## TECNAZENE (115)

EXPLANATION

Tecnazene was reviewed by the JMPR in 1974, 1978, 1981, 1983, 1987 and 1989, and its use on potatoes was evaluated in 1978 and 1981. The 1981 Meeting concluded (FAO/WHO 1982) that while the TMRL of 1 mg/kg for potatoes washed before analysis proposed in 1978 may have been too low, the available data were inadequate to recommend an alternative. Additional residue data were reviewed in 1989 and it was concluded that the 1978 recommendation was lower than was required under current conditions of commercial use.

The 1989 JMPR concluded that residues of tecnazene in the pulp of treated, uncooked potatoes would generally be less than 1 mg/kg and noted that further losses occurred during normal cooking. However the high levels that could be attained in the peel of treated potatoes, up to 100 mg/kg, also had to be noted. The 1989 Meeting concluded that an MRL of 10 mg/kg for potatoes washed before analysis was supported by the new data provided.

Tecnazene has been extensively discussed at the CCPR in 1990, 1991 and 1992, when several countries expressed reservations concerning the definition of the residue, the quality of the residue data, the interpretation of GAP, and toxicological aspects.

Additional updated information on use patterns on potatoes, supervised residue trials, the fate of residues during metabolism and processing, the definition of the residue, and the levels of residues in food in commerce and at consumption was provided for evaluation and is reviewed below.

### IDENTITY

ISO common name: tecnazene

Chemical Name

IUPAC and CA: 1,2,4,5-tetrachloro-3-nitrobenzene

Other: 2,3,5,6-tetrachloronitrobenzene

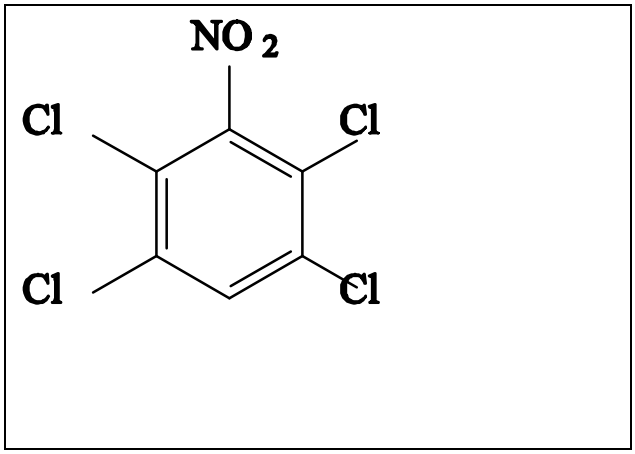
Synonyms: TCNB

CAS No.: 117-18-0

CIPAC No.: 65

1200 tecnazene

Structural formula:




Molecular formula: $C_6HCl_4NO_2$

Molecular weight: 261

Pesticidal class: plant growth regulator (sprout suppressant on potatoes) and fungicide (dry rot on potatoes, *fusarium caerulum*).

**Physical and Chemical Properties**

Pure active ingredient

Vapour Pressure: 0.027 Pa ($2.7 \times 10^{-7}$ atm) at 20°C

0.053 Pa ($5.2 \times 10^{-7}$ atm) at 25°C
1.15 Pa ($1.13 \times 10^{-5}$ atm) at 50°C

Melting Point: 99°C

Octanol-Water Partition Coefficient: Log $P_{ow}$ 4.0 at 25°C

Solubility (at 22°C): water 1.9 mg/l
methanol 36 g/l
acetone 295 g/l
toluene 231 g/l
n-hexane 53 g/l

Specific gravity: 1.744 at 25°C

Hydrolysis: stable to hydrolysis at pH 5, 7 and 9 at 25°C for 30 days in the dark

Photolysis: no information

Technical material

| | |
|---|---|
| Purity: | 98.1%(±0.7%)-100.0% (±0.7%) |
| Melting range: | 100.3-100.8°C |
| Stability: | stable over 2 weeks at 54°C |

**Formulations**

Tecnazene is currently marketed in a range of granular (10% and 5% ai) and dust (3% and 6% ai) formulations. The adjuvants used in the granular and dust formulation are all inert materials or fillers, such as potassium, aluminum or calcium sulphate (Zeneca, letter, 1994). Formulations: Fusarex, Hytec, Hytec 6, Hytec Super, Tecnazene 6% Dust, Hystore 10, New Hystore, Tripart, Arena, Nebulin, Tubodust, Bygran, NewArena, Tubostore, New Quadkeep, Tecnacarb, New Quadstore, Tecgran 100, Storite SS, Storaid Dust, Hortag, Hickstor, Hickstor 3, Hickstor 5, Hickstor 6, Hickstor 6 + MBC, Hickstor 10, Hickstor TBZ6. Formulations for which label information was provided are listed by company in the section "Use pattern".

**Manufacturing process and impurities**

Produced by nitration of 1,2,4,5-tetrachlorobenzene. Analysis of five batches of technical tecnazene showed >99% tecnazene, containing <0.1% hexachlorobenzene (HCB) (Williams, 1992; Zeneca, 1994).

## METABOLISM AND ENVIRONMENTAL FATE

**Animal metabolism**

The metabolism of tecnazene by rabbits and rats has been briefly reviewed previously by the JMPR (1974, p.531; 1978, p.228). The absorption, distribution, metabolism and excretion of [$^{14}$C]tecnazene has been studied in the rat. Earlier metabolism studies with unlabelled tecnazene were also carried out on the rat, rabbit, guinea pig and pigeon. Tecnazene is extensively metabolized in all species. In animals the nitro group is reduced, yielding 2,3,5,6-tetrachloroaniline and 4-amino-2,3,5,6-tetrachlorophenol. These metabolites are excreted in the urine as such or, in the case of the phenol, after the formation of ethereal glucuronide or sulphate conjugates. The nitro group can be replaced by glutathione, leading to the formation of another major metabolite, *S*-(2,3,5,6-tetrachlorophenyl)-*N*-acetylcysteine, which is also excreted in the urine. A similar route is followed in the metabolism of the related fungicide pentachloronitrobenzene (quintozene) in the rabbit and the rat (Betts *et al*., 1955; Renner, 1980).

Figure 1, page 1207, shows the metabolic pathways identified in rats and rabbits. The same metabolites are formed in other species.

Quantitative studies have been described in only one report provided for evaluation (Bratt 1991), in which the disposition of [$^{14}$C]tecnazene and its metabolites was followed in male and female rats dosed at 1 mg/kg bw. After 24 hours the highest tissue concentrations of $^{14}$C were in the kidneys, liver and nasal passages of both sexes. After seven days $^{14}$C residues were low but generally slightly higher in males where the highest concentrations were found in the abdominal fat (0.032 mg/kg, expressed as tecnazene), kidneys (0.016 mg/kg), lungs (0.016), blood (0.014) and heart (0.013 mg/kg). In females, the highest concentration was 0.011 mg/kg in the abdominal fat, blood and ovaries. After

seven days the total proportion of the dose present in the tissues was 0.13% and 0.05% in male and female rats respectively.

The concentrations of $^{14}C$ in the tissues appeared to decrease as a function of time on the evidence of autoradiograms at 24 and 48 hours and liquid scintillation counting at 7 days.

**Plant metabolism**

[$^{14}C$]tecnazene, formulated as a 6% dust, was applied to potatoes at the recommended rate of 135 mg ai or 2.25 g formulation/kg potatoes (Lewis, 1992). Thus the treatment was according to label recommendations at the maximum rate. The potatoes were stored at 8°C (the recommended holding temperatures for ware and crisping potatoes are 7°C and 8-10°C respectively) for periods up to six months in the dark in aerated containers (4 h with moistened air per day).

The treated potatoes were thoroughly washed, as in normal commercial practice, then extracted with acetonitrile and the whole tubers, peel and pulp analysed after 0, 88 and 186 days.

It is clear from Table 1 (Lewis, 1992) that tecnazene was the major component of the residue, accounting for 77% and 64% of the total residue in the whole potatoes after 88 and 186 days storage at 8°C respectively. A high proportion of the residue remained in the peel. Removal of the peel reduced tecnazene residues from 6.8 mg/kg in the whole potato to 0.4 mg/kg in the pulp.

The total $^{14}C$ residues in whole potatoes increased from 0.3 mg/kg tecnazene equivalents at day 0 to 10.7 mg/kg after 186 days.

Table 1. Radioactive residues in potatoes washed before analysis following treatment with [$^{14}C$]tecnazene (Lewis, 1992).

| Storage (8°C), days | Radioactive residue (mg/kg as tecnazene) | | | | | |
|---|---|---|---|---|---|---|
| | peel | | pulp | | whole | |
| | tecnazene | total | tecnazene | total | tecnazene | total |
| 0 | 0.9 | 1.1 | 0.1 | 0.1 | 0.3 | 0.3 |
| 88 | 22.6 | 28.0 | 0.2 | 0.7 | 5.0 | 6.5 |
| 186 | 30.8 | 46.9 | 0.4 | 1.6 | 6.8 | 10.7 |

Goodyear (1992) determined the residue of tecnazene and its metabolites after 186 days in samples from the Lewis (1992) study described above.

Whole potatoes, peel and flesh were analysed separately for metabolites. Samples were extracted with acetonitrile and aqueous acetonitrile and the extractable radioactive compounds partitioned between hexane and water. The hexane extracts were analysed by TLC and HPLC and the aqueous extracts by HPLC. Four non-polar compounds were isolated from the hexane fraction of the hexane/acetonitrile/water partitioning of the potato peel. Three of these were confirmed as tecnazene, 2,3,5,6-tetrachloroaniline (TCA) and 2,3,5,6-tetrachlorothioanisole (TCTA); a fourth was tentatively identified as a trichloroaniline (see Figure 1). Their identities were confirmed by GC-MS (Goodyear, 1992; Lappin and Pritchard, 1992). Table 2 shows the results.

Table 2. Nature of $^{14}C$ residues in peel, pulp and whole tubers of potatoes treated with [$^{14}C$]tecnazene and stored for 186 days (Goodyear, 1992).

| Compound or fraction | Peel | | Pulp | | Tuber | |
|---|---|---|---|---|---|---|
| | %[1] | mg/kg[2] | %[1] | mg/kg[2] | %[1] | mg/kg[2] |
| Tecnazene | 65.6 | 30.8 | 24.8 | 0.4 | 64.2 | 6.8 |
| Tetrachloroaniline (TCA) | ND | ND | 2.3 | 0.04 | 0.08 | ND |
| Tetrachlorothioanisole (TCTA) | ND | ND | 0.7 | 0.01 | 0.02 | ND |
| Trichloroaniline | ND | ND | 1.3 | 0.02 | 0.04 | ND |
| Polar metabolites | 23.3 | 10.9 | 53.5 | 0.9 | 24.3 | 2.6 |
| Unextracted | 7.7 | 3.6 | 8.6 | 0.1 | 7.7 | 0.8 |
| Total | 96.6 | 45.3 | 91.2 | 1.47 | 96.3 | 10.2 |

[1] Of total $^{14}C$ in substrate
[2] Calculated as tecnazene
ND Not detected (<0.01 mg/kg)

The water-soluble polar metabolites were hydrolysed by alkali and the hydrolysate partitioned with diethyl ether/dichloromethane for analysis by HPLC. About 30-40% of the polar mixture was converted to 2,3,5,6-tetrachlorothiophenol and 2,2′,3,3′,5,5′,6,6′-octachlorodibenzene disulphide (the thiophenol is readily oxidized to the disulphide) suggesting that the original polar metabolites were glutathione-related conjugates, similar to those found in the metabolism studies on rats. One of the compounds was identified as methyl 2,3,5,6-tetrachlorophenyl sulphoxide by GC-MS. This accounted for about 1% of the polar fraction at 186 days, i.e. about 0.1 mg/kg (as tecnazene) in the whole tubers (Lappin and Pritchard, 1992). The corresponding sulphone (TCTA sulphone), a suspected metabolite of tecnazene in lettuce, potatoes and soil (Bergman *et al*., 1988), was not detected in these studies. The analysis of the polar fraction is shown in Table 3.

Table 3. Metabolites in hydrolysates of polar fractions from potatoes treated with tecnazene (Goodyear, 1992).

| Compound or fraction | Peel | | Pulp | | Tuber | |
|---|---|---|---|---|---|---|
| | %[1] | mg/kg[2] | %[1] | mg/kg[2] | %[1] | mg/kg[2] |
| Thiophenol | 20.5 | 2.23 | 24.7 | 0.22 | 17.3 | 0.45 |
| Disulphide | 21.7 | 2.21 | 8.9 | 0.08 | 12.9 | 0.34 |
| Methyl 2,3,5,6-tetrachlorophenyl sulphoxide | | | | | 1 | 0.1 |
| Aqueous fraction | 12.6 | 1.29 | 20.2 | 0.18 | 12.4 | 0.32 |
| Total | 54.8 | 5.73 | 53.8 | 0.48 | 42.6 | 1.21 |

[1] Of total $^{14}C$ in substrate
[2] Calculated as tecnazene

In a separate metabolism study (Goodyear and Lewis, 1992), [$^{14}C$]-tetrachloroaniline (TCA) was applied at a rate of 13.5 mg/kg to potatoes which were stored up to 155 days in the dark at 8°C in aerated containers.

The major part (77%) of the $^{14}C$ residue in whole potatoes after 155 days storage was identified as unchanged TCA. A new metabolite, 2,3,5,6-tetrachloro-4-methoxyaniline (MTCA) (see

Figure 1), was identified and represented 8% of the $^{14}C$ in whole potatoes with the majority of the residue located in the pulp. The remainder comprised a mixture of polar material (12.4%) and bound material (5.7%).

The results may be summarized as follows. (i) Tecnazene was the major component of the residue, accounting for about two-thirds of the total residue (10.7 mg/kg) in whole potatoes. (ii) Small quantities of tetrachloroaniline (TCA), trichloroaniline and tetrachlorothioanisole (TCTA) were detected in the pulp (<0.05 mg/kg). Residue levels of these metabolites in the whole potatoes after 186 days were each below 0.1% of the total $^{14}C$ residue and below 0.01 mg/kg. (iii) Trace quantities of 2,3,5,6-tetrachloro-4-methoxyaniline (MTCA) were also formed, (iv) A bound residue constituted about 8% of the total residue in the peel, pulp and tubers. (v) One of the polar metabolites was identified as methyl 2,3,5,6-tetrachlorophenyl sulphoxide. This accounted for 5% or less of the polar fraction at 186 days, i.e. about 0.1 mg/kg.

The metabolic routes for tecnazene in rats, rabbits and potatoes are shown in Figure 1; the chemical names of the structures identified by roman numerals are listed in Table 4.

Table 4. Chemical names of compounds shown in Figure 1.

| Compound | Chemical name |
|---|---|
| I (tecnazene) | 2,3,5,6 tetrachloronitrobenzene |
| II | mercapturic acid of XVI - *N*-acetyl-*S*-(2,3,5,6-tetrachlorophenyl)cysteine |
| III | sulphoxide of II |
| IV | sulphone of II |
| V | 2,3,5,6-tetrachloraniline |
| VI | 4-amino-2,3,5,6-tetrachlorophenol |
| VIa | glucuronide of VI |
| VIb | ethereal sulphate of VI |
| VII | 1,2,4,5-tetrachlorobenzene |
| VIII | 2,3,5,6-tetrachlorophenol |
| IX | 2,3,5,6-tetrachlorothiophenol |
| X | bis(2,3,5,6,-tetrachlorophenyl) disulphide |
| XI | methyl 2,3,5,6-tetrachlorophenyl sulphide |
| XII | methyl 2,3,5,6-tetrachlorophenyl sulphoxide |
| XIII | methyl 2,3,5,6-tetrachlorophenyl sulphone |
| XIV | methyl 2,3,5,6-tetrachlorophenyl disulphide |
| XV | cysteine glycine conjugate of XVII |
| XVI | cysteine conjugate of XV |
| XVII | glutathione conjugate of I |
| XVIII | monodechlorinated product of II - *N*-acetyl-*S*-(trichlorophenyl)cysteine |
| XIX | 2,3,5,6-tetrachloro-4-methoxyaniline |

| Compound | Chemical name |
|---|---|
| I (tecnazene) | 2,3,5,6 tetrachloronitrobenzene |
| XX | 2,3,6-trichloroaniline |

**Environmental fate in soil**

Soil containing residues of tecnazene and its metabolites may be spread onto agricultural land when potato stores are cleaned out, or when sediments are removed from potato washing plants. Several studies were undertaken to determine the fate of tecnazene in soil.

Mackie *et al.* (1991) incubated [U-$^{14}$C]tecnazene with aerobic and anaerobic soils (the type of soil was not identified). A high proportion of the volatile radioactivity may not have been trapped, accounting for the low recovery of $^{14}$C (about 64% after 28 days). TCA was identified, up to 4.3% of the applied dose under aerobic conditions and 45% at 28 days under anaerobic conditions; tetarachloroanisole was not detected in either study.

When [$^{14}$C]tecnazene was incubated for 28 days in a loamy sand soil at 21°C in the dark (1.07 mg/kg) it was slowly degraded under aerobic conditions, but rapidly reduced to tetrachloroaniline under anaerobic conditions with a half-life of 9 days (Mackie and Hall, 1992a). In a closed system 93% of the $^{14}$C was recovered and 24% was identified as tecnazene, 36% as TCA and 0.83% as tetrachlorothioanisole (TCTA); 27% was bound. After 60 days the residue included 82% TCA, 1.64% TCTA and 26% bound; only 0.13% of the radioactivity was detected as $^{14}CO_2$ and 0.23% as organic volatiles. Acid and aqueous ethanol reflux of the bound residue solubilized 15.5% of the $^{14}$C residues as TCA.

TCA was degraded slowly in soil under both aerobic and anaerobic conditions, but was strongly adsorbed and of low mobility (Mackie and Hall, 1992b,c).

When a loamy sand soil was treated with [U-$^{14}$C]tetrachoroaniline at 1.19 mg/kg dry soil (Mackie and Hall, 1992b), 77 and 59% of the TCA remained after 3 and 6 months, and after 6 months 4.3 and 13.2% of the applied radioactivity was from $^{14}CO_2$ and bound $^{14}$C residues respectively. The adsorption and desorption of [$^{14}$C]TCA by sand, sandy loam, silt-clay loam and a clay-loam at 4 concentrations for each soil was reported by Mackie and Hall (1992c). Freundlich isotherms showed high adsorption capacities, resulting in incomplete desorption, which increased with increasing soil cation-exchange capacity, and clay and organic matter content.

Residues of both tecnazene and TCA are lost fairly rapidly from soil in the field, mainly by volatilization.

A clay and a sandy soil were treated with tecnazene (200 mg/kg wet soil) or potato washing sludge (containing 53, 29 and <LOD mg/kg tecnazene, TCA and TCTA respectively). The concentrations of TCTA increased and those of tecnazene decreased with time in both sludge- and tecnazene-treated soils while TCA decreased in the sludge-treated but increased in the tecnazene-treated soils (Sankey, 1993).

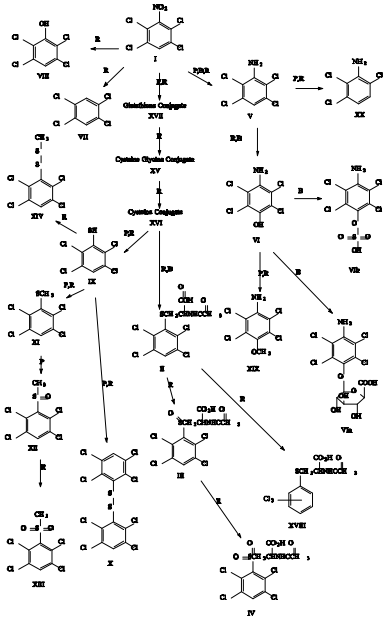


Figure 1. Proposed metabolic routes for tecnazene (I) in rats (R), rabbits (B) and potatoes (P).

### Environmental fate in water/sediment systems

Tecnazene and TCA were kept separately in aqueous solutions, buffered at pH 5, 7 and 9, at 25°C for 30 days. No hydrolysis of either compound occurred (Lewis and Goodyear, 1991; Mamouni, 1992).

The behaviour of radiolabelled tecnazene and TCA has been studied in soil sediment/water systems under anaerobic conditions for periods up to three months. Residues of tecnazene rapidly decreased by volatilization, adsorption and anaerobic degradation in the bottom sediment; the half-life was less than four weeks. TCA was also rapidly lost from the aqueous phase, mainly by volatilization and adsorption to the sediment (Roberts *et al*., 1992; Mackie and Hall, 1992d).

## METHODS OF RESIDUE ANALYSIS

### Extraction

In the metabolism studies [$^{14}$C]tecnazene was applied to potatoes as in commercial practice, and the stored potatoes were extracted with acetonitrile/water and partitioned with hexane. This was shown to transfer all the tecnazene and the major metabolites TCA and TCTA, as well as trichloroaniline, into the hexane phase. Similar solvent extraction procedures are used in the following methods of residue analysis, indicating that they are efficient in removing weathered residues of tecnazene and its metabolites. Furthermore, the residue levels of tecnazene and its metabolites determined by $^{14}$C counting in the metabolism studies were in general agreement with levels determined by chemical analysis.

### Analytical methods

Two methods of analysis of residues of tecnazene in potatoes are widely used.

(a) Gas chromatography with electron capture detection

Chopped samples of potatoes were macerated and extracted with light petroleum and ethanol. After filtration and clean-up by partitioning with sodium chloride and sodium carbonate solutions, the organic layer was dried and an aliquot injected into a gas chromatograph equipped with an electron-capture detector. The external standard method was used to calculate the residue concentration.

Recoveries were reported to be between 80 and 100% from samples spiked in the range 0.5-20.0 mg/kg. The limit of determination was 0.01 mg/kg (Bullock and Connolly, 1991; Swaine *et al*., 1982).

An alternative extraction with methanol followed by partition into toluene (Byast, 1989) has been used. Whole tubers, peel and pulp spiked at 0.53-0.58 mg/kg were analyzed by this method and recoveries ranged between 106 and 116% for all samples.

Kennedy (1990) reported a method for determining TCA and TCTA in the presence of tecnazene. Potatoes were macerated with acetone and cleaned up by partition and adsorption

chromatography on neutral alumina. Quantification was with an external standard. Limits of determination were 0.05 mg/kg TCA and 0.01 mg/kg TCTA. Mean recoveries of both analytes were 83-137% from whole tubers spiked with 0.1-1.0 mg/kg TCA or 0.05-0.5 mg/kg TCTA, and 107-115%.from pulp spiked with 0.1-0.2 mg/kg TCA and 0.05-0.1 mg/kg TCTA.

Problems were encountered with this method, especially with low levels of TCA in the presence of high residues of tecnazene. The close retention times of the two compounds under the chromatographic conditions used, the lower response of the detector to TCA than to tecnazene and the presence in some control extracts of coextractives that interfered with the analysis, may make the method unreliable for the general determination of TCA and TCTA.

An improvement was achieved by using hexane as the extracting solvent. The final determination was with 2,4,6-tribromoaniline as an internal standard. Recoveries were mainly in the range 94-100%, with one high batch giving a mean of 120%, (Harland *et al.*, 1993).

(b) HPLC with UV detection

In this procedure, macerated potato samples are extracted with hexane/acetone, and the hexane layer is separated and repeatedly washed with water to remove residual acetone. An aliquot of the hexane is analysed by normal-phase HPLC (Spherisorb S5 CN column) with hexane as the mobile phase.

This method was found to be suitable for the simultaneous determination of tecnazene, TCA and TCTA, all with LODs of 0.01 mg/kg. Mean recoveries from 12 samples of potatoes each spiked with tecnazene, TCA and TCTA were 94% (SD 9.3%), 95% (SD 6.2%) and 93% (SD 5.8%) respectively (Stanley, 1993).

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

Potatoes were normally transported unfrozen from the potato store to the analytical laboratory. If not already washed they were stored at 4°C in the dark until washed, usually within one day of receipt. After this, potatoes or potato macerates were kept deep frozen at or below -18°C until analysed.

Tecnazene is relatively stable chemically and is reduced to TCA only under anaerobic conditions. The amounts of TCA found on storing tecnazene for periods up to six months at 7-8°C were reported to be very small. Tecnazene and TCA are both stable to water at 20-25°C and pH 5-9. The major losses of tecnazene occur through volatilization. The vapour pressure of tecnazene is markedly dependent on temperature and at -18°C or below would be expected to be negligible, as would any enzymic degradation. Tecnazene and its main degradation products TCA and TCTA were therefore expected to be stable under these conditions. No separate storage stability studies were conducted on frozen samples.

Samples for peeling or cooking were normally kept at 4°C in the dark, usually for no more than a few days. Because of the length of normal storage periods, this additional storage was not expected to influence the results.

Harland *et al.*, (1993) stored washings from tecnazene-treated potatoes at 4°C and analyzed subsamples at several intervals up to 6 weeks. Residue levels of TCA were initially very low (<0.5 mg/l) but increased to 11 mg/l after 6 weeks storage. Tecnazene residues remained nearly constant at 150 mg/l over the same period.

## USE PATTERN

The only use of tecnazene now supported by the manufacturer is the post-harvest application of granular or dust formulations to potatoes (ICI Agrochemicals, 1990).

Tecnazene is applied to potatoes for the control of sprouting and the prevention of weight loss in store. It also controls dry rot (*Fusarium* spp.) and reduces levels of skin spot (*Polyscaytalum pustulans*), gangrene (*Phoma exigua* spp.) and silver scurf (*Helminthosporium solani*). Tecnazene is only applied to potatoes, post-harvest, intended for long-term storage (4-6 months). This use is registered in the UK and tecnazene is currently marketed in a range of granular and dust formulations by various UK-based companies.

The granular formulations contain 5% or 10% and the dusts 3% or 6% of tecnazene. Some of the products also contain thiabendazole or carbendazim. Formulations for which label information was provided are listed in Table 5.

Table 5. Label recommendations for uses of tecnazene.

| Company and formulation | Label information |
|---|---|
| **Zeneca** | |
| Fusarex | granules - 10% w/w tecnazene - 1.25 kg/t |
| Fusarex | dust - 6% w/w tecnazene - 2.25 kg/t |
| MSD Agvet | |
| Storaid dust | dust - 6% tecnazene + 1.8% thiabendazole (TBZ) - 0.135 + 0.041 kg ai/t |
| Storite SS | spray - 0.3 kg tecnazene + 0.1 kg TBZ - 0.12 + 0.04 kg ai/t |
| **Agrichem** | |
| Tubostore | granules - 10% tecnazene - 0.125 kg ai/t |
| New hystore | granules - 5% tecnazene - 0.125 kg ai/t |
| Hystore 10 | granules - 10% tecnazene - 0.125 kg ai/t |
| Hytec | dust - 3% tecnazene - 0.135 kg ai/t |
| Hytec 6 | dust - 6% tecnazene - 0.135 kg ai/t |
| Tubodust | dust - 6% tecnazene - 0.135 kg ai/t |
| Hytec super | dust - 6% tecnazene + 1.8% TBZ - 0.135 +0.041 kg ai/t |
| **Atlas interlates** | |
| Tecgran 100 | granules - 10% tecnazene - 0.125 kg ai/t |
| Tecnazene 6% dust | dust - 6% tecnazene - 0.135 kg ai/t |
| **Hickson & Welsch** | |
| Hickstor 5 | granules - 5% tecnazene - 0.125 kg ai/t |
| Hickstor 10 | granules - 10% tecnazene - 0.125 kg ai/t |
| Hickstor 3 | dust - 3% tecnazene - 0.135 kg ai/t |
| Hickstor 6 | dust - 6% tecnazene - 0.135 kg ai/t |
| Hickstor TBZ6 | dust - 6% tecnazene + 1.8 TBZ - 0.135 kg + 0.041 ai/t |
| Hickstor 6 + MBC | dust - 6% tecnazene +2% carbendazim - 0.135 + 0.045 kg ai/t |

NOTE. The recommended use pattern for TBZ on stored potatoes is one application at 42 g ai/t (JMPR 1977, Table 1, p.443) and for carbendazim (JMPR 1988, Table 1, p.44) 25 g ai/t. The 45 g ai/t used in the Hickstor 6 + MBC formulation greatly exceeds the recommended rate evaluated by the JMPR for the use of carbendazim on stored potatoes (JMPR 1988, p.44).

The products are applied to give 0.125 kg ai as granules or 0.135 kg ai as dust per tonne of potatoes. Thus, a 10% granule formulation would be applied at 1.25 kg product/tonne and a 6% dust at 2.25 kg product/tonne.

This maximum application rate and a minimum 6-week interval between application and sale are statutory requirements in the UK. Only one application to each crop is permitted.

About two-thirds of the annual potato production in the UK is stored and approximately 12.5% of that is treated with tecnazene-based products.

The use and importance of tecnazene to the UK grower for the long-term storage of quality potatoes has been reviewed (Gibbard, 1992).

## RESIDUES IN POTATOES RESULTING FROM SUPERVISED TRIALS

After opening the storage facilities, potatoes are normally washed before distribution to the market. Residue levels of tecnazene in washed potatoes vary according to the period for which they are stored and the extent of washing. Residues previously reported and evaluated by the JMPR are shown in Table 6, together with results not previously reviewed (Byast, 1989).

In the trials carried out in 1982, the maximum residues of tecnazene found in the washed tubers were 7.9, 9.3 and 6.3 mg/kg for the 3% dust, 6% dust and 10% granule respectively, with little difference between the ranges from the three formulations (Swaine, 1982).

In 1989, a 6% dust and 10% granule were used for treating potatoes for 42-56 days and 117-181 days storage. The samples showed ranges of 1-7.4 mg/kg (mean 6.2 mg/kg) and 2.2-8.5 mg/kg (mean 4.9 mg/kg) tecnazene (Dick *et al*., 1989a).

In a separate trial carried out in 1989, tecnazene was applied to potatoes in commercial storage facilities with the 6% dust and/or 10% granule formulation, and tubers were analysed after 6, 9, 12 and 126-133 days (normal opening).

Residues of tecnazene in the washed tubers are shown in Table 6. They were highest (7.8 and 8.5 mg/kg) at the end of the normal storage period of 126-133 days (Byast, 1989).

In a series of supervised residue trials (Table 7) potatoes were treated at commercially recommended rates (116-135 g ai/tonne) with a variety of dust (3% and 6%) and granular (5% and 10%) formulations using mechanical applicators at ten commercial potato storage facilities located in four major potato growing areas of the UK, selected to represent box, bulk ambient and controlled environment stores (Leaper, 1993a).

In a further series of unsupervised trials (Table 8; Leaper, 1993b), 12 commercial stores were selected, as before, to achieve a wide variety of locations and storage procedures involving a range of commercial varieties of second, early, and main-crop potatoes. In both sets of trials samples of potatoes were taken for analysis from the top, middle and bottom of the clamps at normal clamp opening 90-205 days (12-30 weeks) after treatment. Potatoes from the supervised trials were also taken from the top of the clamps 42 days after treatment (Table 9).

Table 6. Residues of tecnazene in washed whole potatoes following treatment with different formulations after various storage periods.

| Storage period (days) | Residues of tecnazene (mg/kg) | | | Reference |
|---|---|---|---|---|
| | 3% dust | 6% dust | 10% granules | |
| 60 | 1.5-3.4(2.4) | - | - | JMPR 1981 |
| 90 | 4.0-5.0 (4.7) | - | - | (Bullock & Cole, 1980) |
| 120 | 2.1-4.8 (3.4) | - | - | |
| 42 | 1.2-7.9 | 0.8-9.3 | 0.7-6.3 | JMPR 1989 |
| 84 | 1.6-2.8 | 1.5-4.6 | 1.1-4.6 | (Swaine, 1982) |
| 112 | 3.1-3.4 | 2.4-3.2 | 3.0-4.0 | |
| 42-56 | - | 1.0-7.4 | 1.4-4.3 | JMPR 1989 |
| 117-181 | - | 2.2-7.6 | 4.8-8.5 | (Dick et al., 1989) |
| 42 | - | 3.1, 3.3 | 2.7 | Byast, 1989 |
| 63 | - | 2.2, 1.8 | 4.3 | |
| 84 | - | 2.1, 4.8 | 2.8 | |
| 126-133 | - | 8.5 | 7.8 | |

The residues of tecnazene after 42 days (the shortest period allowed by GAP) ranged between 2.2 and 9.4 mg/kg (average 6.5 mg/kg) and those of TCA and TCTA averaged 0.045 and 0.036 mg/kg respectively. Potatoes were transported unfrozen to the analytical laboratory within 24 hours of sampling, together with untreated control potatoes. The potatoes were stored at 4°C in the dark until washed, usually within one day of receipt, then deep frozen unless required for cooking. Samples for cooking were kept at 4°C, mostly for no more than one day, before cooking, baking or microwave cooking.

The mean tecnazene residue in the washed potatoes increased from 2.7 mg/kg on the day of application to 6.5 mg/kg after 42 days, but remained at approximately this level (mean 6.8 mg/kg) after further storage, which varied from 50 to 163 days depending upon when the store was opened and the crop sold.

Only three residues of tecnazene were above 10 mg/kg and two of these (14 and 18 mg/kg) were from the same store which was maintained at 5°C for 205 days: low temperature storage is not normal but can occur in practice.

The mean residues of TCA increased from 0.05 to 0.13 mg/kg between six weeks after treatment the final store opening. The corresponding residues of TCTA were 0.04 and 0.06 mg/kg. The mean residues of TCA and TCTA immediately after the application of tecnazene to the potatoes were 0.012 mg/kg and less than the LOD of 0.01 mg/kg. Generally the potatoes stored for the longest periods had the highest levels of TCA and TCTA. The residues of tecnazene, TCA and TCTA were not consistently related to the sampling position (top, middle or bottom) within the store (Tables 7 and 8). Varietal differences were not evident among the 12 varieties studied (Sante, Maris Piper, Cara, Pentland Dell, Desiree, Wilja, Cutra, Estima, Marfona, Pentland Squire, and Kondor) (Harland *et al*., 1993; Stanley, 1993).

Table 7. Tecnazene, TCA and TCTA residues in whole washed potatoes from supervised trials (1991) at normal store opening (92-205 days).

| Trial no. | Sampling location | Residue (mg/kg) | | |
|---|---|---|---|---|
| | | Tecnazene | TCA | TCTA |
| 1 | Top | 6.0 | 0.15 | 0.045 |
| | Middle | 7.5 | 0.11 | 0.03 |
| | Bottom | 7.9 | 0.12 | 0.02 |
| 2 | Top | 6.9 | 0.14 | 0.06 |
| | Middle | 6.6 | 0.14 | 0.05 |
| | Bottom | 5.7 | 0.08 | 0.04 |
| 3 | Top | 8.4 | 0.18 | 0.15 |
| | Middle | - | - | - |
| | Bottom | - | - | - |
| 4 | Top | 7.7 | 0.20 | 0.07 |
| | Middle | 6.8 | 0.16 | 0.06 |
| | Bottom | 7.3 | 0.18 | 0.07 |
| 5 | Top | 5.7 | 0.09 | 0.08 |
| | Middle | 7.5 | 0.09 | 0.08 |
| | Bottom | 2.4 | 0.03 | 0.04 |
| 6 | Top | 6.1 | 0.08 | 0.10 |
| | Middle | 5.8 | 0.06 | 0.09 |
| | Bottom | 4.3 | 0.08 | 0.07 |
| 7 | Top | 4.5 | 0.02 | 0.02 |
| | Middle | 7.6 | 0.03 | 0.02 |
| | Bottom | 7.5 | 0.02 | <0.01 |
| 8 | Top | 9.8 | 0.16 | 0.08 |
| | Middle | 18 | 0.16 | 0.09 |
| | Bottom | 16 | 0.11 | 0.07 |
| 9 | Top | 7.4 | 0.13 | 0.04 |
| | Middle | 7.7 | 0.37 | 0.08 |
| | Bottom | 7.2 | 0.21 | 0.05 |
| 10 | Top | 6.4 | 0.05 | 0.05 |
| | Middle | 8.1 | 0.06 | 0.05 |
| | Bottom | 7.9 | 0.10 | 0.05 |

Table 8. Tecnazene, TCA and TCTA residues in whole washed potatoes from unsupervised trials (1991) at normal store opening (92-205 days).

| Trial no. | Residues (mg/kg) composite of top, middle and bottom | | |
|---|---|---|---|
| | Tecnazene | TCA | TCTA |
| 11 | 5.0 | 0.04 | 0.02 |

| Trial no. | Residues (mg/kg) composite of top, middle and bottom | | |
|---|---|---|---|
| | Tecnazene | TCA | TCTA |
| 12 | 8.7 | 0.05 | 0.03 |
| 13 | 4.5 | 0.04 | 0.03 |
| 14 | 4.3 | 0.29 | 0.06 |
| 15 | 4.9 | 0.03 | 0.02 |
| 16 | 14 | 0.12 | 0.16 |
| 17 | 6.2 | 0.09 | 0.04 |
| 18 | 7.7 | 0.55 | 0.12 |
| 19 | 9.1 | 0.55 | 0.17 |
| 20 | 6.6 | 0.21 | 0.18 |
| 21 | 10 | 0.41 | 0.16 |
| 22 | 6.4 | 0.22 | 0.11 |

## FATE OF RESIDUES IN STORAGE AND PROCESSING

### In Storage

Since tecnazene is used only as a post-harvest treatment for stored potatoes, the fate of residues in storage has been fully discussed above.

### In Processing

The normal commercial procedure after releasing potatoes from storage is to wash the tubers to remove adhering soil and debris. Results reported to the JMPR in 1978, 1981 and 1989 showed that washing removed a significant amount of the tecnazene residue, that most of the residue was in the skin, and that peeling effectively removed over 90% of the residue. Boiling, baking or frying peeled or unpeeled potatoes also reduced residues of tecnazene still further (FAO/WHO, 1979, 1982, 1990). The evidence to support these conclusions was mainly presented in reports by Bullock and Burgess (1973), Bullock and Cole (1980), Dick *et al*. (1989a,b) and Swaine *et al*. (1982).

Residues in peeled potatoes were reduced by 19-35% by boiling, 22-33% by conventional oven baking and 72-74% by microwave baking. Residue levels after frying were similar to those in the peeled potatoes but represented a reduction of about 45% of the total residue in the commodity (Dick *et al*., 1989b).

A later study, not previously reported to the JMPR, reported the reduction of the total amount of tecnazene after boiling, baking or frying (without peeling) when the weight loss on cooking was taken into account. The reduction of tecnazene was least for boiling (0-31%) and greatest for frying potato chips without peeling (78-94%) (Rose, 1989).

A metabolism study on potatoes treated with [$^{14}$C]tecnazene showed that the residues of tecnazene in washed potatoes increased with storage and confirmed that the residue was mainly (90%) associated with the peel (Table 1).

In more detailed cooking studies, using potatoes treated and stored under normal commercial conditions, the potatoes were analysed for TCA and TCTA, as well as tecnazene (Table 9).

Cooking by boiling in skin, oven baking or microwave baking reduced tecnazene residue levels. The mean residues after cooking by the three procedures were 2.1, 1.6 and 2.5 mg/kg respectively, showing a reduction of over 60% of the mean residue of 6.8 mg/kg in uncooked whole potatoes. The

effect of cooking on residues of TCA and TCTA was less clear (Harland *et al.*, 1993; Stanley, 1993).

Table 9. Residues of tecnazene and its metabolites in whole potatoes and cooked samples from supervised trials.

| Storage time or treatment | Residues, range and (mean), mg/kg | | |
|---|---|---|---|
| | Tecnazene | TCA | TCTA |
| 42 days | 2.2-9.4 (6.5) | 0.017-0.07 (0.045) | 0.01-0.12 (0.04) |
| 90-205 days (normal store opening) | 2.4-18.0 (6.8) | 0.022-0.55 (0.13) | <0.01-0.18 (0.06) |
| Boiled (18 samples) | 0.89-5.0 (2.1) | 0.03-0.37 (0.12) | <0.01-0.09 (0.05) |
| Baked (18 samples) | 0.19-3.6 (1.6) | 0.01-0.32 (0.17) | 0.02-0.36 (0.09) |
| Microwave cooked (16 samples) | 0.84-3.8 (2.5) | 0.01-0.44 (0.13) | <0.01-0.15 (0.06) |

Lewis (1992) examined the effects of boiling, oven-baking and microwave-baking on potatoes treated with [$^{14}$C]tecnazene and stored for 140 days at 8°C, then 69 days at 15°C to increase the rate of metabolism and facilitate the identification of metabolites. Potatoes were washed thoroughly before processing. After cooking, $^{14}$C residues in the whole potatoes were approximately 30 mg/kg tecnazene equivalents, of which approximately 5 mg/kg was parent tecnazene. Residues of TCTA and TCA were about 3 and 1 mg/kg respectively in oven-baked potatoes but both <1 mg/kg in microwave-baked and boiled potatoes.

Residues of tecnazene and TCA remained more or less the same during cooking except in oven-baked potatoes where the TCTA residues increased, possibly by thermal degradation of polar glutathione conjugates. As discussed previously the metabolism study showed a complex mixture of at least 25 polar metabolites which represented the balance of the $^{14}$C in the potatoes. No individual metabolite exceeded 10% of the residues (Goodyear, 1992).

## RESIDUES IN POTATOES IN COMMERCE OR AT CONSUMPTION

Between April 1988 and December 1990, tecnazene, TCA and TCTA residues in potatoes in the UK were determined as part of the UK Food Surveillance Programme. The fourth report of the Working Party on Pesticide Residues indicates that during the above period tecnazene residues were found in about 50% of the UK main-crop potato samples analysed (62 samples were analysed in 1988, 57 in 1989 and 80 in 1990) and 5 mg/kg was exceeded in only two 1988 samples. The ranges in the 1989 and 1990 samples were not detected (ND) to 2.7 mg/kg and ND to 4.3 mg/kg respectively (Her Majesty's Stationery Office, 1992a).

Residues of TCA and TCTA were both <0.2 mg/kg. These results support the findings of metabolism studies and recent (1991) supervised and unsupervised field trials according to commercial practice (Tables 7 and 8).

The third annual report of the Working Party on Pesticide Residues, covering the period January to December 1991, includes the results of monitoring potatoes for tecnazene and other post-harvest chemicals (Her Majesty's Stationery Office, 1992b). The data on tecnazene and its metabolites TCA and TCTA taken from Table 8 of the report are reproduced below (Table 10). The pattern of tecnazene residues found in 1991 was similar to that in the previous year, with 45% of main-crop potatoes showing residues compared with 49% in 1990. 38% of the samples contained tecnazene in the range 0.01-1 mg/kg, 6% in the range 1.1-4.6 mg/kg and only one sample (5.5 mg/kg) exceeded 5 mg/kg. Residues of both TCA and TCTA were either undetectable (<0.01 mg/kg) or very low (<0.05

mg/kg).

Table 10. Tecnazene and metabolite residues in retail samples of potatoes (1991).

| Residue | Concentration range (mg/kg) | No. of samples in range |
|---|---|---|
| Tecnazene | <0.01[1] | 97 |
| | 0.01-1 | 67 |
| | 1.1-4.6 | 11 |
| | 5.5 | 1 |
| 2,3,5,6-Tetrachloroaniline (TCA) | <0.01[1] | 149 |
| | 0.01-0.1 | 15 |
| | 0.1-0.5 | 12 |
| 2,3,5,6-Tetrachlorothioanisole (TCTA) | <0.01[1] | 151 |
| | 0.01-0.08 | 25 |

[1] Not detected

## NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was informed that the MRL for tecnazene in potatoes (washed before analysis) in the UK is 10 mg/kg.

## APPRAISAL

Tecnazene was reviewed by the JMPR in 1974, 1978, 1981, 1983, 1987 and 1989. Although CXLs exist for head lettuce and witloof chicory, the only use of tecnazene now supported by the manufacturer is for the post-harvest application of granular or dust formulations to potatoes as a sprout suppressant and fungicide.

A TMRL of 1 mg/kg was recommended for potatoes (washed before analysis) by the 1978 JMPR. Additional residue data were reviewed by the 1989 JMPR which recommended an MRL of 10 mg/kg for potatoes washed before analysis.

The 1989 Meeting noted that residues of tecnazene in the pulp of treated, uncooked potatoes would generally be less than 1 mg/kg and that further losses occurred during normal cooking, but drew attention to the high levels, up to nearly 100 mg/kg, that could be attained in the peel of treated potatoes.

Tecnazene has been extensively debated at the CCPR in 1990, 1991 and 1992, with several countries expressing reservations concerning the definition of the residue, the quality of the residue data, the interpretation of GAP and toxicological aspects.

Additional updated information on use patterns for tecnazene on potatoes, data on residues resulting from supervised trials, on the fate of residues in metabolism and processing, and on residues in food in commerce were provided for evaluation.

New, more detailed, studies of metabolism in the rat confirmed earlier studies and showed results comparable to those found in other species (rabbit, guinea pig and pigeon). Tecnazene was shown to be extensively metabolized and excreted in laboratory animals, mainly via glutathione

conjugation.

The major routes of metabolism of tecnazene in stored potatoes involve both reduction to 2,3,5,6-tetrachloroaniline (TCA) and initial glutathione conjugation with subsequent catabolism. The major component of the residue was tecnazene (64%); TCA and 2,3,5,6-tetrachlorothioanisole (TCTA) were minor components (<1%). A more significant (10%) multicomponent water-soluble fraction could be hydrolysed to 2,3,5,6-tetrachlorothiophenol and was apparently derived from initial glutathione conjugates. The water-soluble metabolites were similar to those in rats.

Peeling removed more than 90% of the residue from treated potatoes, and all methods of cooking reduced residue levels further. The extent of the loss of tecnazene on cooking depended on whether peeled or unpeeled potatoes were used, but was ≥20%.

Post-harvest residue trials were carried out in the UK in 1991 with potatoes treated according to GAP (116-135 g ai/tonne, nominal treatment rate 125 g ai/tonne). Samples were analyzed for tecnazene and the metabolites TCA and TCTA at 92-205 days after treatment (at normal store opening). Residues of TCA and TCTA were 0.02-0.55 mg/kg (average 0.13 mg/kg) and <0.01-0.18 mg/kg (average 0.059`mg/kg) respectively; residues of tecnazene ranged from 2.4 to 18 mg/kg (average 6.8 mg/kg). In treated tubers analyzed 42 days after treatment (42 days is the minimum post-treatment period for removal for use according to GAP) residues of TCA, TCTA and tecnazene, ranges and (means), were 0.017-0.07 (0.045), 0.01-0.12 (0.036) and 2.2-9.0 (6.5) mg/kg respectively.

In summary, ten supervised residue trials showed tecnazene residues from 2.4 to 18 mg/kg in potatoes treated and stored according to GAP, with an average of 6.8 mg/kg. Considerable variations are possible during application, during storage under varying conditions, and in the washing of tubers before analysis. From these considerations, the Meeting concluded that an MRL of 20 mg/kg would be required to cover residues of tecnazene in potato tubers resulting from the post-harvest treatment of potatoes for storage according to GAP, and recommended accordingly.

The Meeting concluded that the residue should be defined as "tecnazene", because the parent compound alone is a good indicator of the total residue and of use according to GAP.

Extensive retail monitoring data in the UK are available for tecnazene. In the most recent survey of 256 potato samples in 1991, tecnazene was not found (<0.01 mg/kg) in 55% of the samples and was ≤1 mg/kg in 95% of the samples. The highest tecnazene residue found was 5.5 mg/kg. TCA and TCTA were found in only about 10% of the samples, the highest levels being 0.5 mg/kg of TCA and 0.08 mg/kg of TCTA.

Potato metabolism and processing studies have shown that 90% of the terminal residues are in the tuber peel. Peels contained up to 47 mg/kg of total residues (66% as tecnazene). The Meeting noted that potato culls, waste, protein concentrates and bakery products were also used as livestock feeds.

No ruminant metabolism or lactating ruminant feeding studies were available. The Meeting was unable to estimate the possible transfer of residues to the meat or milk of cattle.

## RECOMMENDATIONS

On the basis of the new residue data on the post-harvest use of tecnazene on potatoes the Meeting recommended the MRL shown below.

Definition of the residue: tecnazene

| CCN | Commodity | MRL (mg/kg) |
|---|---|---|
| VR 0589 | Potato | 20 Po (washed before analysis) |

The present CXL is 1 mg/kg and there is a proposed amendment at Step 7C of 10 mg/kg.

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