peaches	Canada	10	-
		USA	10	-
		Plums	Canada	5
		USA	5	-
Small fruits and berries	Blueberries	USA	10	
		Netherlands	10	3
	Grapes	Canada	10	-
		USA	10	-
Tropical and sub-tropical fruit	Kiwifruit	Australia	15	-
		Netherlands	15	-
		New Zealand	15	21
		USA	25	-
Tree nuts	Nuts	Netherlands	0.1	-
		USA	0.1	-
Legume vegetables	Peas, fresh	Netherlands	0.2	
Root and tuber vegetables	Sweet potatoes (post-harvest use)	USA	10	-
		Netherlands	10	-
	Potatoes	Netherlands	0.05*	28
		Switzerland	0.05*	-
	USA	0.1	-	
Cereal grains	Fresh corn including sweet corn	USA	0.5	-
Tea		Netherlands	0.1*	
Fodder crops	Alfalfa	USA	40	-
	Field corn	USA	10	-
	Pea forage	USA	10	-
	Other commodities	Netherlands	0.05*	
Animal products	Meat and fat (cattle)	Australia	1	-
		USA	0.2	-
	Milk	Australia	0.2	-
		Netherlands	0.05*	-

\*At or about the limit of determination

## APPRAISAL

Phosmet has been evaluated at several Joint Meetings between 1976 and 1988. MRLs were recommended for a number of commodities of plant and animal origin. Updated information on GAP, and reports of supervised trials and studies of processing, metabolism and the stability of residues in stored analytical samples have been made available for evaluation within the CCPR periodic review programme.

Phosmet is a broad-spectrum organophosphorus insecticide used to control a variety of insect and mite pests which attack pome, stone and citrus fruit. It is also used on field, pasture and forage crops. Phosmet is non-systemic and acts by contact and ingestion as a cholinesterase inhibitor. It is registered in a number of countries, mainly for protecting fruits and vegetables. The direct use of phosmet on livestock for the control of warble fly, ticks and lice of cattle, resulting in residues in animal commodities, was not reported to the Meeting.

Carbonyl-labelled [<sup>14</sup>C]phosmet was used in studies of metabolism and environmental fate.

The absorption, distribution, metabolism and excretion of [ $^{14}\text{C}$ ]phosmet has been studied in rats, goats and hens. The chemical is rapidly absorbed, distributed and excreted, predominantly in the urine, in all three species. Biotransformation also appeared to be similar in the species studied. Hydrolysis of the phosphorus-containing moiety to yield *N*-mercaptomethylphthalimide is followed by methylation and oxidation at the sulfur atom to give sulfoxides and sulfones. These metabolites, together with *N*-mercaptomethylphthalimide, are hydrolysed to generate a series of phthalamic acids and finally phthalic acid.

The principal metabolites in tissues and milk reflect a single metabolic sequence: hydrolytic displacement of the phosphorus-containing moiety to yield *N*-mercaptomethylphthalimide, followed by methylation and oxidation of the thiol group. Hydrolytic degradation via *N*-hydroxymethylphthalimide also occurred. These reactions generated a series of phthalimide derivatives, which were hydrolysed to the analogous phthalamic acids. Treatment of extracted samples with hydrazine solubilized more than half of the bound residues. Solubilized products of hydrazinolysis consisted mostly of phthalohydrazide. The results indicate that bound residues in tissues and milk contain the *N*-substituted phthalimide moiety, with little or no chemical modification. Residues of phosmet do not accumulate significantly in edible tissues or eggs. Although the rat liver microsomal NADPH enzyme system readily converts phosmet to phosmet oxon, neither phosmet nor its oxygen analogue could be detected in the tissues of the goats or hens.

Lactating goats were dosed with [ $^{14}\text{C}$ ]phosmet at the equivalent of 8-8.8 ppm in the diet for four days. Most of each day's dose was recovered in the urine within the following 24 hours. In total, urinary excretion accounted for 60% of the cumulative dose. Less than 6% remained in the edible tissues at slaughter, 13-14 hours after the final dose. The total radioactivity ranged from 0.006 mg/kg phosmet equivalent in the fat to 0.24 mg/kg in the kidneys. Nine metabolites containing the phthalimide moiety were identified. Neither phosmet nor phosmet oxon was detected in the edible tissues (<0.002-0.003 mg/kg) or milk (<0.0004 mg/kg).

Laying hens dosed for seven days at a level equivalent to 10.5 ppm in the diet excreted 89.6% of the cumulative dose. Edible tissues collected at slaughter and eggs accounted for only 0.3% of the cumulative dose. In egg yolks the highest level of  $^{14}\text{C}$  (as phosmet equivalents) was 0.040 mg/kg on day 7, and in whites 0.007 mg/kg on day 4. At slaughter the levels of total radioactivity expressed as phosmet were 0.24 mg/kg in liver, 0.21 mg/kg in kidneys, 0.021 mg/kg in breast muscle, 0.015 mg/kg in thigh muscle, 0.005 mg/kg in fat and 0.068 mg/kg in blood. Phosmet itself was not detected (<0.005 mg/kg) in any of the edible tissues, but 0.001 mg/kg was found in egg yolks. None of the metabolites exceeded 0.005 mg/kg in the edible tissues or eggs. The metabolites identified in the edible tissues and egg yolks were phthalimide and phthalic acid.

Plant metabolism studies on sour cherries, cotton, maize and potatoes were reported. Forty four per cent of the applied radioactivity was absorbed by sour cherries within 4 hours. The main surface residue was the parent compound, while 16 or 17 metabolites occurred in the fruit. Phthalic acid was the major metabolite and accounted for 17-21% of the total radioactivity. Several other metabolites accounting for a small fraction of the radioactivity were identified. These included phosmet oxon, phthalimide, and phthalamic acid derivatives. No benzoic acid or ring-hydroxylated products were detected. Related conjugates of *N*-glycosylphthalimide accounted for 27-32% of the total radioactivity, but phthalic acid accounted for 85-90% of the extractable radioactivity after acid hydrolysis.

In maize the major part of the total residue was present in the maize fodder (267 mg/kg expressed as phosmet equivalent) and forage (31 mg/kg). Cobs (5 mg/kg) and grain (3 mg/kg) contained much lower residues. The metabolism of phosmet in maize involves various hydroxylation (oxidation), hydrolysis and conjugation reactions, giving products that are distinctly more polar than phosmet. The pattern of metabolites was similar in all parts of the plant, but their ratios varied. The parent phosmet amounted to 53% of the total residue in fodder, with the oxon (1.2%) and derivatives of phthalimide and phthalic acid present in small amounts, whereas in the grain phthalic acid was the single identified residue

(61%) and the parent compound was not detectable. Most of the radiocarbon in the unidentified metabolites (32.7%) was accounted for as phthalic acid after acid hydrolysis.

In potatoes the foliage contained most of the residue (14-109 mg/kg), and translocation to tubers (1.4-2.1 mg/kg) was limited. Phthalic acid and phthalamic acid were the major metabolites. Phosmet, its oxygen analogue and hydroxylated phthalic acids were not observed in any of the extracts.

The environmental fate of phosmet was studied in soil and water. Degradation in soil was studied under aerobic followed by anaerobic conditions. Under anaerobic conditions the degradation continued, but at a slower rate. The main components of the residue, expressed as phosmet equivalent, found in aerobic soil were phosmet (36.6%), phosmet oxon (0.5%), *N*-methoxymethylphthalimide (5.68%), *N*-methylsulfonmethylphthalimide (2.59%), *N*-hydroxymethylphthalimic acid (2.44%) and phthalimide (1.53%). In addition, 7 identified metabolites containing the phthalimide moiety (each <1%) and some unidentified intermediate products were also detected. Hydrolysis was shown to be an important factor in limiting the persistence of phosmet in soils, and the initial degradation products were metabolized by soil micro-organisms. After hydrolysis the aryl moiety, with or without a mercapto group depending on the point of cleavage, was further degraded through a variety of reactions including oxidation of the mercapto group to sulfonic acid, its methylation followed by oxidation to the sulfoxide, and imide bond cleavage. Ultimately, mineralization to carbon dioxide occurred. The products under aerobic and anaerobic conditions were largely the same.

Phosmet did not undergo significant photodegradation when exposed on thin layer plates of soil to natural sunlight for a period of 30 days.

Phosmet undergoes fairly rapid hydrolysis at ambient temperatures, with half-lives in water at 25°C of 7.5-9.7 days at pH 5, 9.4 hours at pH 7 and 5.5 minutes at pH 9. Degradation is enhanced by light.

The major hydrolysis products formed at pH 5 in the dark were *O,O*-dimethyl *O*-hydrogen phosphorodithioate (79.4 mol %), *O*-methyl *O,O*-dihydrogen phosphorodithioate, phthalamic acid, phthalimide, and phthalic acid. Following irradiation with a xenon lamp at pH 5, dimethyl hydrogen phosphate, (72.3 mol %), phosphoric acid, methyl dihydrogen phosphate, phthalimide, phthalamic acid and phthalic acid were detected. Other minor products were also detected but not identified.

Residues in rotational crops were studied in radishes, lettuce and wheat which were planted in the soil 30, 120 and 365 days after treatment with [*carbonyl*-<sup>14</sup>C]phosmet at a rate equivalent to 5.6 kg ai/ha. The total radioactive residue taken up by the plants varied from about 2% to 64% depending on the plant and the time between soil treatment and harvest. Neither phosmet nor its oxygen analogue were detected in the plant extracts. The radioactive residue consisted of a number of polar metabolites, most of which were characterized by chemical and enzymatic hydrolysis as esters or conjugates of phthalic acid.

The current analytical methods for residues are based on extraction with acetone or ethyl acetate, clean-up on charcoal, silica gel or SX-3 gel columns, and gas-chromatographic determination. Phosmet and its oxon are determined simultaneously. Recoveries are above 70%. The typical limits of determination in plant materials, milk and animal tissues are 0.01-0.05 mg/kg. In most of the supervised trials the LOD reported was 0.05 mg/kg.

Storage stability studies showed that phosmet is stable at  $-20 \pm 10^\circ\text{C}$  in almonds, apples, soya beans, and wheat grain and straw for a minimum of 2½ years and in alfalfa, maize, oranges, peppers and potatoes for a minimum of 2 years.

#### Definition of the residue

Phosmet is the major residue component; the oxon is either not detected or is less than 10% of the parent compound in most cases. In addition, the other metabolites are water-soluble compounds without the

phosphorodithioate group and are less toxic than the parent compound. The significant residue for both regulatory control and dietary intake purposes is therefore the parent compound.

The Meeting noted that phosmet was previously classified as fat-soluble. On the basis of its octanol/water partition coefficient and the distribution of residues between fat and meat, the Meeting concluded that the compound is not fat-soluble.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake:  
phosmet

### Supervised trials

Supervised trials were conducted on oranges in Argentina and Brazil. In the Argentine trials residues were determined in whole fruit, peel and pulp, but in Brazil only the pulp was analysed and the results cannot be used to estimate maximum residue levels. The application rate in the three Argentine orange trials corresponded with the current use pattern and resulted in residues in the whole fruits of 0.07, 0.13 and 0.32 mg/kg. The pulp did not contain detectable residues (<0.05 mg/kg) in any of the trials.

The data were too limited to estimate a maximum residue level for oranges, and since no residue data were provided for other citrus commodities, the Meeting recommended the withdrawal of the existing CXL for citrus fruits (5 mg/kg).

A number of trials were carried out on apples and pears in Brazil, Canada, Germany, The Netherlands, the UK and the USA. No GAP was reported for Germany, The Netherlands or the UK. Trials were according to current GAP in Canada (1.9 kg ai/ha) and the USA (1.7–4.1 kg ai/ha for apples; 1.7-5.6 kg ai/ha for pears) or at somewhat higher rates. The residues in the fruit were generally below 5 mg/kg at 7 days PHI. The residues in pears (1.7, 1.3 and 0.85 mg/kg) were lower than in apples. The Brazilian trials resulted in residues below 0.05 mg/kg in apples 14 days after application at single or double GAP rates. The residues in apples from the Canadian and US trials at approximately maximum GAP rates in rank order were 1.8, 1.8, 2.8, 3.3, 3.4, 3.4, 3.7, 4.2, 4.3 and 7.3 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg, and an STMR level of 3.4 mg/kg for apples. Owing to the lack of sufficient data, the Meeting concluded that no maximum residue level could be estimated for pears and recommended the withdrawal of the existing CXL (10 mg/kg).

Field trials on apricots, nectarines and peaches treated at rates up to 1.3 times the US GAP rate resulted in residues up to 6.8 mg/kg at 14 days PHI. The residues in apricots (♦) and peaches treated at 0.7-1.3 times the maximum rates according to Canadian and US GAP in rank order were 0.87, 1.2, 1.5, 1.6, 2.9, 4.2♦, 4.7♦, 6.4 and 6.8 mg/kg. The residues in nectarines were lower, 0.45 and 0.55 mg/kg, and could not be combined with those of apricots and peaches.

The Meeting estimated maximum residue levels of 10 mg/kg and STMR levels of 2.9 mg/kg for apricots and peaches, and recommended the withdrawal of the existing CXL for nectarines (5 mg/kg).

Following treatments at about 1-1.3 times current GAP rates, residues in plums of 0.41, 0.55 and 0.48 mg/kg, and in fresh and dried prunes of 2.3 and 2.2 mg/kg were reported. The information was insufficient to estimate a maximum residue level for plums (including prunes).

Grapes were treated at rates of 1.4-2.2 kg ai/ha which accord with GAP for the eastern states of the USA (1.5-2.5 kg ai/ha). Residues up to about 10.2 mg/kg were found 7 days after the last application and up to 9.2 mg/kg after 14 days. The residues from treatments according to GAP in rank order were 0.17, 0.24, 0.61, 2.8, 3.3, 4.0, 4.2 and 9.2 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 3.1 mg/kg for grapes.



In supervised trials on olives in France, Italy and Spain the residues declined to <0.02-0.34 mg/kg after PHIs of 28-30 days. The trials in France were evaluated against Spanish and Italian GAP. The residues from GAP applications in rank order were <0.02, 0.09, 0.12, 0.16, 0.24 and 0.34 mg/kg.

The available information indicates that a maximum residue level of 0.5 mg/kg and an STMR of 0.14 mg/kg for olives would be appropriate, but because there was no suitable supporting processing study the Meeting could not make any recommendation.

Of the supervised residue trials on kiwifruit carried out in New Zealand during 1974-76 only one complied with current GAP. The Meeting recommended the withdrawal of the CXL for kiwifruit (15 mg/kg).

In two supervised trials on peas carried out in two states of the USA, phosmet residues were below the limit of determination (<0.05 mg/kg) in succulent peas, <0.05-0.08 mg/kg in dried peas, 0.15-0.51 mg/kg in succulent pods, 2.7-5.6 mg/kg in succulent pea forage and 2.5-17 mg/kg in dry pea hay. Phosmet oxon residues were <0.05 mg/kg in peas and green forage, and 0.06-0.28 mg/kg in hay. The oxon residue was less than 10% of that of the parent compound.

The Meeting concluded that the data were not sufficient to estimate maximum residue levels, and recommended the withdrawal of the existing CXLs for peas (pods and immature seeds), peas (dry), pea hay or fodder (dry) and pea vines (green).

Numerous trials on potatoes in Canada, The Netherlands and the USA indicated that the translocation of the compound to the tuber was limited, and residues in the tubers following applications at recommended and double rates were <0.05 mg/kg. Residues up to 0.11 mg/kg were detected in trials at fivefold rates however, which indicates that this is not a nil residue situation.

The Meeting estimated a maximum residue level of 0.05\* mg/kg and an STMR of 0.05 mg/kg for potatoes. This is the level of the current CXL.

Residues from six supervised trials on cotton in Brazil at 1.5-4.5 times the GAP rate were all below the limit of determination (0.05 mg/kg).

The Meeting concluded that no detectable residue is likely to occur in cotton seed if GAP is followed, and estimated a maximum residue level of 0.05 mg/kg and an STMR level of 0 mg/kg.

Supervised trials were reported on alfalfa, Bermuda grass, lupins, maize forage, peas, rape and soya bean plants used for animal feed. Most of the trials were on alfalfa.

The residue data on forage and fodder crops showed that residues were generally high (commonly 40-80 mg/kg) immediately after application to alfalfa, but declined fairly rapidly. After 14 days they were mainly in the range 0.2-2 mg/kg. The residues of phosmet on lupins, maize, peas and rape were lower and generally below 2.0 mg/kg 7 days after the last application. The residues in fresh alfalfa from applications according to GAP in rank order were 0.13, 0.21, 0.24, 0.26, 0.3, 0.4, 0.77, 0.84, 0.84, 1.2, 1.6, 2.1, 2.1, 2.24 and 3.5 mg/kg. The Meeting did not estimate any maximum residue levels for animal feed items (see "Animal products" below).

The data, if any, were insufficient to estimate maximum residue levels in blueberries, feijoa, maize, maize fodder and forage, pea hay or fodder, sweet corn, sweet potatoes and tree nuts. The Meeting therefore recommended the withdrawal of the existing CXLs for these commodities.

Animal products. Although no detectable residues of phosmet or its oxon occurred in edible animal products in metabolism studies, the Meeting was not able to estimate any maximum residue levels for animal feeds or animal products because of the high residues in animal feed items and the lack of animal

transfer studies. Consequently, the Meeting recommended the withdrawal of the existing CXLs for alfalfa fodder and forage, cattle meat and milks.

### Processing

Studies have been carried out to determine the effect of processing on residues of phosmet in apples, grapes, peaches, olives, potatoes and prunes.

Field-treated apples containing 12-14 mg/kg phosmet residues were processed to unclarified and clarified juice and wet and dry pomace, which contained 5.3, 1.4, 29 and 89 mg/kg respectively. The oxon residue was less than 1% of the phosmet residue in all samples. Most of the phosmet residue is evidently in or on the peel, since processing decreased residues about 2.5-10 times in the products which were separated from the peel. Fractions which are normally processed with the peel, such as wet and dry pomace and the combined peels and cores, showed about a 2-6-fold concentration of the residues. The Meeting therefore concluded that maximum residues up to 60 mg/kg might occur in dry apple pomace.

Field-treated grapes were processed to raisins and raisin waste by sun-drying, and into wet and dry pomace. There was no concentration of the residue in the raisins but concentration occurred by factors of 12 in raisin waste, 3 in wet pomace, and about 6 in dry pomace.

Potatoes, treated with excessive amounts of phosmet to obtain detectable residues (0.1 mg/kg), were processed to yield potato chips, potato granules, wet peel and dry peel. There was no detectable residue in potato chips or granules (LOD  $\leq$  0.05 mg/kg). Residues in the wet peel were at the same level as in the washed potatoes, but were concentrated about threefold in the dry peel. This was accounted for by an 85% loss of moisture partly offset by the loss of some phosmet during drying (the theoretical residue would be 0.72 mg/kg).

Olives were processed to crude oil and neutralized oil. The residue in the crude oil was about four times that in the original olives, and purification ("neutralization") of the crude oil reduced the residues about threefold. The process used for neutralization was not reported, so the residues in the oil could not be used to estimate those likely to result from industrial processing. The Meeting concluded that the database was not sufficient to estimate maximum residue levels in crude or refined olive oil.

Fresh prunes were processed into dried prunes and both commodities were analysed for phosmet and phosmet oxon. The average phosmet residue in fresh prunes was 2.63 mg/kg, and in dried prunes 0.82 mg/kg. Phosmet oxon was not detectable in any of the samples. The decrease in dried prunes was attributed to the loss of residues during the drying process at 54-60°C, which more than offset the loss of moisture. Since it had not been possible to estimate a maximum residue level for fresh prunes the Meeting could not estimate one for dried prunes.

## **RECOMMENDATIONS**

The unchanged parent compound is the major residue component, phosmet oxon is either not detected or it is present in less than 10% of the parent compound in most cases. In addition, the metabolites are less toxic than the parent compound and they are water soluble compounds without the phosphorodithioate group. Therefore the significant residue for both regulatory control and dietary intake purposes is defined as the parent compound alone. The Meeting noted that the compound was previously classified as fat soluble. Based on its octanol/water partition coefficient and residue distribution in fat and meat, the Meeting concluded that the compound is not fat soluble.

Definition of residue for compliance with MRLs and for estimation of dietary intake: phosmet

Commodity		Recommendation			PHI, <sup>1</sup> days
		MRL mg/kg		STMR mg/kg	
CCN	Name	New	Previous		
AL 1021	Alfalfa forage green	w	40		
FP 0226	Apple	10	10	3.4	7
FS 0240	Apricot	10	5	2.9	7
FB 0020	Blueberries	w	10		
MM 0812	Cattle meat	w	1 (fat) V		
FC 0001	Citrus fruits	w	5		
SO 0691	Cotton seed	0.05		0	14
FI 0335	Feijoa	w	2		
FB 0269	Grapes	10	10	3.1	7-14
FI 0341	Kiwi	w	15		
AF 0645	Maize forage	w	10		
AS 0645	Maize fodder	w	10		
GC 0645	Maize	w	0.05		
ML 0106	Milks	w	0.02 V		
FS 0245	Nectarine	w	5		
AL 0072	Pea hay and fodder	w	10		
AL 0528	Pea vines green	w	10		
FS 0247	Peach	10	10	2.9	14
FP 0230	Pear	w	10	w	
VP 0063	Peas (pods and succulent seeds)	w	0.2		
VD 0063	Peas (dry)	w	0.02*		
VR 0589	Potato	0.05*	0.05	0.05	7
VO 0447	Sweet corn (corn-on-the-cobs)	w	0.05		
VR 0508	Sweet potato	w	10 (Po)		
TN 0085	Tree nuts	w	0.1		

<sup>1</sup>PHI on which the recommendations are based

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