

2-PHENYLPHENOL AND ITS SODIUM SALT (056)

EXPLANATION

2-Phenylphenol (ortho-phenylphenol, OPP), and sodium *o*-phenylphenate, SOPP, were first evaluated by the 1962 JECFA for their use for the post-harvest treatment of fruits and vegetables to protect against microbial damage during storage and distribution in commerce. A second evaluation by the 1964 JECFA provided specifications of the identity and purity of OPP and SOPP, and established an ADI. The 1969 JMPR recommended MRLs for 2-phenylphenol and its sodium salt in several fruits.

2-Phenylphenol was originally scheduled for periodic re-evaluation of residue aspects at the 1994 JMPR. The 1994 CCPR withdrew the compound from the agenda because the manufacturer (Bayer AG) indicated that it was not supporting the existing CXLs, and that the database was considered insufficient to support a periodic review. GAP was available only for citrus fruits and pears. Meanwhile the CCPR requested countries to submit additional data to support the MRLs, in the absence of which they would be deleted. The US delegation to the CCPR requested retention of the CXLs for citrus fruits and pears pending the development of additional information, and the delegate from Spain indicated an interest in an MRL for apples, so only these three CXLs were retained (ALINORM 95/24, para. 143-145). The California Citrus Quality Council (CCQC) and the Oregon Washington California Pear Bureau (now the Pear Bureau Northwest) undertook to support the extensive studies necessary for the re-registration of SOPP by the US EPA for the post-harvest treatment of fresh citrus fruit and pears grown in the USA.

At the 1995 CCPR the periodic re-evaluation of the residue data was scheduled for the 1999 JMPR (ALINORM 95/24A, Appendix IV). In 1997 the CCQC requested the WHO Joint Secretary to schedule a toxicological evaluation of additional studies with OPP/SOPP in experimental animals. The 1998 CCPR scheduled this evaluation for the 1999 JMPR, together with the periodic review of residue aspects. The 1998 CCPR noted that the CXL for apple would be considered for deletion at its next Session if not supported (ALINORM 99/24, para. 47).

The CCQC and the Pear Bureau Northwest provided, through Leng Associates of Midland, Michigan, USA, the information in support of the periodic review of 2-phenylphenol. Additional information was supplied by the governments of The Netherlands and Australia.

IDENTITIES

ISO common names:

2-phenylphenol (accepted in lieu of a common name)
2-phenylphenol-sodium

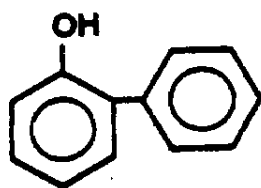
Chemical names:

IUPAC:	biphenyl-2-ol	IUPAC:	sodium biphenyl-2-olate
CA:	(1,1'-biphenyl)-2-ol	CA:	biphenyl-2-ol, sodium salt
CAS No:	90-43-7	CAS No:	132-27-4 (and 6152-33-6)

Synonyms:

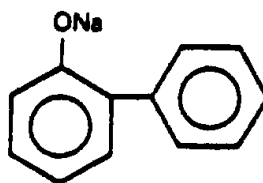
<i>ortho</i> -biphenylol, <i>ortho</i> -phenylphenol, OPP	sodium 2-phenylphenate, SOPP, SOPP•4H ₂ O
<i>ortho</i> -hydroxybiphenyl, 2-hydroxybiphenyl	sodium <i>o</i> -phenylphenate, NaOPP

Structural formulae:



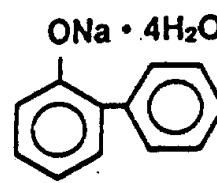
Molecular formula: C₁₂H₁₀O

Molecular weight: 170.2



Molecular formula: C₁₂H₉NaO (and •4H₂O)

Molecular weight: 192.2 (and 264.3)



Physical and chemical properties

Pure active ingredient (OPP)

Vapour pressure: 1.6 x 10⁻³ mm Hg
(2.16 x 10⁻⁴ kPa) at 25°C

Melting point: 57°C

Octanol/water partition coefficient:
log P_{OW}: 3.12 (20° C, pH 7)

Solubility, g/kg solvent (20°C):
0.76 in water (pH 5.67)
496 in methanol
479 in acetone
532 in acetonitrile
529 in octanol
466 in toluene
48.6 in hexane

Density: 1.2 g/ml at 25°C

Hydrolysis: stable (25°C, pH 5, 7, 9)

Photolysis: stable (10 days)

Technical OPP (Dowicide 1)

Purity: >99%

Appearance: white to light buff crystals

Commercial products

“Dowicide 1” Antimicrobial, >99% OPP,
The Dow Chemical Co., Midland MI USA

SOPP anhydrous

1.8 x 10⁻⁹ mmHg (2.4 x 10⁻¹⁰ kPa)
at 25°C

m.p.: 298°C (loss of H₂O at 120°C)

Dissociation constant (tetrahydrate):
pKa: 9.84 at 20°C

Solubility (tetrahydrate): g/kg solvent (20°C)
534 in water (pH 13.61)
526 in methanol
543 in acetone
531 in acetonitrile
439 in octanol
0.53 in toluene
0.047 in hexane

Dissociates in water

Photolysis: stable (10 days)

Technical SOPP tetrahydrate (Dowicide A)

Purity: >97% tetrahydrate

Appearance: white crystalline flakes

“Dowicide A” Antimicrobial, >97% SOPP as
tetrahydrate, The Dow Chemical Co., USA

“Preventol O Extra”, Bayer Corp., USA,
and Bayer AG, Leverkusen, Germany

“Preventol ON Extra”, Bayer Corp., USA,
and Bayer AG, Leverkusen, Germany

Formulations

Many formulated products containing OPP are registered in the USA and are approved world-wide for use as disinfectants, antimicrobials, preservatives, antioxidants, and sanitizing solutions in various industries.

Several formulated products containing SOPP are registered in the USA for the post-harvest treatment of fruits and vegetables to control microbial and fungal infections during storage and distribution.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Two lactating Nubian goats, 2 to 4 years of age, were given single daily oral encapsulated doses of [¹⁴C]2-phenylphenol, labelled in the hydroxylated ring (99.5% chemical and radiochemical purity), for 5 consecutive days at an average level of 13.7 or 53.3 mg/day (Thalacker, 1997). The doses were equivalent to 11.3 ppm (174,500 dpm/μg) and 32.1 ppm (179,300 dpm/μg) of the test material in the diet, based on the actual feed consumption during the test period. A third goat was given placebos. Milk, urine, and faeces were collected daily from each animal. The goats were slaughtered about 23 hours after the last dose, and samples of blood, kidneys, liver, muscle (round), fat (omental and renal, mixed), urine, and gastrointestinal tract were collected and stored at -20°C.

¹⁴C was measured in all the samples. The urine from days 1-5 contained 80-83% of the total administered radioactivity. The faeces contained 4.3% of the low dose and 10% of the high dose. The cage washes contained 7% of the radioactivity from the low dose and 1.3% from the high dose. More than 90% of the administered radioactivity was eliminated from both goats.

The radioactivity in the milk of both animals reached a plateau on day 1 or 2 equivalent to 0.03% of the dose, 0.008 μg/g as phenylphenol for the low-dose goat and 0.043 μg/g for the high-dose goat.

The concentrations of radioactivity in the tissues are shown in Table 1.

Table 1. Radioactivity in tissues after oral administration of [¹⁴C]phenylphenol to lactating goats for 5 consecutive days.

Sample	¹⁴ C, μg/g as phenylphenol	
	11.3 ppm rate	32.1 ppm rate
Fat	<0.0005	0.003
Kidneys	0.005	0.020
Liver	0.004	0.014
Muscle	<0.001	<0.001

Milk samples from each of the five days were extracted with acetone. The acetone was evaporated and the residual aqueous fraction partitioned with hexane. The radioactivity of each fraction was measured. The aqueous fraction contained 87% of the total radioactivity in the milk from the low-dose goat and 76% of that from the high-dose goat. The unextractable ¹⁴C was 5% for the low-dose and 9% for the high-dose goat. Liver and kidney samples were extracted sequentially with acetonitrile and methanol/water (80:20). The residual solids were dried and assayed for radioactivity. About 83% of the total radioactive residue in the kidneys of the low-dose goat partitioned into acetonitrile and 13% into the methanol/water fraction. The proportions were 94% and 8% respectively

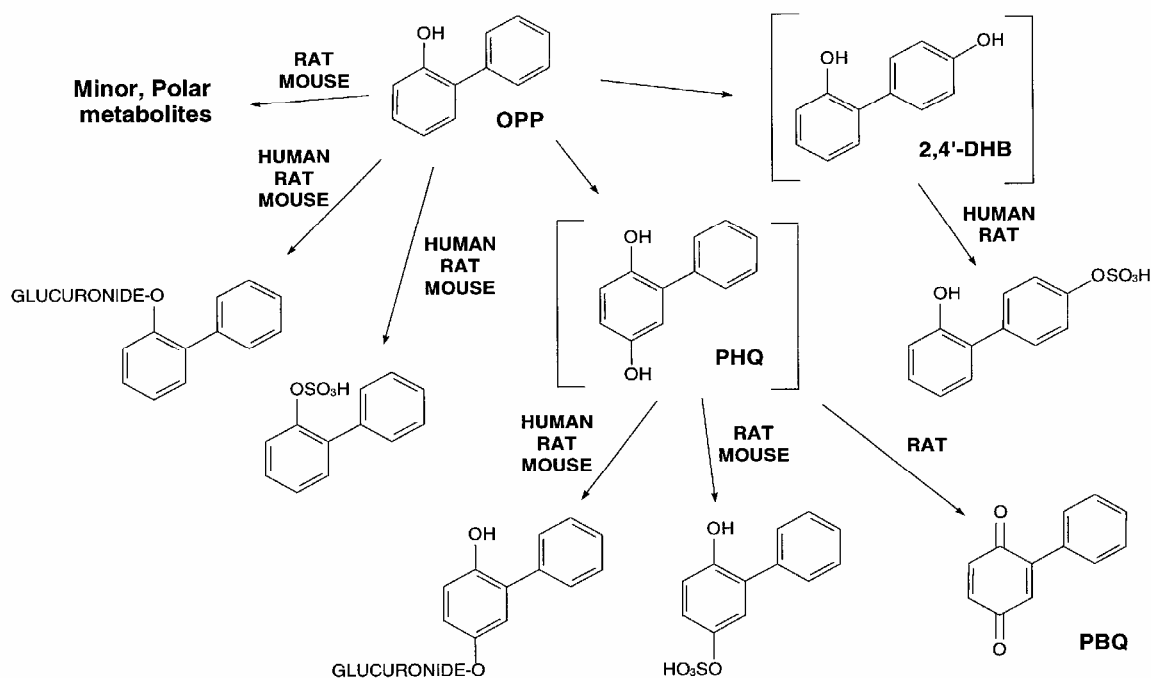
for the high-dose goat. In the liver samples 28% of the total radioactive residue partitioned into acetonitrile from the low-dose and 37% from the high-dose goat. About 20% partitioned into methanol/water from each goat. Unextractable ^{14}C amounted to 56% from the low dose and 45% from the high dose.

The extracts of milk, kidney and liver were analysed by HPLC, except the hexane extracts of milk because the levels of radioactivity were so low. Reference standards included phenyl-1,4-benzoquinone (PBQ), 2-phenylphenol and phenylhydroquinone (PHQ). Most of the attempted identification was by comparison with standards on a MicroBondapak C-18 column with a water/methanol (1.5% formic acid) gradient. No peak corresponded to any of the reference standards in any extract. The highest single residue detected was 0.007 mg/kg as OPP in the acetonitrile extract of kidneys. No other component accounted for more than 0.002 mg/kg.

The high dose rate, equivalent to 32 ppm in the feed, represents approximately six times the theoretical intake of OPP by cattle. This is based on the highest residue found in citrus trials according to GAP, 6.5 mg/kg, the average processing factor for converting oranges to dried pulp, 3.6, and the proportion of citrus pulp in the diet, 20%. At this six-fold rate more than 90% of the residue was eliminated. There was no propensity for the residue to accumulate in fat or muscle. Low levels were found in the milk (0.04 mg/kg), kidneys (0.02 mg/kg) and liver (0.01 mg/kg). The residues in these samples consisted of multiple components, none of which exceeded 0.007 mg/kg. Neither OPP nor PHQ were found. Measurable residues would therefore not be expected to result from the intake of OPP derived from uses according to GAP, assuming that additional bioaccumulation does not occur during exposure for more than 5 days.

The metabolism of 2-phenylphenol in rats, mice and humans was reviewed by Leng (1998). Studies conducted by the Dow Chemical Company and Bayer Corporation indicated the metabolic pathways shown in Figure 1. Metabolism studies have shown that OPP is absorbed well and excreted rapidly in the urine. The major metabolite excreted by rats is OPP sulfate with lesser amounts of the glucuronide conjugates of OPP and its hydroxylated metabolite, 2,5-biphenyldiol (phenylhydroquinone or PHQ). Trace amounts of phenyl-1,4-benzoquinone (PBQ) were also detected in the urine. Formation of the sulfate appeared to become saturated at a dose of about 600 mg/kg bw/day while the other conjugates increased in proportion to the dose up to the highest dose of about 1000 mg/kg bw/day. These metabolites were also found in the urine of mice given 5 daily doses of OPP at 25 or 1000 mg/kg bw and in human male volunteers given a dermal dose of [^{14}C]OPP at 0.006 mg/kg bw. The sulfate conjugate of 2,4'-biphenyldiol (2,4'-dihydroxybiphenyl, DHB) was also identified. Little or no free OPP, and no free PHQ or PBQ, were found in mice, rats or humans.

Figure 1. Metabolism of 2-phenylphenol (OPP) in rats, mice and man deduced from the analysis of urine.



A poultry metabolism study was not submitted, but current GAP does not include use on any poultry feed items.

Plant metabolism

Studies on oranges and pears were reported. Navel oranges (106, weighing from 145 to 191 g each) were dipped in a 0.1% solution and gently agitated for 3 minutes. The solution, maintained at 37°C, consisted of a mixture of ring-¹⁴C-labelled and unlabelled SOPP (Deccosol 122 concentrate) in distilled water adjusted to pH 11.8. The specific activity of the dosing solution was 8667 dpm/μg. This solution left a total residue of about 10 mg/kg on the oranges. Eight more oranges were dipped in a 0.5% solution. The oranges were air-dried on a stainless steel rack for about 2 hours and then packed into an incubator maintained at 90% relative humidity and 11.7°C. After four weeks the incubator temperature was lowered to 5°C to retard fruit spoilage.

Samples of eight oranges were collected after 2 hours, 2 days and 1, 2, 4, 6, 8, 10 and 12 weeks. Each orange was rinsed with methanol to remove surface residues, then peeled and cut into eight slices. The peeled oranges were processed through a juicer to yield juice and pulp, and the peels were chopped and homogenized in liquid nitrogen. The total radioactive residue was determined in each of the three substrates.

Homogenized peel (25 g) was extracted sequentially with hexane and methanol. The residual solid from the 12-week peel only was then sequentially incubated with cellulase (pH 5 buffer, 24 hours, 37°C), refluxed with 1 N HCl (110°C, 4 hours) and refluxed with 25% NaOH (110°C, 26 hours). At each step the aqueous filtrate was extracted with ethyl acetate. The juice from the 12-week sampling only and the pulp from the high-dose treatment (0.5% dip) were also extracted with ethyl acetate. All the extracts and residual solids were radioanalysed.

The methanol rinse and hexane and methanol extracts from the peel at every sampling interval, the ethyl acetate extract from the high-dose pulp and the ethyl acetate extract from the 12-week juice were analysed by reversed-phase HPLC on a Nucleosil 5 C-18 100 A column, with a UV detector (254 nm) and a flow-through radioactivity monitor. Fractions were also collected and analysed by LSC. TLC was also used for separation and purification with normal-phase silica plates, which were scanned with a radioanalytical imaging system. Reference standards were 4,4'-biphenyldiol, phenylhydroquinone (PHQ), 2,2'-biphenyldiol, phenyl-1,4-benzoquinone, OPP, 2-methoxybiphenyl (2-MBP) and dibenzofuran.

Various peaks isolated by HPLC, particularly from rinse samples, were analysed by GC-MS with a double-focusing magnetic sector spectrometer operated in the electron impact mode, connected to an Rt_x 1 column, 30 m x 0.25 mm i.d..

The change in distribution of the radioactive residue with time is shown in Table 2. The residue migrated from the surface of the oranges into the peel, but there was very little further translocation. Less than 0.5% of the TRR was found in the juice or pulp at any time.

Table 2. Distribution of radioactivity in oranges at intervals after a 0.1% dip treatment with radiolabelled OPP.

Time	TRR, mg/kg ¹	Rinse, % of TRR	Juice, % of TRR	Pulp, % of TRR	Peel, % of TRR
2 h	9.8	58	0.17	0.16	42
2 days	12	24	0.21	0.13	76
7 days	10	12	0.30	0.16	94
2 weeks	10	6.0	0.33	0.23	94
4 weeks	8.4	5.8	0.32	0.21	94
6 weeks	8.4	3.9	0.34	0.28	95
8 weeks	9.8	5.8	0.34	0.36	94
10 weeks	9.8	4.7	0.31	0.28	95
12 weeks	9.2	4.8	0.23	0.18	95
12 weeks- 0.5% dip	16	5.3	0.44	0.39	94

¹From ¹⁴C in all fractions of all 8 oranges at each sampling

The distribution of the radioactivity in the peel among the hexane, methanol and residual solid fractions changed with time. The hexane-soluble portion decreased from 88% at 2 h to 65% at 12 weeks, while the methanol-soluble portion increased from 4.3% to 30% and the insoluble fraction increased slightly from 0.54% to 2.5% over the same period.

The methanol rinse (4.7% of the TRR) from the 12-week sample of peel was analysed by TLC and HPLC. OPP constituted 1.3% of the TRR or 0.12 mg/kg, and 2-methoxybiphenyl 0.3% or 0.025 mg/kg. No other compounds could be identified.

The methanol extract of the 12-week peel contained phenylhydroquinone at 2.8% of the TRR or 0.25 mg/kg, and OPP at 1.0% of the TRR or 0.093 mg/kg. All the components in the other bands or peaks, including 25% of the TRR at a 6-minute HPLC retention time, remained unidentified. All the other regions of radioactivity were individually <3% of the TRR. The hexane extract was found to contain only OPP, at 62% of the TRR or 5.7 mg/kg.

In an effort to identify the 6-minute HPLC peak in the methanol extract of the 12-week peel the extract from the high-dose peel was hydrolysed with 1 N HCl. The product mixture was extracted with ethyl acetate, which recovered 98% of the radioactivity. Analysis by TLC and HPLC revealed OPP and PHQ, in a ratio of 88:12 by HPLC. This corresponds to 26% of the TRR as OPP and 3.6% as PHQ. Presumably the increase in the OPP from 1% to 26% may be attributed to a conjugate hydrolysed by the acid.

The high-dose methanol extract was also hydrolysed with β -glucosidase. In the ethyl acetate extract of the hydrolysate, containing 58% of the radioactivity in the original methanol extract, OPP was the only significant compound, indicating that some of the OPP conjugation was with glucose.

The twelve-week post-extraction solid (2.5% of the TRR; 4.3% of the high-dose TRR) was hydrolysed successively with cellulase, 1 N HCl, and 25% NaOH. Cellulase released 0.64% of the TRR, acid released 0.41%, and NaOH released 1.0%. The hydrolysates were not investigated further.

The ethyl acetate extracts of the pulp and juice from the 12-week samples were analysed by HPLC and TLC. The major compound was OPP, representing about 76% of the radioactivity in the pulp extract (0.14% of the TRR, 0.01 mg/kg) and about 51% of that in the juice extract (0.12% of the TRR, 0.01 mg/kg).

The identified radiolabelled compounds in the 12-week peel are shown in Table 3.

Table 3. Compounds identified in the peel of oranges dipped in OPP solution and stored for 12 weeks.¹

Compound	Methanol wash		Hexane extract		Methanol extract (including acid hydrolysate)		Total % of TRR identified	Total mg/kg identified
	% of fraction	% of TRR	% of fraction	% of TRR	% of fraction	% of TRR		
2-phenylphenol (OPP)	27	1.3	100	62	88	26	89	8.2
Phenyl hydro-quinone (PHQ)	-	-	-	-	22	3.6	3.6	0.33
2-methoxy biphenyl (2-MBP)	5.3	0.3	-	-	-	-	0.3	0.03
TOTAL							93	8.6

¹ The pulp and juice each contained 0.2-0.3% of the TRR, the major component of which was OPP.

In a metabolism study (Wu, 1995) a total of 153 pre-weighed Bosc pears were treated with a solution containing [¹⁴C]SOPP labelled in the phenoxide ring plus unlabelled SOPP (Steri-Seal D) at a total concentration of 40 g/kg in sodium silicate solution (pear float) adjusted to pH 13.3 and maintained at 0°C. The specific activity of the solution was 1,237 dpm/ μ g. A preliminary study had indicated that pears so treated and subsequently rinsed with water as recommended would contain a TRR of about 40 mg/kg OPP equivalent. All treated, rinsed pears were stored in sealed cabinets under controlled conditions of 90% humidity at 1-4°C and eight pears were removed at intervals from 2 h to 28 weeks. Each pear was rinsed with 150 ml of methanol to remove surface residues and peeled. The combined peels were homogenized in liquid nitrogen and the peeled pears were cut into slices, combined and homogenized in liquid nitrogen. The TRR in each sample was measured.

The peel and pulp samples were extracted twice with 4:1 acetonitrile/0.1N HCl and the extracts partitioned twice with methylene chloride, giving methylene chloride/acetonitrile (MeCl₂/ACN) and aqueous fractions. The distribution of ¹⁴C was determined in the initial rinse and in each extract by LSC and in the post-extraction solids (PES) by combustion. Initially 80% of the TRR was found in the rinse and 20% in the peel, with only 0.05% in the pulp. After storage, less radioactivity was found in the methanol rinse and more in the peel and pulp. The radioactivity in the pulp increased from 0.05% of the TRR at 2 h to 28% at 24 weeks, that in the peel increased to 66%, and that in the rinse decreased to 8.2%. Significant proportions of the radiolabel were translocated with time to both the peel and pulp.

The proportion of the TRR in the various extracts also changed with time. At 2 h after treatment the peel contained 20% (4.5 mg/kg as OPP), of which 95% was extracted into MeCl₂/ACN, 0.75% was in the water and 3.9% remained in the PES. After 28 weeks the peel contained 66% of the

TRR (27.7 mg/kg) of which 80% was extracted into the MeCl₂/ACN fraction, 10% was in the aqueous fraction and 9.2% was in the PES.

The pulp of pears stored for less than 4 weeks contained only low levels of radioactivity. At 8 weeks it contained 7.6% of the TRR (2.9 mg/kg as OPP), of which 39% was extracted into MeCl₂/ACN, 59% was in the aqueous extract and 1.8% was in the PES. At 28 weeks, the pulp contained 26% of the TRR (11 mg/kg OPP equivalent), of which 56% was in the MeCl₂/ACN extract, 44% in the aqueous fraction and 2.0% in the PES.

The post-extraction solid from the 28-week peel was sequentially hydrolysed with cellulase (37°C, 24 h), 1 N HCl (110°C, 2 h) and 6 N HCl (110°C, 24 h). Each product mixture was partitioned between water and ethyl acetate.

The methanol rinse and all the MeCl₂/ACN and aqueous extracts from the peel and pulp were examined by reversed-phase HPLC, with detection by UV (254 nm) and flow-through radioactivity detectors. Fractions were also collected at timed intervals and analysed by LSC. TLC on normal-phase silica gel plates was used for confirmation of identities and for purification of fractions. Developed plates were scanned with a bio-imaging analyser. Reference standards included 4,4'-biphenyldiol, phenylhydroquinone (PHQ), 2,2'-biphenyldiol, phenyl-1,4-benzoquinone, 2-phenylphenol (OPP), 2-methoxybiphenyl (2-MBP) and dibenzofuran. GC-MS with a double-focusing magnetic sector instrument operated in the electron-impact mode was used for the qualitative identification of some metabolites. Thermospray LC-MS was also used to analyse the rinse and the hydrolysate of the 28-week post-extraction solid of the peel for non-polar metabolites.

The findings are shown in Table 4. Metabolites A, B, C, D, E, F and G were identified as conjugates of OPP by isolation of each metabolite, acid hydrolysis, and analysis of the hydrolysate extract. They are most likely to be sugar conjugates. Dibenzofuran, 4,4'-biphenyldiol, 2,2'-biphenyldiol and phenyl-1,4-benzoquinone were not detected in any extract.

Table 4. Identification of compounds in extracts of pears dipped in OPP and stored for 28 weeks.

Sample	OPP		Metabolites A-F ¹		Metabolite G ²		Total identified	
	% of TRR	mg/kg ³	% of TRR	mg/kg ³	% of TRR	mg/kg ³	% of TRR	mg/kg ³
PEEL								
MeCl ₂ /ACN extract	3.2	1.4	44	18			47	19
Aqueous extract			6.8	2.9			6.8	2.9
EtOAc extract of PES cellulase hydrolysate			0.28	0.12	2.9	1.2	3.2	1.3
PULP								
MeCl ₂ /ACN extract	0.49	0.21	14	4.5			14	4.7
Aqueous extract			12	4.9			12	4.9
RINSE	2.6	1.1	1.3	0.56			3.9	1.7
Total	6.3	2.7	78	31	2.9	1.2	87	35

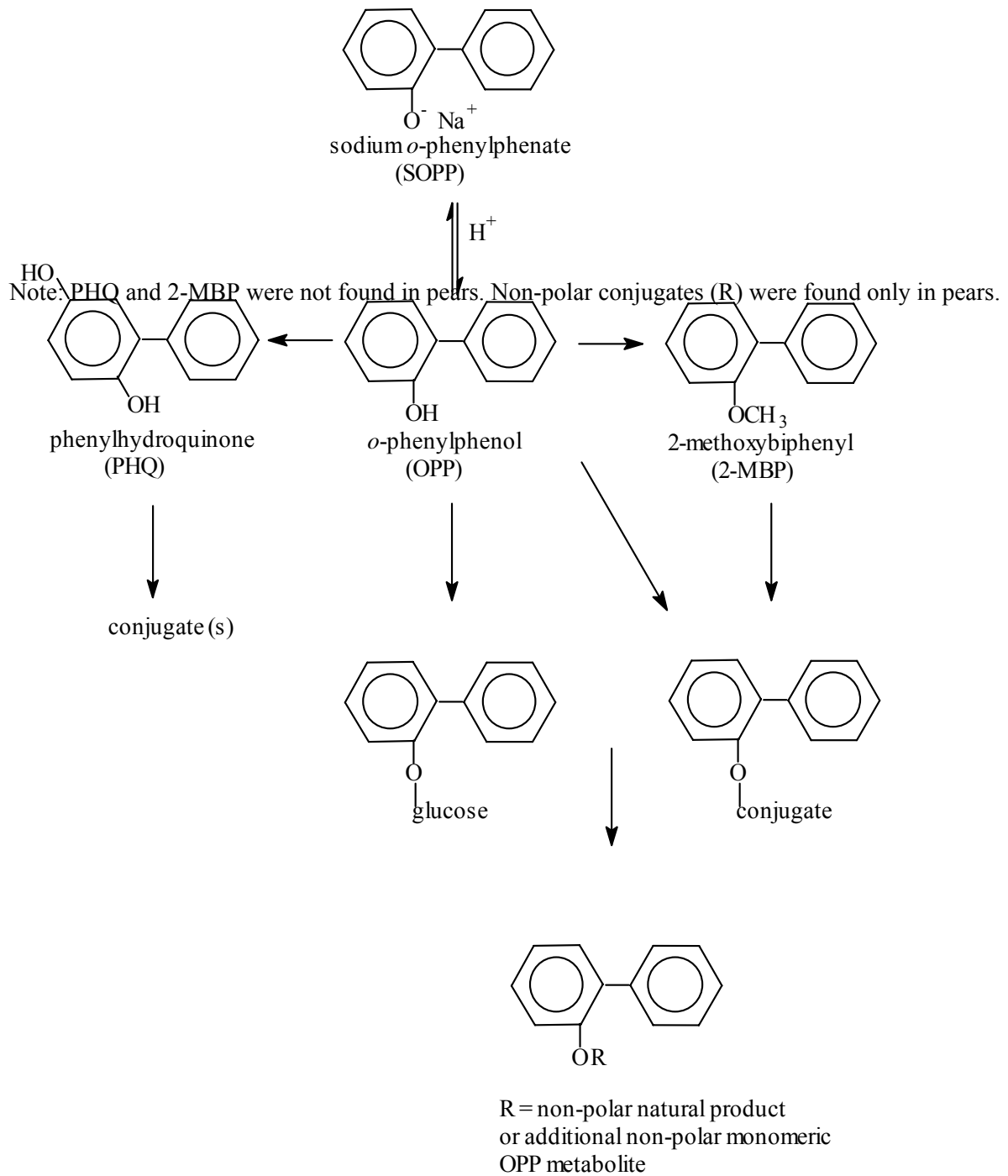
¹ Structures of metabolites A-F were consistent with OPP conjugates.

² Metabolite G was isolated from the ethyl acetate extract of the cellulase hydrolysate of the post-extraction solid. It was hydrolysed with 1 N HCl, purified, and examined by HPLC. The single peak corresponded to OPP. The purified G was also examined by LC-MS. The fragment ions were consistent with a glucose conjugate of OPP.

³ Expressed as OPP.

The metabolism of OPP by oranges and pears is consistent with the pathways shown in Figure 2. In oranges the radiolabelled residue showed no tendency to be translocated beyond the peel. After 12 weeks 95% of the total radioactive residue was in the peel 89% as OPP and 4% as PHQ. Less than 0.5% of the TRR was in the pulp and 76% of that was OPP. The situation was different with pears, where a significant proportion of the TRR was found in the pulp. After 24 weeks 28% of the total radioactive residue was in the pulp, 50% of which was OPP and its conjugates. No PHQ was found.

Figure 2. Metabolic pathways of OPP in pears and oranges.



Environmental fate in soil

OPP is not directly applied to the soil or to planted crops. Its use is for the post-harvest treatment of fruit. No studies were reported, but a review of the breakdown of OPP in soil was provided (Zbozinek, 1984). It is noted that exact information on the specific pathways of OPP metabolism by micro-organisms in soil is lacking, but it is postulated that the breakdown is similar to known pathways for biphenyl. OPP would be oxidized to 3-phenylcatechol which, by analogy with biphenyl, would be converted to acetaldehyde, pyruvate and benzoate. A different pathway involves transformation of OPP into stable polymers which eventually become part of the humus.

Environmental fate in water/sediment systems

The biodegradation of OPP in river water and activated sludge was studied by Gonsior *et al.* (1984). OPP was degraded completely within 2 days in a simulated biological wastewater treatment system at concentrations of 30 and 100 mg/l, but the antimicrobial properties of OPP slowed its degradation at concentrations above 100 mg/l. The biodegradability of OPP at concentrations expected to be found in the environment was determined with [¹⁴C]OPP uniformly labelled in the phenolic ring at concentrations of 123, 12.3 and 1.22 µg/l in water from the Tittabawassee river (Midland, MI), at 20°C in the dark. Analysis by HPLC at intervals showed a reduction to half the initial concentration within about 1 week. The ¹⁴CO₂ reached 50% of its theoretical maximum after 16 days. After 30 days incubation with HgCl₂ added to inhibit biological activity, [¹⁴C]OPP accounted for about 79% of the initial radioactivity in the river water sample; about 8% was from breakdown products extractable with methylene chloride and <0.2% had been converted to ¹⁴CO₂.

The rate of degradation of [¹⁴C]OPP was also studied at an initial concentration of 9.6 mg/l in activated sludge obtained from a wastewater treatment plant. A reduction to half the initial concentration was found within 24 and 3 hours in fresh sludge and sludge pre-treated for 6 days with unlabelled OPP respectively. The ¹⁴CO₂ evolved in 48 hours was two-thirds of the theoretical maximum production in both experiments.

In a 1997 study using a modification of the OECD Method 301B biodegradability test, [¹⁴C]OPP uniformly labelled on the phenolic ring was added at nominal concentrations of 0.2 and 1.0 mg/l to a mineral medium with a microbial inoculum from a municipal wastewater treatment plant. The concentration of suspended solids in the mixed liquor was 30 mg/l. The low concentrations of test material were needed to avoid potential inhibitory effects upon the micro-organisms. Extensive biodegradation of OPP was observed at 23°C in the dark: by day 11, two-thirds of the ¹⁴C added to the reaction mixtures was converted to ¹⁴CO₂. This met the guideline criterion for classification as readily biodegradable (60% of the theoretical ¹⁴CO₂ production obtained within a 10-day window in the 28-day test). The recovery of radioactivity after 28 days ranged from 76% from the killed controls to 87-88% from the biologically active mixtures. In the active reaction mixtures, mineralization to ¹⁴CO₂ accounted for 72-76% of the radioactivity, while 6-7% was incorporated into the biomass or adsorbed onto the solids and 6-8% remained in solution. Since <1% of the radioactivity was evolved as ¹⁴CO₂ in the killed controls, the mineralization was biologically mediated (Gonsior and Tryska, 1997).

METHODS OF RESIDUE ANALYSIS

Analytical methods

The government of The Netherlands supplied a reference to its official method for the determination of OPP (Ministry of Health, Welfare and Sport, 1996). An extract is analysed by GLC with an ion trap detector. Details were not provided. The limit of determination was stated to be 0.01-0.05 mg/kg, and the recovery from various commodities at 0.12 mg/kg to be 99%.

The colorimetric method 180.129 of the US Food and Drug Administration (FDA Pesticide Analytical Manual, 1987) determines OPP and its sodium salt in tomatoes, sweet potatoes and fresh

pineapples with an estimated limit of detection of 3 mg/kg. A 500 g sample is chopped and steam-distilled in 400 ml of water and 100 ml of 85% phosphoric acid. A known volume of the distillate is adjusted to pH 10.3-10.5 and diluted to 190 ml with sodium carbonate buffer. 4-Aminoantipyrine solution (2%, 1 ml) and potassium ferricyanide solution (2%, 1 ml) are added and the volume is adjusted to 200 ml. The absorbance at 500 nm is read after 7-10 minutes. Calibration is by external standards.

In a modification of the US FDA method (Smith, 1999) the distillate, without pH adjustment, is analysed by HPLC with a UV detector (280 nm). The eluant is methanol/water (65:35). No additional details were provided. The method was used for the determination of OPP in pear peel. Calibration was by external standards (0.025-0.50 mg/kg).

Another variation of the FDA procedure was applied to the analysis of citrus fruit by Tanaka *et al.* (1978). Five fruits are chopped and slurried, and 80 g of the slurry is mixed with 70 ml of distilled water, 10 ml heptane and 2 ml sulfuric acid. The mixture is steam-distilled and the distillate collected in traps of 15% sodium hydroxide. The solution in the traps is diluted with water to 500 ml and a 5 ml portion is neutralized and derivatized with pentafluorobenzoyl chloride. The reaction mixture is extracted with heptane and the extract together with 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene as internal standard, is analysed by GLC with an electron capture detector. The recoveries of OPP from lemons, oranges and grapefruit at fortifications of 5 and 10 mg/kg were 95-99%.

A GLC method for the determination of OPP residues in citrus fruit, kiwifruit and cantaloupes was supplied by Elf Atochem (1990). A mixture of 330 g slurried fruit, 15 ml concentrated HCl, antifoam drops, and 14 ml hexane is refluxed for 1.5 hours and distilled. The distillate is made alkaline with 5 N NaOH and partitioned with hexane after adding salt. The aqueous layer is adjusted to pH 2.0 with HCl and extracted with hexane. The final hexane extract is analysed by GLC with a 15 m x 0.53 mm DB-1 column and a flame ionization detector. Calibration is with external standards. The limit of determination is 0.10 mg/kg.

Several HPLC methods are described in the literature (Reeder, 1976; Farrow *et al.*, 1977; Ott, 1978). The most recent version was provided by Sunkist Growers, Inc. (1999). The method has been applied to Navel and Valencia oranges, lemons, tangerines, tangelos, mandarins, minneolas, pummelos and pink and white grapefruit to determine OPP, imazalil and thiabendazole. Ten or 12 fruits are cut into 6 sections each and one section is taken from each fruit. The composite samples (300-350 g) are separated into peel and fruit sacs. The peels are slurried in a blender with ethyl acetate (200 ml), the slurry is filtered and the grinding and filtering process is repeated twice. The extract is analysed by HPLC on a Zorbax ODS, 250 cm x 4.6 mm, column with 30.2% phosphate buffer and 69.8% acetonitrile as the mobile phase at a flow of 1 ml/min. A fluorescence detector with a 254 nm excitation filter is used with calibration by external standards (0.25-3.8 mg/kg). The linear calibration curve is based on duplicate injections at each concentration. The limit of detection is estimated to be 0.05 mg/kg OPP and the limit of determination assumed to be 0.25 mg/kg.

A GC-MS method, validated with radiolabelled compounds, was described for the determination of OPP and the metabolite PHQ (phenylhydroquinone) in citrus fruits and their processed fractions (Harsy, 1996a) and submitted as a proposed enforcement method to the US EPA. Fruit samples are cut into small pieces and ground in liquid nitrogen. Juice samples are frozen as received. To determine OPP, thawed homogenate or juice (10 g) is simultaneously hydrolysed, steam distilled and extracted in a micro-Nielsen-Kryger apparatus, using sufficient HCl to produce a 1 N concentration in the sample. Water and iso-octane are placed in the inner chamber of the apparatus. The mixture is refluxed for 2 hours (pulp overnight). The OPP is derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) to form the trimethylsilyl ethers and determined by GC-MS in the selected ion mode. The ions 227, 242, 170 and 141 are monitored, with a dwell time of 50 msec per ion. The column is a 30 m x 0.25 mm HP-5 (5% phenyl methyl silicone). The ion m/z

227 is used for quantification with external standards. Orange oil is determined by direct injection, monitoring ion m/z 170.

For the determination of PHQ, the homogenized sample or juice (10 g) is hydrolysed in 0.3 N HCl with ascorbic acid and EDTA for one hour at 100°C under argon. The mixture is extracted with methylene chloride and the PHQ derivatized with BSTFA (70°C, 15 min). The derivative is determined by GC-MS, monitoring ions 330 and 229, the former being used for quantification.

Both OPP and PHQ standards showed linear detector response from 0 to 6 or 7 ng injected on the column.

The LOD was 0.05 mg/kg for OPP and 0.2 mg/kg for PHQ in all samples except oil, in which it was 1 mg/kg for both compounds. Some recoveries are shown in Table 5.

Table 5. Recoveries of OPP and PHQ from fortified citrus fruit by GC-MS.

Analyte and sample	Fortification, mg/kg	Mean recovery, %	Number of samples	Range, %	Standard deviation, %
OPP					
Orange	0.05	118	8	104-126	7.0
	1	80	2	78, 82	-
	20	74	2	74, 75	-
Lemon	0.05	92	7	80-104	7.1
	1	65	2	65, 65	-
	20	77	2	76, 77	-
Juice	0.05	88	8	83-93	3.8
	1	96	2	94, 97	-
	20	80	2	80, 80	-
Pulp, dry	0.05	82	8	77-88	3.9
	1	70	2	69, 71	-
	20	93	2	74, 112	-
Oil	0.05	76	8	74-78	1.4
	10	63	2	60, 65	-
	30	71	2	70, 71	-
PHQ					
Orange	0.2	78	8	72-85	4.1
	1	82	2	79, 85	-
	20	83	2	76, 89	-
Lemon	0.2	76	7	65-84	6.0
	1	78	2	78, 78	-
	20	104	2	99, 108	-
Juice	0.2	76	8	69-81	3.8
	1	77	2	77, 78	-
	20	65	2	64, 65	-
Oil	1	76	8	72-79	2.2
	3	66	2	65, 67	-
	5	65	2	64, 66	-
	10	73	2	73, 73	-

The method was validated (Harsy, 1996b) with a 12-week peel sample from the orange metabolism study which contained a total radioactive residue of 28.68 mg/kg as OPP. Analysis of the residue showed it to be 89% OPP and conjugates and 3.6% PHQ and conjugates (see Table 3), giving a residue of OPP and its conjugates of 25.5 mg/kg and PHQ and conjugates of 1.0 mg/kg. The peel was analysed by the GC-MS method and the results compared with those from the metabolism study (Table 6).

Table 6. Validation of the GC-MS method with orange peel containing incurred residues of 25.5 mg/kg [¹⁴C]OPP and conjugates and 1.0 mg/kg [¹⁴C]PHQ and conjugates.

Sample	OPP recovery, %	Total radioactivity - OPP, %	PHQ recovery, %	Total radioactivity - PHQ, %
Peel replicate 1 extract	84	74	109	73
Peel replicate 1 residue		32		20
TOTAL replicate 1		106		93
Peel replicate 2 extract	85	76	111	77
Peel replicate 2 residue		38		19
TOTAL replicate 2		114		96

Stability of pesticide residues in stored analytical samples

The storage stability of OPP and PHQ in raw oranges, grapefruit and lemons, and processed orange products was studied by Johnson and Strickland (1996a-c). Samples of whole grapefruit, lemons, and navel oranges, and navel orange juice, oil and dry pulp were fortified with OPP and PHQ, each at 0.5 mg/kg, and held in frozen storage. Samples were removed at intervals and analysed for OPP and PHQ by the Harsy GC-MS method. Fortified controls were analysed at each interval to establish method recoveries. The results are shown in Table 7. OPP was stable in grapefruit for 6 months, in lemons for 8 months, in oranges for 7 months, in juice for 5 months, in dried pulp for 4 months and in oil for 9 months. PHQ was stable in grapefruit for 5 months and in orange juice for 5 months, but unstable in oranges and oil. The stability in lemons is uncertain, because the concurrent method recoveries were very poor.

Table 7. Recoveries from stored and freshly fortified samples of citrus fruits and processed orange commodities fortified with OPP and PHQ, each at 0.5 mg/kg (10.5 mg/kg in citrus oil) and stored frozen at -20°C.

Commodity	Storage period, months ¹	Recovery from freshly spiked samples, % ²	Recovery from stored samples, %	% of mean fresh recovery after storage
OPP				
Grapefruit	1.0	64, 69 (66)	59, 66	89, 100
	1.9	70, 73 (71)	67, 76	94, 106
	2.8	73, 74 (74)	72, 73	97, 99
	3.8	147, 154 (151)	128, 141	85, 93
	5.9	82, 83 (82)	80, 84	97, 102
Lemons	0.2	93, 119	-	-
	1.00	103, 124 (113)	148, 153	130, 135
	1.9	114, 124 (119)	64, 119	54, 100
	3.1	84, 86 (85)	103, 109	121, 129
	4.1	68, 69 (68)	88, 91	129, 133
	8.4	78, 82 (80)	104, 108	130, 135
Oranges	1.0	56, 59 (58)	71, 74	103, 105
	2.1	69, 69 (69)	71, 72	103, 105
	3.1	83, 84 (84)	75, 85	90, 101
	4.0	70, 79 (75)	73, 76	97, 101
	5.2	148, 155 (151)	123, 142	81, 94
	7.2	76, 77 (77)	80, 83	105, 108
Juice	1.2	77, 88 (82)	79, 82	96, 99
	2.4	72, 72 (72)	76, 78	106, 108
	3.2	85, 153 (119)	81, 89	68, 75
	4.3	79, 83 (81)	82, 87	102, 108
	5.3	141, 150 (145)	145, 146	100, 101
Dried pulp	3.6	71, 72 (72)	68, 73	95, 102
	4.0	94, 150 (122)	123, 141	101, 115

Commodity	Storage period, months ¹	Recovery from freshly spiked samples, % ²	Recovery from stored samples, %	% of mean fresh recovery after storage
	6.2	46, 53 (49)	39, 48	79, 97
Oil ³	0	52, 54 (53)	-	-
	0.9	84, 87 (86)	88, 90	102, 105
	1.9	74, 84 (79)	83, 81	105, 102
	4.5	82, 87 (84)	84, 80	100, 95
	5.0	90, 92 (91)	90, 92	99, 101
	6.1	114, 111 (112)	108, 106	96, 95
	7.7	99, 102 (100)	96, 105	96, 105
	9.1	83, 86 (84)	89, 91	106, 108
PHQ				
Grapefruit	3.4	53, 102 (77)	82, 131	106, 171
	4.8	80, 87 (83)	87, 87	104, 104
	6.1	47, 54 (50)	50, 53	101, 105
	9.4	36, 40 (38)	42, 43	111, 113
Lemons	7.5	31, 88 (60)	136, 171	228, 287
	8.6	23, 33 (28)	40, 44	143, 156
	9.8	31, 32 (31)	49, 59	155, 187
Oranges	3.2	67, 78 (72)	38, 55	52, 76
	4.7	42, 76 (59)	19, 71	32, 121
	5.8	81, 81 (74)	50, 59	62, 72
	7.5	67, 81 (74)	16, 32	22, 44
Juice	1.9	78, 79 (78)	73, 92	92, 116
	3.2	61, 66 (63)	74, 84	116, 132
	4.7	75, 78 (77)	77, 79	101, 103
Oil	0	71, 75 (73)	-	-
	0.9	94, 103 (99)	41, 51	41, 52
	1.9	61, 59 (60)	<10, <10	<17, <17
	2.5	95, 98 (97)	<10, <10	<10, <10

¹ Initial samples, except of oil, were not analysed.

² Values in parenthesis are means of two independently fortified and analysed fresh control samples.

³ Control samples contained significant concentrations of OPP (1.2-2.1 mg/kg). Results were corrected.

Definition of the residue

The current definition is “sum of 2-phenylphenol and 2-phenylphenate, expressed as 2-phenylphenol”.

In studies of metabolism in oranges and pears OPP and its conjugates constituted 90% of the total radioactive residue (TRR) in oranges and 87% of the TRR in pears. PHQ was found in orange peel at low concentrations (<4% of the TRR). It is therefore appropriate to define the residue for both enforcement and for the estimation of dietary exposure as the sum of 2-phenylphenol and sodium 2-phenylphenate, free and conjugated, expressed as 2-phenylphenol. This applies to plant commodities only.

USE PATTERN

Information was supplied by the California Citrus Quality Council (CCQC), the Pear Bureau Northwest and the governments of Australia, The Netherlands and Germany. Germany and The Netherlands indicated that they had no registered uses. The only uses are for the post-harvest treatment of citrus fruit and pears, most commonly to control green mould and sour rot. The information is shown in Table 8.

Table 8. Registered uses of 2-phenylphenol.

Crop	Country	Formulation	mg ai/kg fruit or solution concentration, kg ai/hl	Method	Comments
Citrus	Australia	SP, 950 g/kg	1.9 (as Na OPP tetrahydrate)	Dip	Adjust dip pH to 12. Wash fruit after dip.
Citrus	USA	Wax liquid with 0.40% OPP	4.2 mg/kg fruit	Spray	Spray without dilution on to clean and dry citrus, 1 gal (8.5 lbs) per 8000 lbs fruit
Citrus	USA	SC, 25% SOPP	0.97 kg ai/hl 8.1 mg ai/kg fruit	Wax emulsion	Use wax foamer or sprayer. Do not rinse.
Citrus	USA	Foaming cleaner, 14.5% SOPP; 24% SOPP	1.6 (as Na OPP) 2.0 (as Na OPP tetrahydrate)	Mechanical foamer or spray	10-30 second treatment with 14.5% followed by fresh water rinse. For 14.5%, dilute 1 gal with 9 gal water. 1 gal = 9.0 lbs. 30-60 second treatment for 24%, followed by a water rinse. 1 gal = 3.1 lbs. Na OPP tetrahydrate.
Citrus	USA	SC, 14.5% anhydrous Na OPP	0.05 (500 ppm)	Bin drench	Dilute with water. 1 gal = 8.93 lbs.
Citrus	USA	SC, 14.5% SOPP anhydrous; 25% SOPP tetrahydrate	0.34 (3500 ppm) for SOPP anhydrous; 0.5 for SOPP tetrahydrate	Washing tank.	Wash in tank 2-5 minutes, after adjusting pH to >11.6. Wash citrus after treatment with fresh water. For 14.5%, 1 gal = 9.18 lbs. Dilute 1 gal with 46 gal water minimum. For 25%, 1 gal = 3.33 lbs. SOPP tetrahydrate. Dilute 1 gal with 80 gal water.
Pears	USA	Foaming cleaner, 14.5% SOPP; 24% SOPP	1.3 (as Na OPP) 1.9% (as Na OPP tetrahydrate)	Mechanical foamer or spray	For 14.5%, dilute 1 gal with 11 gal water. Foam and brush onto pears for 15-30 seconds. Rinse with fresh water. 1 gal = 9.0 lbs. For the 24%, dilute one gallon with 19 gallons of water. Treat for 15-30 seconds. 1 gal = 3.1 lbs. SOPP tetrahydrate.
Pears	USA	SC, 14.5% SOPP anhydrous; SC, 25% SOPP	0.35 (3500 ppm) for 14.5%; 0.5 for 25%	Dip	For 14.5%, add 1 gal to 44 gallons of water. Dip for 1.5 to 4 minutes and then rinse thoroughly with fresh water. 1 gal = 9.18 lbs. For 25%, add 1 gal to 80 gal water, adjust pH to 11-12, dip or flood for 0.5-2 min and rinse. 1 gal = 3.33 lbs SOPP tetrahydrate.

RESIDUES RESULTING FROM SUPERVISED TRIALS

In 8 US trials (Johnson and Strickland, 1996) commercially grown citrus fruit from southern California (lemons, Navel oranges and grapefruit) and central Florida (grapefruit) were treated with SOPP. Scarred fruit were used, as they tend to show higher residues of OPP. Lemons were treated with a storage wax containing 2,4-D and imazalil and stored at 7-18°C for six weeks before the trial. Navel oranges and grapefruit were treated with SOPP within four days of harvest.

Lemons, oranges and grapefruit were given a foamer wash treatment for 30 seconds with a solution containing 1.45% anhydrous SOPP (2.0% SOPP tetrahydrate), followed by a fresh water rinse. The label specifies 1.6 kg ai/hl as anhydrous SOPP. A sample of the treated fruit was collected immediately after the water rinse. Control samples received a foaming wash without OPP.

The foamer wash experiments were conducted in duplicate with individually prepared solutions. The foamer wash solution is applied as a high-volume flush over the fruit as it moves across a series of parallel brushes that generate the foam. The application rate is dependent on the time spent on the brushes and not the volume output of the sprayer, provided the brushes are thoroughly soaked.

The remaining fruit from the foaming wash/water rinse were treated with a shipping wax that contained 1.0% anhydrous SOPP. The treatment was in duplicate with individually prepared wax solutions. GAP specifies approximately 1 kg ai/hl, or 1%. The wax was applied with a bank of parallel stiff brushes that carried fruit under a pair of ultra low volume spray heads or under a wax drip system which kept the brushes saturated with wax. The pumps supplying the wax were adjusted to deliver it at one gallon of wax solution per 10000 pounds of fruit, as specified by the label.

The samples which had not received the wax treatment were frozen on the day of treatment and kept frozen until analysis, a period of 1-8 months. The remaining control and foam-treated samples which received the wax treatment were placed in storage that simulated commercial conditions. Lemons were stored at temperatures of 10-11°C and relative humidities of 96-97%. Navel oranges were stored at 5.5-10.5°C and relative humidities of 75 to 84%. California grapefruit were stored at 5-11°C and relative humidities of 71 to 83%, and Florida grapefruits at 12-15°C and 74 to 98%. Samples were taken after 4 and 8 weeks and frozen until analysis. The usual interval between post-harvest SOPP treatment and citrus consumption is estimated to be 8 weeks.

The fruit samples were analysed by the Harsy method (one-step hydrolysis/steam distillation/extraction, followed by GC-MS). Both OPP and PHQ were determined. The results are shown in Table 9. Fortified control samples were analysed concurrently with the results shown in Table 10.

Table 9. OPP and PHQ residues in oranges, lemons and grapefruit treated with 1.45% anhydrous SOPP foamer wash and 1.00% anhydrous SOPP in shipping wax.

Trial no. (site)	Treatment and storage period, days							
	Foamer wash (day 0)		Foamer wash + wax (day 0)		Foamer wash + wax (day 28)		Foamer wash + wax (day 56)	
	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg
Navel oranges								
1	1.7, 1.4 (1.6)	<0.2, <0.2	7.0, 6.4 (<u>6.7</u>)	<0.2, <0.2 (<0.2)	5.8, 7.0 (6.4)	<0.2, <0.2 (<0.2)	4.9, 6.1 (5.5)	0.27, 0.33 (0.30)
2	1.8, 1.5 (1.6)	<0.2, <0.2 (<0.2)	6.2, 6.8 (<u>6.5</u>)	<0.2, <0.2 (<0.2)	5.7, 6.0 (5.8)	<0.2, <0.2 (<0.2)	6.5, 6.4 (6.4)	0.25, 0.26 (0.26)
Control	<0.05	<0.2	0.057	<0.2	0.083	<0.2	0.066	<0.2
Lemons								
1	2.4, 2.7 (2.6)	<0.2, <0.2 (<0.2)	4.5, 3.8 (4.2)	<0.2, <0.2 (<0.2)	4.6, 5.2 (4.9)	0.34, 0.34 (0.34)	4.9, 5.9 (<u>5.4</u>)	0.34, 0.31 (0.32)
2	3.4, 3.2 (3.3)	<0.2, <0.2 (<0.2)	4.5, 4.6 (4.6)	<0.2, <0.2 (<0.2)	5.8, 4.8 (5.3)	0.32, 0.35 (0.34)	5.0, 5.3 (<u>5.2</u>)	0.33, 0.40 (0.36)
Control	<0.05	<0.2	0.062	<0.2	0.062	<0.2	0.077	<0.2
Grapefruit								
1 (Calif)	1.1, 0.73 (0.91)	<0.2, <0.2 (<0.2)	1.9, 2.3 (2.1)	<0.2, <0.2 (<0.2)	2.3, 1.9 (2.1)	0.47, 0.44 (0.46)	3.5, 1.3 (<u>2.4</u>)	0.50, 0.23 (0.36)
2 (Calif)	1.3, 1.7 (1.5)	<0.2, <0.2 (<0.2)	2.4, 2.1 (2.2)	<0.2, <0.2 (<0.2)	2.1, 2.5 (2.3)	0.47, 0.37 (0.42)	2.5, 2.4 (<u>2.4</u>)	0.49, 0.40 (0.44)
Control (Calif)	<0.05	<0.2	<0.05	<0.2	<0.05	<0.2	<0.05	<0.2
3 (Florida)	0.31, 0.48 (0.40)	<0.2, <0.2 (<0.2)	3.4, 2.0 (<u>2.7</u>)	<0.2, <0.2 (<0.2)	1.8, 1.6 (1.7)	<0.2, <0.2 (<0.2)	1.9, 1.4 (1.7)	0.21, <0.2 (0.21)

Trial no. (site)	Treatment and storage period, days							
	Foamer wash (day 0)		Foamer wash + wax (day 0)		Foamer wash + wax (day 28)		Foamer wash + wax (day 56)	
	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg
4 (Florida)	0.65, 0.83 (0.74)	<0.2, <0.2 (<0.2)	2.0, 2.4 (2.2)	<0.2, <0.2 (<0.2)	2.2, 1.6 (1.9)	<0.2, <0.2 (<0.2)	3.0, 1.8 (<u>2.4</u>)	0.46, 0.22 (0.34)
Control (Florida)	<0.05	<0.2	0.063	<0.2	<0.05	<0.2	<0.05	<0.2

Table 10. Recovery of OPP and PHQ from fortified citrus samples analysed concurrently with the treated samples of Table 9.

Analyte and sample	Fortification, mg/kg	Number of samples	Recovery range, %	Mean recovery, %
OPP				
Orange	0.05	4	80-99	86
	0.5	5	58-104	72
	1	5	69-95	84
	5	4	69-95	88
Lemon	0.25	5	73-93	83
	0.5	2	74, 78	76
	1	9	69-93	80
	5	2	81, 109	95
Grapefruit (California)	0.05	3	97 - 139	119
	0.5	6	68-99	86
	1	5	73-99	90
	5	4	70-101	86
Grapefruit (Florida)	0.05	4	89-105	96
	0.5	4	66-74	71
	0.25	1	104	-
	1	5	88-101	93
	5	4	78-92	85
PHQ				
Orange	0.2	9	55-117	85
	1	9	54-119	86
Lemon	0.2	9	64-93	78
	1	9	61 - 96	77
Grapefruit (California)	0.2	9	68-95	80
	1	9	66-95	78
Grapefruit (Florida)	0.2	9	60-125	77
	1	9	61-118	80

Two trials at the same location with the same equipment, but with two independently prepared treatment solutions, were conducted with Anjou pears in Oregon, USA, in 1995 (Thompson, 1996). Pears after 4 months cold storage were dipped in a float tank for 120 seconds in a solution containing 0.49% SOPP (Steriseal D, 24.4% anhydrous SOPP by analysis, nominal 22.6% on label). The pears were rinsed under flowing water and dried briefly with a hair dryer. This is consistent with US GAP. Controls were dipped in a solution that did not contain SOPP. In each trial, a 4.54 kg sample of pears was collected and a 2.27 kg sub-sample was frozen within 3 h (day 0). In one trial the remaining 2.27 kg of fruit was divided into two sub-samples, which were stored at -2 to 2°C and >90% relative humidity for 60 or 120 days. In the other trial the remaining 2.27 kg was again divided into two portions, which were stored under controlled conditions at -1 to 0°C and 90-95% relative humidity for 60 or 113 days. The samples were all immediately frozen and kept frozen until analysed. The maximum interval from sampling to analysis was about 6 months for the day 0 samples and correspondingly less for the samples stored before freezing.

Storage stability studies showed acceptable or marginally acceptable recoveries at all intervals up to 4 months, but recoveries from the 6-month samples were below 50%, suggesting that the initial trial samples (stored frozen for 6 months) may have contained twice the measured residues. It is also to be noted that the stability study was with a pear homogenate, not with whole fruit. A freshly fortified sample was not analysed with each set of stored samples to provide information on analytical recoveries. The results of the storage stability trials are shown in Table 11.

Table 11. Recovery of OPP from fortified pear homogenate after frozen storage.

Storage period, days	Fortification, mg/kg	Recovery, % ¹
0	1.18	79
	18.1	100
30	1.51	57
	17.9	70
60	1.50	78
	19.9	106
120	1.50	83
	24.8	109
210	1.51	43
	15.5	44

¹ Not corrected for concurrent analytical recovery

Samples and controls were analysed by the Harsy GC-MS method. All residues in control samples were below the LOD (<0.15 mg/kg). Fortified controls (12 determinations) gave recoveries ranging from 71% to 103% at fortification levels of 0.1-15 mg/kg. The residues in the treated samples are shown in Table 12.

Table 12. Residues of OPP on pears after a dip treatment for 120 seconds in a 0.49% aqueous solution of SOPP.

Trial	Post-treatment storage period, days	OPP, mg/kg
1	0	1.7, 1.1 (Mean <u>1.4</u>)
	60	0.93, 1.5 (Mean 1.2)
	120	0.69, 1.0 (Mean 0.87)
2	0	0.85, 0.79 (Mean <u>0.82</u>)
	60	0.82, 0.74 (Mean 0.78)
	120	0.70, 0.57 (Mean 0.63)

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information, except on stability in stored analytical samples.

In processing

In a processing study (Johnson and Strickland, 1996) commercially grown Navel oranges from Tulare County, California, were scarified before an exaggerated treatment with a foamer wash solution

containing SOPP at 14.5 g/kg (or SOPP tetrahydrate at 20 g/kg) for 120 sec rather than the usual 30 sec. This was followed by application of a shipping wax solution containing SOPP at 10 g/kg (14 g/kg as SOPP tetrahydrate), thiabendazole at 3500 mg/kg and imazalil at 2000 mg/kg. Control samples received similar treatments with foamer wash and shipping wax solutions containing no SOPP. Two lots of each treatment solution were prepared for duplicate applications. A sample weighing about 50 kg was collected from control and treated oranges after storage periods of 0, 28 and 56 days and 4.5 kg of each initial sample was selected randomly to produce two 1.4 to 1.8 kg sub-samples, which were frozen immediately and shipped frozen to the laboratory for analysis.

The remaining 45 kg of each of the initial samples was sent to an experimental processing facility and processed into juice, dry pulp and oil. Two sub-samples were randomly selected from the whole fruit and from each process fraction. Two replicates from each sub-sample were frozen immediately for analysis for OPP and PHQ.

The remaining control and treated samples were placed in commercial storage for 28 or 56 days (5-10°C, 75-84% relative humidity), then treated in the same way as the initial samples.

The raw oranges were processed by simulated standard industrial procedures. After washing for five minutes substandard fruits were removed by hand and the remainder (5-10 kg) were scarified for 0.5-5 minutes in a modified vegetable peeler, simulating the Brown Machinery commercial procedure. The collected flavedo and oil/water emulsion were passed through a 180 µm mesh screen to remove flavedo fragments and the emulsion was broken by freezing. After thawing, the floating oil was centrifuged at 2600 rpm for 10 minutes to effect the final separation of pure oil. In a commercial operation the emulsion would be screened and centrifuged at 10000 rpm.

The scarified oranges were transferred to a Hollymatic juice extractor which halved the fruit and then used auger reamers to remove the juice from the halves. This simulates closely the Brown Machinery juice extractor used commercially. The extracted juice was passed through a pulper finisher with a 0.4-0.6 mm screen to remove the vesicular membranes, seeds, segment membranes and peel fragments.

In commercial operations, most peel and rag from the juicer and finisher are sold as fresh or dried animal feed. The peel may also be used to make specialized products such as pectins, essential oils, candied peel, marmalade and citrus molasses. In the laboratory procedure, the flavedo from the scarification process (to produce oil) and the rag and seeds from the juice and finisher extraction processes were added to the shredded peel to produce wet pulp.

Citrus molasses is produced by reacting the peel with lime, pressing the peel to extract the juice and concentrating the juice. In the present study the wet pulp was mechanically shredded and lime was added to a pH of 8-10 and mixed for 15-20 minutes. The pulp mixture was then hydraulically pressed and the expressed liquid was vacuum-evaporated to 50° Brix. The residual peel was air-dried to less than 10% moisture.

All samples were analysed by the Harsy GC-MS method after storage for 1-4 months, except oil which was stored for as long as 9 months. Control samples of fruit and processed commodities were fortified and analysed concurrently with the treated samples. The recovery data are shown in Table 13 and the residues found in the treated oranges and their processed commodities in Table 14.

Table 13. Recovery of OPP and PHQ from fortified control oranges and processed products.

Sample	OPP added, mg/kg	OPP recovery, %	PHQ added, mg/kg	PHQ recovery, %
Whole orange	0.5	71, 71	0.2	67, 78
	1	86, 86	1	67, 82
	5	86, 82, 86, 82, 89, 89		
Juice	0.25	73	0.2	64, 70

Sample	OPP added, mg/kg	OPP recovery, %	PHQ added, mg/kg	PHQ recovery, %
	1	88, 75, 89	1	69, 67
	5	89, 83		
Dry pulp	0.05	90	-	
	0.5	89	-	
	1	100, 80	-	
	5	85, 90		
Oil	2	89, 96	1	44, 43
	5	79, 90	5	56, 52

Table 14. Concentrations of OPP and PHQ in oranges treated with a foaming cleaner (1.45%) and a storage wax (1.0%) and their processed products.

Sample	Day 0 residue, mg/kg	Day 28 residue, mg/kg	Day 56 residue, mg/kg	Day 0 processing factor	Day 28 processing factor	Day 56 processing factor
OPP						
Whole orange						
1	13.6, 13.4 (13.5)	8.90, 8.16 (8.53)	9.86, 10.1 (9.98)	-	-	-
2	18.4, 15.6 (17.0)	10.1, 13.5 (11.8)	7.85, 8.89 (8.37)	-	-	-
Juice						
1	0.263, 0.302 (0.283)	0.278, 0.320 (0.299)	0.344 0.325 (0.335)	0.021	0.035	0.034
2	0.314, 0.307 (0.311)	0.438, 0.426 (0.432)	0.324, 0.351 (0.338)	0.018	0.037	0.040
Dry pulp						
1	40.1, 38.5 (39.3)	38.7, 10.9 (24.8)	38.1, 36.3 (37.4)	3.0	2.9	3.7
2	39.2, 35.0 (37.1)	52.1, 52.2 (52.2)	45.9, 43.6 (44.8)	2.2	4.4	5.4
Oil						
1	1168, 1183 (1176)	866, 795 (831)	622, 693 (658)	88	97	66
2	1378, 1232 (1305)	933, 974 (954)	876, 877 (877)	77	81	105
PHQ						
Orange						
1	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	0.247, 0.225 (0.236)	-	-	-
2	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	-	-	-
Juice						
1	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	~1	~1	~1
2	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	~1	~1	~1

Sample	Day 0 residue, mg/kg	Day 28 residue, mg/kg	Day 56 residue, mg/kg	Day 0 processing factor	Day 28 processing factor	Day 56 processing factor
Oil						
1	<1.0, <1.0 (<1.)	<1.0, <1.0 (<1.0)	<1.0, <1.0 (<1.0)	-	-	-
2	<1.0, <1.0 (<1.0)	<1.0, <1.0 (<1.0)	<1.0, <1.0 (<1.0)	-	-	-

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Residues of OPP in fresh citrus fruits reported by citrus packing houses in the USA

Fresh citrus fruit treated with various formulations containing SOPP are often sampled at packing houses in the USA to check that the fruit has been treated according to label directions and that residues of OPP do not exceed the established US tolerance of 10 mg/kg. Reports of such monitoring by several US formulators of SOPP products were supplied.

The Brogdex Company provided residue data for 63 samples of Navel oranges, lemons and Valencia oranges treated with SOPP at 3 to 20 g/kg in 1998 (Appel, 1999). The residues ranged from 0.5 to 4.37 mg/kg, with an overall average of 2.24 mg/kg.

Elf Atochem North America provided extensive data on OPP residues in citrus fruit as determined in their laboratory from 1994 to 1998 (Wartanessian, 1999). All of the samples were of fruit that had been treated with OPP. Analyses were by method 415B. Residues of OPP in about 500 samples of grapefruit (mainly Florida) ranged from 0.1 to 2.5 mg/kg, with annual averages of 0.3 to 0.6 mg/kg; in about 330 samples of California lemons from 0.1 to 6.6 mg/kg, with annual averages of 0.8 to 1.6 mg/kg; in about 500 samples of Navel and Valencia oranges from California and Florida from 0.1 to 7.6 mg/kg, with annual averages of 0.4 to 0.9 mg/kg, and in 38 samples of (mainly Florida) tangerines from 0.1 to 0.8 mg/kg, with annual averages of 0.3 to 0.5 mg/kg.

FMC Food Tech, Citrus Systems, provided results of analyses in 1998 for OPP in >100 samples of grapefruit, lemons and Navel and Valencia oranges that had been treated with OPP (Nguyen, 1999). The residues ranged from 0.1 to 6.8 mg/kg in lemons. The highest residue found in 40 samples of oranges was 6.0 mg/kg.

Sunkist Growers reported residues of OPP found in 1996 and 1997 in about 1200 samples of Ruby Red and white grapefruit, Navel and Valencia oranges, lemons, tangerines, tangelos, mandarins, minneola, pummelo and oroblanco, grown in Arizona and California and treated in affiliated packing houses. The OPP residues ranged from 0.12 to 7.81 mg/kg, with the majority below 3 mg/kg (Mulligan, 1999). A large number of OPP residues were reported as "non-detected," possibly because the fruit had been treated with fungicides other than OPP. The LOD was 0.10 mg/kg in the method used by Sunkist.

Data on residues of OPP in pears were not available from packing houses in the Pacific Northwest.

Residues of OPP in citrus fruit and pears reported by government laboratories

The US FDA has reported the results of a special pesticide residue monitoring study in which 4000 samples of infant foods and adult foods eaten by infants or children were analysed (Yess *et al.*, 1993). Samples of fresh fruit were collected from markets in four geographic areas in the USA and analysed

as the whole, unwashed, unpeeled product. Residues of OPP were found in only 12 of 862 samples of oranges (1.4%), with a maximum of 4.4 mg/kg. No OPP was detected in the 571 samples of pears analysed in the study.

A later study by the US FDA focused on the incidence and level of pesticide residues in domestic and imported pears and tomatoes (Roy *et al.*, 1995). One of the pesticides determined was OPP in a total of 710 domestic and 949 imported pear samples. About 95% of the fresh pears consumed in the USA are domestically grown, with about 97% of the production located in northwestern States (California, Oregon and Washington). Although Bartlett pears are grown on the largest area, only 30% of this early variety are sold as fresh fruit. Sampling was at a total of 227 domestic pear establishments, with 2.3 kg of pears taken from randomly selected cartons destined for retail markets. Analyses for residues of OPP were by HPLC with an acetone-water mobile phase and a fluorescence detector. The limit of determination was 0.10 mg/kg. All significant residues were determined with a second column and detector combination or by GC-MS to confirm the identity of the residues. Residues of OPP were found in 125 of 710 samples of domestic pears (18%) with a maximum of 2.6 mg/kg and in 28 of 949 samples of imported pears (3%) with a maximum of 2.2 mg/kg.

The Residue Branch of the USDA recently provided a summary and details of the incidence and level of OPP residues found in grapefruit, oranges, orange juice and pears analysed in 1992-1997 as part of the Pesticide Data Program (Fry, 1999). The samples were collected and analysed by participating State Laboratories in California, Florida, Michigan, North Carolina, New York, Ohio, Texas and Washington, using sensitive multiresidue screening methods (GLC with EC detection, GC-MS, HPLC with post-column derivatization and fluorescence detection). A total of 788 samples of grapefruit were analysed for OPP in 1992-1993 with 14 detections at levels between 0.015 and 0.055 mg/kg, 2116 samples of oranges during 1992-1996 with 283 between 0.010 and 3.6 mg/kg, 601 samples of orange juice in 1997 with 16 between 0.017 and 0.033 mg/kg, and 654 samples of pears in 1997 with 21 between 0.005 and 11 mg/kg.

Most of the OPP residues found in these commodities were <0.1 mg/kg, with 45 samples containing between 0.1 and 1 mg/kg and 32 samples containing >1 mg/kg. The highest residues were in pears collected in 1997, when post-harvest treatment with OPP increased because other fungicides such as benomyl were no longer available to control decay in stored pears.

The government of The Netherlands submitted data on residues of OPP in food in commerce in 1997 and in the period 1994-1996. In 1997, 30 of 177 citrus samples (17%) contained residues above 1 mg/kg, but below the MRL of 12 mg/kg. In 1994-1997, 254 of 665 citrus samples (38%) contained >1 mg/kg of OPP, three of them at or above the national MRL at 12-14 mg/kg.

NATIONAL MAXIMUM RESIDUE LIMITS

Leng (1999) compiled a Table of national MRLs for 2-phenylphenol and its sodium salt from information in the 1990 Canadian compendium. The governments of The Netherlands and Australia also reported their national MRLs.

Country	MRL, mg/kg	Commodities
Argentina	5	orange, grapefruit, lemon, lime, kumquat
Australia	25	pears
	20	carrots, peaches
	15	plums, prunes, sweet potatoes,
	10	melons (except watermelon), citrus fruit, cucumbers, peppers, pineapples, tomatoes
	3	cherries, nectarines
Austria	10	citrus fruit
Canada	25	Apples, pears, carrots, peaches, plums, sweet potatoes
	10	cantaloupes, citrus fruits, cucumbers, bell peppers, pineapples, tomatoes

Country	MRL, mg/kg	Commodities
Czechoslovakia	25	pears
	20	peaches
	15	plums, sweet potatoes
	10	gourds, citrus fruits, cucumbers, pineapples, tomatoes, green peppers
	3	nectarines, cherries
Denmark	5	citrus fruit (subsequently raised to 12 mg/kg?)
	0.1	others (cereal grains excluded)
Germany	10	citrus fruits
Hungary	25	apple, pear
	20	peach, carrot
	10	pineapple, melon, cucumber, tomato, black (?) pepper
	3	cherry, nectarine
Israel	15	plums
	10	citrus fruit, pineapple
Kenya	120	cantaloupes (whole)
	25	pears
	20	carrots, peaches
	15	sweet potatoes, apples, plums (including fresh prunes)
	10	citrus fruit, cucumbers, peppers, cantaloupes (edible portion), pineapples, tomatoes
Netherlands	12	citrus fruit, marmelades
	25	pome fruit
	20	peaches, carrots
	15	plums, sweet potatoes
	10	kiwifruit, pineapples, fruiting vegetables
	3	cherries, nectarines
	1	other food commodities
South Africa	10	citrus (for local use)
Spain	12	citrus fruit
	10	pears, apples, melons
	0.1	other plant products
Sweden	10	fruits and vegetables
Switzerland	10	citrus fruit (whole)
USA	125	cantaloupes (no more than 10 in edible portion)
	25	apples, pears
	20	carrots, peaches, plums (fresh prunes), kiwifruit
	15	sweet potatoes
	10	cantaloupes (edible portion), citrus fruits, cucumbers, peppers (bell), pineapples, tomatoes
	5	cherries, nectarines

APPRAISAL

The 1969 JMPR recommended MRLs for 2-phenylphenol (OPP) and its sodium salt (SOPP) in several fruits. 2-Phenylphenol was originally scheduled for periodic re-evaluation of residues by the 1994 JMPR, but was withdrawn because the manufacturer indicated that it was not supporting the existing CXLs and the data base was considered insufficient to support a periodic review. OPP was rescheduled for periodic re-evaluation of residues by the 1999 JMPR (ALINORM 95/24A, Appendix IV). The California Citrus Quality Council (CCQC) and the Pear Bureau Northwest provided information in support of the periodic review. Additional information was supplied by the governments of Australia and The Netherlands.

Animal metabolism

Two lactating Nubian goats 2 to 4 years of age were dosed orally by capsule with [¹⁴C]2-phenylphenol, labelled in the phenoxy ring daily for 5 consecutive days at an average dose level of 13.7 and 53.3 mg/kg b w/day. The doses were equivalent to 11.3 ppm and 32.1 ppm of the test

material in the diet, based on actual feed consumption during the test period. Milk, urine and faeces were collected daily from each animal. The goats were slaughtered about 23 hours after the last dose.

All samples were radioanalysed. In both goats >90% of the administered radioactivity was eliminated, mainly in the urine. The radioactivity in the milk reached a plateau on day 1 or 2 for both animals at 0.03% of the administered dose, 0.008 µg OPP equivalents/g from the low dose and 0.043 µg/g from the high dose. Radioactive residues from the low dose were ≤0.005 mg/kg in the fat, kidney, liver and muscle, and from the high dose 0.003 mg/kg in the fat, 0.020 mg/kg in kidney, 0.014 mg/kg in liver and <0.001 mg/kg in muscle.

The extracts of kidneys and liver were analysed by HPLC. The organic solvent extracts of milk was not analysed because of the very low levels of radioactivity. Reference standards included phenyl-1,4-benzoquinone (PBQ), OPP and phenylhydroquinone (PHQ). No peak corresponded to a reference standard in any extract. The largest single component detected was 0.007 mg/kg as OPD in the acetonitrile extract of kidney. In general, no other component accounted for more than 0.002 mg/kg. Extracts were not hydrolysed to release possible conjugates because of the low radioactivity.

The metabolism of OPP in rats, mice and humans was summarized without supporting details. Metabolism studies have shown that OPP is well absorbed and rapidly excreted in the urine. The main metabolite excreted by rats was OPP sulfate with lesser amounts of glucuronide conjugates of OPP and its hydroxylated metabolite phenylhydroquinone (PHQ). Trace amounts of phenyl-1,4-benzoquinone (PBQ) were also detected in urine. These metabolites were also found in the urine of mice given 5 daily doses of OPP at 25 and 1000 mg/kg bw and in human male volunteers given a dermal application of [¹⁴C]OPP at 0.006 mg/kg bw. The sulfate conjugate of 2,4'-dihydroxybiphenyl (DHB) was also identified. Little or no free OPP and no free PHQ or PBQ was found in mice, rats and humans.

The Meeting concluded that the metabolism of OPP in ruminants is adequately understood. OPP and/or its metabolites are eliminated in the urine and do not accumulate in any tissues or milk. OPP, PBQ and PHQ were not found in milk or tissues. Studies with rats and mice indicate that OPP is converted directly to the glucuronide and sulfate conjugates, and via a postulated 2,4'-DHB to a sulfate and via a postulated PHQ to PHQ glucuronide and sulfate.

Plant metabolism

The metabolism of OPP applied post-harvest to oranges and pears was reported. Oranges were dipped in either a 0.1% or 0.5% solution of radiolabelled OPP and were then stored for intervals from 2 hours–12 weeks under commercial storage conditions for pears at 1–4°C. Upon removal from storage, the oranges were rinsed with methanol to remove surface residues and then peeled. Pulp containing 6.2 mg/kg as OPP and juice 7.0 mg/kg as OPP from the 0.5% treatment after 12 weeks were extracted and analysed by HPLC. Peels taken at intervals were subjected to sequential extraction and enzyme, acid, and base hydrolysis.

The calculated total radioactive residue on whole oranges was 9–12 mg/kg from the 0.1% dip and 16 mg/kg from the 0.5% dip. Most of the radiolabelled residue (>95% of the TRR) remained in the rinse or the peel at all intervals. The main compound in the juice and pulp samples was OPP, 75% of the radioactivity in the pulp extract (0.14% of the TRR, 0.01 mg/kg) and about 51% of that in the juice extract (0.12% of the TRR, 0.01 mg/kg). Orange peel contained OPP and OPP conjugates (89% of the TRR) and phenylhydroquinone (3.6%).

Bosc pears were treated with an aqueous dipping solution of 40 g/kg unlabelled and (U-*phenoxy*-¹⁴C]OPP. The pears were rinsed after treatment and stored at 1–4°C and 90% humidity for various periods (2 h–28 weeks). Pears taken from storage were rinsed with methanol to remove surface residues and peeled. Peels and pulp were extracted separately. Extracts were analysed by HPLC and GC-MS and LC-MS were used for qualitative identifications.

The pears sampled 28 weeks after treatment contained 42.2 mg/kg OPP equivalents. About 66% of the TRR was in the peel and 26% in the pulp. About 57% of the TRR in the peel and 23% in the pulp was identified as OPP and OPP conjugates, one a glucose conjugate. The rinse contained 4% of the TRR

The Meeting concluded that the metabolism of OPP in plants is adequately understood. Most of the residue in oranges and pears is OPP and OPP conjugates. PHQ (4% of the TRR) was found in orange peel. OPP did not translocate beyond the peel of oranges, but migrated substantially into the pulp of pears.

Environmental fate

Information was presented on the biodegradation of OPP in river water, activated sludge and municipal waste-water with a microbial inoculum (OECD Method 301B). In river water radiolabelled OPP at concentrations ranging from 1.2 to 120 µg/l was degraded to about 50% of the initial concentration in one week. The addition of HgCl₂ to inhibit biological activity reduced the decrease to only 10% after 30 days. In activated sludge, radiolabelled OPP at 9.6 mg/l was degraded to 50% of the initial concentration in 24 hours. OPP meets the criteria to be classed as readily biodegradable. Mineralization to ¹⁴CO₂ accounted for about 66% of the radioactivity after 11 days. In HgCl₂-treated controls <1% of the radioactivity was evolved as ¹⁴CO₂.

The Meeting concluded that OPP is readily degraded in surface waters and municipal waste mixtures and that the degradation is biologically mediated. The Meeting also concluded that information on the fate in soil is not required because OPP is used only as a post-harvest treatment in packing houses and similar indoor structures. Contamination of the soil is highly unlikely.

Analytical methods

Numerous methods exist for the determination of 2-phenoxyphenol and sodium 2-phenylphenate in crops. No methods are available for livestock commodities. The official enforcement method in the USA is a photometric method with an estimated limit of detection of 3 mg/kg. The chopped sample is steam distilled in aqueous phosphoric acid, the distillate is derivatized, and the absorbance at 500 nm is measured. Many laboratories now measure absorption after HPLC. With this variation the limit of determination is about 0.025 mg/kg.

Several HPLC methods that do not require distillation are described in the literature. One such method is routinely applied to citrus fruit by a major US citrus grower. A composite fruit sample is slurried and extracted with ethyl acetate. The extract is analysed by HPLC with fluorescence detection. The limit of detection is estimated to be 0.05 mg/kg OPP.

A GLC method is used industrially to measure residues in citrus fruit, kiwifruit and cantaloupes. Elf Atochem Method 415B involves reflux distillation with HCl and hexane. The distillate is extracted and analysed by GLC with a flame ionization detector and a capillary column. The limit of determination is 0.1 mg/kg.

The method used for trials and a processing study and proposed for enforcement in the USA is a GC-MS procedure. The blended fruit sample is simultaneously acid-hydrolysed, steam distilled and extracted in a micro-Nielson-Kryger apparatus. The extract is derivatized with BSTFA. The resulting trimethylsilyl ether is analysed by GC-MS in the selected ion mode. Ions monitored for OPP were 227, 242, 170 and 141, with m/z 227 used for quantification ion. The method can be adapted to determine PHQ. The limit of determination for OPP was 0.05 mg/kg in all citrus products except oil, in which it was 1 mg/kg.

The Meeting concluded that adequate methods exist for data collection and for MRL enforcement for OPP in fruit and fruit products.

Stability of residues in stored analytical samples

In storage stability studies on citrus OPP was stable at freezer temperatures in grapefruit for 6 months, lemons for 8 months, oranges for 7 months, orange juice for 5 months and orange oil for 9 months. PHQ was stable in grapefruit for 5 months and orange juice for 5 months, but unstable in oranges and orange oil. The PHQ data for lemons could not be interpreted.

A storage stability study on pears was conducted concurrently with the residue trials. OPP was stable in pears stored frozen for about 4 months.

The Meeting concluded that adequate storage stability data had been presented for OPP in citrus and processed citrus commodities and in pears.

Definition of the residue

In studies of metabolism in oranges and pears OPP and its conjugates constituted 90% of the total radioactive residue (TRR) in oranges and 87% of the TRR in pears. PHQ was found in orange peel at low concentrations (<4% of the TRR). It is therefore appropriate to define the residue for both enforcement and for the estimation of dietary exposure as the sum of 2-phenylphenol and sodium 2-phenylphenate, free and conjugated, expressed as 2-phenylphenol. This applies to plant commodities only.

Residues resulting from supervised trials

Citrus fruits. US GAP encompasses only post-harvest fruit treatments. The trials complied with a foamer cleaning with brushes and spray for 10–60 sec at 1.45 kg sodium *o*-phenylphenate (SOPP) per hl or a waxing with brushes and spray at 0.97 kg SOPP per hl, with an application rate of the final mixture at 0.83 ml/kg fruit (1 gal/10,000 lbs.). Additional GAP not covered by the trials specifies (1) a dip/wash for 2–5 minutes with 0.36 kg SOPP per hl, followed by a fresh water rinse; and (2) a bin drench at 0.87 g SOPP per hl, with no rinse. The foamer cleaning would give the highest exposure to OPP.

Supervised trials were reported on lemons, oranges and grapefruits, two each on lemons and oranges in California, two on California grapefruit and two on Florida grapefruit. In each trial the fruit were subjected to a foamer cleaning with brushes using 1.45% anhydrous SOPP with a 30-second exposure. This was followed by the application of shipping wax containing 1.0% anhydrous SOPP, at 1 l of wax solution per 1200 kg of fruit, corresponding to maximum GAP; only one application of OPP is usually made. Some control samples contained OPP above the limit of determination (0.05 mg/kg), the range being <0.05–0.08 mg/kg. The concentration in the controls was at most about 2% of that in the treated samples and was not considered significant.

The residues in the whole fruit in rank order were 2.4 (3), 2.7, 5.2, 5.4, 6.5 and 6.7 mg/kg. The median is 3.95 mg/kg. The pulp samples were not analysed separately from peel, but the study of orange metabolism indicated that no more than 5% of the radioactive residue was likely to be found in the pulp. The STMR for pulp may be estimated as 0.05 x 3.93 mg/kg, and 0.20 mg/kg.

The number of trials is inadequate for any individual commodity, but 8 trials are acceptable for the citrus group. The Meeting estimated an STMR of 3.9 mg/kg and a maximum residue level of 10 mg/kg, confirming the existing MRL for citrus fruits.

Pears. US GAP specifies the post-harvest treatment of pears as (1) foamer and spray cleaning with 1.3 kg SOPP/hl for 15–30 seconds followed by a rinse, or (2) dipping in 0.35 kg SOPP/hl solution for 1.5–4 minutes, followed by a rinse.

In two trials in the USA, pears were dipped in a 0.49% solution of SOPP for 2 minutes, followed by a water rinse. The trials were according to maximum GAP and the residues were highest on the day of treatment. The residues were 0.82 and 1.4 mg/kg.

The Meeting could not estimate an STMR or maximum residue level as there were only two trials, and recommended the withdrawal of the existing MRL.

Apples. No trials were reported. The Meeting recommended the withdrawal of the existing MRL.

Animal feeding studies

No studies were reported. Orange pulp is used in cattle feed. The ruminant metabolism study showed no detectable residues of OPP or PHQ. Conjugates were not determined. The high-dose rate, equivalent to 32 ppm in the feed, represents approximately 6 times the theoretical maximum intake of OPP by cattle. This is based on the highest residue found in citrus trials according to GAP, 6.7 mg/kg, the average processing factor for converting citrus to dried pulp, 3.6 and the percentage of citrus pulp in the diet, 20%, and $6.7 \text{ mg/kg} \times 3.6 \times 0.2 = 4.8 \text{ ppm}$. At the sixfold rate, more than 90% of the residue was eliminated. There was no propensity for the residue to accumulate in fat and muscle. Low levels of residues were found in the milk (0.04 mg/kg), kidney (0.02 mg/kg) and liver (0.01 mg/kg). These residues consisted of multiple components, none of which exceeded 0.007 mg/kg. Neither OPP nor PHQ was found. Measurable residues from the ingestion of OPP would not be expected from current treatments according to GAP. This assumes that additional bioaccumulation does not occur with exposure periods greater than 5 days.

The Meeting concluded that maximum residue levels need not be estimated for animal commodities.

Processing

Studies of the conversion of treated oranges into orange juice, orange oil and dried pulp were reported. Oranges were treated by a foamer cleaning with a 14.5 g/kg solution of SOPP for 120 seconds, followed by application of shipping wax containing 10 g SOPP per kg. The oranges were scarified before treatment to increase the uptake of OPP. The treatments represented maximum GAP, but the scarification would be expected to produce higher residues. Oranges were processed on the day of treatment and 28 and 56 days later. Two independent trials were conducted on each day, giving a total of six trials.

The residues decreased in converting oranges to juice. The processing factors were 0.018, 0.021, 0.034, 0.035, 0.037 and 0.040, an average processing factor of 0.031. The Meeting estimated an STMR for orange juice of 0.12 mg/kg, based on the STMR for citrus of 3.9 mg/kg and the average processing factor. The Meeting also estimated a maximum residue level for orange juice of 0.5 mg/kg, based on the maximum residue level for citrus of 10 mg/kg and the maximum processing factor of 0.040.

The residues increased in orange oil. The processing factors were 66, 77, 81, 88, 97 and 105, an average of 86. The Meeting estimated an STMR for orange oil of 340 mg/kg from the STMR for

citrus of 3.9 mg/kg and the average processing factor, and a maximum residue level of 1000 mg/kg from the maximum residue level for citrus of 10 mg/kg and the maximum processing factor of 105.

The residues were increased slightly in dried pulp, an animal feed item. The processing factors were 2.2, 2.9, 3.0, 3.7, 4.4 and 5.4. The Meeting estimated a maximum residue level for dried orange pulp of 60 mg/kg, based on the citrus maximum residue level and the maximum processing factor, $10 \times 5.4 = 54$ mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLS.

Definition of the residue for plant commodities, for compliance with MRLs and for the estimation of dietary intake: sum of 2-phenylphenol and sodium 2-phenylphenate, free and conjugated, expressed as 2-phenylphenol.

CCN	Commodity Name	MRL, mg/kg		STMR, mg/kg
		New	Previous	
FP 0226	Apple	W	25 Po	-
FC 0001	Citrus fruits	10	10 Po	0.20
AB 0001	Citrus pulp, dried	60	-	-
JF 0004	Orange juice	0.5	-	0.12
-	Orange oil	-	-	340
FP 0230	Pear	W	25 Po	-

FURTHER WORK OR INFORMATION

Desirable

A ruminant feeding study at the level of the estimated dietary intake based on citrus pulp consumption and at 10 and 100 times that level. Milk and tissues should be analysed for OPP and PHQ, free and conjugated.

DIETARY RISK ASSESSMENT

Chronic intake

STMRs for one raw commodity and one processed commodity were used for a chronic dietary intake assessment. The International Estimated Daily Intakes for the 5 GEMS/Food regional diets, based on these STMRs, were all 0% of the ADI. The Meeting concluded that the intake of residues of 2-phenylphenol resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The Meeting concluded that an acute RfD for 2-phenylphenol is unnecessary. This conclusion was based on a determination that the pesticide is unlikely to present an acute toxicological hazard, and residues are therefore unlikely to present an acute risk to consumers.

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