# QUINOXYFEN (222)

*First draft prepared by Stephen Funk, Health Effects Division, US Environmental Protection Agency, Washington, DC, USA*

## EXPLANATION

Quinoxyfen is a fungicide used for protection against powdery mildew diseases on a variety of crops. At the 36th session of the CCPR (ALINORM 04/27/24), quinoxyfen was listed as a candidate for evaluation of a new compound by the 2006 JMPR. It was furthermore identified as a candidate for work sharing.

The sponsor has submitted study reports on the metabolism in lactating goats, wheat, sugar beet, grapes, cucumber, and tomato, on the environmental fate (aerobic soil metabolism, hydrolytic degradation, photochemical degradation, and confined rotational crops), on analytical methods for the determination of quinoxyfen in various matrices, and on the storage stability of quinoxyfen in stored frozen analytical samples. Crop field trials were supplied for cherries, grapes, strawberries, currants, melons, peppers, lettuce, wheat, barley, hops, sugar beets and sugar beet tops. GAP information (labels) was also supplied. Processing studies were submitted for wheat, barley, and grapes, and dairy cow and laying hen feeding studies were provided. National use information was supplied by Australia, the Netherlands, and the USA. Germany provided field trial data for currants.

## IDENTITY

| | |
|---|---|
| ISO common name: | Quinoxyfen |
| IUPAC name: | 5,7-dichloro-4- quinolyl 4 fluorophenyl ether |
| Chemical Abstract name: | 5,7-dichloro-4-(4-fluorophenoxy)quinoline |
| CAS No.: | 124495-18-7 |
| CIPAC No.: | 566 |
| Synonyms: | XR-795; XDE-795; DE-795 |
| Molecular Formula: | $C_{15}H_8Cl_2FNO$ |
| Structural Formula: | |

F
Cl O
Cl N

| | |
|---|---|
| Molecular Weight: | 308.14 |
| Minimum purity | 97% |

## PHYSICAL AND CHEMICAL PROPERTIES

Pure Active Ingredient:

| Chemical/physical property | Results | | Reference |
|---|---|---|---|
| Appearance | Off-white flocculent solid | | 21129, Cowlyn and Boothroyd, 1994 |
| Melting point | 106 – 107.5ºC | | |
| Relative density | 1.56 | | |
| Solvent solubility, 20ºC | Hexane<br>Methanol<br>Toluene | 9.64 g/L<br>21.5 g/L<br>272 g/L | |

| Chemical/physical property | Results | | Reference |
|---|---|---|---|
| | Dichloromethane 589 g/L<br>Acetone 116 g/L<br>Ethyl acetate 179 g/L | | |
| Water solubility, 20ºC | pH | µg/L | 8605, Cowlyn and Boothroyd, 1994 |
| | 6.45<br>5<br>7<br>9 | 116 ± 5.1<br>128<br>47<br>36 | |
| Vapour pressure | $1.2 \times 10^{-5}$ Pa @ 20ºC | | |
| | $2.0 \times 10^{-5}$ Pa @ 25ºC | | |
| Volatility, Henry's Law Constant @ 20ºC | Calculation:<br>$3.19 \times 10^{-2}$ Pa.m$^3$. mole$^{-1}$ | | |
| Partition coefficient, 20ºC and pH 6.6 | Log $P_{OW}$ = 4.66 ± 0.002 | | |

Technical Material

| Chemical/physical property | Results | Reference |
|---|---|---|
| Melting point | 100 - 106ºC | 27304, Cowlyn, 1994 |
| Relative density | 1.49 | |
| Solvent solubility, 20ºC | n-heptane 10.2 g/L<br>Methanol 24.6 g/L<br>Xylene 200 g/L<br>Dichloromethane 236 g/L<br>Acetone 111 g/L<br>Ethyl acetate 138 g/L<br>Acetonitrile 22.8 g/L<br>n-Octanol 37.9 g/L | |
| Dissociation constant | pKa of protonated DE-795 = 3.63;<br>equivalent Ka = $2.37 \times 10^{-4}$ | |

***Formulations***

Quinoxyfen is a protectant fungicide. In order to provide both protective and curative control, some formulations have been developed consisting of Quinoxyfen with a curative fungicide. Quinoxyfen is available in the following formulations.

| Formulation | Active ingredient content |
|---|---|
| Suspension concentrate (SC), containing only Quinoxyfen as the active ingredient | 250 g/L Quinoxyfen<br>(EF-1295) |
| | 500 g/L Quinoxyfen<br>(EF-1186) |
| Suspension concentrate (SC), containing a mixture of Quinoxyfen and Cyproconazole | 200 g/L Quinoxyfen + 60 g/L Fenarimol<br>(EF-1303) |
| | 75 g/L Quinoxyfen + 80 g/L Cyproconazole<br>(EF-1406) |
| Emulsion, oil in water (EW), containing a mixture of Quinoxyfen and Fenpropimorph | 66 g/L Quinoxyfen + 250 g/L Fenpropimorph.<br>(EF-1288) |

The supervised trials reported to the Meeting used either the EF-1295, EF1186, or EF-1303 formulations.

## METABOLISM AND ENVIRONMENTAL FATE

The various metabolism studies were conducted using quinoxyfen radio-labelled with the $^{14}C$ label in the phenyl ring (phenoxy label) or on the second carbon of the quinoline ring (quinoline label).

**Phenyl-Ring Labelled [$^{14}$C]Quinoxyfen**

**Quinoline-Ring Labelled [$^{14}$C]Quinoxyfen** [labelled on the second carbon of the quinoline ring]

The following table summarizes the metabolites identified in the various metabolism and environmental fate studies.

Table 1: Summary of metabolites and degradates.

| Common Name/Code | Chemical Name | Structure |
|---|---|---|
| Quinoxyfen<br>DE-795 | 5,7-dichloro-4-(4-fluorophenoxy)quinoline | |

| Common Name/Code | Chemical Name | Structure |
|---|---|---|
| 2-Oxo DE-795[1]<br>2-Oxo Quinoxyfen | 5,7-dichloro-4-(4-fluorophenoxy)-2-oxo-quinoline | |
| DE-795 n-oxide<br>Quinoxyfen n-oxide | 5,7-dichloro-4-(4-fluorophenoxy)quinoline-N-oxide | |
| 3-OH DE-795[1]<br>3-hydroxy Quinoxyfen | 5,7-dichloro-4-(4-fluorophenoxy)-3-hydroxy-quinoline | |
| CFBPQ | 2-chloro-10-fluoro(1)benzopyrano (2,3,4-de)quinoline | |
| 4-Fluorophenol. | 4-Fluorophenol | |

| Common Name/Code | Chemical Name | Structure |
|---|---|---|
| DCHQ | 5,7-dichloro-4-hydroxyquinoline | Cl OH Cl N |

[1] For all radiolabelled studies (plant, livestock, rat and environmental fate) the metabolite identified as 3-hydroxy quinoxyfen is in fact 2-oxo quinoxyfen.

***General for all radiolabelled quinoxyfen studies***

The manufacturer has reported that in all studies utilizing radio-labelled quinoxyfen, a metabolite has been misidentified (18219, N. R. Pearson and G. L Reeves, 2005). The metabolite identified as 3-hydroxy quinoxyfen was subsequently positively identified as 2-oxoquinoxyfen by X-ray diffraction. Text and figures have been corrected to reflect this change of structure assignment.

***Animal metabolism***

Metabolism in lactating goats- adapted in part from the evaluation of Australia

The Meeting received a report on the metabolism, distribution, and elimination of $^{14}C$-quinoxyfen, labelled either in the phenoxy ring or the quinoline ring, in lactating dairy goats (n=5; 51-60 kg bw), (29257, Dunsire and Paul, 1995). Two goats were orally dosed with phenoxy $^{14}C$-quinoxyfen (purity > 98%), twice daily for 5 consecutive days, at a rate of 10.7 mg quinoxyfen/kg feed (equivalent to 0.20 mg ai/kg bw, 91.16 mg total over 5 days). Similarly, two goats were treated with quinoline $^{14}C$-quinoxyfen, twice daily for 5 consecutive days, at a rate of 11.7 mg quinoxyfen/kg feed (equivalent to 0.21 mg ai/kg bw, 101.2 mg total over 5 days). The remaining goat was used as the untreated control animal.

Urine and faeces were collected at intervals of 24 hours until sacrifice. The metabolism cages were washed with water at the time of excreta collection and the cage washings were retained for analysis of the TRRs. Milk samples were collected prior to the first treatment with quinoxyfen, and then twice daily throughout the study period (at about 8:00 am and 4:00 pm) until animals were sacrificed. The weights of urine, faeces, cage wash and milk samples were recorded and total radioactivity were measured using liquid scintillation counting (LSC). Faecal samples were homogenised with water and subjected to combustion analysis before analysis by LSC.

Goats were sacrificed 16 hours after the final dose, and samples of the following fluids/tissues were collected for TRR analysis: whole blood, plasma, liver, kidney, skeletal muscle, subcutaneous fat, omental fat, perirenal fat, GI tract and contents, and carcass. Tissue samples were analysed for their TRR content using combustion analysis and LSC.

The distribution of quinoxyfen TRRs recovered from goats after 10 twice daily oral doses of radio-labelled quinoxyfen (approximately10 mg ai/kg feed/day) are tabulated below. Results are expressed as a percentage of administered dose, and as μg equiv/kg (where applicable).

Table 2. Distribution of the radiolabelled residue in the body fluids and tissues of goats (29257).

| Sampling time/period (h) | % Administered (µg equiv./kg) | | | | |
|---|---|---|---|---|---|
| | Control | Phenoxy $^{14}C$-quinoxyfen | | Quinoline $^{14}C$-quinoxyfen | |
| | Animal 1 | Animal 2 | Animal 3 | Animal 4 | Animal 5 |
| Urine | | | | | |
| 0-24 | 0.0 | 5.8 | 1.2 | 1.6 | 1.20 |
| 24-48 | 0.0 | 8.3 | 14. | 2.5 | 2.4 |
| 48-72 | 0.0 | 7.9 | 9.1 | 2.8 | 0.05 |
| 72-96 | 0.0 | 9.1 | 9.8 | 3.0 | 5.7 |
| 96-120 | 0.0 | 9.2 | 10. | 2.8 | 2.9 |
| ***Subtotal*** | ***NA*** | ***40.*** | ***44.*** | ***13.*** | ***12.*** |
| Faeces | | | | | |
| 0-24 | 0.0 | 3.2 | 0.86 | 4.5 | 1.4 |
| 24-48 | 0.02 | 8.5 | 6.1 | 13. | 10. |
| 48-72 | 0.01 | 7.1 | 15. | 7.0 | 12. |
| 72-96 | 0.01 | 10. | 6.8 | 16. | 21. |
| 96-120 | 0.15 | 9.5 | 8.6 | 16. | 20. |
| ***Subtotal*** | ***NA*** | ***39.*** | ***38.*** | ***56.*** | ***65.*** |
| Cage wash | | | | | |
| 0-24 | 0.0 | 0.07 | 0.03 | 0.03 | 0.02 |
| 24-48 | 0.0 | 0.29 | 0.20 | 0.04 | 0.06 |
| 48-72 | 0.0 | 0.13 | 0.29 | 0.04 | 0.03 |
| 72-96 | 0.0 | 0.26 | 0.28 | 0.06 | 0.57 |
| 96-120 | 0.0 | 0.44 | 0.61 | 0.16 | 0.10 |
| ***Subtotal*** | ***NA*** | ***1.2*** | ***1.4*** | ***0.33*** | ***0.78*** |
| Milk | | | | | |
| 0-8 | 0.0 | 0.03 (28.) | 0.02 (29.) | 0.02 (20.1) | 0.01 (26.) |
| 8-24 | 0.0 | 0.09 (53.) | 0.08 (71.) | 0.06 (36.5) | 0.06 (56.) |
| 24-32 | 0.0 | 0.06 (66.) | 0.07 (107.6) | 0.04 (46.4) | 0.03 (77.) |
| 32-48 | 0.0 | 0.11 (68.) | 0.11 (96.) | 0.06 (44.6) | 0.07 (72.) |
| 48-56 | 0.0 | 0.06 (76.) | 0.07 (120.) | 0.04 (50.2) | 0.04 (88.) |
| 56-72 | 0.0 | 0.10 (74.) | 0.12 (109.) | 0.06 (48.0) | 0.08 (76.) |
| 72-80 | 0.0 | 0.10 (90.) | 0.09 (140.) | 0.05 (59.0) | 0.05 (101.) |
| 80-96 | 0.0 | 0.12 (75.) | 0.13 (110) | 0.08 (54.4) | 0.07 (74.) |
| 96-104 | 0.0 | 0.06 (81.) | 0.07 (130.) | 0.05 (62.5) | 0.06 (120.) |
| 104-120 | 0.0 | 0.10 (74.) | 0.13 (110.) | 0.06 (48.8) | 0.06 (64.) |
| Subtotal | NA | 0.83 | 0.89 | 0.52 | 0.53 |
| Tissues | | | | | |
| Liver | 0.0 | 0.92 | 0.92 | 0.69 | 1.3 |
| Kidney | 0.0 | 0.04 | 0.05 | 0.03 | 0.02 |
| GI tract wall | 0.0 | 3.1 | 3.3 | 6.9 | 2.5 |
| GI tract contents | 0.0 | 8.3 | 11. | 11.76 | 13. |
| Carcass | 0.01 | 2.1 | 3.4 | 1.7 | 2.3 |
| ***Subtotal*** | ***NA*** | ***14.*** | ***19.*** | ***21.*** | ***19.*** |
| | | | | | |
| **Total** | **NA** | **95.** | **103** | **91** | **98** |

Concentrations of total radioactivity in tissues for the phenoxy label were liver, 1.03 and 0.93 mg/kg; kidney, 0.29 and 0.34 mg/kg; muscle, 0.022 and 0.032 mg/kg; perirenal fat, 0.18 and 0.19 mg/kg; omental fat, 0.20 and 0.17 mg/kg; and subcutaneous fat, 0.12 and 0.12 mg/kg. Concentrations of total radioactivity in tissues for the quinoline label were liver, 0.94 and 1.5 mg/kg; kidney, 0.22 and 0.17 mg/kg; muscle, 0.015 and 0.032 mg/kg; perirenal fat, 0.13 and 0.32 mg/kg; omental fat, 0.12 and 0.26 mg/kg; and subcutaneous fat, 0.073 and 0.19 mg/kg. TRR levels in milk at 16 hours after the final dose were 0.074 and 0.11 mg/kg for the phenoxy label and 0.049 and 0.064 mg/kg for the quinoline label.

Samples were extracted with methanol. Liver was also subjected to protease digestion (pepsin, 0.1 M HCl, 37°C, overnight), enzyme deconjugation (β-glucuronidase with sulphatase activity) of the methanol extract, mild base hydrolysis, and/or strong base (6 N NaOH) or strong acid (6 N HCl) hydrolysis (reflux, 6 hour). Kidney was subjected to protease digestion. Some extraction efficiencies are summarized in Table 3.

Table 3. Extraction efficiencies of pooled tissue and milk samples (29257).

| Matrix | Treatment Step | Extraction Efficiency (% TRR) | |
|---|---|---|---|
| | | Phenoxy label | Quinoline label |
| Milk | Methanol extraction | 85 | 87 |
| Kidney | Methanol extraction | 71 | 45 |
| Kidney | Protease digestion | 100 | 100 |
| Liver | Methanol extraction | 42 | 25 |
| Liver | Protease digestion | 100 | 100 |
| Liver | 1M NaOH hydrolysis at 40° C | 94 | 92 |
| Muscle | Methanol extraction | 84 | 76 |
| Omental fat | Methanol extraction | 100 | 100 |
| Subcutaneous fat | Methanol extraction | 93 | 91 |
| Perirenal fat | Methanol extraction | 100 | 100 |

The TRRs in excreta (urine, faeces), milk and tissues (kidney, liver, fat) from goats were characterized and/or identified. Extracts were analyzed by TLC and HPLC, and some identifications (from urine and faeces only) were confirmed by GC/MS. Available standards (not labelled) included dichlorohydroxyquinoline (DCHQ), N-oxide quinoxyfen, 4-fluorophenol, 2-oxo quinoxyfen, and 6-hydroxy quinoxyfen. Values are expressed as a percentage of the TRR (except as noted) and as mg equiv. /kg (in parenthesis) in Table 4.

Table 4. Characterization/Identification of the radiolabelled residue in excreta, milk, and tissues (29257).

| Sample matrix | Extraction method | Percentage TRR (mg equiv./kg)[1] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Label | Quinoxyfen | Isomeric hydroxy quinoxyfens[2] | 4-FP | DCHQ | 2-oxo | Not identified[4] |
| Urine | Direct (none) | Phenoxy | ND[3] | ND | 3-6 | ND | ND | 89-92 |
| | | Quinoline | ND | ND | ND-21 | 11-12 | ND | 67-82 |
| | Acid hydrolysed + methanol | Phenoxy | ND-3.5 | ND-5[7] | 35-58 | ND | ND | 25-55 |
| | | Quinoline | ND-3.5 | ND-22[7] | ND-19 | 38-56 | ND | 15-38 |
| Faeces | Methanol | Phenoxy | 27-31 | 49-55[6] | ND-1.1 | ND | ND | 10-13 |
| | | Quinoline | 24-26 | 59-62[6] | ND | 2.5 | ND | 6-10 |
| Milk | Methanol | Phenoxy | 30-42 (0.027-0.038) | ND-0.94 (ND-0.0008) | ND (ND) | ND (ND) | ND-1.4 (ND-0.001) | 36-42 (0.032-0.038) |
| | | Quinoline | 37-42 (0.021-0.023) | ND (ND) | ND (ND) | ND-3.0 (ND-0.002) | ND (ND) | 38-40 (0.021-0.022) |
| Kidney | Methanol | Phenoxy | 1.6-2.3 (0.005-0.008) | ND (ND) | ND (ND) | ND (ND) | ND (ND) | 63-66[5] (0.21-0.22) |
| | | Quinoline | 2.4-3.5 (0.005-0.07) | ND (ND) | ND (ND) | ND-1.6 (ND-0.003) | ND (ND) | 31-39 [5] (0.59-0.75) |
| Liver | Methanol | Phenoxy | ND-1.2 (ND-0.012) | ND-2.1 (ND-0.022) | ND-6.7 (ND-0.068) | ND (ND) | ND (ND) | 30-34 (0.30-0.35) |
| | | Quinoline | 1.8-3.8 (0.022-0.047) | ND (ND) | ND (ND) | ND-3.2 (ND-0.041) | ND (ND) | 3.8-20 (0.050-0.25) |
| | Enzyme deconjugate (of MeOH extract) | Phenoxy | 10.5 (0.051) | 3.0 (0.015) | 13.2 (0.064) | ND (ND) | ND (ND) | 60.4 (0.29) |
| | | Quinoline | 18.3 (0.054) | 10.4 (0.031) | ND (ND) | 19.7 (0.058) | ND (ND) | 29.0 (0.085) |
| | Protease digest | Phenoxy | 6-7 (0.059-0.070) | ND (ND) | ND-8.3 (ND-0.085) | ND (ND) | ND (ND) | 70-74 (0.64-0.71) |
| | | Quinoline | 9-15 | ND | ND | ND | ND | 50-56 |

| Sample matrix | Extraction method | Percentage TRR (mg equiv./kg)[1] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Label | Quinoxyfen | Isomeric hydroxy quinoxyfens[2] | 4-FP | DCHQ | 2-oxo | Not identified[4] |
| | | | (0.12-0.20) | (ND) | (ND) | (ND) | (ND) | (0.62-0.72) |
| | Protease digest + acid hydrolysis | Phenoxy | 5-11 (0.043-0.099) | ND-1.2 (ND-0.011) | ND-22.4 (ND-0.201) | ND (ND) | ND-1.3 (ND-0.012) | 59-68 (0.52-0.61) |
| | | Quinoline | 2-13.5 (0.019-0.128) | ND (ND) | ND (ND) | ND-15.3 (ND-0.144) | ND (ND) | 48-71 (0.45-0.67) |
| | Protease digest + enzyme deconjugate[6] | Phenoxy | ND-74 | ND-8.5 | ND | ND | ND-90 | ND-22. |
| | | Quinoline | ND-84 | ND-4.8 | ND | 5.5-7.0 | ND-81 | 5.2-8.1 |
| Omental fat | MeOH extract | Phenoxy | 51-98 (0.099-0.19) | ND (ND) | ND (ND) | ND (ND) | ND (ND) | 1.8-26. (0.004-0.050) |
| | | Quinoline | 53-96 (0.100-0.18) | ND (ND) | ND (ND) | ND (ND) | ND (ND) | ND-22 (ND-0.041) |
| Perirenal fat | MeOH extract | Phenoxy | 70-96 (0.13-0.18) | ND (ND) | ND (ND) | ND (ND) | ND (ND) | 1.2-14.4 (0.002-0.028) |
| | | Quinoline | 90-97 (0.19-0.20) | ND (ND) | ND (ND) | ND (ND) | ND (ND) | ND-3.4 (ND-0.007) |
| Subcutaneous fat | MeOH extract | Phenoxy | 76-83 (0.096-0.10) | ND-1.5 (ND-0.002) | ND (ND) | ND (ND) | ND (ND) | 3.7-5.4 (0.005-0.007) |
| | | Quinoline | 75-94 (0.061-0.076) | ND (ND) | ND (ND) | ND (ND) | ND (ND) | 1.9-6.5 (0.002-0.005) |

[1] 4-FP = 4-fluorophenol; DCHQ = 5,7-dichloro-4-hydroxyquinoline; 2-oxo = the 2-oxo derivative of quinoxyfen. Calculated on a %TRR basis by the JMPR reviewer using percent of radioactivity in the extract and extraction efficiency.

[2] Radioactive material that co-chromatographed (TLC, HPLC) with the N-Oxide quinoxyfen standard in faeces extracts was shown by GC-MS to be comprised of several isomeric hydroxy-quinoxyfen metabolites. Other extracts were not subjected to GC/MS/ Thus, identifications of N-oxide in various tissue extracts are not confirmed.

[3] not detected.

[4] Generally characterized as "polar material" by TLC and HPLC.

[5] Deconjugation with mixed glucuronidase/sulphatase treatment did not change the profile.

[6] Percentage of total radioactivity in the final extract.

[7] N-oxide quinoxyfen was identified by HPLC in acid-hydrolysed urine but was not confirmed by TLC.

The major component identified in liver was a conjugated form of quinoxyfen (approximately 10–15% TRR). The only components identified in kidney were quinoxyfen (approximately 3% TRR) and DCHQ (about 2% TRR), with no apparent quinoxyfen conjugates present. In both kidney and liver, major portions of the TRR were characterized as polar based on TLC and HPLC behaviour. The major component present in fat was quinoxyfen (approximately 90% TRR), while milk contained quinoxyfen (about 40% TRR) and some very polar material. Small amounts of radioactivity corresponding to 4-fluorophenol, DCHQ, and several hydroxy-quinoxyfen metabolites were also present in the liver. Small amount of radioactivity corresponding to 2-oxo quinoxyfen, DCHQ, and isomeric hydroxy quinoxyfens were found in the milk. For both labels, hydroxy metabolites and parent compound were the major components present in faeces, while urine contained mainly a polar component which was easily hydrolysed to 4-fluorophenol or DCHQ. A proposed metabolic pathway is presented in Figure 1.

The metabolism in goat and rat (7474, Schumann, 1995) are qualitatively similar. Cleavage of the ether linkage to form 4-fluorophenol and DCHQ is seen in both animals. Isomers of fluorophenyl-ring hydroxylated quinoxyfen were found in the rat (bile, faeces), whereas isomers of quinoline-ring hydroxylated quinoxyfen (2-oxo) were found in the goat metabolism study. The latter were at very low levels (< 0.1% of the administered dose for the 2-oxo quinoxyfen) in the rat.

Figure 1: Proposed Metabolic Pathway for Quinoxyfen in the Lactating Goat

*Metabolism in poultry*

The Meeting did not receive a poultry metabolism study. Likewise, the evaluations of Australia, the EC, and the USA do not include a poultry metabolism study. However, see the poultry feedings study below, where radiolabelled quinoxyfen was utilized.

## Plant metabolism

*Wheat – adapted from the Evaluation of the EC (UK)*

The Meeting received two study reports on the metabolism of quinoxyfen in wheat (31757, Haq and Brown, 1995a; 31659; Haq, MacDonald, and Brown, 1995). In the first study, which was a probe study, $^{14}$C-quinoxyfen was applied to winter wheat plants at growth stage BBCH 32. Another application was made to previously untreated plants at growth stage BBCH 57 (70% of inflorescence emerged). Samples were collected at various time intervals and assayed for total radioactivity.

In the second study, UK trials were carried out in 1993, with [4-flurophenoxy-U-$^{14}$C]- or [2-quinoline-$^{14}$C]-quinoxyfen (radiochemical purities > 98%) formulated as emulsifiable concentrates and applied to winter wheat grown in outdoor pots in single applications of 250 g ai/ha at BBCH 32(stem elongation phase – 2nd node) or in one application of 250 g ai/ha at BBCH 49 (late booting stage – first awns visible). To aid characterisation of metabolites, applications at 1000 g ai/ha were also made at BBCH 32. Plants receiving an application at BBCH 32 were sampled at days 0, 14, 29 and 105 (harvest) after treatment. Plants receiving an application at BBCH 49 were sampled at days 0 and 78 (harvest) after treatment.

Roots were separated from aerial parts and, for harvest samples, grain separated from straw. A series of solvent washes were used to remove residues from the surface: methanol: water; dichloromethane; methanol. Remaining material was extracted with acidified acetonitrile. Samples were combusted both before and after extraction to determine total radioactivity. Radioactivity remaining in the post-extraction residual material (non-extractable) was determined by combustion/LSC. Radioactive fractions were further characterised by TLC, HPLC, and mass spectrometry. Grain samples from harvest were further separated into grain and chaff. The sequence of washes and extraction procedures employed for grain were similar to those used for straw. Only grain from plants receiving the late season application was used for studying the distribution and characterisation of radioactivity.

The distribution of radioactive residues is presented in Table 5. Total radioactivity in straw at harvest was 3–5 mg/kg for the higher application rate. Total radioactivity in grain was 0.03–0.05 mg/kg.

Table 5. The distribution of radioactivity in winter wheat straw and grain following treatment with phenoxy- and quinoline-labelled [$^{14}$C] quinoxyfen (% TRR and mg/kg) (31757; 31659).

| Sample[1] | Aqueous wash | | dichloromethane wash | | methanol wash | | Total wash | | Acetonitrile extract | | Non extractable | | Total Activity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | mg/kg |
| STRAW: P-label, , BBCH 32 | | | | | | | | | | | | | |
| Day0 1N | 15.7 | 0.672 | 25.6 | 1.10 | 39.4 | 1.70 | 80.7 | 3.50 | 15.4 | 0.66 | 3.86 | 0.166 | 4.3 |
| 4N | 14.9 | 3.03 | 26.8 | 5.40 | 35.8 | 7.30 | 77.5 | 15.7 | 17.0 | 3.40 | 5.50 | 1.12 | 20.4 |
| Day 14 1N | 10.4 | 0.212 | 20.8 | 0.42 | 23.4 | 0.48 | 54.6 | 1.11 | 21.3 | 0.43 | 24.1 | 0.49 | 2.04 |
| 4N | 10.8 | 1.16 | 23.2 | 2.50 | 24.8 | 2.05 | 58.9 | 6.28 | 20.7 | 2.20 | 20.4 | 2.18 | 10.7 |
| Day 29 1N | 8.14 | 0.070 | 8.72 | 0.07 | 20.7 | 0.17 | 37.6 | 0.30 | 30.8 | 0.25 | 31.5 | 0.26 | 0.8 |
| 4N | 7.93 | 0.370 | 11.3 | 0.54 | 22.2 | 1.05 | 41.5 | 1.90 | 25.9 | 1.22 | 32.6 | 1.60 | 4.7 |
| Harvest1N | 8.97 | 0.090 | 5.19 | 0.052 | 14.4 | 0.14 | 28.6 | 0.28 | 10.8 | 0.11 | 60.6 | 0.60 | 1.0 |
| 4N | 11.7 | 0.6 | 10.8 | 0.52 | 24.4 | 1.16 | 46.9 | 2.24 | 11.4 | 0.55 | 42.0 | 2.00 | 4.8 |
| STRAW: P-label, , BBCH 49 | | | | | | | | | | | | | |
| Day 0 1N | 5.10 | 0.08 | 23.0 | 0.35 | 38.2 | 0.58 | 66.4 | 1.01 | 30.8 | 0.47 | 2.81 | 0.04 | 1.53 |
| Harvest1N | 7.53 | 0.16 | 5.47 | 0.12 | 12.8 | 0.28 | 25.8 | 0.56 | 10.7 | 0.23 | 63.5 | 1.37 | 2.16 |
| STRAW: Q-label, BBCH 32 | | | | | | | | | | | | | |
| Day 0 1N | 15.2 | 0.804 | 24.6 | 1.30 | 45.7 | 2.41 | 85.5 | 4.52 | 9.18 | 0.485 | 5.33 | 0.281 | 5.28 |
| 4N | 14.4 | 5.11 | 34.0 | 12.0 | 42.2 | 15.0 | 90.6 | 32.1 | 6.49 | 2.30 | 2.88 | 1.02 | 35.4 |
| Day 14 1N | 6.61 | 0.113 | 16.5 | 0.283 | 22.9 | 0.393 | 46.0 | 0.789 | 17.1 | 0.294 | 36.9 | 0.633 | 1.72 |
| 4N | 6.29 | 0.563 | 28.2 | 2.53 | 24.8 | 2.22 | 59.3 | 5.31 | 14.8 | 1.32 | 26.0 | 2.33 | 9.00 |
| Day 29 1N | 5.64 | 0.065 | 10.0 | 0.116 | 19.3 | 0.223 | 35.0 | 0.404 | 21.1 | 0.243 | 43.9 | 0.507 | 1.15 |
| 4N | 7.16 | 0.323 | 14.3 | 0.643 | 20.4 | 0.922 | 41.9 | 1.89 | 23.8 | 1.07 | 34.3 | 1.55 | 4.51 |
| Harvest1N | 12.2 | 0.262 | 6.43 | 0.138 | 14.5 | 0.311 | 33.1 | 0.712 | 8.77 | 0.189 | 58.2 | 1.25 | 2.15 |
| 4N | 10.6 | 0.555 | 8.75 | 0.460 | 16.5 | 0.867 | 35.8 | 1.88 | 9.91 | 0.520 | 54.2 | 2.85 | 5.25 |

| Sample[1] | Aqueous wash | | dichloromethane wash | | methanol wash | | Total wash | | Acetonitrile extract | | Non extractable | | Total Activity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | % | mg/kg | mg/kg |
| STRAW: Q-label, , BBCH 49 | | | | | | | | | | | | | |
| Day 0 1N | 8.22 | 0.290 | 24.8 | 0.88 | 29.5 | 1.04 | 62.5 | 2.21 | 34.3 | 1.21 | 3.18 | 0.112 | 3.53 |
| Harvest1N | 9.65 | 0.330 | 4.54 | 0.155 | 10.3 | 0.353 | 24.5 | 0.838 | 12.0 | 0.410 | 63.5 | 2.17 | 3.42 |
| GRAIN: P-label, BBCH 49 | | | | | | | | | | | | | |
| Harvest1N | 2.48 | 0.0009 | 0.92 | 0.0003 | 0.82 | 0.0003 | 4.22 | 0.0015 | 7.91 | 0.0028 | 87.9 | 0.0307 | 0.0349 |
| GRAIN: Q-label, , BBCH 49 | | | | | | | | | | | | | |
| Harvest1N | 2.64 | 0.0014 | 0.20 | 0.0001 | 0.54 | 0.0003 | 3.38 | 0.0018 | 7.12 | 0.0038 | 89.5 | 0.048 | 0.0535 |

[1] 1 N = 250 g ai/ha; 4N = 1000 g ai/ha. Harvest = 105 days after treatment for early application, 78 days after treatment for late application. There were many additional whole plant sample analyses reported, but without sufficient information to calculate TRRs in mg equivalents/kg.

Table 6. Distribution and characterisation of total residues obtained from aqueous and solvent washes and acetonitrile extraction following treatment with [$^{14}$C] quinoxyfen. (31757; 31659).

| Sample | quinoxyfen | | Metabolite A[2] | | Metabolite B | | Metabolite C | | Metabolite E | | Metabolite F | | Metabolite G | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg |
| STRAW: P-label, BBCH 32 | | | | | | | | | | | | | | |
| Day 0 1N[1] | 69. | 3.0 | | | 0.88 | 0.038 | | | 1.2 | 0.052 | | | 1.1 | 0.047 |
| 4N | 75. | 15. | | | 0.81 | 0.16 | | | 1.5 | 0.31 | | | 0.75 | 0.15 |
| Day 14 1N | 34. | 0.68 | 16. | 0.33 | 15. | 0.31 | 4.5 | 0.091 | 2.9 | 0.060 | 1.4 | 0.029 | 1.9 | 0.038 |
| 4N | 39. | 4.2 | 17. | 1.8 | 11. | 1.2 | 6.2 | 0.66 | 1.2 | 0.13 | 1.2 | 0.12 | 1.4 | 0.15 |
| Day 29 1N | 16. | 0.13 | 23. | 0.18 | 4.0 | 0.033 | 15. | 0.12 | 4.7 | 0.039 | 1.7 | 0.014 | 1.7 | 0.014 |
| 4N | 16. | 0.77 | 18. | 0.83 | 7.8 | 0.37 | 14. | 0.67 | 2.6 | 0.12 | 0.91 | 0.043 | 7.3 | 0.35 |
| Harvest 1N | 8.3 | 0.083 | 23. | 0.23 | | | 1.9 | 0.019 | 4.5 | 0.045 | | | 1.4 | 0.015 |
| 4N | 27. | 1.3 | 22. | 1.0 | 0.70 | 0.034 | 1.8 | 0.087 | 5.5 | 0.26 | | | 1.4 | 0.067 |
| STRAW: P-label, BBCH 49 | | | | | | | | | | | | | | |
| Harvest 1N | 11. | 0.23 | 17. | 0.36 | 0.45 | 0.01 | 2.0 | 0.044 | 4.3 | 0.093 | | | 1.5 | 0.032 |
| STRAW: Q-label, BBCH 32 | | | | | | | | | | | | | | |
| Day 0 1N | 75.6 | 4.0 | | | 0.35 | 0.018 | | | 1.5 | 0.081 | | | 1.4 | 0.074 |
| 4N | 85. | 30. | 0.08 | 0.028 | | | | | 0.96 | 0.34 | | | 0.95 | 0.34 |
| Day 14 1N | 30. | 0.52 | 24. | 0.40 | 1.5 | 0.026 | 2.2 | 0.038 | 1.7 | 0.029 | 2.1 | 0.037 | 1.3 | 0.023 |
| 4N | 47. | 4.2 | 20. | 1.8 | | | | | 1.1 | 0.101 | 1.6 | 0.14 | 0.85 | 0.076 |
| Day 29 1N | 17. | 0.20 | 27. | 0.32 | 4.4 | 0.051 | | | 4.0 | 0.046 | 0.50 | 0.006 | 2.1 | 0.024 |
| 4N | 33. | 1.5 | 29. | 1.3 | | | | | 2.5 | 0.11 | 0.57 | 0.026 | 1.1 | 0.051 |
| Harvest 1N | 7.9 | 0.17 | 27. | 0.58 | 1.8 | 0.038 | 1.1 | 0.025 | 2.9 | 0.062 | | | 1.2 | 0.025 |
| 4N | 20. | 1.00 | 22. | 1.2 | | | 1.1 | 0.057 | 3.3 | 0.17 | | | | |
| STRAW: Q-label, BBCH 49 | | | | | | | | | | | | | | |
| Harvest 1N | 5.0 | 0.17 | 24. | 0.83 | | | 1.4 | 0.049 | 3.8 | 0.13 | | | 1.8 | 0.060 |

| Sample | quinoxyfen | | Metabolite A[2] | | Metabolite B | | Metabolite C | | Metabolite E | | Metabolite F | | Metabolite G | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg | % TRR | amount mg/kg |
| GRAIN: P-label, BBCH 49 | | | | | | | | | | | | | | |
| Harvest 1N | 0.11 | .00004 | 8.6 | 0.003 | | | 2.5 | .00088 | 0.68 | .00021 | | | 0.24 | .00007 |
| GRAIN: Q-label, BBCH 49 | | | | | | | | | | | | | | |
| Harvest 1N | 0.03 | .00002 | 9.0 | 0.0048 | | | 1.23 | .00069 | 0.10 | .00006 | | | 0.03 | .00002 |

[1] 1N = 0.250 g ai/ha, 4N = 100 g ai/ha

[2] A is 6 or more components, possibly organic acids.

Levels of the quinoxyfen in straw declined 4–8 fold from time 0 to harvest. At harvest, 58–63% of total radioactive residue (TRR) was non-extractable, approximately 0.1–0.2 mg/kg quinoxyfen were found in day 105 samples following application at BBCH 32 and about 0.2 mg/kg quinoxyfen were found in day 78 samples following application at BBCH 49. In grain at harvest, total radioactivity was approximately 0.04–0.05 mg/kg, of which > 90% was unextractable. Less than 0.001 mg/kg quinoxyfen was found.

No qualitative differences were found between the metabolite profiles of the phenyl- and quinoline-labelled forms.

The distribution and characterisation of metabolite residues in straw and grain are summarised in Table 7. The extractable fraction (solvent wash and acidified acetonitrile extract) was found to contain 4–6 metabolites (designated A, B, C, E, F, and G) accounting for approximately (A) 0.2–0.8 mg/kg (several components), (C) 0.02–0.1 mg/kg, (E) 0.03-0.1 mg/kg and (G) 0.02–0.06 mg/kg. It was suggested that E and G were formed from quinoxyfen by hydroxylation and loss of Cl, respectively, however no structure was given for E. Metabolite G was tentatively identified as a photodegradation product since it exhibited similar chromatographic characteristics to the product of aqueous photolysis of quinoxyfen, CFBPQ (see Figure 2). In grain, qualitatively similar metabolites were found to those found in straw, although levels were lower and were < 0.01 mg/kg.

Further experiments to increase the amount of extractable residue were carried out on samples from plants that had received a treatment at BBCH 49. Extraction of the 'non-extractable' straw fraction remaining after acetonitrile extraction involved extraction in 0.1M sodium hydroxide, followed by Soxhlet extraction in 0.2M sodium hydroxide in methanol. Grain was extracted with 0.1M sodium hydroxide. Straw was also subjected to enzyme hydrolysis using either pancreatin (a mixture that includes amylase, trypsin, lipase, ribonuclease, and protease), glucosidase, glucuronidase or cellulase.

The resulting extracts of base hydrolysis were analysed by TLC, LSC and combustion/LSC. Extracts from enzyme hydrolyses were partitioned with methyl t-butyl ether under both acidic and basic conditions. The distribution of the radioactivity between the organic and residual aqueous phases was determined by LSC. The ratio of radioactivity in the organic and aqueous partitions was compared to aliquots of material that had not been incubated in the presence of enzymes.

Alkaline hydrolysis of the straw resulted in up to ca. 82% of the previously unextracted radioactive residue being released (approximately 41% TRR in straw). TLC profiling of the hydrolysed extract indicated that the resulting radiolabelled compounds were polar in nature, as all the radioactivity remained at the origin of the chromatogram.

Alkaline hydrolysis of the grain resulted in up to 38% of the previously unextracted radioactive residue being released (approximately. 33% TRR in grain). Due to the gelatinous nature of the extracts the applicant stated that it was not possible to carry out profiling of these extracts.

Enzyme hydrolysis of straw resulted in comparable levels of radioactivity in the organic portion of the resulting extracts compared to samples following the same partitioning process that had not been incubated with enzymes. This indicated that the previously unextracted radioactivity that the

hydrolysis systems released (approximately 70% pancreatin, 94% glucosidase, 89% glucuronidase and 93% cellulase) were polar species.

Potassium permanganate was used as an oxidising agent on straw samples which had been previously extracted with acetonitrile. The agent was buffered with iron nitrate and silver nitrate. The remaining fibre was rinsed with a solution of oxalic acid in ethanol. The radioactivity in the washes and remaining fibre were determined by LSC and combustion/LSC. This system will oxidise lignin but not cellulose and therefore provided an estimate of the partition of 'unextracted' radioactivity between cellulose (direct measurement) and lignin (remainder by mass balance). Of the 64 and 73% of TRR remaining in the acetonitrile extracted tissue, approximately 37 and 40% (about 24 and 29% TRR) have been shown be associated with cellulose. The balance is considered to be associated with lignin (about 31 and 45% TRR). All values quoted are for phenyl- and quinoline labels, respectively.

Direct measurement of lignin associated radioactivity was made on straw samples which had been previously extracted with acetonitrile. The straw was soaked in dioxane: water and shaken for 4 days at room temperature, then filtered. The process was repeated for a further 2 days at 60°C, it was then centrifuged. The centrifuge pellet was extracted again as before but for 5 days at 50°C. The radioactivity of the supernatants was determined by LSC. This method of estimating lignin associated radioactivity resulted in an estimate of lignin associated radioactivity of 16 and 21% TRR for the phenyl- and quinoline-labels, respectively.

Measurement of the starch related residue of the wheat grain was carried out by finely milling the grain which was then extracted using dimethyl sulphoxide, centrifuged and the starch containing supernatant was decanted. The starch was precipitated from the supernatant with anhydrous ethanol and separated by centrifugation. The radioactivity of the different fractions was determined by combustion/LSC or LSC. These data showed that around 13 and 53% of the TRR in grain was precipitated from the system by the addition of ethanol and is therefore probably incorporated into starch. Approximately 59 and 38% of the residue remained in the supernatant (dimethyl: sulphoxide:ethanol:water) from which the starch was precipitated. All values quoted are for phenoxy and quinoline labels, respectively.

Further characterisation of the polar, origin associated 'metabolite A' in the normal phase TLC system was carried out. Hydrochloric acid was used to hydrolyse the aqueous wash samples at 85°C from the BBCH 49 application. TLC analysis demonstrated that no quinoxyfen or related material was released, by the hydrolysis. Partial hydrolysis of the quinoxyfen was observed but ca. 70% of the parent compound remained unhydrolysed. To better characterise 'metabolite A', derivatization of the aqueous washes of samples from the BBCH 49 application was carried out. Acetylation was used, dried samples were suspended in pyridine: acetic acid at 95°C, to facilitate the partitioning of the 'metabolite' into toluene. This acetylation enabled 42 and 26% of the radioactivity in the washes to be partitioned into toluene for the phenyl- and quinoline-labelled treatments, respectively. The resulting solutions were evaporated to dryness and re-suspended in acetonitrile. Reverse and normal phase TLC of the acetylated extract indicated that 'metabolite A' was (after undergoing an acetylation procedure) made up of several (at least six components).

Reverse phase HPLC analysis of washes and extracts of samples from the BBCH 49 application resulted in a broad peak within 1 minute of the solvent front. When the mobile phase was acidified (2% acetic acid) a broad peak resolved from the solvent front was observed. The applicant suggests this is evidence that 'metabolite A' and the other uncharacterised components are acidic anions. They propose that the acidification of the mobile phase results in the retention of the component on the reverse phase column, but that the multiple components of the metabolite are not resolved by this system. It was noted that in all the chromatograms the UV profile closely mirrored the radio-chromatogram, indicating that the metabolites were very similar to/may be the same as the matrix material. The use of a reverse phase ion exchange column in the chromatographic system resulted in several broad poorly resolved peaks being observed.

Tricapryl methyl ammonium chloride, (a lipophilic quaternary ammonium salt) was used as an ion pair reagent to try to extract the postulated organic acids that are proposed as constituting 'metabolite A' into dichloromethane. This system was used on the aqueous washes of the mature

samples from all the treatment regimes. At pH 2, 30% of the radioactivity was extracted into the dichloromethane. At pH 10, 82% of the radioactivity is extracted into the dichloromethane. This provides further evidence for the acidic anionic nature of the metabolites.

LC-MS studies (electrospray interface) on the ion pair extracts described above identified only one poorly resolved peak when negative ion mode was employed. The retention time of the peak matched a peak in the radioactive trace. A reasonable mass spectrum was produced with a postulated molecular ion at m/z 501, with a strong base peak at m/z305. However a corresponding peak in the UV trace at the same retention time was proposed by the applicant as indicating that 'metabolites' such as the 'metabolite A' complex and wheat natural products were in fact the same and resulted from natural incorporation.

Aqueous photolysis studies were conducted on aliquots of the parent material and resulted in the production of polar material, demonstrating that polar components were generated on photo-degradation of quinoxyfen. Chromatographic analysis of the ion paired product of this polar material showed that it was not the same as the polar material that comprised Metabolite A. This demonstrates that the metabolites produced are not simply photo-degradation products of quinoxyfen.

To support the proposal that polar metabolites represented by the 'metabolite A' complex may have arisen by the incorporation of small carbon units (derived from quinoxyfen) into natural products, an investigation into the nature of the matrix natural products extracted with surface wash solvents used was carried out. The study demonstrated that the surface washes were relatively inefficient at extracting the dislodgeable matrix material from the plant, (third or fourth extractions still removed material). 13C-NMR analysis of the aqueous and methanol wash material demonstrated that it comprised largely sugar moieties (either as mono, oligo or polysaccharides). The same analysis of the dichloromethane wash indicated that long chain hydrocarbons were present (waxes).

*Metabolism in sugarbeets- adapted in part from the Evaluation of the USA*

The metabolism of $^{14}$C-quinoxyfen in sugarbeet roots and leaves following maximum seasonal application (for European use) of 300 g ai/ha applied in two applications, as a suspension concentrate formulation was reported to the Meeting (81925, Graper and Balcer, 2001). The last application was delivered 60 days after the first application and 26 days before the mature harvest. Immature samples were taken between the first and second applications.

Additional higher rate plots (600 g ai/ha) were included to facilitate the characterization and identification of radioactive residues. One application was made and only immature crops were harvested. Half of the plots at either rate were treated with $^{14}$C-quinoxyfen labelled in the phenoxy ring and the other half labelled at the quinoline ring.

Sampling intervals for immature leaves and roots were 0, 7, 14, and 28 days after treatment, except that no root and leaf samples were taken from the 600 g ai/ha plot at 0 DAT. The radioactive residues in the samples were isolated and characterized by liquid extraction, partition, and chromatography.

Half of the immature top samples were sequentially surface washed with a dilute surfactant solution (0.1% aqueous solution of Aerosol OT) and dichloromethane. The remaining half of immature tops along with mature tops, and immature and mature root samples were not surface washed. Radioactivity was determined by liquid scintillation counting (LSC) for liquid samples (surface washings) and by combustion/LSC for solid samples (roots and tops). The limit of detection (LOD) and limit of quantitation (LOQ) were reported at 0.002 and 0.007 mg/kg, respectively. TRRs were calculated by summing the radioactivity determined for the surface washings and the respective tissue sample. The TRRs are presented in Table 7.

Table 7. TRRs in /on sugarbeet root and top samples following applications of phenyl- and quinoline-labelled [$^{14}$C]Quinoxyfen. (81925).

| Timing and Method of application | Matrix | PHI (days) | TRR (mg/kg) [1] | |
|---|---|---|---|---|
| | | | Phenyl-label | Quinoline-label |
| Two foliar applications for a total application of 0.35-0.36 kg ai/ha | Whole plant | 0 after 1st application | 6.56 (8.60) | 9.00 (10.0) |
| | Immature sugar beet root | 7 after 1st application | 0.123 | 0.077 |
| | | 14 after 1st application | 0.067 | 0.067 |
| | | 28 after 1st application | 0.014 | 0.025 |
| | Mature sugar beet root | 26 after 2nd application | 0.078 | 0.049 |
| | Mature "split" sugar beet root | 26 after 2nd application | 0.059 | -- |
| | Immature tops | 7 after 1st application | 3.28 (2.74) | 3.08 (4.68) |
| | | 14 after 1st application | 0.952 (1.15) | 1.12 (2.44) |
| | | 28 after 1st application | 0.503 (0.300) | 1.08 (0.345) |
| | Mature tops | 26 after 2nd application | 1.89 | 2.20 |
| Single foliar application at 0.59-0.65 kg ai/ha | Immature sugar beet root | 7 after 1st application | 0.287 | 0.124 |
| | | 14 after 1st application | 0.087 | 0.172 |
| | | 28 after 1st application | 0.063 | 0.081 |
| | Immature tops | 7 after 1st application | 18.3 (19.8) | 19.0 (16.0) |
| | | 14 after 1st application | 9.72 (9.13) | 7.30 (12.7) |
| | | 28 after 1st application | 2.75 (3.47) | 6.09 (2.60) |

[1] TRR of surface-washed top samples are given in parentheses and are sum of the radioactivity determined in surface washings and residual tissue.

For both labels, it was found that the majority of the radioactivity was extractable in 80:20 acetonitrile/water (68–77% TRR root; 55% [quinoline label] –74% TRR leaf).

Chromatographic analyses of the acetonitrile: water extract showed the nature of radioactivity to be similar between the phenyl and quinoline labels. The parent quinoxyfen was identified as the principal residue component accounting for: 26% of TRR in phenyl-labelled roots, 25% of TRR in quinoline-labelled roots, 30% of TRR in phenyl-labelled tops, and 19% of TRR in quinoline-labelled tops. The remainder of radioactivity was characterized as polar residues consisting of multiple metabolites

The organic extracts, partitioning phases, and hydrolysates of sugar beet roots and tops were initially analyzed by HPLC conducted on a YMS ODS-AQ C18 column with a gradient mobile phase of ACN and water each with 0.1% acetic acid, using in-line radioactivity detection and UV detection (225 or 290 nm). Radioactive residues were identified by co-chromatography with the following non-labelled reference standards: quinoxyfen, 2-oxo quinoxyfen, 6-hydroxy quinoxyfen, DCHQ, and 4-fluorophenol.

Thin-layer chromatography (TLC) analysis of the initial aqueous ACN extract was performed to confirm the identity of quinoxyfen. TLC analyses were conducted using silica gel F254 plates and a toluene: acetone (75:25, v:v) solvent system. Reference standards were observed under UV light (254 nm) and radioactive residues were quantitated using phosphor imaging.

Using TLC, the minor peak which co-chromatographed with the 2-oxo metabolite by HPLC analysis, chromatographed near the 6-OH metabolite. This metabolite was not further identified, but is thought to possibly be the CFBPQ [2-chloro-10-fluoro(1)benzopyrano(2,3,4-de)quinoline] metabolite. The CFBPQ metabolite co-chromatographed with the 2-Oxo standard using HPLC analysis in a separate tomato metabolism study (see below). Because CFBPQ was the main metabolite observed in

an aqueous photolysis study (see below), this metabolite is likely formed via photolysis on the surface of the leaves and may have been absorbed and possibly further metabolized.

The aqueous phase of the quinoline-labelled extract was also analyzed by an additional HPLC system with a gradient phase over a longer period and an even more multicomponent profile was observed. The parent and DCHQ metabolite eluted near the standards, but a definitive identification could *not* be made.

Polar metabolites released by acid hydrolysis of the phenyl-labelled aqueous phase were further isolated by C18 SPE. The fraction containing the highest radioactivity was analyzed by HPLC and LC/MS. HPLC analysis was similar to the aqueous phase with 4-fluorophenol identified as the major residue, while LC/MS demonstrated that none of the radioactivity co-eluted with 4-fluorophenol, 2-Oxo, or quinoxyfen. It was proposed that the residues were metabolites which had lost the quinoline portion of the quinoxyfen molecule and which contain the chlorine atoms, such as conjugates of 4-fluorophenol. The isolated SPE fraction was also acid hydrolysed and partitioned with dichloromethane. HPLC and LC/MS analysis confirmed that the majority of radioactivity was 4-fluorophenol. Because the 4-fluorophenol metabolite was identified by co-chromatography prior to acid hydrolysis in the aqueous phase and was determined from the organic phase following acid hydrolysis, the petitioner stated that the 4-fluorophenol metabolite is present as a conjugate in the SPE fraction. The 4-fluorophenol conjugate(s) was confirmed by LC/MS.

The nonextractable residues, after initial extraction of samples with acetonitrile: water, were 23.2–32.0% of TRR for roots and 17.8–35.9% of TRR for tops. No further attempts were made to characterize bound residues in roots since the TRR was ≤ 0.02 mg/kg. To characterize bound residues in tops, sub-samples were subjected to acid detergent fibre, cellulose, and lignin isolation procedures. The results of these procedures showed that most of the radioactivity was associated with lignin.

Table 8. Summary of residue characterization/Identification in mature sugarbeet roots and tops following two foliar applications of phenyl-or quinoline-Label [$^{14}$C]Quinoxyfen (81925).

| Metabolite/Fraction | Root | | Tops | |
|---|---|---|---|---|
| | % TRR [a] | mg/kg[a] | % TRR | mg/kg |
| Phenyl-Label Quinoxyfen | TRR = 0.078 mg/kg | | TRR = 1.9 mg/kg | |
| Quinoxyfen | 26 | 0.020 | 30 | 0.56 |
| 4-Fluorophenol | -- | -- | 17 | 0.32 |
| CFBPQ [b] | -- | -- | 5.0 | 0.094 |
| Multiple Unknowns, Rt = 6 minutes | 37 | 0.029 | -- | -- |
| Multiple Unknowns, Rt = 25 minutes | -- | -- | 19 | 0.36 |
| Other unknowns | 7.4 | 0.008 | 8.5 | 0.16 |
| Total Extractable | 77 | 0.060 | 74 | 1.4 |
| Total Identified | 26 | 0.020 | 52 | 0.98 |
| Total Characterized [c] | 44 | 0.037 | 28 | 0.52 |
| Total Unresolved | Not reported (NR) | NR | NR | NR |
| Total Unextractable [d] | 23 | 0.018 | 18 | 0.34 |
| TOTAL | 100 | 0.078 | 92 | 1.7 |
| Quinoline-Label Quinoxyfen | TRR = 0.049 mg/kg | | TRR = 2.2 mg/kg | |
| Quinoxyfen | 25 | 0.012 | 19 | 0.43 |
| DCHQ | -- | -- | 6.9 | 0.15 |
| CFBPQ [b] | -- | -- | 3.0 | 0.065 |
| Unknown Rt = 6 minutes | 18 | 0.009 | -- | -- |
| Other unknowns | 16 | 0.007 | 25. | 0.56 |

| Metabolite/Fraction | Root | | Tops | |
|---|---|---|---|---|
| | % TRR [a] | mg/kg[a] | % TRR | mg/kg |
| Total Extractable | 68 | 0.033 | 55 | 1.2 |
| Total Identified | 25 | 0.012 | 29 | 0.64 |
| Total Characterized [c] | 34 | 0.016 | 25 | 0.56 |
| Total Unresolved | NR | NR | NR | NR |
| Total Unextractable [d] | 32 | 0.016 | 36 | 0.79 |
| TOTAL | 100 | 0.049 | 91 | 2.0 |

[a] Values were normalized in the report to compensate for non-homogeneity problems in roots.

[b] Co-eluted with 2-oxo standard using HPLC, but eluted near the 6-OH standard with TLC; this metabolite was not further identified, but is thought to possibly be the CFBPQ metabolite, (2-chloro-1)-fluoro[1]benzopyrano[2,3,4-de]quinoline.

[c] Total Characterized = sum of all unidentified/characterized metabolites.

[d] Total Unextractable = TRR - Total Extractable, as stated in report. Much of the unextractable residue in tops was characterized as lignin.

*Metabolism in grapes- adapted from the Evaluation of the USA*

The Meeting received a study report on the metabolism of quinoxyfen in/or grape vines (42894, Caley and Kingsley, 1995). $^{14}$C-quinoxyfen, labelled in either the phenoxy ring or the quinoline ring, was formulated as a suspension concentrate and applied either at the rate of 375 mg/L or 750 mg/L active ingredient. Both radiolabelled compounds had a radiopurity > 97% (by TLC) and specific activities of 91.45 µCi/mg for the phenoxy label and 82.50 µCi/mg for the quinoline label, as determined by liquid scintillation counting. Applications were made to grape vines grown in a glasshouse, either as a direct spray to berries at approximately 18 days after the end of flowering (1st application) *or* 5 weeks later when fruits were about 70% of mature size (2nd application). In addition, at each application time point, part of a whole vine was treated with 375 mg ai/L suspension to investigate translocation into untreated parts of the vine. Fruits treated at the 'early stage' were collected at pre-harvest intervals (PHIs) of 0, 30, and 45 days; fruits treated at the 'late stage' were collected at PHIs of 0 and 10 days.

The harvested fruits were surface washed sequentially with water, dichloromethane, and methanol. Treated vines samples from the translocation studies were not surface washed. Plant tissue (vines and grapes) samples were then frozen in dry ice and homogenized using a blender. Radioactivity was determined by liquid scintillation counting (LSC) for liquid samples (surface washings) and by combustion/LSC for solid samples (vines and grapes). The TRRs were calculated by summing the radioactivity determined for the surface washings and the respective tissue sample.

Table 9. TRRs in /on the fruits and vines of grapes following a single direct spray application of phenyl- and quinoline-labelled [$^{14}$C]Quinoxyfen. (42894).

| Timing and Method of Application | Grape Matrix | PHI (days) | TRR (mg/kg)[1] | |
|---|---|---|---|---|
| | | | Phenyl-label | Quinoline-label |
| Early application at 375 mg ai/L | Fruit | 0 | 13.3 | 9.12 |
| | | 30 | 2.95 | 2.21 |
| | | 45 | 2.51 | 1.98 |
| Late application at 375 mg ai/L | Fruit | 0 | 4.86 | 4.95 |
| | | 10 | 2.91 | 4.24 |
| Early application at an exaggerated rate of 750 mg ai/L | Fruit | 45 | 6.76 | 5.27 |
| Translocation experiment: Early application to the vine at 375 mg ai/L | Treated fruit | 45 | 1.16 | 1.50 |
| | Untreated fruit | 45 | 0.008 | 0.007 |
| | Treated vines (stems/leaves) | 45 | 15.9 | 23.4 |
| | Untreated vines (stems/leaves) | 45 | nd [2] | nd |

| Timing and Method of Application | Grape Matrix | PHI (days) | TRR (mg/kg)[1] | |
|---|---|---|---|---|
| | | | Phenyl-label | Quinoline-label |
| Translocation experiment: Late application to the vine at 375 mg ai/L | Treated grape fruit | 10 | 2.85 | 1.88 |
| | Untreated grape fruit | 10 | 0.006 | 0.006 |
| | Treated vines (stems/leaves) | 10 | 18.0 | 17.4 |
| | Untreated vines (stems/leaves) | 10 | nd | nd |

[1] TRR reported for grapes is the total of radioactivity determined in surface washings and tissue.

[2] Not detected.

The fruit's TRR decreased from the 0-day sampling interval to subsequent sampling intervals. The majority of radioactivity was removed from the grapes by surface washing; > 98% of the TRR was released at 0 day and > 81% TRR was released at maturity. TRR in untreated grapes were 0.002 mg/kg. The TRRs of grapes from the exaggerated rate study were basically proportional to the increase in the application rate.

In the translocation study, low levels (< 0.01 mg/kg) of radioactivity were observed in untreated grapes, and non-detectable residues were observed in the untreated vines (stems/leaves). No translocation of radioactivity from the treated vine and grapes to the untreated vines (stems/leaves) or grapes appeared to have occurred.

Surface washings, extracts, and hydrolysates (0.1 N NaOH) of grape fruit and vines were analyzed by normal-phase TLC and reversed-phase HPLC. HPLC analyses were conducted on Spherisorb ODS 2 (guard and analytical) columns with a gradient mobile phase of ACN and water, using in-flow radio-detection and UV detection (295 nm). TLC analyses were conducted on $60F_{254}$ silica plates using a mobile phase of toluene:isopropyl alcohol:acetic acid (8:2:1, v:v:v). Radioactive residues were identified by co-chromatography with the following non-labelled reference standards: quinoxyfen, quinoxyfen n-oxide, 4-fluorophenol, and DCHQ (dichloro-hydroxy quinoline). Reference standards were observed under UV light (254 nm), and radioactive residues were quantitated using phosphor imaging.

Table 10. Summary of characterization/identification of residues in mature grapes following a single direct spray application of phenoxy- and quinoline-Labelled [$^{14}$C]Quinoxyfen at 375 mg ai/L. (42894).

| Metabolite/Fraction | Early application 45-day PHI | | Late application 10-day PHI | |
|---|---|---|---|---|
| | % TRR | mg/kg | % TRR | mg/kg |
| Phenoxy-label Quinoxyfen | TRR = 2.51 mg/kg | | TRR = 2.91mg/kg | |
| Quinoxyfen | 93. | 2.3 | 97. | 2.8 |
| Unknown Peak 1 | 3.3 | 0.083 | 3.0 | 0.088 |
| Unknown Peak 3 | 0.7 | 0.018 | -- | -- |
| NaOH hydrolysate | 2.0 | 0.049 | -- | -- |
| Total Extractable | 99 | 2.5 | 99 | 4.2 |
| Total Identified | 93 | 2.3 | 97 | 2.8 |
| Total Characterized[1] | 6.0 | 0.15 | 3.0 | 0.088 |
| Total Unresolved | Not reported (NR) | NR | NR | NR |
| Total Unextractable [2] | 4.2 | 0.10 | 1.4 | 0.041 |
| TOTAL | 103. | 2.6 | 101. | 2.9 |
| | | | | |

| Metabolite/Fraction | Early application 45-day PHI | | Late application 10-day PHI | |
|---|---|---|---|---|
| | % TRR | mg/kg | % TRR | mg/kg |
| Quinoline-label Quinoxyfen | TRR = 1.985 mg/kg | | TRR = 4.235 mg/kg | |
| Quinoxyfen | 94 | 1.8 | 98. | 4.1 |
| Unknown Peak 1 | 2.1 | 0.042 | 0.3 | 0.011 |
| Aqueous | 1.5 | 0.030 | 0.3 | 0.011 |
| NaOH hydrolysate | 1.2 | 0.024 | -- | -- |
| Total Extractable | 98 | 1.9 | 99. | 4.2 |
| Total Identified | 94 | 1.8 | 98. | 4.2 |
| Total Characterized [a] | 4.8 | 0.096 | 0.6 | 0.022 |
| Total Unresolved | NR | NR | NR | NR |
| Total Unextractable [b] | 4.6 | 0.091 | 1.2 | 0.051 |
| TOTAL | 103 | 2.04 | 100. | 4.2 |

[1] Total Characterized = sum of all unidentified/characterized metabolites

2 Total Unextractable = TRR - Total Extractable; actual value presented in report.

*Metabolism in cucumber – adapted from the Evaluation of the USA*

The Meeting received a study report on the metabolism of $^{14}$C-quinoxyfen in cucumbers grown in a glasshouse (45725, Chapleo and Caley, 1996). $^{14}$C-quinoxyfen, labelled in either the phenoxy ring or the quinoline ring, was formulated as a suspension concentrate containing 75 mg ai/L and was applied with a compressed air sprayer to the fruit and foliage of plants as a spray at the commencement of fruit ripening, 592 mg/plant. Further applications were made to the same plants 10 days and 23 days after the initial treatment. Both radio-labelled forms were applied to separate groups of plants at each application point. Immature fruits and foliage were harvested from a single plant on the day of the first application, and prior to the second and third applications. Mature fruits and foliage were harvested from the remaining two plants 7 days following the third application. Efforts where focused on the characterization of the nature of the residue in mature samples collected from the 3 treatment regime.

In a separate experiment, $^{14}$C-quinoxyfen, labelled in either the phenoxy ring or the quinoline ring and formulated as the suspension concentrate, was applied to the foliage only of two plants. Foliage and fruits were harvested 21 days after the single application.

Mature fruits were washed sequentially with water, dichloromethane and methanol and the levels of radioactivity were determined in the washes and fruit. . The TRR for each matrix was calculated by summing the radioactivity determined for the surface washings and the respective foliage or fruit tissue sample. Greater than 88% of the total radioactive residue (TRR) was removed by surface washes from samples taken immediately after the initial treatment. Much less was removed at subsequent harvests, and at the final harvest 7 days after last application, 57% TRR (phenyl label) and 36% TRR (quinoline label) were removed by surface washing. The TRR levels at various harvest intervals are summarized in Table 11.

Table11. TRRs in /on cucumber fruit and foliage following application(s) of phenoxy- and quinoline-Labelled [$^{14}$C]Quinoxyfen (45725).

| Timing and Method of application | Cucumber Matrix | PHI | TRRs (mg/kg) [1] | |
|---|---|---|---|---|
| | | | phenoxy-label | quinoline-label |
| One to three spray treatments were made to the fruits and foliage of cucumbers beginning at the commencement of fruit ripening at an average rate of 75 mg ai/L per application | Fruit | Just after 1st application | 0.12 | 0.14 |
| | | Prior to 2nd application | 0.025 | 0.050 |
| | | Prior to 3rd application | 0.017 | 0.017 |
| | | 7 days (after final application) | 0.079 | 0.076 |
| | Foliage | Just after 1st application | 2.7 | 2.0 |
| | | Prior to 2nd application | 2.1 | 1.4 |
| | | Prior to 3rd application | 3.5 | 2.9 |
| | | 7 days (after final application) | 4.2 | 3.4 |
| For the translocation experiment, one spray application was made | Fruit | 23 days (coincided with 3rd application above) | 0.005 | 0.014 |
| | Foliage | 23 days (coincided with 3rd application above) | 0.97 | 1.1 |

[1] TRR reported is the total of radioactivity determined in surface washings and tissue.

A sub-sample of treated fruit, that had been surface washed for TRR determination, was extracted (2×) with acetonitrile (ACN): water:1 M HCl (94:5:1, v:v:v) and then centrifuged. The extracts were combined and concentrated for thin-layer chromatography (TLC) analysis. The concentrated extract was re-dissolved in methanol and a precipitate formed. The precipitate was removed by centrifugation and re-dissolved in water.

To investigate the nature of non-extractable ('bound') residues, a sub-sample of fruit which had undergone initial extraction as described above was subjected to acid hydrolysis (refluxed with 1 M HCl for 18 hours). The hydrolysate was partitioned (3×) with hexane, and the hexane fractions were combined. Low levels of radioactivity were partitioned into the hexane phase; therefore, TLC analysis was not performed.

A sub-sample of treated foliage, that had been surface washed for TRR determination, was extracted (2×) with ACN:water:1 M HCl (94:5:1, v:v:v) and then centrifuged. The extracts were combined and concentrated for TLC analysis. Separate sub-samples of the methanol surface washings and extracts were subjected to enzyme hydrolysis to further investigate the nature of polar radioactive components. Residues were re-dissolved in 0.1 M sodium acetate buffer, pH 5. Then β-glucuronidase in sodium acetate buffer was added, and the mixture was incubated at 37°C for 18 hours.

To investigate the nature of non-extractable residues, a sub-sample of non-extractable residues following the initial extraction of residues was subjected to acid hydrolysis (refluxed with 1 M HCl for 18 hours). The hydrolysate was partitioned (3×) with hexane, and the hexane fractions were combined and concentrated for TLC analysis. The aqueous fraction was subjected to solid-phase extraction (SPE) with a phenyl Bond-Elute cartridge; residues were eluted with methanol. Radioactivity was determined in the water fraction (flow-through), methanol fraction, and solid-phase gel. The water fraction was concentrated by freeze-drying, and the methanol fraction was concentrated by rotary evaporation for TLC analysis.

Surface washings, extracts, and hydrolysates of cucumber fruit and foliage were initially analyzed by TLC conducted on $60F_{254}$ silica plates using a mobile phase of toluene:isopropyl alcohol:acetic acid (8:2:1, v:v:v). Radioactive residues were identified by co-chromatography with the following non-labelled reference standards: quinoxyfen, 2-oxo quinoxyfen, quinoxyfen n-oxide and DCHQ (dichloro-hydroxy quinoline). Reference standards were observed under UV light (254 nm) and radioactive residues were quantitated using phosphor imaging.

To confirm results, the surface washings and extracts of phenyl-and quinoline-labelled fruit and foliage samples were also analyzed by high-performance liquid chromatography (HPLC). HPLC analyses were conducted on a Spherisorb ODS 2 (guard and analytical) columns with a gradient mobile phase of ACN and water, using in-flow radio-detection and UV detection (295 nm). Identification of quinoxyfen residues was also confirmed by liquid chromatography/mass spectroscopy (LC/MS) analysis. A summary of residue characterization and identification is presented below in Table 12.

Table 12. Summary of residue characterization/identification in cucumber fruit and foliage harvested 7 days following the last of three spray treatments of phenoxy-or quinoline-labelled $[^{14}C]$Quinoxyfen at an average rate of 75 mg ai/L per application.(45725).

| Metabolite/Fraction | Cucumber Fruit | | Cucumber Foliage | |
|---|---|---|---|---|
| | % TRR | mg/kg | % TRR | mg/kg |
| Phenoxy-labelled Quinoxyfen | TRR = 0.079 mg/kg | | TRR = 4.2 mg/kg | |
| Quinoxyfen | 74 | 0.058 | 74 | 3.1 |
| Quinoxyfen n-oxide | 2.8 | 0.002 | 1.4 | 0.057 |
| 2-Oxo quinoxyfen | -- | -- | 3.7 | 0.16 |
| Unknown A | 4.1 | 0.003 | 0.7 | 0.028 |
| Unknown F | -- | -- | 0.1 | 0.002 |
| Origin | 7.8 | 0.005 | 15[3] | 0.64 |
| Water surface wash | 3.7 | 0.003 | -- | -- |
| Precipitate | 1.0 | 0.001 | -- | -- |
| SPE gel | -- | -- | < 0.1 | 0.002 |
| Total Extractable | 93 | 0.074 | < 95 | 4.0 |
| Total Identified | 77 | 0.060 | 79 | 3.3 |
| Total Characterized [1] | 17 | 0.012 | < 16 | 0.67 |
| Total Unresolved | Not reported (NR) | NR | NR | NR |
| Total Unextractable [2] | 13 | 0.010 | 13 | 0.56 |
| TOTAL | 107 | 0.082 | 108 | 4.6 |
| Quinoline-Label Quinoxyfen | TRR = 0.076 mg/kg | | TRR = 3.4 mg/kg | |
| Quinoxyfen | 64 | 0.049 | 56 | 1.9 |
| Quinoxyfen n-oxide | 2.5 | 0.001 | 3.3 | 0.11 |
| Unknown A | 1.5 | 0.001 | 0.6 | 0.02 |
| Unknown B | -- | -- | 0.3 | 0.011 |
| Unknown F | 2.1 | 0.002 | 0.2 | 0.006 |
| Origin | 10 | 0.008 | 27[3] | 0.91 |
| Water surface wash | 2.6 | 0.002 | -- | -- |
| Precipitate | 3.1 | 0.002 | -- | -- |
| Acid hydrolysate; hexane phase | 0.1 | < 0.001 | 0.1 | 0.002 |
| Acid hydrolysate; aqueous phase | 8.1 | 0.006 | -- | -- |
| SPE gel | -- | -- | 0.3 | 0.010 |
| Total Extractable | 95 | < 0.072 | 88 | 3.0 |
| Total Identified | 67 | 0.050 | 60 | 2.0 |
| Total Characterized [1] | 28 | < 0.022 | 28 | 0.96 |
| Total Unresolved | NR | NR | NR | NR |
| Total Unextractable [2] | 17 | 0.013 | 11 | 0.39 |
| TOTAL | 111 | 0.084 | 99 | 3.4 |

[1] Total Characterized = sum of all unidentified/characterized metabolites

[2] Total Unextractable = TRR - Total Extractable.

[3] A polar mixture associated with the baseline of TLC plates. Found in the TLC analysis of the aqueous and methanol surface washes, initial tissue extracts, and various extracts from the acid hydrolysates of the tissue remaining following solvent extractions. Shown not to be glucose conjugates.

*Metabolism in tomato – adapted from the US Evaluation*

The Meeting received a study report on the application of $^{14}$C-quinoxyfen labelled either in the phenoxy or quinoline ring to tomatoes at the US maximum seasonal rate of 600 g ai/ha (five weekly applications of 120 g ai/ha), (78962, Byrne *et al.,* 2000). Tomato plants were grown to maturity outdoors in separate plots treated either with $^{14}$C-phenoxy and $^{14}$C-quinoline quinoxyfen. Immature fruit was collected at 0, 7, 14, and 28 days after the first application. Mature fruit was collected 14 days after the 5$^{th}$ and final application (42 days after the first application). Vines were collected and analyzed 0, 7, and 42 days after the first application.

Treated tomato samples from all sampling intervals were surface washed sequentially with a dilute soap (0.01%) solution and methylene chloride. Treated vines samples, collected prior to the third application and were not analyzed. Surface-washed plant tissue (fruit and foliage) samples were then frozen in dry ice and homogenized using a mill. Radioactivity was determined by liquid scintillation counting (LSC) for liquid samples (surface washings) and by combustion/LSC for solid samples (homogenized fruit and foliage tissue). The limit of detection (LOD) and limit of quantitation (LOQ) were reported as 0.0029 and 0.011 mg/kg, respectively. The TRRs presented in Table 13 below were calculated by summing the radioactivity determined for the surface washings and the respective tissue sample.

Table 13. TRRs in /on tomato fruits and foliage following application(s) of phenoxy- and quinoline-labelled [$^{14}$C] Quinoxyfen (78962).

| Timing and Method of application | Matrix | PHI (days) | TRR [1] | |
|---|---|---|---|---|
| | | | Phenoxy-label | Quinoline-label |
| One to five post-emergence foliar applications were made at a nominal rate of 0.12 kg ai/ha per application. | Immature fruit | 0 after 1$^{st}$ application | 0.057 | 0.092 |
| | | Prior to 2$^{nd}$ application | 0.042 | 0.063 |
| | Immature fruit | Prior to 3$^{rd}$ application | 0.083 | 0.093 |
| | | Prior to 5$^{th}$ application | 0.13 | 0.19 |
| | Mature fruit | 14 after 5$^{th}$ application | 0.19 | 0.243 |
| | Immature foliage | 0 after 1$^{st}$ application | 5.4 | 6.6 |
| | | Prior to 2$^{nd}$ application | 4.2 | 3.6 |
| | Mature foliage | 14 after 5$^{th}$ application | 11 | 14 |

The soap (aqueous) and DCM surface-washings of mature fruits contained sufficient radioactivity for chromatographic analysis (HPLC and thin-layer chromatography (TLC)); the DCM surface-washings were concentrated, and residues were re-dissolved in ACN and water prior to analysis.

Sub-samples of post-rinsed samples were extracted (3x) with ACN: water (80:20, v:v) and then centrifuged. The extracts were combined, and an aliquot was concentrated in the aqueous phase and partitioned with DCM: ACN (80:20, v:v). The organic phase was concentrated and diluted with ACN and water for HPLC analysis; the aqueous phase was directly analyzed by HPLC.

To investigate the nature of non-extractable ('bound') residues, a sub-sample of non-extractable residues following the initial extraction was subjected to acid hydrolysis (1 N HCl refluxed for 4 hours) and then vacuum filtered. The acidified pellet was rinsed with water, centrifuged, and filtered. The rinsate was combined with the acid hydrolysate. The nonextractable residues remaining following acid hydrolysis were then extracted with ACN to remove acid-labile, non-water soluble residues.

A separate but larger sub-sample of milled tomato fruit was subjected to a series of fractionation procedures in order to elucidate the nature of bound residues. These sub-samples were extracted and acid hydrolysed as described above, and the nonextractable residues were subjected to ADF isolation, or lignin or cellulose determinations. Briefly, nonextractable residues were refluxed for 1 hour in acid detergent solution (hexadecyltrimethylammonium bromide in 2 N sulfuric acid).

The solids were collected by vacuum filtration and dried in an oven ($80^{o}$ C) overnight. The dried solid acid detergent fibre (ADF) fraction and liquid ADF rinsate were analyzed by LSC or combustion/lSC. To isolate lignin, chilled sulphuric acid was added to nonextractable residues, and the sample was refrigerated overnight. The sample was diluted with water, refluxed for 2 hours, cooled, and vacuum filtered. The solids were dried in an oven ($60^{o}$ C) overnight, and the solid (lignin) fraction was determined by LSC; the liquid filtrate is *assumed* to contain primarily dissolved cellulose. To isolate cellulose, buffered saturated potassium permanganate was added to nonextractable residues, and the sample was filtered. Additional potassium permanganate was added and filtered to ensure complete oxidation/solubilisation of lignin. Excess potassium permanganate was removed from the oxidized solid by the addition of oxalic and hydrochloric acids in ethanol, after which the solids were sequentially washed with ethanol and acetone. The solids were dried in an oven ($60^{o}$C) overnight, and the solid (cellulose) fraction was determined by LSC; the liquid filtrate is *assumed* to contain primarily oxidized lignin.

Surface washings of phenyl- and quinoline-labelled mature tomatoes contained 57% and 62% TRR, respectively, with the largest amount of radioactivity recovered in the organic surface-washing. The remainder of radioactivity (20–27% TRR) was largely extracted using ACN:water (80:20, v:v). Approximately half of the extract was partitioned into organic solvent. Phenyl- and quinoline-labelled bound residues of mature tomatoes were subjected to sequential acid hydrolysis (1 N HCl at reflux) and ACN extraction, which released an additional 2.4–4% TRR. Bound residues remaining following simple extraction and hydrolysis accounted for 4.0% and 3.9% of TRRs in phenyl- and quinoline-labelled tomatoes, respectively. The levels of radioactivity in the surface washings, extracts, and bound fractions were similar for phenyl- and quinoline-labelled tomato fruit.

Individual surface washings, and the organic and aqueous extracts were subjected to HPLC analysis for characterization/identification of residues. Most of the radioactivity in all of the surface washings was identified as quinoxyfen (51−54% TRR). Quinoxyfen was also detected as the major residue present at approximately 12% TRR in the organic and aqueous extracts. An unknown peak eluting at approximately 42 minutes and present at < 2% TRR was observed in the organic extract (both labels). This peak had a similar retention time as the 2-oxo metabolite. The remainder of the peaks detected in the aqueous and organic extracts were minor polar unknowns, each present at < 5% TRR. The residue profiles for the phenyl- and quinoline-labelled fruit were similar. An additional 2.4–4% TRR was released from non-extractable residues with acid hydrolysis and subsequent ACN extraction.

A larger sample of surface-washed fruit tissue was extracted and subjected to acid hydrolysis and ACN extraction for further characterization of non-extractable residues. Bound residues were characterized to be associated with ADF (10–12% TRR, 0.020-0.028 mg/kg) containing lignin, cellulose, and hemicellulose.

Tomato foliage samples harvested 14 days following five applications were subjected to extensive investigation. The soap (aqueous) and methylene chloride (DCM) surface-washings contained sufficient radioactivity for chromatographic analysis (HPLC and TLC); the DCM surface-washings were concentrated, and residues were re-dissolved in ACN and water prior to analysis.

A sub-sample of post-rinsed foliage was extracted (3x) with ACN: water (80:20, v:v) and then centrifuged. The extracts were combined, and an aliquot was concentrated in the aqueous phase and partitioned with DCM:ACN (80:20, v:v). The organic phase was concentrated and diluted with ACN and water for HPLC analysis; the aqueous phase was directly analyzed by HPLC.

To investigate the nature of nonextractable residues, a sub-sample of nonextractable residues from the initial extraction was subjected to acid hydrolysis (1 N HCL refluxed for 4 hours) and vacuum filtered. The acidified pellet was rinsed with water, centrifuged, and filtered. The rinsate was combined with the acid hydrolysate. The nonextractable residues remaining following acid hydrolysis were then extracted with ACN to remove acid-labile, non-water soluble residues. The acid hydrolysate was partitioned with DCM: ACN (80:20, v:v). The DCM phase was concentrated, and the organic and aqueous phases were analyzed by HPLC.

A separate but larger sub-sample of milled tomato foliage was subjected to extraction, acid hydrolysis, and ACN extraction. The nonextractable residues following acid hydrolysis and ACN extraction were subjected to ADF isolation, or lignin or cellulose determinations. The similar procedures described for fruits were employed for this purpose.

Non-extractable residues were subjected to sequential acid hydrolysis (1 N HCl at reflux) and ACN extraction, which released an additional 8.4–9.7% TRR. Bound residues remaining following simple extraction and hydrolysis accounted for 5.9% and 6.7% TRR in phenyl- and quinoline-labelled foliage, respectively. Levels of radioactivity in the surface washings, extracts, and bound fractions were similar for phenyl- and quinoline-labelled tomato foliage.

Individual surface washings and the organic and aqueous extracts were subjected to HPLC analysis for characterization/identification of residues. Most of the radioactivity in all of the surface washings was identified as quinoxyfen (31.6–34.5% TRR). Quinoxyfen was also detected as the major residue present at ≤ 9–12% TRR in the organic extract. 4-fluorophenol was identified as a minor residue (0.9% TRR) in the phenyl-labelled organic extract only. An unknown peak eluting at approximately 42 minutes and present at ≤ 3.2% TRR was observed in the organic extract (both labels). This peak had a similar retention time as the 2-oxo metabolite standard. An additional unknown peak (Rt = 35 minutes) was detected at ≤ 7% TRR, and the remainder of the peaks detected in the organic extracts were minor polar unknowns each present at < 1% TRR. The aqueous extracts of both phenyl- and quinoline-labelled foliage were comprised of more polar unknown peaks each present at ≤ 3.3% TRR. The residue profiles for the phenyl- and quinoline-labelled foliage were similar.

A larger sample of surface-washed foliage tissue was extracted and subjected to acid hydrolysis and ACN extraction. The majority of the bound residues were associated with ADF (3.7–4.6% TRR) containing lignin, cellulose, and hemicellulose.

The surface washings, extracts, and hydrolysates of tomato fruits and foliage were analyzed by HPLC. HPLC analyses were conducted on a YMC ODS-AQ column with a gradient mobile phase of ACN and water each containing 0.1% acetic acid, using in-flow radiodetector and UV detector (295 nm). Radioactive residues were identified by co-chromatography with the following non-labelled reference standards: quinoxyfen, 4-fluorophenol, 2-Oxo (2-oxo quinoxyfen), 6-OH (6-hydroxy quinoxyfen), and DCHQ (dichloro-hydroxy quinoline).

Residues of quinoxyfen were confirmed in the surface-washings and organic phase of the initial extraction by TLC analysis. TLC analyses were conducted on $60F_{254}$ silica plates using a mobile phase of toluene: acetone (75:25, v:v). Reference standards were observed under UV light (254 nm) and radioactive residues were quantitated using a linear detector.

Minor peaks observed by HPLC analysis of the DCM surface-wash of foliage samples eluted with potential photolysis products in the fruit, such as 2-oxo metabolite. However, these peaks did not co-chromatograph with the 2-oxo standard using TLC. These degradates were, therefore, further isolated using an open column system. The phenyl-labelled DCM surface-wash was applied to a medium bore silica column and one-minute fractions were collected for HPLC and LC/MS analysis. In all but the first fraction collected, some radioactivity eluted similar to the 2-oxo metabolite using gradient HPLC; however, multiple components were observed using isocratic HPLC (water: ACN each with 0.1% acetic acid; 4:6, v:v). It is reasonable to conclude that the residue consists of a range of components instead of a single metabolite accounting for > 10% of the radioactivity present.

The major residue identified by HPLC in fractions 1 and 2 was quinoxyfen, and was confirmed by LC/MS. In fraction 3, the major component was analyzed by LC/MS which did not demonstrate fragmentation across the ether linkage; the degradate was proposed to be CFBPQ (2-chloro-10-fluoro[1]benzopyrano[2,3,4-de]quinoline) based on the accurate mass. The spectrum of the degradate, by $^{1}H$ NMR analysis, was consistent with CFBPQ. The CFBPQ degradate was the main degradate identified in an aqueous photolysis study; therefore, CFBPQ may be formed via photolysis on the surface of the tomatoes or leaves.

In fraction 4, residues similar to the parent, but more polar and with different fragmentation patterns by LC/MS analysis, were thought to be rearrangement isomers of quinoxyfen. The chemical structures could not be conclusively determined with NMR. Analysis of fraction 5 by LC/MS indicated possible structures of a *p*-hydroxyphenoxy degradate and 2-oxo metabolite.

Table 14 lists the summary of residues identified and characterized from this study.

Table 14. Summary of characterization/identification of $^{14}$C-residues in mature tomato fruits and foliage harvested 14 days following the last of five foliar applications of phenyl- or quinoline-Label [$^{14}$C]Quinoxyfen for a total rate of 600 g ai/A. (78962).

| Metabolite/Fraction | Tomato Fruit 14-day PHI | | Tomato Foliage 14-day PHI | |
|---|---|---|---|---|
| | % TRR | mg/kg | % TRR | mg/kg |
| Phenoxy-labelled Quinoxyfen | TRR = 0.191 mg/kg | | TRR = 10.716 mg/kg | |
| Quinoxyfen | 63 | 0.12 | 43 | 4.6 |
| 4-Fluorophenol | -- | -- | 0.9 | 0.096 |
| Unknown Rt = 35 minutes | -- | -- | 7.0 | 0.75 |
| Unknown Rt = 42 minutes | 1.9 | 0.003 | 3.2 | 0.34 |
| “Other” unknowns | each ≤ 5.0 | each ≤ 0.008 | each ≤ 3.3 | each ≤ 0.36 |
| Acid hydrolysate | 3.6 | 0.007 | 7.6 | 0.81 |
| ACN extract | 0.4 | 0.001 | 2.1 | 0.22 |
| Total Extractable | 88 | 0.17 | 87 | 9.3 |
| Total Identified | 63. | 0.12 | 44 | 4.7 |
| Total Characterized [1] | > 11 [2] | > 0.019 [2] | > 23. | > 2.5 |
| Total Unresolved | Not reported (NR) | NR | NR | NR |
| Total Unextractable [3] | 4.0 | 0.008 | 5.9 | 0.64 |
| TOTAL [4] | 92 | 0.18 | 93 | 10 |
| | | | | |
| Quinoline-label Quinoxyfen | TRR = 0.24 mg/kg | | TRR = 14. mg/kg | |
| Quinoxyfen | 65 | 0.16 | 43 | 6.1 |
| Unknown Rt = 35 minutes | -- | -- | 6.5 | 0.92 |
| Unknown Rt = 42 minutes | 1.8 | 0.004 | 2.2 | 0.304 |
| “Other” unknowns | each ≤ 1.6 | each ≤ 0.002 | each ≤ 2.1 | ≤ 0.30 |
| Acid hydrolysate | 2.1 | 0.005 | 6.6 | 0.93 |
| ACN extract | 0.3 | 0.001 | 1.8 | 0.26 |
| Total | 84 | 0.20 | 85 | 12 |
| Total Identified | 65 | 0.16 | 43 | 6.1 |
| Total Characterized [1] | > 5.8 [2] | > 0.012 [2] | > 19. [2] | > 2.7 |
| Total Unresolved | NR | NR | NR | NR |
| Total Unextractable [3] | 3.9 | 0.009 | 6.7 | 0.9 5 |
| TOTAL [4] | 88 | 0.21 | 92 | 13 |

1 Total Characterized = sum of all unidentified/characterized metabolites

2 Because only the maximum single unknown level was reported; the total identified does not include unknowns below the maximum value.

3 Total Unextractable = TRR - Total Extractable; actual value presented in the report.

4 Total as presented in the report.

*In summary,* quinoxyfen was metabolized in plants with portions of the molecule becoming associated with natural plant constituents. The main residue identified in the roots, leaves, and fruits at harvest, was the parent compound, quinoxyfen. Hydroxylation of the quinoline or phenoxy rings was

observed. Cleavage of the ether bond was a minor pathway (sugar beet). CFBPQ was formed, perhaps via surface photolysis. There was no evidence of significant translocation from treated foliage to other parts of the plant. The metabolic pathways are indicated in Figure 2.

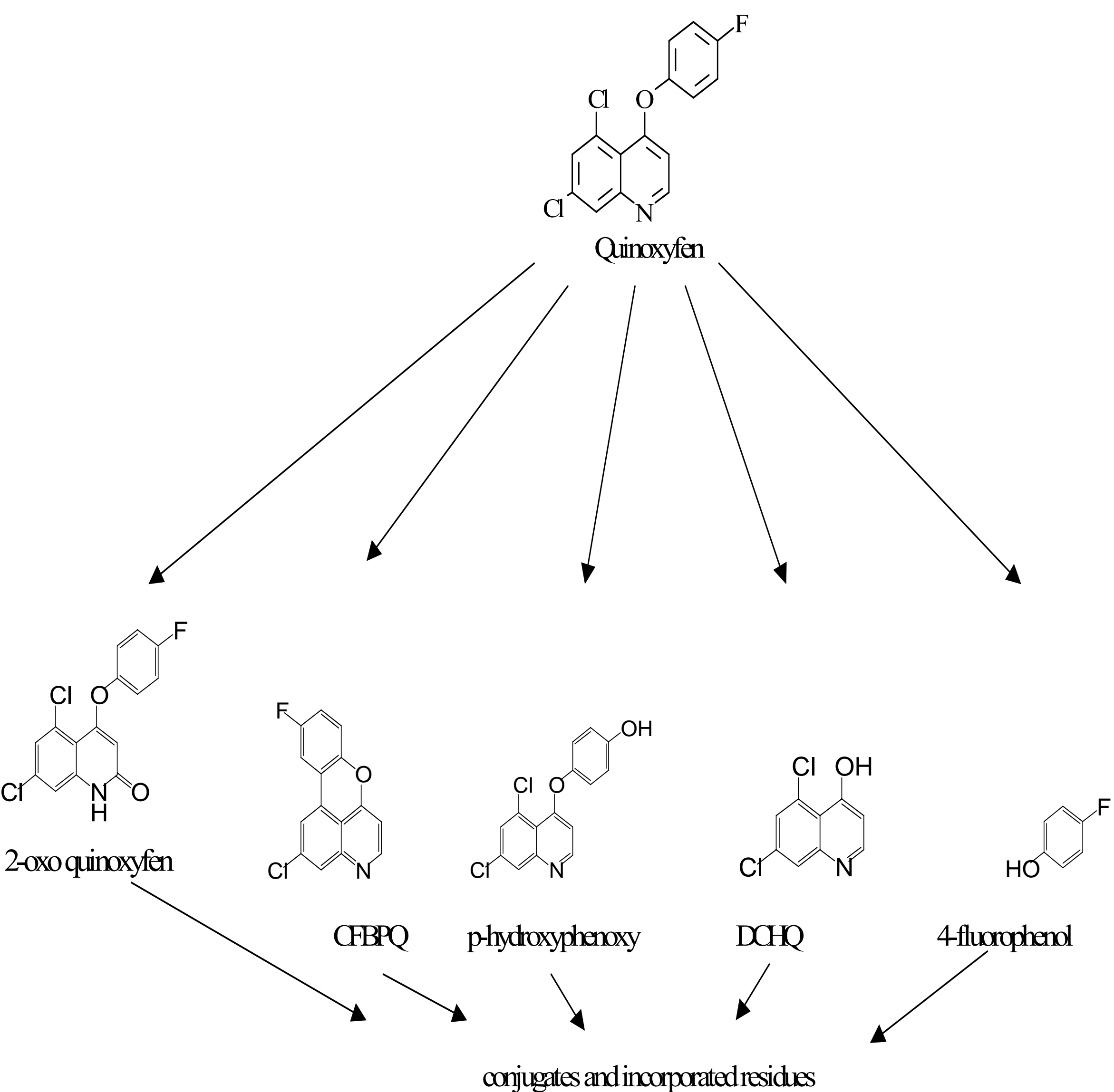


Figure 2. Proposed quinoxyfen metabolic pathway in plants.

## *Environmental fate*

### *Aerobic soil metabolism*

The Meeting received a study report on the aerobic soil metabolism of quinoxyfen (6357, Reeves, 1993; 8411, Ghosh and Portwood, 1994; and 29386, Cracknell *et al.,* 1995). In a laboratory study, one standard (Speyer 2.2) and three UK agricultural soils (Castle Rising, Marcham, and Wereham) were treated with quinoline-labelled [$^{14}$C]-quinoxyfen at a rate equivalent to 250 g ai/ha and incubated at 40% moisture content and 20ºC in the dark for up to 200 days. Under these conditions parent compound slowly degraded to give 5,7-dichloro-4-(4-fluorophenoxy)-2-oxo-quinoline 2-oxo-DE-795). In the three agricultural soils this did not exceed *ca* 8% of applied radioactivity (AR) at any time, although it did reach 27% AR at 200 days in non-agricultural Speyer 2.2 soil. The pattern of 2-oxo-DE-795 formation was such that no significant plateau and decline could be detected in any soil during the test period. A second metabolite identified as 5,7-dichloro-4-hydroxyquinoline (DCHQ) was also formed as a minor component in Speyer 2.2 soil, and as the only degradation product in acidic Wereham soil (pH4.2), where it reached 6% AR at 100 days. Non-extractable residue (NER; up to 25% AR) and small amounts of $CO_2$ (< 2% AR) were also seen. The distribution of radioactivity in the four soils is summarized in Table 15.

Table 15. Summary of aerobic soil degradation in various soil types (6357; 8411; 29386).

| | Days After Treatment (% Applied Radioactivity) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Matrix | 0 | 4 | 8 | 16 | 36 | 64 | 100 | 150 | 200 |
| DE-795 | 96 - 101 | 94 - 100 | 90 - 99 | 88 - 97 | 86 - 96 | 80 - 95 | 74 - 85 | 58 - 81 | 53 - 81 |
| 2-OH-quinoxyfen[1] | 0 | 0 | 0 | 0 - 3 | 0 - 6 | 0 - 11 | 0 - 15 | 0 - 22 | 0 - 27 |
| DCHQ | 0 | 0 | 0 | 0 | 0 | 0 | 0 - 6 | 0 - 6 | 0 - 5 |
| $CO_2$ | 0 | trace | trace | trace | < 1 | < 1 | < 2 | < 2 | < 2 |
| NER | 1 - 5 | 2 - 6 | 3 - 10 | 3 - 11 | 5 - 14 | 7 - 16 | 10 - 18 | 14 - 25 | 15 - 25 |
| Total | 101 - 103 | 98 - 103 | 100 - 102 | 99 - 101 | 99 - 102 | 99 - 102 | 99 - 102 | 100 - 102 | 100 - 102 |

[1] Misidentified as 3-OH-quinoxyfen (18219, N. R. Pearson and G. L. Reeves, 2005)

At 150 days, the NER was further extracted by sonication with methanol at 55°C, and the extracts shown to contain between 34–46% of the NER as DE-795, 2-Oxo-DE-795 and DCHQ (in proportions similar to their content in the original soil extracts) that had become bound to the soil with time.

The proposed route of aerobic soil degradation is shown in Figure 3.

quinoxyfen

(Major)

(Minor, predominantly acidic soil)

2-oxo Quinoxyfen

DCHQ

$CO_2$ (Very Minor) + NER

Figure 3. Pathway for the aerobic soil degradation of quinoxyfen.

$DT_{50}$ and $DT_{90}$ values were calculated for the soils from the above study as well as in a second standard soil (Speyer 2.1) as part of the aged residue column leaching study (24033, Reeves, 1994). The application rate was equivalent to 250 g ai/ha (1× rate) throughout. Comparative work was also done to investigate the effect of soil moisture content (Castle Rising at 60%moisture content), temperature (Speyer 2.2 at 10ºC and 30ºC) and application rate (Speyer 2.2 at 4× and ¼× rate) upon the degradation kinetics (K01). Table 16 shows the kinetic data (calculated assuming first-order kinetics) obtained under the various test regimes.

Table 16. Quinoxyfen laboratory aerobic soil degradation half-lives (1× = 250 g ai/ha) (24033).

| Soil | Moisture content | Temp. | Application Rate | $DT_{50}$ (days) | $DT_{90}$ (days) |
|---|---|---|---|---|---|
| Speyer 2.2 | 40% | 20°C | 1× | 220 | ca 730 |
| Castle Rising | 40% | 20°C | 1× | 510 | ca 1700 |
| Marcham | 40% | 20°C | 1× | 300 | ca 1000 |
| Wereham | 40% | 20°C | 1× | 470 | ca 1500 |
| Speyer 2.2 | 40% | 20°C | ¼×, 4× | 220 | ca 730-760 |

| Soil | Moisture content | Temp. | Application Rate | $DT_{50}$ (days) | $DT_{90}$ (days) |
|---|---|---|---|---|---|
| Speyer 2.2 | 40% | 10°C | 1× | 870 | - |
| Speyer 2.2 | 40% | 30°C | 1× | 87 | ca 270 |
| Castle Rising | 60% | 20°C | 1× | 450 | ca 1500 |
| Speyer 2.1 | 40% | 20°C | 1× | 300 | - |

The results showed that quinoxyfen is *slowly* degraded in soil under dark aerobic conditions. There was an apparent decline in the degradation rate in all soils after 100 days, particularly in Marcham soil, suggesting biphasic or non-linear degradation. Therefore, the $DT_{50}$ and $DT_{90}$ values presented were calculated using only data to 100 days. The rate decline could not be attributed to any significant decrease in microbial biomass.

*Hydrolytic degradation*

The hydrolysis of Quinoxyfen was investigated in sterile buffer solutions (pH 4, 7 and 9) at a nominal concentration of 0.5 µg ai/mL (8557, Reeves, and Ghosh, 1994). Acetone was used as a 1% co-solvent to facilitate solubility. The degradation was studied at 50°C and all pH values, and at pH4 at 25°C and 40°C using [$^{14}$C]-quinoline labelled quinoxyfen. The rates of hydrolytic degradation ($t_{½}$) under the various test regimes are summarized in Table 17.

Table 17. Hydrolytic degradation of quinoxyfen (8557).

| Temperature | Half-life (t½) | | |
|---|---|---|---|
| | pH4 | pH7 | pH9 |
| 50°C | 7 days | Stable | Stable |
| 40°C | 16 days | ND | ND |
| 25°C | 75 days | ND | ND |

Stable = no degradation after 5 days and <1% degradation after 21 days

ND = not determined due to stability seen at 50°C

At a temperature closer to environmental conditions (25°C), quinoxyfen was stable at pH 7 and pH 9 but degraded at pH 4 with a half-life of 75 days. At 25°C, DCHQ reached approximately 41% AR at 46 days (*ca* 33% AR at 30 days). The extent of hydrolysis confirmed that seen in early-stage environmental fate probe studies. The single hydrolysis product (which was seen at all temperatures) was identified as DCHQ by chromatographic analysis and mass spectrometry.

The effect of buffer (phthalate and citrate), quinoxyfen concentration (0.5 and 0.06 µg/mL) and co-solvent (acetone and THF) were further investigated in a hydrolysis study at pH 4 and 50ºC (6328, Baloch, R, *et al.,* 1997). The results confirmed the findings of the previous study by Reeves and Ghosh in showing that quinoxyfen was degraded at pH 4 (half-life of approximately 5 days; compared to 7 days from the Reeves study to give DCHQ). This was irrespective of buffer type, quinoxyfen concentration, or co-solvent.

*Photochemical degradation*

The Meeting received several study reports on the photochemical degradation of quinoxyfen. The photolysis quantum yield of quinoxyfen was determined in water/acetonitrile (8:2 v/v) at concentrations of between 4.6–17.9 mg ai/L using artificial light at the absorption maximum (298 nm) at 20°C (4429, Rüdel, 1995). The acetonitrile was shown to have no effect upon light absorption. Quinoxyfen degraded rapidly under these conditions with a quantum yield of 1.2 (± 0.2) × $10^{-2}$. This value was then used to calculate photolysis half-lives in dilute aqueous solution at latitude 52°N using the ABIWAS program which is based on the model of Frank and Klopffer (1988). This gave half-lives of 1.7 hours in June and 22.8 hours in December, assuming average light intensities and weather

conditions. The maximal or expected 'worst case' half-lives for March (earliest application) and June (latest application) were 16.4 hours and 6.8 hours, respectively.

Quinoxyfen degraded to give two main photoproducts. The main degradate (up to 30% at 8 hours), with a chromatographic polarity between quinoxyfen and 5,7-dichloro-4-hydroxy quinoline (DCHQ), was identified by mass spectrometry as 2-chloro-10-fluoro[1]benzopyrano[2,3,4-de]quinoline (CFBPQ) (Portwood, D., 1996; Report GHE-P 4721). A second degradation product (up to 11%) matched DCHQ by HPLC. At 6 hours, a quantitative mass balance was seen in the irradiated solution compared to a dark control, indicating no volatile loss of radioactivity.

In order to investigate the photo degradation of quinoxyfen in aqueous solution under sunlight conditions, and to determine the rate and extent of formation of CFBPQ and its subsequent degradation, a non-guideline outdoor photolysis study was carried out (48846, MacDonald., 1997) using quinoxyfen radiolabelled [$^{14}$C] on the C-2 of the quinoline ring. This was performed at Letcombe Regis, UK (latitude around 50°N) using natural lake water, pH 7 buffer, and natural water/sediment, with exposure during August-September, 1996. Favourable conditions existed for photolysis with non-turbid, shallow water being used. The application rate was 0.5 µg/mL. Further samples without sunlight exposure were used as dark controls.

After 1 day in the light exposed samples, no significant levels of quinoxyfen were detected in either the natural water system or the water/sediment system. The water contained only CFBPQ and a very polar, multi-component material. Subsequent analysis of water samples to 28 days after treatment showed that CFBPQ rapidly degraded with a half-life of about 1−2 days in the natural water/buffer test systems, and approximately 4 days in the natural water with sediment present. The degradation of CFBPQ was followed by increasing amounts of very polar, multi-component material (7−27 components). On day 1, the water test system contained 54% of the applied radioactivity as CFBPQ, 27% as polar metabolite(s), and 0% as quinoxyfen. On day 14, 0.47% of applied radioactivity was CFBPQ, 73% polar material. The buffered water test system yielded similar results. The dark natural water controls consisted largely of quinoxyfen (108% applied radioactivity day 1, 74% day 14, 51% on day 28, with no degradates identified). The dark buffered water controls showed no degradation of quinoxyfen over 14 days and about 20% degradation from day 14 to day 28.

The photochemical degradation of quinoxyfen on soil was also studied (31076, Reeves, 1995). Speyer 2.2 soil (loamy sand) was surfaced treated with [$^{14}$C]-quinoxyfen labelled at the 2 position of the quinoline ring at a rate of 250 g ai/ha. The soil was maintained in a stainless steel incubation chamber covered with an airtight quartz glass plate. Irradiation was performed in 12 hour cycles of light and dark, using sun simulation lamps. Temperatures during the light and dark cycles were about 25°C and 18°C, respectively. Control samples were maintained under the same conditions, but with no light. At 1, 3, 7, 14, 21, and 30 days after treatment the headspace was purged and analyzed for carbon dioxide and volatiles. Soil samples were taken at the same intervals and immediately after application.

Quinoxyfen degraded under the artificial light conditions with a half-life of about 200 days, estimated to be equivalent to > 1 year in natural sunlight in the spring in England. The main degradation product, up to 6.5% of applied radioactivity, remained unidentified. DCHQ was found (2.5% maximum of applied radioactivity). Very little organic volatiles or carbon dioxide was found (< 1% applied radioactivity). Total recovery of radioactivity ranged from 96% to 103%. Greater than 70% of the applied radioactivity was identified as quinoxyfen after 30 days. The non-extractable residue in soil increased to a maximum of 11% of applied radioactivity on day 30. No degradation occurred with the dark controls, the non-extractable residue did not exceed 4% of applied radioactivity, and about 94% of applied radioactivity was identified as quinoxyfen.

*Residues in succeeding crops (Confined rotational crop)*

Uptake of quinoxyfen from soil into three succeeding crops was investigated (75502, Haq and Brown, 1995). Two radiolabelled forms of quinoxyfen (phenoxy-labelled and quinoline-labelled) were prepared as an emulsifiable concentrate spray solution and applied separately to Mendip loam soil to give an even distribution on the soil surface using a DeVilbiss spray gun. The emulsifiable

concentrate was diluted with water to give a final concentration of 400 g ai/hectare. To assess if the treated tubs received the required amount of quinoxyfen, the soil was sampled within 24 hours after application.

The three succeeding crops studied were, turnips (root crop), sunflowers (oilseed crop) and cabbage (leafy crop). The crops were sown into the soil, at the appropriate depth and density for the crop, 30 days after the application. The crops were sampled at harvest (118 days after treatment for cabbage and turnip, 150 days after treatment for sunflower) and separated into above-ground and below-ground portions. The latter were water washed to remove adhering soil. Crop matrix samples were homogenized and the total radioactivity determined by combustion.

Soil samples were extracted sequentially with acetonitrile and acetone. Extraction released about 88% of the radioactivity from day zero soils and about 80% of the radioactivity from harvest day soils. Extracts were analyzed by normal phase TLC and reverse phase HPLC (UV detection 295 nm and radioactivity monitor). Analysis of the soil extracts of Day 0 samples showed only quinoxyfen to be present. Analysis of the soil extracts of harvest samples indicated only quinoxyfen (> 95% of soil radioactivity) and very low levels of metabolites (< 5%), more polar than the parent. Thus, metabolism of quinoxyfen does not occur extensively over the time course of the study (150 days). It is possible that the more polar metabolites were available for uptake into the plants.

The raw agricultural commodity (RAC, i.e. turnip root, cabbage leaves and sunflower head) were homogenized and the total radioactive content of the homogenized fractions determined by combustion. Results are given in Table 18.

Table 18. Total radioactive residue (TRR) content of rotational crops (75502).

| Commodity | [$^{14}$C] Label | μg/kg |
|---|---|---|
| Cabbages (leaves) | Phenoxy | 0.43 |
| Cabbages (leaves) | Quinoline | 0.49 |
| Cabbages (leaves) | Control | - |
| Sunflowers (Head) | Phenoxy | 1.2 |
| Sunflowers (Head) | Quinoline | 0.28 |
| Sunflowers (Head) | Control | - |
| Turnips (Root) | Phenoxy | 3.5 |
| Turnips (Root) | Quinoline | 3.4 |
| Turnips (Root) | Control | - |

The levels of radioactivity taken up from soil treated with $^{14}$C-quinoxyfen into the RAC of the three succeeding crops studied (turnip, cabbage and sunflower) were below 4 μg/kg quinoxyfen equivalents. The residue levels observed were too low to allow for chromatographic analysis.

## RESIDUE ANALYSIS

### *Analytical Methods*

Analytical methods for determination of residues of quinoxyfen have been developed for a wide range of substrates. The methods have been extensively validated with numerous recoveries on a wide range of substrates. The analytical methods for determination of residues of quinoxyfen in plant and animal matrices follow similar partitioning, clean-up and quantification procedures. Generally, quinoxyfen residues are extracted from plants and animal tissues samples with acidic acetonitrile. After addition of sodium bicarbonate solution to an aliquot of the extract, quinoxyfen is partitioned into hexane, which is then evaporated to dryness. The residue is reconstituted in hexane prior to an aminopropyl solid phase extraction using 1% acetone in hexane to elute quinoxyfen residues. The eluate is evaporated to dryness and reconstituted in 0.1% corn oil in tri-methyl pentane (TMP). Quinoxyfen is

quantified either by gas chromatography with mass selective detection (GC-MSD) or by HPLC with UV absorbance. This basic method has been modified and validated for use in various matrices. Validation study results were corrected for control values which were typically < 1% of the lowest fortification level. Matrix-specific methods are summarized below.

The Meeting received several methods for the determinate of quinoxyfen in grapes and processed grape commodities Method ERC 94.29 – Determination of grapes by reverse phase HPLC using UV absorbance detection at 235 nm (105043, Khoshab, 1995); Independent laboratory validation (41039, Khoshab, 1995) was used in all supervised trials on grapes conducted in various European countries and was used for some supervised trials on grapes conducted in Australia. The method involves extraction of quinoxyfen from the crop by macerating with acidic acetone. After addition of sodium bicarbonate solution to an aliquot of the extract, the residue was partitioned into hexane which is then evaporated to dryness. The residue is reconstituted in hexane prior to an aminopropyl solid phase extraction using 1% acetone in hexane to elute the quinoxyfen. The eluate is evaporated to dryness and reconstituted in acetonitrile/water. Quinoxyfen is quantified by reverse phase HPLC using UV absorbance detection at 235 nm. Confirmation is by GC/MSD (237 and 272 amu ions).

The method was validated by analysis of fortified samples for residues of quinoxyfen in grapes over the range of 0.01 – 1.0 mg/kg. The method was independently validated by an external laboratory, where samples were fortified with quinoxyfen over the range of 0.01–10 mg/kg. Table 19 summarizes the recovery data.

Table 19. Recovery of quinoxyfen from fortified grapes (Method ERC94.29) (105043; 41039).

| Fortification levels | % Recovery[1] | |
|---|---|---|
| | Original method | Independent validation |
| Mean control values | 0.0000 (n=6) | 0.0002 (n=6) |
| 0.01 | 94, 100[2] | 82, 83[2] |
| 0.01 | 98, 86 | 84, 95 |
| 0.01 | 95, 100 | 89, 88 |
| 0.20 | 99, 100 | 100, 93 |
| 1.0 | 98, 99 | 110, 103 |
| 10.0 | Not fortified at this level | 101, 100 |
| Mean (overall) | 97 ± 4.4 | 94 ± 9 |
| % RSD over validated range (0.01-10.0 mg/kg) | 4.5 (n=10) | 9.5 (n=12) |
| % RSD at lowest validated level (0.01 mg/kg) | 5.5 (n=6) | 5.6 (n=6) |
| Mean at lowest validated level (0.01 mg/kg) | 96 ± 5.3 | 87 ± 4.9 |

[1] Corrected for control value and moisture content

[2] Duplicate samples.

<u>Method ERC 95.26</u> – Determination of quinoxyfen in grapes, must, wine, and pomace by gas chromatography with mass selective detection (GC-MSD) (105334, Khoshab and Roberts, 1996; 83731, Thompson, 2002) was used in processing studies for grapes carried out in European countries and in field trials and processing studies conducted in the US. In this method, quinoxyfen residues were extracted from grapes, pomace, and raisins and analyzed as in ERD 94.29. The final residue was reconstituted in 0.1% corn oil in tri-methyl pentane (TMP).

Quinoxyfen residues in grape must, grape juice, and wine were extracted by addition of sodium bicarbonate solution followed by partitioning into hexane which was then evaporated to dryness and reconstituted in 0.1% corn oil in TMP.

Quinoxyfen was quantified by gas chromatography with mass selective detection (GC-MSD). The m/z 237.0 was used for confirmation, and the m/z 306.9 ion for quantification. The method was validated by fortifying control samples with quinoxyfen at levels of 0.01 mg/kg to 2.0 mg/kg. Recovery experiments were performed in 4 batches by two analysts. Table 20 summarizes the recovery data, including the relative standard deviation at the lowest validated level as well as over the validated range.

Table 20. Recovery of quinoxyfen from fortified grape wine, must, pomace (Method ERC95.26) (105334).

| Matrix | Fortification level (mg/L) | % Recovery[1] | Average % recovery | % RSD |
|---|---|---|---|---|
| Wine | 0.01 | 88, 90[2] | 87 ± 4 | 4.6 (n=8) |
| | 0.01 | 85, 85 | | |
| | 0.01 | 93, 88 | | |
| | 0.01 | 84, 80 | | |
| | 0.05 | 102, 99 | | |
| | 0.05 | 107, 111 | | |
| | 0.05 | 111, 117 | | |
| | 0.05 | 105, 103 | | |
| | 0.20 | 108, 107 | | |
| | 0.20 | 110, 104 | | |
| | 0.01 – 0.20 | 80 - 117 | 99 ± 11.2 | 11.3 (n=20) |
| Must | 0.01 | 87, 76 | 88 ± 12.5 | 14.2 (n=6) |
| | 0.01 | 102, 101 | | |
| | 0.01 | 92, 72 | | |
| | 0.05 | 99, 100 | | |
| | 0.05 | 118, 115 | | |
| | 0.05 | 105, 101 | | |
| | 0.2 | 99, 112 | | |
| | 0.5 | 100, 99 | | |
| | 0.01 – 0.5 | 72 - 118 | 99 ± 12.4 | 12.5 (n=16) |
| Pomace | 0.05 | 77, 80 | 78 ± 2.7 | 3.4 (n=6) |
| | 0.05 | 80, 73 | | |
| | 0.05 | 79, 79 | | |
| | 0.20 | 69, 72 | | |
| | 0.50 | 85, 98 | | |
| | 1.0 | 75, 75 | | |
| | 2.0 | 76, 77 | | |
| | 0.05 – 2.0 | 69 - 98 | 78 ± 6.9 | 8.9 (n=14) |

[1] Corrected for control Mean control values: wine = 0.0000 (n=8); must= 0.0000 (n=6); pomace= 0.0000 (n=6)

[2] Duplicate samples.

Table 21. Recovery of quinoxyfen from grapes, juice, and raisins (Method ERC95.26) (83731).

| Matrix | Fortification level (mg/L) | % Recovery | Average % recovery | % RSD |
|---|---|---|---|---|
| Grapes | 0.01<br>0.01<br>0.01 | 100<br>97<br>99 | 99 ± 1 | 1.5 (n=3) |
| | 0.10<br>0.10<br>0.10 | 89<br>98<br>89 | 92 ± 5 | 5.6 (n=3) |
| | 1.0<br>1.0<br>1.0 | 78<br>95<br>95 | 89 ± 10 | 11 (n=3) |
| | 0.01 – 1.0 | 78 – 100 | 93 ± 7 | 7.5 (n=9) |
| Juice | 0.01<br>0.01<br>0.01 | 89<br>87<br>86 | 88 ± 2 | 1.6 (n=3) |
| | 0.10<br>0.10<br>0.10 | 76<br>76<br>76 | 76 ± 0 | 0 (n=3) |
| | 1.0<br>1.0<br>1.0 | 73<br>70<br>69 | 71 ± 2 | 3 (n=3) |
| | 0.01 – 1.0 | 69 - 89 | 78 ± 7.5 | 9.6 (=9) |
| Raisins | 0.01<br>0.01<br>0.01 | 78<br>77<br>78 | 78 ± 1 | 1(n=3) |
| | 0.10<br>0.10<br>0.10 | 96<br>96<br>97 | 96 ± 1 | 0 (n=3) |
| | 1.0<br>1.0<br>1.0 | 89<br>90<br>85 | 88 ± 3 | 0.8 (n=3) |
| | 0.01 – 1.0 | 77 - 97 | 87 ± 8 | 9.4 (n=9) |

Method GRM 99.02 – Determination of quinoxyfen in grapes and dried grapes by gas chromatography with mass selective detection (GC-MSD) (74780, Teasdale, 2000) Independent laboratory validation (102718, Dobbs, 2001) was used for determination of quinoxyfen in supervised trials on grapes in Australia. Sample preparation is similar to that of ERC95.26. Quinoxyfen was quantified by gas chromatography with mass selective detection (GC-MSD). The quantitation ion is 237 amu, and the confirmation ion is 272 amu.

At least two samples (in duplicate) were fortified at quinoxyfen concentration levels of 0.01 to 0.5 mg/kg. A summary of the recovery data are summarized in Table 22.

The independent laboratory validation (Dobbs, 2001) conducted for the determination of residues of quinoxyfen on raisins using Method GRM 99.02 showed average recoveries of 94 ± 8% over the concentration range of 0.01 mg/kg to 0.1 mg/kg. Individual recovery values were within the acceptable range of 70–120%. The results are included in Table 22.

Table 22. Recovery of quinoxyfen from fortified grapes and dried grapes (Method GRM99.02) (74780, 102718).

| Fortification level (mg/kg) | n | Recovery range (%) | Mean (%) | Standard deviation | % RSD |
|---|---|---|---|---|---|
| GRAPES | | | | | |
| 0.01 | 8 | 98 - 105 | 101 | 2.6 | 2.6 |
| 0.05 | 3 | 78 - 104 | 102 | 20.5 | 20.1 |
| 0.2 | 4 | 91- 115 | 103 | 11.1 | 10.8 |
| 0.5 | 4 | 94 - 98 | 96 | 1.7 | 1.8 |
| 0.01 - 0.5 | 19 | 78 - 115 | 100 | 8.8 | 8.8 |
| DRIED GRAPES | | | | | |
| 0.01 | 4 | 68 - 95 | 82 | 11.9 | 14.5 |
| 0.05 | 4 | 84 - 99 | 92 | 7.4 | 8.0 |
| 0.2 | 4 | 77 - 115 | 93 | 15.8 | 17.0 |
| 0.5 | 4 | 70 - 95 | 79 | 10.8 | 13.7 |
| 0.01 - 0.5 | 20 | 68 -115 | 86 | 12.4 | 14.4 |
| DRIED GRAPES (ILV) | | | | | |
| 0.01 | 5 | 84 - 86 | 85 | 0.84 | 9.8 |
| 0.02 | 3 | 98 - 103 | 101 | 2.6 | 2.6 |
| 0.10 | 5 | 95 - 106 | 100 | 4.3 | 4.3 |
| 0.01 – 0.1 | 13 | 84 - 106 | 94 | 8 | 8.5 |

Mean control values: Grapes = 0.0002 mg/kg (n=8); Dried grapes = 0.003 mg/kg (n=8).

Method ERC 95.26 – Validation of method for determination of quinoxyfen in cherries by GC-MSD (102722, Chen, 2002) was validated for use in the supervised trials on cherries conducted in the US. Untreated samples of cherries were fortified at concentration levels of 0.01mg/kg to 1.0 mg/kg. The recovery results are summarized in Table 23.

Table 23. Recovery of quinoxyfen from fortified cherries (102722).

| Fortification level (mg/L) | % Recovery[1] | Average % recovery | % RSD |
|---|---|---|---|
| 0.01 | 92 | 94 ± 2 | 2.13% |
| 0.01 | 96 | | |
| 0.01 | 94 | | |
| 0.1 | 94 | 96 ± 2 | 2.16% |
| 0.1 | 97 | | |
| 0.1 | 98 | | |
| 1.0 | 79 | 92 ± 11 | 11.9% |
| 1.0 | 98 | | |
| 1.0 | 98 | | |
| 0.01 – 1.0 | 79 - 98 | 94 ± 6 | 6..4% (n=9) |

Method ERC 95.26 – Validation of method for the determination of quinoxyfen residues in lettuce by GC-MSD (208698, Barney, 2005)- was validated for use on lettuce samples collected from trials in the US after minor modifications of ERC95.26 such as changes in the filtration procedure or volume of solvent used, which did not affect the performance of the method. Method validation was carried out at fortification levels of 0.01, 0.1, and 1.0 mg/kg of quinoxyfen. The results are summarized in Table 24.

Table 24: Recovery of quinoxyfen from fortified leaf lettuce samples (Method ERC95.26) (208698).

| Fortification level (mg/L) | % Recovery[1] | Average % recovery | % RSD |
|---|---|---|---|
| 0.01 | 87 | 88 ± 2.2 | 2.5 |
| 0.01 | 87 | | |
| 0.01 | 89 | | |
| 0.01 | 91 | | |
| 0.01 | 90 | | |
| 0.01 | 85 | | |
| 0.10 | 86 | 88 ±2.1 | 2.4 |
| 0.10 | 87 | | |
| 0.10 | 90 | | |
| 1.0 | 84 | 89 ± 4.5 | 5.0 |
| 1.0 | 89 | | |
| 1.0 | 93 | | |
| 0.01 – 1.0 | 84 - 93 | 88 ± 2.6 | 2.9 (n=12) |

Method ERC 96.16 – Independent laboratory validation for the determination of quinoxyfen residues in melon peel and pulp by GC-MSD (45724, Khoshab, and Rawle, 1996) was used in the supervised trials on melons conducted in European countries and involved extraction of quinoxyfen with acidic acetone and partitioning into hexane after addition of sodium bicarbonate solution. The extract was evaporated to dryness and the residue was reconstituted in hexane prior to an aminopropyl solid phase extraction using 1% acetone in hexane to elute the quinoxyfen. The eluate was then evaporated to dryness and reconstituted in tri-methyl pentane containing 1% corn oil and 1,4-dibromonaphthalene as internal standard. Quinoxyfen was measured by gas chromatography with mass selective detection using m/z 237 ion. The m/z 286 ion was used for quantification of the internal standard.

Method 96.16 was independently validated by an external laboratory and the results were consistent with recovery data and chromatography generated on the original method (Table 25).

Table 25. Recovery of quinoxyfen from fortified melon peel and pulp (Method ERC 96.16) (45724).

| Fortification level (mg/kg) | % Recovery | |
|---|---|---|
| | Original method | Independent Validation |
| MELON PEEL | | |
| 0.01 | 82, 82 | 103, 87 |
| 0.01 | 88, 89 | 87, 86 |
| 0.01 | 101, 100 | 92, 95 |
| 0.01 | 93, 92 | 77, 86 |
| 0.05 | 92, 92 | 96, 94 |
| 0.20 | 94, 104 | 84, 93 |
| 0.50 | 100, 97 | 97, 105 |
| 1.0 | 101, 98 | 101, 100 |
| Mean Overall | 94 ± 6.6 | 92 ± 7.7 |
| % RSD (0.01-1.0 mg/kg) | 7.0 (n=16) | 8.4 (n=16) |
| Mean (0.01 mg/kg) | 91 ± 7.2 | 89 ± 7.7 |
| % RSD (0.01 mg/kg) | 7.9 (n=6) | 8.6 (n=6) |
| MELON PULP | | |
| 0.01 | 91, 94 | 102, 83 |
| 0.01 | 92, 95 | 89, 89 |
| 0.01 | 92, 100 | 98, 84 |
| 0.01 | 91, 96 | 86, 98 |

| Fortification level (mg/kg) | % Recovery | |
|---|---|---|
| | Original method | Independent Validation |
| 0.05 | 92, 98 | 89, 98 |
| 0.20 | 103, 105 | 93, 89 |
| 0.50 | 102, 101 | 102, 101 |
| 1.0 | 99, 99 | 100, 104 |
| Mean Overall | 97 ± 4.6 | 94 ± 7.0 |
| Mean (0.01 mg/kg) | 94 ± 3.1 | 91 ± 7.2 |
| % RSD (0.01-1.0 mg/kg) | 4.7 (n=16) | 7.5 (n=16) |
| % RSD (0.01 mg/kg) | 3.3 (n=6) | 7.9 (n=6) |

Method ERC 96.08 – Validation of method for the determination of quinoxyfen residues in peppers (76968, Khoshab and MacMillan, 1996; 08006, Chen, 2003) uses an extraction and clean-up scheme and analysis method similar to ERC 96.16, for use in trials on peppers in the US.

Table 26. Recovery of quinoxyfen from fortified samples of peppers (Method ERC 96.08) (76968; 08006).

| Fortification level (mg/L) | Range% Recovery | Average % recovery | % RSD |
|---|---|---|---|
| 0.01 | 78 - 120 | 87.7 ± 10 | 11.3 (n=18) |
| 0.05 | 92 - 102 | 99.1 ± 4.1 | 4.2 (n=14) |
| 2.0 | 101 - 107 | 103.5 ± 2.6 | 2.6 (n=4) |
| 0.01 – 2.0 | 78 - 120 | 93.9 ± 9.8 | 10.4 (n=36) |

Method GRM 99.04 – Determination of residues of quinoxyfen in sugar beet roots and tops by GC-MSD (74779, Teasdale, Lyons, Rhodes, and Patel, 2000) was used in trials in European countries. The method uses the extraction, clean-up, and analysis schemes of ERC 96.16. The validation was performed in 4 batches by 2 analysts. The results are summarized in Table 27.

Table 27. Recovery of quinoxyfen from fortified sugar beet roots and tops (74779).

| Fortification level (mg/kg) | % Recovery[1] | Average % recovery | % RSD |
|---|---|---|---|
| SUGAR BEET ROOTS | | | |
| 0.01<br>0.01<br>0.01<br>0.01 | 103, 100<br>92, 98<br>97, 87<br>103, 118 | 100 ± 9.2 | 9.2 (n=8) |
| 0.05<br>0.05 | 98, 96<br>100, 102 | 99 ± 2.6 | 2.6 (n=4) |
| 0.2<br>0.2 | 90, 103<br>101, 102 | 99 ± 61 | 6.2 (n=4) |
| 0.5<br>0.5 | 89, 91<br>89, 86 | 89 ± 2.1 | 2.4 (n=4) |
| 0.01 – 0.5 | 86 - 118 | 97 ± 7.6 | 7.8 (n=20) |
| SUGAR BEET TOPS | | | |
| 0.1<br>0.1<br>0.1<br>0.1 | 104, 104<br>101, 105<br>110, 87<br>109, 105 | 103 ± 7.1 | 6.9 |
| 0.5<br>0.5 | 99, 100<br>100, 97 | 99 ± 1.4 | 1.4 |
| 2.0<br>2.0 | 97, 96<br>92, 101 | 96 ± 3.7 | 3.8 |

| Fortification level (mg/kg) | % Recovery[1] | Average % recovery | % RSD |
|---|---|---|---|
| 5.0<br>5.0 | 97, 96<br>98, 96 | 97 ± 0.6 | 0.6 |
| 0.1 – 5.0 | 87 - 110 | 100 ± 5.5 | 5.5 |

[1] Corrected for control value and moisture content.

Mean control values: Sugar beet roots = 0.0001 mg/kg (n=8); tops = 0.0002 mg/kg (n=8)

Method ERC 94.5 – Determination of quinoxyfen residues in wheat and barley straw and grain by GC-MSD (63697, Gambie and Nicholson, 1994); Independent laboratory validation (31621, Gambie, Rawle, and Shaw, 1995) was used in supervised trials conducted on wheat and barley in various European countries. After extraction of the residues in acidic acetone, sodium bicarbonate was added and the extract was partitioned into hexane which was evaporated to dryness. The residue was next reconstituted in hexane and the resulting solution cleaned up in an aminopropyl solid phase extractor using 1% acetone in hexane. The eluate was evaporated to dryness and reconstituted in 0.1% corn oil in tri-methyl pentane containing 1,4-dibromonaphthalene as internal standard. Quinoxyfen was quantified by gas chromatography with mass selective detection. Ions monitored were 237 and 272 m/z for quinoxyfen and 286 m/z for the internal standard. This method is very similar to method ERC 96.16.

The method was validated by fortification of samples of wheat and barley grain at quinoxyfen concentration levels of 0.01–1.0 mg/kg and samples of straw at levels of 0.05–10 mg/kg. Two independent external laboratories also performed recovery experiments at the same levels of fortification. The results are summarized in Table 28.

Table 28. Summary of recoveries of quinoxyfen from fortified wheat and barley grain and straw samples (63697; 31621).

| Fortification level (mg/kg) | % Recovery[1] | | |
|---|---|---|---|
| | Original method, ERC 94.5 | Independent validation lab 1 | Independent validation lab 2 |
| WHEAT AND BARLEY GRAIN | | | |
| 0.01 | 80, 91[2] | 92, 81[2] | 100, 93 |
| 0.01 | 95, 86 | 107, 107 | 98, 93 |
| 0.01 | 92, 86 | 86, 80 | 88, 107 |
| 0.05 | 93, 96 | 119, 119 | - |
| 0.10 | 84, 94 | 73, 80 | 97, 110 |
| 0.5 | - | - | 104, 105 |
| 1.0 | 103, 144 | - | |
| Mean | 92 ± 7.2 | 94 ± 17.2 | 99.5 ± 7 |
| Mean control values | 0.0003 mg/kg (n=6) | 0.0002 (n=6) | 0.000 (n=3) |
| % RSD over the validated range | 7.9 (n=12) | 18.2 (n=10) | 7 (n=10) |
| % RSD at the lowest validated value (0.01 mg/kg) | 6.1 (n=6) | 13.3 (n=6) | 6.9 (n=6) |
| WHEAT AND BARLEY STRAW | | | |
| 0.05 | 87, 88 | 89, 92 | 87, 91 |
| 0.05 | 76, 80, 76, 78 | 88, 83 | 89, 85 |
| 0.05 | 90, 92, 93 | 79, 71 | 94, 87 |
| 0.05 | 82, 86 | - | - |
| 0.20 | 82, 88 | - | 97, 94 |
| 0.20 | 80, 88 | - | - |

| Fortification level (mg/kg) | % Recovery[1] | | |
|---|---|---|---|
| | Original method, ERC 94.5 | Independent validation lab 1 | Independent validation lab 2 |
| 0.50 | 95, 89 | 77, 85 | 103, 95 |
| 1.0 | 90, 96,98 | 85, 89 | - |
| 5.0 | 76, 83 | - | - |
| 10.0 | 76, 82 | 72, 85 | 88, 86 |
| Mean Overall | 85 ± 6.8 | 82.9 ± 6.8 | 91.3 ± 5.4 |
| Mean (0.05 mg/kg) | | | |
| Mean control values | 0.0029 (n=12) | 0.0003 (n=6) | 0.0096 (n=3) |
| % RSD over the validated range | 7.9 (n=24) | 8.2 (n=12) | 5.9 (n=12) |
| % RSDat the lowest validated value (0.05 mg/kg) | 7.4 (n=11) | 9,2 9 (n=6) | 3.7 (n=6) |

1 Corrected for control values.

2 Replicate samples.

Method ERC 95.16 – Determination of quinoxyfen residues in flour, bran and bread by GC-MSD (31600, Gambie and Press, 1995) was used in the processing study on wheat and involved extraction and clean-up of quinoxyfen residues by the procedure of Method ERC 94.5. Quinoxyfen was quantified by gas chromatography with mass selective detection. Ions monitored are 286 amu for the internal standard and 237 amu (quantitation ion) and 272 amu (confirmation) for quinoxyfen. Ion 307 is also considered if the ratio of 237/272 is not within ± 10% of the value of the bracketing standard.

The method was validated for each analyte (flour, bran and bread) by fortification with quinoxyfen at concentration levels of 0.01 mg/kg to 0.20 mg/kg. The results are summarized in Table 29.

Table 29: Recovery of quinoxyfen from fortified wheat flour, bran, and bread (31600).

| Fortification level (mg/kg) | % Recovery[1] | | |
|---|---|---|---|
| | FLOUR | BRAN | BREAD |
| 0.01 | 77, 88 | 75, 73 | 86, 96 |
| 0.01 | 107, 107 | 101, 101 | 98, 98 |
| 0.01 | 90, 87 | 80, 86 | 91.90 |
| 0.05 | 86, 77 | 73, 77 | 84, 90 |
| 0.20 | 87, 94 | 86, 89 | 104, 98 |
| Mean Overall | 90 ± 10.4 | 84 ± 10.4 | 94 ± 6.3 |
| Mean control values | 0.0002 mg/kg (n=6) | 0.0004 mg/kg (n=6) | 0.000 (n=6) |
| % RSD over the validated range (0.01-0.20 mg/kg) | 11.6 (n=10) | 12.4 (n=10) | 6.7 (n=10) |
| % RSD at the lowest validated value (0.01 mg/kg) | 12.9 (n=6) | 14.3 (n=6) | 5.3 (n=6) |

[1]Corrected for appropriate control value

Method ERC 95.10 – Determination of quinoxyfen residues in beer by GC-MSD (63705, Teasdale and Press, 1995)-was used in the study involving processing of barley into beer. Quinoxyfen residues were extracted from beer samples with methyl-tertiary-butyl ether after addition of sodium bicarbonate solution and acetone. The extract was evaporated to dryness and the residue was reconstituted in 0.1% corn oil in tri-methyl pentane. Quinoxyfen was quantified by gas chromatography with mass selective detection. The ions monitored are 237 amu and 272 amu for quinoxyfen.

The method was validated by recovery experiments carried out in 2 batches by 2 analysts. Beer samples were fortified with quinoxyfen at concentration levels of 0.01 mg/kg to 0.5 mg/kg.

Table 30. Recovery of quinoxyfen from fortified beer samples (63705).

| Fortification level (mg/L) | % Recovery[1] | Average % recovery | % RSD |
|---|---|---|---|
| 0.01<br>0.01<br>0.01 | 75, 72<br>80, 72<br>92, 92 | 80.5 ± 9.4 | 11.6 (n=6) |
| 0.05<br>0.05 | 86, 84<br>68, 81 | 79.8 ± 8.1 | 10.2 (n=4) |
| 0.10<br>0.10 | 90, 92<br>72, 78 | 83 ± 9.6 | 11.6 (n=4) |
| 0.50<br>0.50 | 94, 94<br>75, 86 | 87.3 ± 9 | 10.3 (n=4) |
| 0.01 – 0.50 | 68 - 94 | 82.4 ± 8.8 | 10.6 (n=18) |

1 Corrected for control value.

Mean control value = 0.000 mg/kg (n=6)

Method ERC 95.26.S1 – Determination of residues of quinoxyfen in hops by gas chromatography with mass selective detection (73994, Oberwalder, 1998; 81400, West, S., 2001); Independent laboratory validation (80416, Eckert, J. and West, S., 2000) was used in trials on hops conducted in the US. It is a modification of Method 95.26 which was originally developed and validated for grapes. The procedure for hops was the same as for grapes, with minor modifications such as increase in volume of extracting solvent and proportionate increase in the volumes of sodium bicarbonate and hexane. Recovery data were generated for hops by an independent laboratory by fortifying untreated control samples with quinoxyfen at concentration levels of 0.05 mg/kg and 0.1 mg/kg.

Table 31. Recovery of quinoxyfen from fortified samples of hops (73994; 80416; 81400).

| Fortification level (mg/L) | % Recovery | Average % recovery | % RSD |
|---|---|---|---|
| 0.05<br>0.05<br>0.05 | 113<br>117<br>87 | 106 ± 16 | 15.4 (n=3) |
| 0.10<br>0.10<br>0.10 | 100<br>102<br>104 | 102 ± 2 | 2 (n=3) |
| 0.05 –0.10 | 87 - 117 | 104 ± 10.6 | 10.6 (n=6) |

Method ERC 94.7 – Determination of residues of quinoxyfen in skimmed milk, whole milk, and cream by GC-MSD (135047, Class, 2003) was developed for quantitative determination of quinoxyfen residues in skimmed milk, whole milk and cream. This method was used in the cattle feeding study. Quinoxyfen was extracted from the milk fraction by shaking with methanol. After addition of sodium bicarbonate solution, quinoxyfen was partitioned into hexane which was then evaporated to dryness. The residue was reconstituted in 1% acetone in hexane and applied to an aminopropyl SPE cartridge using a further volume of 1% acetone in hexane to elute the residue.

For cream samples, the eluate was evaporated to dryness and reconstituted in 5% methanol in dichloromethane prior to clean-up using gel permeation chromatography. For skimmed milk and whole milk, the residue was reconstituted in hexane and further purified using a silica SPE cartridge using 10% methyl-tertiary-butyl ether in hexane to elute quinoxyfen. The eluates were evaporated to dryness and the residue reconstituted in 0.1% corn oil in tri-methyl pentane. Quinoxyfen was quantified by gas chromatography with mass selective detection. The 237 m/z fragment ion was used for quantification, and the 272 m/z and 274 m/z fragment ions were used for confirmation.

The method was validated at fortification levels of 0.001 to 0.1 mg/kg quinoxyfen.

Table 32. Recovery of quinoxyfen from fortified samples of whole milk, skimmed milk, and cream (Method ERC 94.7) (135047).

| Fortification level (mg/kg) | % Recovery[1] | | |
|---|---|---|---|
| | SKIMMED MILK | WHOLE MILK | CREAM |
| 0.001 | 87, 93 | 88, 79 | 64, 100 |
| 0.001 | 90, 96 | 83, 78 | 97, 110 |
| 0.001 | 99, 86 | 77, 85 | 90, 83 |
| 0.01 | 86, 85 | 80, 81 | 99, 99 |
| 0.1 | 79, 80 | 78, 84 | 87, 86 |
| Mean | 88 ± 6.5 | 81 ± 3.6 | 92 ± 12.6 |
| Mean control values | 0.000 mg/kg (n=6) | 0.000 mg/kg (n=6) | 0.000 (n=6) |
| % RSD over the validated range (0.001 – 0.1 mg/kg) | 7.3 (n=10) | 4.4 (n=10) | 13.8 (n=10) |
| % RSD over the lowest validated range | 5.6 (n=6) | 5.3 (n=6) | 17.6 (n=6) |

1Corrected for appropriate control value

The independent laboratory validation consisted of fortification of skimmed milk and cream samples with quinoxyfen at concentration levels of 0.001 mg/kg and 0.1 mg/kg.

Table 33: Summary of ILV results for recovery of quinoxyfen from fortified skimmed milk and cream (Method ERC 94.7) (130457)

| Matrix | Fortification level (mg/kg) | n | % Recovery (range) | Average % recovery | % RSD |
|---|---|---|---|---|---|
| Skimmed milk (1.5% fat) | 0.001 | 5 | 76 - 113 | 101 | 15 |
| | 0.1 | 5 | 85 - 98 | 91 | 5 |
| | Overall fortification | 10 | 76 - 113 | 96 ± 11.5 | 12 |
| Cream (30% fat) | 0.001 | 4 | 69 - 81 | 75[1] | 9 |
| | 0.1 | 4 | 70 - 78 | 74[2] | 4 |
| | Overall fortification | 8 | 69 - 81 | 74 ± 4.4 | 6 |

[1] One result, 39% was identified by Dixon-Test as an outlier and was not included in the calculations.

[2] One result, 55%, was identified by Dixon-Test as an outlier and was not included in the calculations.

Method ERC 94.20 – Determination of residues of quinoxyfen in bovine muscle, kidney, and fat by GC-MSD (63682, Hastings, M. and Gambie, A., 1995); Independent laboratory validation (135044, Class, 2003) is applicable to the quantitative determination of quinoxyfen residues in bovine muscle, kidney, and fat down to the lowest validated level of 0.01 mg/kg. Quinoxyfen was extracted from the tissue by shaking with methanol. After addition of water, quinoxyfen was partitioned into hexane which was then evaporated to dryness. The residue was reconstituted in dichloromethane prior to clean-up using gel permeation chromatography. The eluate was evaporated to dryness and reconstituted in 0.1% corn oil in tri-methyl pentane. Quantification was by gas chromatography with mass selective detection. The 237 m/z fragment ion was used for quantification, and the 272 m/z and 274 m/z fragment ions were used for confirmation.

The method has been validated by the analysis of untreated and fortified samples for residues of quinoxyfen in muscle, kidney, and fat over the range of 0.01-1.0 mg/kg.

Table 34. Recovery of quinoxyfen from fortified samples of bovine muscle, kidney, and fat (Method ERC 94.20) (63682).

| Fortification level (mg/kg) | % Recovery[1] | | |
|---|---|---|---|
| | MUSCLE | KIDNEY | FAT |
| 0.01 | 92, 100 | 91, 91 | 104, 116 |
| 0.01 | 93, 113 | 97, 98 | 108, 100 |
| 0.01 | 102, 112 | 94, 98 | 92, 95 |
| 0.10 | 110, 107 | 78, 86 | 109, 109 |
| 1.0 | 99, 96 | 95, 94 | 80, 93 |
| Overall Mean | 102 ± 7.7 | 92 ± 6.2 | 101 ± 10.7 |
| Mean at lowest validated value (0.01 mg/kg) | 102 ± 9.0 | 95 ± 3.3 | 102 ± 8.8 |
| Mean control values | 0.0007 mg/kg (n=6) | 0.000 mg/kg (n=6) | 0.000 (n=6) |
| % RSD over the validated range (0.01- 1.0 mg/kg) | 7.6 (n=10) | 6.7 (n=10) | 10.6 (n=10) |
| % RSD over the lowest validated range (0.01 mg/kg) | 8.8 (n= 6) | 3.5 (n=6) | 8.6 (n=6) |

[1] Corrected for appropriate control value

For the independent laboratory validation, bovine meat and fat samples were fortified with quinoxyfen at levels of 0.01 mg/kg and 1.0 mg/kg.

Table 35. Summary of ILV recovery results for quinoxyfen residues in fortified bovine meat and fat (Method ERC 94.20) (135044).

| Matrix | Fortification level (mg/kg) | n | % Recovery (range) | Average % recovery | % RSD |
|---|---|---|---|---|---|
| Bovine meat | 0.01 | 4[1] | 68 - 93 | 84 | 14 |
| | 1.0 | 5 | 86 - 105 | 92 | 9 |
| | 0.01- 1.0 | 8 | 80 - 105 | 88 ± 10.6 | 12 |
| Bovine fat | 0.01 | 5 | 70 - 96 | 80 | 13 |
| | 1.0 | 5 | 80 - 96 | 84 | 8 |
| | 0.01 -1.0 | 10 | 70 - 96 | 82 ± 8.2 | 10 |

[1] One result, 60% was caused by a partial loss of extract during partition and was not included in the calculation.

Method ERC 94.30 – Determination of residues of quinoxyfen in bovine liver by GC-MSD (63683, Hastings and Gambie, 1995); Independent laboratory validation (135046, Class, 2003) was used in the cattle feeding study. The liver sample was first digested with aqueous hydrochloric acid/pepsin in order to extract quinoxyfen residue. After centrifuging, the remaining solid tissue was extracted with methanol and again centrifuged. The methanol was decanted and removed by evaporation. The residue was reconstituted in the original acid/pepsin extract which was then treated with buffer and β-glucuronidase to breakdown any conjugated residues. After addition of water, quinoxyfen was partitioned into hexane which was then evaporated to dryness. The residue was reconstituted in dichloromethane prior to clean-up using gel permeation chromatography. The eluate was evaporated to dryness and reconstituted in 0.1% corn oil in tri-methyl pentane, and quinoxyfen was quantified by gas chromatography with mass selective detection. Ion 237 m/z is used for quantification, and ions 272 m/z and 274 m/z are used for confirmation.

The method has been validated by analysis of untreated and fortified samples for residues of quinoxyfen in liver over the range of 0.01 – 1.0 mg/kg. An independent laboratory validation resulted in unacceptable results, while in the repeated tests the recoveries remained poor (Table 37).

Table 36. Recovery of quinoxyfen from fortified samples of bovine liver (Method ERC 94.30) (63683).

| Fortification level (mg/kg) | % Recovery | Average % Recovery | % RSD |
|---|---|---|---|
| 0.01<br>0.01 | 67, 73<br>61, 67 | 67 ± 3.8 | 5.6 (n=6) |
| 0.01 | 68, 68 | | |
| 0.10<br>1.0 | 62, 63<br>62, 64 | | |
| 0.01 - 1.0 | 61 - 73 | 66 ± 3.7 | 5.7 (n=10) |

Mean control value = 0.000 (n=6)

Table 37. Summary of ILV recovery results for quinoxyfen residues in fortified bovine Liver, Second Attempt (Method ERC 94.30) (135046).

| Fortification level (mg/kg) | % Recovery | Average % Recovery | % RSD |
|---|---|---|---|
| 0.01<br>0.01<br>0.01<br>0.01<br>0.01 | 49<br>46<br>46<br>36<br>44 | 44 ± 4.9 | 11 (n=5) |
| 1.0 | 53<br>56<br>55<br>51 | 54 ± 2.2 | 4.1 (n=4) |
| 0.01 - 1.0 | | | |

Control values < 0.0005 and 0.0009 mg/kg. One sample at the 1.0 mg/kg fortification level (recovery 41% was excluded because of partial loss of hexane extract on evaporation.

Method ERC 98.05 – Determination of quinoxyfen residues in eggs by GC-MSD (64399, Khoshab et.al, 1998); Independent laboratory validation (135045, Class, 2003)-was used in the poultry feeding study. Quinoxyfen was extracted from whole egg and egg yolk by macerating and shaking with an acidic acetone solution. After addition of sodium bicarbonate solution, quinoxyfen was partitioned into hexane which was then evaporated to dryness. The residue was reconstituted in 2% acetone in hexane and applied to an aminopropyl SPE cartridge using a further volume of 2% acetone in hexane to elute quinoxyfen. The eluate was evaporated to dryness and reconstituted in dichloromethane prior to clean-up using gel permeation chromatography. The eluate was evaporated to dryness and reconstituted in 0.1% corn oil in tri-methyl pentane containing 1,4-dibromonaphthalene as an internal standard. Quinoxyfen was quantified by gas chromatography with mass selective detection. The 1,4-dibromonaphthalene quantification ion is 286 amu; the quinoxyfen quantification ion is 272 amu, with confirmation ions 237 amu and 307 amu.

The method has been validated by the analysis of untreated samples and samples of whole eggs and egg yolks fortified with quinoxyfen over the range of 0.01 mg/kg to 1.0 mg/kg. Results of the independent laboratory validation were consistent with the initial validation results.

Table 38. Recovery of quinoxyfen from fortified samples of eggs (64399).

| Fortification level (mg/kg) | % Recovery[1] | Average % Recovery | % RSD |
|---|---|---|---|
| 0.01 | 109, 105[2] | 98 ± 7.3 | 7.4 (n=8) |
| 0.01 | 101, 95 | | |
| 0.01 | 101, 96 | | |
| 0.01 | 85, 95 | | |
| 0.10 | 93, 97 | 97 ± 2.6 | 2.7 (n=4) |
| 0.10 | 98, 99 | | |
| 0.5 | 92, 90 | 94 ± 4 | 4.3 (n=4) |
| 0.5 | 96, 99 | | |
| 1.0 | 93, 87 | 87 ± 4.5 | 5.2 (n=4) |
| 1.0 | 87, 82 | | |
| 0.01-1.0 | 82 - 109 | 95 ± 6.7 | 7.1 (n=20) |

[1] Mean control values: whole eggs = 0.0000 (n=6); yolk = 0.0000 (n=6).

[2] Replicate samples.

Table 39. Summary of ILV recovery results for quinoxyfen residues in fortified eggs (135045).

| Matrix | Fortification level (mg/kg) | n | % Recovery (range) | Average % recovery | % RSD |
|---|---|---|---|---|---|
| Whole eggs | 0.01 | 5 | 73 - 104 | 85 | 15 |
| | 1.0 | 5 | 79 - 105 | 92 | 13 |
| | 0.01 - 1.0 | 8 | 73 - 105 | 88 ± 12.3 | 14 |
| Egg yolk | 0.01 | 5 | 73 - 78 | 76 | 3 |
| | 1.0 | 5 | 73 - 84 | 81 | 6 |
| | 0.01 – 1.0 | 10 | 73 - 84 | 78 ± 4.7 | 6 |

[1]Corrected from appropriate control value

*Multi-residue Methods*

Multi-residue method testing for quinoxyfen according to US FDA PAM I, Appendix II**,** as updated January 1994 was reported to the Meeting (80711, Hackert Anderson and West, S., 2001).

Quinoxyfen was analyzed according to the FDA Multiresidue Method Testing guidelines in PAM, Vol. I, Appendix II (1/94). Protocol A. Quinoxyfen was evaluated to see if it was naturally fluorescent. With an excitation wavelength of 245 nm and 300 nm, the compound showed no emission response above that of the methanol blank. Therefore, quinoxyfen does not naturally fluoresce.

Protocol C. The gas chromatographic behaviour of quinoxyfen was evaluated according with three column types (DB-1, DB-17, and DB-225) in combination with electron capture detection (ECD) or nitrogen-phosphorous detection (NPD). Quinoxyfen chromatographed within acceptable limits under Level I guidelines using the DB-1, DB-17, and DB-225 with ECD at 200ºC and also on the DB-1 with NPD at 200ºC.

Protocol D. Testing (without Florisil cleanup) for recovery of quinoxyfen from grapes utilizing NPD as a specific detector resulted in an average recovery of 27% at 0.1 mg/kg and 75% at 0.05 mg/kg.

Protocols E and F required Florisil cleanup. For the C1 elution system, the majority of quinoxyfen eluted in fraction 2. The majority of quinoxyfen eluted in the third fraction for the C2 system.

Protocol E testing with grapes yielded total average quinoxyfen recoveries of 37% (low fortification) and 102% (high fortification) for Florisil cleanup C1. The results show incomplete recovery of quinoxyfen at low fortification level (0.05 mg/kg) and complete recovery at the high fortification level (0.5 mg/kg). Since quinoxyfen is recoverable through the method with the C1 Florisil cleanup, the testing was repeated using the C2 Florisil cleanup. Average recoveries from grapes were 94% (low fortification) and 88% (high fortification) for Florisil cleanup C2, showing complete recovery through the method.

Protocol F testing with ground beef yielded total average quinoxyfen recoveries of 12% (low fortification) and 70% (high fortification) for Florisil cleanup C1 and 30% (low fortification) and 93% (high fortification) for Florisil cleanup C2. The results show incomplete or partial recovery at the low fortification level (0.05 mg/kg) and complete recovery at the high fortification level (0.5 mg/kg) with the C1 and C2 Florisil cleanup.

Multi-residue Method DFG S19 – Validation of method for determination of quinoxyfen in wheat, barley, grapes, strawberries, melons and other matrices by GC-ECD or GC-MSD (31651, Hastings and Schmidt, 1995)

A multi-residue method, DFG S19 was validated for use in the analysis of quinoxyfen in a number of plant matrices. The method involves extraction of plant samples with acetone: water solution (maintained constant at a ratio of 2:1, v/v). The extract was saturated with sodium chloride and diluted with dichloromethane, resulting in separation of excess water. The organic phase was separated and evaporated to dryness. The residue remaining was taken up in dichloromethane and was cleaned up by gel permeation chromatography. The eluate was concentrated and after supplemental clean up on a small silica gel column, quinoxyfen residues are determined by gas chromatography using capillary column and electron capture detector or mass selective detector.

Strawberry samples were extracted after adding sodium bicarbonate solution, since the original method resulted in unacceptable recoveries (about 60%).

Control samples of various matrices were each fortified with quinoxyfen at levels of 0.01 mg/kg and 0.5 mg/kg. The results are summarized in Table 40.

Table 40. Summary of recoveries of quinoxyfen from wheat, barley, melons, strawberries, and grapes at fortification levels of 0.01 and 0.5 mg/kg (MRM DFG S19) (31651).

| Analyte | Recovery range (%) | Mean recovery (%) | % RSD |
|---|---|---|---|
| Winter wheat | | | |
| Grain | 90 – 99 | 96 | 4 (n=4) |
| Straw | 87 – 99 | 93 | 6 (n=4) |
| Winter barley | | | |
| Grain | 84 – 98 | 91 | 7 (n=4) |
| Straw | 79 – 100 | 92 | 10 (n=4) |
| Melons | | | |
| Peel | 90 – 97 | 94 | 3 (n=1) |
| Pulp | 95 – 97 | 96 | 1 (n=1) |
| Strawberries | 69 – 88 | 78 | 10 (n=4) |
| Grapes | 74 – 87 | 81 | 7 (n=4) |

Method DFG S19 for the determination of residues of quinoxyfen on hops by GC-MSD (73994, Oberwalder, 1999), modified, was used for the supervised trials on hops conducted in Germany. The method was validated for hops by fortification of untreated samples with quinoxyfen at concentration levels of 0.01 mg/kg to 1.0 mg/kg. Recovery data are summarized in Table 41.

Table 41. Recovery of quinoxyfen in fortified samples of fresh and dried hops with MRM DFG S19 (73994).

| Matrix | Fortification level (mg/L) | % Recovery |
|---|---|---|
| FRESH HOPS CONES | 0.01<br>0.01<br>0.02<br>0.02<br>0.02<br>0.50<br>0.50<br>1.0<br>1.0 | 150[1]<br>70<br>85<br>70<br>90<br>90<br>73<br>91<br>93 |
| Mean | 0.01-1.0 | 85 ± 11 |
| % RSD over the validated range (0.01-1.0 mg/kg) | | 12 (n=8) |
| DRIED HOPS CONES | 0.02<br>0.02<br>0.50 | 105<br>100<br>93 |
| Mean | 0.02-0.50 | 99 ± 6 |
| % RSD over the validated range (0.02 – 0.5 mg/kg) | | 6.1 (n=3) |

1 Outlier according to Dixon Test; not included in calculation of the mean.

***Stability of Pesticide Residues in Stored Analytical Samples***

Frozen storage stability studies were reported to the Meeting for a variety of substrates that include animal tissues and plants. Control samples were fortified with known concentrations of quinoxyfen and then placed in frozen storage at approximately -20 C or less. The fortified samples were analyzed periodically for residues of quinoxyfen using the same analytical method as that used for the residue field trial or processing samples.

The stability of frozen samples was evaluated as part of the supervised trials on cherries (102721, 102722, Chen, 2002). The maximum storage interval for field-treated samples was 77 days. To evaluate stability of residues during this period, control samples of each matrix were fortified with 1.0 mg/kg quinoxyfen and analyzed after 80 days of frozen storage at -18ºC. All samples were analyzed within 1 day of extraction. Method ERC 95.26, which was validated and used for the determination of quinoxyfen in the supervised trials for cherries, was used for the storage stability test. Concurrent recoveries from samples fortified on the day of analysis were comparable to the test samples.

Table 42. Stability of quinoxyfen residues in cherries after frozen storage (102721, 102722).

| Matrix | Fortification level (mg/kg) | No. of days in frozen storage | Quinoxyfen conc (mg/kg) | % Remaining | % Concurrent recovery[1] | Reference |
|---|---|---|---|---|---|---|
| Cherry fruit | 1.0<br>1.0<br>1.0 | 80<br>80<br>80 | 0.908<br>0.926<br>0.918 | 91<br>93<br>92 | 94<br>94<br>95 | Chen, H., 2002a<br>IR-4 Study 07757 |
| | | | Average | 92 | 94 | |

[1] Concurrent recovery is from samples fortified on the day of analysis. % remaining was not corrected for the concurrent method recovery.

Numerous field trials on grapes were conducted in Europe, Australia, and the US. Throughout these trials, samples of grapes were stored frozen from 5.5 to about 11 months before analysis. A study was undertaken to determine the stability of quinoxyfen residues in samples of grapes stored

frozen (47234, Williams, 1996). Untreated samples of macerated grapes from one of the trials conducted in Europe were combined and mixed briefly in a Waring blender. Thirty six aliquots, each being 10 g of the grape sample, were fortified with 0.10 mg/kg quinoxyfen. A further 36 aliquots of 10 g each were left unfortified. All samples were stored below -16ºC and a proportion of both fortified and untreated samples were analyzed at intervals of 0, 3, 6, 9, and 12 months of storage.

Samples were analyzed according to Method ERC 94.29, which was previously validated over the range of to a lowest validated level of 0.01mg/kg for grapes and was used in the supervised trials. The results are summarized in Table 43.

Untreated samples of grapes (approximately 10 g each) were taken from the trial in the US in which portion of the harvest was processed and fortified with 0.10 mg/kg quinoxyfen (Thompson, 2001a; IR-4 Study 07256). Untreated juice and raisin samples were likewise collected after processing and fortified with 0.1 mg/kg quinoxyfen. All samples were then frozen at –18ºC. Frozen grape samples were analyzed after 206 days of storage, while juice and raisin samples were analyzed after 155 and 254 days of frozen storage, respectively. All samples were analyzed using method ERC 95.26, which had previously been validated for use on grapes and its processed fractions, with a lowest validated level of 0.01 mg/kg. The results are included in Table 43.

Table 43. Residues of quinoxyfen in grapes and grape processed fractions during frozen storage (47234).

| Matrix | Storage Period, Days | Fortification mg/kg | % Remaining | Concurrent % Recovery[1] | Reference |
|---|---|---|---|---|---|
| Grapes | 0 | 0.1 | 90 | 93 | Khoshab, A. and Williams, M., 1996 (GHE-P-5423) |
| | | 0.1 | 93 | 93 | |
| | | 0.1 | 88 | | |
| | | 0.1 | 90 | | |
| | | 0.1 | 102 | | |
| | | 0.1 | 100 | | |
| | | Average | 93.8 | 93 | |
| Grapes | 90 | 0.1 | 110 | 101 | |
| | | 0.1 | 104 | 97 | |
| | | Average | 107 | 99 | |
| Grapes | 180 | 0.1 | 96 | 93 | |
| | | 0.1 | 96 | 95 | |
| | | Average | 96 | 94 | |
| Grapes | 270 | 0.1 | 93 | 90 | |
| | | 0.1 | 94 | 92 | |
| | | Average | 93.5 | 91 | |
| Grapes | 365 | 0.1 | 97 | 100 | |
| | | 0.1 | 98 | 99 | |
| | | Average | 97.5 | 99.5 | |
| Grapes | 206 | 0.10 | 87 | 92 | Thompson, 2001a (IR-4 Study 07256) |
| | | 0.10 | 86 | 91 | |
| | | 0.10 | 85 | | |
| | | Average | 86 | 91.5 | |
| Grape juice | 255 | 0.01 | 93 | 89 | |
| | | 0.01 | 93 | 93 | |
| | | 0.01 | 81 | | |
| | | Average | 89 | 91 | |
| Raisins | 254 | 0.01 | 99 | 99 | |
| | | 0.01 | 100 | 101 | |
| | | 0.01 | 98 | | |
| | | Average | 99 | 100 | |

[1] Concurrent recovery is from samples fortified on the day of analysis. % remaining was not corrected for concurrent method recovery.

Samples of wheat grain and straw were taken from one of the supervised trials conducted in Europe. These samples were prepared with dry ice in a mill. Aliquots of each substrate (10g for grain

and 5g for straw) were weighed into 57 labelled 150 mL polypropylene pots. Thirty samples of grain were fortified with 0.1 mg/kg quinoxyfen, while 30 samples of straw were fortified with 1.0 mg/kg quinoxyfen. The remaining 27 samples of each substrate were retained as controls. All samples were then transferred to a freezer and kept frozen at temperatures ranging from -18ºC to -24ºC during the study with an average temperature of -23ºC. The storage intervals were 0, 98, and 267 days for grain and 0, 97, and 280 days for straw (31748, Gambie 1995). Grain samples were kept frozen and analyzed after 534 days. Straw samples were analyzed after 536 days (47586, Gambie, 1996)

Samples were analyzed using method ERC 94.5, which had previously been validated with a lowest validated level of 0.01 mg/kg for grain and 0.05 mg/kg for straw. The results from both studies are summarized in Table 44.

Table 44. Residues of quinoxyfen in cereal grain and straw during frozen storage (31748; 47586).

| Matrix | Storage Period, Days | Fortification mg/kg | % Remaining | Concurrent% Recovery[1] | Reference |
|---|---|---|---|---|---|
| Grain | 0 | 0.1 | 92 | 108 | Gambie, A. and Long, T., 1995 (GHE-P-4409) |
| | | 0.1 | 81 | 109 | |
| | | 0.1 | 97 | | |
| | | 0.1 | 91 | | |
| | | 0.1 | 100 | | |
| | | 0.1 | 103 | | |
| | | Average | 94 | 108 | |
| Grain | 98 | 0.1 | 100 | 102 | |
| | | 0.1 | 99 | 101 | |
| | | 0.1 | 100 | | |
| | | Average | 99 | 102 | |
| Grain | 267 | 0.1 | 106 | 89 | |
| | | 0.1 | 92 | 101 | |
| | | 0.1 | 97 | | |
| | | Average | 98 | 95 | |
| Grain | 453 | 0.1 | 106 | 105 | Gambie, A., 1996 (GHE-P-5438) |
| | | 0.1 | 111 | 107 | |
| | | 0.1 | 113 | | |
| | | Average | 110 | 106 | |
| Grain | 534 | 0.1 | 75 | 73 | |
| | | 0.1 | 77 | 75 | |
| | | 0.1 | 74 | | |
| | | Average | 75 | 74 | |
| Straw | 0 | 0.1 | 91 | 88 | Gambie, A. and Long, T., 1995 (GHE-P-4409) |
| | | 0.1 | 95 | 87 | |
| | | 0.1 | 92 | | |
| | | 0.1 | 92 | | |
| | | 0.1 | 97 | | |
| | | 0.1 | 96 | | |
| | | Average | 94 | 88 | |
| Straw | 97 | 0.1 | 72 | 75 | |
| | | 0.1 | 79 | 73 | |
| | | 0.1 | 80 | | |
| | | Average | 77 | 74 | |
| Straw | 280 | 0.1 | 85 | 88 | Gambie, A. and Long, T., 1995 (GHE-P-4409) |
| | | 0.1 | 86 | 87 | |
| | | 0.1 | 87 | | |
| | | Average | 86 | 87 | |
| Straw | 456 | 0.1 | 87 | 101 | Gambie, A., 1996 (GHE-P-5438) |
| | | 0.1 | 96 | 94 | |
| | | 0.1 | 93 | | |
| | | Average | 92 | 97 | |

| Matrix | Storage Period, Days | Fortification mg/kg | % Remaining | Concurrent% Recovery[1] | Reference |
|---|---|---|---|---|---|
| Straw | 536 | 0.1 | 75 | 78 | |
| | | 0.1 | 78 | | |
| | | 0.1 | 74 | | |
| | | Average | 75 | 78 | |

[1] Concurrent recovery is from samples fortified on the day of analysis. % remaining was not corrected for concurrent method recovery.

The stabilities of frozen samples of hops, lettuce, strawberry, peppers, and cantaloupe (melon) were evaluated as part of the supervised trials (83727, Thompson, 2001; 208698, Barney, W., 2005; 208697, Barney, 2005; 8006, Chen, 2003; 208696, Corley, 2004). To evaluate the stability of residues during this period, control samples of commodity were fortified with quinoxyfen and analyzed after some days of frozen storage at -15ºC. Samples were generally analyzed on the day of extraction. No samples were analyzed on day 0. Method ERC 95.26 was used for the storage stability tests.

Table 45. Residues of quinoxyfen in hops (dried), lettuce, strawberry, peppers, and melon during frozen storage.

| Matrix | Storage Period, Days | Fortification mg/kg | % Remaining | Concurrent % Recovery[1] | Reference |
|---|---|---|---|---|---|
| Hops | 113 | 0.5 | 105 | 109 | 83727 |
| | | 0.5 | 104 | 107 | |
| | | 0.5 | 110 | 106 | |
| | | Average | 106 | 108 | |
| Lettuce (leaf) | 280 | 0.10 | 93 | 95 | 208698 |
| | | 0.10 | 94 | 96 | |
| | | 0.10 | 88 | 95 | |
| | | Average | 92 | 95 | |
| Strawberry | 162 | 0.10 | 92 | 98 | 208697 |
| | | 0.10 | 97 | 94 | |
| | | 0.10 | 94 | 97 | |
| | | Average | 94 | 96 | |
| Melon (cantaloupe) | 251 | 0.50 | 89 | 94 | 208696 |
| | | 0.50 | 95 | 95 | |
| | | 0.50 | 91 | 93 | |
| | | Average | 92 | 94 | |
| Peppers, Bell | 318 | 1.0 | 98 | - | 8006 |
| | | 1.0 | 104 | - | |
| | | 1.0 | 104 | - | |

[1] Concurrent recovery is from samples fortified on the day of analysis. % remaining was not corrected for concurrent method recovery.

Samples of whole milk from the dairy cow feeding study were stored for up to 87 days prior to analysis. In order to assess the stability of residues of quinoxyfen in stored frozen samples, twelve 10-g samples of untreated whole milk were fortified with 0.1 mg/kg and kept frozen until analysis. In order to simulate the conditions in the study, milk was initially stored for 4 days at + 4ºC, prior to deep freezing (31599, Gambie and Long, 1995).

Fortified samples, together with untreated samples were analyzed using method ERC 94.7, which has previously been validated with an LOQ of 0.001 mg/kg for milk. Samples were removed from storage and analyzed after 0, 161 and 238 days of frozen storage. Two untreated samples were fortified with 0.1 mg/kg on each day of analysis and analyzed for concurrent recoveries. The results are summarized in Table 46.

Table 46. Residues of quinoxyfen in whole milk samples during frozen storage (31599).

| Matrix | Storage Period, Days | Fortification mg/kg | % Remaining | Concurrent % Recovery |
|---|---|---|---|---|
| Milk | 0 | 0.1 | 93 | 90 |
| | | 0.1 | 90 | 89 |
| | | 0.1 | 91 | |
| | | 0.1 | 90 | |
| | | 0.1 | 90 | |
| | | 0.1 | 89 | |
| | | Average | 90 | 90 |
| Milk | 161 | 0.1 | 82 | 76 |
| | | 0.1 | 81 | 85 |
| | | 0.1 | 83 | |
| | | Average | 82 | 80 |
| Milk | 238 | 0.1 | 86 | 89 |
| | | 0.1 | 91 | 88 |
| | | Average | 88 | 88 |

The liver, kidney, muscle, subcutaneous and peritoneal fat samples were stored up to 244, 190, 209, and 218 days, respectively during the cow feeding study (31599, Gambie, and Long,1995). In order to evaluate the stability of quinoxyfen residues on frozen storage, tissue samples from the control group were fortified with 0.1 mg/kg quinoxyfen and frozen at < 20ºC until analysis. Liver samples were analyzed using method ERC 94.30, which has been previously validated with an LOQ of 0.01 mg/kg. The rest of the tissues were analyzed with method ERC 94.20, with a lowest validated level of 0.01 mg/kg. Concurrent recoveries were run with control samples fortified with 0.1 mg/kg quinoxyfen on the day of analysis. The results are summarized in Table 47.

Table 47. Residues of quinoxyfen in animal tissue samples during frozen storage (31599).

| Matrix | Storage Period, Days | Fortification mg/kg | % Remaining | Concurrent% Recovery[1] |
|---|---|---|---|---|
| Liver | 242 | 0.1 | 64 (107[1]) | 61 |
| | | 0.1 | 60 (100[1]) | 61 |
| | | 0.1 | 44 (44[1]) | |
| | | Average | 56 (93[1]) | 61 |
| Liver | 292 | 0.1 | 65 | 67 |
| | | 0.1 | 69 | 66 |
| | | 0.1 | 64 | |
| | | Average | 66 | 66.5 |
| Kidney | 188 | 0.1 | 90 | 94 |
| | | 0.1 | 94 | 91 |
| | | 0.1 | 94 | |
| | | Average | 93 | 92.5 |
| Muscle | 194 | 0.1 | 87 | 91 |
| | | 0.1 | 86 | 91 |
| | | 0.1 | 84 | |
| | | Average | 86 | 91 |

| Matrix | Storage Period, Days | Fortification mg/kg | % Remaining | Concurrent% Recovery[1] |
|---|---|---|---|---|
| Subcutaneous fat | 207 | 0.1<br>0.1<br>0.1<br>Average | 93<br>94<br>101<br>96 | 90<br>89<br><br>89.5 |
| Peritoneal fat | 216 | 0.1<br>0.1<br>0.1<br>Average | 80<br>79<br>87<br>82 | 79<br>89<br><br>84 |

[1] Values in parenthesis are corrected for concurrent recoveries. No other % Remaining values were corrected for concurrent method recoveries.

## USE PATTERN

Quinoxyfen is a protectant fungicide for the control of powdery mildew diseases in a range of crops. Quinoxyfen does not control existing or latent powdery mildew infections and therefore, it must be applied before symptoms of the disease appear, on a protectant schedule. The product is diluted with water and applied as foliar spray or broadcast treatment using conventional spray equipment.

Quinoxyfen is registered for use in a wide range of crops in several countries. Only the registered uses in countries where supervised trials have been conducted or in countries with GAPs similar to where the supervised trials were carried out, are provided and summarized in Table 48. This summary is based on official labels provided by the sponsor and by use information supplied by the governments of Australia, Germany, and the Netherlands.

Table 48. Summary of GAP uses for quinoxyfen.

| Crop | Country | Formulation | Application | | | | PHI days |
|---|---|---|---|---|---|---|---|
| | | | Method | Rate, kg ai/ha | Spray conc. kg ai/hL | No. or max (kg ai/ha/ season) | |
| Blueberry | Germany | 250 g/L SC | Foliar | 0.075 | | 3 | 14 |
| Cereals (Wheat, barley, oats, rye, triticale) | UK | 500 g/L SC | Foliar | 0.15 | 0.0375 – 0.075 | 2<br>0.3 kg ai/ha | ~60<br>Zadoks 49 (first awns) |
| Cereals (Wheat, barley, oats, rye, triticale) | UK | 250 g/L SC | Foliar | 0.15 | 0.0375 – 0.075 | 2<br>0.3 kg ai/ha | ~60<br>Zadoks 49 (first awns) |
| Cereals (Wheat, barley, oats, rye, triticale) | UK | 66.7 g/L + 250 g/L Fenpropimorph | Foliar | 0.1 – 0.2 | | 2 | ~60<br>Zadoks 49 (first awns) |
| Cherry | USA | 250 g/L SC (2.08 lbs/gal) | Foliar | 0.12 | | 5, maximum 0.63 kg ai/ha/year<br>7-day intervals | 7 |
| Currants | Germany | 250 g/L SC | Foliar | 0.075 | | 3 | 14 |
| Gooseberries | Germany | 250 g/L SC | Foliar | 0.075 | | 3, | 14 |
| Grapes | Australia | 250 g/L SC | Foliar | 0.05 (calculated) | 0.0025 at 7-10-day intervals; 0.005 at 10-14-day intervals | 3 | 14 |

| Crop | Country | Formulation | Application | | | | PHI days |
|---|---|---|---|---|---|---|---|
| | | | Method | Rate, kg ai/ha | Spray conc. kg ai/hL | No. or max (kg ai/ha/ season) | |
| Grapes, table and wine | France | 250 g/L SC | Foliar | 0.05 | | 3, 7-10-day intervals between 2 leaves unfolded and end of bunch closure | 21 |
| Grapes, table and wine | Germany | 200 g/L + 60 g/L fenarimol | Foliar | 0.08 | 0.005 | 4, 10-14-day intervals | 21 |
| Grapes, table and wine | Italy | 250 g/L SC | Foliar | | 0.0075 | 5, 8-14-day intervals | 28 |
| Grapes, table and wine | Spain | 250 g/L SC | Foliar | 0.075 | 0.0075 | 5, 10-18-day intervals | 30 (wine) 21 (table) |
| Grapes | USA | 250 g/L SC | Foliar | 0.018 – 0.12 0.036 at 7 day interval 0.072 at 14 day interval 0.12 at 21 day interval | | 5, 7-21-day intervals; maximum 0.60 kg ai/ha/year | 14 |
| Grapes, and wine | France | 200 g/L (+ 60 g/L fenarimol) SC | Foliar | 0.04 | | 3, 7 – 10 day-intervals | 21 |
| Grapes, table and wine | Italy | 200 g/L (+ 60 g/L fenarimol) SC | Foliar | | 0.005 – 0.0075 | 5, 8 – 10 day intervals | 28 |
| Grapes, table and wine | Spain | 200 g/L (+ 60 g/L fenarimol) SC | Foliar | | 0.005 – 0.0075 | 5, 10-19-day intervals | 30 (wine) 21 (table) |
| Hops | Germany | 250 g/L SC | Foliar | 0.0675 – 0.15 | 0.005 – 0.011 | 4, 10-14-day intervals, maximum 0.5 kg ai/ ha/ season | 28 |
| Hops | USA | 250 g/L SC | Foliar | 0.073 – 0.15 | | 4, 7-day intervals; maximum 0.60 kg ai/ha/year | 21 |
| Lettuce, head and leaf | USA | 250 g/L SC | Foliar | 0.073 – 0.11 | 0.026 -0.039 (calculated) | 4, maximum 0.44 kg ai/ha/season. 10 – 14 day intervals | 1 |
| Melons | Italy | 250 g/L SC | Foliar | | 0.004 – 0.006 | 10-12 days intervals | 7 |
| Melons | Italy | 200 g/L (+ 60 g/L fenarimol) SC | Foliar | | 0.005 – 0.006 | 10-12-days interval | 7 |

| Crop | Country | Formulation | Application | | | | PHI days |
|---|---|---|---|---|---|---|---|
| | | | Method | Rate, kg ai/ha | Spray conc. kg ai/hL | No. or max (kg ai/ha/ season) | |
| Melons | Spain | 250 g/L SC | Foliar | 0.075 | 0.0075 | 3, 5 – 7 day interval | 7 |
| Melons | Spain | 200 g/L (+ 60 g/L fenarimol) SC | Foliar | | 0.005 – 0.0075 | 3, 10-14 day interval | 7 |
| Melons | USA | 250 g/L SC | Foliar | 0.073 – 0.11 | 0.039 (calculated) | 4, maximum 0.44 kg ai/ha/season | 3 |
| Peppers (all) | USA | 250 g/L SC | Foliar | 0.15 | 0.02 (calculated) | 4, maximum 0.60 kg ai/ha/season 7 day interval | 3 |
| Strawberry | Germany | 250 g/L SC | Foliar | 0.125 | 0.006 | 2, 7-21-day intervals. Field and glasshouse | 14 |
| Strawberry | USA | 250 g/L SC | Foliar | 0.073 – 0.11 | 0.026 – 0.039 (calculated) | 4, maximum 0.44 kg ai/ha/season 10 – 14 day interval | 1 |
| Sugarbeets | France | 500 g/L SC | Broadcast | 0.15 | 0.05 – 0.1 | 1 | 28 |
| Sugarbeets | Germany | 500 g/L SC | Broadcast | 0.12 | 0.031- 0.062 | 2 | 28 |
| Sugarbeets | UK | 500 g/L | Broadcast | 0.15 | 0.038 – 0.075 | 2 0.2 kg ai/ha | 28 |
| Sugarbeets | UK | 250 g/L | Broadcast | 0.15 | 0.038 – 0.075 | 2 0.2 kg ai/ha | 28 |
| Watermelons | Italy | 250 g/L SC | Foliar | | 0.004 – 0.006 | 10-12 days intervals | 7 |
| Watermelons | Italy | 200 g/L (+ 60 g/L Fenarimol) SC | Foliar | | 0.005 – 0.006 | 10-12-days interval | 7 |
| Watermelons | Spain | 250 g/L SC | Foliar | 0.075 | 0.0075 | 3, 5 – 7 day interval | 7 |
| Watermelons | Spain | 200 g/L (+ 60 g/L Fenarimol) SC | Foliar | | 0.005 – 0.0075 | 3, 10-14 day interval | 7 |
| Wheat and Barley | France | 500 g/L SC | Foliar | 0.15 | 0.05 – 0.1 | 1 | 56 |
| Wheat and Barley | France | 200 g/L + (66.7g/L fenpropimorph) SC | Foliar | 0.1 | 0.03 – 0.07 | 1 | 56 |
| Wheat and Barley | Germany | 500 g/L SC | Foliar | 0.15 | 0.025 – 0.075 | 2 0.25 kg ai/ha | 49 (first awns visible) |
| Wheat and Barley | Germany | 500 g/L SC | Foliar | 0.25 | - | 1 | BBCH 25 - 32 |
| Wheat | Netherlands | 500 g/L SC | Foliar | 0.15 | 0.025-0.075 | 1 | 60 |

| Crop | Country | Formulation | Application | | | | PHI days |
|---|---|---|---|---|---|---|---|
| | | | Method | Rate, kg ai/ha | Spray conc. kg ai/hL | No. or max (kg ai/ha/ season) | |
| Wheat | Netherlands | 500 g/L SC | Foliar | 0.15 | 0.025-0.075 | 1 | 60 |

.

## RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of supervised trials are shown in Tables 50 to 64. Where multiple samples were taken from a single plot or multiple analyses conducted on a single sample, the average value is reported. Where results from separate plots with distinguishing characteristics such as different formulations, varieties or treatment schedules were reported, results are listed for each plot Results have not been corrected for concurrent method recoveries unless indicated. The following table summarizes information on residues resulting from supervised trials.

Table 49: Field trials.

| Group | Commodity | Table No. |
|---|---|---|
| Stone fruit | Cherries | 50 |
| Berries and other small fruits | Grapes | 51 |
| | Strawberries | 52 |
| | Currants | 53 |
| Fruiting vegetables, cucurbits | Melons | 54 - 55 |
| Fruiting vegetables other than cucurbits | Peppers | 56 |
| Leafy vegetables | Lettuce | 57 |
| Root and tuber vegetables | Sugar Beets | 58 |
| Cereal grains | Wheat | 59 |
| | Barley | 60 |
| Straw, fodder and forage of cereal grains and grasses (straws and fodder dry) | Wheat | 61 |
| | Barley | 62 |
| Dried herbs | Hops | 63 |
| Miscellaneous fodder and forage crops | Sugar beet tops | 64 |

*Stone fruit – adapted in part from the Evaluation of the USA*

A total of 13 supervised field trials on cherries were conducted in major cherry growing areas of the USA in 2000 and 2001 (102722; 102721, Chen, 2002). Each treated plot received five foliar-directed applications of a suspension concentrate formulation containing 250 g/L quinoxyfen at the rate of approximately 0.12 kg ai/ha (0.11 lbs/acre) per application. There were no adjuvants in the tank mix. The retreatment interval was 6 – 8 days, typically 7 days. The period of time from harvest to analysis ranged from 35 to 77 days. Cherries were pitted prior to analysis.

Table 50. Quinoxyfen residues in cherries (pitted) from foliar directed application in the USA.

| Cherries country, year (variety) | Application | | | | | PHI days | Residues[1], mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | | |
| GAP, USA | 250 g/L SC | 0.12 | | | 5, max 0.63 kg ai/ha/ year | 7 | | |
| Trial 00-M121 Michigan, USA, 2000 (Montmorency) | 250 g/L SC | 0.12 | 0.013 | 929- 951 | 5, total = 0.62 kg ai/ha/yr | 7 | 0.13 | 102722 |
| Trial 00-M122 Michigan, USA, 2000 (Montmorency) | 250 g/L SC | 0.12 | 0.013 | 932- 946 | 5, total = 0.62 kg ai/ha/yr | 7 | 0.08 | 102722 |
| Trial 00-M123 Michigan, USA, 2000 (Montmorency) | 250 g/L SC | 0.12 | 0.013 | 930- 948 | 5, total = 0.62 kg ai/ha/yr | 7 | 0.11 | 102722 |
| Trial 00-M124 Michigan, USA, 2000 (Montmorency) | 250 g/L SC | 0.12 | 0.013 | 930- 945 | 5, total = 0.62 kg ai/ha/yr | 7 | 0.14 | 102722 |
| Trial 00-M125 Michigan, USA, 2000 (Emperor Francis) | 250 g/L SC | 0.13 | 0.022 | 571- 575 | 5, total = 0.63 kg ai/ha/yr | 7 | 0.12 | 102722 |
| Trial 00-M126 Michigan, USA, 2000 (Hedelfinger) | 250 g/L SC | 0.13 | 0.022 | 571- 579 | 5, total = 0.63 kg ai/ha/y | 7 | 0.13 | 102722 |
| Trial 00-WA39 Washington, USA, 2000 (Bing) | 250 g/L SC | 0.13 | 0.009-0.010 | 1312-1399 | 5, total = 0.63 kg ai/ha/yr | 7 | 0.14 | 102722 |
| Trial 00-WA40 Washington, USA, 2000 (Bing) | 250 g/L SC | 0.12 | 0.011 | 1102-1159 | 5, total = 0.61 kg ai/ha/yr | 7 | 0.11 | 102722 |
| Trial 00-WA41 Washington, USA, 2000 (Montmorency) | 250 g/L SC | 0.12 | 0.005-0.006 | 2144-2178 | 5, total = 0.62 kg ai/ha/yr | 6 | 0.05 | 102722 |
| Trial 00-CO01 Colorado, USA, 2000 (Montmorency) | 250 g/L SC | 0.11- 0.12 | 0.006 | 1765-1914 | 5, total = 0.60 kg ai/ha/yr | 6 | 0.15 | 102722 |
| Trial 00-PA01 Pennsylvania, USA , 2000 (Montmorency) | 250 g/L SC | 0.12 – 0.13 | 0.011 | 1122-1159 | 5, total = 0.63 kg ai/ha/yr | 6 | 0.27 | 102722 |
| Trial 01-CA49 California, USA, 2001 (Brooks) | 250 g/L SC | 0.12 | 0.009-0.010 | 1239-1360 | 5, total = 0.61 kg ai/ha/yr | 7 | 0.03 | 102721 |
| Trial 01-CA50 California, USA, 2001 (Brooks) | 250 g/L SC | 0.13 | 0.008-0.009 | 1469-1624 | 5, total = 0.63 kg ai/ha/yr | 8 | 0.08 | 102721 |

[1] Average of duplicate field samples from the same plot.

*Berries and other small fruits*

A total of 57 supervised trials were conducted on grapes in the following countries: France (9), Germany (6), Italy (11), Spain (6), US (13), Canada (4), and Australia (8). Results are summarized in Table 51.

A typical residue decline curve from the foliar application to grapes is that from Trial R94-049 in Spain. Six applications were made at 9 – 10 day intervals, and grape samples were taken at intervals of 1 – 62 days after the final treatment. The half-life is 19 days for first-order kinetics.

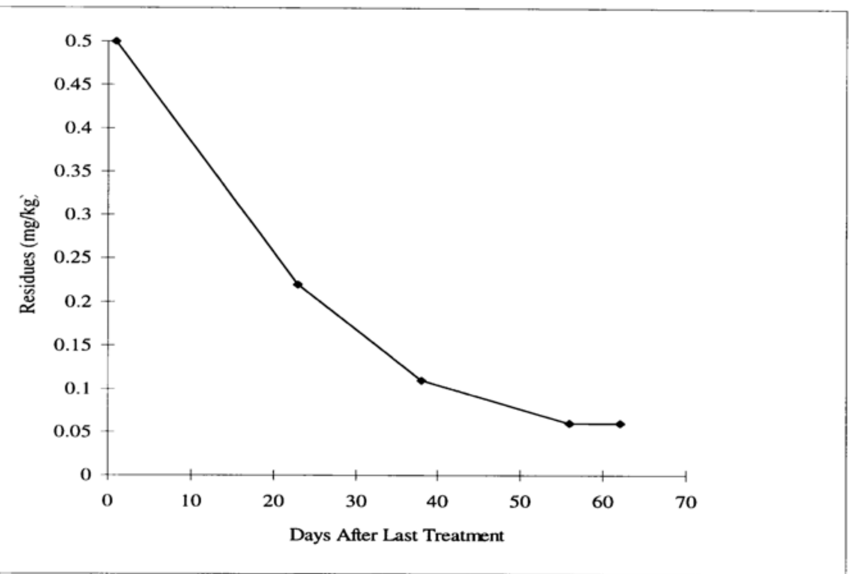


Table 51. Quinoxyfen residues in grapes from foliar applications in France, Germany, Italy, Spain, USA, Canada and Australia.

| Grapes country, year (variety) | Application[1] | | | | | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | | |
| GAP, France (Table and wine) | 250 g/L SC | 0.05 | | | 3 appl/yr at 7-10-day intervals | 21 | | |
| Trial D3T6S361 France, 1993 (Cinsault, Wine) | 500 g/L SC | 0.029 – 0.045 | 0.0074-0.0076 | 390-730 | 6 at 8-11 days interval | 64 | 0.03 | 42674 |
| Trial D3T6S361 France, 1993 (Cinsault, Wine) | 500 g/L SC | 0.031 – 0.058 | 0.0074-0.0076 | 410- 770 | 8 at 8-11 days interval | 43 | 0.04 | |
| Trial D3T6S361 France, 1993 (Cinsault, Wine) | 500 g/L SC | 0.031-0.055 | 0.0075 | 410-730 | 10 at 8-11 days interval | 22 | 0.06 | 42674 |
| Trial R94-014 France, 1994 (Italia, table) | 250 g/L SC | 0.05 | 0.025 | 200 | 6 at 6-13 days interval | 0<br>7<br>15<br>22<br>30 | 0.12<br>0.06<br>0.05<br>0.04<br>0.04 | 43622 |
| Trial R94-015 France, 1994 (Gamay, Wine) | 250 g/L SC | 0.05 | 0.025 | 200 | 6 at 8-13 days interval | 0<br>6<br>13<br>20<br>27 | 0.39<br>0.10<br>0.07<br>0.13<br>0.07 | 43621 |
| Trial R94-016B France, 1994 (Pinot Noir, Wine) | 250 g/L SC | 0.05 | 0.027 | 190 | 6 at 8-12 days interval | 32 | 0.04 | 43620 |

| Grapes country, year (variety) | Application[1] Form | kg ai/ha | kg ai/hL | water, L/ha | no. | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| Trial R94-017 France, 1994 (Pinot Meunierr, Wine) | 250 g/L SC | 0.05 | 0.024 | 210 | 6, at 11-13 days interval | 0<br>10<br>21<br>28<br>34 | 0.05<br>0.04<br>0.02<br>0.02<br>0.02 | 43816 |
| Trial R94-017 France, 1994 (Pinot Noir, Wine) | 250 g/L SC | 0.05 | 0.027 | 190 | 6, at 8-13 days interval | 0<br>11<br>18<br>25<br>32 | 0.12<br>0.06<br>0.05<br>0.04<br>0.05 | |
| Trial R95-037 France, 1995 (Chenin, Wine) | 250 g/L SC | 0.06 | 0.047 | 130 | 6, at 11-14 days interval | 0<br>5<br>9<br>15<br>20 | 0.10<br>0.08<br>0.11<br>0.08<br>0.09 | 45716 |
| GAP, Germany (Table and wine) | 250 g/L SC Or 200 g/L + 60 g/L fenarimol SC | 0.08 | 0.005 | 1600 | Max 4, at 10-14 day interval | 21 | | |
| Trial R95-038A Germany, 1995 (Silvaner, Wine) | 200 g/L SC + 60 g/L fenarimol | 0.068-0.072 | 0.010- 0.012 | 610-810 | 7, at 11-12 days interval | 1<br>5<br>10<br>15<br>21 | 0.35<br>0.24<br>0.21<br>0.21<br>0.24 | 45717 |
| Trial R95-038A Germany, 1995 (Silvaner, Wine) | 200 g/L SC + 60 g/L fenarimol | 0.020-0.021 | 0.003- 0.004 | 610- 810 | 7, at 11-12 days interval | 1<br>5<br>10<br>15<br>21 | 0.05<br>0.06<br>0.06<br>0.06<br>0.04 | |
| Trial R95-038B Germany, 1995 (Silvaner, Wine) | 200 g/L SC + 60 g/L fenarimol | 0.020-0.021 | 0.003- 0.004 | 610- 810 | 7, at 11-12 days interval | 1<br>5<br>10<br>15<br>21 | 0.20<br>0.25<br>0.28<br>0.10<br>0.36 | 45717 |
| Trial R95-038B Germany, 1995 (Silvaner, Wine) | 200 g/L SC + 60 g/L fenarimol | 0.019-0.022 | 0.003- 0.004 | 600- 840 | 7, at 11-12 days interval | 1<br>5<br>10<br>15<br>21 | 0.04<br>0.06<br>0.05<br>0.06<br>0.05 | |
| Trial R95-039A Germany, 1995 (Riesling, Wine) | 200 g/L SC + 60 g/L fenarimol | 0.066-0.077 | 0.009- 0.012 | 600-840 | 7, at 11-13 days interval | 21 | 0.21 | 45718 |
| Trial R95-039B Germany, 1995 (Riesling, Wine) | 200 g/L SC + 60 g/L fenarimol | 0.062-0.068 | 0.009- 0.012 | 560-770 | 7, at 11-12 days interval | 21 | 0.16 | |
| GAP, Italy (Table and wine) | 250 g/L SC OR 200 g/L +60 g/L fenarimol | | 0.008 | | Max 5/year, at 8 – 14 days interval | 28 | | |

| Grapes country, year (variety) | Application[1] Form | kg ai/ha | kg ai/hL | water, L/ha | no. | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| Trial R94-046A Italy, 1994 (Wine-White Marzemino) | 250 g/L SC | 0.094 | 0.008 | 1200 | 6 at 11-12 days interval | 0<br>6<br>10<br>15<br>20<br>30 | 0.50<br>0.36<br>0.20<br>0.20<br>0.13<br>0.17 | 42673 |
| Trial R94-046B Italy, 1994 (Wine-White Marzemino) | 250 g/L SC | 0.125 | 0.010 | 1200 - 1300 | 6 at 10-12 days interval | 0<br>6<br>10<br>15<br>20<br>30 | 0.65<br>0.34<br>0.48<br>0.43<br>0.36<br>0.30 | |
| Trial R94-047A Italy, 1994 (Italia, Table) | 250 g/L SC | 0.96- 0.103 | 0.008 | 1300 - 1400 | 6 at 10-11 days interval | 0<br>4<br>9<br>14<br>19<br>30 | 0.30<br>0.24<br>0.24<br>0.26<br>0.24<br>0.18 | 43416 |
| Trial R94-047B Italy, 1994 (Italia, Table) | 250 g/L SC | 0.136-0.138 | 0.010 | 1400 | 6 at 10-11 days interval | 0<br>4<br>9<br>14<br>19<br>30 | 0.55<br>0.25<br>0.52<br>0.36<br>0.34<br>0.10 | |
| Trial R94-048A Italy, 1994 (Cardinale, Table) | 250 g/L SC | 0.083-0.111 | 0.01 | 830-1100 | 6 at 9-11 days interval | 21<br>32 | 0.10<br>0.06 | 43179 |
| Trial R94-048B Italy, 1994 (Cardinale, Table) | 250 g/L SC | 0.05- 0.083 | 0.008 | 670-1100 | 6 at 9-11 days interval | 21<br>32 | 0.07<br>0.04 | |
| Trial R95-027 Italy, 1995 (Prosecco, Wine | 250 g/L SC | 0.062-0.065 | 0.006 | 1000 | 7 at 3-13 days interval | 20 | 0.30 | 44917 |
| Trial R95-028A Italy, 1995 (Garganega, Wine) | 200 g/L SC+ 60 g/L fenarimol | 0.07-0.072 | 0.007 | 1000 | 7 at 10-12 days interval | 21 | 0.49 | 45173 |
| Trial R95-028B Italy, 1995 (Prosecco, Wine) | 200 g/L SC+ 60 g/L fenarimol | 0.07-0.071 | 0.007 | 1000 | 7 at 10-13 days interval | 20 | 0.28 | 45173 |
| Trial R95-029A Italy, 1995 (Italia, Table) | 200 g/L SC+ 60 g/L fenarimol | 0.062-0.065 | 0.006 | 1000 | 7 at 10-13 days interval | 20 | 0.32 | 45715 |
| Trial R95-029B Italy, 1995 (Italia, Table) | 200 g/L SC+ 60 g/L fenarimol | 0.069-0.073 | 0.007 | 1000 | 7 at 10-13 days interval | 20 | 0.25 | 45715 |
| GAP, Spain (Table and wine) | 250 g/L SC | 0.075 | 0.008 | | Max 5/ season, at 10 – 18 day intervals | 30, wine grapes; 21, table grapes | | |

| Grapes country, year (variety) | Application[1] Form | kg ai/ha | kg ai/hL | water, L/ha | no. | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| Trial R94-049 Spain, 1994 (Malabeo, Wine) | 250 g/L SC | 0.042<br>0.052<br>0.039<br>0.047<br>0.050<br>0.050 | 0.008 | 520- 690 | 6 at 9-10 days interval | 1<br>23<br>38<br>56<br>62 | 0.50<br>0.22<br>0.11<br>0.06<br>0.06 | 43180 |
| Trial R94-050 Spain, 1994 (Malabeo, Wine) | 250 g/L SC | 0.038<br>0.040<br>0.044<br>0.040<br>0.058<br>0.056 | 0.0075 | 510- 780 | 6 at 9-10 days interval | 62 | 0.04 | 43181 |
| Trial R95-032 Spain, 1995 (Italia, Table) | 200 g/L SC+ 60 g/L fenarimol | 0.070 | 0.007 | 950 | 6 at 11-14 days interval | 21 | 0.08 | 45531 |
| Trial R95-033 Spain, 1995 (Blanca Apireta, Table) | 250 g/L SC | 0.060- 063 | 0.01 –0.013 | 480- 610 | 5 at 12-14 days interval | 0<br>5<br>10<br>15<br>21 | 0.15<br>0.10<br>0.06<br>0.10<br>0.04 | 45532 |
| Trial R95-034 Spain, 1995 (Palomino Fino, Wine) | 250 g/L SC | 0.060- 073 | 0.010 | 570- 700 | 6 at 13-15 days interval | 21 | 0.02 | 45513 |
| Trial R95-035 Spain, 1995 (Macabeo, Wine) | 200 g/L SC + 60 g/L fenarimol | 0.070- 0.073 | 0.014 | 500- 520 | 7 at 9-15 days interval | 20 | 0.15 | 45692 |
| GAP, USA | 250 g/L SC | 0.12<br>0.036 at 7 day interval<br>0.072 at 14 day interval<br>0.12 at 21 day interval | | | 5, Max 0.60 kg ai/ha/year at 7 –21 days interval | 14 | | |
| Trial 99-NY06 New York, USA, 1999 (Chardonnay) | 250 g/L SC | 0.094- 0.118 | 0.006 –0.007 | 1600 | 5, at interval of 6-7 days; Total = 0.567 kg ai/season | 14 | 0.22 | 83731 |
| Trial 99-PA02 Pennsylvania, USA, 1999 (Cayuga) | 250 g/L SC | 0.118 – 0.123 | 0.012 | 1000 | 5, at interval of 6-7 days; Total = 0.60 kg ai/season | 15 | 0.13 | |
| Trial 99-CA38 California, USA, 1999 (Perlette) | 250 g/L SC | 0.22<br>0.22<br>0.12<br>0.12<br>0.12 | 0.009 –0.017 | 1300- 1400 | 5, at interval of 6-8 days; Total = 0.8 kg ai/season | 14 | 0.06 | |
| Trial 99-CA39 California, USA, 1999 (Thompson seedless) | 250 g/L SC | 0.118 – 0.121 | 0.009 | 1328- 1400 | 5, at interval of 6-8 days; Total = 0.598 kg ai/season | 14 | 0.09 | |

| Grapes country, year (variety) | Application[1] | | | | | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | | |
| Trial 99-CA68 California, USA, 1999 (Thompson seedless) | 250 g/L SC | 0.120 – 0.121 | 0.009 | 1300 - 1400 | 5, at interval of 6-7 days; Total = 0.612 kg ai/season | 14 | 0.15 | |
| Trial 99-CA69 California, USA, 1999 (Thompson seedless) | 250 g/L SC | 0.115 – 0.123 | 0.009 | 1300 - 1400 | 5, at interval of 6-7 days; Total = 0.595 kg ai/season | 14 | 0.08 | |
| Trial 99-CA70 California, USA, 1999 (Thompson seedless) | 250 g/L SC | 0.119 – 0.121 | 0.009 | 1300 | 5, at interval of 6-7 days; Total = 0.598 kg ai/season | 14 | 0.18 | |
| Trial 99-CA71 California, USA, 1999 (Thompson) | 250 g/L SC | 0.169 – 0.120 | 0.009 | 1300 | 5, at interval of 6-7 days; Total = 0.592 kg ai/season | 14 | 0.24 | |
| Trial 99-CA96 California, 1999 (Sauvignon Blanc) | 250 g/L SC | 0.23 0.12 0.12 0.12 0.12 | 0.010- 0.018 | 1200 | 5, at interval of 6-8 days; Total = 0.71 kg ai/season | 14 | 0.15 | |
| Trial 99-ID16 Idaho, USA, 1999 (Chardonnay) | 250 g/L SC | 0.118 – 0.123 | 0.010 | 1100 - 1200 | 5, at interval of 6-7 days; Total = 0.607 kg ai/season | 13 | 0.08 | |
| Trial 99-WA10 Washington, USA, 1999 (Concord) | 250 g/L SC | 0.120 – 0.122 | 0.009- 0.012 | 1000- 1300 | 5, at interval of 6-7 days; Total = 0.605 kg ai/season | 15 | 0.15 | |
| Trial 99-WA11 Washington, USA, 1999 (Concord) | 250 g/L SC | 0.120 – 0.121 | 0.009- 0.012 | 1000 - 1400 | 5, at interval of 6-7 days; Total = 0.604 kg ai/season | 14 | 0.13 | |
| Trial 99-FL43 Florida, USA, 1999 (Summit Muscadine) | 250 g/L SC | 0.123- 0.128 | 0.013 | 960- 990 | 5, at interval of 7-8 days; Total = 0.625 kg ai/season | 14 | 0.44 | |
| GAP, USA (applied to Canadian trials) | 250 g/L SC | 0.018-0.12 0.036 at 7 day interval 0.072 at 14 day interval 0.12 at 21 day interval | | | 5, Max 0.60 kg ai/ha/year at 7 –21days interval | 14 | | |
| Trial 99-ON06 Ontario, Canada, 1999 (Concord) | 250 g/L SC | 0.117- 0.121 | 0.013 | 880- 920 | 5 at intervals of 6-7 days; Total = 0.594 kg ai/season | 14 | 0.22 | 83731 |
| Trial 99-ON06 Ontario, Canada, 1999 (C0ncord) | 250 g/L SC | 0.058- 0.062 | 0.007 | 880-930 | 5 at intervals of 6-7 days; Total = 0.30 | 14 | 0.09 | |

| Grapes country, year (variety) | Application[1] Form | kg ai/ha | kg ai/hL | water, L/ha | no. | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| Trial 99-ON07 Ontario, Canada, 1999 (SU-23512) | 250 g/L SC | 0.115-0.120 | 0.013 | 860- 910 | 5 at intervals of 6-7 days; Total = 0.594 kg ai/season | 14 | 0.29 | |
| Trial 99-ON07 Ontario, Canada, 1999 (SU-23512) | 250 g/L SC | 0.058-0.061 | 0.007 | 870- 920 | 5 at intervals of 6-7 days; Total = 0.297 kg ai/season | 14 | 0.13 | |
| GAP, Australia | 250 g/L SC | 0.05 (calculated) | 0.0025 at 7-10 day interval;0.005 at 10-14 day interval | 1000 (for dilute) | 3 | 14 | | |
| Trial 98483-01 Australia, 2000 (Rhine Reisling) | 250 g/L SC | 0.075 | 0.0025 | 3000 | 3 | 14 | 0.15 | 1951 |
| | | 0.15 | 0.005 | 3000 | 3 | 14 | 0.45 | |
| | | 0.30 | 0.010 | 3000 | 3 | 14 | 0.99 | |
| Trial 98483-02 Australia, 2000 (Chardonnay) | 250 g/L SC | | 0.0025 | - | 3 | 14 | 0.23 | |
| | | | 0.005 | - | 3 | 14 | 0.82 | |
| | | | 0.010 | - | 3 | 14 | 1.32 | |
| Trial 98483-03 Australia, 2000 (Black Shiraz) | 250 g/L SC | 0.025 | 0.0025 | 1000 | 3 | 14 | < 0.01 | |
| | | 0.05 | 0.005 | 1000 | 3 | 14 | 0.09 | |
| | | 0.10 | 0.010 | 1000 | 3 | 14 | < 0.01 | |
| | | 0.05 | 0.005 | 1000 | 3 | 14 | 0.09 | |
| | | 0.10 | 0.010 | 1000 | 3 | 14 | < 0.01 | |
| Trial 99050-01 Australia, 1999 (Chardonnay) | 250 g/L SC | 0.025 | 0.0025 | 1000 | 7 | 14 | 0.06 | 2148 |
| | | 0.050 | 0.005 | 1000 | 7 | 14 | 0.18 | |
| | | 0.10 | 0.010 | 1000 | 7 | 14 | 0.39 | |
| Trial 99050-02 Australia, 1999 (Verdelho) | 250 g/L SC | 0.025 | 0.0025 | 1000 | 6 | 82 | 0.02 | |
| | | 0.043 | 0.005 | 850 | 6 | 82 | 0.05 | |
| | | 0.083 | 0.010 | 830 | 6 | 82 | 0.09 | |
| Trial 99051-01 Australia, 2000 (Cabernet) | 250 g/L SC | 0.035 | 0.0025 | 1400 | 3 | 0 | 0.05 | 2149 |
| | | | | | | 3 | 0.05 | |
| | | | | | | 7 | 0.04 | |
| | | | | | | 14 | 0.03 | |
| | | | | | | 21 | 0.03 | |
| | | | | | | 28 | 0.05 | |
| | | 0.073 | 0.005 | 1500 | 3 | 0 | 0.22 | |
| | | | | | | 3 | 0.27 | |
| | | | | | | 7 | 0.17 | |
| | | | | | | 14 | 0.15 | |
| | | | | | | 21 | 0.10 | |
| | | | | | | 28 | 0.11 | |
| | | 0.15 | 0.010 | 1500 | 3 | 0 | 0.50 | |
| | | | | | | 3 | 0.43 | |
| | | | | | | 7 | 0.23 | |
| | | | | | | 14 | 0.25 | |
| | | | | | | 21 | 0.18 | |
| | | | | | | 28 | 0.19 | |

| Grapes country, year (variety) | Application[1] | | | | | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | | |
| Trial 99051-03 Australia, 2000 (Chardonnay) | 250 g/L SC | 0.065 | 0.0025 | 2600 | 3 | 0 | 0.19 | 2149 |
| | | | | | | 3 | 0.21 | |
| | | | | | | 7 | < 0.01 | |
| | | | | | | 14 | 0.17 | |
| | | | | | | 21 | 0.08 | |
| | | | | | | 28 | | |
| | | 0.13 | 0.005 | 2600 | 3 | 0 | 0.60 | |
| | | | | | | 3 | 0.51 | |
| | | | | | | 7 | 0.39 | |
| | | | | | | 14 | 0.54 | |
| | | | | | | 21 | 0.30 | |
| | | | | | | 28 | 0.22 | |
| | | 0.26 | 0.010 | 2600 | 3 | 1 | 1.2 | |
| | | | | | | 3 | 1.0 | |
| | | | | | | 7 | 0.70 | |
| | | | | | | 14 | 0.65 | |
| | | | | | | 21 | 0.50 | |
| | | | | | | 28 | 0.53 | |
| Trial 99051-04 Australia, 2000 (Thompson seedless) | 250 g/L SC | 0.17 | 0.0025 | 6700 | 3 | 1 | 0.51 | 2149 |
| | | | | | | 3 | 0.83 | |
| | | | | | | 7 | 0.80 | |
| | | | | | | 14 | 0.41 | |
| | | | | | | 21 | 0.60 | |
| | | | | | | 28 | 0.40 | |
| | | 0.33 | 0.005 | 67 00 | 3 | 1 | 1.5 | |
| | | | | | | 3 | 1.6 | |
| | | | | | | 5 | 1.7 | |
| | | | | | | 14 | 1.1 | |
| | | | | | | 21 | 1.0 | |
| | | | | | | 28 | 1.0 | |
| | | 0.67 | 0.010 | 6700 | 3 | 1 | 3.2 | |
| | | | | | | 3 | 4.3 | |
| | | | | | | 7 | 3.3 | |
| | | | | | | 14 | 3.2 | |
| | | | | | | 21 | 3.1 | |
| | | | | | | 28 | 2.6 | |

Note: For US trials, residue value is the average of duplicate samples.

A total of eleven supervised trials were conducted on strawberries in Germany from 1999 to 2000 (11110, Kunz, 2001). Eight supervised trials were conducted in strawberry growing areas in the USA (208697, Barney, W., 2005).

Table 52. Quinoxyfen residues in strawberries from foliar applications in Germany and the USA.

| Strawberry country, year (variety) | Application[1] | | | | | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | | |
| GAP, Germany | 250 g/L SC | 0.12 | 0.006 | 2000 | 2 | 14 | | |
| Trial OR901 (Field) Germany, 1999 (Polka) | 500 g/L SC | 0.12 | 0.013 | 1000 | 2 | 21 | 0.01 | 11110 |
| Trial B/FO 27/99 (Glasshouse) Germany, 1999 (Polka) | 500 g/L SC | 0.12 | 0.013 | 1000 | 2 | 0 | 0.08 | 11110 |
| | | | | | | 7 | 0.04 | |
| | | | | | | 14 | 0.02 | |
| | | | | | | 21 | 0.01 | |

| Strawberry<br>country, year (variety) | Application[1] | | | | | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | | |
| Trial RU-F-53 00 RPMZ 1/1<br>(Plastic tunnel)<br>Germany, 1999<br>(Elsanta) | 250 g/L SC | 0.12 | 0.013 | 1000 | 2 | 0<br>7<br>14<br>21 | 0.37<br>0.01<br>0.05<br>0.01 | 11110 |
| Trial RU-L-39 99 MZ<br>(Plastic tunnel)<br>Germany, 1999<br>(Honeoye Frigo) | 500 g/L SC | 0.12 | 0.013 | 1000 | 2 | 7<br>14<br>21 | 0.26<br>0.07<br>0.01 | 11110 |
| Trial PSD-O-19/99<br>(Glasshouse)<br>Germany, 1999<br>(Elsanta) | 500 g/L SC | 0.12 | 0.013 | 1000 | 2 | 21 | 0.04 | 11110 |
| Trial 11312 (Plastic tunnel)<br>Germany, 2000<br>(Elsanta) | 250 g/L SC | 0.12 | 0.013 | 1000 | 2 | 14<br>21 | 0.16<br>0.07 | 11110 |
| Trial 11312 (plastic tunnel)<br>Germany, 2000<br>(Elsanta) | 500 g/L SC | 0.12 | 0.013 | 1000 | 2 | 14<br>21 | 0.09<br>0.07 | 11110 |
| Trial PSD-O-26/00<br>(Glasshouse)<br>Germany, 2000<br>(Elsanta) | 250 g/L SC | 0.12 | 0.013 | 1000 | 2 | 14<br>21 | 0.12<br>0.02 | 11110 |
| Trial B/FO 36/00<br>(Glasshouse)<br>Germany, 2000<br>(Avalon grün) | 250 g/L SC | 0.12 | 0.013 | 1000 | 2 | 0<br>7<br>14 | 0.24<br>0.12<br>0.04 | 11110 |
| Trial OR0001 (Field)<br>Germany, 2000<br>(Elsanta) | 250 g/L SC | 0.12 | 0.013 | 1000 | 2 | 21 | < 0.01 | 11110 |
| Trial 00/022 (Field)<br>Germany, 2000<br>(Elsanta) | 250 g/L SC | 0.12 | 0.013 | 1000 | 2 | 14 | 0.01 | 11110 |
| GAP, USA | 250 g/L SC | 0.11 | | 280 | 4, max 0.44 /kg ai/season | 1 | | |
| Trial 02-WI12<br>Wisconsin, USA, 2002<br>(Honoeye) | 250 g/L SC | 0.14-0.15 | | 400 – 440 | 4, max 0.58 kg ai/ ha/season | 1 | 0.16 | 208697 |
| Trial 02-NJ25<br>New Jersey USA, 2002<br>(Chandler) | 250 g/L SC | 0.14 - 0.15 | | 500 - 520 | 4, max 0.58 kg ai/ ha/season | 1 | 0.18 | 208697 |
| Trial 02-NC16 North Carolina, USA, 2002<br>(Camarosa) | 250 g/L SC | 0.14 – 0.15 | | 320 – 330 | 4, max 0.58 kg ai/ ha/season | 1<br>3<br>6 | 0.41<br>0.25<br>0.18 | 208697 |
| Trial 02-FL43,<br>Florida, USA<br>2002<br>(Sweet Charlie) | 250 g/L SC | 0.14 – 0.15 | | 370 - 380 | 4, max 0.58 kg ai/ ha/ season | 1 | 0.56 | 208697 |
| Trial 02-WA29<br>Washington, USA, 2002<br>(Totem) | 250 g/L SC | 0.15 - 0.17 | | 390 - 660 | 4, max 0.65 kg ai/ ha/ season | 1 | 0.05 | 208697 |

| Strawberry country, year (variety) | Application[1] | | | | | PHI days | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | | |
| Trial 02-CA97 California, USA, 2002 (Hecker) | 250 g/L SC | 0.15 | | 460 - 470 | 4, max 0.58 kg ai/ ha/ season | 1<br>3<br>7 | 0.46<br>0.33<br>0.16 | 208697 |
| Trial 02-CA98 California, USA, 2002 (Hecker) | 250 g/L SC | 0.14 - 0.15 | | 460 - 480 | 4, max 0.58 kg ai/ ha/ season | 1 | 0.24 | 208697 |
| Trial 02-CA99 California, USA, 2002 (Hecker) | 250 g/L SC | 0.15 | | 470 – 480 | 4, max 0.60 kg ai/ ha/ season | 1 | 0.53 | 208697 |

Supervised trials were conducted on black currants in Germany (20062, Fuchsbichler, 2002; 20061, Fuchsbichler, 2002). The trials were conducted by a government agency in Germany to support the establishment of MRLs in the EU.

Table 53. Quinoxyfen residues in currants from foliar application in Germany (20061; 20062)[1].

| Currants (black) Trial No., country, year (variety) | Application | | | | | PHI days | Residues[2] mg/kg |
|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | |
| GAP, Germany | 250 g/L SC | 0.075 | 0.0075 | 1000 | 3 | 14 | |
| RIP2003-487 (148) Germany, 2001 (Ben Navis) | 250 g/L SC | 0.075 | 0.0075 | 1000 | 3 | 14 | 0.20 |
| RIP2003-490 (244) Germany, 2002 (Tenah) | 250 g/L SC | 0.075 | 0.0094 | 800 | 3 | 0<br>7<br>10<br>14<br>21 | 0.30<br>0.11<br>0.08<br>0.06<br>0.03 |
| RIP2003-492 (246) Germany, 2002 (Titania) | 250 g/L SC | 0.075 | 0.017 | 429 | 3 | 14 | 0.05 |
| RIP2003-449 (147) Germany, 2002 (Titania) | 250 g/L SC | 0.075 | 0.01 | 750 | 3 | 0<br>7<br>10<br>14<br>21 | 0.25<br>0.09<br>0.04<br>0.04<br>0.02 |
| RIP2003-483 (146) Germany, 2002 (Blackdown) | 250 g/L SC | 0.075 | 0.0075 | 1000 | 3 | 0<br>7<br>10<br>14<br>21 | 0.63<br>0.43<br>0.39<br>0.40<br>0.34 |
| RIP2003-489 (243) Germaany, 2002 (Titania) | 250 g/L SC | 0.075 | 0.0075 | 1000 | 3 | 0<br>7<br>10<br>14<br>21 | 0.60<br>0.47<br>0.44<br>0.30<br>0.11 |
| RIP2003-491 (245) Germany, 2002 (Ben Tirran) | 250 g/L SC | 0.075 | 0.0075 | 1000 | 3 | 14 | 0.28 |

[1]Only the report on the analytical phase of the study was available to the Meeting.

[2]All control samples were <LOQ (0.01 or 0.02 mg/kg).

*Fruiting vegetables, Cucurbits*

Sixteen supervised trials on melons were conducted in Spain, Italy, and Greece during 1995 and 1996 (46957; 46958; 46956; 46954, Khoshab, 1995; 48081; 48080; 47141, Khoshab, 1996). Quinoxyfen was determined in the peel and the pulp. Residues in the whole fruit were calculated using percentage weight composition of melons from a standard text (The Composition of Foods by Paul, A. and Southgate, D), i.e., 59% pulp and 41% peel.

Table 54. Quinoxyfen residues on melons from supervised trials in Italy, Greece and Spain.

| Melons | Application | | | PHI | Residues, mg/kg | | | |
|---|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/hL | no. | days | Whole fruit | Peel | Pulp | Reference |
| GAP, Italy | 250 g/L OR 200 g/L + 60 g/L fenarimol | 0.004- 0.006 | | 7 | | | | |
| Trial R95-025A Italy, 1995 (0328 Numens) | 200 g/L + 60 g/L fenarimol | 0.0075 | 3 | 7 | 0.03 | 0.07 | < 0.01 | 46957 |
| Trial R95-025B Italy, 1995 (0328 Numens) | 200 g/L 60 g/L fenarimol | 0.0070 | 3 | 7 | 0.02 | 0.06 | < 0.01 | |
| Trial R96-041A Italy, 1996 (vector) | 250 g/L | 0.0075 | 3 | 8 | 0.03 | 0.04 | 0.02 | 48081 |
| Trial R96-041B Italy, 1996 (vector) | 200 g/L + 60 g/L fenarimol | 0.0075 | 3 | 8 | 0.02 | 0.03 | 0.02 | |
| Trial R96-043A Italy, 1996 (Supermarket) | 250 g/L | 0.0055 | 3 | 7 | 0.02 | 0.02 | < 0.01 | 48080 |
| Trial R96-043B Italy, 1996 (Supermarket) | 200 g/L + 60 g/L fenarimol | 0.0050 | 3 | 7 | 0.01 | 0.01 | < 0.01 | |
| Trial R96-097A Greece, 1996 (Yuppie Hylond) | 250 g/L | 0.0075 | 3 | 7 | 0.02 | 0.06 | < 0.01 | 47141 |
| Trial R96-097B Greece, 1996 (Yuppie Hylond) | 200 g/L + 60 g/L fenarimol | 0.0070 | 3 | 7 | 0.01 | 0.04 | < 0.01 | |
| GAP, Spain | 200 g/L + 60 g/L fenarimol | 0.005- 0.0075 | 3 | 7 | | | | |
| Trial R95-030A Spain, 1995 (Galia-Revigal) | 250 g/L | 0.0075 | 3 | 0<br>4<br>7 | 0.05<br>0.01<br>0.02 | 0.08<br>0.02<br>0.06 | < 0.01<br>< 0.01<br>< 0.01 | 46958 |
| Trial R95-030A Spain, 1995 (Galia-Revigal) | 200 g/L + 60 g/L fenarimol | 0.0070 | 3 | 7 | 0.02 | 0.04 | ND | |
| Trial R95-030B Spain, 1995 (Doral) | 250 g/L | 0.0074 | 3 | 0<br>4<br>7 | 0.03<br>0.01<br>0.01 | 0.07<br>0.04<br>0.02 | < 0.01<br>ND<br>ND | |

| Melons | Application | | | PHI | Residues, mg/kg | | | |
|---|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/hL | no. | days | Whole fruit | Peel | Pulp | Reference |
| Trial R95-030B Spain, 1995 (Doral) | 200 g/L + 60 g/L fenarimol | 0.0070 | 3 | 0<br>4<br>7 | 0.02<br>0.02<br>0.01 | 0.06<br>0.06<br>0.03 | ND<br>ND<br>ND | |
| Trial R95-031A Spain, 1995 (Cantaloupe) | 250 g/L | 0.0077 | 3 | 0<br>4<br>7 | 0.02<br>0.02<br>0.01 | 0.06<br>0.02<br>0.02 | ND<br>< 0.01<br>ND | 46956 |
| Trial R95-031B Spain, 1995 (Cantaloupe) | 200 g/L + 60 g/L fenarimol | 0.0072 | 3 | 0<br>4<br>7 | 0.02<br>< 0.01<br>< 0.01 | 0.04<br>0.01<br>< 0.01 | ND<br>ND<br>ND | 46956 |
| Trial R96-045A Spain, 1996 (Regal) | 250 g/L | 0.0075 | 3 | 7 | 0.02 | 0.04 | < 0.01 | 46954 |
| Trial R96-045B Spain, 1996 (Regal) | 200 g/L + 60 g/L fenarimol | 0.0070 | 3 | 7 | 0.02 | 0.04 | < 0.01 | |

ND = 0.002 mg/kg (20% of LOQ)

A total of 11 supervised field trials on cantaloupes were conducted in major growing areas of the USA and Canada in 2002 and 2003 (208696, Corley, 2004).

Table 55. Summary of quinoxyfen residue data on melons from treatments according to the GAP in the US (208696).

| Melons | Application | | | | PHI days | Residues[1] mg/kg |
|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | water, L/ha | no. | | |
| GAP, USA | 250 g/L SC | 0.073-0.11 | 280 | 4 | 3 | |
| Trial 01-BC01 BC, Canada, 2001 (Athena) | 250 g/L SC | 0.14 – 0.15 | 540 - 560 | 4, total 0.58 kg ai/ha | 4 | 0.03 |
| Trial 01-ON01 ON, Canada, 2001 (Athena) | 250 g/L SC | 0.11 – 0.17 | 520 - 760 | 4, total 0.57 kg ai/ha | 2 | 0.05 |
| Trial 01-QC03 Quebec, Canada 2001 (Early Dawn) | 250 g/L SC | 014 – 0.15 | 470 - 490 | 4, total 0.58 kg ai/ha | 4 | 0.03 |
| Trial 01-CA60 CA, USA, 2001 (Aclaim) | 250 g/L SC | 0.15 | 370 - 480 | 4, total 0.58 kg ai/ ha | 3 | 0.03 |
| Trial 01-CA82 CA, USA, 2001 (Hale's Best) | 250 g/L SC | 0.15 – 0.16 | 470 - 480 | 4, total 0.62 kg ai/ ha | 3 | 0.04 |
| Trial 01-CA83 CA, USA, 2001 (Hearts of Gold) | 250 g/L SC | 0.15 – 0.16 | 480 - 490 | 4, total 0.62 kg ai/ ha | 2 | 0.02 |
| Trial 01-NM09 NM, USA, 2001 (Hale's Best Jumbo) | 250 g/L SC | 0.15 | 340 - 370 | 4, total 0.58 kg ai/ ha | 3 | 0.02 |
| Trial 01-NJ20 NJ, USA, 2001 (Ambrosia) | 250 g/L SC | 0.15 | 380 - 390 | 4, total 0.60 kg ai/ ha | 0<br>3<br>7<br>14 | 0.04<br>0.03<br>0.03<br>0.02 |
| Trial 01-TX323 TX, USA, 2001 (Explorer) | 250 g/L SC | 0.15 - 0.16 | 320 - 340 | 4, total 0.61 kg ai/ ha | 0<br>3<br>7<br>14 | 0.07<br>0.02<br>0.02<br>< 0.01 |

| Melons | Application | | | | PHI days | Residues[1] mg/kg |
|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | water, L/ha | no. | | |
| Trial 01-TX324 TX, USA, 2001 (Mission) | 250 g/L SC | 0.15 | 290 - 300 | 4, total 0.60kg ai/ ha | 2 | 0.05 |
| Trial 01-GA16 GA, USA, 2001 (Vienna) | 250 g/L SC | 0.15 | 280 - 290 | 5, total 0.75 kg ai/ ha | 2 | < 0.01 |

[1] Average of duplicate samples from the same plot.

*Fruiting vegetables, other then Cucurbits*

*Peppers, sweet*

A total of eleven supervised trials were conducted on peppers (six on bell peppers and five on non-bell peppers) in commercial growing areas in the United States during 2001 (8006, Chen, 2003). Samples of marketable pepper were collected by hand from each plot, placed in plastic bags and shipped to the laboratory, where they were kept frozen at about -20ºC until analysis (255 days maximum).

Table 56. Quinoxyfen residues in sweet peppers from supervised trials in the USA (8006).

| PEPPERS | Application | | | | | PHI | Residues[1] mg/kg |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | days | |
| GAP, USA | 250 g/L SC | 0.15 | 0.020 | 750 | 4, max 0.60 kg ai/ha/yr | 3 | |
| Trial 01-NJ19 NJ, USA, 2001 (Bell- King Arthur) | 250 g/L SC | 0.14 | | 370 - 390 | 4, total 0.58 kg ai/ha/yr | 2 | 0.15 |
| Trial 01-FL27 FL, USA, 2001 (Bell- Camelot) | 250 g/L SC | 0.14 | | 320 – 340 | 4, total 0.58 kg ai/ha/yr | 0<br>3<br>7<br>14 | 0.41<br>0.16<br>0.06<br>0.02 |
| Trial 01-FL28 FL, USA, 2001 (Bell- Camelot) | 250 g/L SC | 0.14 | | 320 - 340 | 4, total 0.58 kg ai/ha/yr | 3 | 0.15 |
| Trial 01-TX20 TX, USA, 2001 (Bell- Jupiter) | 250 g/L SC | 0.14 | | 360 - 380 | 4, total 0.58 kg ai/ha/yr | 2 | 0.17 |
| Trial 01-CA58 CA, USA, 2001 (Bell - Jupiter) | 250 g/L SC | 0.14 | | 460 - 480 | 4, total 0.58 kg ai/ha/yr | 0<br>3<br>7<br>14 | 0.03<br>0.01<br>0.01<br>0.01 |
| Trial 01-CA59 CA, USA, 2001 (Bell- Jupiter) | 250 g/L SC | 0.14 | | 480– 490 | 4, total 0.58 kg ai/ha/yr | 3 | 0.02 |
| Trial 01-OH15 OH, USA, 2001 (Non-bell) | 250 g/L SC | 0.14 | | 470- 550 | 4, total 0.58 kg ai/ha/yr | 2 | 0.09 |
| Trial 01-NM07 NM, USA, 2001 (Non-bell- Big Jim) | 250 g/L SC | 0.14 | | 320 - 370 | 4, total 0.58 kg ai/ha/yr | 4 | 0.12 |

| PEPPERS<br>country, year (variety) | Application | | | | | PHI<br>days | Residues[1] mg/kg |
|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | |
| Trial 01-FL29<br>FL, USA, 2001<br>(Non-bell -Cheyane) | 250 g/L SC | 0.14 | | 320 - 330 | 4,<br>total 0.58 kg ai/ha/yr | 3 | 0.64 |
| Trial 01-TX21<br>TX, USA, 2001<br>(Non-bell- Sonora Anaheim) | 250 g/L SC | 0.14 | | 420 – 590 | 4,<br>total 0.58 kg ai/ha/yr | 2 | 0.23 |
| Trial 01-GA14<br>GA, USA, 2001<br>(Non-bell - Jalapeno) | 250 g/L SC | 0.14 | | 470 - 480 | 4,<br>total 0.58 kg ai/ha/yr | 5 | 0.52 |

[1] Average of duplicate samples in the same plot.

*Leafy vegetables*

*Lettuce*

A total of sixteen supervised trials were conducted on lettuce (eight on leaf lettuce and eight on head lettuce) in commercial growing areas in the United States during 2002 (208698, Barney, 2005). A minimum of 4 pounds of head lettuce (with wrapper leaves) or leaf lettuce (with wrapper leaves) was collected per sample. At all of the trials, lettuce samples were harvested randomly across the plots avoiding the ends of the plots. Two samples were collected from each treated plot and one from each untreated plot. Lettuce samples were placed in labelled sample bags and held in frozen storage until analysis (19 to 187 days).

Table 57. Quinoxyfen residues on lettuce with wrapper leaves from supervised trials in the USA (208698).

| Lettuce<br>(head and leaf)<br>country, year (variety) | Application | | | | | PHI<br>days | Residues[1] mg/kg |
|---|---|---|---|---|---|---|---|
| | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | | |
| GAP, USA | 250 g/L SC | 0.11 | | 280 | 4 ,<br>max of 0.44 kg ai/ha/season | 1 | |
| Trial 02-CO09<br>CO, USA, 2002<br>(Head -Raider) | 250 g/L SC | 0.14 – 0.15 | | 360 - 400 | 4,<br>total 0.58 kg ai/ ha/yr | 1 | 1.4 |
| Trial 02-FL40<br>FL, USA, 2002<br>(Head - Salinas) | 250 g/L SC | 0.15 | | 330 | 4,<br>total 0.58 kg ai/ ha/yr | 1 | 5.3 |
| Trial 02-NC15<br>NC, USA, 2002<br>(Head - Maverick) | 250 g/L SC | 0.14 – 0.15 | | 321 | 4,<br>total 0.58 kg ai/ ha/yr | 1 | 1.2 |
| Trial 02-CA89<br>CA, USA, 2002<br>(Head -Sharp Shooter) | 250 g/L SC | 0.15 – 0.16 | | 550 - 740 | 5,<br>total 0.74 kg ai/ ha/yr | 1 | 0.86 |
| Trial 02-CA91<br>CA, USA, 2002<br>(Head - Titan) | 250 g/L SC | 0.14 - 0.15 | | 590 - 650 | 4,<br>total 0.58 kg ai/ ha/yr | 1 | 1.0 |

| Lettuce (head and leaf) | Application | | | | | PHI | Residues[1] mg/kg |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | days | |
| Trial 02-CA93 CA, USA, 2002 (Head – Sharp Shooter) | 250 g/L SC | 0.14 – 0.15 | | 720 - 750 | 4, total 0.59 kg ai/ ha/yr | 1 | 0.91 |
| Trial 02-CA94 CA, USA, 2003 (Head – Wellton) | 250 g/L SC | 0.14 | | 380 - 400 | 4, total 0.58 kg ai/ ha/yr | 1 | 3.1 |
| Trial 02-CA87 CA, USA, 2002 (Head – Empire) | 250 g/L SC | 0.14 – 0.15 | | 370 - 380 | 4, total 0.58 kg ai/ ha/yr | 1 | 2.1 |
| Trial 02-CO10 CO, USA, 2002 (Leaf – Capistrano) | 250 g/L SC | 0.14 – 0.17 | | 360 - 440 | 4, total 0.62 kg ai/ ha/yr | 1 | 1.8 |
| Trial 02-MD09 MD, USA, 2002 (Leaf – Grand Rapids) | 250 g/L SC | 0.14 – 0.15 | | 400 - 410 | 4, total 0.58 kg ai/ ha/yr | 1 | 2.9 |
| Trial 02-CA90 CA, USA, 2002 (Leaf – Green Gene's #1) | 250 g/L SC | 0.15 | | 450 - 620 | 4, total 0.74 kg ai/ ha/yr | 1<br>4<br>7<br>14 | 2.2<br>1.4<br>0.76<br>0.29 |
| Trial 02-CA92 CA, USA, 2002 (Leaf – Panther) | 250 g/L SC | 0.14 – 0.15 | | 660 - 760 | 4, total 0.58 kg ai/ ha/yr | 1 | 1.3 |
| Trial 02-NM11 NM, USA, 2002 (Leaf – Salad Bowl) | 250 g/L SC | 0.14 | | 380 - 510 | 4, total 0.57 kg ai/ ha/yr | 1 | 3.4 |
| Trial 02-CA95 CA, USA, 2002 (Leaf – Marin) | 250 g/L SC | 0.14 – 0.15 | | 400 - 470 | 4, total 0.58 kg ai/ ha/yr | 1 | 13 |
| Trial 02-CA88 CA, USA, 2002 (Leaf – Waldemans Green) | 250 g/L SC | 0.15 | | 370 - 380 | 4, total 0.58 kg ai/ ha/yr | 1 | 4.3 |
| Trial 02-FL41 FL, USA, 2003 (Leaf – Waldemans Dark Green MTO) | 250 g/L SC | 0.15 | | 330 | 4, total 0.58 kg ai/ ha/yr | 1<br>3<br>7<br>14 | 6.9<br>6.1<br>5.2<br>1.8 |

[1] Average of results from duplicate samples taken for each plot.

*Root and Tuber vegetables*

*Sugar beet roots*

A total of eight supervised trials were conducted on sugar beets in Northern Europe (Germany, Northern France and the UK) 76690, (Jones, 2000; 83187, Kang, 2001,). The first application was made at growth stage BBCH 16–33 and the second at growth stage BBCH 45–49. Samples were immediately frozen and kept in frozen storage at about -18ºC up to 4 months (1999 trials) or 179 days (2000 trials), until analysis.

Table 58. Quinoxyfen residues in sugar beet roots from supervised trials in Germany, UK, and France.

| Sugar Beets | Application | | | | | PHI | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | days | | |
| GAP, Germany | 500 g/L SC | 0.12 | 0.062 | | 2 | 28 | | |
| Trial R99-021C<br>Germany, 1999<br>(Aries) | 500 g/L | 0.15<br>0.15 | 0.075 | 200 | 2 | 28 | < 0.01 | 76690 |
| Trial CEMS-1348C<br>Germany, 2000<br>(Beta vulgaris) | 500 g/L | 0.15<br>0.15 | 0.075 | 200 | 2 | 28 | 0.01 | 83187 |
| Trial CEMS-1348D<br>Germany, 2000<br>(Beta vulgaris) | 500 g/L | 0.16<br>0.15 | 0.075 | 210 | 2 | 28 | 0.01 | 83187 |
| GAP, UK | 500 g/L SC | 0.15 | 0.075 | 200 | 2<br>0.2 kg ai/ha/yr | 28 | | |
| Trial R99-021A<br>UK, 1999<br>(Madison) | 500 g/L | 0.15<br>0.15 | 0.075 | 200 | 2 | 28 | < 0.01 | 76690 |
| Trial R99-021B<br>UK, 1999<br>(Madison) | 500 g/L | 0.15<br>0.15 | 0.075 | 200 | 2 | 28 | < 0.01 | 76690 |
| Trial CEMS-1348A,<br>UK, 2000<br>(BEA VA/ Chorus) | 500 g/L | 0.14<br>0.16 | 0.075 | 180-210 | 2 | 28 | 0.02 | 83187 |
| Trial CEMS-1348B,<br>UK, 2000<br>(BEA VA/ Jackpot) | 500 g/L | 0.15<br>0.14 | 0.075 | 190-210 | 2 | 28 | 0.01 | 83187 |
| GAP, France | 500 g/L | 0.15 | 0.10 | | 1 | 28 | | |
| Trial R99-021D<br>France (northern), 1999<br>(Access) | 500 g/L | 0.15 | 0.075 | 200 | 2 | 28 | < 0.01 | 76690 |

*Cereal grains*

*Wheat*

A total of 38 supervised trials were conducted on wheat during 1993 and 1994 (10 in Germany (31265, 31266, 31633, 31262, Gambie, 1995), eight in the UK (24035, 63697, Gambie and Nicholson, 1994; 31080, Gambie, 1995; 29405, Gambie, Nicholson, and Wood, 1995; 31268, Gambie and Wood, 1995), six in northern France (31620, 29912, 31241, Gambie, 1995), 10 in southern France (29406, 31644, 31234, Gambie, 1995), and four in Greece (31231, Gambie, 1995). The trials received either one application of a suspension concentrate formulation containing 500 g/L quinoxyfen at the rate of 0.25 kg ai/ha or two applications, one at 0.25 kg ai/ha, the second at 0.15 kg ai/ha. The applications were made around the stem elongation growth stages (BBCH 31-33) with a second one at around the booting stage when first awns are visible (BBCH 47–49). Samples of grain and straw were collected at harvest. Whole plants were cut above ground level by hand with subsequent threshing in a combine harvester. Samples were stored frozen at -18ºC until analysis, 9 to 15 months later.

Table 59. Quinoxyfen residues on wheat grain from foliar applications in France, Greece, Germany, and UK

| Wheat grain | Application | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | Water L/ha | no. | days | Grain[1] | |
| GAP, France | 500 g/L SC | 0.15 | 130-300 | 1 | 56 | | |
| Trial R93-28A S. France, 1993 (Durum, Lloyd) | 500 g/L SC | 0.25 | 230 | 1 | 79 | < 0.01 | 29406 |
| Trial R93-28A S. France, 1993 (Durum, Llyod) | 500 g/L SC | 0.15 +0.25 | 230-460 | 2 | 64 | < 0.01 | |
| Trial R93-28B S. France, 1993 (Winter, Soissons) | 500 g/L SC | 0.25 | 180 | 1 | 67 | ND | |
| Trial R93-28B S. France, 1993 (Winter, Soissons | 500 g/L SC | 0.15 + 0.25 | 180 | 2 | 55 | ND | |
| Trial R94-018 S. France, 1994 (Winter, Fortal) | 500 g/L SC | 0.25 | 300 | 1 | 99 | ND | 31644 |
| Trial R94-018 S. France, 1994 (Winter, Fortal) | 500 g/L SC | 0.15 + 0.25 | 300 | 2 | 66 | ND | 31644 |
| Trial R94-019A S. France, 1994 (Durum, Neodor) | 500 g/L SC | 0.25 | 200 | 1 | 87 | ND | 31234 |
| Trial R94-019A S. France, 1994 (Durum, Neodor) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 67 | ND | |
| Trial R94-020A S. France, 1994 (Winter, Soisson) | 500 g/L SC | 0.25 | 316 | 1 | 83 | ND | 31234 |
| Trial R94-020A S. France, 1994 (Winter, Soisson) | 500 g/L SC | 0.15 + 0.25 | 308 | 2 | 27 | ND | |
| Trial R93-29A N. France, 1993 (Winter, Sidereal) | 500 g/L SC | 0.25 | 333 | 1 | 95 | ND | 29912 |
| Trial R93-29A N. France, 1993 (Winter, Sidereal) | 500 g/L SC | 0.15 + 0.25 | 333 | 2 | 75 | < 0.01 | |
| Trial R93-30B N. France, 1993 (Winter, Arche) | 500 g/L SC | 0.25 | 200 | 1 | 115 | ND | 31620 |
| Trial R93-30B N. France, 1993 (Winter, Arche) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 87 | ND | |

| Wheat grain | Application | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | Water L/ha | no. | days | Grain[1] | |
| Trial R94-023A N. France, 1994 (Spring, Furio) | 500 g/L SC | 0.25 | 200 | 1 | 65 | ND | 31241 |
| Trial R94-023A N. France, 1994 (Spring, Furio) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 50 | ND | |
| GAP, France applied to trials in Greece | 500 g/L SC | 0.15 | 130-300 | 1 | 56 | | |
| Trial R93-36A Greece, 1993 (Hard wheat, Mexicali) | 500 g/L SC | 0.25 | 200 | 1 | 82 | ND | 31231 |
| Trial R93-36A Greece, 1993 (Hard wheat, Mexicali) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 60 | 0.02 | |
| Trial R93-36B Greece, 1993 (Soft wheat, Yecora) | 500 g/L SC | 0.25 | 200 | 1 | 58 | 0.02 | |
| Trial R93-36B Greece, 1993 (Soft wheat, Yecora) | | 0.15 + 0.25 | 200 | 2 | 48 | 0.09 | |
| GAP, Germany | 500 g/L SC | 0.15 | 200-400 | 2, 0.25 kg ai/ha/yr | 49 | | |
| | 500 g/L SC | 0.25 | - | 1 | BBCH 25 – 32 | | |
| Trial RF93-31S Germany, 1993 (Winter, Ares) | 500 g/L SC | 0.25 | 400 | 1 | 84 | ND | 31266 |
| Trial RF93-31S Germany, 1993 (Winter, Ares) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 70 | ND | |
| Trial RF93-31C Germany, 1993 (Winter, Astron) | 500 g/L SC | 0.25 | 400 | 1 | 100 | ND | 31266 |
| Trial RF93-31C Germany, 1993 (Winter, Astron) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 78 | < 0.01 | |
| Trial RF93-32C Germany, 1993 (Winter, Astron) | 500 g/L SC | 0.25 | 400 | 1 | 86 | ND | 31265 |
| Trial RF93-32C Germany, 1993 (Winter, Astron) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 73 | ND | |

| Wheat grain | Application | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | Water L/ha | no. | days | Grain[1] | |
| Trial RF94-038A Germany, 1994 (Winter, Kanzler) | 500 g/L SC | 0.25 | 400 | 1 | 85 | ND | 31262 |
| Trial RF94-038A Germany, 1994 (Winter, Kanzler) | 500 g/L SC | 0.18 + 0.25 | 437 | 2 | 50 | ND | |
| Trial R94-041A Germany, 1994 (Winter, Kanzler) | 500 g/L SC | 0.25 | 400 | 1 | 84 | ND | 31633) |
| Trial R94-041A Germany, 1994 (Winter, Kanzler) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 49 | ND | |
| GAP, UK | 250 g/L or 500 g/L SC | 0.15 | 200-400 | 2 | ~60 Zadoks 49 | | |
| Trial R93-34A UK, 1993 (Winter, Mercia) | 500 g/L SC | 0.25 | 200 | 1 | 113 | ND | 24035 |
| Trial R93-34A UK, 1993 (Winter, Mercia) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 91 | ND | |
| Trial R93-35A UK, 1993 (Winter, Brock) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 62 | ND | 24035 |
| Trial R93-35A UK, 1993 (Winter, Clarine) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 69 | 0.05 | |
| Trial R93-33A UK, 1993 (Winter, Apollo) | 500 g/L SC | 0.25 | 200 | 1 | 113 | ND | 29405 |
| Trial R93-33A UK, 1993 (Winter, Apollo) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 70 | < 0.01 | |
| Trial R94-002A UK, 1994 (Winter, Spark) | 500 g/L SC | 0.25 | 200 | 1 | 104 | ND | 31080 |
| Trial R94-002A UK, 1994 (Winter, Spark) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 71 | < 0.01 | 31080 |

[1] ND = 0.002 mg/kg for wheat grain (< 20% of LOQ).

*Barley*

A total of 22 supervised trials were conducted on barley during 1993 and 1994, eight in Germany (31263, 31261, 31648, 31635, Gambie, 1995); seven in the UK (24035, Gambie and Nicholson, 1994; 31267, Gambie and Wood, 1995; 31235, Gambie, 1995), five in northern France (31620, 29912, 31646, Gambie, 1995) and two in southern France in 1998 (69430, Khoshab and Clements, 1999). The applications were made around the stem elongation growth stages (BBCH 31-33) with a second one at around the booting stage when first awns are visible (BBCH 45-49). Samples of grain and

straw were collected at harvest. Whole plants were cut above ground level by hand with subsequent threshing in a combine harvester. Samples were stored frozen at -18ºC until analysis, 8 to 18 months later.

Residues of quinoxyfen were determined by gas chromatography with mass selective detection, following method ERC 94.5.

Table 60. Quinoxyfen residues in barley grain from supervised trials in Germany, UK, and France.

| BARLEY | Application | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | Water L/ha | no. | days | Grain[1] | |
| GAP, France | 500 g/L SC | 0.15 | 130-300 | 1 | 56 | | |
| Trial R98-002A S. France, 1998 (Winter, Majestic) | 500 g/L SC | 0.15 + 0.16 | 253 | 2 | 65 | 0.04 | 69430 |
| Trial R98-002A S. France, 1998 (Winter, Nevada) | 500 g/L SC | 0.15 + 0.16 | 246 | 2 | 55 | < 0.01 | |
| Trial R93-30A N. France, 1993 (Winter, Energy) | 500 g/L SC | 0.25 | 200 | 1 | 75 | 0.01 | 31620 |
| Trial R93-30A N. France, 1993 (Winter, Energy) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 55 | 0.11 | |
| Trial R93-29B N. France, 1993 (Winter, Plaisant) | 500 g/L SC | 0.25 | 300 | 1 | 58 | < 0.01 | 29912 |
| Trial R93-29B N. France, 1993 (Winter, Plaisant) | 500 g/L SC | 0.15 + 0.25 | 300 | 2 | 47 | 0.12[2] | |
| Trial R94-021 N. France, 1994 (Spring, Alexis) | 500 g/L SC | 0.25 | 260 | 1 | 65 | ND | 31646 |
| GAP, Germany | 500 g/L SC | 0.1 - 0.15 | 200-400 | 2 | 49 | | |
| | 500 g/L SC | 0.25 | - | 1 | BBCH 25 – 32 | | |
| Trial RF93-114A Germany, 1993 (Winter, Igri) | 500 g/L SC | 0.25 | 400 | 1 | 66 | 0.02 | 31263 |
| Trial RF93-114A Germany, 1993 (Winter, Igri) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 58 | 0.04 | |
| Trial RF93-115S Germany, 1993 (Winter, Iastrid) | 500 g/L SC | 0.25 | 400 | 1 | 75 | ND | 31261 |
| Trial RF93-115S Germany, 1993 (Winter, Iastrid) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 65 | ND | |
| Trial RF94-039A Germany, 1994 (Winter, Grete) | 500 g/L SC | 0.25 | 400 | 1 | 66 | < 0.01 | 31635 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Trial RF94-039A Germany, 1994 (Winter, Grete) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 54 | 0.05 | |
| Trial RF94-040A Germany, 1994 (Winter, Jana) | 500 g/L SC | 0.25 | 400 | 1 | 72 | < 0.01 | 31648 |
| Trial RF94-040A Germany, 1994 (Winter, Jana) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 55 | 0.01 | |
| GAP, UK | 250 g/L OR 500 g/L | 0.15 | 200-400 | 1-2 | ~60 Zadoks 49 | | |
| Trial R93-34A UK, 1993 (Winter, Pasoral) | 500 g/L SC | 0.25 | 200 | 1 | 96 | ND | 24035 |
| Trial R93-34A UK, 1993 (Winter, Pasoral) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 82 | ND | |
| Trial R93-85A UK, 1993 (Spring, Alexis) | 500 g/L SC | 0.25 | 200 | 1 | 76 | 0.02 | 31267 |
| Trial R93-85A UK, 1993 (Spring, Alexis) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 64 | 0.15 | |
| Trial R94-003A UK, 1994 (Winter, Halcyon) | 500 g/L SC | 0.25 | 200 | 1 | 91 | ND | 31235 |
| Trial R94-003A UK, 1994 (Winter, Halcyon) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 70 | < 0.01 | |

[1] ND = 0.002 mg/kg for barley grain (< 20% of LOQ).

[2] Trials not included in estimation of MRL due to very late application at growth stage BBCH 58.

*Straw, fodder and forage of cereal grains and grasses (straws and fodders dry)*

*Wheat*

Table 61. Quinoxyfen residues on wheat straw from foliar applications in France, Germany, Greece, and UK.

| Wheat Straw | Application[1] | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | Water L/ha | no. | days | Straw[1] | |
| GAP, France (South) | 500 g/L SC | 0.15 | 130-300 | 1 | 56 | | |
| Trial R93-28A S. France, 1993 (Durum, Lloyd) | 500 g/L SC | 0.25 | 230 | 1 | 79 | 0.10 | 29406 |
| Trial R93-28A S. France, 1993 (Durum, Llyod) | 500 g/L SC | 0.15 + 0.25 | 230-460 | 2 | 64 | 0.24 | |
| Trial R93-28B S. France, 1993 (Winter, Soissons) | 500 g/L SC | 0.25 | 180 | 1 | 67 | 0.33 | |
| Trial R93-28B S. France, 1993 (Winter, Soissons | 500 g/L SC | 0.15 + 0.25 | 180 | 2 | 55 | 0.32 | |

| Wheat Straw | Application[1] | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | Water L/ha | no. | days | Straw[1] | |
| Trial R94-018 S. France, 1994 (Winter, Fortal) | 500 g/L SC | 0.25 | 300 | 1 | 99 | < 0.05 | 31644 |
| Trial R94-018 S. France, 1994 (Winter, Fortal) | 500 g/L SC | 0.15 + 0.25 | 300 | 2 | 66 | 0.13 | 31644 |
| Trial R94-019A S. France, 1994 (Durum, Neodor) | 500 g/LSC | 0.25 | 200 | 1 | 87 | 0.07 | 31234 |
| Trial R94-019A S. France, 1994 (Durum, Neodor) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 67 | 0.17 | |
| Trial R94-020A S. France, 1994 (Winter, Soisson) | 500 g/L SC | 0.25 | 320 | 1 | 83 | < 0.05 | 31234 |
| Trial R94-020A S. France, 1994 (Winter, Soisson) | 500 g/L SC | 0.15 + 0.25 | 310 | 2 | 27 | 0.06 | |
| Trial R93-29A N. France, 1993 (Winter, Sidereal) | 500 g/L SC | 0.25 | 330 | 1 | 95 | 0.19 | 29912 |
| Trial R93-29A N. France, 1993 (Winter, Sidereal) | 500 g/L SC | 0.15 + 0.25 | 330 | 2 | 75 | 0.23 | |
| Trial R93-30B N. France, 1993 (Winter, Arche) | 500 g/L SC | 0.25 | 200 | 1 | 115 | < 0.05 | 31620 |
| Trial R93-30B N. France, 1993 (Winter, Arche) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 87 | 0.13 | 31620 |
| Trial R94-023A N. France, 1994 (Spring, Furio) | 500 g/L SC | 0.25 | 200 | 1 | 65 | 0.19 | 31241 |
| Trial R94-023A N. France, 1994 (Spring, Furio) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 50 | 0.58 | |
| GAP, France (South) applied to trials in Greece | 500 g/L SC | 0.15 | 130-300 | 1 | 56 | | |
| Trial R93-36A Greece, 1993 (Hard wheat, Mexicali) | 500 g/L SC | 0.25 | 200 | 1 | 82 | 0.11 | 31231 |
| Trial R93-36A Greece, 1993 (Hard wheat, Mexicali) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 60 | 1.06 | |
| Trial R93-36B Greece, 1993 (Soft wheat, Yecora) | 500 g/L SC | 0.25 | 200 | 1 | 58 | 2.99 | |

| Wheat Straw | Application[1] | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | Water L/ha | no. | days | Straw[1] | |
| Trial R93-36B Greece, 1993 (Soft wheat, Yecora) | | 0.15 + 0.25 | 200 | 2 | 48 | 7.22 | |
| GAP, Germany | 500 g/L SC | 0.1 - 0.15 | 200-400 | 2 | 49 | | |
| | 500 g/L EC | 0.25 | - | 1 | BBCH 25- 32 | | |
| Trial RF93-31S Germany, 1993 (Winter, Ares) | 500 g/L SC | 0.25 | 400 | 1 | 84 | ND | 31266 |
| Trial RF93-31S Germany, 1993 (Winter, Ares) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 70 | < 0.05 | |
| Trial RF93-31C Germany, 1993 (Winter, Astron) | 500 g/L SC | 0.25 | 400 | 1 | 100 | 0.07 | 31266 |
| Trial RF93-31C Germany, 1993 (Winter, Astron) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 78 | 0.11 | |
| Trial RF93-32C Germany, 1993 (Winter, Astron) | 500 g/L SC | 0.25 | 400 | 1 | 86 | 0.13 | 31265 |
| Trial RF93-32C Germany, 1993 (Winter, Astron) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 73 | 0.36 | |
| Trial RF94-038A Germany, 1994 (Winter, Kanzler) | 500 g/L SC | 0.25 | 400 | 1 | 85 | < 0.05 | 31262 |
| Trial RF94-038A Germany, 1994 (Winter, Kanzler) | 500 g/L SC | 0.18 + 0.25 | 440 | 2 | 50 | 0.26 | |
| Trial R94-041A Germany, 1994 (Winter, Kanzler) | 500 g/, SC | 0.25 | 400 | 1 | 84 | < 0.05 | 31633 |
| Trial R94-041A Germany, 1994 (Winter, Kanzler) | 500 g/, SC | 0.15 + 0.25 | 400 | 2 | 49 | 0.12 | |
| GAP, UK | 250 g/, or 500 g/L SC | 0.15 | 200-400 | 1-2 | ~60 Zadoks 49 | | |
| Trial R93-34A UK, 1993 (Winter, Mercia) | 500 g/, SC | 0.25 | 200 | 1 | 113 | 0.19 | 24035 |
| Trial R93-34A UK, 1993 (Winter, Mercia) | 500 g/, SC | 0.15 + 0.25 | 200 | 2 | 91 | 0.27 | |
| Trial R93-35A UK, 1993 (Winter, Brock) | 500 g/, SC | 0.15 + 0.25 | 200 | 2 | 62 | 0.37 | 31268 |

| Wheat Straw | Application[1] | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | Water L/ha | no. | days | Straw[1] | |
| Trial R93-35A UK, 1993 (Winter, Clarine) | 500 g/, SC | 0.15 + 0.25 | 200 | 2 | 69 | 1.61 | |
| Trial R93-33A UK, 1993 (Winter, Apollo) | 500 g/, SC | 0.25 | 200 | 1 | 113 | 0.09 | 29405 |
| Trial R93-33A UK, 1993 (Winter, Apollo) | 500 g/, SC | 0.15 + 0.25 | 200 | 2 | 70 | 0.57 | |
| Trial R94-002A UK, 1994 (Winter, Spark) | 500 g/, SC | 0.25 | 200 | 1 | 104 | 0.21 | 31080 |
| Trial R94-002A UK, 1994 (Winter, Spark) | 500 g/, SC | 0.15 + 0.25 | 200 | 2 | 71 | 0.87 | 31080 |

[1] ND = 0.01 mg/kg for straw (< 20% of LOQ).

*Barley*

Table 62. Quinoxyfen residues in barley straw from foliar applications in Germany, UK, and France.

| Barley straw | Application | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | Kg ai/ha | Water L/ha | no. | days | Straw[1] | |
| GAP, France | 500 g/L SC | 0.15 | 130-300 | 1 | 56 | | |
| Trial R98-002A S. France, 1998 (Winter, Majestic) | 500 g/L SC | 0.15 + 0.16 | 253 | 2 | 65 | 1.34 | 69430 |
| Trial R98-002A S. France, 1998 (Winter, Nevada) | 500 g/L SC | 0.15 + 0.16 | 246 | 2 | 55 | 1.77 | |
| Trial R93-30A N. France, 1993 (Winter, Energy) | 500 g/L SC | 0.25 | 200 | 1 | 75 | 1.23 | 31620 |
| Trial R93-30A N. France, 1993 (Winter, Energy) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 55 | 2.10 | |
| Trial R93-29B N. France, 1993 (Winter, Plaisant) | 500 g/L SC | 0.25 | 300 | 1 | 58 | 1.13 | 29912 |
| Trial R93-29B N. France, 1993 (Winter, Plaisant) | 500 g/L SC | 0.15 + 0.25 | 300 | 2 | 47 | 1.77 | |
| Trial R94-021 N. France, 1994 (Spring, Alexis) | 500 g/L SC | 0.25 | 260 | 1 | 65 | 0.13 | 31646 |
| GAP, Germany | 500 g/L SC | 0.15 | 200-400 | 2, 0.25 kg ai/ha/season | 49 | | |
| | 500 g/L SC | 0.25 | - | 1 | BBCH25 – 32 | | |

| Barley straw | Application | | | | PHI | Residues, mg/kg | Reference |
|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | Kg ai/ha | Water L/ha | no. | days | Straw[1] | |
| Trial RF93-114A Germany, 1993 (Winter, Igri) | 500 g/L SC | 0.25 | 400 | 1 | 66 | 1.56 | 31263 |
| Trial RF93-114A Germany, 1993 (Winter, Igri) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 58 | 1.76 | |
| Trial RF93-115S Germany, 1993 (Winter, Iastrid) | 500 g/L SC | 0.25 | 400 | 1 | 75 | 0.22 | 31261 |
| Trial RF93-115S Germany, 1993 (Winter, Iastrid) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 65 | 0.38 | |
| Trial RF94-039A Germany, 1994 (Winter, Grete) | 500 g/L SC | 0.25 | 400 | 1 | 66 | 0.29 | 31635 |
| Trial RF94-039A Germany, 1994 (Winter, Grete) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 54 | 0.54 | |
| Trial RF94-040A Germany, 1994 (Winter, Jana) | 500 g/L SC | 0.25 | 400 | 1 | 72 | 0.20 | 31648 |
| Trial RF94-040A Germany, 1994 (Winter, Jana) | 500 g/L SC | 0.15 + 0.25 | 400 | 2 | 55 | 0.86 | |
| GAP, UK | 250 g/L OR 500 g/L | 0.15 | 200-400 | 1-2 | ~60 Zadoks 49 | | |
| Trial R93-34A UK, 1993 (Winter, Pasoral) | 500 g/L SC | 0.25 | 200 | 1 | 96 | 0.30 | 24035 |
| Trial R93-34A UK, 1993 (Winter, Pasoral) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 82 | 0.58 | |
| Trial R93-85A UK, 1993 (Spring, Alexis) | 500 g/L SC | 0.25 | 200 | 1 | 76 | 2.94 | 31267 |
| Trial R93-85A UK, 1993 (Spring, Alexis) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 64 | 5.25 | |
| Trial R94-003A UK, 1994 (Winter, Halcyon) | 500 g/L SC | 0.25 | 200 | 1 | 91 | 0.22 | 31235 |
| Trial R94-003A UK, 1994 (Winter, Halcyon) | 500 g/L SC | 0.15 + 0.25 | 200 | 2 | 70 | 1.15 | |

[1] ND = 0.002 mg/kg for barley grain (< 20% of LOQ).

*Dried herbs*

*Hops*

Table 63. Quinoxyfen residues on dried hops from foliar applications in the US and Germany.

| Hops, dry | Application | | | | | PHI | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | days | | |
| GAP, Germany | 250 g/L SC | 0.15 | 0.011 | | 4 or max 0.5 kg ai/ha/season | 28 | | |
| Trial RF98-200A<br>Germany, 1998<br>(Hallertauer tradition) | 250 g/L SC | 0.16 - 0.24 | 0.007 | | 3, total 0.62 kg ai/ha/season | 27[1]<br><br>35 | (0.03)<br>0.04<br>0.04 | 73994 |
| Trial RF98-200B<br>Germany, 1998<br>(Hallertauer tradition) | 250 g/L SC | 0.16-0.24 | 0.007 | | 3, total 0.63 kg ai/ha/season | 27[1]<br><br>35 | (0.02)<br>0.03<br>< 0.02 | 73994 |
| Trial RF98-200C<br>Germany, 1998<br>(Hallertauer tradition) | 250 g/L SC | 0.160 - 0.24 | 0.007 | | 3, total 0.61 kg ai/ha/season | 27[1]<br><br>35 | (0.03)<br>0.04<br>0.07 | 73994 |
| Trial RF98-200D<br>Germany, 1998<br>(Spalter) | 250 g/L SC | 0.20 - 0.251 | 0.007 | | 3, total 0.69 kg ai/ha/season | 28[1]<br><br>35 | (0.19)<br>0.27<br>0.05 | 73994 |
| Trial G99033R<br>Germany, 1999<br>(Spalter) | 250 g/L SC | 0.24-0.250 | 0.007 | | 3, total 0.69 kg ai/ha/season | 28<br>30 | 0.76<br>0.28 | 74050 |
| Trial G99085R<br>Germany, 1999<br>(Perle) | 250 g/L SC | 0.15- 0. 25 | 0.007 | | 3, total 0.60 kg ai/ha/season | 28<br>35 | 0.55<br>0.34 | 74050 |
| Trial G99086R<br>Germany, 1999<br>(Perle) | 250 g/L SC | 0.16-0.25 | 0.007 | | 3, total 0.62 kg ai/ha/season | 28<br>35 | 0.37<br>0.23 | 74050 |
| Trial G99087R<br>Germany, 1999<br>(Perle) | 250 g/L SC | 0.16-0.24 | 0.007 | | 3, total 0.62 kg ai/ha/season | 28<br>35 | 0.41<br>0.28 | 74050 |
| GAP, USA | 250 g/L SC | 0.15 | | | 4 or max 0.6 kg ai/ha/season | 21 | | |
| Trial 99-WA09<br>Washington, USA<br>1999<br>(Nugget hops) | 250 g/L SC | 0.15-0.22 | 0.018 | | 3, total 0.59 kg ai/ha/season | 20 | 0.39[2] | 83727 |
| Trial 99-OR12<br>Oregon, USA<br>1999<br>(Nugget hops) | 250 g/L SC | 0.15-0.23 | 0.020 | | 4, total 0.75 kg ai/ha/season | 21 | 1.22[2] | 83727 |
| Trial 99-ID03<br>Idaho, USA, 1999<br>(Nugget tops) | 250 g/L SC | 0.15-0.22 | 0.021 | | 3, total 0.61 kg ai/ha/season | 21 | 2.17[2] | 83727 |

[1] Residues in parenthesis were levels on fresh hops as actually determined. The residues in dried hops were estimated assuming fresh hops have a moisture content of 80% and dried hops, about 10%, i.e., a concentration of about 70% in residues after drying.

[2] Average of two replicate samples (from the same plot).

*Miscellaneous Fodder and Forage crops*

*Sugar beet Tops*

The eight supervised trials conducted on sugar beets in Northern Europe (Germany, Northern France and the UK) were described above. Samples were immediately frozen and kept in frozen storage at about -18ºC up to 4 months (1999 trials) or 179 days (2000 trials), until analysis.

Table 64. Quinoxyfen residues in sugar beet tops from foliar applications in Germany, the UK, and northern France.

| Sugar beet tops | Application | | | | | PHI | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | days | | |
| GAP, Germany | 500 g/L SC | 0.12 | 0.062 | 200-400 | 2 | 28 | | |
| Trial R99-021C Germany, 1999 (Aries) | 500 g/L SC | 0.15 | 0.075 | 200 | 2 | 28 | 0.27 | 76690 |
| Trial CEMS-1348C Germany, 2000 (Beta vulgaris) | 500 g/L SC | 0.153<br>0.152 | 0.075 | 202-204 | 2 | 28 | 0.10 | 83187 |
| Trial CEMS-1348D Germany, 2000 (Beta vulgaris) | 500 g/L SC | 0.155<br>0.154 | 0.075 | 205-207 | 2 | 28 | 0.10 | 83187 |
| GAP, UK | 500 g/L SC | 0.15 | 0.075 | 200-400 | 2 | 28 | | |
| Trial R99-021A UK, 1999 (Madison) | 500 g/L SC | 0.15 | 0.075 | 200 | 2 | Whole plant<br>0<br>7<br>14<br>21<br><br>Tops<br>28 | <br><br>1.0<br>0.43<br>0.10<br>0.06<br><br><br>0.22 | 76690 |
| Trial R99-021B UK, 1999 (Madison) | 500 g/L SC | 0.15 | 0.075 | 200 | 2 | Whole plant<br>0<br>7<br>14<br>21<br><br>Tops<br>28 | <br><br>0.71<br>0.69<br>0.24<br>0.14<br><br><br>0.37 | 76690 |
| Trial CEMS-1348A, UK 2000 (BEA VA/ Chorus) | 500 g/L SC | 0.136<br>0.158 | 0.075 | 180-210 | 2 | Whole Plant<br>0<br>7<br>14<br>21<br><br>Tops<br>28 | <br><br>1.3<br>0.57<br>0.41<br>0.23<br><br><br>0.36 | 83187 |

| Sugar beet tops | Application | | | | | PHI | Residues mg/kg | Reference |
|---|---|---|---|---|---|---|---|---|
| country, year (variety) | Form | kg ai/ha | kg ai/hL | water, L/ha | no. | days | | |
| Trial CEMS-1348B, UK 2000 (BEA VA/ Jackpot) | 500 g/L SC | 0.154<br>0.144 | 0.075 | 192-205 | 2 | Whole plant<br>0<br>7<br>14<br>21<br><br>Tops<br>28 | <br><br>1.4<br>0.55<br>0.23<br>0.14<br><br><br>0.13 | 83187 |
| GAP, France | 500 g/L SC | 0.15 | 0.10 | | 1 | 28 | | |
| Trial R99-021D France (northern), 1999 (Acces) | 500 g/L SC | 0.15 | 0.075 | 200 | 2 | 28 | 0.07 | 76690 |

## FATE OF RESIDUES IN STORAGE AND IN PROCESSING

### *In storage*

No information was provided on the fate of quinoxyfen residues under commercial storage conditions.

### *In processing*

Two processing studies were conducted in northern France and the United Kingdom in 1994 to determine the residues in processed fractions of flour and bread from winter wheat samples treated with quinoxyfen (31600; 31607, Gambie and Press, 1995).

Grains from foliar application to wheat at GAP rate were first cleaned to remove non-wheat material such as broken kernels and straw. Before milling, samples were conditioned by adding water and again cleaned. The samples were then milled at a feed rate of 5 kg per hour. Each passage and consequent sieving in the milling resulted in flour fractions called respectively the 1st, 2nd and 3rd reduction flour. In all milling experiments, approximately 200 g of sample material were taken for residue analysis from the 1st reduction, the white bread flour and the finished offal. These samples were rapidly deep frozen. The flour fractions were blended by weight and starting with 5 kg of flour, dough's were mixed, dough pieces moulded and placed in greased aluminium-coated tins. Baking was done in a rotary oven at 240ºC for 30 minutes for white bread and 15 minutes for wholemeal bread, with steam injection at the start of baking.

All grain samples (RAC) and processed fractions for residue analysis were frozen at -20ºC until analysis about 280 days later. Residues of quinoxyfen in the RAC were determined by gas chromatography with mass selective detection, following method ERC 94.5, which had a lowest validated level of 0.01 mg/kg for grain. Residues of quinoxyfen in flour, bran and bread were determined using gas chromatography with mass selective detection, following method ERC 95.16, which had a lowest validated level of 0.01 mg/kg.

Table 65. Residues in wheat grain and processed fractions.

| Processed Fraction | Residues mg/kg | Reference |
|---|---|---|
| Wheat grain (RAC)<br>Flour, 1st reduction<br>Flour, 74% extraction | < 0.01<br>ND<br>ND | 31600 |

| Processed Fraction | Residues mg/kg | Reference |
|---|---|---|
| Wholemeal flour | < 0.01 | |
| Bran | 0.01 | |
| White bread | ND | |
| Wholemeal bread | < 0.01 | |
| Wheat grain (RAC) | ND | 31607 |
| Flour, 1st reduction | ND | |
| Flour, 76% extraction | < 0.01 | |
| Bran | 0.01 | |
| White bread | ND | |

ND = < 0.002 mg/kg

The residues of quinoxyfen after processing barley grain following treatment with quinoxyfen into beer was investigated in the UK in 1994 (31624, Gambie and Teasdale, 1995). To ensure that the grain for brewing had sufficient residues, spring barley was treated with two applications of a suspension concentrate formulation containing quinoxyfen at 500 g/L, at double the maximum recommended application rate. After collecting about 1 kg of grain for the determination of residues in the RAC, the remaining grain was bulked and sent for processing into beer.

The grain samples were cleaned by sieving prior to processing following commercial practices. Barley malt was prepared. A 200g sample of malt was frozen for residue analysis. The remainder was milled and then mashed and the wort filtered. The spent grains from the filtration process were homogenized and a 1kg sub-sample frozen for analysis. After adjustment of the pH the wort was boiled and the sugar content adjusted prior to fermenting. After storage of the green beer for one month at 0-4ºC, the beer was filtered, bottled, and pasteurised. Five litres of beer in bottles were stored at 10ºC prior to shipment for residue analysis.

Grain, malt, and spent grain samples were analyzed by method ERC 94.5 using gas chromatography with mass selective detection. The LOQ for the method was 0.01 mg/kg. Procedural recoveries were 88% for grain, 90% for malt, and 88% for spent grains. Residues of quinoxyfen in beer were quantified by gas chromatography with mass selective detection according to method ERC 95.19. The LOQ for the method was 0.01 mg/kg. Procedural recovery for beer was 73%.

Table 66. Residues in barley grain and processed fractions (31624).

| Matrix | Residues mg/kg | Processing factor |
|---|---|---|
| Barley grain (RAC) | 0.02 | - |
| Malt | 0.01 | 0.5 |
| Spent grain | 0.01 | 0.5 |
| Beer | ND (< 0.002) | 0.1 |

Several processing studies were carried out in 1995 in Italy, France, and Germany on red and white wine grapes (46975; 47145; Khoshab, 1996 and 47868 Khoshab and Volle, 1996). In the trials in France, vines received seven sequential applications of a suspension concentrate formulation containing 250 g/L quinoxyfen, at 11–15 day intervals between post-flowering and 20–21 days before harvest. Grape samples were taken at normal harvest (20–21 days after final application). Samples of the grapes for the RAC were frozen immediately for residue analysis. Additional samples were taken and transported to the processing facility on the same day. Processing was carried out within 48 hours of harvest.

Residue trials on red and white wine grapes were also carried out at two locations in Germany during 1995. The wine grape vines received seven sequential applications of a suspension concentrate formulation containing a mixture of 200 g/L quinoxyfen and 60 g/L fenarimol, at a rate of about 0.07 kg ai/ha. Applications were made between post flowering and 22 days before harvest at approximately equal intervals. Grape samples were taken at normal harvest. Samples for the RAC were immediately frozen after harvest. Additional samples taken for wine processing were processed within 8 hours of harvest.

Trials on white wine grapes were conducted in Italy in the same period. The vines were also treated with seven sequential applications of a suspension concentrate formulation containing 250 g/L quinoxyfen at the rate of 0.065 kg ai/ha. Applications were made between post flowering and 21 days before harvest at approximately equal intervals. Grape samples were taken at normal harvest (21 days after the last application). Samples for the RAC were frozen immediately for residue analysis. Additional samples were collected and transported the same day for processing into wine. Processing started within 7 hours after arrival at the processing facility.

For the trials in France, processing was carried out according to the VITI R&D methods VINIF/001 and VINIF/002 for white and red grapes, respectively. The processing method used by the German and Italian trials was according to the BBA Guideline Part IV, 3-4. Both these methods follow commercial practices.

In addition to the grapes (RAC), samples of pomace, must and wine were taken in each trial for residue analysis. Grapes were separated from stalks and prepared in a cutter without dry ice. Grape pomace samples were prepared in a homogeniser with dry ice. No preparations were required for must and wine. All prepared samples were stored deep frozen until analysis. Samples were kept frozen at about -20ºC for a period of 9 to 12 months before analysis. All samples were analyzed following the methods described below.

Residues of quinoxyfen in grape samples were determined using method ERC 94.29 which has a lowest validated level of 0.01 mg/kg. Residues in grape pomace, must and wine samples were determined using method ERC 95.26 which has a lowest validated level of 0.05 mg/kg for pomace and 0.01 mg/kg for must and wine.

Table 67. Residues in grapes and processed fractions.

| Matrix | Residues mg/kg | Processing factor | Reference |
|---|---|---|---|
| Red wine grapes (RAC) | 0.08 | | 47868 |
| Must | < 0.01 | 0.13 | |
| Pomace | 0.25 | 3.1 | |
| Wine (2 months) | ND (< 0.002) | 0.03 | |
| Wine (6 months) | ND < 0.002) | 0.03 | |
| White wine grapes (RAC) | 0.15 | | 47868 |
| Must | < 0.01 | 0.07 | |
| Pomace | 0.78 | 5.2 | |
| Wine (2 months) | ND (< 0.002) | 0.01 | |
| Wine (6 months) | ND (< 0.002) | 0.01 | |
| Red wine grapes (RAC) | 0.46 | | 46975 |
| Must | 0.02 | 0.04 | |
| Pomace | 1.00 | 2.2 | |
| Young wine | ND (< 0.002) | 0.004 | |
| Mature wine | ND (< 0.002) | 0.004 | |
| White wine grapes (RAC) | 0.14 | | 46975 |
| Must | 0.01 | 0.07 | |
| Pasteurized must | < 0.01 | 0.07 | |
| Pomace | 0.72 | 5.1 | |
| Young wine | ND (< 0.002) | 0.01 | |

| Matrix | Residues mg/kg | Processing factor | Reference |
|---|---|---|---|
| Pasteurized young wine | ND (< 0.002) | 0.01 | |
| Mature wine | ND (< 0.002) | 0.01 | |
| Pasteurized mature wine | ND (< 0.002) | 0.01 | |
| White wine grapes | 0.52 | | 47145 |
| Must | 0.03 | 0.06 | |
| Pomace | 1.72 | 3.3 | |
| Wine (2 months) | ND (< 0.002) | 0.004 | |
| Wine (6 months) | ND (< 0.002) | 0.004 | |
| | | AVERAGE (n = 5) | MEDIAN |
| Grapes (RAC) | | - | |
| Must | | 0.07 | |
| Pomace | | 3.8 | |
| Young wine/ 2 months | | 0.01 | 0.01 |
| Mature wine/ 6 months | | 0.01 | 0.01 |

One of the trials conducted in California in 1999 to determine the residues of quinoxyfen in grapes (RAC) included a determination of the residues on juice and raisins (83731, Thompson, 2001). Mature fruits were harvested 14 days after the last application and sent to the processing laboratory on the day of sampling and kept frozen until processing. A representative sample was taken for RAC residues and the rest of the bulk sample was processed into grape juice and raisins, simulating commercial practices.

Grapes were passed through a crusher/destemmer. The stems were discarded, the crush was transferred to a steam-jacketed kettle, and pectinase enzyme was added. The crush was then heated to 120–130ºF for a minimum of 2 hours. The depectinized grape crush slurry was passed through a screw press to extract unclarified juice and wet pomace, which was discarded. The unclarified juice was heated to inactivate the added enzyme and then cooled in a refrigerator for argol settling. After 34 days, the argol-settled juice was filtered using a plate-and frame filter press with depth filter pads and filter aid. The filtered juice was heated to canning temperature, put in jars and sealed. Once cool, the jars were weighed, labelled, bagged, and placed in frozen storage (-10º to -5ºF) until shipment to the analytical laboratory for analysis of residues.

Grape bunches were spread on stainless steel drying trays and placed outdoors with adequate protection from birds, insects, and animals. The grapes were turned about once a week during the drying process, which took approximately 1 month. When dry, the moisture content was measured, and the dried grapes were placed in plastic bags and stored at 70ºF for approximately 13 days to achieve moisture equilibrium. The dried grapes were frozen, gently rubbed on 4-mesh screen for destemming and cap stem removal, and immersed in 77ºF water for approximately 15 minutes for rehydration to raisins. Excess water was drained, and the raisins were placed in plastic bags and returned to storage to achieve moisture equilibrium. After 12 days the moisture content was again measured , and the raisins were weighed, bagged, labelled and placed in frozen storage (-10º to -5ºF) until shipment to the analytical laboratory.

Samples were analyzed using method ERC 95.26, which had a lowest validated level of 0.01 mg/kg quinoxyfen for grapes and processed fractions. Residues of quinoxyfen were quantified by gas chromatography with mass selective detection.

Table 68. Residues in grapes, juice, and raisins (83731).

| Matrix | Residues mg/kg | Processing factor |
|---|---|---|
| Grapes (RAC) | 0.177 | |
| Raisins | 0.117 (0.109, 0.110, 0.115, 0.132)[1] | 0.66 |
| Juice | < 0.01 (< 0.01 (4))[1] | 0.06 |

[1] Replicate sub-samples.

## RESIDUES IN ANIMAL COMMODITIES

### *Farm animal feeding studies*

Two cattle feeding studies were conducted in 1994. One of the studies was conducted using fourteen lactating Friesian cows aged between 4 and 9 years old with weight range of 480 to 644.5 kg and daily milk yield of at least 10 kg/day (31599; Gambie and Long, 1995). The animals were divided into the following treatment groups:

| Dose Group | Number of animals | Treatment | |
|---|---|---|---|
| | | ppm total diet per day | mg/animal/day |
| 1 | 3 | Untreated | 0 |
| 2 | 3 | 0.2 | 4 |
| 3 | 3 | 0.6 | 12 |
| 4 | 5 | 2.0 | 40 |

The animals received a feed concentrate twice daily. On each occasion, the appropriate amount of quinoxyfen was added to the feed concentrate as a corn oil solution, based on a daily food consumption of 20 kg. The untreated group of animals received 20 ml corn oil. The animals were dosed for 28 days. Milk samples were taken throughout the study for residue analysis. In addition whole milk samples from days 14 and 27 were separated into cream and skimmed milk and samples taken for both residue analysis and determination of fat content. Milk samples were stored frozen at about -20ºC until analysis in about 51 days. .

After 28 days of dosing, all cows except two from the highest treatment group were sacrificed. The remaining two cows were maintained on a basal diet from day 29 and were sacrificed 7 and 14 days after the end of the dosing period (days 36 and 43, respectively).

At sacrifice, samples of the following tissues were taken for residue analysis: subcutaneous fat, peritoneal fat (perirenal and omental pooled fat), skeletal muscle (pooled from the pectoralis and abductor muscle of the thigh), liver and kidney. The samples were coarsely chopped before freezing and storage at -20ºC until analysis in 76-255 days.

A supplementary study (31634; Gambie, Teasdale, and Press, 1995) was undertaken with higher feeding levels of quinoxyfen. The study used six lactating Friesian cows aged between 4 and 6 years old with a weight range of 500-620 kg and daily milk yield at least 11 kg/day. Three cows were treated at dose level of 20 ppm total diet/day, equivalent to 400 mg/animal/day. The other three animals received no treatments. The animals were dosed for 28 days and 16 hours after the last dose, they were sacrificed. The same tissue samples as the other study were collected and frozen.

Samples of whole milk, skimmed milk, and cream were analyzed for residues of quinoxyfen using method ERC 94.7, which had a lowest validated level of 0.001 mg/kg. Mean procedural recoveries were 81% for whole milk and 80% for cream. The fat content of whole milk and cream samples was determined by the Rose-Gottlieb gravimetric method (BS 1741: Part 3: 1987).

Method ERC 94.30 was used for the determination of residues of quinoxyfen in liver, where quantification was done by gas chromatography with mass selective detection. The method had an LOQ of 0.01 mg/kg. Procedural recoveries for liver samples were below 70%.

For analysis of residues of quinoxyfen in kidney, muscle and fat, method ERC 94.20, which had a lowest validated level of 0.01 mg/kg, was used. Mean procedural recoveries of up to 94% for kidney, 92% for muscle, and 84% to 92% for fat were obtained from samples fortified at levels of 0.01mg/kg to 1.0 mg/kg.

In all these methods, quinoxyfen residues were quantified by gas chromatography with mass selective detection. All residues equivalent to less than 20% of the lowest validated level were classified as “not detected” (ND).

From the first study (31599), milk sampled on Days 14 and 27/28 was separated into cream and skimmed milk and both the fat content and quinoxyfen residues were determined.

During the withdrawal period from day 29 to 42, residues in whole milk decreased from 0.007 to < 0.001 mg/kg within 4 days after dosing ceased. After 14 days depuration period, no residues were detected in milk. Tissue residues were determined after 7 and 14 day depuration period. After 7 and 14 days, residues in peritoneal fat were 0.05 mg/kg and < 0.01 mg/kg, respectively. Residues in other tissues were either < 0.01 mg/kg or not detected during the depuration period.

Table 69. Mean residues of quinoxyfen in whole milk over 28 days oral administration of quinoxyfen to dairy cows (31599; 31634).

| DAY | Concentration of quinoxyfen, mg/kg<br>Treatment groups (ppm feed/day) | | | | |
|---|---|---|---|---|---|
| | Untreated | 0.2 | 0.6 | 2.0 | 20 |
| -1 | ND | ND | ND | ND | ND |
| 1 | - | - | - | < 0.001 | 0.017 |
| 3 | - | - | - | 0.006 | 0.085 |
| 5 | - | - | - | 0.007 | - |
| 7 | < 0.001 | 0.001 | 0.002 | 0.007 | 0.37 |
| 10 | - | - | - | 0.009 | 0.19 |
| 14 | ND | 0.001 | 0.002 | 0.009 | 0.18 |
| 18 | - | - | - | 0.009 | - |
| 21 | ND | < 0.001 | 0.002 | 0.007 | 0.15 |
| 24 | - | - | - | 0.007 | 0.16 |
| 28* | - | < 0.001 | 0.002 | 0.007 | - |
| MEAN | < 0.0005 | 0.001 | 0.002 | 0.007 | 0.16 |
| 30 | - | - | - | 0.005 | 0.11 |
| 32 | - | - | - | < 0.001 | - |
| 35 | - | - | - | < 0.001 | - |
| 37 | - | - | - | < 0.001 | - |
| 40 | - | - | - | < 0.001 | - |
| 42 | - | - | - | ND | - |

* Final day of dosing; - No analysis; ND = not detected (< 0.0002 mg/kg)

Table 70. Residues in whole milk, skim milk, and cream on days 14 and 27/28 following oral administration of quinoxyfen to dairy cows (31599; 31634).

| Treatment, ppm in feed/day | | Quinoxyfen residues[1] (mg/kg) | | | Quinoxyfen ratio: cream/whole milk | Fat ratio: cream/whole milk |
|---|---|---|---|---|---|---|
| | | Whole milk | Skim milk | Cream | | |
| Day 14 | | | | | | |
| 0.2 | Min | < 0.001 | ND[2] | < 0.001 | - | 12.5 |
| | Max | < 0.001 | ND | 0.007 | >7 | 9.8 |
| | Mean | < 0.001 | ND | 0.003 | >3 | 10.7 |
| 0.6 | Min | 0.002 | ND | 0.016 | 8.0 | 11.6 |
| | Max | 0.002 | ND | 0.022 | 11.0 | 15.2 |

| Treatment, ppm in feed/day | | Quinoxyfen residues[1] (mg/kg) | | | Quinoxyfen ratio: cream/whole milk | Fat ratio: cream/whole milk |
|---|---|---|---|---|---|---|
| | | Whole milk | Skim milk | Cream | | |
| | Mean | 0.002 | ND | 0.018 | 9.2 | 12.9 |
| 2.0 | Min | 0.010 | 0.005 | 0.046 | 4.6 | 3.1 |
| | Max | 0.007 | < 0.001 | 0.077 | 11.0 | 12.9 |
| | Mean | 0.0088 | 0.0022 | 0.068 | 7.9 | 9.3 |
| Day 27 | | | | | | |
| 0.2 | Min | < 0.001 | < 0.001 | 0.006 | >6 | 12.2 |
| | Max | < 0.001 | < 0.001 | 0.007 | >7 | 12.9 |
| | Mean | < 0.001 | < 0.001 | 0.0067 | >7 | 12.0 |
| 0.6 | Min | 0.002 | ND | 0.011 | 5.5 | 12.3 |
| | Max | 0.002 | ND | 0.02 | 10.0 | 14.8 |
| | Mean | 0.002 | ND | 0.015 | 7.3 | 13.4 |
| 2.0 | Min | 0.009 | 0.004 | 0.041 | 4.6 | 9.7 |
| | Max | 0.007 | 0.001 | 0.079 | 11.3 | 13.7 |
| | Mean | 0.007 | 0.002 | 0.059 | 8.6 | 11.4 |

[1]Min and Max refer to the ratio of quinoxyfen in cream/quinoxyfen in whole milk on a per cow basis within each treatment group.

.[2]ND = not detected (< 0.0002)

Table 71. Summary of residues in tissues following 28 days oral administration of quinoxyfen to dairy cows (31599; 31634).

| Treatment, ppm feed/day (Reference) | | Residues, mg/kg | | | | |
|---|---|---|---|---|---|---|
| | | Liver | Kidney | Skeletal muscle | Subcutaneous fat | Peritoneal fat |
| 0.2 (GHE-P-4161) | Min | ND | ND | ND | ND | < 0.01 |
| | Max | ND | < 0.01 | ND | < 0.01 | 0.02 |
| | Mean | ND | < 0.01 | ND | < 0.01 | 0.01 |
| 0.6 (GHE-P-4161) | Min | ND | ND | ND | < 0.01 | < 0.01 |
| | Max | < 0.01 | < 0.01 | ND | < 0.01 | 0.02 |
| | Mean | < 0.01 | < 0.01 | ND | < 0.01 | 0.012 |
| 2.0 (GHE-P-4161) | Min | < 0.01 | < 0.01 | < 0.01 | 0.02 | 0.09 |
| | Max | < 0.01 | < 0.01 | < 0.01 | 0.04 | 0.10 |
| | Mean | < 0.01 | < 0.01 | < 0.01 | 0.03 | 0.09 |
| 20.0 GHE-P-4185) | Min | 0.04 | 0.07 | 0.06 | 0.78 | 1.1 |
| | Max | 0.21 | 0.29 | 0.18 | 2.0 | 3.2 |
| | Mean | 0.12 | 0.19 | 0.11 | 1.4 | 2.2 |

ND = 0.002 mg/kg

A poultry feeding study conducted in 1995 consisted of four groups of 10 Isa Brown laying hens (5-6 months old, weighing *ca* 1-2 kg) fed at the following dose levels: 0.1, 0.3, and 1.0 mg/kg of diet/ day based on the average daily intake of food in the group (31744, Jack. and Dunsire, 1995). The fourth group of hens served as controls and were dosed with empty gelatin capsules. The hens were

fed gelatin capsules containing radiolabelled (mixture of $^{14}C$-quinoline label and $^{14}C$-phenoxy label) $^{14}C$-quinoxyfen. Each daily dose was administered in a single capsule at the same time each day for 28 days.

Within each dose group, the ten hens were subdivided into 3 sub-groups of 3 or 4 hens. All samples were pooled by sub-group prior to analysis. Eggs were collected daily from all hens and pooled for residue analysis. On days 14 and 28, the egg samples were separated into whites and yolks, which were analyzed separately.

At the end of the dosing period (approximately 23 hours after last dose on day 28), the hens were sacrificed and the following edible tissues retained for analysis: skin with fat, breast muscle, thigh muscle, liver, kidney, and abdominal fat pad. An approximately equal weight of tissue from each bird in each sub-group was combined and thoroughly mixed.

With the exception of eggs, samples not analyzed immediately were stored frozen at -20ºC until analysis. Eggs were stored at 4ºC until analysis. After combustion of the samples, radioactivity was measured by LSC.

Table 72. Residues in eggs over 28 days oral administration of $^{14}C$-quinoxyfen to laying hens (31744).

| Dose period, Day | Residues (TRR), µg equivalent/g<br>Treatment (ppm feed/day) | | |
|---|---|---|---|
| | 0.1 ppm | 0.3 ppm | 1.0 ppm |
| 1 | 0.000 | 0.000 | 0.000 |
| 2 | 0.000 | 0.001 | 0.003 |
| 3 | 0.001 | 0.002 | 0.006 |
| 4 | 0.001 | 0.004 | 0.009 |
| 5 | 0.002 | 0.005 | 0.014 |
| 6 | 0.002 | 0.006 | 0.018 |
| 7 | 0.002 | 0.007 | 0.021 |
| 8 | 0.002 | 0.007 | 0.024 |
| 9 | 0.002 | 0.008 | 0.023 |
| 10 | 0.002 | 0.008 | 0.023 |
| 11 | 0.002 | 0.008 | 0.024 |
| 12 | 0.002 | 0.008 | 0.023 |
| 13 | 0.002 | 0.008 | 0.023 |
| 14 (whites) | 0.000 | 0.001 | 0.002 |
| 15 (yolks) | 0.008 | 0.025 | 0.071 |
| 15 | 0.002 | 0.008 | 0.023 |
| 16 | 0.003 | 0.008 | 0.025 |
| 17 | 0.003 | 0.009 | 0.024 |
| 18 | 0.003 | 0.009 | 0.025 |
| 19 | 0.003 | 0.009 | 0.023 |
| 20 | 0.003 | 0.009 | 0.024 |
| 21 | 0.003 | 0.010 | 0.024 |
| 22 | 0.003 | 0.009 | 0.024 |
| 23 | 0.003 | 0.009 | 0.023 |
| 24 | 0.003 | 0.009 | 0.025 |
| 25 | 0.003 | 0.010 | 0.025 |
| 26 | 0.003 | 0.010 | 0.025 |
| 27 | 0.003 | 0.011 | 0.025 |

| Dose period, Day | Residues (TRR), µg equivalent/g<br>Treatment (ppm feed/day) | | |
|---|---|---|---|
| | 0.1 ppm | 0.3 ppm | 1.0 ppm |
| 28 (white) | 0.000 | 0.001 | 0.002 |
| 28 (yolks) | 0.010 | 0.036 | 0.072 |

Table 73. Residues in poultry tissues following 28 days oral administration of $^{14}$C-quinoxyfen to laying hens (31744).

| Treatment, ppm feed/day (Reference) | | Residues (TRR), mg equivalent/kg | | | | | |
|---|---|---|---|---|---|---|---|
| | | Liver | Kidney | Breast muscle | Thigh muscle | Skin with fat | Abdominal fat pad |
| 0.1 (GHE-P-4394) | Min | 0.009 | 0.003 | 0.000 | 0.000 | 0.003 | 0.007 |
| | Max | 0.009 | 0.004 | 0.000 | 0.000 | 0.008 | 0.013 |
| | Mean | 0.009 | 0.003 | 0.000 | 0.000 | 0.005 | 0.010 |
| 0.3 (GHE-P-4394) | Min | 0.035 | 0.016 | 0.000 | 0.001 | 0.012 | 0.028 |
| | Max | 0.040 | 0.018 | 0.000 | 0.001 | 0.017 | 0.037 |
| | Mean | 0.038 | 0.017 | 0.000 | 0.001 | 0.014 | 0.034 |
| 1.0 (GHE-P-4394) | Min | 0.087 | 0.039 | 0.001 | 0.005 | 0.034 | 0.080 |
| | Max | 0.097 | 0.049 | 0.002 | 0.009 | 0.063 | 0.12 |
| | Mean | 0.093 | 0.045 | 0.001 | 0.007 | 0.051 | 0.10 |

## APPRAISAL

***Chemical name:*** 5,7-dichloro-4-quinolyl 4 fluorophenyl ether

### *Animal metabolism*

The Meeting received results of an animal metabolism study in lactating goats. Two goats were orally dosed with phenoxy $^{14}$C-quinoxyfen (purity > 98%), twice daily for five consecutive days, at a rate of 10.7 mg quinoxyfen/kg feed. Similarly, two goats were treated with quinoline $^{14}$C-quinoxyfen, twice daily for five consecutive days, at a rate of 11.7 mg quinoxyfen/kg feed.

Urine, faeces and cage wash accounted for 77–80% of the total administered dose. Milk contained 0.5–0.9%, liver 0.9–1.3%, and kidney 0.0–0.05%. The radioactive residue appeared to plateau in milk on day 4. Total radioactive residues (TRRs) in tissues and milk from use of the phenoxy labelled quinoxyfen were 0.34 mg/kg in kidney, 1.0 mg/kg in liver, 0.032 mg/kg in muscle, 0.20 mg/kg in omental fat, and 0.11 mg/kg in milk (16 hours after final dose); and from the use of the quinoline labelled quinoxyfen, 1.5 mg/kg in liver, 0.22 mg/kg in kidney, 0.032 mg/kg in muscle, 0.32 mg/kg in perirenal fat, and 0.064 mg/kg in milk.

Quinoxyfen was identified in milk (30–40% TRR), kidney (2–4% TRR), liver (10–20% TRR), and fat (50–97% TRR). DCHQ (5,7-dichloro-4-hydroxyquinoline) and/or 4-fluorophenol, resulting from cleavage of the ether linkage, was/were found in small amounts (< 5% TRR) in milk, kidney, and liver. Enzyme deconjugation of liver extracts indicated additional substantial quantities of these two compounds (13–20% TRR) present as conjugates. Less than 5% TRR was attributed to isomeric hydroxy quinoxyfens in liver, milk, and subcutaneous fat. 2-Oxo-quinoxyfen was found in milk at a maximum of 1.4% TRR.

The metabolism in goat and rat are qualitatively similar. Cleavage of the ether linkage to form 4-fluorophenol and DCHQ is seen in both animals. Isomers of fluorophenyl-ring hydroxylated quinoxyfen were found in the rat (bile and faeces), whereas isomers of quinoline-ring hydroxylated quinoxyfen (2-oxo) were found in the goat metabolism study. The latter were at very low levels (< 0.1% of the administered dose for the 2-oxo quinoxyfen) in the rat.

The Meeting concluded that the major metabolite in ruminant commodities from the oral administration of quinoxyfen is the parent quinoxyfen. Degradation from cleavage of the ether linkage generates free DCHQ and 4-fluorophenol. Another minor pathway involves formation of hydroxy derivatives.

### *Plant metabolism*

The Meeting received plant metabolism studies for the foliar application of phenoxy- and quinoline-labelled [$^{14}$C] quinoxyfen, in separate experiments, to winter wheat, sugar beets, grapes, cucumber and tomato.

In each crop tested, parent quinoxyfen was found to be a significant to very major portion of the TRR: 8–27% TRR in wheat straw, 25% TRR in sugar beet root, 19–30% TRR in sugar beet tops, 93–98% TRR in grapes, 64–74% TRR in cucumber fruit, and 63–65% TRR in tomato fruit. DCHQ (7% TRR) and 4-fluorophenol (17% TRR) were found in sugar beet tops, indicative of ether bond cleavage. CFBPQ (2-chloro-10-fluoro(1)benzopyrano (2,3,4-de)quinoline), a product of photolysis, was also found in sugar beet tops (3–5% TRR) and possibly in wheat straw at 2% TRR. The 2-oxo quinoxyfen and p-hydroxyphenoxy quinoxyfen metabolites were tentatively identified at low concentrations (< 5% TRR) in several crops. Much of the unidentified extractable radioactivity in wheat straw was found to be multicomponent and of an acidic anionic nature (about 20% TRR) not related to conjugates of quinoxyfen with natural products.

About ≥ 20% of the TRR in mature wheat straw was characterized as lignin, and 25% was associated with cellulose. About 13–53% TRR in wheat grain (100% TRR = 0.03 mg/kg) was associated with starch. About 10% TRR in tomato was associated with lignin, cellulose, and hemicellulose.

Quinoxyfen was shown to have no tendency to translocate in grape vines. Radiolabeled material applied only to some vine leaves did not move to the fruit or to untreated leaves.

The Meeting concluded that quinoxyfen is a major portion of the residue when applied in a foliar fashion to several crop types (grapes, cucumber and tomato). In wheat quinoxyfen was extensively metabolized with portions of the molecule becoming associated with natural plant constituents. Minor metabolic pathways were cleavage of the ether bond, photolysis, and hydroxylation of the quinoline or phenyl rings.

### *Environmental fate*

The Meeting received information on the aqueous hydrolysis, aerobic soil metabolism, aqueous photolysis, and soil photolysis of quinoxyfen. Confined rotational crop studies with radiolabeled quinoxyfen were also provided.

Quinoxyfen is stable under aqueous hydrolysis at pH 7 and 9, but degrades slowly under acidic hydrolysis conditions. The half-life at pH 4 at 25 $^{o}$C is about 75 days. The hydrolysis product was identified as DCHQ.

Quinoxyfen is relatively stable under conditions of dark aerobic soil metabolism. After 200 days, 53–81% of the quinoxyfen applied to various soil types remained. Some 0–27% had been converted to 2-oxo quinoxyfen, and 0–5% was present as DCHQ. About 15–25% of the original quinoxyfen had become bound to the soil. Less than 2% had been converted to carbon dioxide. Half lives of 90 to 500 days were calculated for the various soil types.

Quinoxyfen degraded in aqueous solution under artificial light (298 nm) to yield CFBPQ and DCHQ (minor). Half lives under typical use conditions were calculated to vary from 7 to 16 hours. Other work under natural sunlight conditions in water and water sediment systems showed the rapid loss of quinoxyfen, with no quinoxyfen remaining after 1 day. CFBPQ formed, but rapidly degraded

In contrast, quinoxyfen degraded slowly on the surface of sandy loam soil when exposed to simulated natural light. The half life was estimated to be equivalent to > 2 years in spring in England. DCHQ was identified in minor amounts, but the major metabolite remained unknown.

The uptake of radiolabeled quinoxyfen from soil into three succeeding crops (turnips, sunflower and cabbage) was reported. The quinoxyfen was applied at a rate equivalent to 400 g ai/ha, typical of the maximum seasonal use rate. Mature crop parts contained very low levels of radioactive residue, 0.4–3.5 μg/kg.

The Meeting concluded that quinoxyfen is relatively stable under aerobic conditions in soil and at neutral and alkaline pH in water, it undergoes rapid photolytic degradation in water systems, and that residues of quinoxyfen in rotational crops are unlikely.

### *Methods of Analysis*

The Meeting received information for analytical methods for the quantitative determination of quinoxyfen in a variety of crops. The methods were used for data collection in the supervised field trials and livestock feeding studies, and several of the methods were validated by independent laboratories for use as enforcement methods. The methods were typically validated at 0.01 mg quinoxyfen/kg matrix for fruits, vegetables, and grains, with some exceptions (sugarbeet tops 0.2 mg/kg; barley and wheat straw and hops, 0.05 mg/kg). The methods were validated at 0.001 mg/kg for milk, and at 0.01 mg/kg for muscle, kidney, fat, and eggs. Bovine liver was problematic, and adequate recoveries were not achieved at levels of 0.01–1.0 mg/kg. Recovery in liver was 40% to 60%.

The various analytical methods for determination of residues of quinoxyfen in plant and animal matrices follow similar partitioning, clean-up and quantification procedures. Generally, quinoxyfen residues are extracted from plants and animal tissues samples with acidic acetonitrile. After addition of sodium bicarbonate solution to an aliquot of the extract, quinoxyfen is partitioned into hexane, which is then evaporated to dryness. The residue is reconstituted in hexane prior to an aminopropyl solid phase extraction using 1% acetone in hexane to elute quinoxyfen residues. The eluate is evaporated to dryness and reconstituted in 0.1% corn oil in tri-methyl pentane (TMP). Quinoxyfen is quantified either by gas chromatography with mass selective detection (GC-MSD) or by HPLC with UV absorbance. Specific methods differ in the clean-up steps, e.g., the use of gel permeation chromatography for livestock matrices.

The Meeting concluded that adequate analytical methods exist for the determination of quinoxyfen in crops and livestock commodities (except liver) both for data collection and MRL enforcement purposes.

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

The Meeting received information on the stability of quinoxyfen in a variety of crop and livestock matrices. In all cases, quinoxyfen was shown to be stable in the macerated matrices under conditions of frozen storage for an interval at least as great as the storage interval of supervised field trial or livestock feeding samples.

Quinoxyfen was stable under conditions of frozen storage for at least 80 days in cherries, 365 days in grapes, 255 days in grape juice and raisins, 530 days in wheat grain and straw, 110 days in dried hops, 280 days in lettuce, 980 days in strawberry, 320 days in bell peppers, 250 days in melons, 240 days in milk, 190 days in kidney and muscle, and 220 days in fat. Quinoxyfen appeared to be unstable in liver, 60% remaining at 240 days, but the correction for the average concurrent recovery yields a percent remaining of 93%.

The Meeting concluded that quinoxyfen is stable in a variety of analytical crop, processed commodity, and livestock commodity samples under frozen storage conditions.

### *Residue definition*

The plant and ruminant metabolism studies show that a major portion of the residue is parent quinoxyfen. There was no indication that substantial portions of quinoxyfen exist as conjugates in the metabolic mixtures. In plant studies, significant degradation with reincorporation of the radiolabel into natural products was indicated.

No metabolism study in poultry was provided. The poultry feeding study utilized radiolabeled quinoxyfen, but no attempts were made to identify the radiolabeled residues in eggs and tissues.

The available analytical methods determine only quinoxyfen.

The residue definition in Australia, the European Union, and the United States is quinoxyfen.

Ruminant feeding studies show that quinoxyfen preferentially accumulates in fat as opposed to muscle (10:1). Likewise the quinoxyfen ratio between cream and whole milk was about 8 to 1. The goat metabolism study indicated that the TRR in the various fats was about 10× those in muscle. Finally, the octanol/water partition coefficient for quinoxyfen is 4.7.

The Meeting concluded that the residue definition for both enforcement and dietary exposure considerations for plant commodities and for farm animal commodities is quinoxyfen. The Meeting also decided that quinoxyfen is fat-soluble.

### *Results of supervised trials on crops*

The Meeting received supervised trials data for the foliar application of quinoxyfen as a suspension concentrate formulation (SC) to a variety of crops, including cherries, grapes, strawberries, currants, melons, peppers, lettuce, sugar beets, wheat, barley, and hops.

#### *Cherries*

Field trials are reported from the USA (GAP: 250 g/L SC, 0.12 kg ai/ha, five applications per season, 7 day PHI). The ranked order of residue values on cherries (pitted) for 13 trials conducted at maximum GAP is: 0.03, 0.05, 0.08 (2), 0.11 (2), 0.12, 0.13 (2), 0.14 (2), 0.15, and 0.27 mg/kg. The Meeting estimated an STMR of 0.12 mg/kg, HR of 0.27 mg/kg and a maximum residue level of 0.4 mg/kg.

#### *Grapes*

Field trials are reported from France (GAP: 250 g ai/L SC, 0.05 kg ai/ha, three applications per year at 7–10 day intervals, 21 day PHI), Germany (GAP: 250 g ai/L EC, 0.005 kg ai/hL, four applications maximum at 10–14 day intervals, 21 day PHI, the application volume depends on the growth stage), Italy (GAP: 250 g ai/L SC, 0.008 kg ai/hL, five applications maximum per year at 8–14 day intervals, 28 day PHI), Spain (GAP: 250 g ai/L SC, 0.075 kg ai/ha, 0.008 kg ai/hL, five applications maximum per year at 10–18 day intervals 30 day PHI for wine grapes, 21 day PHI for table grapes), US (GAP: 250 g ai/L SC, 0.12 kg ai/ha, five applications maximum per season or 0.60 kg ai/ha/year at 7–21 day interval, 14 day PHI), Canada (GAP: no label, use USA), and Australia (GAP: 250 g ai/L SC, 0.005 kg ai/hL, three applications maximum at 7–14 day intervals, 14 day PHI).

The trials in France and Germany consisted of 6, 7, or 10 repeat applications. Applications made more than 30 days before harvest will not contribute significantly to the final residue. With the 6–13 day retreatment intervals and a 21 day PHI, only the last three applications will contribute to the residue. The ranked order of residues from trials conducted at the maximum GAP with the additional repeat applications (n=9) in France and Germany is: 0.02, 0.04, 0.04, 0.05, 0.05, 0.06, 0.09, 0.13, and 0.36 mg/kg.

The ranked order of the residue values on grapes for eight trials conducted at the maximum GAP in Italy is: 0.04, 0.06, 0.07, 0.10, 0.17, 0.18, 0.30, 0.49 mg/kg. The ranked order of the residue values on grapes for trials conducted at the maximum GAP in Spain is: 0.02, 0.04, 0.08, 0.22 mg/kg.

The ranked order for 13 trials in the US conducted at the maximum GAP is: 0.06, 0.08 (2), 0.09, 0.13 (2), 0.15 (3), 0.18, 0.22, 0.24, 0.44 mg/kg. The ranked order for two trials in Canada conducted at the maximum GAP of the US is: 0.22, 0.29 mg/kg.

Fifteen trials conducted in Australia comply with the PHI of 14 days, 0.01, 0.05, 0.06, 0.09 (2), 0.15 (2), 0.17, 0.18, 0.23, 0.41, 0.45, 0.54, 0.82, 1.1 mg/kg

The trial residue values from France, Germany, Italy, Spain, Canada, US, and Australia appear to be from the same population and are combined (n = 51) in rank order: 0.01, 0.02 (2), 0.04 (4), 0.05 (3), 0.06 (4), 0.07, 0.08 (3), 0.09 (4), 0.10, 0.13 (3), 0.15 (5), 0.17 (2), 0.18 (3), 0.22 (3), 0.23, 0.24, 0.29, 0.30, 0.36, 0.41, 0.44, 0.45, 0.49, 0.54, 0.82, and 1.1 mg/kg. The Meeting estimated an STMR of 0.13 mg/kg, HR of 1.1 mg/kg and a maximum residue level of 2 mg/kg.

*Strawberries*

Field trials were reported to the Meeting from Germany (GAP: 250 g ai/L SC, 0.12 kg ai/ha, 0.006 kg ai/hl, two applications per season, 14 day PHI) and the USA (250 g ai/L SC, 0.11 kg ai/ha, four applications per season (0.44 kg ai/ha/season), 1 day PHI).

The residue values in ranked order from the eight trials in Germany at maximum GAP were: 0.01, 0.02, 0.04, 0.05, 0.07, 0.09, 0.12, and 0.16 mg/kg.

The residue values in ranked order from the six trials in the USA at maximum GAP are: 0.16, 0.18, 0.24, 0.41, 0.46, and 0.56 mg/kg. The values of Germany and the USA are not from the same population.

Using the residue values (n=6) from the USA, the Meeting estimated as STMR of 0.32 mg/kg, HR of 0.56 mg/kg and a maximum residue level of 1 mg/kg.

*Currants*

Supervised field trial studies for the foliar application of quinoxyfen to black currants in Germany were reported to the Meeting. The GAP is: 240 g ai/L, 0.075 kg ai/ha, 0.0075 kg ai/hL, three applications per year, 14 day PHI.

The residue values in ranked order (n=7) for trials conducted at maximum GAP were: 0.04, 0.05, 0.06, 0.20, 0.28, 0.30, and 0.40 mg/kg.

The Meeting estimated an STMR of 0.20 mg/kg, HR of 0.40 mg/kg and a maximum residue level of 1 mg/kg.

*Melons*

Field trials on melons were reported from Spain (GAP: 250 g ai/L SC, 0.0075 kg ai/hL, three applications per year, 7 day PHI), Italy (GAP: 250 g ai/L SC, 0.006 kg ai/hL, 7 day PHI), Greece (No label available, use GAP Italy), and the USA (GAP: 250 g ai/L SC, 0.11 kg ai/ha, four applications per year, 3 day PHI).

The residues in ranked order for whole melons from six trials at maximum GAP in Italy and two trials in Greece are: 0.01 (2), 0.02 (4), and 0.03 (2) mg/kg; and the residues in ranked order for the pulp only were: < 0.01 (6) and 0.02 (2) mg/kg.

The residues in ranked order for whole melons from eight trials at maximum GAP in Spain are: 0.01 (4) and 0.02 (4) mg/kg; and the residues in ranked order for the pulp only are: ND - < 0.01 (8) mg/kg.

The residues in ranked order for whole melons (cantaloupes) from six trials at maximum GAP in the USA (taking into account the permitted maximum total seasonal rate) are: < 0.01, 0.02, 0.03 (3), and 0.05 mg/kg. No data were provided on pulp.

The data from the various countries are from the same population and are combined (n=22) in ranked order, for whole melon: 0.01 (7), 0.02 (9), 0.03 (5), and 0.05 mg/kg; and for pulp (n=16), 0.01 (14) and 0.02 (2) mg/kg.

The Meeting estimated an STMR of 0.01 mg/kg and HR of 0.02 mg/kg for quinoxyfen in melon pulp and a maximum residue level of 0.1 mg/kg for quinoxyfen in/on whole melon, except watermelon in both cases.

*Peppers*

A field trial residue study was reported from the USA (GAP: 250 g ai/L SC, 0.15 kg ai/ha, four applications per year, 0.60 kg ai/ha/year, 3 day PHI).

The residues (n=11) in ranked order for quinoxyfen residues on peppers from application at maximum GAP were: 0.01, 0.02, 0.09, 0.12, 0.15 (2), 0.16, 0.17, 0.23, 0.52, and 0.64 mg/kg.

The Meeting estimated an STMR of 0.15 mg/kg, HR of 0.64 mg/kg and a maximum residue level of 1 mg/kg for peppers (bell and non-bell).

*Lettuce*

A field study report was provided for the foliar application of quinoxyfen to lettuce (leaf and head) in the USA. The GAP in the USA is: 250 g ai/L SC, 0.11 kg ai/ha, four applications per season and 0.44 kg ai/ha/season, and a PHI of 1 day.

Seven trials on head lettuce were at maximum GAP, with residues in ranked order of: 0.91, 1.0, 1.2, 1.4, 2.1, 3.1, and 5.3 mg/kg. Six trials on leaf lettuce were at maximum GAP, with residues in ranked order of: 1.3, 2.9, 3.4, 4.3, 6.9, and 13 mg/kg.

The Meeting estimated an STMR of 1.4 mg/kg, HR of 5.3 mg/kg and a maximum residue level of 8 mg/kg for lettuce (head).

The Meeting estimated an STMR of 3.8 mg/kg, HR of 13 mg/kg and a maximum residue level of 20 mg/kg for lettuce (leaf).

*Sugar beet roots*

Field trial data were received from Germany (GAP: 500 g ai/LC SC, 0.12 kg ai/ha, two applications per season, 28 day PHI), UK (GAP: 500 g ai/L SC, 0.15 kg ai/ha, two applications, 28 day PHI), and France (GAP: 500 g ai/L SC, 0.15 kg ai/ha, one application, 28 day PHI).

The residue values for trials conducted in the three European countries at maximum GAP in ranked order are: < 0.01 (4), 0.01 (3), 0.02 mg/kg.

The Meeting estimated an STMR of 0.01 mg/kg and a maximum residue level of 0.03 mg/kg for sugar beet roots.

*Wheat grain*

Wheat grain trials were reported from France, Germany, and the UK. The GAPs are: 500 g ai/L SC, 0.15 kg ai/ha, one application in France with a PHI of 56 days; 500 g ai/L SC, 0.25 kg ai/ha, one

application in Germany at growth stages BBCH 25–32 (tillering), and in the UK 500 g ai/L SC, 0.15 kg ai/ha, two applications until growth stage BBCH 49 (about 60 days PHI).

Some trials in Greece were evaluated against the GAP of France. The trials in North France were evaluated against the GAP of Germany.

The trials in Greece were not within the maximum GAP of France. The trials were conducted at rates in excess of the maximum GAP, and they resulted in finite residue values (> LOQ). Some trials (n=21 ) in France, Germany, and the UK conducted at or in excess of the maximum GAP of the respective countries yielded residue values below the LOQ. The residue values in ranked order were: < 0.01 (21) mg/kg.

The Meeting estimated an STMR of 0.01 mg/kg and a maximum residue level of 0.01 (*) mg/kg for wheat grain.

*Barley grain*

Barley grain trials were reported from France, Germany, and the UK. The GAPs are: 500 g ai/L SC, 0.15 kg ai/ha, one application in France with a PHI of 56 days; 500 g ai/L SC, 0.25 kg ai/ha, one application in Germany at growth stages BBCH 25–32 (tillering), and in the UK 500 g ai/L SC, 0.15 kg ai/ha, two applications until growth stage BBCH 49 (about 60 days PHI).

All trials in Europe were conducted above the maximum GAP. Eight trials provided residue values below the limit of quantitation. The ranked order of residues is < 0.01 (8) mg/kg.

The Meeting estimated an STMR of 0.01 mg/kg and a maximum residue level of 0.01 (*) mg/kg for barley grain.

*Wheat straw*

Wheat trials were reported from France, Germany, and the UK. The GAPs are: 500 g ai/L SC, 0.15 kg ai/ha, two applications per season one application in France with a PHI of 56 days; 0.25 kg ai/ha, one application in Germany at growth stages BBCH 25–32 (tillering), and in the UK 500 g ai/L SC, 0.15 kg ai/ha, two applications until growth stage BBCH 49 (about 60 days PHI). Some trials in Greece were evaluated against the GAP of France (South). The trials in the UK and in North France were evaluated against the GAP of Germany.

The residues in rank order in wheat straw (n=16) were: < 0.05 (5), 0.07, 0.09, 0.11, 0.13 (2), 0.19 (2), 0.21, 0.23, 0.27, 0.36 mg/kg. On a dry weight basis (88% DM) the values are: < 0.06 (5), 0.08, 0.10, 0.12, 0.15 (2), 0.22 (2), 0.24, 0.26, 0.31, 0.41 mg/kg. The Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR of 0.14 mg/kg.

*Barley straw*

Barley trials were reported from France, Germany, and the UK. The GAPs are: 500 g ai/L SC, 0.15 kg ai/ha, two applications per season one application in France with a PHI of 56 days; 0.25 kg ai/ha, a application in Germany at growth stages BBCH 25–32 (tillering), and 500 g ai/L SC, 0.15 kg ai/ha, two applications until growth stage Zadoks 49 (about 60 days PHI) in the UK. The trials in the UK and in North France were evaluated against the GAP of Germany.

The residues in barley straw in rank order (n=6) are: 0.22 (2), 0.30, 0.58, 1.23, 2.94 mg/kg. On a dry weight basis (89% DM) the values are: 0.25 (2), 0.34, 0.65, 1.38, 3.30 mg/kg. The Meeting estimated a maximum residue level of 5 mg/kg and an STMR of 0.50 mg/kg. The highest residue is 3.3 mg/kg.

*Hops (dry)*

Hops trials were reported from Germany (GAP: 250 g/L SC, 0.011 kg ai/hL, four applications or 0.5 kg ai/ha/season, PHI 28 days) and from the USA (GAP: 250 g/L SC, 0.15 kg ai/ha, four applications or 0.6 kg ai/ha/season, PHI 21 days).

Six trials in Germany were conducted at the maximum seasonal GAP, but with three applications rather than four. The sum of the three applications was within 30% of the seasonal maximum GAP. The residue values in ranked order were: 0.03, 0.04, 0.07, 0.37, 0.41, and 0.55 mg/kg.

Four trials in the USA were conducted at the maximum season GAP, with three applications rather than four. The residue values in ranked order were: 0.39, 1.2, and 2.2 mg/kg.

The trials in the USA and in Germany are not from the same population. The three trials in the USA provide insufficient data for the estimation of an STMR and maximum residue level.

Using the six trials from Germany, the Meeting estimated and STMR of 0.22 mg/kg and a maximum residue level of 1 mg/kg for residues of quinoxyfen in hops (dry).

*Spices*

Using a default processing (dehydration) factor of 10, the Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 1.5 mg/kg for dried chili peppers based on the maximum residue level and STMR of pepper

*Sugar beet tops*

Field trial data were received from Germany (GAP: 500 g ai/LC SC, 0.12 kg ai/ha, two applications per season, 28 day PHI), UK (GAP: 500 g ai/L SC, 0.15 kg ai/ha, two applications, 28 day PHI), and France (GAP: 500 g ai/L SC, 0.15 kg ai/ha, one application, 28 day PHI).

Three trials from Germany and four trials from the UK were conducted at the maximum GAP. The residue values from Germany in ranked order were: 0.10 (2) and 0.27 mg/kg. The residue values from the UK in ranked order are: 0.13, 0.22, 0.36, and 0.37 mg/kg. The combined values (n=7) in ranked order were: 0.10 (2), 0.13, 0.22, 0.27, 0.36, and 0.37 mg/kg.

The Meeting estimated an STMR of 0.22 mg/kg and a highest residue level of 0.37 mg/kg.

### *Fate of residues in storage*

The effect of storage upon the fate of quinoxyfen residues was not reported to the Meeting.

### *Fate of residues during processing*

Information on the fate of quinoxyfen in the processing of wheat, barley, and grapes was reported to the Meeting. No information was supplied on the fate of radiolabeled quinoxyfen under general processing conditions.

Winter wheat which had received foliar treatment with quinoxyfen was processed into flour and bread in separate studies in France and the UK. The wheat grain contained no residues (< 0.01 mg/kg) and while there was no apparent concentration of residue in bran, flour, or bread, no processing factors could be calculated.

Barley in the UK was treated at an exaggerated rate with quinoxyfen, and the grain at normal harvest was processed into malt and beer by a simulated commercial process. The processing factor for malt was 0.5 and that for beer was < 0.1. Using the STMR for barley (0.01 mg/kg), the Meeting estimated an STMR-P of 0.001 mg/kg for beer.

Processing studies for the conversion of grapes to wine were reported from France, Germany, and Italy. In all cases, the grapes had quantifiable field incurred residues of quinoxyfen. Three trials were conducted for the preparation of white wine and two for the preparation of red wine. The processing factor varied from 0.004 to 0.03, with a median and average value of 0.01. Applying this processing factor to the STMR of grapes (0.15 mg/kg), the Meeting estimated an STMR-P of 0.015 mg/kg for wine (from grapes).

A processing study for the conversion of grapes to raisins and grape juice was reported from the USA. Grapes with a quantifiable field incurred residue of quinoxyfen were processed in separate commercial-type procedures into raisins and pasteurised grape juice. The processing factors for raisins and juice were 0.66 and 0.06, respectively. Using the STMR value for grapes (0.15 mg/kg), the Meeting estimated STMR-Ps of 0.099 mg/kg and 0.009 mg/kg for raisins and grape juice, respectively.

### *Farm animal dietary burden*

The Meeting estimated the dietary burden of quinoxyfen residues in farm animals on the basis of the diets listed in Appendix IX of the *FAO Manual*. Calculation from MRLs, highest residues and STMR-P values provides the levels in feed suitable for estimating MRLs for animal commodities, while calculation from STMR and STMR-P values for feed is suitable for estimating STMR values for animal commodities. The percentage of dry matter is taken as 100% when MRLs and STMR values are already expressed as dry weight.

*Estimated maximum dietary burden of farm animals*

| Commodity | Group | Residue (mg/kg) | Basis of Residue | Dry matter (%) | Diets | | | Residue contribution (mg/kg) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Beef cattle | Dairy cattle | Poultry | Beef cattle | Dairy cattle | Poultry |
| Barley grain | GC | 0.01 | MRL | 88 | 50 | 30 | 80 | 0.006 | 0.005 | 0.009 |
| Sugar beet leaves (tops) | AV | 0.37 | HR | 23 | 20 | 10 | - | 0.32 | 0.16 | - |
| Barley Straw | AS | 3.3 | HR | 89 | 10 | 60 | | 0.33 | 1.98 | |
| TOTAL | | | | | 80 | 100 | 80 | 0.66 | 2.14 | 0.01 |

The calculated maximum dietary burdens for beef cattle, dairy cows and poultry are 0.66, 2.1, and 0.01 ppm, respectively.

*Estimated STMR dietary burden of farm animals*

| Commodity | Group | Residue (mg/kg) | Basis of Residue | Dry matter (%) | Diets | | | Residue contribution (mg/kg) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Beef cattle | Dairy cattle | Poultry | Beef cattle | Dairy cattle | Poultry |
| Barley grain | GC | 0.01 | STMR | 88 | 50 | 30 | 80 | 0.006 | 0.003 | 0.009 |
| Sugar beet leaves (tops) | AV | 0.22 | STMR | 23 | 20 | 10 | - | 0.19 | 0.10 | - |
| Barley Straw | AS | 0.50 | STMR | 89 | 10 | 60 | - | 0.05 | 0.30 | |
| TOTAL | | | | | 80 | 100 | 80 | 0.25 | 0.40 | 0.01 |

The calculated STMR dietary burdens for beef cattle, dairy cows and poultry are 0.25, 0.40, and 0.01 ppm, respectively.

### *Farm animal feeding studies*

The Meeting received two feeding studies for dairy cattle and a radiolabeled quinoxyfen feeding study for poultry (chickens). Friesian cows were fed for 28 consecutive days with diets containing 0.2, 0.6, 2.0, or 20 ppm quinoxyfen. Residues in whole milk reached a plateau by day 7 of 0.001, 0.002, and 0.007 mg/kg for 0.2, 0.6, and 2.0 ppm dosing levels, respectively. At the 20 ppm dosing level, the quinoxyfen residue spiked to 0.37 mg/kg on day 7 and then declined to an apparent plateau of 0.16 ppm by the final day.

At the 0.2 ppm feeding level, the maximum and average (n=3 cows) residue in whole milk (day 27) was < 0.001 mg/kg. In cream, the maximum residue was 0.007 mg/kg and the average residue was 0.003 mg/kg. At the 0.6 ppm feeding level, the maximum and average (n=3 cows) in whole milk (day 27) was 0.002 mg/kg and 0.002 mg/kg, respectively. In cream, the maximum residue was 0.02 mg/kg, and the average residue was 0.015 mg/kg.

At the 0.2 ppm feeding level, the maximum and average residues in liver, kidney, muscle, and fat were ND and ND, < 0.01 and < 0.01 mg/kg, ND and ND, and 0.02 and 0.01 mg/kg, respectively. At the 0.6 feeding level, the maximum and average residues in liver, kidney, muscle, and fat were < 0.01 and < 0.01 mg/kg, < 0.01 and < 0.01 mg/kg, ND and ND, and 0.02 and 0.012 mg/kg, respectively.

At the 0.6 ppm feeding level, the maximum and average residues in milk were 0.002 mg/kg each. The maximum and average values in cream were 0.022 mg/kg and 0.016 mg/kg, respectively. The maximum and average residue values in liver and kidney were < 0.01 mg/kg each. The maximum and average values in muscle were ND (< 0.002 mg/kg). The maximum and average values in fat were 0.02 and 0.12 mg/kg, respectively.

At the 2 ppm feeding level, the maximum and average residues in milk were 0.010 and 0.0088 mg/kg, respectively. The maximum and average residues in cream were 0.077 and 0.068 mg/kg, respectively. The maximum and average residues in liver, kidney, and muscle were < 0.01 mg/kg. The maximum residue in fat was 0.10 mg/kg, and the average was 0.09 mg/kg.

*Quinoxyfen total residues, mg/kg*

| Dietary burden (ppm)<br>Feeding level [ppm] | | Cream | Milk | Muscle | | Liver | | Kidney | | Fat | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Mean | Mean | Highest | Mean | Highest | Mean | Highest | Mean | Highest | Mean |
| MRL, beef cattle | (0.66)<br>[0.6] | | | (< 0.01)<br>[< 0.002] | | (< 0.01)<br>[< 0.01] | | (< 0.01)<br>[< 0.01] | | (0.02)<br>[0.02] | |
| MRL, dairy cattle | (2.1)<br>[2] | (0.068)<br>[0.068] | (0.0088)<br>[0.0088] | | | | | | | | |
| STMR beet cattle | (0.25)<br>[0.2] | | | | (0.002)<br>[< 0.002] | | (0.002)<br>[< 0.002] | | (< 0.01)<br>[< 0.01] | | (0.01)<br>[0.01] |
| STMR dairy cattle | (0.40)<br>[0.2/0.6] | (0.01)<br>[0.003/0.016] | (0.002)<br>[< 0.001/0.002] | | | | | | | | |

A *poultry feeding* study consisted of four groups of 10 Isa Brown laying hens fed at the following dose levels: 0.1, 0.3, and 1.0 ppm of diet/ day. The hens were fed gelatin capsules containing a *radiolabelled* (mixture of $^{14}$C-quinoline label and $^{14}$C-phenoxy label) $^{14}$C-quinoxyfen. Each daily dose was administered in a single capsule at the same time each day for 28 days. Only TRR was determined in the eggs and tissues. These levels were very low at a 0.1 ppm diet with maximum values of 0.003 mg/kg in eggs, 0.009 mg/kg in liver, 0.004 mg/kg in kidney, 0.0 mg/kg in muscle, and 0.013 mg/kg in fat. At the 1.0 ppm feeding level, TRR values were 0.025 mg/kg in eggs, 0.097 mg/kg in liver, 0.049 mg/kg in kidney, 0.009 mg/kg in muscle, and 0.063 mg/kg in fat. However, the TRR was not characterized or identified.

*Animal commodity maximum residue levels*

The Meeting estimated the following maximum residue levels for mammalian commodities, based on the cow feeding studies and the calculated dietary intake (see above): muscle, 0.01 (*) mg/kg; fat, 0.02 mg/kg; edible offal, 0.01 (*) mg/kg; milk fat, 0.2 mg/kg; milk, 0.01 mg/kg. The Meeting likewise estimated the following STMR values: muscle, 0.002 mg/kg; fat, 0.01 mg/kg; edible offal 0.01 mg/kg; milk fat, 0.02 mg/kg; milk, 0.002 mg/kg. The milk fat estimations assume that cream is 50% fat. Although the metabolic profile in poultry was not determined, the feeding study with radiolababelled quinoxyfen demonstrated very low levels of total residue at a feeding level of 0.1 ppm, the estimated dietary burden of poultry. Therefore, the MRLs for poultry commodities are estimated at the LOQs of the analytical method, 0.01 (*) mg/kg for each of poultry egg and edible offal, and 0.02 mg/kg meat (fat). The STMRs are based on the TRR values and are estimated to be: eggs, 0.003 mg/kg; offal, 0.009 mg/kg; muscle, 0 mg/kg; and fat 0.013 mg/kg.

## RECOMMENDATIONS

The Meeting estimated the maximum residue levels and STMR values shown below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue: Plant and animal commodities.

Definition of the residue (for compliance with MRL and estimation of dietary intake): *quinoxyfen.*

The residue is fat soluble.

| CCN | Commodity Name | MRL, mg/kg | | STMR or STMR-P, mg/kg | HR, mg/kg |
|---|---|---|---|---|---|
| | | New | Previous | | |
| GC0640 | Barley | 0.01 (*) | | 0.01 | |
| | Beer | | | 0.001 | |
| FS0013 | Cherries | 0.4 | | 0.12 | 0.27 |
| FB0278 | Currants, black | 1 | | 0.20 | 0.40 |
| DF0269 | Dried grapes (=Currant, Raisins and Sultanas) | | | 0.099 | |
| MO105 | Edible offal (mammalian) | 0.01 (*) | | 0.01 | |
| PE0112 | Eggs | 0.01 (*) | | 0.003 | |
| FB0269 | Grapes | 2 | | 0.13 | 1.1 |
| JF0269 | Grape juice | | | 0.009 | |
| DH1100 | Hops, dry | 1 | | 0.22 | |
| VL0482 | Lettuce, head | 8 | | 1.4 | 5.3 |
| VL0483 | Lettuce, leaf | 20 | | 3.8 | 13 |
| MM0095 | Meat (from mammals other than marine mammals) | 0.01 * (muscle)<br>0.02 (fat) | | 0.01 fat<br>0.002 muscle | |
| VC0046 | Melons, except watermelon | 0.1 | | 0.01 | 0.02 |
| ML0106 | Milks (excl. processed products) | 0.01 | | 0.002 | |
| FM0183 | Milk fats | 0.2 | | 0.02 | |
| VO0051 | Peppers | 1 | | 0.15 | 0.64 |
| ? | Peppers, chili, dried | 10 | | 1.5 | |
| PO 0111 | Poultry, edible offal of | 0.01 (*) | | 0.009 | |
| PM 0110 | Poultry meat | 0.02 | | 0.013 fat<br>0.0 muscle | |
| FB0275 | Strawberry | 1 | | 0.32 | 0.56 |
| VR0596 | Sugar beet root | 0.03 | | 0.01 | |
| AV1051 | Sugar beet leaves or tops | | | 0.22 | |
| GC0654 | Wheat | 0.01 (*) | | 0.01 | |
| | Wine of grapes | | | 0.015 | |

## DIETARY RISK ASSESSMENT

### *Long-term intake*

The International Estimated Daily Intakes (IEDI) of quinoxyfen, based on the STMRs estimated for 15 commodities for the thirteen GEMS/Food cluster diets were in the range of 0% to 1% of the ADI (Annex 3 of the 2006 JMPR Report). The Meeting concluded that the long-term intake of residues of quinoxyfen resulting from its uses that have been considered by JMPR is unlikely to present a public health concern.

### *Short-term intake*

The 2005 JMPR decided that an acute RfD is unnecessary. The Meeting therefore concluded that the short-term intake of quinoxyfen residues is unlikely to present a public health concern.

## REFERENCES

**Author, Date, Title, Institute, Report Reference, Document No. GLP/Non-GLP.**

Baloch, R., Paterson, G. and Kamaludin, J., 1997, Effects of Buffer and CO-Solvent on the Hydrolysis of DE-795. DowElanco Report No. GHE-P 6328. GLP. Unpublished. 02 May 1997.

Barney, W., 2005, Quinoxyfen: Magnitude of the Residue on Strawberry. IR-4 Project, Center for Minor Crop Pest Management Technology Center of New Jersey, Rutgers, IR-4 Study No.08382. GLP. Unpublished. 26 July 2005.

Barney, W., 2005a, Quinoxyfen: Magnitude of the Residue on Lettuce (Head and Leaf). IR-4 Project, Center for Minor Crop Pest Management Technology Center of New Jersey, Rutgers, IR-4 Study No.08367. GLP. Unpublished. 26 July 2005.

Byrne, S, Balcer, J, Gilbert, J., and Thornburg, S., 2000, A Nature of the Residue Study with $^{14}$C-labelled Quinoxyfen Fungicide Applied to Tomatoes, Dow AgroSciences, Indianapolis; USA, Study No. 990044, Report No. GH-C 514. GLP. Unpublished.

Caley, C. and Kingsley, R., 1995, The Metabolism of XDE-795 in Grapes, Inveresk Research International, Study No. 12216, DowElanco Report No. GHE-P-4801. GLP. Unpublished. 18 December 1995

Chapleo, S. and Caley, C., 1996, The Metabolism of XDE-795 in Cucumbers, Inveresk Research International, Study No. 12887, DowElanco Report No. GHE-P-5412. GLP. Unpublished. 17 July 1995

Chen, H., 2002, Quinoxyfen: Magnitude of the Residue in Cherry, IR-4 Project, Center for Minor Crop Pest Management Technology Center of New Jersey, Rutgers, IR-4 Study No. A7757. GLP. Unpublished. 18 June 2002.

Chen, H., 2002a, Quinoxyfen: Magnitude of the Residue in Cherry, IR-4 Project, Center for Minor Crop Pest Management Technology Center of New Jersey, Rutgers, IR-4 Study No.07757. GLP. Unpublished. 18 June 2002.

Chen, H., 2003, Quinoxyfen: Magnitude of the Residue on Peppers (Bell & Non-Bell). IR-4 Project, Center for Minor Crop Pest Management Technology Center of New Jersey, Rutgers, IR-4 Study No.08006. GLP. Unpublished. 31 July 2003

Class, T., 2003, Independent Laboratory Validation of Dow AgroSciences LLC Method ERC 94.20 – Determination of XDE-795 in Bovine Muscle, Kidney and Fat, PTRL Europe, Ulm, Germany, Study No. P/B 681 G 030020, DowElanco Report No. GHE-P-10436, GLP. Unpublished. 2 May 2003

Class, T., 2003a, Independent Laboratory Validation of Dow AgroSciences LLC Method ERC 98.05 – Determination of Resides of Quinoxyfen in Eggs, PTRL Europe, Ulm, Germany, Study No. P/B 684 G 030023 11344019-5008-4, DowElanco Report No. GHE-P-10434. GLP. Unpublished. 14 May 2003.

Class, T., 2003b, Independent Laboratory Validation of Dow AgroSciences LLC Method ERC 94.30 – Determination of XDE-795 Residues in Bovine Liver, PTRL Europe, Ulm, Germany, Study No. P/B 682 G 030021 11344019-5008-2, DowElanco Report No. GHE-P 10437. GLP. Unpublished. 27 July 2003

Class, T., 2003c, Independent Laboratory Validation of Dow AgroSciences LLC Method ERC 94.7 – Determination of XDE-795 Residues in Skimmed Milk, Whole Milk and Cream, PTRL Europe, Ulm, Germany, Study No. P/B 683 G 030022 11344019-5008-3, DowElanco Report No. GHE-P-10435. GLP. Unpublished. 13 May 2003

Corley, J., 2004, Quinoxyfen: Magnitude of the Residue on Cantaloupe. IR-4 Project, Center for Minor Crop Pest Management Technology Center of New Jersey, Rutgers, IR-4 Study No.07252. GLP. Unpublished.12 October 2004

Cowles, J., 2000, Residues of quinoxyfen in Australian grapes after three consecutive applications of EF-1295 in 1999, Study no. GHF-P-1951, Dow Agro Sciences Australia, Unpublished, 2000.

Cowles, J., 2000a, Residues of quinoxyfen in Australian grapes after multiple consecutive applications of EF-1295 in 1999 - 2000, Study no. GHF-P-2148, Dow Agro Sciences Australia, Unpublished, 2000.

Cowles, J., 2000b, Residues of quinoxyfen in Australian grapes after three consecutive applications of EF-1295 in 2000, Study no. GHF-P-2149, Dow Agro Sciences Australia, Unpublished, 2000.

Cowlyn, T., 1994, XDE 795 (Technical): Determination of Physico-chemical Properties, Pharmaco L.S.R., Ltd. Study No. 92016/CE, DowElanco Report No.GHE-P-3906. GLP. Unpublished. 21 December 1994

Cowlyn, T. and Boothroyd, S, 1994, Determination of Vapour Pressure, Water Solubility and Partition Coefficient of XDE 795 (Pure), L.S.R Limited, Study No. 92016/CA, DowElanco Report No. GHE-P-3105R. GLP. Unpublished 9 July 1994

Cowlyn, T. and Boothroyd, S, 1994a, XDE 795 (Purea): Determination of the Physico-chemical Properties, L.S.R. Limited, Study No. 92016/CD, DowElanco Report No. GHE-P-3597, GLP. Unpublished. 21 April 1994

Cracknell, M., Duriatti, A, Ghosh, D, Graupner, P and Portwood, D, 1995, Identification of Soil Metabolite of XDE-795, DowElanco Europe, Report No. GHE-P-3889. GLP. Unpublished. 9 March 1995

Dobbs, L., 2001, Independent Laboratory Validation of Dow AgroSciences LLC Method GRM 99.02 - Determination of Quinoxyfen Residues in Grapes and Dried Grapes by Gas Chromatography with Mass Selective Detection, Central California Research Laboratories Inc.(CCRL), USA, Study No. 010112 CCRL 990100. Dow AgroSciences Report No. GH-C 5495. GLP. Unpublished. 7 December 2001

Dunsire, J. and Paul, H., 1995, The Disposition of [14C]-XDE-795 in the Lactating Goat, Inveresk Research International, Study ID 10043, DowElanco Report No. GHE-P 4126. GLP. Unpublished. 25 February 1995

Eckert, J. and West, S., 2001, Independent Laboratory Validation for Quinoxyfen in Hops Using Dow AgroSciences Method ERC 95.26, Enviro-Bio-Tech. Ltd, USA, Study No. DOW-08-00, Dow AgroSciences Report No. GH-C 5166. 11 June 2001. GLP. Unpublished.

Fuchsbichler, G., 2002, Determination of the residues of Quinoxyfen in black currant, Bayerische Hauptversuchsanstalt fur Landwirtschaft. Study HVA 21/02. 13 December 2002. Unpublished.

Fuchsbichler, G., 2002a, Determination of the residues of Quinoxyfen in balck currant and gooseberry. Bayerische Hauptversuchsanstalt fur Landwirtschaft, Study HVA 37/01. 08 January 2002. Unpublished.

Gambie, A. and Long, T., 1995, Residues of XDE-795 in Milk and Tissues of Dairy Cows Following Oral Administration of XDE-795 and in Dairy Process Fractions – 1994, DowElanco Europe H.R.C. Ltd., Campden & Chorleywood, FRA, Report No. GHE-P-4161 (DWC685/943019, DWC715/950264, DWC715/950264). GLP. Unpublished. 24 July 1995

Gambie, A. and Nicholson, A., 1994, Residues of XDE-795 in Winter Wheat and Winter Barley, Grain and Straw, at Harvest Following Application of EF 1186, UK – 1993, DowElanco Europe, Report No. GHE-P-3724. GLP. Unpublished. 17 August 1994

Gambie, A. and Nicholson, A., 1994a, Determination of XDE-795 Residues in Wheat and Barley (Immature Plant, Straw and Grain), DowElanco Europe, Report No. ERC 94.5. GLP. Unpublished. 18 August 1994

Gambie, A. and Press, A., 1995, Residues of XDE-795 in Winter Wheat at Harvest Together with the Process Fractions Flour and Bread Following Applications of EF-1186, UK – 1994, DowElanco Europe, Report No. GHE-P-4164. GLP. Unpublished. 17 July 1995

Gambie, A. and Press, A., 1995a, Residues of XDE-795 in Winter Wheat (soft) at Harvest together with the Process Fractions Flour and Bread following Applications of EF-1186, Northern France - 1994., DowElanco Europe, Report No. GHE-P-4171. GLP. Unpublished. 20 July 1995

Gambie, A. and Teasdale, R., 1995, Residues of XDE-795 in Spring Barley at Harvest and in Brewing Process Fractions following Applications of EF-1186, UK – 1994, DowElanco Europe, Report No. GHE-P-4165. GLP. Unpublished. 6 July 1995.

Gambie, A. and Wood, S., 1995, Residues of XDE-795 in Spring Barley, Grain and Straw, at Intervals Following Application of EF 1186, UK – 1993. DowElanco Europe, Report No. GHE-P-3785. GLP. Unpublished. 7 June 1995

Gambie, A., & Wood, S., 1995a, Residues of XDE-795 in Winter Wheat, and Winter Barley, Grain and Straw, at Harvest Following Application of EF 1186, UK – 1993, DowElanco Europe, Report No. GHE-P-3784. GLP. Unpublished. 7 June 1995

Gambie, A., Nicholson, A & Wood, S., 1995, Residues of XDE-795 in Winter Wheat, Grain and Straw, at Intervals Following Application, DowElanco Europe, Report No. GHE-P-3786. GLP. Unpublished. 10 April 1995

Gambie, A., Rawle, N., and Shaw, I., 1995, Independent Validation of DowElanco Method ERC-94.5 for the Determination of XDE-795 Residues in Immature Plant, Grain and Straw, DowElanco Europe, Report No. GHE-P-3783. GLP. Unpublished. 30 August 1994

Gambie, A., Teasdale, R and Press, A., 1995, Residues of XDE-795 in Milk and Tissues of Dairy Cows Following Oral Administration of XDE-795 (Extended Dose Level). – 1995, DowElanco Europe, I.R.I. Ltd. Report No. GHE-P-4185 (IRI 12106). GLP. Unpublished. 21 July 1995

Gambie, A., 1995, Residues of XDE-795 in Winter Hard Wheat and Winter Soft Wheat at Intervals following Application of EF-1186, Southern France – 1993, DowElanco Europe, Report No. GHE-P-3787. GLP. Unpublished. 10 April 1995

Gambie, A., 1995a, Residues of XDE-795 in Winter Soft Wheat at Intervals and Winter Barley at Harvest following Application of EF-1186, Northern France – 1993, DowElanco Europe, Report No. GHE-P-3788. GLP. Unpublished. 16 May 1995

Gambie, A., 1995b, Residues of XDE-795 in Winter Wheat at Intervals following Application of EF-1186, UK – 1994, DowElanco Europe, Report No. GHE-P-4162. GLP. Unpublished. 22 May 1995

Gambie, A., 1995c, Residues of XDE-795 in Hard and Soft Wheat, Grain and Straw, at Harvest Following Application of EF 1186, Greece – 1993, DowElanco Europe, Report No. GHE-P-3792. GLP. Unpublished. 23 May 1995.

Gambie, A., 1995d, Residues of XDE-795 in Durum Wheat at Intervals following Applications of EF-1186, Southern France – 1994, DowElanco Europe, Report No. GHE-P-4168. GLP. Unpublished. 14 June 1995

Gambie, A., 1995e, Residues of XDE-795 in Winter Barley at Intervals following Application of EF-1186, UK – 1993, DowElanco Europe, Report No. GHE-P-4163. GLP. Unpublished. 2 June 1995

Gambie, A., 1995f, Residues of XDE-795 in Spring Wheat at Intervals following Application of EF-1186, Northern France – 1994, DowElanco Europe, Report No. GHE-P-4172. GLP. Unpublished. 14 June 1995

Gambie, A., 1995g, Residues of XDE-795 in Winter Barley Grain and Straw at Harvest following Application of EF-1186, Germany – 1993, DowElanco Europe, Report No. GHE-P-4160. GLP. Unpublished. 14 June 1995

Gambie, A., 1995h, Residues of XDE-795 in Winter Wheat at Intervals following Application of EF-1186, Germany – 1994, DowElanco Europe, Report No. GHE-P-4178. GLP. Unpublished. 16 June 1995

Gambie, A., 1995i, Residues of XDE-795 in Winter Barley Grain and Straw at Intervals following Application of EF-1186, Germany – 1993, DowElanco Europe, Report No. GHE-P-4159. GLP. Unpublished. 14 June 1995

Gambie, A., 1995j, Residues of XDE-795 in Winter Wheat at Harvest following Application of EF-1186, Germany – 1993, DowElanco Europe, Report No. GHE-P-3791. GLP. Unpublished. 14 June 1995

Gambie, A., 1995k, Residues of XDE-795 in Winter Wheat at Intervals following Application of EF-1186, Germany - 1993., DowElanco Europe, Report No. GHE-P-3789. GLP. Unpublished. 9 June 1995

Gambie, A., 1995l, Residues of XDE-795 in Winter Soft Wheat and Barley, Grain and Straw, at Harvest, following Application of EF-1186, Northern France – 1993, DowElanco Europe, Report No. GHE-P-3790. GLP. Unpublished. 29 June 1995

Gambie, A., 1995m, Residues of XDE-795 in Winter Wheat at Harvest following Application of EF-1186, Germany – 1994, DowElanco Europe, Report No. GHE-P-4181. GLP. Unpublished. 7 July 1995

Gambie, A., 1995n, Residues of XDE-795 in Winter Barley at Intervals Following Applications of EF-1186, Germany – 1994, DowElanco Europe, Report No. GHE-P-4179. GLP. Unpublished. 17 July 1995

Gambie, A., 1995o, Residues of XDE-795 in Winter Soft Wheat, Grain and Straw, at Harvest, after Applications of EF-1186, Southern France – 1994, DowElanco Europe, Report No. GHE-P-4167. GLP. Unpublished. 6 July 1995

Gambie, A., 1995p, Residues of XDE-795 in Spring Barley, Grain and Straw, at Harvest following Applications of EF-1186, Northern France – 1994, DowElanco Europe, Report No. GHE-P-4170. GLP. Unpublished. 7 July 1995

Gambie, A., 1995r, Residues of XDE-795 in Winter Barley at Harvest following Application of EF-1186, Germany – 1994, DowElanco Europe, Report No. GHE-P-4180. GLP. Unpublished. 5 July 1995

Gambie, A., 1995s, The Stability of XDE-795 in Cereal Immature Plant, Grain and Straw Under Frozen Storage Conditions (INTERIM REPORT), DowElanco Europe, Report No. GHE-P-4409. GLP. Unpublished. 7 July 1995

Gambie, A., 1995t, Overview of Residue Transfer Studies in the Dairy Cow Following Oral Administration of DE-795, DowElanco Europe, Milk Marque Product Development Centre, Report No. GHE-P-4486. GLP. Unpublished. 24 July 1995

Gambie, A., 1996, The Stability of XDE-795 in Cereal Immature Plant, Grain and Straw Under Frozen Storage Conditions, DowElanco Europe, Report No. GHE-P-5438. GLP. Unpublished. 27 September 1996

Ghosh, D. and Portwood, D., 1994, Identification of Soil Metabolism Products of XDE-795 by Particle Beam Liquid Chromatography Mass Spectrometry and Thermospray Liquid Chromatography Mass Spectrometry, DowElanco Europe, Report No. GHE-P-3079. GLP. Unpublished. 28 January 1994

Graper, L. and Balcer, J., 2001, A Nature of the Residue Study with $^{14}$C-Labelled Quinoxyfen Fungicide Applied to Sugar Beets, Dow AgroSciences, Indianapolis; USA, Study No. 990045, Report No. GH-C 5201. GLP. Unpublished. 2 March 2001

Hackert Anderson, C. and West, S., 2001, Multi-Residue Method Testing For Quinoxyfen According to PAN I, Appendix II, as Updated January, 1994, ABC Laboratories, Columbia, USA, Study No. ACFS-45995, Dow AgroSciences Report No. GH-C 5165. GLP. Unpublished. 23 January 2001

Haq, R. and Brown, G., 1995, The Metabolism of XDE-795 in Winter Wheat - A Probe Study, DowElanco Europe, Report No. GHE-P-4418. GLP. Unpublished. 11 July 1995

Haq, R. and Brown, G., 1995a, Uptake of XDE-795 into Three Succeeding Crops, DowElanco Europe, Report No. GHE-P-4322. GLP. Unpublished. 11 July 1995

Haq, R., MacDonald, A and Brown, G. , 1995, The Metabolism of XDE-795 in Winter Wheat, DowElanco Europe, Report No. GHE-P-4391. GLP. Unpublished. 7 July 1995

Hastings, M. and Gambie, A., 1995, Determination of XDE-795 Residues in Bovine Muscle, Kidney and Fat. DowElanco Europe, Report No. ERC 94.20. GLP. Unpublished. 16 May 1995

Hastings, M. and Gambie, A., 1995a, Determination of XDE-795 Residues in Bovine Liver, DowElanco Europe, Report No. ERC 94.30. GLP. Unpublished. 8 June 1995

Hastings, M. and Schmidt, F. , 1995, The Suitability of the DFG Method S 19 for the Determination of XDE-795 Residues in Winter Wheat, Winter Barley, Grapes, Melons, Cucumbers, Strawberries, Squashes and Soil, DowElanco Europe, Study No. DOW-9502, Report No. GHE-P-4427. GLP. Unpublished. 27 June, 1995

Jack, L. and Dunsire, J., 1995, Investigation of Total XDE-795 Derived Residues in Eggs and Edible Tissues Following 28 day Oral Administration (A Feeding Study), Inveresk Research International , Study No. 155622, DowElanco Report No. GHE-P-4394. GLP, Unpublished. 26 June 1995

Jones, S., 2000, Residues of Quinoxyfen in Sugar Beet at Intervals and Harvest Following Multiple Applications of FORTRESS (EF-1186), Northern Europe – 1999, CEMAS, UK, Study No. CEMS-1072, DowElanco Report No. GHE-P-8687. GLP. Unpublished. 18 January 2000

Kang, J., Kingdom, N., and Womack, J., 2001, Residues of Quinoxyfen in Sugar Beet at Intervals and At-harvest Following Multiple Applications of FORTRESS, CEMAS, UK, Study No. CEMS-1348, DowElanco Report No. GHE-P-9212. GLP. Unpublished. 4 April 2001

Khoshab, A. and Clements, B., 1999, Residues of Quinoxyfen in Barley at Harvest Following Multiple Applications of Fortress (EF-1186), Southern France – 1998, Dow AgroSciences, Report No. GHE-P-7972. GLP. Unpublished. 19 June 1999

Khoshab, A. and Roberts, R., 1996, Determination of DE-795 Residues in Grape, Wine, Must and Pomace, DowElanco Europe, Report No. ERC 95.26. GLP. Unpublished. 19 February 1996

Khoshab, A. and Volle C. , 1996, Residues of DE-795 in Wine Grapes at Harvest, Must, Wine and Pomace Following Multiple Applications of EF-1295, Northern and Southern France – 1995, DowElanco Europe, Report No. GHE-P-5171. GLP. Unpublished. 13 November 1996

Khoshab, A., Boothroyd, S, Gale, D and Frewer, N., 1998, Determination of Quinoxyfen Residues in Eggs, Dow AgroSciences, Report No. ERC 98.05. GLP. Unpublished

Khoshab, A., 1995, Independent Validation of DowElanco Method ERC-94.29 for the Determination of XDE-795 in Grapes, DowElanco Europe, Report No. GHE-P-4588. GLP. Unpublished. 24 October 1995

Khoshab, A., 1995a, Residues of XDE-795 in Wine Grapes at Intervals following multiple Applications of EF-1295, Italy 1994, DowElanco Europe, Report No. GHE-P-4594. GLP. Unpublished. 20 December 1995

Khoshab, A., 1995b, Residues of XDE-795 in Grapes at Harvest following 6, 8 or 10 Applications of EF-1186, France – 1993, DowElanco Europe, Report No. GHE-P-4587. GLP. Unpublished. 5 December 1995

Khoshab, A., 1995c, Determination of XDE-795 Residues in Grapes, DowElanco Europe, Report No. ERC 94.29. GLP. Unpublished. 8 February 1995

Khoshab, A., 1996, Residues of DE-795 in Table Grapes at Harvest following multiple Applications of EF-1295, Italy 1994, DowElanco Europe, Report No. GHE-P-4596. GLP. Unpublished. 1 February 1996

Khoshab, A., 1996a, Residues of DE-795 in Wine Grapes at Intervals following multiple Applications of EF-1295, Spain – 1994, DowElanco Europe, Report No. GHE-P-4597. GLP. Unpublished. 1 February 1996

Khoshab, A., 1996b, Residues of DE-795 in Wine Grapes at Harvest following multiple Applications of EF-1295, Spain – 1994, DowElanco Europe, Report No. GHE-P-4598. GLP. Unpublished. 1 February 1996

Khoshab, A., 1996c, Residues of DE-795 in Table Grapes at Intervals following multiple Applications of EF-1295, Italy 1994, DowElanco Europe, Report No. GHE-P-4595. GLP. Unpublished. 14 February 1996

Khoshab, A., 1996d, Residues of DE-795 in Wine Grapes at Harvest following multiple Applications of EF-1295, Northern France – 1994, DowElanco Europe, Report No. GHE-P-4592. GLP. Unpublished. 7 February 1996

Khoshab, A., 1996e, Residues of DE-795 in Wine Grapes at Intervals following multiple Applications of EF-1295, Southern France – 1994, DowElanco Europe, Report No. GHE-P-4591. GLP. Unpublished. 7 February 1996

Khoshab, A., 1996f, Residues of DE-795 in Table Grapes at Intervals following multiple Applications of EF-1295, Southern France – 1994, DowElanco Europe, Report No. GHE-P-4590. GLP. Unpublished. 7 February 1996

Khoshab, A., 1996g, Residues of DE-795 in Wine Grapes at Intervals following multiple Applications of EF-1295, Northern France – 1994, DowElanco Europe, Report No. GHE-P-4593. GLP. Unpublished. 21 March 1996

Khoshab, A., 1996h, Residues of DE-795 in Wine Grapes at Intervals following multiple Applications of EF-1295, Italy 1995, DowElanco Europe, Report No. GHE-P-5164. GLP. Unpublished. 28 May 1996.

Khoshab, A., 1996i, Residues of DE-795 and Fenarimol in Wine Grapes at Harvest following multiple Applications of EF-1303, Italy – 1995, DowElanco Europe, Report No. GHE-P-5165. GLP. Unpublished. 12 June 1996

Khoshab, A., 1996j, Residues of DE-795 in Wine Grapes at Harvest following multiple Applications of EF-1295, Spain 1995, DowElanco Europe, Report No. GHE-P-5169. GLP. Unpublished. 3 July 1996

Khoshab, A., 1996k, Residues of DE-795 and Fenarimol in Table Grapes at Harvest following multiple Applications of EF-1303, Spain – 1995, DowElanco Europe, Report No. GHE-P-5167. GLP. Unpublished. 3 July 1996

Khoshab, A., 1996l, Residues of DE-795 in Table Grapes at Intervals following multiple Applications of EF-1295, Spain 1995, DowElanco Europe, Report No. GHE-P-5168. GLP. Unpublished. 3 July 1996

Khoshab, A., 1996m, Residues of DE-795 and Fenarimol in Table Grapes at Harvest following multiple Applications of EF-1295 or EF-1303, Italy – 1995, DowElanco Europe, Report No. GHE-P-5166. GLP Unpublished. 5 August 1996

Khoshab, A., 1996n, Residues of DE-795 in Wine Grapes at Intervals following multiple Applications of EF-1295, Northern France 1995, DowElanco Europe, Report No. GHE-P-5172. GLP. Unpublished. 2 August 1996

Khoshab, A., 1996o, Residues of DE-795 and Fenarimol in Wine Grapes at Intervals following multiple Applications of EF-1303, Germany – 1995, DowElanco Europe, Report No. GHE-P-5173. GLP. Unpublished. 2 August 1996.

Khoshab, A., 1996p, Residues of DE-795 and Fenarimol in Wine Grapes at Harvest following multiple Applications of EF-1303, Germany – 1995, DowElanco Europe, Report No. GHE-P-5174. GLP. Unpublished. 2 August 1996

Khoshab, A., 1996r, Residues of DE-795 and Fenarimol in Melons at Intervals Under Field Conditions Following Multiple Applications of EF-1303 or EF-1295, Spain – 1995, DowElanco Europe, Report No. GHE-P-5488. GLP. Unpublished. 5 September 1996

Khoshab, A., 1996s, Residues of DE-795 and Fenarimol in Greenhouse Grown Melons at Intervals Following Multiple Applications of EF-1303 or EF-1295, Spain – 1995, DowElanco Europe, Report No. GHE-P-5422. . GLP. Unpublished. 6 September 1996

Khoshab, A., 1996t, Residues of DE-795 and Fenarimol in Melons at Harvest, Grown Under Open Air Conditions, Following Multiple Applications of EF-1303 or EF-1295, Italy – 1995, DowElanco Europe, Report No. GHE-P-5420. GLP. Unpublished. 28 August 1996

Khoshab, A., 1996u, Residues of DE-795 and Fenarimol in Melons at Intervals Grown Under Open Air Conditions and Residues of DE-795 and 2-oxo-DE-795 Metabolite in Soil at Harvest Following Multiple Applications of EF-1303 and EF-1295, Spain – 1995, DowElanco Europe, Report No. GHE-P-5421. GLP. Unpublished. 29 August 1996

Khoshab, A., 1996v, Residues of DE-795 and Fenarimol in Wine Grapes at Harvest, Must, Wine and Pomace Following Multiple Applications of EF-1303, Germany – 1995, DowElanco Europe, Report No. GHE-P-5175. GLP. Unpublished. 22 August 1996

Khoshab, A., 1996z, Residues of DE-795 and Fenarimol in Melons at Harvest, Under Field Conditions, Following Multiple Applications of EF-1303 or EF-1295, Greece – 1996, DowElanco Europe, Report No. GHE-P-5489. GLP. Unpublished. 23 September 1996

Khoshab, A., 1996x, Residues of DE-795 in Wine Grapes at Harvest, Must, Wine and Pomace Following Multiple Applications of EF-1295, Italy – 1995, DowElanco Europe, Report No. GHE-P-5176. GLP. Unpublished. 6 September 1996

Khoshab, A., 1996y, Residues of DE-795 and Fenarimol in Melons at Harvest, Under Field Conditions, Following Multiple Applications of EF-1295 or EF-1303, Italy – 1996, DowElanco Europe, Report No. GHE-P-5487. GLP. Unpublished. 26 November 1996

Khoshab, A., 1996w, Residues of DE-795 and Fenarimol in Melons at Intervals Under Cover Following Multiple Applications of EF-1295 or EF-1303, Italy – 1996, DowElanco Europe, Report No. GHE-P-5485. GLP. Unpublished. 13 November 1996

Khoshab, A. and Macmillan, H. , 1996, Determination of DE-795 Residues in Courgettes and Cucumbers, DowElanco Europe, Report No. ERC 96.08A. GLP. Unpublished. 10 June 1996

Khoshab, A. and Macmillan, H. , 1996a, Determination of DE-795 Residues in Melon Peel and Pulp, DowElanco Europe, Report No. ERC 96.16. GLP. Unpublished. 3 June 1996

Khoshab, A. and Rawle, N. , 1996, Independent Laboratory Confirmation of DowElanco Analytical Method ERC-96.16 for the Determination of DE-795 in Melon Peel and Pulp, DowElanco Europe, Report No. GHE-P-5406. GLP. Unpublished. 8 August 1996

Khoshab, A., 1996, Residues of DE-795 and Fenarimol in Wine Grapes at Harvest following multiple Applications of EF-1303, Spain – 1995, DowElanco Europe, Report No. GHE-P-5170. GLP. Unpublished. 18 July 1996

Kunz, A., 2001, Determination of Residues Following Use of Quinoxyfen in Strawberries – Germany 1999 and 2000. Dow AgroSciences GMBH. Report GHE-P 11110. GLP. Unpublished. 16 March 2001.

MacDonald, A., 1997, The Photolysis of $^{14}$C-DE-795 under Natural Conditions, DowElanco Europe, Report No. GHE-P-5932. GLP. Unpublished. 25 February 1997

Oberwalder, C., 1999, Determination of Residues of Quinoxyfen Applied as EF-1295 in Hops. Four Sites in Germany, 1998, GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH, Study No. 98251/G1-FPHO: RF98-200, DowElanco Report No. GHE-P-8483. GLP. Unpublished. 31 May 1999

Pollmann, B., 2000, Determination of Residues of Quinoxyfen Applied as EF-1295 in Hops. Four Sites in Germany, 1999, GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH, Study No. 99255/G1-FPHO: RF99-027, DowElanco Report No. GHE-P-8484. GLP. Unpublished. 20 March 2000

Portwood, D., 1996, Identification of DE-795 Photolysis Products, DowElanco Europe, Report No. GHE-P-4721. GLP. Unpublished. 10 May 1996.

Reeves, G., 1993, The Aerobic Soil Degradation/Metabolism of [$^{14}$C] -XDE-795 and the Effect of Environmental Conditions on its Degradation Rate, DowElanco Europe, Report No. GHE-P-2990. GLP. Unpublished. 24 August 1993

Reeves, G., 1994, The Leaching Characteristics of Aged {$^{14}$C }-XDE-795 Soil Residues, DowElanco Europe. Report No. GHE-P-3552. GLP. Unpublished. 12 August 1994

Reeves, G., 1995, The Soil Photolysis of XDE-795, DowElanco Europe, Report No. GHE-P-4111. GLP. Unpublished. 19 May 1995

Reeves, G. and Ghosh, D., 1994, The Hydrolysis of [$^{14}$C] - XDE-795, DowElanco Europe, Report No. GHE-P-3137. GLP. Unpublished. 23 March 1994

Rudel, H., 1995, Determination of the Quantum Yield of XDE-795 in Water. DowElanco Europe Study Code No. DOW-025/7-21. Report No. GHE-P 4429.

GLP. Unpublished. 13 June 1995.

Schumann, A.M., Dryzga, M.D., Pottenger, L.H.., Stewart, H.S., and Bartels, M.J., 1995, XDE-795: Tissue Distribution and Metabolism of $^{14}$C-labelled XDE-795 in Fischer 344 Rats, Dow Chemical Company, Study No. DECO-HET DR-0325-7474-006. Unpublished. 1995

Teasdale, R. and Press, A., 1995, Determination of XDE-795 Residues in Beer, DowElanco Europe, Report No. ERC 95.10. 3 July 1995. GLP. Unpublished

Teasdale, R., Lyons, S, Rhodes, H and Patel, K. , 2000, Determination of Quinoxyfen Residues in Sugar Beet Roots and Tops, Dow AgroSciences, Letcombe, UK, Method No. GRM 99.04. GLP. Unpublished. 4 May 2000. - METHOD

Teasdale, R., 2000, Determination of Residues of Quinoxyfen in Grapes and Dried Grapes, Dow AgroSciences Europe, Method No. GRM 99.02,. Report No. RV99-002, Unpublished. 5 May 2000. GLP

Thompson, D., 2001, Quinoxyfen: Magnitude of the Residue on Hops, IR-4 Project, Center for Minor Crop Pest Management Technology Center of New Jersey, Rutgers, IR-4 Study No. 07350. GLP. Unpublished. 30 March 2001

Thompson, D., 2001, Quinoxyfen: Magnitude of the Residue on Grape, IR-4 Project, Center for Minor Crop Pest Management Technology Center of New Jersey, Rutgers, IR-4 Study No. 07256. GLP. Unpublished. 30 March 2001

West, S., 2001, Method Validation Report for the Determination of Quinoxyfen (DE-795) in Hops by Dow AgroSciences Method ERC 95.26.S1, Enviro-Bio-Tech. Ltd, USA, Report No. GH-C 5175. GLP. Unpublished. 15 February 2001

Williams, M., 1996, The Stability of XDE-795 under Frozen Storage Conditions in Grapes, Severn Trent Labs, Coventry, UK, Study No. 21442/1. DowElanco Report No. GHE-P-5423. GLP. Unpublished. 3 September 1996.

## CROSS REFERENCES

| Author | Trial code | Year |
|---|---|---|
| Cowles, J. | 1951 | 2000 |
| Cowles, J. | 2148 | 2000a |
| Cowles, J. | 2149 | 2000b |
| Rudel, H. | 4429 | 1995 |
| Baloch, R., Paterson, G. and Kamaludin, J. | 6328 | 1997 |
| Reeves, G. | 6357 | 1993 |
| Schumann, A.M., Dryzga,M.D.., Pottenger, L.H.., Stewart, H.S.,a nd Bartels, M.J. | 7474 | 1995 |
| Chen, H. | 8006 | 2003 |

| | | |
|---|---|---|
| Ghosh, D and Portwood, D. | 8411 | 1994 |
| Reeves, G. and Ghosh, D. | 8557 | 1994 |
| Cowlyn, T and Boothroyd, S | 8605 | 1994 |
| Kunz, A. | 11110 | 2001 |
| Fuchsbichler, G. | 20061 | 2002 |
| Fuchsbichler, G. | 20062 | 2002a |
| Cowlyn, T and Boothroyd, S | 21129 | 1994a |
| Reeves, G. | 24033 | 1994 |
| Gambie, A and Nicholson, A. | 24035 | 1994 |
| Cowlyn, T | 27304 | 1994 |
| Dunsire, J and Paul, H. | 29257 | 1995 |
| Cracknell, M, Duriatti, A, Ghosh, D, Graupner, P and Portwood, D | 29386 | 1995 |
| Gambie, A, Nicholson, A & Wood, S. | 29405 | 1995 |
| Gambie, A. | 29406 | 1995 |
| Gambie, A. | 29912 | 1995a |
| Reeves, G. | 31076 | 1995 |
| Gambie, A. | 31080 | 1995b |
| Gambie, A. | 31231 | 1995c |
| Gambie, A. | 31234 | 1995d |
| Gambie, A. | 31235 | 1995e |
| Gambie, A. | 31241 | 1995f |
| Gambie, A. | 31261 | 1995g |
| Gambie, A. | 31262 | 1995h |
| Gambie, A. | 31263 | 1995i |
| Gambie, A. | 31265 | 1995j |
| Gambie, A. | 31266 | 1995k |
| Gambie, A and Wood, S. | 31267 | 1995 |
| Gambie, A, & Wood, S. | 31268 | 1995a |
| Gambie, A and Long, T. | 31599 | 1995 |
| Gambie, A and Press, A. | 31600 | 1995 |
| Gambie, A and Press, A. | 31607 | 1995a |
| Gambie, A. | 31620 | 1995l |
| Gambie, A, Rawle, N., and Shaw, I. | 31621 | 1995 |
| Gambie, A and Teasdale, R. | 31624 | 1995 |
| Gambie, A. | 31633 | 1995m |
| Gambie, A, Teasdale, R and Press, A. | 31634 | 1995 |
| Gambie, A. | 31635 | 1995n |
| Gambie, A. | 31644 | 1995o |
| Gambie, A. | 31646 | 1995p |
| Gambie, A. | 31648 | 1995r |
| Hastings, M and Schmidt, F. | 31651 | 1995 |
| Haq, R, MacDonald, A and Brown, G. | 31659 | 1995 |
| Jack, L and Dunsire, J. | 31744 | 1995 |
| Gambie, A. | 31748 | 1995s |
| Gambie, A. | 31753 | 1995t |
| Haq, R and Brown, G. | 31757 | 1995 |
| Khoshab, A. | 41039 | 1995 |
| Khoshab, A. | 42673 | 1995a |
| Khoshab, A. | 42674 | 1995b |
| Caley, C.and Kingsley, R. | 42894 | 1995 |
| Khoshab, A. | 43179 | 1996 |
| Khoshab, A. | 43180 | 1996a |
| Khoshab, A. | 43181 | 1996b |
| Khoshab, A. | 43416 | 1996c |
| Khoshab, A. | 43620 | 1996d |
| Khoshab, A. | 43621 | 1996e |
| Khoshab, A. | 43622 | 1996f |
| Khoshab, A. | 43816 | 1996g |
| Portwood, D. | 44553 | 1996 |
| Khoshab, A. | 44917 | 1996h |

| | | |
|---|---|---|
| Khoshab, A. | 45173 | 1996i |
| Khoshab, A. | 45513 | 1996j |
| Khoshab, A. | 45531 | 1996k |
| Khoshab, A. | 45532 | 1996l |
| Khoshab, A., | 45692 | 1996 |
| Khoshab, A. | 45715 | 1996m |
| Khoshab, A. | 45716 | 1996n |
| Khoshab, A. | 45717 | 1996o |
| Khoshab, A. | 45718 | 1996p |
| Khoshab, A. and Rawle, N. | 45724 | 1996 |
| Chapleo, S. and Caley, C | 45725 | 1996 |
| Khoshab, A. | 46954 | 1996r |
| Khoshab, A. | 46956 | 1996s |
| Khoshab, A. | 46957 | 1996t |
| Khoshab, A. | 46958 | 1996u |
| Khoshab, A. | 46975 | 1996v |
| Khoshab, A. | 47141 | 1996z |
| Khoshab, A. | 47145 | 1996x |
| Williams, M. | 47234 | 1996 |
| Gambie, A. | 47586 | 1996 |
| Khoshab, A and Volle C. | 47868 | 1996 |
| Khoshab, A. | 48080 | 1996y |
| Khoshab, A. | 48081 | 1996w |
| MacDonald, A. | 48846 | 1997 |
| Hastings, M and Gambie, A. | 63682 | 1995 |
| Hastings, M and Gambie, A. | 63683 | 1995a |
| Gambie, A and Nicholson, A. | 63697 | 1994a |
| Teasdale, R and Press, A. | 63705 | 1995 |
| Khoshab, A, Boothroyd, S, Gale, D and Frewer, N. | 64399 | 1998 |
| Khoshab, A and Clements, B. | 69430 | 1999 |
| Oberwalder, C. | 73994 | 1999 |
| Pollmann, B. | 74050 | 2000 |
| Teasdale, R, Lyons, S, Rhodes, H and Patel, K. | 74779 | 2000 |
| Teasdale, R. | 74780 | 2000 |
| Haq, R and Brown, G. | 75502 | 1995a |
| Jones, S. | 76690 | 2000 |
| Khoshab, A. and Macmillan, H. | 76968 | 1996 |
| Byrne, S, Balcer, J, Gilbert, J., and Thornburg, S. | 78962 | 2000 |
| Eckert, J and West, S. | 80416 | 2001 |
| Hackert Anderson, Cand West, S. | 80711 | 2001 |
| West, S. | 81400 | 2001 |
| Graper, L and Balcer, J. | 81925 | 2001 |
| Kang, J., Kingdom, N., and Womack, J. | 83187 | 2001 |
| Thompson, D. | 83727 | 2001 |
| Thompson, D. | 83731 | 2001 |
| Dobbs, L | 102718 | 2001 |
| Chen, H | 102721 | 2002 |
| Chen, H | 102722 | 2002a |
| Khoshab, A. | 105043 | 1995c |
| Khoshab, A and Roberts, R. | 105334 | 1996 |
| Khoshab, A. and Macmillan, H. | 105351 | 1996a |
| Class, T | 135044 | 2003 |
| Class, T | 135045 | 2003a |
| Class, T | 135046 | 2003b |
| Class, T | 135047 | 2003c |
| Corley, J. | 208696 | 2004 |
| Barney, W. | 208697 | 2005 |
| Barney, W. | 208698 | 2005a |