2,4-D (20)

EXPLANATION

2,4-D was first evaluated in 1970 (T, R), and the last evaluations are from 1986/87 (R) and 1996 (T). The 1997 JMPR evaluated effects on the environment.

2,4-D was proposed for re-evaluation by the Working Group on Priorities at the 1989 CCPR as the ADI was established before 1976 (ALINORM 89/24A, para 299 and Appendix V). It was stated at the 1990 CCPR that there was continued use and manufacturers might be able to submit data (ALINORM 91/24 para 360, Appendix V part I). The review was tentatively scheduled for 1994. The compound was later rescheduled to the 1996 JMPR, and then to the 1998 Meeting.

The present evaluation is within the CCPR Periodic Review Programme.

The members of the industry taskforce which supplied most of the information were AGRO-GOR, Dow Elanco, Nufarm and Rhône Poulenc, who provided data on metabolism and environmental fate, analytical methods, use patterns, residue trials and national MRLs. Information on residue analytical methods, GAP and national MRLs was also provided by the government of The Netherlands.

IDENTITY (Free acid)

ISO common name: 2,4-D
Chemical name

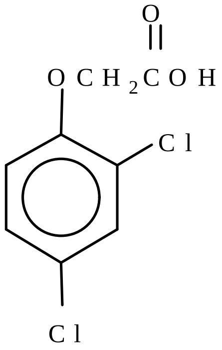
IUPAC: 2,4-dichlorophenoxyacetic acid

CA: (2,4-dichlorophenoxy)acetic acid

CAS Registry No.: 94-75-7

CIPAC No.: 1

Structural formula:



Molecular formula: $C_8H_6Cl_2O_3$

Molecular weight: 221.0

Physical and chemical properties

Pure active ingredient

Appearance: white to brown crystals, granules, flakes, powder or lumps

Vapour pressure: 1.9×10^{-5} Pa at 25°C (Chakrabarti and Gennrich, 1987a)

Melting point: 140.5°C

Octanol/Water partition coefficient at 25°C:
log P_{OW} = 2.7 at pH 1; 0.18 at pH 5; -0.83 at pH 7; -1.01 at pH 9
(Bailey and Hopkins, 1987)

Solubility: in water at 25°C (Hopkins,1987c)

pH 1 buffered	311 ± 4 mg/l
pH 5 buffered	20031± 1149 mg/l
pH 7 buffered	23180 ±590 mg/l
pH 9 buffered	34196 ± 1031 mg/l
pH 5 unbuffered	29934 ± 2957 mg/l
pH 7 unbuffered	44558 ± 674 mg/l
pH 9 unbuffered	43134 ± 336 mg/l

Hydrolysis: stable at pH 5, 7, 9 at 25°C (Anon. 1989a)

Photolysis: aqueous photolysis pH 7 $t_{1/2}$ = 13 days (Anon. 1989b)
soil photolysis very stable

Rate of dissociation: ~200 minutes at 25°C

Dissociation constant: pK_a 3 at 25.2°C (Reim, 1989a; Gallacher, 1991)

Thermal stability: stable at melting point

Technical material

Minimum purity: 96%

Main impurities:

water	1.5% max.
free phenols	0.3% max. (calculated as 2,4-dichlorophenol)
sulphated ash	0.5% max.
triethanolamine insolubles	0.1% max.

Melting range: 137-141°C

Stability: stable indefinitely

Formulations

Commercially available formulations: TC, WP, SP, WG. Also compounded as alkali metal salts, organic amines and esters.

IDENTITY (dimethylamine salt)

ISO common name: 2,4-D-dimethylamine

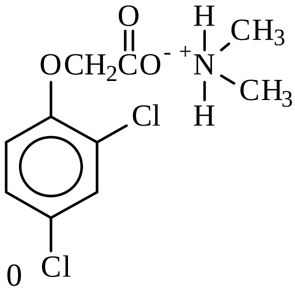
Chemical name
IUPAC: dimethylamine (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, dimethylamine salt

CAS Registry No.: 2008-39-1

CIPAC No.: 1

Synonyms: 2,4-D DMA

Structural formula:



Molecular formula: $C_{10}H_{13}Cl_2NO_3$

Molecular weight: 266.13

Physical and chemical properties

Pure active ingredient

Appearance: amber to brown liquid; white to brown crystals or powder

Vapour pressure: <1.33 x 10^{-5} Pa at 26°C (Douglas, 1993a; MacDaniel and Weiler, 1987)

Octanol/Water partition coefficient: refer to 2,4-D acid

Solubility (water: Hopkins, 1987a,b; organic solvents: Kinnunen, 1994a):

water	pH 5	320632 ± 3645 mg/l at 25°C
	pH 7	729397 ± 86400 mg/l at 25°C
	pH 9	663755 ± 94647 mg/l at 25°C
acetonitrile		1.02 g/100 ml at 20°C
methanol		>50 g/100 ml at 20°C
hexane		3.59 g/100 ml at 20°C
1-octanol		5.37 g/100 ml at 20°C
toluene		0.165 g/100 ml at 20°C

Specific gravity: 1.23 - 1.24 g/cm^3 at 20°C (Dow Chemical Co., 1989a)

Hydrolysis: refer to 2,4-D acid

Photolysis: refer to 2,4-D acid

Rate of dissociation: <1 minutes

Thermal stability: stable

pH: 6.8 -9

Technical material

Minimum purity: to be prepared from 2,4-D acid 96% min.

Main impurities: proportional to 2,4-D content except water

Melting range: 118–120°C ± 1°C (Murphy, 1993a)

Formulations

Commercially available formulations: TK, SL, SP.

IDENTITY (2-ethylhexyl ester)

ISO common name: 2,4-D-ethylhexyl

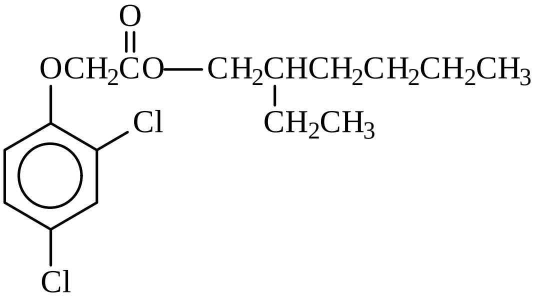
Chemical name
IUPAC: 2-ethylhexyl (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, 2-ethylhexyl ester

CAS Registry No.: 1928-43-4

CIPAC No.: 1

Synonyms: 2,4-D EHE

0
Structural formula:



Molecular formula: $C_{16}H_{22}Cl_2O_3$

Molecular weight: 333.27

Physical and chemical properties

Pure active ingredient

Appearance: amber to brown liquid

Vapour pressure: 4.8×10^{-4} Pa at 25°C (Chakrabarti and Gennrich, 1987b)

Boiling point: >200°C under degradation (Kinnunen, 1994b)

Octanol/Water partition coefficient: log $P_{OW} = 5.78$ at 25°C (Helmer, 1987a)

Solubility: water 0.0867 mg/l at 25°C (Helmer, 1987b)
industrial water 0.0324 ± 0.0032 mg/l at 12°C (Potter, 1990)

Specific gravity: 1.152 g/cm^3 at 20°C (Dow Chemical Co., 1989b)

Hydrolysis: in sterile aqueous solutions at 25°C (Concha *et al.*, 1993a):
pH 5 $t_{1/2}$ 99.7 days
pH 7 $t_{1/2}$ 48.3 days
pH 9 $t_{1/2}$ 52.2 hours
in natural water (river water) pH 7.8 at 25°C:
$t_{1/2}$ 6.2 hours
in soil slurries at 25°C (Concha *et al.*, 1993b):
$t_{1/2}$ in Catlin silty clay soil slurry 1.25 hours
$t_{1/2}$ in Hanford sandy loam soil slurry 1.45 hours

Photolysis: sterile aqueous photolysis 25°C $t_{1/2}$ 128 days (Concha and Shepler, 1993b)
UV stable (Schriber and Tiszai, 1991)

Technical material

Minimum purity: 92%

Main impurities: proportional to 2,4-D content except:
free acid 1.5% max., suspended solids 0.1% max., water 1% max.

Stability: no appreciable change in 2 years in sealed containers. will decompose before boiling.

Formulations

Commercially available formulations: TK, EC, EW and OL.

IDENTITY (diethanolamine salt)

ISO common name: 2,4-D-diethanolamine

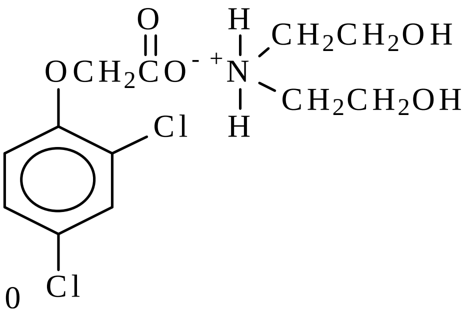
Chemical name
IUPAC: diethanolamine (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, diethanolamine salt

CAS Registry No.: 5742-19-8

CIPAC No.: 1

Synonyms: 2,4-D DEA

Structural formula:



Molecular formula: $C_{12}H_{17}Cl_2NO_5$
Molecular weight: 326.18

Physical and chemical properties

Pure active ingredient

Appearance: cream solid powder

Vapour pressure: $<1.33 \times 10^{-5}$ Pa at 25°C and 45°C (Douglas, 1993a)

Melting point: 83°C (Malone, 1993)

Octanol/Water partition coefficient: log $P_{OW} = -1.65$ at 25°C (Douglas, 1993b)

Solubility:

acetonitrile	47 mg/g	at 25°C
ethanol	280 mg/g	at 25°C
n-octanol	36 mg/g	at 25°C
water	806 mg/g	at 25°C (Douglas, 1993c)

Specific gravity: 0.762 g/cm^3 at 25.5°C (Wojcieck, 1992a)

Photolysis: stable under light

Rate of dissociation: 3 minutes at 25°C

Thermal stability: stable up to 150°C (Malone, 1993)

pH: 7.48 at 25°C (Furlong, 1992)

Technical material

No information was received.

FORMULATIONS

Commercially available formulations: SL.

IDENTITY (2-butoxyethyl ester)

ISO common name: 2,4-D-butoxyethyl

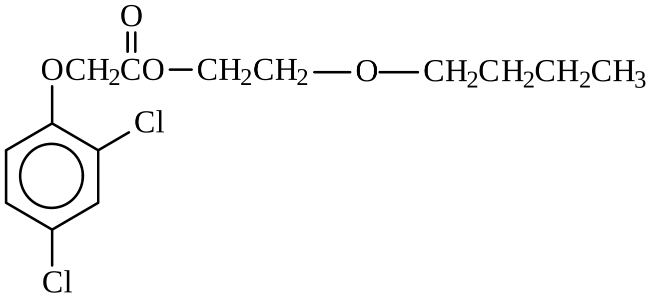
Chemical name
IUPAC: 2-butoxyethyl (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, 2-butoxyethyl ester

CAS Registry No.: 1929-73-3

CIPAC No.: 1

Synonyms: 2,4-D BEE

Structural formula:



Molecular formula: $C_{14}H_{18}Cl_2O_4$

Molecular weight: 321.20

Physical and chemical properties

Pure active ingredient

Appearance: amber liquid

Vapour pressure: 3.2×10^{-4} Pa at 25°C (Chakrabarti, 1989)

Boiling point: 89°C (Kinnunen, 1994c)

Octanol/Water partition coefficient: log $P_{OW} = 4.1$ at 25°C (Heimerl, 1990)

Specific gravity: 1.0 - 1.2 g/ml at 20°C (Dow Chemical Co., 1989c)

Hydrolysis: in sterile water buffered at 25°C (Shepler *et al.*, 1990)
pH5 $t_{1/2}$ 196 days
pH7 $t_{1/2}$ 74 days
pH9 $t_{1/2}$ 55 minutes
soil/water slurry (Racke, 1989)
61% hydrolysed in 20 minutes

Photolysis: (aqueous) $t_{1/2}$ 74 days, stable to photodegradation (Marx and Shepler, 1990)

Thermal stability: stable up to 50°C (Schriber, 1992)

Technical material

Minimum purity: 92.0%

Stability: stable for a minimum of 2 years in sealed container.

Formulations

Commercially available formulations: EC, TK.

IDENTITY (isopropylamine salt)

ISO common name: 2,4-D-isopropylamine

Chemical name

IUPAC: isopropylamine (2,4-dichlorophenoxy)acetate

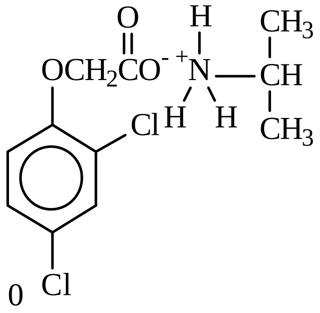
CA: (2,4-dichlorophenoxy) acetic acid, isopropylamine salt

CAS Registry No.: 5742-17-6

CIPAC No.: 1

Synonyms: 2,4-D IPA

Structural formula:



Molecular formula: $C_{11}H_{15}Cl_2NO_3$

Molecular weight: 280.04

Physical and chemical properties

Pure active ingredient

Appearance: amber liquid

Vapour pressure: $<1.33 \times 10^{-5}$ Pa (Chakrabarti, 1990a)
(salt decomposed in temperature range -3.9 to 24°C)

Octanol/Water partition coefficient: refer to 2,4-D acid

Melting point: 121°C ± 1°C (Murphy, 1993b)

Solubility (Kinnunen, 1994d):

water	pH5	17.4 g/100 ml
	pH7	43.6 g/100 ml
	pH9	33.1 g/100 ml
acetonitrile		2.1 g/100 ml

methanol	>50 g/100 ml
hexane	4.36×10^{-3} g/100 ml

Specific gravity: 1.15 g/ml at 20°C (Dow Chemical Co., 1989d)

Photolysis: refer to 2,4-D acid

Dissociation rate: <1 min at 21°C (Reim, 1989b)

Thermal stability: stable up to 50°C (Schriber, 1991a)

Technical material

Minimum purity: 48.4%

Stability: stable for minimum of 2 years in sealed container

Formulations

Commercially available formulations: SL.

IDENTITY (isopropylamine salt)

ISO common name: 2,4-D-isopropylamine

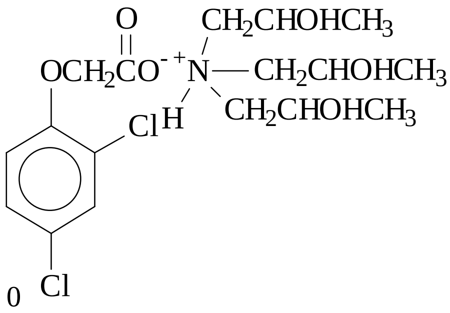
Chemical name
IUPAC: tri-isopropanolamine (2,4-dichlorophenoxy)acetate
CA: (2,4-dichlorophenoxy) acetic acid, tri-isopropanolamine salt

CAS Registry No.: 32341-80-3

CIPAC No.: 1

Synonyms: 2,4-D TIPA

Structural formula:



Molecular formula: $C_{17}H_{27}Cl_2NO_6$

Molecular weight: 412.31

Physical and chemical properties

Pure active ingredient

Appearance: amber liquid

Vapour pressure: <1.33 x 10^{-5} Pa at 14.2 - 28.0°C (Chakrabarti, 1990b)

Octanol/Water partition coefficient: refer to 2,4-D acid

Melting point: 88.0°C - 110.5°C (Kinnunen, 1994)

Solubility (Schriber, 1991b):

water	pH5	46.1 wt % ai
	pH7	46.1 wt % ai
	pH9	10.4 wt % ai
acetonitrile		12.3 wt % ai
acetone		11.7 wt % ai
n-octanol		7.6 wt % ai

Specific gravity: 1.2 g/ml at 20°C (Dow Chemical Co., 1989e)

Photolysis: refer to 2,4-D acid

Dissociation rate: <1 min at 21°C (Reim, 1989b)

Thermal stability: stable up to 50°C (Schriber, 1991c)

Technical material

Minimum purity: 68.8%

Melting range: 88°C - 110.5°C (Kinnunen, 1994e)

Stability: stable at minimum for 2 years in sealed container

Formulations

Commercially available formulations: SL.

IDENTITY (isopropyl ester)

ISO common name: isopropyl

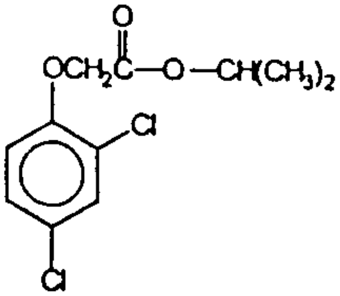
Chemical name
IUPAC: (2,4-dichlorophenoxy)acetate, isopropyl ester
CA: (2,4-dichlorophenoxy) acetic acid, isopropyl ester

CAS Registry No.: 94-11-1

CIPAC No.: 1

Synonyms: 2,4-D IPE

Structural formula:



Molecular formula: $C_{11}H_{12}Cl_2O_3$

Molecular weight: 263.12

Physical and chemical properties

Pure active ingredient

Appearance: light amber liquid

Vapour pressure: 1.87 Pa at 25°C (Fisher, 1989)

Octanol/Water partition coefficient: log P_{ow} = 4.2 at 25°C (Fisher, 1989)

Solubility: practically insoluble in water (Fisher, 1989)

Specific gravity: 1.25 g/cm^3 at 20°C (Fisher, 1989)

Hydrolysis:	under sterile conditions at 25°C		
	pH 5	no hydrolysis in 30 days	
	pH 7	$t_{1/2}$	89 days
	pH 9	$t_{1/2}$	22.4 hours (Burke, 1994a)

Thermal stability: stable to approximately 240°C (Fisher, 1989)

Technical material

Minimum purity: 92%

Main impurities: proportional to 2,4-D content (except free acid 1,5% max. suspended solids 0.1% max., water 1% max.)

Stability: no appreciable change in 2 years in sealed containers. Decomposes before boiling.

Formulations

Commercially available formulations: TK and EC.

METABOLISM AND ENVIRONMENTAL FATE

Metabolism and environmental fate studies were conducted with uniformly ring-^{14}C-labelled 2,4-D:

^{14}C-labelled 2,4-dichlorophenoxyacetic acid ([^{14}C]2,4-D): mouse, rat, goat, poultry, fish.

^{14}C-labelled 2,4-dichlorophenoxyacetic acid dimethylamine salt ([^{14}C]2,4-D DMA): apple.

^{14}C-labelled 2,4-dichlorophenoxyacetic acid 2-ethylhexyl ester ([^{14}C]2,4-D EHE): potato, wheat.

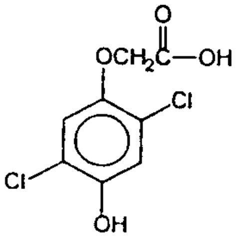
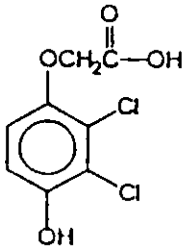
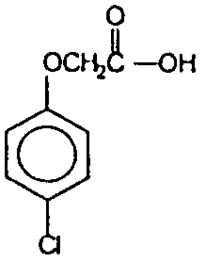
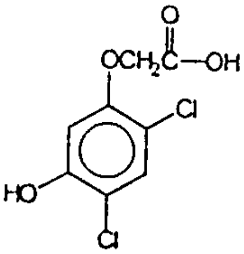
^{14}C-labelled 2,4-dichlorophenoxyacetic acid isopropylester ([^{14}C]2,4-D IPE): lemon.

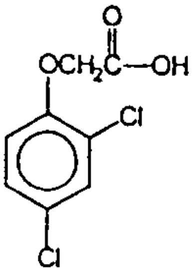
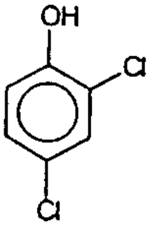
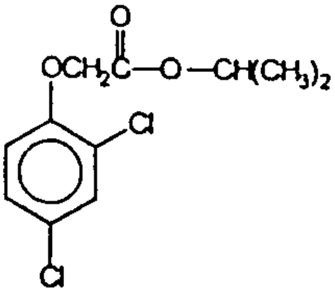
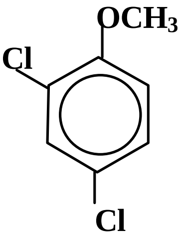
Furthermore, the label on the ester moiety is also used:

2,4-Dichlorophenoxyacetic acid 2-ethylhexyl-1-^{14}C ester (2,4-D EHE-1-^{14}C): rat.

For the chemical names, structures and abbreviations of metabolites used in the text see Table 1.

Table 1. Structures of metabolites of 2,4-D.

Chemical name, abbreviation	Structure
2,5-Dichloro-4-OH-phenoxyacetic acid (4-Hydroxy-2,5-D)	
2,3-Dichloro-4-OH-phenoxyacetic acid (4-Hydroxy-2,3-D)	
4-Chlorophenoxyacetic acid (4-CPAA)	
2,4-Dichloro-5-OH-phenoxyacetic acid (5-Hydroxy-2,4-D)	

Chemical name, abbreviation	Structure
4-Chlorophenol (4-CP)	
2, 4-Dichlorophenoxyacetic acid (2,4-D)	
2,4-Dichlorophenol (2,4-DCP)	
2,4-Dichlorophenoxyacetic acid isopropyl ester (2,4-D IPE)	
2,4-Dichloroanisole (2,4-DCA)	

Animal metabolism

Mice (Eiseman, 1984). The pharmacokinetics of [^{14}C]2,4-D (purity, 98%) were studied in groups of 26 male B6C3F1 mice after single oral doses at 5, 45, or 90 mg/kg bw and single intravenous administrations of 90 mg/kg bw. To evaluate the excretion balance groups of five mice were given the same single doses of [^{14}C]2,4-D by gavage or intravenous doses of 5 or 90-mg/kg bw. Plasma, liver and kidneys were analysed for the radiolabel 0.083, 0.25, 0.5, 1, 2, 4, 6, 8, 12, 24, 36, 48 and 72 hours after treatment. Urine was collected before and after treatment at 0-6, 6-12, 12-24, 24-36, 36-48, 48-72 hours and then every 24 hours up to 168 hours. Faeces were collected before and 0-12, 12-24 and every 24 hours up to 168 hours after treatment. The animals were then slaughtered and the blood, liver, kidneys and residual carcases were sampled for measurement of total radioactive residues (TRR).

The disappearance of the label from plasma in animals at each dose was examined by reiteratively weighted non-linear regression analysis to obtain the apparent pharmacokinetic parameters by both the oral and intravenous routes. Because of the apparent lag in clearance at the higher doses and the high levels of 2,4-D-derived ^{14}C in plasma during the first 4 hours after dosing, a two-compartment model with Michaelis-Menten limited clearance was used. The half-lives were calculated to be 28-45 hours. At least 50% of the dose was cleared within 12 hours however, suggesting that the estimates are lower than the actual clearance constants.

After oral administration, the area under the curve (AUC) of time v. concentration increased more than proportionally with the dose.

The main route of elimination of ^{14}C was the urine, accounting for 63, 84, 71, 53 and 65% of doses at 5 mg/kg bw orally, 5 mg/kg intravenously, 45 mg/kg bw orally, 90 mg/kg bw orally, and 90 mg/kg intravenously respectively. 7.6% of the dose in animals receiving 5 mg/kg bw orally and 5.2% at 5 mg/kg bw intravenously was excreted in the faeces. The proportions increased to 15% at 45 mg/kg bw orally, 16% at 90 mg/kg bw orally, and 12% at 90 mg/kg bw intravenously. Most of the TRR was eliminated in the urine 0-6 hours after treatment at 5 mg/kg bw intravenously, 0-12 hours after at 5 mg/kg bw orally, and 6-24 hours after at 45 or 90 mg/kg bw. 168 hours after treatment very little ^{14}C was detected. None was found in blood or plasma in the animals dosed intravenously, and only one animal of those dosed orally had a detectable, low level of radiolabel in the plasma. The liver and kidneys contained similar levels of TRR at each dose. Less than 1.1% of the dose was retained in the animals seven days after administration of [^{14}C]2,4-D, irrespective of the dose and administration route. The urinary clearance of 2,4-D appeared to be a saturable process in male mice at doses of $\geq$45 mg/kg bw.

Rats. Smith *et al.* (1980) examined the pharmacokinetics of the elimination of [^{14}C]2,4-D (radiochemical purity, >99%) after oral and intravenous administration to several groups of male Fischer 344 rats to investigate the fate of the compound as a function of the dose and to identify the approximate dose at which the kinetics of elimination begin to show evidence of saturation. Three groups of three rats with jugular cannulae received oral doses of 10, 50, or 150 mg/kg bw, and two similar groups received intravenous doses of 5 or 90 mg/kg bw. The concentrations of TRR were determined 1, 2, 3, 6, 9, 12,15, 18, 24, 36, 48, 60 and 72 hours after treatment; ^{14}C levels in the urine were measured at 6-hourly intervals for the first 24 hours and at 12-hour intervals thereafter up to 72 hours; faecal samples were collected at 24-hour intervals.

To determine the effect of dose five groups of six rats were given single oral doses of 10, 25, 50, 100 or 150 mg/kg bw and were killed 6 hours after treatment. Absorption of 2,4-D after oral administration was complete as >85% of the dose within the first 12 hours and a total of 97% of the 10 mg/kg bw oral dose and 95% of the 150 mg/kg bw dose was excreted in the urine. After intravenous doses 99 and 86% of the 5- and 90-mg/kg bw doses were recovered within the first 12 hours and 100 and 91% after 72 hours. Saturable clearance from the plasma was detected and was confirmed by the disproportionate increase in the AUC, which probably reflects saturable urinary excretion, in view of the concomitant increasing ratio of plasma:kidney ^{14}C concentrations with increasing dose.

The elimination was biphasic. The mean half-lives for the intravenous and oral routes were 55 minutes and 1 hour respectively for the ∀-phase and 14 and 18 hours for the ∃-phase. The rapid elimination of the ^{14}C in the urine and the small contribution of the ∃-phase indicate low potential accumulation of 2,4-D in rats.

Timchalk (1990) examined the absorption, distribution, metabolism and excretion of [^{14}C]2,4-D after oral and intravenous administration to Fischer 344 rats. Four groups of five male and five female rats each received [^{14}C]2,4-D as a single oral dose by gavage at 1 or 100 mg/kg bw, or as a single intravenous dose at 1 mg/kg bw, or were given 14 daily oral doses of unlabelled 2,4-D at 1 mg/kg bw followed by a single oral dose of [^{14}C]2,4-D at the same rate on day 15. Two additional groups of four male rats were given single oral doses and then 1 or 100 mg/kg bw through jugular cannulae to define the concentration-time course in the plasma. Plasma concentrations were determined for 24 hours after treatment.

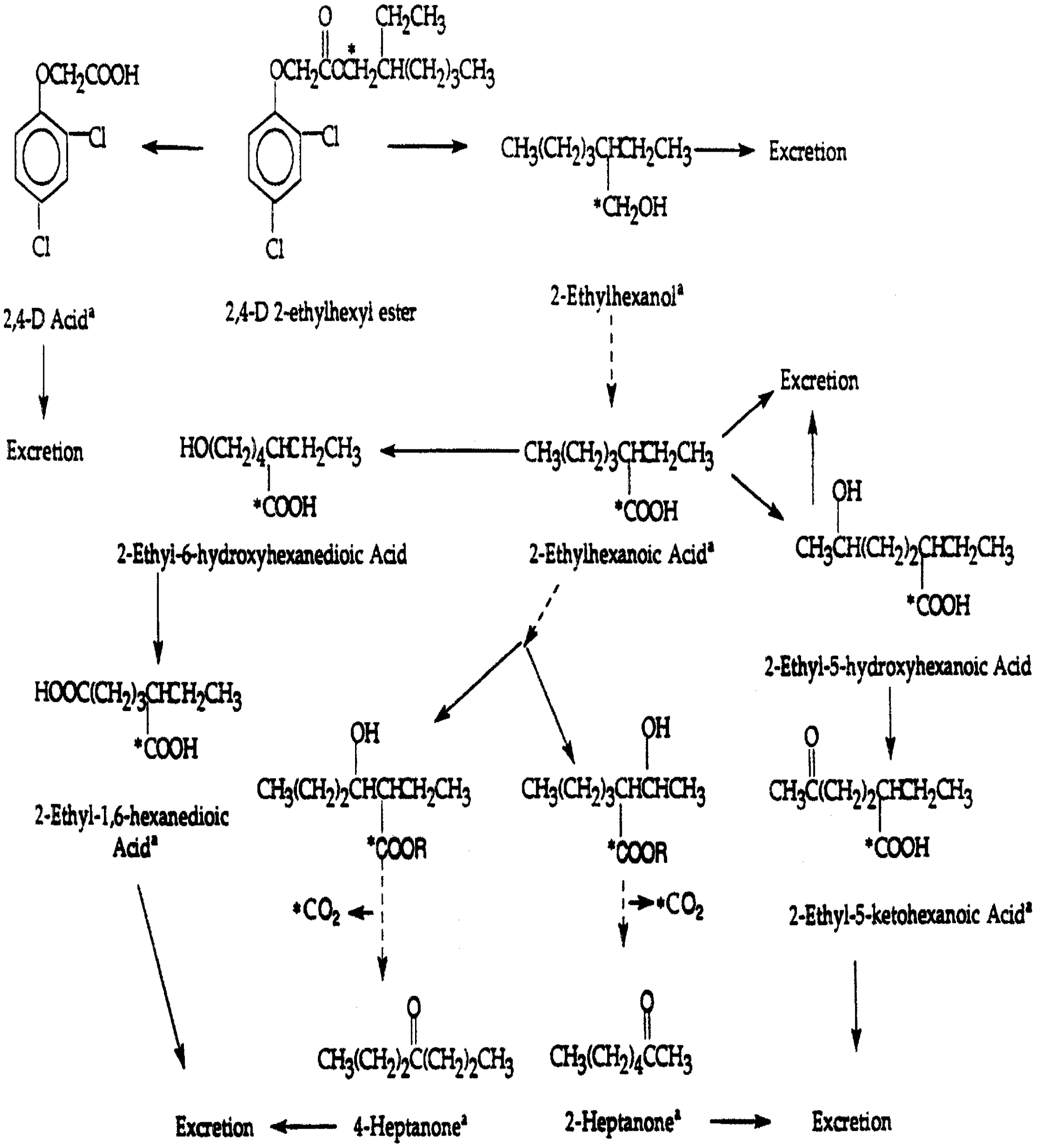
In all groups >94% of the dose was recovered within 48 hours after treatment, mainly in the urine (85-94%), with 2-11% in the faeces. No sex-related difference was seen, and repeated oral dosage did not alter the excretory route. Peak plasma levels were attained about 4 hours after treatment. The disproportionate AUCs and the delayed urinary excretion of ^{14}C strongly imply dose-dependent non-linear kinetics however. Although the elimination of the radiolabel was saturated during the first few hours after the 100 mg/kg bw dose its excretion was rapid, most of the dose having been excreted 36 hours after treatment in all groups. Rapid excretion of [^{14}C]2,4-D is also indicated by the approximate half-life of 5 hours for urinary excretion after oral administration. The analysis of all major tissues and organs for residual ^{14}C activity indicated that only a small fraction of the dose was present 48 hours after treatment. The tissues and organs of animals treated at the low dose contained <0.7% of the administered [^{14}C]. These results indicate that the fate of [^{14}C]2,4-D in rats is independent of dose and sex and that the compound is rapidly and almost completely eliminated, essentially by the urinary route, and is unlikely to accumulate.

Unlabelled 2,4-D EHE was administered as a single oral dose to male and female 11 week old Fischer 344 rats to investigate the pharmacokinetic characteristics of this ester in relation to 2,4-D itself (Frantz and Kropscott, 1984). Eight groups of animals (3/sex/group) were given oral doses of 130 mg/kg of the 2-ethylhexyl ester (equivalent to 86.3 mg/kg 2,4-D acid) in maize oil and killed after 15 and 30 min, and 1, 2, 4, 8, 24 and 72 hours for blood samples. Urine samples were taken at 12 hour intervals from the 72-hour group. A control group (3/sex) was dosed with maize oil only and a terminal blood sample was taken after 3 hours. Both ester and acid were determined by GLC and GC-MS with detection limits of 0.01 and 0.1 :g/ml respectively.

The most significant finding was the absence of any 2-ethylhexyl ester ([0.01 :g/ml) in either blood or urine as measured up to 72 hours after dosing. The acid was found in both blood and urine. Log-linear plots of 2,4-D acid concentration in the blood v. time were similar for male and female rats, with peak blood levels appearing at 2 hours for females and 4 hours for males. No acid was detectable at 72 hours in either male or female blood samples. Urine levels of 2,4-D acid peaked at 12 hours in both sexes and clearance was nearly complete by 36 hours; only small amounts of acid were detectable at 72 hours. The cumulative recovery of 2,4-D acid in urine (as a percentage of the equivalent administered) was 94.8 ± 9.2% for males and 84.3 ± 4.5% for females. These data indicate that the 2-ethylhexyl ester of 2,4-D is converted very rapidly to 2,4-D acid, and the acid is then excreted in the urine.

The absorption, distribution, excretion and biotransformation of [*EHE*-1-^{14}C]2,4-D were studied in male Fischer 344 rats after a single oral dose of 15 mg/kg bw (Dryzga *et al.*, 1992). Blood was collected from each rat 0.5, 1, 1.5, 2, 4, 6, 8, 12, 18 and 24 hours after treatment and the plasma was analysed for the radiolabel; urine was collected 6, 12, 24 and 48 hours after treatment, and the radiolabel in the urine and the cage rinse was combined for each collection interval and expressed as radiolabel excreted in the urine. Faeces were collected at 24-hour intervals and analysed for radiolabel; expired [^{14}C]carbon dioxide collected at 6, 12, 24 and 48 hours was trapped in a solution of monoethanolamine and 1-methoxy-2-propanol, and the TRR was quantified. No tissue samples were analysed. Metabolites were characterized in pooled urine (0-6 and 6-12 hours) and in faeces (0-24 hours) by GC-MS, and unchanged ester in the urine and faecal extracts was determined by HPLC.

Figure 1. Proposed metabolic pathways of 2,4-Dd EHE in rats (Dryzga *et al.*, 1992).



[a] Compounds actually identified

,4-D EHE-1-^{14}C was rapidly absorbed, with a peak plasma concentration of 1.0 mg/g 4 h after treatment, decreasing with a half-life of 9 hours. Once absorbed, the ester was extensively metabolized and eliminated in the urine and faeces, and as expired $^{14}CO_2$. It was rapidly hydrolysed to 2,4-D and 2-ethylhexanol, since no ester was found in the blood, urine, or faeces. The principal route of excretion was the urine (62-66%), with less in the faeces (14-21%) and expired carbon dioxide (9-12%). The metabolites in both urine and faeces were 2-ethylhexanol, 2-ethylhexanoic acid, 2-ethylhexane-1,6-dioic acid and 2,4-D. Metabolites found in only in the urine were 2-ethyl-5-oxohexanoic acid, 2-ethyl-5-hydroxyhexanoic acid, 2-heptanone and 4-heptanone (Figure 1). These metabolites were previously reported as metabolites of [^{14}C]2-ethylhexanol. The ethylhexyl ester of 2,4-D is thus converted rapidly to 2,4-D, which is then excreted in the urine.

Goats. Guo and Stewart (1993) dosed a lactating goat orally with [^{14}C]2,4-D at a level equivalent to 483 ppm in the feed intake, for 3 consecutive days. Urine, faeces and milk were sampled during the dosing phase and tissues were collected after slaughter. ^{14}C was determined by combustion and/or liquid scintillation counting. Approximately 82 and 8% of the total dose was recovered in the urine and faeces respectively. Less than 0.1% of the dose was recovered in the other samples.

The ^{14}C residues in the samples except excreta and liver were extracted with organic and aqueous solvents. Liver was first treated with pancreatin and then extracted with organic solvents. Urine was analysed directly by HPLC with radiometric detection. HPLC was used to determine the total ^{14}C as 2,4-D equivalents in the various extracts. The major ^{14}C component was identified as 2,4-D by mass spectrometry, HPLC and thin-layer chromatography. The results of these analyses are shown in Table 2.

Table 2. Metabolism of 2,4-D in goats. Identity and distribution of ^{14}C components in the extractable fractions urine, milk and tissues (Guo and Stewart, 1993).

Sample	Total ^{14}C mg/kg	% 2,4-D	% DCP[1]	% CPAA[2]	% NP1	% NP2[3]	% NP3	% Not[4] identified
Urine	320	97.8	ND[5]	1.8	ND[5]	ND[5]	ND[5]	0.4
Milk	0.202	47.0	5.0	6.9	1.0	ND[5]	ND[5]	35.1
Liver	0.224	20.5	ND[5]	ND[5]	14.7	17.9	5.4	36.6
Kidney	1.44	53.6	ND[5]	ND[5]	10.3	22.0	4.1	9.9
Fat	0.088	45.4	2.3	ND[5]	3.4	13.6	ND[5]	21.7
Muscle	0.037	37.8	ND[5]	ND[5]	2.7	24.3	ND[5]	19.0

[1] DCP: 2,4-dichlorophenol

[2] CPAA: 2-*o* and 2-*p*-chlorophenoxyacetic acid

[3] The GC/MS profile for NP2 matched 2,4-dichloroanisole, but the compound was not later confirmed (Guo and Stewart 1994)

[4] Total % extracted - Total % identified. In general, this radioactivity is associated with several different fractions and with radioactivity that was unaccounted for after HPLC analysis. Thus, no single unidentified component is present at the level shown here.

[5] Not detected

2,4-dichlorophenoxyacetic acid was found to be the predominant component in the urine, kidneys, fat, liver and muscle. Free 2,4-D and polar conjugates hydrolysed to 2,4-D under acidic conditions were the major ^{14}C components in the milk. Low levels of DCP were tentatively identified in the milk and fat by HPLC.

The ^{14}C in the am and pm milk samples ranged from 0.22 to 0.34 mg/kg and 0.036 to 0.055 mg/kg, as 2,4-D respectively. Free [^{14}C]2,4-D was identified as the most significant residue in milk (38% of the TRR, 0.077 mg/kg). Certain polar conjugates were observed in the milk, from which 2,4-D was readily released by acid hydrolysis. The total 2,4-D after a 1-hour hydrolysis was about 47.0% of the TRR or 0.095 mg/kg. Approximately 0.009 mg/kg (4.5% of the TRR) and 0.01 mg/kg (5.0% of the TRR) of the residues in milk were tentatively identified as *o*- and *p*-

chlorophenoxyacetic acid (CPA) and 2,4-dichlorophenol (DCP) respectively. It is possible that CPA derived from an impurity in the original test substance.

The highest ^{14}C concentration in the tissues was in the kidneys (1.4 mg/kg). Lower levels were found in the liver (0.22 mg/kg), fat (0.088 mg/kg) and muscle (0.037 mg/kg). The main component identified in the residues of each tissue was 2,4-D. About 0.002 mg/kg of DCP (2.3% of the TRR) was found in the fat.

Poultry. Residues in the tissues, eggs and excreta were measured in laying hens (3 groups of 5, each bird weighting 1.5 kg) dosed orally for 7 days with radiolabelled capsules of 2,4-D approximately equivalent to 18 ppm in the feed intake (112-119 g/bird/day). The eggs and excreta were collected throughout the 7 days, and the birds were killed 22-24 hours after the final dose (Puvanesarajah and Bliss, 1992).

Samples collected included excreta, egg, fat, gizzard, heart, kidney, liver, breast muscle and thigh muscle. Except for the eggs (production of which from each treatment group was good) all the samples were composited for each group before analysis. The weights of the comparable samples from the three groups were very similar.

The TRR levels in the samples were determined either by direct radio-analysis or combustion and radio analysis (the latter corrected for sample and oxidizer recoveries). Recoveries in the hens ranged from 95.8 to 101.6%, approximately 90% in the excreta. The residues in the breast muscle were <0.002 mg/kg; thigh muscle 0.006 mg/kg; fat 0.028 mg/kg and liver 0.03 mg/kg. The mean residue levels in eggs increased steadily from less than quantifiable at day 1 to 0.018 mg/kg at day 7. The tissues and eggs contained <0.1% of the total dose (Table 3).

Table 3. 2,4-D acid equivalents and % total dose recoveries in body tissues, eggs and excreta of hens (Puvanesarajah and Bliss, 1992).

Sample	Group II		Group III		Group IV	
	TRR, mg/kg[1]	% Total dose recovered	TRR, mg/kg[1]	% Total dose recovered	TRR, mg/kg[1]	% Total dose recovered
Egg 1[2]	<LOD[4]	<0.1	<MQL[4]	<0.1	<MQL[4]	<0.1
Egg 2	0.002	<0.1	0.003	<0.1	0.003	<0.1
Egg 3	0.006	<0.1	0.006	<0.1	0.006	<0.1
Egg 4	0.010	<0.1	0.010	<0.1	0.010	<0.1
Egg 5	0.014	<0.1	0.013	<0.1	0.009	<0.1
Egg 6	0.016	<0.1	0.016	<0.1	0.018	<0.1
Egg 7[3]	0.018	<0.1	0.017	<0.1	0.019	<0.1
Fat	0.029	<0.1	0.032	<0.1	0.023	<0.1
Kidney	0.705	<0.1	0.065	<0.1	0.791	<0.1
Liver	0.025	<0.1	0.019	<0.1	0.046	<0.1
Breast muscle	<MQL[4]	<0.1	<MQL[4]	<0.1	0.002	<0.1
Thigh muscle	0.005	<0.1	0.004	<0.1	0.008	<0.1
Heart	0.011	<0.1	0.008	<0.1	0.028	<0.1
Gizzard	0.142	<0.1	0.038	<0.1	0.118	<0.1
Excreta[5]	16 - 21	95.9	15 - 19	89.9	15 - 21	89.4
Total dose recovered		96.0		90.0		89.5

[1] Numbers listed are the means of triplicate determinations of pooled samples.

[2] First day of dose

[3] Last day of dose

[4] Limit of determination (0.002 mg/kg)

[5] Range of values for the day 1-7 samples

The ^{14}C components present as free residues in the eggs and liver were 2,4-D and 2,4-dichlorophenol (Table 4). A large proportion of the fat activity was released only after base hydrolysis, which suggested that 2,4-D conjugates constituted most of the extractable ^{14}C.

Table 4. Components of extractable ^{14}C residues in hens (Puvanesarajah and Bliss, 1992).

		% of extractable ^{14}C (free and conjugated)		
Sample	Total ^{14}C mg/kg	2,4-D	2,4-Dichlorophenol	Not identified
Egg	0.0178	23.0	7.3	56.8
Fat	0.0271	25.1		67.6
Liver	0.0297	18.2	4.4	59.7

Fish. Bluegill sunfish (*lepomis macrochirus*) were exposed to approximately 11 mg/kg of [^{14}C]2,4-D in their water under static conditions for 4 consecutive days (Premkumar and Stewart, 1994). The whole fish and the water were sampled daily and the fish on day 4 were dissected into fillet and viscera. The [^{14}C]2,4-D equivalent TRR levels in the whole fish, fillet and viscera and the water were determined by combustion and/or liquid scintillation counting.

The fillet and viscera residues were extracted with polar and nonpolar organic solvents. Most of the residues were acetonitrile-extractable. <5% of the TRR was hexane-soluble, and approximately 10% was unextractable with solvents. Acid and base hydrolyses released the unextractable residues in the fillets.

Radio analyses of the whole fish showed a steady increase from day 1 (0.41 mg/kg) to day 3 (0.6 mg/kg). The TRR in the day 4 viscera and fillet were 1.9 and 0.41 mg/kg respectively. The treated fillet had small amounts of hexane-soluble residues (0.005 mg/kg, 1.2% of the TRR) and unextractable ^{14}C (0.041 mg/kg, 10% of the TRR). Most of the ^{14}C was soluble in acetonitrile (0.34 mg/kg, 84% of the TRR).

HPLC radio-analysis was used to characterize the ^{14}C residues in the extracts (Table 5). 2,4-D (70.4% of the TRR, 0.29 mg/kg), 2,4-DCP (4.7% of the TRR, 0.019 mg/kg), and a conjugate (4.4% of the TRR, 0.018 mg/kg) were identified in the acetonitrile-soluble residue. Acid hydrolysis of the polar conjugate released 2,4-D and 2,4-DCP. Acid and base hydrolyses of the unextractable fillet pellet released additional 2,4-D (6.4 and 3.9% of the TRR, 0.029 and 0.016 mg/kg respectively) and 2,4-DCP (0.5% of the TRR, 0.002 mg/kg). The identities of 2,4-D and 2,4-DCP in the fillet tissue were confirmed by GC-MS.

Table 5. Components of extractable ^{14}C residues in fish exposed for 4 days to 11 mg/kg in their water (Premkumar and Stewart, 1994).

TRR		Extractable ^{14}C in					
		2,4-D	2,4-DCP	2,4-DCA	polar unknown	CPA and CP	not identified
Fillet, TRR	% of TRR[1]	80[2]	7.9[2]		2.2	N/A[3]	1.0
0.41 mg/kg	mg/kg[1,2]	0.33	0.03		0.009	N/A[3]	0.004
Viscera, TRR	% of TRR[1]	30[2]	28[2]	0.3[3]	5.8	40	1.6
1.9 mg/kg	mg/kg[1,2]	0.57	0.53	0.006	0.11	0.76	0.03

[1] Sum of free and conjugated
[2] Expressed as 2,4-D
[3] Identity confirmed by GC-MS

Plant metabolism

Apples. Smith (1991) sprayed [^{14}C]2,4-D on the turf beneath the canopy of a dwarf apple tree in accordance with label instructions. The test material consisted of the dimethylamine salt of 2,4-D acid in aqueous solution applied at 2.2 kg ae/ha (2 applications 42 days apart). Soil samples were taken after 42 days and 97 days, and fruit samples after 97 days (maturity) .

Combustion analysis and liquid scintillation counting were used to determine ^{14}C residues in the soil and plant samples. All residues were corrected for oxidizer recovery and matrix effects, and those in the soil for moisture content. Most residues were in the 0-7.5 and 7.5-15 cm layers with considerably less (<0.05 mg/kg as 2,4-D) in the 15-22.5, 22.5-30 and 30-45 cm layers. The TRR in was 0.53 mg/kg and 0.042 mg/kg 0-7.5 and 7.5-15 cm layers at day 42 and 0.93 mg/kg and 0.15 mg/kg at day 97. Combustion analysis of the apples gave TRR levels of 0.009 mg/kg. The apples were lyophilized and exhaustively extracted with methanol/acetic acid (95:5). The extract was then concentrated, re-suspended in water, and extracted with hexane/diethyl ether/acetic acid (47.5:47.5:5), leaving 56% as water-soluble residue with no quantifiable residue (<0.0008 mg/kg) in the organic extract and 44% remaining in the post-extraction solids as determined by combustion.

Lemons. Wu (1994) treated lemons with an aqueous emulsion of [^{14}C]2,4-D isopropyl ester resulting in an average residue level of 2.4 mg/kg expressed as 2,4-D on the fruit. The lemons were stored inside a constant temperature incubator at an average temperature of 5.5 ± 0.7°C, with relative humidity of about 85%. The stored lemons were sampled at 2 hours, 2, 7, 14 and 28 days, and 6, 8, 10, 12, 16, 20 and 24 weeks after treatment.

At sampling, each lemon was rinsed with 200 ml of acetone to remove the surface residues, then cut into eight slices and peeled and processed through a juice extractor. The peel was diced, and homogenized in liquid nitrogen and dry ice. The TRR level was determined for each type of sample.

All the samples were extracted twice with methylene chloride, and the remaining solids in the pulp and peel samples were extracted twice with a mixture of acetonitrile and 0.1 N hydrochloric acid. The distribution of ^{14}C in each extracted fraction was monitored. The acetone rinses and all organosoluble and aqueous fractions obtained at each sampling were analysed by both TLC and reversed-phase HPLC.

Most of the TRR was found in the peel and rinse at all samplings, with very little in the pulp and juice. Radioactivity in the peel increased from 57% of the TRR at 2 hours to 97% at 2 weeks, and remained at about the same level for the 24-week storage period. Radioactivity in the pulp increased from 0.17% at 2 hours to 3.8% at 24 weeks, and in juice from 0.09% at 2 hours to 2.5% at 10 weeks, maintaining a level of about 2% for the remaining weeks. Surface residues removed by acetone decreased from 43.02% to 0.85% after 24 weeks. Solvent extraction of the peel showed 76%, 23% and 1.15% of the peel radioactivity in methylene chloride, aqueous acetronitrile, and post-extraction solid (PES) fractions respectively 2 hours after treatment, and 19.9, 73.5 and 6.6% respectively 24 weeks after treatment. The corresponding proportions in the pulp were about 31-38%, 54-62% and 6-8%, and in juice about 32-44%, 29-33% and 26-35%.Table 6 shows the distribution of ^{14}C in the rinse, peel, pulp and juice at each sampling.

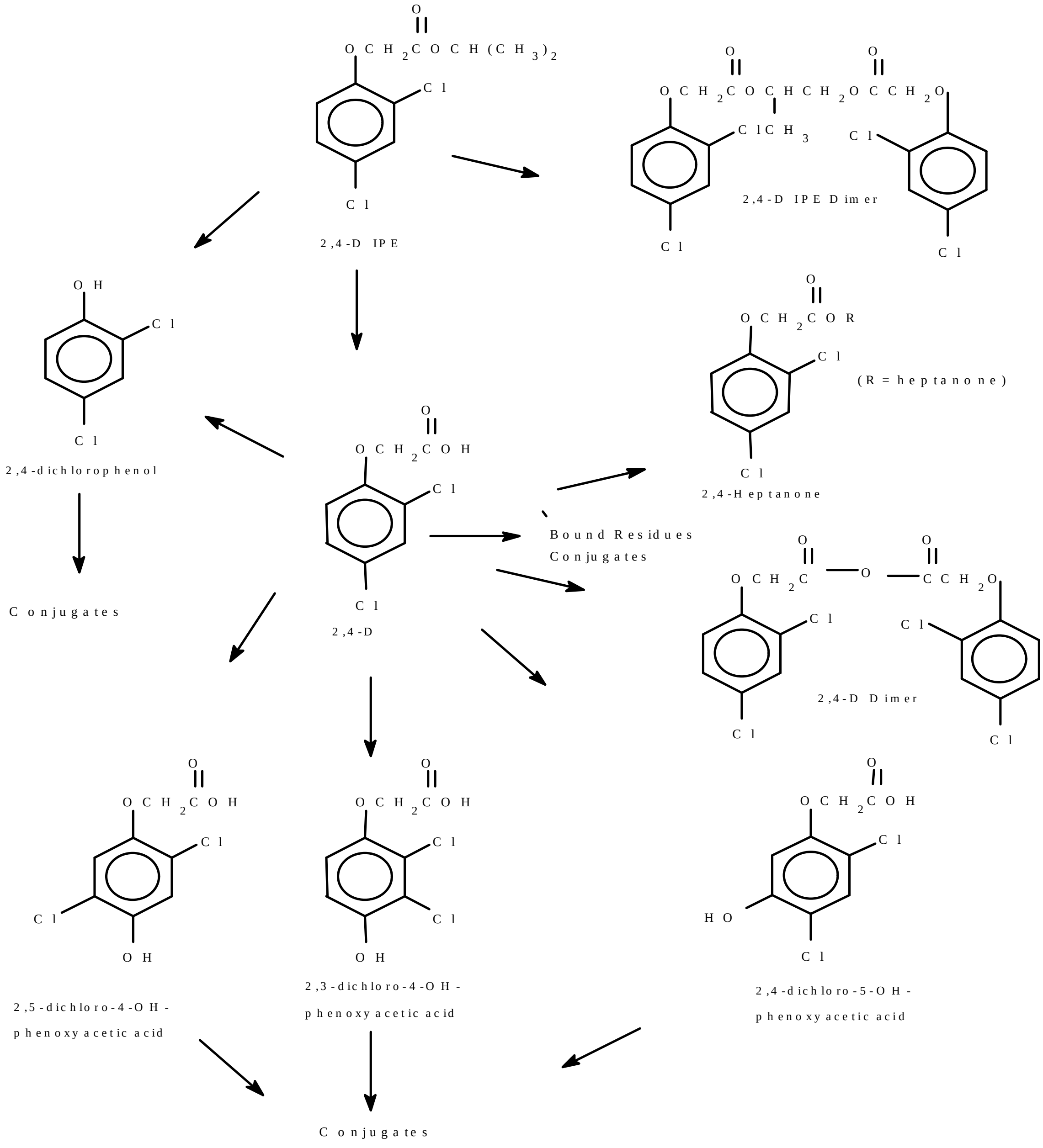
Table 6. Distribution of radioactivity in lemons at various sampling intervals (Wu, 1994).

Sampling	TRR, mg/kg as 2,4-D	Pan wash & rinse % of TRR	mg/kg	Juice % of TRR	mg/kg	Pulp % of TRR	mg/kg	Peel % of TRR	mg/kg
2 h	2.8	43	1.2	0.09	0.003	0.17	0.005	56.7	1.6
2 days	2.3	4.9	0.11	0.10	0.002	0.20	0.005	94.8	2.2
7 days	2.3	3.2	0.07	0.31	0.007	0.55	0.01	96.0	2.2
14 days	2.3	2.1	0.05	0.51	0.01	0.66	0.02	96.8	2.3

Sampling	TRR, mg/kg as 2,4-D	Pan wash & rinse		Juice		Pulp		Peel	
		% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
28 days	2.1	1.6	0.03	0.93	0.02	1.3	0.03	96.1	2.0
6 weeks	2.2	1.2	0.03	1.2	0.03	1.7	0.04	95.9	2.2
8 weeks	2.3	1.1	0.03	1.8	0.04	2.3	0.05	94.8	2.2
10 weeks	2.4	1.1	0.03	2.5	0.06	3.1	0.07	93.3	2.3
12 weeks	2.4	1.0	0.025	1.9	0.05	2.7	0.07	94.4	2.3
16 weeks	2.3	0.80	0.02	1.5	0.035	2.3	0.06	95.4	2.2
20 weeks	2.3	0.93	0.02	2.0	0.05	3.5	0.08	93.5	2.1
24 weeks	2.4	0.85	0.02	1.9	0.05	3.8	0.09	93.4	2.3
Average	2.34								

Metabolites were determined by HPLC and TLC with radiometric detection. Most of the low-level residues (0.64% of the TRR, 0.015 mg/kg) in the 20-week rinse were detected at HPLC retention times of about 36-50 minutes. Four metabolites were tentatively identified by GC-MS: a heptanone ester of 2,4-D, a 2,4-D dimer postulated as 2,4-D anhydride, a dimer of 2,4-D IPE, and a substituted 2,4-dichlorophenol. 2,4-D (0.12% of the TRR, 0.003 mg/kg) and 2,4-D IPE (0.05% of the TRR, 0.001mg/kg) were also found in the rinse. The lemon peel at 20 weeks contained 93.5% of the TRR (2.1 mg/kg). Most of these residues consisted of free and conjugated forms of 2,4-D (64% of the TRR, 1.45 mg/kg). Other metabolites found in minor quantities were free and bound 2,4-D IPE (0.73% of the TRR, 0.017 mg/kg), 4-hydroxy-2,3-D or 5-hydroxy-2,4-D (0.58%, 0.013 mg/kg), 4-hydroxy-2,5-D (0.44%, 0.01 mg/kg) and 2,4-dichlorophenol (0.72%, 0.016 mg/kg). Small amounts of ester-like metabolites similar to those found in the rinses were detected (0.92% of the TRR, 0.02 mg/kg). The main metabolites found in the pulp and juice were also free and conjugated 2,4-D (2.9% of the TRR, 0.07 mg/kg, in the pulp, and 0.99% of the TRR, 0.02 mg/kg, in the juice).

Figure 2. Proposed metabolic pathways of 2,4-D IPE in stored lemons (Wu, 1994).



0 Proposed Metabolic Pathways of 2,4-D IPE in Stored Lemons

The post-extraction solid fraction PES-1 (5.3% of the TRR, 0.12 mg/kg) from the 20-week peel was hydrolysed with cellulase, then 1 *N* HCl and finally 6 *N* HCl. Each hydrolysate was partitioned with ethyl acetate (EtOAc). The organic and aqueous fractions, as well as the final PES, were monitored for ^{14}C. Cellulase released about 27% of the PES radioactivity; 17.6% was soluble in EtOAc (EtOAc-1), and 9.4% remained in the aqueous fraction (Aq-1). Hydrolysis of the resulting PES-2 with *N* HCl released 13.2% of the radioactivity; 10.2% was soluble in EtOAc (EtOAc-2), and 3% remained in the aqueous fraction (Aq-2). Hydrolysis of the remaining PES-3 with 6 *N* HCl released 43% of the radioactivity, 39.5% soluble in EtOAc (EtOAc-3) and 3.7% remaining in the aqueous fraction (Aq-3), while 57% remained in final PES-4. Owing to the low residue levels only the EtOAc-1 fraction was analysed by HPLC and two-dimensional TLC. Four metabolites were detected in this fraction; the main metabolite (about 89% of EtOAc-1, <0.1% of the TRR) had a similar TLC R_f value to 2,4-D, but the HPLC retention times did not match.

Potatoes. [^{14}C]2,4-D ethylhexyl ester was applied as an over-the-top spray to the immature foliage of potato plants grown in a greenhouse (Puglis and Smith, 1992). The diluted emulsified concentrate was applied twice at 0.067 kg acid equivalent (ae)/ha, the first application to three to four week-old plants and the second approximately one week later, according to the registered use of the herbicide on potatoes. Phytotoxicity was observed on the foliage, and the tuber yield was reduced by 56% compared to the control plant. The specific activity of the formulated [^{14}C]2,4-D ethylhexyl ester was 4.08 mCi/mmol (41,000 dpm/µg ae), and the radiochemical purity was 99%. The tubers were harvested at maturity 82 days after the last application. The TRR in the tubers was determined by combustion of tissue aliquots to $^{14}CO_2$ and subsequent radio-analysis. Aliquots of the ground potato tubers were extracted by two methods, one to determine free residues and the other total free and acid-hydrolysable residues. The free residues were isolated by extraction of a 5 *N* hydrochloric acid slurry of the ground potato tuber with diethyl/ether petroleum ether (3:1). The total free and acid-hydrolysable residues were isolated after heating a 5 *N* hydrochloric acid extract of the ground tuber with 5 *N* sulfuric acid and extracting the hydrolysate with the ether mixture (Table 7).

Table 7. Distribution of ^{14}C residues in potato tubers (Puglis and Smith, 1992).

Total ^{14}C, mg/kg as 2,4-D	Free ^{14}C, %		Sample of free and acid-hydrolysable ^{14}C, %	
	aqueous	ether	aqueous	ether
0.0054	46	17	65	30

The total ^{14}C residue in the potato tubers was very low. In an attempt to characterize the organosoluble residue, a 50 g sample was subjected to acid hydrolysis followed by extraction with diethyl ether. The ^{14}C activity in the partially purified extract was observed at an R_f value that did not match the R_f of either the 2-ethylhexyl ester or the free acid. The unknown ^{14}C-labelled compound from the TLC zone was fortified with unlabelled 2,4-D acid and reanalysed by TLC. The added 2,4-D was found at the same R_f value as the unknown compound, and the identity was confirmed by mass spectrometry and high-performance liquid chromatography. Thus, if 2,4-D were present in the treated tubers, it would chromatograph in the same region as the unknown ^{14}C activity. Further characterization of the unknown ^{14}C component(s) was not possible owing to the very low concentration (<0.001 mg/kg 2,4-D ae) and the significant interference of other sample components with the chromatography. An exaggerated application rate was not used to achieve higher residue levels in the tubers because an unacceptable phytotoxic response to rates above 0.067 kg ae/ha.

A second study was conducted with [^{14}C]2,4-D EHE formulated as an emulsifiable concentrate solution (Premkumar and Vengurlekar, 1994). Two foliar applications were made to the plants, the first when the tubers were about the size of a pea 58 days after planting, the second 14 days later. The average radiochemical purity of the formulated solution was 95.4%, and the specific activity 1.55 x 10^5 dpm/mg 2,4-D acid equivalents. The formulated [^{14}C]2,4-D EHE was applied at an average exaggerated rate of 0.35 kg acid equivalents/ha (0.33 and 0.37 kg ae/ha for the first and second applications respectively), 4.4 times the maximum label rate of 0.078 kg ae/ha.

Foliage, vine and tuber samples were analysed for ^{14}C. The vines sampled 1, 7 and 20 days after the second application had residues of 15, 10 and 6.3 mg/kg as 2,4-D respectively, and the tubers collected at the same times contained total ^{14}C residues of 0.32, 0.65 and 0.58 mg/kg respectively. Because the watering of the plants after application was directed to the soil to avoid wash-off from the foliage, these results suggest that the [^{14}C]2,4-D EHE and/or its metabolites were translocated from the plant tops to the tubers.

The ^{14}C residues in the mature tubers were extracted with acidified acetonitrile, which extracted 105% of the TRR (0.61 mg/kg) and 5.4% (0.031 mg/kg) remained unextracted. HPLC of the extracts showed that 8.3% of the TRR (0.048 mg/kg) was the parent 2,4-D EHE. The main identifiable metabolite was 2,4-D (46% of the TRR, 0.27 mg/kg) and the remaining radioactivity was distributed among four or more polar components. When the extract was concentrated and re-analysed by HPLC the profile changed considerably in the polar region and the parent was found to be unstable during the concentration process, being reduced to 1.6% of the TRR, 0.009 mg/kg. Also the 2,4-D concentration decreased to 36.4% of the TRR (0.21 mg/kg).

The extraction, concentration and analysis procedure was validated by fortifying control samples with 2,4-D EHE at 0.62 mg/kg. Upon chromatographic analysis, 95% of the parent compound remained unchanged. The remainder was hydrolysed to 2,4-D (3.4%) and an unknown component (1.9%).

The treated tubers were then extracted with acetonitrile. This extracted 96% of the TRR (0.55 mg/kg) and 9% (0.052 mg/kg) remained in the post-extraction solids (PES). HPLC analysis of the acetonitrile extract demonstrated that 0.5% of the TRR (0.003 mg/kg) was present as 2,4-D EHE, and 40% (0.23 mg/kg) as free 2,4-D. The remaining radioactivity was distributed among several polar components. During concentration and analysis some parent was again lost and changes were observed in the polar components but the 2,4-D remained unchanged (43% of the TRR, 0.25 mg/kg) indicating that the parent ester and some polar components (perhaps conjugates) were not stable during concentration.

The extracted ^{14}C residues were subjected to acid hydrolysis. HPLC of the hydrolysate showed three major compounds which were tentatively identified as 4-hydroxy-2,5-D (15% of the TRR, 0.084 mg/kg), 4-chlorophenoxyacetic acid (4-CPAA; 24% of the TRR, 0.14 mg/kg) and 2,4-D (39.5% of the TRR, 0.23 mg/kg). The amount of 2,4-D in the extract remained unchanged after hydrolysis, suggesting that the polar components in the extract could be conjugates of 4-hydroxy-2,5-D and 4-CPAA. All three major products were isolated and methylated: GC-MS of the methyl esters confirmed the identification of 4-hydroxy-2,5-D, 4-CPAA and 2,4-D.

Acid hydrolysis released some bound ^{14}C residues from the PES (9.0% of the TRR, 0.052 mg/kg) and the pellet remaining after the concentration of the acetonitrile extract (4.9% of the TRR, 0.028 mg/kg). The acetonitrile phase contained 8.7% of the TRR (0.05 mg/kg) and 6.4% of the TRR (0.037 mg/kg) remained unextracted. HPLC radio-analysis of the released ^{14}C residues demonstrated the presence of 2,4-D (2.3% of the TRR, 0.013 mg/kg), 4-CPAA (1.6% of the TRR, 0.009 mg/kg) and 4-hydroxy-2,5-D (0.9% of the TRR, 0.005 mg/kg). The components were characterized on the basis of their retention times. A total of 1.4% of the TRR (0.008 mg/kg) was eluted in the void volume and remained unidentified.

Figure 3. Metabolic pathways of 2,4-D EHE in potato tubers (Premkumar and Vengurlekar, 1994).

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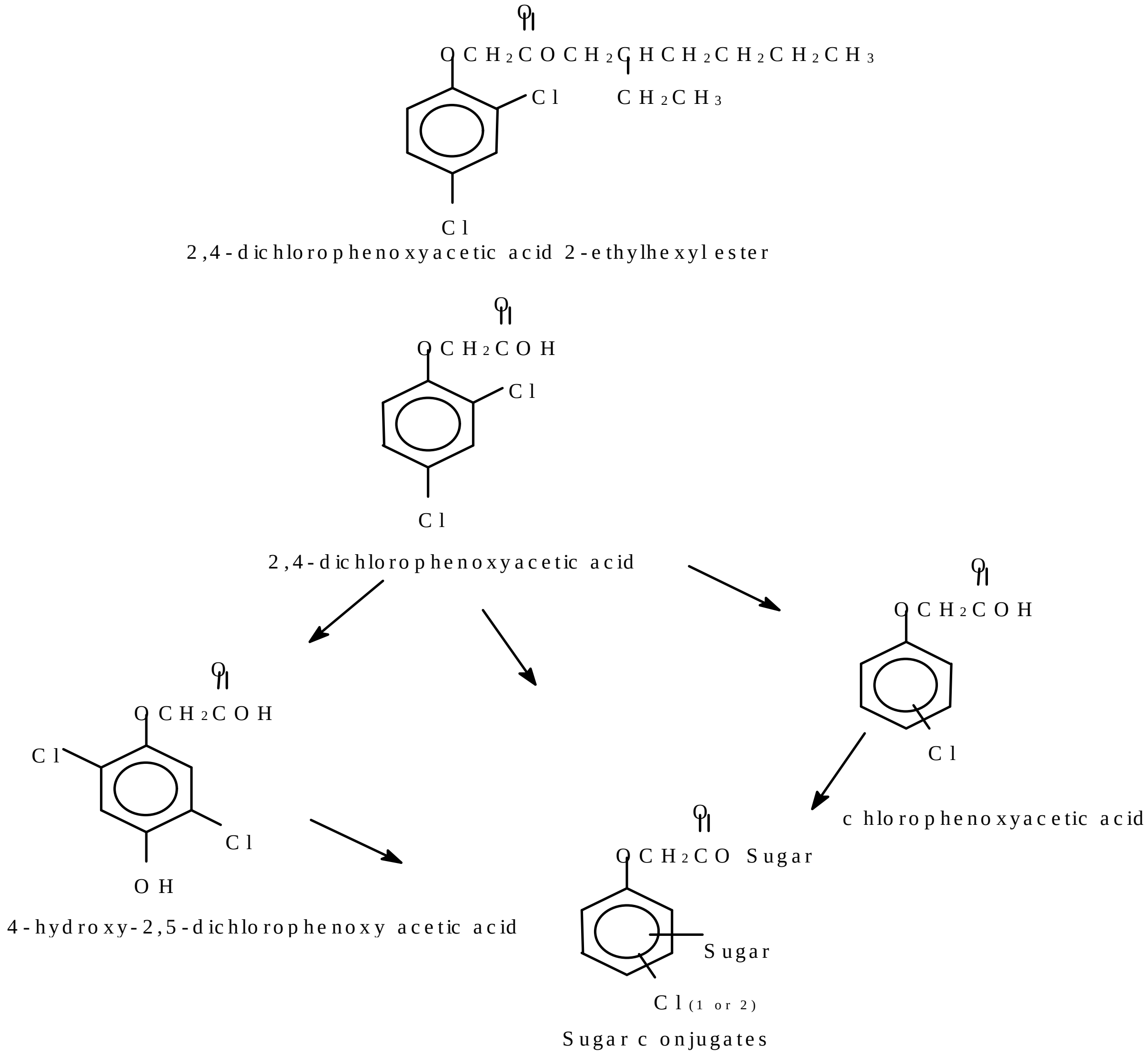

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The distribution of the ^{14}C components is shown in Tables 8 and 9.

Table 8. Distribution of ^{14}C residues (0.58 mg/kg) in extracts of mature potato tubers treated with 2,4-D EHE (Premkumar and Vengurlekar, 1994).

Residue	Acidified acetonitrile extract		Acetonitrile extract	
component	% TRR	mg/kg[1]	% TRR	mg/kg[1]
Polar unknown[2]	27.7	0.16	9.5	0.055
4-hydroxy-2,5-D	18.4	0.11	6.4	0.04
4-CPAA	1.0	0.006	4.3	0.025
2,4-D	46.3	0.27	40.4	0.23
2,4-D 2-EHE	8.3	0.05	0.5	0.003

Residue component	Acidified acetonitrile extract		Acetonitrile extract	
	% TRR	mg/kg[1]	% TRR	mg/kg[1]
Unidentifiable	3.3	0.019	28.6	0.17
Unaccounted for	-	-	6.0	0.03
Unextractable	5.4	0.031	9.0	0.05
Total	110.3	0.64	104.7	0.6

[1] 2,4-D acid equivalents
[2] Eluting in the void volume

Table 9. Distribution of ^{14}C residues in acid hydrolysates of unextracted ^{14}C residues (Premkumar and Vengurlekar, 1994).

Residue component	CH_3CN extract of acid hydrolysis		Post extraction solid (PES) from acid hydrolysate		Total in tuber	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
4-Hydroxy-2,5-D	14.6	0.08	0.9	0.005	15.5	0.09
4-CPAA	24.4	0.14	1.6	0.009	26.0	0.15
2,4-D	39.5	0.23	2.3	0.01	41.8	0.24
Unidentified	8.5	0.05	3.9	0.02	12.4	0.07

Wheat. In a wheat metabolism study [^{14}C]2,4-D EHE formulated as an emulsifiable concentrate solution was applied in a single over-the-top spray to spring wheat, at about the tiller stage, at 1.68 kg ae/ha which is in excess of the maximum label rate (Puvanesarajah, 1992). The radio purity of the formulated solution was 98% and the specific activity was 20,070 dpm/µg ae (2.0 mCi/mmol). The plants were grown under partially enclosed greenhouse conditions.

The TRR levels, as 2,4-D equivalents, in the forage, straw and grain samples were determined by combustion radio-analysis and liquid scintillation counting (LSC). The ^{14}C in the forage, straw and grain was extracted with organic and aqueous/organic solvents and 0.5 M KOH in aqueous methanol. The remaining residues were treated with enzymes. Diethyl ether and aqueous ethanol extraction recovered a large proportion of the residues in the forage and straw. Most of the residues recovered from the grain were in the aqueous and aqueous/methanolic KOH extracts. The distribution of the ^{14}C is shown in Table 10.

Table 10. Wheat. Distribution of ^{14}C in extraction solvents (Puvanesarajah, 1992).

Sample	Total ^{14}C, mg/kg[1]	% in ether	% in EtOH	% in AcN/H_2O	% in H_2O	% in KOH	% in enzyme digest	% in Aq. HCL	% un-extracted
10-day forage	34	20	66	N/A	N/A	12	0.04		0.4
49-day straw	56	14	63	N/A	N/A	19	1.7		0.4
49-day grain	0.30	N/A	N/A	3.7	7.7	28	10	22	8.9

[1] As 2,4-D ae

The radioactive residues in the extracts were separated by HPLC. Owing to the many metabolites and conjugates, quantification of the components by direct HPLC analysis of the extracts was not possible. Base and acid hydrolyses of the ether and ethanol extracts converted most of the metabolites to exocons which were separated by HPLC and their identities confirmed by MS and/or TLC (Table 11).

Table 11. Distribution of the components of extractable residues in wheat (Puvanesarajah, 1992).

Sample	Total^{14}C, mg/kg [1]	% of Total ^{14}C extracts[4]					
		2,4-D EHE	2,4-D	2,4-dichloro phenol	Hydroxydichloro-phenoxyacetic acids[5]	In natural constituents	Not identified[6]
10-day forage	34	3.1 [2]	74 [2]	0.5 [3]	8 [3,]		9.8
49-day straw	56	2.0 [2]	70 [2]	0.9 [3]	8.5 [3]		12
49-day grain	0.3	-	6	-	-	45 [7]	41

[1] As 2,4-D acid ae

[2] Identity confirmed by MS, TLC and HPLC

[3] Identity confirmed by MS and HPLC

[4] Total of free and conjugated

[5] 4-Hydroxy-2,5-dichlorophenoxyacetic acid and two other structural isomers H_2 & H_3

[6] In general, this radioactivity is associated with many different fractions over a wide range of retention times and/or with radioactivity which was unaccounted for after HPLC analysis. Thus, no single unidentified component is present at the level shown.

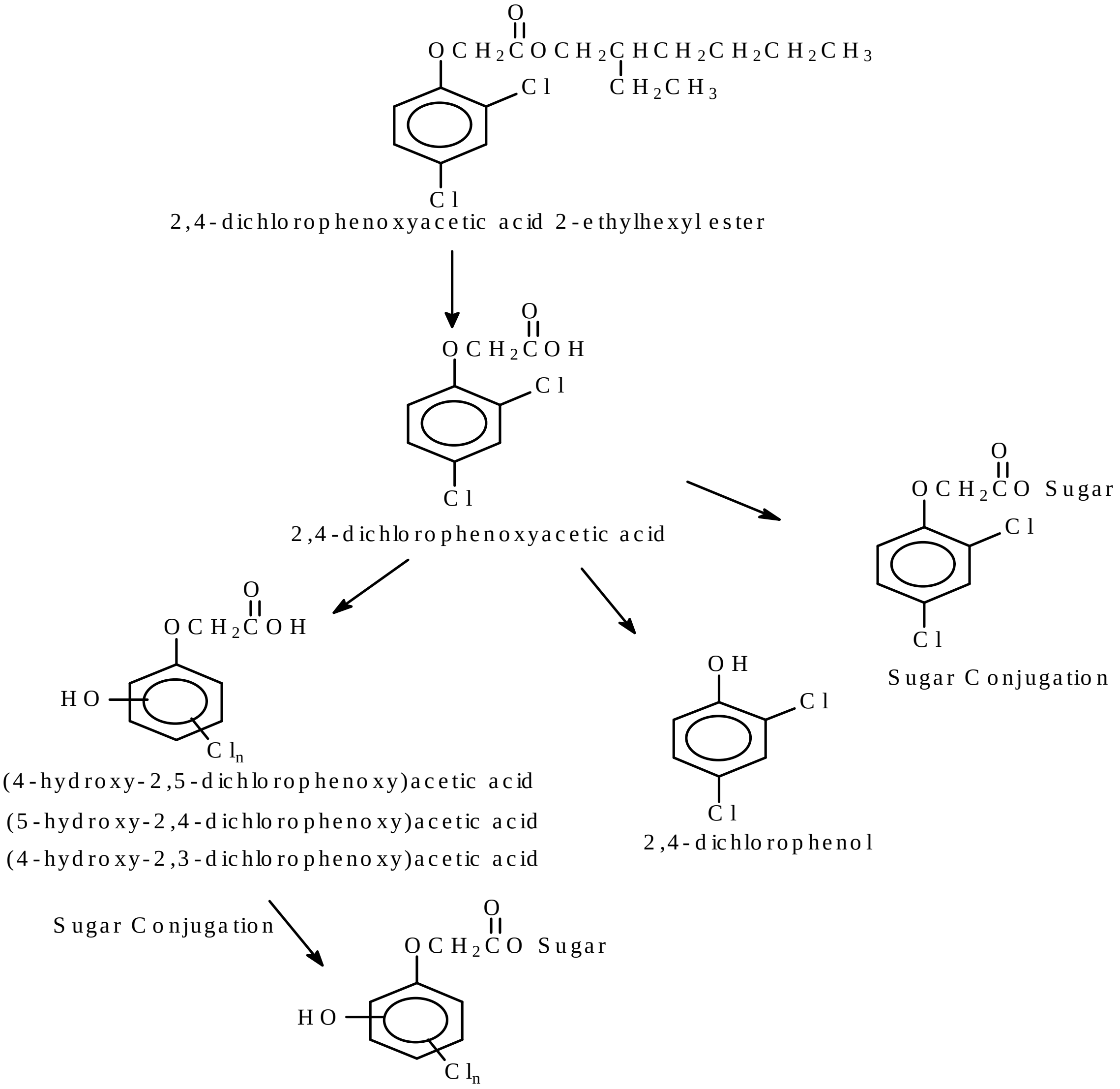
[7] Incorporated into protein, starch and cellulose fractions

In forage and straw unconjugated 2,4-D was found at 9% and 6% respectively, and base-labile 2,4-D conjugates accounted for 64% of the total residues. The hydrolysis of these 2,4-D conjugates by a mild base suggests esterification with indigenous substances, presumably sugars. Approximately 33% of the total ring-hydroxylated 2,4-D derivatives identified in the forage were free residues extractable in ether, and the others were found as polar conjugates in the ethanol extract. These polar conjugates were stable to bases but were readily cleaved under acidic conditions, which suggests they were phenolic glycosides. A large portion (about 77%) of the ring-hydroxylated metabolites in the straw were polar conjugates. Side-chain degradation of 2,4-D to give 2,4-dichlorophenol was a minor pathway (see Table 11).

2,4-D residues identified in the grain extracts represented $\leq$6% of the total grain residues. 45% from the incorporation of ^{14}C into proteins, starch and cellulose. Untreated control samples had residues of 0.17 mg/kg. This ^{14}C contamination was attributed to the proximity of the control and treated wheat to another plot in which $^{14}CO_2$ was generated from the microbial breakdown of 2,4-D EHE applied to soil. Both the treated and control samples were analysed by the same schemes for the extraction of residues and isolation of natural products to distinguish between the residues resulting from treatment of wheat with [^{14}C]2,4-D EHE and that resulting from the uptake of $^{14}CO_2$. These parallel analyses demonstrated that the presence of ^{14}C in the control grain samples did not affect the conclusions on the nature of the residue in wheat grain after treatment of young wheat plants with [^{14}C]2,4-D EHE.

In later work on samples from the above study (Pither, 1992) the two isomeric hydroxydichlorophenoxyacetic acids reported as H_2 and H_3 in wheat forage and straw (at 1.4 to 2.5% of the total ^{14}C residue) were identified from their chromatographic mobilities and mass spectral data as 4-hydroxy-2,3-dichlorophenoxyacetic acid and 5-hydroxy-2,4-dichlorophenoxyacetic acid. These compounds had HPLC elution ranges of 15.0-17.5 min and 18.5-21.5 min respectively. The presence of the ^{14}C components with HPLC elution ranges similar to those of 2,4-D EHE and 2,4-D in the basic extract of control wheat grain was re-examined, and the presence of 2,4-D in the extracts of control and treated wheat grain was confirmed by the re-analysis. 2,4-D EHE could not be detected in the basic extract from control wheat grain when precautions were taken to eliminate contamination by carry-over during HPLC analysis.

Figure 4. Metabolic pathways of 2,4-D EHE in spring wheat (Puvanesarajah, 1992; Puvanesarajah and Ilkka, 1992).



0 Metabolic Pathway for 2,4-D 2-EHE in Spring Wheat

Environmental fate in soil

Aerobic degradation

Concha. and Shepler (1994a) studied the aerobic degradation of [^{14}C]2,4-D in unsterilized Catlin silty clay soil applied at a rate of 5.1 mg/kg for 16 days. The samples were incubated at about 25°C throughout the study. Recoveries of radiocarbon averaged 95.6 ± 6.3%.

The 2,4-D was degraded rapidly and represented 0.5% of the applied dose after 16 days of exposure. The calculated half-life was 1.7 days based on pseudo-first order kinetics.

The main degradation product was CO_2, which accounted for 51.2% of the applied dose at the end of the study period. Two major products were 2,4-DCP (2,4-dichlorophenol) and 2,4-DCA (2,4-dichloroanisole) which rose and fell over the 16-day period. 2,4-DCP reached its maximum of 3.5% of the applied dose at day 2, then decreased to 0.4% at the end of the study period, while 2,4-DCA represented 2.5% of the applied dose at day 9 and decreased to 1.5%; and the unextractable residue was 36% of the TRR. Separation of the fulvic and humic acid fractions of an extracted sample at day 5 afforded 16% of the applied dose in the former and 11% in the latter. Further analysis of the fulvic acid fraction by HPLC recovered 6.1% of the applied dose as 2,4-D.

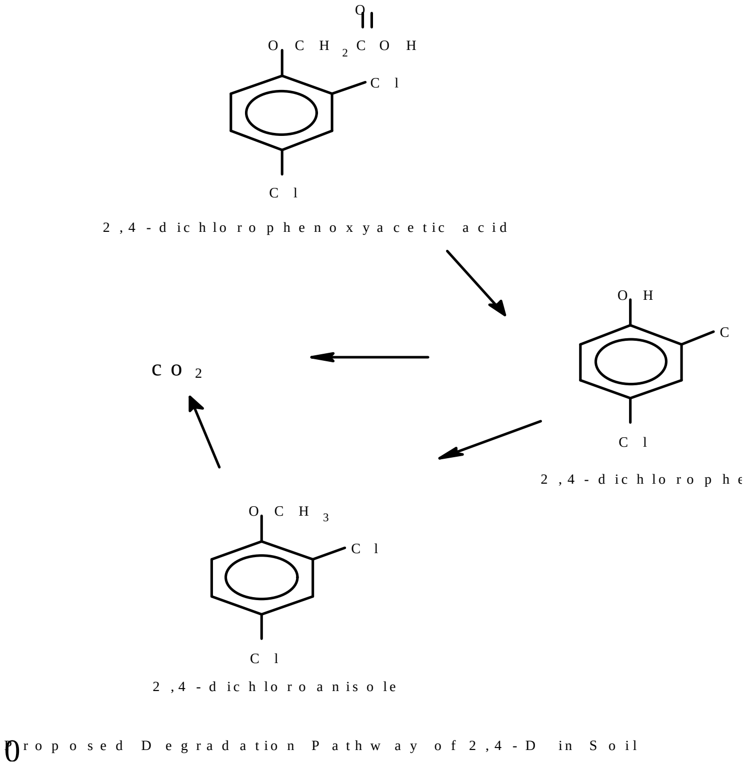
The results indicate that 2,4-D and its degradation products should dissipate rapidly from the soil environment mainly by mineralization and incorporation into the soil organic matter.

Reynolds (1994) determined the fate of the 2-ethylhexyl moiety of 2,4-D EHE by incubating ^{14}C-labelled 2-ethylhexanol in an aerobic soil system at 10 mg/kg under laboratory conditions at 25 ± 1°C in the dark. Sampling was at 0, 2, 4, 8, 12, 18, 24, 48, 168 and 336 hours after treatment.

Degradation was rapid. Initially most of the applied radioactivity was extracted into the organic solvent (methanol/methylene chloride) but the percentage of ^{14}C extracted decreased rapidly from 91% to 13% during the first 48 hours. By days 7 and 14, the organic extract accounted for 6.9% and 6.4% of the total applied radioactivity. The percentage of ^{14}C in the post-extraction solids (PES) remained fairly constant for the first 8 hours then began to increase dramatically, reaching its highest level (48% of the applied ^{14}C) at 48 hours. By day 14 the ^{14}C in the PES accounted for 22% of the total applied radioactivity.

During the first 24 hours the evolved acidic volatiles, including $^{14}CO_2$, increased gradually. Between 24 and 48 hours, however, the level detected in the KOH solution had quadrupled to 47%. Volatile ^{14}C accounted for a maximum of 70% of the applied ^{14}C on day 14.

Figure 5. Proposed degradation pathways of 2,4-D in soil (Concha and Shepler, 1994a).



Recoveries of ^{14}C from days 0 to 14 ranged from 93% to 108%. The average overall recovery of the applied radioactivity was 99%.

Analyses of the organosoluble fraction by reversed-phase HPLC showed one main product, which reached a maximum of 84% at 18 hours, in addition to 2-ethylhexanol. This was identified by GC-MS as 2-ethylhexanoic acid. Low levels of 5 other compounds were observed at later sampling times, but none of these exceeded 2.6% of the total applied radioactivity.

The PES fraction from day 14 was subjected to various procedures which included shaking for 4 hours with acetonitrile/water/acetic acid and refluxing for 1 hour with 0.25 *N* HCl, followed by shaking with 0.5 *N* NaOH for 24 hours to release the bound residues. The radioactivity extracted by $CH_3CN/H_2O/HOAc$ accounted for 1.6% of the total; 4% could be extracted from the solids following reflux with 0.25 *N* HCL for about 1 hour. The radioactivity that was extracted into the acid hydrolysate remained mostly in the aqueous fraction after partitioning with EtOAc. Less than 0.38% of the total applied radioactivity was detected in the EtOAc fraction. Most of the radioactivity in the solids appeared to be incorporated into natural soil constituents (fulvic acid, humic acid and humins). The ^{14}C in the fulvic and humic acids and humins was 4.2%, 4.6% and 7.5% of the total applied radioactivity respectively.

The half-life of 2-ethylhexanol in soil under the aerobic test conditions at 25°C was calculated to be 5.3 hours.

Reynolds (1995e) investigated the fate of the diethanolamine moiety from the diethanolamine salt by incubating diethanolamine with soil (10 mg/kg) under identical conditions to the above. [^{14}C]diethanolamine labelled on the 1-carbons was degraded rapidly with a calculated half-life in sandy loam soil of 1.35 days.

Analyses were by HPLC and TLC comparisons and LSC.

The parent compound steadily decreased throughout the study with the Hanford sandy loam soil. Two days after dosing, less than 38% of the total applied radioactivity was attributable to the parent compound. Its level had decreased to 0.9% of the applied ^{14}C by day 14 and to less than 0.6% at 90 days.

A total of ten products (M1-M10) were observed during the 90-day study. M2 accounted for 9.91% of the total applied radioactivity at day 0 but was not detected at day 1. Low levels of M2 appeared at day 2, reached a maximum of 1.4%, but then decreased to 0.1%.

The main product was M3 which, as determined by reversed-phase HPLC, reached 7.9% at day 2 and then steadily decreased to less than 1% at the end of the study. TLC analysis of the same fraction indicated that M3 consisted of three or four compounds, none of which exceeded 3% of the applied radioactivity.

Low levels of glycine (M4) and ethanolamine (M5) were also detected. Glycine reached a maximum of 5% at day 3, but at 90 days was less than 0.4%. Ethanolamine did not exceed 2.6% of the total radioactivity.

None of the products M6, M7, M8, M9 or M10 exceeded 0.8% of the dosed ^{14}C.

Up to 60% of the dosed ^{14}C in the sandy loam soil was converted to CO_2. The levels of bound residues reached a maximum of 33% at day 7. At day 90, the level of radioactivity detected in the post extraction solids (PES) accounted for 24% of the total applied ^{14}C.

The PES fraction from day 7 was subjected to acid hydrolysis for 4 hours followed by a 24-hour shaking with 0.5 *N* NaOH. Acid hydrolysis released 20% of the ^{14}C. Less than 1% of the radioactivity extracted by 0.25 *N* hydrochloric acid could be partitioned into ethyl acetate. TLC analysis of the aqueous fraction showed five or six compounds. The remaining radioactivity in the solids was incorporated into fulvic acid (4.4%), humic acid (3.7%) and humins (5%), indicating that diethanolamine is incorporated into the natural soil constituents and then mineralized to CO_2.

Adsorption/desorption

Cohen (1991b) determined the adsorption/desorption of unaged [^{14}C]2,4-D in unsterilized Louisiana rice paddy sediment by the batch equilibrium technique.

Two preliminary studies were conducted to determine the adsorption and desorption equilibrium times (24 and 8 hours respectively). It was also demonstrated that 2,4-D acid does not bind to glass surfaces.

A definitive study was conducted at five different concentrations (0.1, 0.51, 1, 2.47 and 5.02 mg/kg) at 22 ± 1°C. The K_d value for 2,4-D acid was 1.22 (K_{oc} = 58.1) indicating adsorption to sediment from water during the adsorption phase of the study. However, in the desorption phase, the K_d value of 1.64 (K_{oc} =78.1) indicated that 2,4-D is moderately to highly mobile in rice paddy sediment. The average ^{14}C recovery for the five concentrations tested was 98.9%.

Fathulla (1996b) studied the adsorption and desorption characteristics of [^{14}C]2,4-D on four representative agricultural soils. Samples were prepared at a soil:solution ratio of 1g:1ml, with nominal concentrations of [^{14}C]2,4-D in aqueous 0.01 *M* calcium chloride of 10, 5, 2.5 and 1 mg/ml. The samples were equilibrated in a shaking water bath for 24 hours at 25 ± 1°C, followed by vortexing and centrifugation. ^{14}C was measured in the resulting supernatant by LSC to determine the adsorption of the test material to the soil. The supernatant was then removed from each sample and replaced with an equal volume of untreated 0.1 *M* $CaCl_2$. The samples were equilibrated for 24 hours at 25 ± 1°C, followed by vortexing and centrifugation. ^{14}C in the supernatant was determined by LSC and the radioactivity remaining in the soil after desorption was determined by oxidation followed by LSC.

Linear regression analysis of the adsorption and desorption data for all the soils demonstrated that adsorption and desorption of [^{14}C]2,4-D followed the Freundlich equation. The adsorption and desorption equilibrium constants ($K_{d\text{-}a}$ and $K_{d\text{-}d}$ respectively), and coefficients $K_{oc\text{-}a}$ and $K_{oc\text{-}d}$ are shown in Table 12.

Table 12. Adsorption and desorption data of 2,4-D in soils (Fathulla, 1996b).

	Adsorption		Desorption	
Soil	$K_{d\text{-}a}$	$K_{oc\text{-}a}$	$K_{d\text{-}d}$	$K_{oc\text{-}d}$
Plainfield sand	0.36	76	1.16	247
California sandy loam	0.17	70	0.81	338
Mississippi loam	0.28	117	1.48	617
Arizona silty clay loam	0.52	59	1.90	216

The test material was largely stable in the test system in all the soils. After 24 hours, the total amounts of unchanged [^{14}C]2,4-D in the adsorption solution and soil extract were 95% of the original for Arizona silty clay loam, 109% for California sandy loam, 97% for Mississippi loam, and 98% for Plainfield sand. [^{14}C]2,4-D was stable over a 24-hour period and in aqueous 0.01 *M* $CaCl_2$, 100% of radioactivity in the desorption solution was owing to unchanged [^{14}C]2,4-D after 48 hours,.

The potential for [^{14}C]2,4-D to leach though soil, based solely on estimations of relative mobility using $K_{oc\text{-}a}$ values, is high for all the soils tested.

Fathulla (1996c) determined the adsorption and desorption characteristics of the soil degradation product 2,4-dichloroanisole (2,4-DCA) on the same four soils. Samples were prepared at a soil:solution ratio of 1g:5ml with nominal concentrations of [^{14}C]2,4-DCA in aqueous 0.01 *M* calcium chloride of 5, 2.5, 1 and 0.5 mg/ml. Other experimental details were as described above (Fathulla, 1996b).

Linear regression analysis of the data demonstrated that the adsorption and desorption of [^{14}C]2,4-DCA followed the Freundlich equation. The adsorption and desorption equilibrium constants and coefficients are shown in Table 13.

Table 13. Adsorption and desorption of 2,4-DCA in soils (Fathulla, 1996c).

	Adsorption		Desorption	
Soil	$K_{d\text{-}a}$	$K_{oc\text{-}a}$	$K_{d\text{-}d}$	$K_{oc\text{-}d}$
Plainfield sand	2.05	436	3.4	721
California sandy loam	1.6	667	2.4	996
Mississippi loam	3.46	1,442	4.5	1,867
Arizona silty clay loam	5.42	616	8.6	975

The test material was again stable in all the test systems. After 24 hours, the total amounts of unchanged [^{14}C]2,4-DCA in the adsorption solution and soil extract were 94% of the original for

Arizona silty clay loam, 105% for California sandy loam, 105% for Mississippi loam and 103% for Plainfield sand. After 48 hours 100% of the radioactivity in the desorption solution was due to unchanged [^{14}C]2,4-DCA.

The potential for 2,4-DCA to leach though the four soils, on the basis of the K_{oc-a} values is medium to low.

Fathulla (1996d) also studied the adsorption and desorption characteristics of 2,4-dichlorophenol in the four agricultural soils. Samples were prepared at a soil:solution ratio of 1g:2ml, with nominal concentrations of [^{14}C]2,4-DCP in aqueous 0.01 *M* calcium chloride of 10, 5, 2.5 and 1 mg/ml. Other experimental details were as described above (Fathulla, 1996b).

The adsorption and desorption of [^{14}C]2,4-DCP again followed the Freundlich equation. The adsorption and desorption equilibrium constants and the adsorption and desorption coefficients are shown in Table 14.

Table 14. Adsorption and desorption of 2,4-DCP in soils (Fathulla, 1996d).

Soil	Adsorption		Desorption	
	K_{d-a}	K_{oc-a}	K_{d-d}	K_{oc-d}
Plainfield sand	1.7	368	3.8	813
California sandy loam	1.97	821	6.3	2,625
Mississippi loam	2.9	1,204	5.6	2,325
Arizona silty clay loam	3.3	374	7.1	807

The test material was largely stable in all four test systems. After 24 hours, the total amounts of unchanged [^{14}C]2,4-DCP in the adsorption solutions and soil extracts were 92.5% of the original for Arizona silty clay loam, 93% for California sandy loam, 92% for Mississippi loam and 92% for Plainfield sand. [^{14}C]2,4-DCP was shown to be stable for 24 hours in aqueous 0.01 *M* $CaCl_2$, and for 48 hours in the desorption solution.

The potential for [^{14}C]2,4-DCP to leach though the tested soils is low, on the basis of the K_{oc-a} values.

Mobility

Burgener (1993) used lysimeters to represent an agricultural ecosystem in which to study the translocation of [^{14}C]2,4-D and its degradation products in a 120 cm soil and the effects of precipitation and vegetation of leaching. Information on the uptake of the pesticide by plants after soil application, as well as the ^{14}C balance after 725 days, was also obtained.

Two lysimeters were covered with summer wheat. On 15 June 1990, the herbicide was applied as the DMA salt at its recommended field rate, 750 g ae/ha. Husbandry and crop rotation followed common agricultural practice. Winter rye was sown in November 1990, followed by winter rape after harvest of the rye in summer 1991.

Water samples were taken regularly and ^{14}C was determined by LSC to estimate the contribution of dissolved $^{14}CO_2$ from the mineralization of the test compound. The remaining radioactivity was characterized by chromatographic techniques. The radioactivity taken up by the plants as well as that in the soil at the conclusion of the experiment was determined by combustion, while $^{14}CO_2$ and other volatile substances emitted to the atmosphere were calculated by difference.

In lysimeter 1 the ^{14}C recovered in the leachate after 2 years was 0.196% of the total applied radioactivity, corresponding to 0.14 mg parent equivalents. The total mean recovery of radioactivity, all leachate samples included, represented a concentration of 0.14 mg parent equivalents/l. After subtraction of $^{14}CO_2$, which represented 0.099% of the applied radioactivity, the remaining concentration was reduced to 0.07 mg/l. During the whole experimental period, 958 l of water (about 48% of the total precipitation, including irrigation) had been collected.

In lysimeter 2 the radioactivity in the water after two years was 0.25% of the total applied corresponding to 0.17 mg parent equivalents. The total mean recovery of radioactivity, all leachate samples included, represented 0.175 mg parent equivalents/l and 0.058% of the total applied radioactivity was $^{14}CO_2$. After subtracting this, the mean content of ^{14}C as 2,4-D was 0.13 mg/l. During this period, 994 l of water was collected, representing about 50% of the total precipitation, including irrigation.

No volatile substances except for $^{14}CO_2$ were detected in the leachates by TLC or HPLC.

[^{14}C]2,4-D DMA salt, the free acid and its known degradation products 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol were not detected in any of the leachates. In both lysimeters, a maximum of three unknown radioactive fractions were detected. The main unknown fraction was present in all the analysed leachate samples. It amounted in total to 0.043% of the applied radioactivity (AR) in lysimeter 1 and to 0.087% in lysimeter 2. The radioactivity evidently originated from very polar residues, and may be assumed in part to be derived from cleaved ring fragments bound to humic and fulvic acids.

At the conclusion of the experiment, soil cores were sectioned into 12 horizontal segments of about 10 cm thickness. In lysimeter 1, the TRR in the soil profile amounted to 21% of the AR, 11% in the top layer. For lysimeter 2 the corresponding proportions were 17% and 8.8%. In both lysimeters, only about 0.1% of the AR was found in the soil below 57 cm.

The extractable radioactivity in the soil again originated from three unknown fractions, the patterns and amounts of which in the soil extracts from the two lysimeters compared well and were nearly identical. Radioactivity was found as deep as 17 cm and amounted in total to 0.26% of the AR in the soil of lysimeter 1 and 0.29% in lysimeter 2. The decomposition products 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol were not detectable in any of the six analysed soil layers, which covered a depth of 57 cm.

The water collected during the experiment represented about 50% of the total precipitation. In June 1990, a series of exceptionally heavy rainfalls started one week before the application. Although the total amount in this month was nearly twice the monthly average for the region, the unfavourable conditions did not yield high concentrations of radioactivity.

The number and levels of the compounds found in the leachate and soil samples compared well in the two lysimeters. The results obtained indicated that [^{14}C]2,4-D and its decomposition products are not mobile in the sandy soil used in the experiment and 2,4-D is therefore not considered to have any potential to leach into ground-water. The leached radioactivity originated entirely from very polar unidentified residues.

Uptake by rotational crops

Burnett and Ling (1994) determined the level and nature of the 2,4-D residues taken up by rotational crops from soil treated with [^{14}C]2,4-D, applied by broadcast spray to bare ground on each of three plots at a rate equivalent to 2.2 kg ae/ha. Rotational crops, wheat, icicle white radish and lettuce, were planted 30 days after treatment (DAT) and 139 DAT.

Soil residues decreased significantly during the initial 30 DAT and chromatographic analysis of soil extracts indicated substantial degradation of 2,4-D during this period. Only 8.7% of the soil residues at 30 DAT were soluble in ether compared to an average of 97.5% at 0 DAT. The radioactivity recovered from soil cores at 0 DAT was identified as being from 2,4-D by HPLC, but at 30 DAT only 1.1% of the applied radioactivity was tentatively attributed to 2,4-D.

The TRR as 2,4-D equivalents in the 30 DAT crops except wheat forage ranged from 0.01 mg/kg to 0.06 mg/kg:

Sample	TRR, mg/kg as 2,4-D	
	30 DAT	139 DAT
Radish top	0.043	0.01
Radish root	0.01	0.011
Lettuce	0.019	0.013
Wheat forage	<0.001	0.03
Wheat straw	0.06	0.084
Wheat grain	0.049	0.06

No ether-soluble residues above 0.01 mg/kg were found in any plant samples, whereas in control tissues fortified with 2,4-D more than 65% of the activity was ether-soluble. All samples contained ethanol-soluble residues, but these exceeded 0.01 mg/kg only in radish tops and wheat straw (30 DAT radish tops 0.011 mg/kg, 30 DAT wheat straw 0.017 mg/kg, 139 DAT wheat straw 0.014 mg/kg).

Most of the radioactivity in the plants was not extractable with ether or acidic aqueous ethanol. Hydrolysis of the bound residues solubilized varying amounts of ^{14}C but only traces of ether-soluble residues, none above 0.004 mg/kg. Radioactive components at the retention times of 2,4-D and a hydroxylated product were observed on HPLC analysis of the ether extract of acid-hydrolysed radish tops at [0.001 mg/kg.

In the wheat straw at 30 DAT, crude lignin and cellulose contained 0.01 mg/kg and 0.007 mg/kg respectively. Wheat grain from both planting intervals was shown to contain ^{14}C incorporated into glucose isolated from the starch. The amount of [^{14}C]glucose was consistent with the amount of starch in typical wheat grain (60-70%).

The results showed no ether-soluble residues from free or conjugated 2,4-D or its known wheat metabolites at levels above 0.01 mg/kg after a 30-day planting interval. Extraction, hydrolysis and chromatographic characterization, supported by the detection of ^{14}C in glucose from starch, indicate that the radioactive residues in the rotational crops at both 30 and 139 DAT were owing to natural incorporation.

Terrestrial field dissipation

Fifteen terrestrial field soil dissipation studies were conducted with 2,4-D EHE (Barney, 1995a-d, j; Hatfield, 1995c-j; Silvoy, 1995a,b), and 18 with 2,4-D DMA (Barney, 1995e-i; Burgener, 1993; Hatfield, 1995k-r; Silvoy, 1994a-d). The results were summarized by Wilson *et al.* (1997).

Each test substance was characterized before use. Maximum label rates and treatment sequences were applied to each crop. In some of the trials, test plots were established in bare soil as well as in cropped areas.

In 1993, test sites in Colorado, North Carolina, and Texas (USA) were treated with commercial liquid formulations of 2,4-D DMA or 2,4-D EHE applied as diluted sprays. The Colorado and North Carolina trials included wheat and turf cropping practices with adjacent bare soil treatments, while the Texas plots included pasture cropping.

The wheat and bare soil plots had 1.4 kg ae/ha applied in May and again in July. In Colorado the soil was sandy clay loam with 1.3 to 1.8% organic matter (OM) and pH 7.8 to 8.1 (total precipitation plus irrigation 32 to 36 cm); in North Carolina sand with 0.77 to 1.4% OM, pH 5.4 to 6.9 pH (total precipitation plus irrigation 52 to 86 cm). Turf and adjacent bare soil treatments in North Carolina and pasture treatments in Texas consisted of 2.2 kg ae/ha applied in May and June. In Texas, the soil varied from sandy loam to silt loam with 1.5 to 1.6% OM, pH 6.0 to 6.1 (total precipitation plus irrigation 94cm).

In 1994 the test sites were in California, Nebraska, North Dakota, and Ohio. Sprays of both the amine salt and ester were applied to bare soil following a treatment regime for maize in Nebraska and Ohio, wheat in North Dakota, and pasture, bare soil, and turf in California. A commercial granular formulation of 2,4-D DMA was applied to bare soil and turf in North Dakota, and a 2,4-D EHE granular formulation to bare soil and turf in Ohio.

The maize treatment regime consisted of applications to bare soil of 2.2 kg ae/ha in May, 1.1 kg ae/ha in June, 0.56 kg ae/ha in July, and 1.7 kg ae/ha in September/October. In Nebraska the soil was silt loam with 2.9 to 3.5% OM and pH 5.7 to 6.7. Total precipitation plus irrigation was 79.5 cm. In Ohio the soils included a silty clay loam, clay loam, and silt loam with 2.0 to 5.0% OM and pH 6.5 to 7.1. Total precipitation plus irrigation was 47 to 97 cm. The wheat treatments consisted of 1.4 kg ae/ha applied in June and August. In North Dakota the soils ranged from sandy loam to loam with 2.9 to 6.4% OM and pH 5.9 to 7.7. The total precipitation plus irrigation ranged from 33 to 34 cm. Turf, pasture, and adjacent bare soil treatments consisted of 2.2 kg ae/ha applied in March through July with second applications in April through August. In California, soils varied from a sandy loam to loamy sand with 0.7 to 3.9% OM and pH 6.3 to 7.9. Total precipitation plus irrigation ranged from 67 to 142 cm.

In addition to 2,4-D, the analytical method employed was designed to extract and determine the ester 2,4-D EHE, 2,4-dichlorphenol and 2,4-dichloroanisole. The last two were shown to be relevant in soil degradation studies. The analytes were extracted from soil samples by a combination of three solvent systems and sonication. The combined extracts were diluted with water and concentrated on a C-18 solid-phase cartridge. The analytes were eluted sequentially with two solvent systems that yielded two eluates. The first eluate, containing 2,4-D EHE, 2,4-DCP, and 2,4-DCA, was chromatographed without derivatization. The second contained 2,4-D which was methylated with BF_3/methanol and partitioned into hexane. The first eluate and the hexane solution were combined for analysis by GC-MS. Recoveries of 2,4-D from fortified soil ranged from 91% at 0.01 mg/kg to 76% at 10 mg/kg with an LOD of 0.01 mg/kg.

Half-lives ($t_{1/2}$) for 2,4-D in soil were calculated for each trial by regression analysis of the residue data. Verification techniques showed applications to be generally close to the targeted levels. Soil half-life values were calculated using only the residues found in the 0- to 15-cm soil layer. The lower layers were not included because the residues were generally low (0 or <10% of those in the 0-15 cm layer), and the rate of degradation has been shown to decrease with increasing soil depth.

Tables 15 and 16 show 2,4-D residues found at various samplings after the maximum number of applications in the 1993 and 1994 trials respectively. For the 2,4-D EHE treatments, the residues shown are the sum of 2,4-D plus the remaining 2,4-D EHE expressed as 2,4-D. Half-lives are also shown for each trial. These were determined from regression analyses using all sampling intervals, and from analyses using the highest residue value found as the initial value. When two half-life values are shown, the first was calculated from all the samplings and the second by taking the highest residue as the initial value.

Table 15. 2,4-D residues and half-lives in 1993 trials. All spray applications (Wilson *et al.*, 1997).

Type of trial, location	Compound applied	$t_{1/2, days}$	Residues, mg/kg, at days after application

			0	1	3	7	14	30	64
Bare soil	Amine	5.1-4.3	0.35[1]	0.38	0.36	0.53	0.05		
Wheat-CO	Ester	2.2	0.52[2]	0.48	0.35	0.16	0.01		
Bare soil	Amine	3.0	0.3	0.28	0.12	0.14	0.01[4]		
Wheat-NC	Ester	3.0-2.5	0.19	0.3	0.34[3]	0.05	0.01[4]		
Wheat	Amine	9.3-7.1	0.2	0.31	0.23	0.27	0.08		
CO	Ester	2.6-2.3	0.22	0.31	0.28[5]	0.04	<0.01		
Wheat	Amine	3.1-2.9	0.26	0.28	0.1[5]	0.17	<0.01[4]		
NC	Ester	6.1-6.5	0.12	0.12	0.17[3]	0.06[6]		<0.01	
Bare soil	Amine	2.5	0.89	0.38	0.16[3]	0.03[7]	0.013		
Turf-NC	Ester	1.7	0.62	0.63	0.36[3]	0.03[7]	<0.01		
Turf	Amine	2.3	0.88	0.57	0.13[3]	0.095[7]	<0.01		
NC	Ester	3.9	0.63	0.38	0.39[3]	0.04[7]	<0.01	<0.01[8]	
Pasture	Amine	10.7	0.44	0.38	0.21	0.15	0.09[4]	0.05	<0.01
TX	Ester	12.8	0.33	0.29	0.22	0.1	0.05[4]	0.05	<0.01

[1] Residues from amine applications are 2,4-D acid

[2] Residues from ester applications are the sum of 2,4-D acid and 2,4-D EHE expressed as 2,4-D ae

[3] Two days

[4] Fifteen days.

[5] Four days.

[6] Eight days.

[7] Five days.

[8] Thirty five days.

[9] Twenty five days.

Table 16. 2,4-D residues and half-lives in 1994 trials, spray and granule applications (Wilson *et al.*, 1997).

Type of trial	Compound applied	$t_{1/2, \text{days}}$	Residues, mg/kg, at days after application						
			0	1	3	7	14	30	60
Spray									
Bare soil	Amine	2.8	0.59[1]			0.32	0.05		
maize NE	Ester	4.1	0.52[2]			0.21	0.13	0.003	
Bare soil	Amine	16.1-15.9	0.47	0.75	0.73	0.5	0.44	0.07	0.01
maize OH	Ester	6.7-5.2	0.59	0.59	0.87	0.78	0.48	0.03	
Wheat	Amine	4.5	0.64	0.53	0.21	0.11	0.07	0.005	
ND	Ester	5.3	0.51	0.49	0.39	0.19	0.09	0.009	
Pasture	Amine	30.6-31.2	0.34	0.56	0.39	0.13	0.15	0.09[3]	0.04[4]
CA	Ester	25.6-27.5	0.29	0.34	0.15	0.09	0.08	0.08[3]	0.04[4]
Turf	Amine	7.5	0.12	0.09	0.08	0.21	0.02		
CA	Ester	8.5	0.15	0.13	0.04	0.09	0.02	0.01[5]	5
Bare soil	Amine	2.3-2.1	0.83	1.4	0.82	0.13	0.02		
turf CA	Ester	11.0	0.42	0.29	0.30	0.28	0.15		
Granular									
Turf ND	Amine	5.1-4.0	0.1	0.11	0.74	0.07	0.02	<0.01	
Bare soil turf ND	Amine	14.6-14.5	1.2	1.6	1.9	1.7	0.89	0.27	0.03[7]
Turf OH	Ester	296-84	0.18	0.74	0.28	0.25	0.19	0.07[6]	<0.01[4]
Bare soil turf OH	Ester	9.9	1.6	1.1	1.3	1.3	1.5	0.05[6]	0.01[4]

[1] Residues from amine applications are 2,4-D acid.

[2] Residues from ester applications are the sum of 2,4-D acid and 2,4-D EHE expressed as 2,4-D.

[3] Twenty nine days.

[4] Fifty eight days.

[5] Twenty days.

[6] Thirty one days.

[7] Sixty two days

Environmental fate in water/sediment systems

Aquatic degradation

Cohen (1991a) studied the aerobic aquatic degradation of uniformly ring-labelled [^{14}C]2,4-D at a concentration of 4.6 mg/kg in a mixture of sieved (2-mm), unsterilized Louisiana rice paddy sediment (clay soil) and water (320 g sediment, 534 g water, 854 g total). The untreated mixture was pre-incubated under aerobic aquatic conditions in darkness at 25°C for 218 days to activate microbes, then [^{14}C]2,4-D in acetonitrile was mixed thoroughly with the sediment/water in the incubation flask and aerobically incubated in darkness at 25°C for 30 days. The soil was continuously purged with humidified air at 30 ml/minute to flush any volatile compounds formed into a series of trapping solutions (ethylene glycol, 1 *M* sulfuric acid and 5% sodium hydroxide).

Samples of the test system were taken immediately after treatment (day 0) and at 2, 5, 12, 20, 27 and 30 days after treatment. Sediment/water samples were separated by centrifugation and aliquots of sediment were combusted and the ^{14}C determined by LSC. The remaining sediment samples were extracted with 1.5 *M* phosphoric acid mixed with ethyl ether, washed with water, and re-extracted with 1 *N* sodium hydroxide solution. ^{14}C was measured in aliquots of all extracts and in duplicate samples of the supernatant and trapping solutions by LSC.

The sediment extracts and the water supernatant were analysed by HPLC with both UV (280 nm) and radio detection in series. Radioactive flow detection allowed identification of 2,4-D and its aerobic degradation products at a level of 0.01 mg/kg (limit of detection 0.005 mg/kg).

Analysis of the sediment/water samples showed that the half-life of 2,4-D acid was 15 days under aerobic aquatic conditions.

The degradation product chlorohydroquinone reached a maximum concentration of 17% (0.78 mg/kg) of the initial radioactivity on day 27 and decreased to 11% (0.52 mg/kg) by day 30. A minor product, 2,4-dichlorophenol, accounted for 4.9% (0.23 mg/kg) and CO_2 for 16% (0.74 mg/kg) of the initial ^{14}C by day 30.

The recovery of ^{14}C during the study (soil extractable and unextractable + water-soluble + cumulative volatiles) ranged from 69 to 100% of the initial radioactivity.

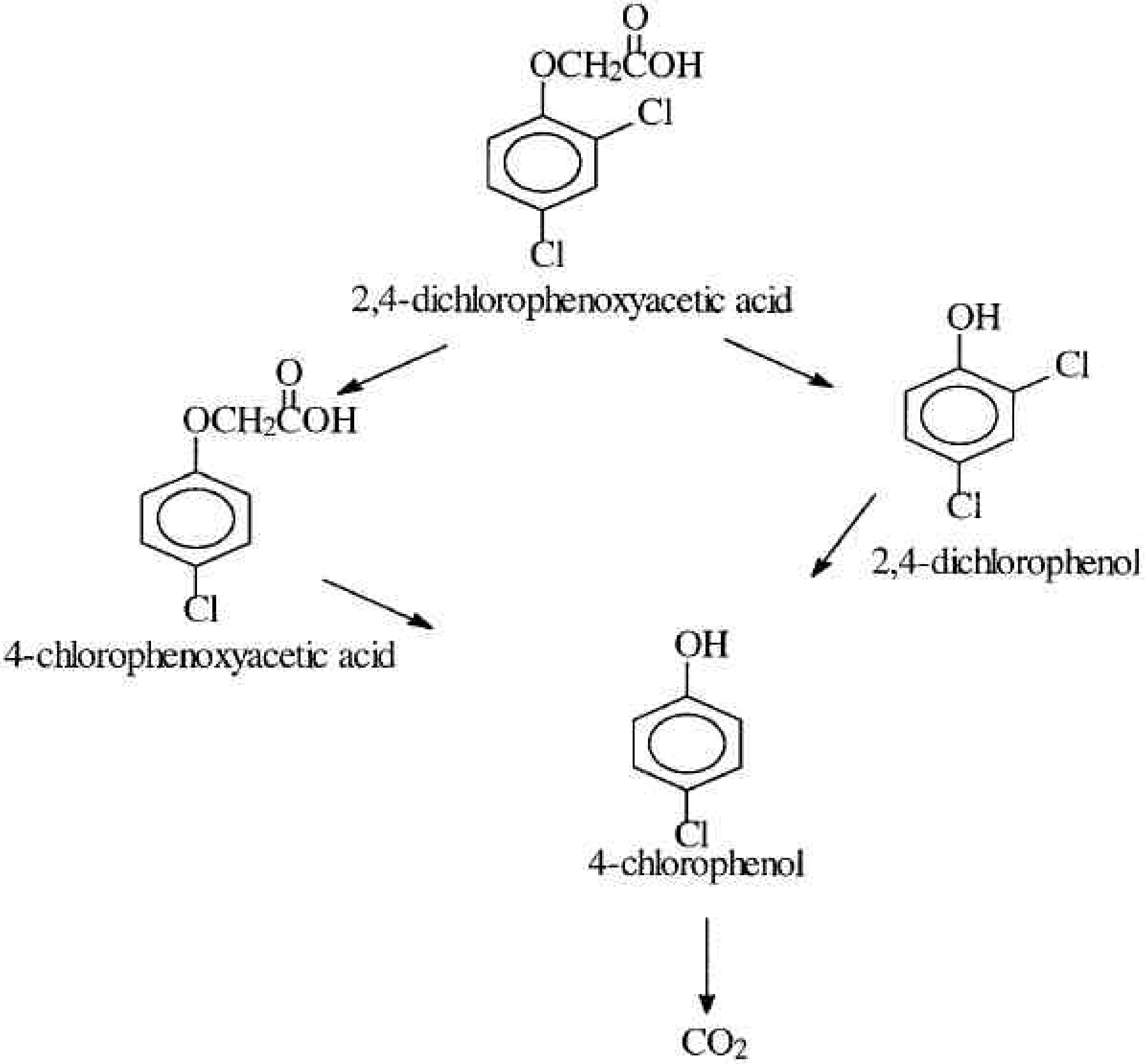
Concha and Shepler (1993a) studied aerobic aquatic degradation of [^{14}C]2,4-D in pond sediment and water samples from Henry County, Illinois with an application rate of 5 mg/kg for up to 46 days, and incubation at 25°C. The aqueous phase was monitored at each sampling for pH (7 to 8) and dissolved oxygen content (2.7 to 6.75 mg/kg).

[^{14}C]2,4-D acid was degraded slowly in the first 25 days and represented $\leq$75% of the applied dose at 25 days. It decreased rapidly n the next 10 days, and at 46 days it represented 0.5% of the applied radiocarbon. Its half-life was 4.5 days.

The main degradation product was CO_2 (64% of the applied radiocarbon at 46 days). 2,4-DCP, 4-CPA and 4-chlorophenol were present in both the water and sediment extracts. 2,4-DCP accounted for 1.1% of the applied ^{14}C at day 35 and decreased to 0.1% at day 46, and 4-CPA rose to 1.1% at day 14 and decreased to untraceable amounts. 4-chlorophenol represented 1.4% of the applied radiocarbon after 20 days and decreased slowly to zero by day 46. An unknown product was observed in the water phase of the samples after 35 days (1.1% of the applied dose); it was unstable when stored frozen or refrigerated and was converted to CO_2 and other volatile products upon acidification of the water-phase. No organic volatiles were detected above 0.1%. The unextractable residue increased with exposure time and constituted about 16% of the applied dose at day 46.

Radiocarbon recoveries averaged 93 ± 7%. During the lag time (25 days) most of the radiocarbon (>64%) was found in the water, and approximately 10 to 14% was extracted from the sediment in an alkaline solvent and about 4% in acidic acetone. After the lag time the radiocarbon distribution shifted dramatically as 2,4-D acid was degraded. At day 46 3% of the applied dose was recovered in the water phase, with 1.0% and 0.6% extracted in base and acidic solvents respectively. The overall material balance dropped slightly at day 35 but increased at day 46. This decrease is attributed to the rapid, massive production of CO_2 after the lag period that may not have been trapped efficiently which the trapping solutions were being changed. A separate sample was incubated and left unopened for 39 days, and higher recovery (92%) confirmed that the loss of radiocarbon was owing to the loss of untrapped CO_2 in the headspace.

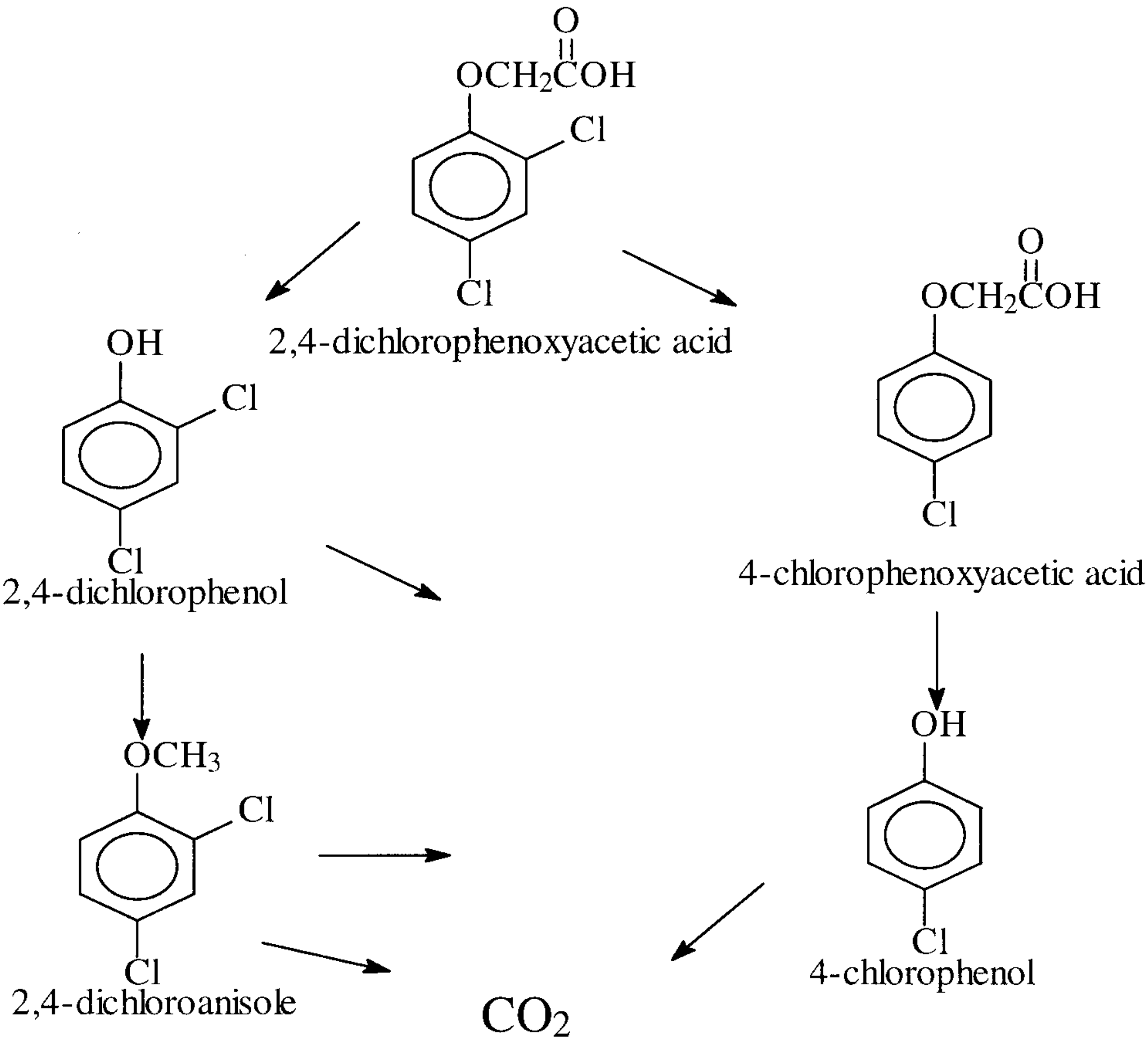
Figure 6. Degradation pathways of 2,4-D in an aerobic pond sediment/water system (Concha and Shepler, 1993a).



Concha and Shepler (1994b) studied the anaerobic aquatic degradation of [^{14}C]2,4-D (4.9 mg/kg) in raw pond sediment and water in Henry County, Illinois for one year. Samples were incubated at 25°C throughout the study and the aqueous phase was monitored at each sampling for pH (7.6-9.6). CLICK HERE for continue

Radiocarbon recoveries averaged 101 ± 5.2%. The distribution of ^{14}C varied depending on the extent of degradation observed in individual samples. The radiocarbon in the aqueous phase amounted to 24-85.5% of the applied ^{14}C and that in the organic extracts of sediment to 11-42%. Bound radiocarbon increased with increased degradation and after 240 days 35% of the applied ^{14}C remained unextracted. A sample taken on day 240 contained 2.4% of the ^{14}C in the humic acid and 14.9% in the fulvic acid fraction, with 23.5% remaining unextracted. Organic volatiles in the foam plugs accounted for up to 2.3% of the applied dose and $^{14}CO_2$ trapped in caustic solutions reached an average of 22% after 365 days.

Figure 7. Degradation pathways of 2,4-D in an anaerobic pond sediment/water system (Concha and Shepler, 1994b).



Compounds in the water, sediment extracts and foam plug extracts were identified by HPLC or two-dimensional TLC. The main component in the aqueous phase was 2,4-D, which represented 26% of the applied dose after 365 days. In the sediment extracts the parent compound constituted 13% of the applied radiocarbon at that time, giving a total of 39% 2,4-D in the test system. The two major degradation products were 2,4-DCP, which rose to 22% at day 30 and subsequently decreased to 4.2% after 365 days, and CO_2. Small unidentified peaks with various retention times were detected in some HPLC radiochromatograms. The largest unknown after 365 days represented 1.5%

of the dose. Small quantities of volatiles were extracted from the foam plugs, and at 365 days they included 4-chlorophenol (1.9%), 2,4-dichloroanisole (0.7%) and 2,4-DCP (0.7%).

The approximate half-life of 2,4-D was calculated to be 312 days ($r^2 = 0.69$).

Fathulla (1996a) studied the aerobic aquatic degradation of [^{14}C]2,4-D in representative sediment and water from Lake Mendota, Dane County, Madison, Wisconsin (USA).

Eighteen samples were prepared by placing approximately 3 g (dry-weight equivalent) of 2-mm sieved sediment and 30 ml lake water in glass containers. The test material was added to each sample in solution at a nominal concentration of 10 mg/kg. The day 0 samples were analysed as soon as possible after dosing. The other sample containers were gently shaken, and the water level was marked on each container. To maintain aerobic conditions and to collect volatile components, the sample vessels were connected to a glass manifold which was attached to a series of traps: ethylene glycol, 0.1 *N* sulfuric acid and two containing 2 *N* KOH. Air was sucked continuously through the traps and the test apparatus maintained in a dark, temperature-controlled room at 25°C. The pH, oxidation-reduction potential (Eh) and dissolved oxygen (DO) were monitored for all samples and throughout the study to ensure that the aerobic conditions were maintained.

The water layer and sediment were separated by centrifugation. The concentration of radioactivity in the water was determined by LSC, and the radioactive compounds separated by HPLC. The sediment samples were extracted first with 5% v/v acetic acid (HOAc) in methanol (MeOH), then with 50:50 MeOH/5% HOAc and finally with 5% aqueous HOAc. The three extracts were combined, the concentration of radioactivity was determined by LSC and the extract analysed by HPLC.

The recovery of radioactivity ranged from 97 to 103%, almost all of it (94-101%) in the water layer. The radioactivity in the sediment extracts did not exceed 3.1% of that applied, and the mean did not exceed 0.1%. Radioactive carbon dioxide was the only volatile component determined in the traps, increasing from 0.015% of the total applied radioactivity at day 1 to 0.28% at day 30.

The radioactivity in the water layers and sediment extracts from days 0 through 30 was almost entirely owing to [^{14}C]2,4-D, with mean percentages of the applied ^{14}C ranging between 103% at day 0 and 97% at day 8. Because no significant degradation was observed it was not possible to calculate the half-life. A single minor component, detected only in one replicate at day 30, accounted for 0.1% of the total applied radioactivity. The identity of [^{14}C]2,4-D was confirmed by two-dimensional TLC and HPLC co-chromatography with an unlabelled reference standard.

Under aerobic aquatic conditions, [^{14}C]2,4-D was not significantly degraded during a 30-day incubation period. In addition to [^{14}C]2,4-D, small amounts of $^{14}CO_2$ (accounting for 0.28% of the initial ^{14}C) and one other component (0.1%) were detected by day 30.

Levine (1990) studied the aquatic degradation of [^{14}C]2,4-D at a concentration of 4.9 mg/kg in sieved (2 mm), unsterilized Louisiana rice paddy sediment (clay soil) and water. The untreated mixture was pre-incubated under anaerobic conditions in darkness at 25 ± 0.8°C for approximately 138 days to activate soil microbes. After the activation period, [^{14}C]2,4-D acid in acetonitrile was mixed thoroughly with the sediment/water mixture in the incubation flask, which was then anaerobically incubated in darkness at 25 ± 0.8°C for 365 days. The mixture was continuously purged with humidified nitrogen at 45-50 ml/minute to flush any volatile compounds formed into a series of trapping solutions (ethylene glycol, 1 *M* sulfuric acid, ethanolamine and 5% sodium hydroxide).

Samples of the test mixture were taken immediately after treatment and after 1, 6, 13, 22, 35, 70, 85, 120, 160 224, 281, 338 and 365 days. The sediment and water were separated by centrifugation and replicate sediment samples were combusted and analysed for total radioactivity by LSC. Additional duplicate samples were extracted with 1.5 *M* phosphoric acid mixed with ethyl ether, washed with water and finally re-extracted with 1 *N* sodium hydroxide solution. ^{14}C was measured in all the extracts and in replicate supernatant water samples and trapping solutions by LSC.

The water samples and sediment extracts were analysed by HPLC with a UV (280 nm) detector and a radioactive flow detector connected in series. Radioactive flow detection allowed identification of 2,4-D and its degradation products at μ0.01 mg/kg. TLC was used as a confirmatory method of identification.

Analysis showed that 2,4-D acid was degraded with a half-life of 41 days under anaerobic aquatic conditions. The main product formed during the 365-day incubation period was 4-chlorophenol, and 2-chlorophenol was a minor product. All ^{14}C residues at or above 0.01 mg/kg were identified.

CO_2 production reached 71% of the initial radioactivity (3.5 mg/kg as 2,4-D) by the end of the study.

The extraction of ^{14}C from the sediment samples ranged from 90 to 102% of the radioactivity present at each sampling, and the total recovery (sediment extractable and unextractable + water supernatant + cumulative volatiles) ranged from 52 to 98% of the day 0 radioactivity. The incomplete recovery was owing to loss of the volatile $^{14}CO_2$.

The results indicate that 2,4-D acid is not likely to remain long in the environment under anaerobic aquatic conditions.

Reynolds (1995b) showed that ^{14}C-labelled 2-ethylhexanol was degraded quickly when incubated at approximately 10 mg/kg in flooded soil under anaerobic conditions at 25 ± 1°C.

The percentage of ^{14}C in the supernatant fraction decreased from 75% at day 0 to 59% at day 3 where it seemed to stabilize throughout the remainder of the study. The proportion of radioactivity that could be extracted from the solid fraction into CH_3OH/CH_2Cl_2 remained at a level of 22 to 26% for the first 30 days. By 60 days, 14% of the initial radioactivity was found in the CH_3OH/CH_2Cl_2 fraction and this proportion stayed fairly constant throughout the remaining period. The percentage of ^{14}C in the post-extraction solids fraction ranged from 6.7% (day 3) to 1.9% (day 179) but remained fairly constant from day 14 to day 270.

The evolved acidic volatiles, including $^{14}CO_2$, increased gradually with time, accounting for 14% and 25% at 30 and 270 days respectively. Barium salt precipitation from the KOH solution at each sampling indicated that there were other volatiles besides $^{14}CO_2$. The mean $^{14}CO_2$ ranged from 1.1% (day3) to a maximum of 9.1% (day 179) of the applied radioactivity. Analysis of a composite of day 224 KOH samples showed the main component to be 2-ethylhexanol.

The water samples and organosoluble extracts were analysed by reversed-phase HPLC. The main compounds were 2-ethylhexanoic acid and 2-ethylhexanol.

The parent 2-ethylhaxanol decreased quickly accounting for 22% of the total applied radioactivity after 30 days, 5.1% after 60 days and was undetectable at 270 days. The 2-ethylhexanoic acid was first observed at day 7 (9.3%) and reaching a maximum of 61% at 120 days, then remaining stable. At 270 days, 59% of the applied dose was still 2-ethylhexanoic acid.

The radioactivity from 2-ethylhexanol in the CH_3OH/CH_2Cl_2 fraction decreased from 24% of the applied radioactivity at day 0 to 2% at day 30, 0-0.53% was detected in the remaining samples. The main product was again 2-ethylhexanoic acid, at 19% after 30 days. It decreased slightly thereafter but then remained stable until the last sampling.

There were four other minor products, none exceeding 2.4% of the total applied radioactivity. Recoveries of ^{14}C ranged from 97% to 105% with a mean of 99%.

In summary under anaerobic conditions, [^{14}C]2-ethylhexanol at an application rate of 10 mg/kg was degraded to 2-ethylhexanoic acid and further mineralized to $^{14}CO_2$ by micro-organisms in the sediment/water test system. Significant levels of 2-ethylhexanol were also detected in the KOH trapping solution together with $^{14}CO_2$. The half-life of 2-ethylhexanol was 14 days.

Reynolds (1995a) established that under laboratory conditions at 25 ± 1°C and in the dark, dimethylamine (DMA) was degraded very quickly in an aerobic water/sediment system containing approximately 10 mg/kg. The estimated half-life was 2.8 days.

Analyses were by comparative HPLC and TLC with LSC.

Quantitative recoveries of ^{14}C were obtained throughout the 14 days of the study from all samples, with an average of 99.6%.

Nine degradation products were observed. The main product, monomethylamine (MMA), was detected at day 0 and accounted for 5.9% of the total applied radioactivity. It gradually decreased with time and accounted for 1.2% of the total initial radioactivity at the end of the period. None of the other products accounted for more than 0.29% of the applied ^{14}C in any sample.

The evolved acidic volatiles trapped in KOH solution increased dramatically during the 14 days, accounting for an average of 63% of the applied radioactivity. Neutral volatiles trapped in ethylene glycol were negligible, amounting to about 0.08% of the applied ^{14}C. Barium salt precipitation from the KOH solution confirmed that most of the trapped radioactivity was due to $^{14}CO_2$.

Sediment-bound residues increased gradually to reach a maximum of 41% at 5 days; these were released by various techniques. Refluxing with 0.25 *N* HCl released 29% of the applied radioactivity which was not extracted by organic solvents. After the acid hydrolysed aqueous fraction was derivatized with benzoyl chloride organic solvent partition extracted 26% of the applied ^{14}C. Chromatographic analysis of the derivatized aqueous fraction showed the presence of a component which was identified as *N*,*N*-dimethylbenzamide, indicating that the parent compounds had become bound to soil constituents.

Soil fractionation of the remaining bound residues yielded 3.1%, 3.96% and 5.1% of the applied radioactivity in humic acid, fulvic acid and humin fractions respectively.

In an identical experiment ,but with an anaerobic water/sediment system (Reynolds, 1995c) DMA was degraded very slowly at 10 mg/kg. The estimated half-life was approximately 1610 days.

Analyses were as before and quantitative recoveries of ^{14}C were obtained throughout the 180-day test period for all samples. The average recovery was 109%.

The total DMA in the water and sediment ranged from an average level of about 99% of the applied chemical on day 0 to 88% by day 180. Eight degradation products were detected. The main one, monomethylamine appeared at day 0 when it accounted for 5.3% of the total applied radioactivity, with levels ranging from 5.5% at 14 days to 3.2% at 90 days with no obvious pattern of formation or decrease. None of the other seven products accounted for more than 0.63% of the initial ^{14}C.

Less than 2% of the applied ^{14}C was evolved as acidic volatiles, including $^{14}CO_2$, which was trapped in KOH solution. Barium salt precipitation confirmed that most of the trapped radioactivity was due to $^{14}CO_2$.

Acid hydrolysis released 7% of the applied ^{14}C, of which almost all (6.9%) remained in the aqueous fraction after partitioning with ethyl acetate. When the aqueous fraction was derivatized 5.9% of the initial ^{14}C could be extracted into dichloromethane and the main component of the extract was DMA, as *N,N*-dimethylbenzamide. A KOH trap used during the acid reflux procedure was found to contain 0.03% of the initial ^{14}C, indicating that no volatiles were formed during reflux. Low levels of radioactivity were detected as fulvic acid (0.51%), humic acid (0.38%) and humins (0.87%).

Reynolds (1995d) also incubated ^{14}C-labelled isopropanol in the dark at 25 ± 1°C in flooded sediment at 10 mg/kg under anaerobic conditions. Degradation was rapid. The evolved acidic volatiles trapped in 1 *N* KOH including $^{14}CO_2$ increased steadily and after 120 days accounted for 65% of the applied ^{14}C, but barium chloride precipitation and HPLC showed that much of the volatile ^{14}C consisted of acetone and isopropanol. Other minor products were observed but not identified.

The half-life of the [2-^{14}C]isopropanol was 15 days. Under the anaerobic aquatic test conditions isopropanol was degraded to acetone and further mineralized to $^{14}CO_2$.

Reynolds (1995f) showed that under the same laboratory conditions diethanolamine was degraded very quickly in an aerobic water/sediment system at 10 mg/kg. The estimated half-life was 10.3 days. Analyses were by HPLC and TLC with LSC.

Nine degradation products were observed in addition to the parent chemical and ethanolamine. The main product, described as M3, accounted for 4.1% of the total applied radioactivity at day 0, 8.2 % after 7 days, decreasing to 2.1% at the end of the study. None of the other products including ethanolamine exceeded 4.3% in any sample.

Sediment-bound residues increased gradually to reach 27% at 21 days. Those from day 14 were examined further. A refluxing solvent released 13% of the applied radioactivity which was not organosoluble. Chromatographic analysis of the polar residues identified a number of components, none of which exceeded 3% of the AR.

Soil fractionation of the remaining bound residues gave 3.4%, 2.2% and 5.5% of the ARR in humic acid, fulvic acid and humin fractions respectively.

In the corresponding anaerobic system, under otherwise identical conditions (Reynolds, 1996) degradation was too slow to estimate a half-life during the study period of 365 days.

Four degradation products in addition to the parent chemical and ethanolamine were observed. The main product, M1, accounted for 1.4% of the total applied radioactivity at day 0, and 6.4% after 14 days, but decreased to 0.84% at 365 days. None of the other products observed, including ethanolamine, exceeded 4.7% in any sample.

Sediment-bound residues accounted for 20% of the ARR at 59 days and 9.1% at 91 days. Acid hydrolysis of the PES from 59 days released 14% of the applied ^{14}C, less than 0.5% of which could be partitioned into ethyl acetate. TLC of the aqueous fraction showed a radioactive spot with the same Rf value as the parent compound. During acid refluxing a KOH trap was found to contain less than 0.25% of the applied dose, indicating that no volatiles were formed. Low levels of the applied radioactivity were detected in fulvic acid (2.75%), humic acid (1.4%) and humins (1.4%).

Recoveries of ^{14}C during the 365days ranged from 102 to 110%, with an average total recovery of 105%.

Aquatic field dissipation

In June 1993 a study was initiated in Louisiana to investigate the dissipation and mobility of 2,4-D DMA and its major products, 2,4-D, 2,4-DCP, 2,4-DCA, 4-CPAA and 4-CP when applied to rice in flooded Mowata silt loam (Barney, 1994). One aerial spray was applied at 2 kg ae/ha. Soil and water samples were taken from the treated and control plots before and after the application on day 0. Soil samples were also taken at 1, 3, 7, 15, 30, 45, 60, 90, 120 and 180 days and water samples at 1, 3, 7, 15 and 30 days. Soil was sampled to a depth of 30 cm at each sampling except on day 0 when samples were taken to a depth of 10 cm. The water samples were taken before soil cores to prevent contamination from disturbed sediment. At each sampling three subsamples of water, each about 200 ml, were collected from different parts of the test site.

Water samples were analysed for 2,4-D, 2,4-DCP, 2,4-DCA, 4-CPAA and 4-CP. The highest 2,4-D residue (mean 1.4 mg/kg) occurred on day 0 and then decreased to a mean of 0.54 mg/kg at day 1 and 0.19 mg/kg at day 3. No 2,4-D was detected above the LOD (0.01 mg/kg) in water samples at 7, 15 or 30 days. Residues of 2,4-DCP and 4-CPAA were detected in the first three samplings, but below the LOD (0.01 mg/kg). Apparent residues of 2,4-DCP and 4-CPAA at day 0 were undetectable at day 7. Traces of 2,4-DCP, 2,4-DCA, 4-CPAA and 4-CP were observed at day 15. The half-life for the dissipation of 2,4-D in water was 1.1 days.

Soil samples were analysed for 2,4-D, 2,4-DCP and 2,4-DCA in 10 cm increments to a depth of 30 cm. The highest 2,4-D residue (0.04 mg/kg; mean total of 3 depths) occurred 1 day after application and decreased to 0.013 mg/kg after 3 days. Residues of 2,4-D, slightly above the LOD of 0.01 mg/kg, were detected below 10 cm only at the day 1 sampling. This suggests contamination by the sampling equipment rather than any mobility to lower depths. Degradation products (2,4-DCP and 2,4-DCA) were not detected above the LOD (0.01 mg/kg) at any sampling. The half-life for the dissipation of 2,4-D in soil was calculated as 1.5 days.

Aquatic pond dissipation

Hatfield (1995a,b) studied the dissipation and mobility in soil of 2,4-D DMA, 2,4-D, 2,4-DCP, 2,4-DCA, 4-CPAA and 4-CP in an aquatic environment (small pond) in North Carolina (NC) and North Dakota (ND). The soils were Bibb sandy loam in NC and Runaff sandy loam in ND. Two applications were made by subsurface injection to the pond, the first at 45 kg ae/ha and the second 30 days later at 50 kg ae/ha in NC, and both at 47 kg ae/ha, 31 days apart, in ND. Soil and water samples were taken from the treated and control plots before and after the applications (day 0), and 1, 3, 7, 14 and 21 days after the first applications and 1, 3, 7, 14, 21, 30, 60, 90 and 120 days (and 180 days in ND) after the second. Soil was sampled to a depth of 20 cm at each sampling, and a composite sample of water was taken from the top 90 cm (NC) or 120 cm (ND) of the pond water.

In NC water residues of 2,4-D increased from 0.54 mg/kg (day 0, first application) to 2.1 mg/kg (day 3) and then decreased to 0.86 mg/kg just before the second application. The concentration of 2,4-D at day 0 after the second application was 2.8 mg/kg and decreased to 0.01 mg/kg by day 21. No subsequent samples had residues above the LOD (0.001 mg/kg).

The mean residues of 2,4-DCP in water fluctuated from 0.006 mg/kg (days 7 and 14 after the first application and the day of the second application) to the LOD at day 21 (second application). 2,4-DCA was undetectable throughout the study. The mean residues of 4-CPAA were similar to 2,4-DCP with the highest concentration (0.012 mg/kg) on day 0 and day 1 after the second application. Low levels of 4-CP were reported on day 14 (0.002 mg/kg) and day 30 (0.001mg/kg) after the second application.

The half-lives of 2,4-D in water were 20 and 7.6 days after the first and second applications respectively.

The average residues of 2,4-D in 0-5 cm soil/sediment layers were 1.1, 1.2, 1.3, 1.5 and 0.79 mg/kg at 0, 1, 3, 7 and 14 days after the first application. At day 21, 2,4-D was detected throughout the 0-20 cm depth at a total concentration of 0.33 mg/kg, and 2,4-DCP was found at 0.22 mg/kg.

After the second application the average residues of 2,4-D in the 0-5 cm soil fractions decreased from 0.62 mg/kg (day 0) to 0.13 mg/kg by day 14 and were undetectable thereafter. Low levels of 4-CP and 4-CPAA were reported from day 21 (first application) to day 7 (second application), but only in the 0-5 and 5-10 cm depths.

The half-life of 2,4-D in soil/sediment was calculated to be 7.6 and 2.0 days after the first and second applications respectively

In ND residues of 2,4-D in water decreased from 4.7 mg/kg (day 0, first application) to 1.2 mg/kg on the day before the second application. The concentration of 2,4-D on day 0 after the second application was 3.1 mg/kg and decreased to 1.5 mg/kg by day 30. Samples taken after day 60 had no residues above the LOD (0.001 mg/kg).

The mean residue of 2,4-DCP in water was 0.01 mg/kg on days -1, 3 and 21 after the second application and decreased to below the LOD after day 60. There were no detections of 2,4-DCA throughout the study. The mean residues of 4-CPAA followed 2,4-DCP with the highest concentration (0.008 mg/kg) on day 0 after the second application.

The half-lives of 2,4-D in water were 14 and 6.5 days for the first and second applications respectively.

The average residues of 2,4-D in the 0-5 cm soil/sediment layers were 0.25, 0.61, 0.35, 0.37 and 1.2 mg/kg at 0, 1, 3, 7 and 14 days after the first application respectively. At day 21, 2,4-D was detected throughout the 0-20 cm depth at a total concentration of 1.05 mg/kg.

After the second application the average residues of 2,4-D in the 0-5 cm fractions decreased from 1.6 mg/kg (day 3) to 0.016 mg/kg (day 180).

Low levels of 4-CP and 4-CPAA were reported only from day 21 (first application) and day 60 (second application) in the 5-10 and 10-15 cm depths.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The official method of analysis in The Netherlands (Anon. 1996) is based on the extraction of samples with a basic aqueous solution before solid-phase extraction (SPE) on a C-18 bonded silica cartridge for concentration and isolation of the analytes followed by clean-up on a silica- or aminopropyl-bonded cartridge. SPE extracts are further processed by column-switched reversed-phase LC using a pre-column packed with internal-surface reversed-phase (ISRP) material and a C-18 bonded analytical column. The analytes are detected by UV at 118 nm. The LOD was reported to be 0.02 mg/kg for meat and 0.05-0.1 mg/kg for cereals and vegetables.

Plants, general method

James (1994) validated EN-CAS method No. ENC-2.93 used to determine the residues in wheat forage, straw and grain.

Table 17 compares the 2,4-D concentrations reported in forage, grain and straw samples from a metabolism study conducted by ABC Laboratories (Puvanesarajah, 1992) with the averaged 2,4-D residues found in the same samples by the EN-CAS method. The results show that method ENC-2/93 is adequate for determining 2,4-D in wheat plants which have been treated during growth.

Table 17. Comparison of analytical methods for 2,4-D in wheat (James, 1994; Puvanesarajah, 1992).

Wheat fraction	^{14}C, mg/kg, 2,4-D equivalents					2,4-D, mg/kg by GLC
	Total ABC Labs	2,4-D, ABC Labs	Total, ENC-2/93	Extracted, ENC-2/93	in final volume from ENC-2/93	in final volume from ENC-2/93
Forage	33.6	24.8	32.2	32.3	24.8	30.6
Straw	55.7	39.0	53.1	53.8	37.1	52.4
Grain	0.299	0.017	0.323	0.120	0.025	0.037

The analytical procedure was as follows. The residues were extracted by shaking with 0.5 M KOH in 1:1 EtOH/H_2O and filtering. After the addition of 0.2 M HCl to an aliquot, the mixture was refluxed for 1 hour on a hot plate. The extract was cleaned up by octadecylsilyl solid-phase (ODS) extraction and solvent partitioning. The dry sample was methylated with boron trifluoride in methanol and the methyl ester was cleaned up by solvent partition followed by alumina column chromatography. ^{14}C was measured by liquid scintillation counting (Optiphase HiSafe® scintillation cocktail with LKB 1214 RackBeta counter).

The 2,4-D residues were determined as the methyl ester by GLC with an ECD. A fused silica 15 m x 0.32 mm DB-1701 column with a 0.25 µm film thickness was used for wheat grain and straw and a 30.m x 0.32 mm DB-17 column with a 0.25 µm film thickness for forage.

Most samples yield good recoveries for forage with good chromatographic baselines with the method as described. A permanganate oxidation as an extra clean-up step is needed for soya beans (forage and seed), rice straw and sugar cane.

Table 18 shows the recoveries of 2,4-D from fortified processed fractions by EN-CAS Method No. ENC-2/93.

Table 18. Recoveries of 2,4-D from fortified processed fractions by EN-CAS method No. ENC-2/93 (James, 1994).

Crop	Sample	Fortification level, mg/kg	Number of samples [1]	% Recovery
Wheat	patent flour	0.01 0.50	5 2	74-101 73, 80
	bran	0.01 0.50	2 2	86, 110 77, 79
	middlings	0.01 0.50	2 2	74, 76 84, 90
	shorts	0.01 0.50	2 2	77, 85 85, 97
	aspirated grain fractions	0.10 1.00	2 2(1)	113, 116 111, 125

Crop	Sample	Fortification level, mg/kg	Number of samples [1]	% Recovery
Maize	starch	0.01 0.50	6 (1) 2	65-87 75, 85
	grits	0.01 0.50	2 2	92, 105 89, 92
	meal	0.01 0.50	2 2	96, 100 86, 91
	flour	0.01 0.50	6 2	81-100 72, 80
	crude oil	0.01 0.50	6 2	71-104 84, 88
	refined oil	0.01 0.50	2 2	92, 98 81, 90
	aspirated grain fractions	0.01 0.50	2 2	93, 99 95, 97
Sorghum	starch	0.01 0.50	2 2	77, 86 82, 84
	flour	0.01 0.50	2 2	88, 94 73, 77
Sugar cane	molasses	0.01 5.00	6 2	82-98 87, 89
	bagasse	0.01 5.00	6 2	72-110 83, 83
	sugar	0.01 2.00	6 2	100-107 73, 80
Rice	hulls	0.01 0.10	2 (1) 2	68, 78 74, 82
	bran	0.01 0.50	2 2	87, 88 90, 97
	polished rice	0.01 0.10	6 2	70-90 78, 80

[1] Figures in parentheses are the numbers of samples with recoveries outside the 70-120% range

Table 19 shows concurrent recoveries of 2,4-D from fortified control samples of field maize, grass, rice, sorghum and sugar cane and processed fractions of field maize, rice, sorghum, sugar cane and wheat.

Table 19. Recoveries of 2,4-D from fortified samples (Carringer, 1995a-x, Rosemond, 1995a-c).

Crop (Reference)	Sample	Fortification level, mg/kg	Number of samples[1]	% recovery
Field maize	forage	0.01-10	15	73-95
(Carringer, 1995d,e,f)	silage	0.01-10	14	78-110
	grain	0.01-20	23	73-112
	fodder	0.01-100	22	80-109

Crop (Reference)	Sample	Fortification level, mg/kg	Number of samples[1]	% recovery
Field maize	starch	0.01, 1	2	93, 95
(Carringer, 1995c)	grits	0.01, 1	2	86, 86
	meal	0.01, 0.05	2	106, 109
	flour	0.01, 0.05	2	111, 121
	crude oil	0.05, 0.1	4	85-107
	refined oil	0.01, 0.05	2	100, 128
	grain	0.01-0.1	4	86-110
	aspirated grain fractions	0.01-5	4	79-102
Grass	forage	0.01-1000	65 (7)	64-112
(Carringer, 1995j,k,o,u,v,w,x) (Rosemond, 1995a,b,c)	hay	1.0-1500	58 (4)	65-100
Rice	grain	0.01-0.5	10	81-118
(Carringer, 1995p,q)	straw	0.01-0.5	8	72-97
Rice	grain	0.01, 0.05	2	70, 82
(Carringer, 1995n)	hulls	0.01, 0.5	2	99, 119
	bran	0.01, 0.5	2	84, 114
	milled white rice	0.01, 0.05	2	93, 103
Sorghum	forage	0.01-0.1	14 (1)	67-114
(Carringer, 1995g,h,i)	grain	0.01-0.1	14	74-93
	fodder	0.02-1	12 (3)	100-133
Sorghum	starch	0.01, 0.05	2	91, 94
(Carringer, 1995m)	flour	0.01, 0.05	2	96, 88
	grain	0.02-0.2	4	70-93
Sugar cane	forage	0.01-0.5	8	90-117
(Carringer, 1995r,s)	cane	0.01-0.2	8	76-108
Sugar cane	cane	0.05, 0.5	2	79, 93
(Carringer, 1995l)	molasses	0.01, 0.05	4	85-116
	bagasse	0.01, 0.05	2	90, 96
	sugar	0.01, 0.05	2	87, 100
Wheat	Forage	0.01-10	19 (1)	60-110
(Carringer, 1995a,b,t)	grain	0.001-20	15	71-113
	straw	0.01-20	17 (2)	69-127

Crop (Reference)	Sample	Fortification level, mg/kg	Number of samples[1]	% recovery
Wheat (Carringer, 1995a)	bran	0.01-10	4	83-100
	low grade flour	0.01, 0.05	2	97, 93
	patent flour	0.01, 0.05	2	97, 100
	middlings	0.01-5.0	4	76-107
	shorts	0.01-5.0	4	72-93
	grain	0.01, 0.05	2 (1)	63, 86
	aspirated grain fractions	0.10-100	3	86-107

[1] Figures in parentheses are the numbers of samples with recoveries outside the 70-120% range.

In an independent laboratory validation of EN-CAS Method No. ENC-2/93 by Centre Analytical Laboratories, Inc. (Zheng 1995) control samples of wheat forage, straw and grain were fortified with 2,4-D at 0.01 mg/kg (the LOD) and at either 5 or 20 mg/kg. Recoveries from all the samples averaged 94%, ranging from 82% for wheat forage to 103% wheat straw.

Citrus fruits

(Siirila 1995). 2,4-D residues in oranges and grapefruit were extracted from 10 g samples of citrus fruit by refluxing with 0.2 M NaOH for 1 hour. An aliquot of the extract was acidified with sulfuric acid and extracted with ethyl ether. The 2,4-D was then methylated with boron trifluoride in methanol. After the addition of water, the residue was extracted into hexane and determined by GC-MSS.

The same method was used for lemons, lemon juice and wet lemon pulp, except that 0.7 M NaOH solution was used for the initial extraction. For lemon molasses, dry lemon pulp and lemon oil, samples of 5, 2 and 1 g were extracted with 0.2, 0.7 and 0.2 M NaOH respectively.

The Olds were 0.05 mg/kg for oranges, grapefruit, lemons, lemon juice and wet lemon pulp, 0.2 mg/kg for dry lemon pulp and molasses and 0.5 mg/kg for lemon oil. Table 20 shows recoveries of 2,4-D from fortified control samples of citrus fruits and processed citrus commodities.

Table 20. Recoveries of 2,4-D from citrus fruit and processed fractions (Johnson and Strickland, 1995a-c).

Sample	Reference	Fortification level, mg/kg	Number of samples [1]	% recovery
Grapefruit	Johnson and Strickland, 1995c	0.5	16 (4)	70.8-140
	Johnson and Strickland, 1995a	0.05 0.1 0.25	10 (2) 6 (2) 4	79.2-133 110-138 90.4-100
Lemons	Johnson and Strickland, 1995c	0.5	6	85.0-104
	Johnson and Strickland, 1995a	0.05 0.25	11 (2) 11	76.6-191 84-114
Oranges	Johnson and Strickland, 1995a	0.05 0.25	6 6	89.6-118 92.8-107

Sample	Reference	Fortification level, mg/kg	Number of samples [1]	% recovery
Lemon juice	Johnson and Strickland, 1995c	0.5	6 (2)	90.2-126
	Johnson and Strickland, 1995b	0.05 0.25	6 6	107-114 96-104
Wet lemon pulp	Johnson and Strickland, 1995c	0.5	6	92.0-105
	Johnson and Strickland, 1995b	0.05 0.025	7 (1) 7	97.6-126 83.2-104
Dry lemon pulp	Johnson and Strickland, 1995c	0.5 1	2 6	98.2-104 76.4-97.6
	Johnson and Strickland, 1995b	0.4 2	6 6	85.5-114 94.0-103
Lemon molasses	Johnson and Strickland, 1995c	1	8	96.3-119
	Johnson and Strickland, 1995b	0.4 2	6 6 (1)	97.8-115 95.0-121
Lemon oil	Johnson and Strickland, 1995c	1	8	77.7-116
	Johnson and Strickland, 1995b	1 5	4 4	74.2-98.1 80.8-95.4

[1] Figures in parentheses are the numbers of samples with recoveries outside the 70-120% range.

Animal products

(Howard 1996a). Procedures were developed to extract and quantify residues of 2,4-D in beef muscle, liver, kidneys, fat and milk.

2,4-D is extracted from beef muscle by homogenizing the tissue with acidified acetonitrile. The homogenate is centrifuged, filtered and diluted with water. The analyte is partitioned into diethyl ether and then into 0.1% NaOH solution. The residual organic solvent is removed by rotary evaporation. The extract is acidified and passed through C-8 and C-18 solid-phase extraction (SPE) columns in series. The analyte is eluted with *tert*-butyl methyl ether (MTBE). The MTBE is concentrated, and the analyte is methylated with ethereal diazomethane or boron trifluoride in methanol (BF_3/MeOH).

Beef fat is homogenized in hexane and 2,4-D is extracted from the homogenate with 0.1% NaOH solution. The basic extract is acidified and partitioned with diethyl ether. The analysis is completed as described for beef muscle.

Beef liver is refluxed for one hour in 2 *N* hydrochloric acid. After cooling, the aqueous extract is diluted with acetonitrile and sodium chloride is added. After phase separation the acetonitrile layer is passed through a hand-packed Florisil column to remove some interferences, the eluate is diluted with 1% NaOH solution and the acetonitrile is removed by rotary evaporation. The aqueous extract is acidified and the analyte transferred to 10% ethyl acetate in hexane, which is passed through a hand-packed neutral alumina column. The analyte is eluted with a solution of 10% methanol in 1% NaOH which is acidified and partitioned with MTBE. The MTBE layer is concentrated and the analyte is methylated with ethereal diazomethane or BF_3/MeOH.

Beef kidney is homogenized in acidified acetonitrile. The homogenate is centrifuged and filtered, and the analysis is completed as described for beef liver.

Milk is acidified to 2 *N* with hydrochloric acid. It is then refluxed for one hour and allowed to cool. Acetonitrile and sodium chloride are added to the sample. The analysis is completed as for liver.

GLC conditions:

Instrument:	HP 5890
Column:	60 m, J&W DB-1, 0.32 mm, 5 µm film
Injector temperature:	250°C
Carrier:	Helium at 2 ml/min
Detector:	ECD at 325°C
Detector make-up:	Nitrogen at 58 ml/min
Column temperature programme	220°C, 5 min, 2°C/min 230°C, 30 or 40 min, 40°C/min 300°C, 10 or 15 min
Injector volume:	4 µl splitles
Retention time:	Approximately 28 to 30 minutes

The LOD was 0.05 mg/kg for beef muscle, beef liver, beef kidney and beef fat, and 0.01 mg/kg for milk.

Howard (1996b) developed and validated procedures to extract and quantify 2,4-D in poultry muscle, liver, fat and eggs.

Residues of 2,4-D are extracted from poultry muscle and fat as described for beef muscle and fat.

2,4-D is extracted from eggs by homogenization with acidified acetonitrile. The homogenate is centrifuged, filtered, and passed through a hand-packed Florisil column to remove interferences. The eluate is diluted with 1% NaOH solution and the acetonitrile removed by rotary evaporation. The aqueous extract is acidified and the analyte partitioned into 10% ethyl acetate in hexane. The organic phase is separated and passed through a hand-packed neutral alumina column. The analyte is eluted with a solution of 10% methanol in 1% NaOH and the eluate is acidified and partitioned with MTBE. The MTBE layer is concentrated and the analyte methylated with BF_3/MeOH. Water is added to the reaction mixture and the methyl ester of 2,4-D is partitioned into hexane for determination by GLC.

Poultry liver is refluxed for 1 hour in 2 *N* HCl. After cooling, acetonitrile and NaCl are added to the hydrolysate, the acetonitrile layer is removed and passed through a hand-packed Florisil column and the analysis is completed as described for eggs.

The GLC conditions are the same as for beef and milk.

The LOD was 0.05 mg/kg for poultry muscle, fat and liver, and 0.01 mg/kg for eggs.

Soil, water and sediment

(Hatfield 1995r). Soil samples were analysed for 2,4-D EHE (when applicable), 2,4-D acid, 2,4-DCP and 2,4-DCA. Residues of these analytes were extracted by sonicating successively with 5% acetic acid in methanol, 5% acetic acid in 50% aqueous methanol and finally 5% acetic acid in water. The combined extracts were diluted with water, acidified and concentrated on a C-18 SPE cartridge. The cartridge was eluted with 2% acetone in hexane and then with 20% methanol in hexane. The first eluate contained 2,4-DCP, 2,4-DCA and 2,4-D EHE if present. The second contained 2,4-D which was concentrated, methylated with BF_3/methanol, partitioned into petroleum ether, and combined with the first (underivatized) eluate. The combined solution in hexane was concentrated and analysed by gas chromatography with a mass selective detector. The LOD was 0.01 mg/kg.

GC-MSD conditions

Instrumentation:	Hewlett-Packard model 5890 Series II gas chromatograph/model 5971A mass selective detector
Column:	Durabond-1 (DB-1), 15 m x 0.25 mm i.d., 0.25 µm with DF film
Pre-column:	Stabilwax, 1 m x 0.25 mm i.d., with 0.25 µm DF film
Oven temperature:	Hold at 60° for 2 minutes, then 60-150°C at 10°C/minute, then 150-200°C at 45°C/minute, then 200-240°C at 10°C/minute, then hold at 240°C for 2 minutes
Injector temperature:	250°C
Transfer line temperature:	280°C
Carrier gas:	Helium
Carrier gas flow rate:	~40-60 cm/second (internal flow sensor)
Head pressure:	5 psi
Injection mode:	Splitless
Injection liner:	Silanized dual taper
Injector purge delay:	1.5 minutes
Septum purge:	~7.5 ml/minute
Injection volume:	2 µl
Ionization potential:	70 eV
Electron multiplier voltage:	1400-1900 V (typical)
Dwell time:	50-200 msec

(Hatfield 1995b). Extraction, concentration on a C-18 column, and elution were identical to the procedures for soil. Water samples were analysed for 2,4-D acid, 2,4-DCP, 2,4-DCA, 4-CPA and 4-CP. The first eluate now contained 2,4-DCP, 2,4-DCA and 4-CP and the second contained 2,4-D and 4-CPA. The analysis was completed as for soil, with the same GC-MS condition. The LOD was 0.001 mg/kg.

(Hatfield 1995b). Sediment samples were analysed for 2,4-D acid, 2,4-DCP, 2,4-DCA, 4-CP and 4-CPA. A 10 g sample was vortexed and sonicated as before. The extracts were decanted and filtered after each extraction, combined and brought to a known volume. 2,4-D acid and its products were fractionated by liquid-liquid partition of separate aliquots. The residues were quantified by gas chromatography with mass selective detection. The LOD for all the analytes was 0.01 mg/kg.

GC-MS conditions:

Instrumentation:	Hewlett-Packard model 5890 Series II gas chromatograph/model 5972 mass selective detector
Column:	HP-5MS, 0.25 mm i.d. x 30 m, 0.25 µm film thickness
Oven temperature:	Hold at 50°C for 1 minutes, then 50-100°C at 5°C/minute, then 100-260°C at 10°C/minute then hold 5 minutes
Injector temperature:	240°C
Transfer line temperature:	280°C
Carrier gas:	Helium
Carrier gas flow rate:	1 ml/minute
Head pressure:	12 psi
Injection mode:	Splitless
Injection liner:	Silanized single taper
Injector purge delay:	1.5 minutes
Septum purge:	50 ml/minute
Injection volume:	2 µl
Ionization potential:	70 eV
Electron multiplier voltage:	1400-1900 V (typical)
Dwell time:	100 msec

Stability of pesticide residue in stored analytical samples

Barker (1995) determined the stability of residues of 2,4-D during freezer storage for one year (the longest period of storage of samples from the residue trials) in raw agricultural commodities (maize grain, forage and fodder, sorghum grain, wheat grain, forage and straw, sugar cane, rice grain, rangeland grass and hay and soya bean seed) and processed fractions (maize starch, flour and crude oil, wheat flour, sugar, molasses and bagasse, and rice bran and hulls). The results are shown in Tables 21 and 22. Freezer storage temperatures were monitored daily and were -12°C to -27°C. Fortification levels ranged from 0.1 to 5 mg/kg. Analyses of stored samples, but not 0-day samples, were corrected for procedural recoveries if these were less than 100%. Procedural recoveries from samples fortified at 0.1 to 5 mg/kg which were analysed concurrently with stored samples yielded an overall mean and standard deviation of 89 ± 10% (n = 232).

Table 21. Storage stability of residues of 2,4-D in raw agricultural commodities (Barker, 1995).

Sample	2,4-D, % of initial residue after days				
	0	30	90	180	365
Maize grain	95 118 88	82 104	101, 108	105 99	91 93
Maize forage	95 91 89	97 94	90 94	93 98	104 96

Sample	2,4-D, % of initial residue after days				
	0	30	90	180	365
Maize fodder	97 96 96	96 95	98 92	82 85	74 78
Sorghum grain	84 83 91	89 89	92 91	99 103	87 88
Wheat grain	79 80 84 87	105 105	90 81	92 94	98 98
Wheat forage	84 82	102 102	93 99	96 97	91 92
Wheat straw	81 86 93 99	103 102	95 93	100 88	100 105
Sugar cane	83 86 79	94 90	102 104	96 97	93 101
Rice grain	110 107 109	98 94	99 101	87 95	100 97
Rangeland grass	88 91 89 98	96 91	100 101	97 89	83 86
Rangeland hay	94 86 89	99 86	96 93	115 110	90 86
Soya bean seed	86 93	93 95	98 92	90 71	96 93

Table 22. Storage stability of incurred residues of 2,4-D in processed agricultural commodities (Barker, 1995).

Sample	2,4-D, % of initial residue after days				
	0	30	90	180	365
Maize starch	98 102 105	106 112	106 104	101 111	98 103
Maize flour	74 64 81	90 89	106 105	89 80	91 100
Crude maize oil	92 92 91	100 88	99 86	94 87	90 93

Sample	2,4-D, % of initial residue after days				
	0	30	90	180	365
Wheat flour	91 84 84	95 94	98 101	89 94	82 100
Cane sugar	94 86 81	95 95	92 89	91 83	88 77
Sugar molasses	84 85 86	98 95	95 98	114 112	100 94
Sugar bagasse	73 68 75	91 96	92 96	90 87	86 84
Rice bran	84 92 91	104 96	96 79	100 102	88 88
Rice hulls	72 73 70	98 98	103 105	81 78	99 80

Johnson and Strickland (1995c) determined the storage stability of 2,4-D in fortified grapefruit, lemons and lemon products stored at ≤-20°C (Table 23).

Table 23. Storage stability of 2,4-D in fortified citrus commodities (Johnson and Strickland, 1995c).

Sample	Fortification level, mg/kg	Storage period, days	Recovery, %	Corrected recovery, %[1]
Grapefruit	0.5	0	91, 90	--
		28	82, 83	92, 93
		56	111, 111	105, 105
		86	69, 93	96, 130
		119	104, 108	91, 95
		150	120, 125	103, 107
		181	134, 135	97, 98
		212	92, 96	79, 82
Lemons	0.5	0	101, 103	-
		28	98, 97	110, 109
		59	105, 104	103, 102
Lemon juice	0.5	0	120, 126	-
		28	129, 136	108, 114
		58	104, 87	111, 92
Wet lemon pulp	0.5	0	96, 94	-

Sample	Fortification level, mg/kg	Storage period, days	Recovery, %	Corrected recovery, %[1]
		28	102, 93	107, 98
		59	99, 101	95, 97
Dry lemon pulp	1	0	96, 78	-
		28	99, 97	123, 121
		58	61, 93	60, 92
		92	107, 107	112, 112
Lemon molasses	1	0	96, 102	-
		28	112, 112	103, 103
		59	108, 106	100, 98
		104	114, 108	98, 93
Lemon oil	1	2	106, 102	-
		28	107, 95	129, 114
		59	100, 99	112, 111
		97	112, 112	99, 99

[1] Corrected for average concurrent procedural recoveries

The stability of 2,4-D in other crops is shown in Table 24.

Table 24. Frozen storage stability of 2,4-D in other fortified crops.

Crop (Reference)	Sample	Fortification, mg/kg	Storage, days	Recovery [1], %
Apple (Barney and Kunkel, 1995b)	Fruit	0.1, 0.5	573	75-101
Asparagus (Kunkel, 1995a)	Spears	0.1	~630 [2]	56, 55, 56, 71
		1	~630 [2]	42, 54, 52, 49
		1	14 [3]	93, 92, 92
Cherry (Barney and Kunkel, 1995c)	Fruit	0.05	862	99, 97, 94
Cranberry (Barney and Kunkel, 1995a)	Fruit	0.05	876	96-102
Filbert (Kunkel, 1996a)	Kernel	0.5	151	77, 96, 99
Grapes (Kunkel, 1996b)	Fruit	0.5	467	101, 92, 101
	Juice	0.5	466	108, 103, 103
	Raisins	0.5	414	87, 91, 88
Peach (Barney and Kunkel, 1995d)	Fruit	0.1	271	99, 96
		0.5	271	94, 91
Pear (Kunkel, 1996d)	Fruit	0.1, 0.5	563-567	92-97

Crop (Reference)	Sample	Fortification, mg/kg	Storage, days	Recovery [1], %
Pecan (Kunkel, 1996c)	Kernel	0.5	182	89, 90, 99
Pistachio (Barney, 1995e)	Kernel	0.5	171	58, 88, 85
Plum/fresh prune (Barney and Kunkel, 1995f)	Fruit	0.02	235	77
		0.1	235	101
		0.5	235	107
Prune (Barney, 1995f)	Fruit	0.02	195	110
		0.1	195	70
		0.5	195	91
Potato (Barney and Kunkel, 1995g)	Tuber	0.05	747	93, 102, 102
Strawberry (Kunkel, 1995e)	Fruit	0.5	59	114-117
Sweet corn (Kunkel, 1995c)	Kernel and cob [4]	0.5	104	81-113

[1] Corrected for concurrent procedural recoveries of 89-117% for asparagus, 75% for cherries, 77% for peaches, 93% for pistachios, 83% for plums, 79% for prunes, 77% for grapes, 87% for grape juice and 69% for raisins.

[2] Storage stability study with fortified 1992 field trial control samples

[3] Storage stability study with fortified 1994 field trial control samples

[4] With husks removed

The stored fortified samples of asparagus showed an average decrease in 2,4-D content of 46% after about 20 months. As these samples were only analysed after a single storage period and 2,4-D residues are stable at -20°C in other commodities, it is unclear whether the decrease reflects actual degradation of 2,4-D or procedural error.

Krautter and Downs (1996) determined the storage stability of 2,4-D in frozen cattle liver, kidney, muscle, fat and milk. Homogenized tissue and milk were fortified with 2,4-D and analysed on the day of preparation and after about 2 and 4 months of frozen storage.

Mean recoveries of 2,4-D from freshly prepared liver, kidney, muscle, fat and milk samples were 99, 71, 111, 85 and 71% respectively. Results of analyses of stored samples were corrected for concurrently determined procedural recoveries. Mean corrected recoveries from liver, kidney, muscle, fat and milk were 115, 112, 106, 112 and 81% respectively after 2 months and 107, 124, 110, 117 and 109% after 4 months. These findings demonstrated that 2,4-D is stable in the analysed cattle products when stored frozen for at least 4 months.

USE PATTERN

2,4-D as acid, salt or ester is a selective hormone-type phenoxy herbicide. It is readily absorbed by leaves and roots causing abnormalities in growth and plant structure with subsequent necrosis. Plant protection products containing 2,4-D are used as foliar-applied herbicides for the post-emergence control of broad-leaved weeds. The registered uses are shown in Table 25.

Table 25. Registered uses of 2,4-D. Application rates are expressed as acid equivalents (kg ae/ha or ae/hl).

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
Almonds	USA	directed to the orchard floor	1.6	61		2	60

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
Apple	Nether-lands	spraying of aerial parts after flowering[1]	0.9-2.1	500		1	
	USA	directed to the orchard floor, retreatment interval of 75 days	2.2	183		2	14
Asparagus	Canada		1.3	50		1	
	USA		2.2	183		2	3
Barley	Australia	boom application aerial application	1.6 1.1	70 10		1	7
	Canada	aerial application ground application, depends on design	0.52	30 50		1	b
	USA	apply after grain is fully tillered but before forming joints in stems, apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Barley, spring	EU[3]	forage application	0.42	200-600	0.07-0.21		
	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Barley, winter	EU[3]	forage application	0.90	200-600	0.15-0.45		
	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Blueberries	USA	directed or spot applications to row middles	1.6			2	30
Cereals	Belarus		0.6	200		1	
	France		1.4	200		1	
	Hungary		0.81	300		1	
	Kazakhstan		1.4	200		1	
	Poland		0.90	200		1	
	Russia		1.6	200		1	
	Ukraine		0.84	300		1	
Cereals, spring	Austria		0.72	200		1	
Cereals, winter	Austria		0.72	200		1	
	EU[3]	forage application (2,4-D EHE)	0.56	200		1	
	Nether-lands	spraying of aerial parts before coming of the ear	0.9-1	600		1	
Cherries	USA	directed to the orchard floor	1.6	183		2	14
Cranberry	USA	make directed wipe of spot applications, make directed or spot applications when weed tops are above crop	4.5 1.3			2	
Grapefruit	USA	ground application to increase fruit size			0.0012 - 0.0024	1	7
Grapes	USA	direct application at least 3 months before harvest	1.6	476		1	100
Grass, pastures cultures of grass seed	Australia	boom application aerial application	4.5 2.8	30 10		1	7
	Canada		3.1	100		1	b
	EU[3]	forage application	0.9-1.5	200-600	0.15-0.75		
	Germany		1.0	600		1	28
	Hungary		1.4	300		1	
	Poland		1.3-1.5	200-300	0.42-0.73	1	
	Nether-lands	spraying of aerial parts	0.9-1.5	600		1	d, e
	USA	allow 30 days between applications, do not cut for hay with in 7 days of application	2.2	18		2	
Hazelnuts	USA	spray to wet leaves and stems of			0.12	4	45

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
		suckers during April through August, 30 days between applications					
Lemon	USA	post harvest packing house application			0.050	1	
Maize	Australia	boom application aerial application	0.67 1.1	25 10		1	
	Belarus		0.6	200		1	
	Canada		0.52	50		1	b
	EU[3]	direct spray to weeds	1.2	200-600	0.2-0.6		
	Hungary		0.68	300		1	
	Kazakhstan		1.1	200		1	
	Netherlands	spraying till crop height 5-60 cm	0.9-1	200		1	
	Russia		1.6	200		1	
	Slovakia		0.63	400		1	
	Thailand		0.71-1.0	500	0.15-0.20		
	Ukraine		0.84	300		1	
	USA	preplant or pre-emergence post-emergence, layby treatment, apply after hard dough stage	1.1 0.56 1.7	18 18 18		3	7
Millet	Australia	boom application aerial application	0.67 0.72	25 10		1	
	USA	1. apply after grain is fully tillered but before forming joints in stems, 2. apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Oats	Australia	boom application aerial application	1.6 1.1	70 10		1	7
	Germany		0.75	200		1	F
	USA	1. apply after grain is fully tillered but before forming joints in stems, 2. apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Oranges	USA	ground application to increase fruit size; aerial application; apply in fall oil, water or whitewash sprays, prevent pre-harvest drop			0.0012-0.0024 0.02 0.0004-0.0024	1 1 1	7 - -
Peach	USA	directed to the orchard floor	1.6	183		2	14
Peanut	Australia	boom application aerial application	2.3 2.3	25 10		1	
Pear	Netherlands	spraying of aerial parts after flowering [6]	0.9-2.1	500		1	
	USA	directed to the orchard floor, retreatment interval of 75 days	2.2	183		2	14
Pecan	USA	directed to the orchard floor	1.6	61		2	60
Pistachio nut	USA	directed to the orchard floor, retreatment interval 30 days	1.6	183		2	50
Plums	Netherlands	spraying of aerial parts of weeds after flowering[6]	1.8	600		1	
Plums (incl. Prunes)	USA	directed to the orchard floor	1.6	183		2	14
Pome fruits	Poland	ground application	0.72-0.90	200-300	0.24-0.45	1	
	USA	directed to the orchard floor,	2.2	183		2	14

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
		retreatment interval of 75 days					
Potato	Australia	aerial application	1.6	10		1	28
	USA	first application at pre-bud stage, second application 10-14 days later	0.078	183		2	
Raspberries	Canada	any time except during bloom	0.52	100		1	
	USA	24 days before harvest and post-harvest	3.1	275		2	24
Rice	Thailand		0.75-1.0	500	0.15-0.20		
	USA	usually 6-9 weeks after emergence	1.7	18		1	60
Rye	Australia	boom application aerial application	1.6 1.1	70 10		1	7
	Canada	aerial application ground application, depends on design	0.52	30 50		1	B
	USA	apply after grain is fully tillered but before forming joints in stems, apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Rye, spring	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Rye, winter	EU[3]		0.90	200-600	0.15-0.45		
	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Sorghum	Australia	boom application aerial application	0.67 0.72	25 10		1	
	USA	apply when sorghum is 15 to 38 cm tall	0.56 (only EHE) 1.1	18		1	30 (for forage)
Soya bean	USA	apply not less than 7 days before planting, apply not less than 15 days before planting	0.56 (only EHE) 1.1	18 18		1	
Strawberry	Canada	after planting – before rooting of runners	0.52	100		1	
	Netherlands	spraying of aerial part of weeds after harvest	1.4	500		1	
	USA	broadcast application, dormant	1.7	183		1	
Sugar cane	Australia	boom application aerial application	3.9 3.2	30 10		1	
	EU[3]		1.4	400-600	0.24-0.36		
	Thailand		0.75-1.0	500	0.15-0.2		
	USA	pre-emergence before canes appear, post-emergence after cane emerges and through canopy closure	2.2	18		2	
Sweet corn	Australia	boom application aerial application	0.67 1.1	25 10		1	
	USA	broadcast application, 1. pre-emergence 2. post-emergence	1.1 0.56	183		2	7 (for forage)
Tangelo	USA	apply in fall oil, water or whitewash sprays, prevent pre-harvest drop			0.0004-0.0024	1	
Tree nuts	USA	directed to the orchard floor	1.6	61		2	60
Triticale	Australia	boom application aerial application	1.6 1.1	70 10		1	7
	Germany[7]		0.75	200		1	F
	Poland		1.3	200-300	0.42-0.62	1	
Wheat	Australia	boom application	1.6	70		1	7

Crop	Country	Application					PHI, days
		Method	Rate, kg ae/ha	Minimum spray, l/ha	Spray conc, kg ae/hl	No.	
		aerial application	1.1	10			
	Canada	aerial application ground application	0.52	30 50		1	b
	USA	1. apply after grain is fully tillered but before forming joints in stems, 2. apply when grain is in the dough stage	1.4 0.56	18 18		2	14
Wheat, spring	EU[3]	forage application	0.42	200-600	0.07-0.21		
	Germany		0.75	200		1	F
	Poland		1.3	200-300	0.28-0.64	1	
Wheat, winter	EU[3]	forage application	0.9	200-600	0.15-0.45		
	Germany		0.75	200		1	F
	Netherlands	spraying of aerial parts at crop height 15-20 cm, before coming of ears[8]	1	600		1	
	Poland		1.3	200-300	0.28-0.64	1	
Wild rice	USA	apply in the 1 to 2 aerial leaf through early tillering stage	0.28	18		1	60

[1] Other herbicides mixed with 2,4-D used for apples (trees over 3 years old): benazolin, dicamba, MCPA, mecoprop.

[2] Do not permit lactating dairy animals to graze treated fields within 7 days after application. Do not harvest forage of cut hay within 30 days after application. Withdraw meat animals from treated fields at least 3 days before slaughter

[3] Proposed uses

[4] Re-entry of cattle not within 1 week after application

[5] Other herbicides mixed with 2,4-D used for grass: benazolin, dicamba, MCPA, mecoprop

[6] Other herbicides mixed with 2,4-D used for pears or plums (trees over 2 years old): dicamba, mecoprop

[7] Pending

[8] Other herbicides mixed with 2,4-D used for wheat: benazolin, dicamba, MCPA

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of supervised residue trials on agricultural crops are shown in Tables 26-53. All trials were carried out in the USA.

Table 26. Grapefruit.
Table 27. Oranges.
Table 28. Lemons.
Table 29. Pome fruit.
Table 30. Stone fruit.
Table 31. Berries.
Table 31. Sweet corn.
Table 33. Potatoes.
Table 34. Asparagus.
Table 35. Maize forage.
Table 36. Maize fodder.
Table 37. Maize grain.
Table 38. Rice grain.
Table 39. Rice straw.
Table 40. Wild rice.
Table 41. Sorghum grain.
Table 42. Sorghum forage.
Table 43. Sorghum fodder.
Table 44. Wheat forage.
Table 45. Wheat grain.
Table 46. Wheat straw.
Table 47. Sugar cane forage.
Table 48. Sugar cane.
Table 49. Tree nuts.
Table 50. Soya bean forage.
Table 51. Soya bean hay.
Table 52. Soya bean seed.
Table 53. Pasture grass, forage and hay.

Residues, application rates and spray concentrations have generally been rounded to two significant figures or, for residues below 0.1 mg/kg, to one. Only when residues were quantifiable in control samples are they recorded in the Tables. Multiple values from the same trial are replicate field samples. Underlined residue values were used for the estimation of maximum residue levels and/or STMRs.

Treatment of citrus fruits

2,4-D is registered in the USA as a growth regulator (1) to reduce drop of mature fruit (2) to increase fruit size (3) to reduce leaf and fruit drop after pesticide sprays, and (4) to inhibit abscission of buttons on harvested fruit (lemons).

Treatments (1)-(3) are applied as diluted pre-harvest sprays to the trees, whereas (4) is a post-harvest packing house treatment applied in a water-wax emulsion or as a diluted flush or spray. Residue trials for (1)-(3) were carried out on grapefruit and oranges (Tables 26 and 27) and for (4) on lemons (Table 28).

Grapefruit . Critical GAP (USA): 1 x 2.4 g ae/hl, PHI 7 days. Trials were conducted at two sites in Riverside County, California, on grapefruit with three broadcast applications of 2,4-D IPE. The first application was at concentrations of approximately 2.4 g ae/hl in early July to trees bearing mature (1994) and immature (1995) fruit. The second application was about three months later at a rate of 0.4 g ae/hl in spray oil (1.25% v/v) to trees bearing immature (1995) fruit, and the final application after a further nine months at 2.3 g ae/hl with ground equipment (Johnson and Strickland, 1995a).

After the first application, three treated and control samples of mature fruit (1994) were collected from each trial site at PHIs of 0 and 7 days. After the second application, three treated samples of immature fruit (1995) were collected from each site at a 0-day PHI after the spray had dried. After the final application, three treated samples of mature fruit (1995) were collected at each site at PHIs of 0 and 7 days. Two of each set of samples were analysed for residues. The LOD for 2,4-D in grapefruit is 0.05 mg/kg.

Table 26. Residues of 2,4-D in grapefruit, Riverside County, California (Johnson and Strickland, 1995a).

	Crop variety	Application rate		Dates	Growth stage at treatment	Sample	Residue, mg/kg	PHI, days	Remarks
		g ae/ha (g ae/hl)	water l/ha						
Site 1	Marsh	113 (2.4)	4690	7/8/94	Mature fruit & immature fruit	Fruit	<0.05 (2) <0.05 (2)	0 7	
		83 (0.4)	20932	10/7/94	Immature fruit	Immature fruit	<0.05 (2)	0	Contained spray oil at conc. of 1.25% v/v
		113 (2.3)	4896	7/6/95	Mature fruit	Mature fruit	0.08 (2) 0.08, 0.07	0 7	
Site 2	Ruby Red	113 (2.5)	4477	7/7/94	Mature fruit & immature fruit	Fruit	<0.05 (2) <0.05 (2)	0 7	
		83 (0.4)	19982	10/7/94	Immature fruit	Immature fruit	<0.05 (2)	0	Contained spray oil at conc. of 1.25% v/v
		113 (2.4)	4674	7/6/95	Mature fruit	Fruit	0.05, 0.08 0.06, 0.07	0 7	

Oranges. Critical GAP (USA): 1 x 2.4 g ae/hl, PHI 7 days. Four trials were conducted in California on navel oranges harvested after a single pre-harvest application of 2,4-D IPE, applied alone or in hydrated lime solution using ground equipment, in two trials at each site.

Table 27. Residues of 2,4-D in navel oranges, California (Johnson and Strickland, 1995a).

Site/location	Application		Dates	Sample	Residue, mg/kg	PHI, days	Remarks
	g ae/ha (g ae/hl)	water l/ha					
Site 1	75 (1.6)	4628	11/15/94	Fruit	<0.05 (2) <0.05 (2)	0…… 7	
Tulare County	113 (2.4)	4628	11/15/94	Fruit	<0.05, 0.06 <0.05 (2)	0 7	included 56 kg/ha hydrated lime
Site 2	75 (1.6)	4572	11/21/94	Fruit	<0.05 (2) <0.05 (2)	0 7	
Kern County	113 (2.5)	4572	11/21/94	Fruit	<0.05 (2) <0.05 (2)	0 7	included 56 kg/ha hydrated lime

Lemons. Critical GAP: (USA) 1 x 0.05 kg ae/hl as post-harvest use. Lemon trees were treated once pre-harvest at 1.2-1.3 g ae/hl (approximately 56 g ae/h) with 2,4-D IPE. Lemons were picked before treatment, on day 0 (after the treated fruit had dried) and day 7.

On day 7, pre-harvest treated "light-green" lemons were treated according to GAP with a water-wax emulsion, with a commercial storage wax containing 50 g ae/hl. Samples were taken on the day of treatment after drying and some were stored at 5.6-16°C, and removed 28, 56 and 112 days after the post-harvest treatment for analysis.

Table 28. Residues of 2,4-D in lemons, California (Johnson and Strickland, 1995a).

Site/location	Variety	Application		Date	Growth stage at treatment	Sample	Residue, mg/kg	PHI or WHP, days	Remarks
		g ae/ha (g ae/hl)	water l/ha						
Site 1 Tulare County	Eureka	56 (1.3)	4456	12/6/94	Immature fruit	Fruit	0.06, 0.05 <0.05(2)	0 7	Pre-harvest
		(50)		12/15/94		Fruit	0.42 0.29 0.61 0.41	0 28 56 112	Post-harvest storage, days
Site 2	Lisbon	56 (1.2)	4663	12/20/94	Immature fruit	Fruit	<0.05, 0.05 <0.05(2)	0 7	Pre-harvest
Ventura County		(50)		12/28/94		Fruit	0.54 0.4 0.52 0.5	0 28 56 112	Post-harvest storage, days

WHP: Withholding period (interval between post-harvest treatment and sampling)

Use as herbicide on fruits

2,4-D is directed to the orchard floor. Residue trials were carried out on apples and pears (Table 29), cherries, peaches and plums (Table 30) and on berries (Table 31). All broadcast spray treatments.

Pome fruits. Critical GAP (USA): 2 x 2.2 kg ae/ha, PHI 14 days. Five trials were conducted in four US states to determine the residues of 2,4-D in apples harvested 14 days after the second of two applications. In four of the trials, 2,4-D DMA was applied twice as a broadcast spray at 2.2 kg ae/ha with a retreatment interval of 69 to 110 days. In an additional trial in New York, 2,4-D was applied as above except that an exaggerated rate of 11 kg ae/ha was used. Samples from this trial were used for a related processing study (Barney and Kunkel, 1995b).

Six trials were conducted in four US states to determine the residues of 2,4-D in pears harvested about 14 days after the second of two applications of 2,4-D DMA at 2.2-2.7 kg ae/ha with a retreatment interval of 28 to75 days, with a total seasonal application rate of 4.5 kg ae/ha (Kunkel, 1995d).

The LOD for 2,4-D was 0.01 mg/kg.

Table 29. Residues of 2,4-D in apples and pears.

Crop, Reference Report no.,. Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		kg ae/ha	water l/ha				
Apples (Barney and Kunkel, 1995b)							
4182.92-NY13	Oregon Spur & Bisbee	2.2 + 2.2	374	6/12/92 + 9/14/92	Fruit	<0.01 (4)	14
	Oregon Spur & Bisbee	11 + 11	374	6/12/92 + 9/14/92	Fruit	<0.01 (4)	14
					Juice	<0.01	14
					Wet pomace	<0.01	14
					Dry pomace	0.014	14
4182-92-MI09	spur MacIntosh MM106	2.2 + 2.2	187	6/17/92 + 8/25/92	Fruit	<0.01 (4)	14
4182.92-WA*14	Red Delicious	2.2 + 2.2	281	5/20/92 + 8/27/92	Fruit	<0.01 (4)	14
4182.92-CA55	Granny Smith	2.2 + 2.2	430	4/22/92 + 8/10/92	Fruit	<0.01 (4)	14
Pears (Kunkel, 1995d)							
4256.92-WA16	Bartlett	2.2 + 2.2	280	5/8/92 + 7/21/92	Fruit	<0.01 (2)	14
4256.92-NY18	Mixed	2.7 + 2.7	374	6/12/92 + 8/31/92	Fruit	<0.01 (2)	14
4256.92-CA64	Unknown	2.2 + 2.2	467	6/19/92 + 7/17/92	Fruit	<0.01 (2)	14
4256.93-OR21	Bartlett	2.2 + 2.2	187	6/10/93 + 8/24/93	Fruit	<0.01 (2)	14
4256.95-CA78	Bartlett	2.2 + 2.2	308	6/23/95 + 7/31/95	Fruit	<0.01 (2)	15
4256.95-CA79	Bartlett	2.2 + 2.2	308	6/14/95 + 7/28/95	Fruit	<0.01 (2)	13

Stone fruits. Critical GAP (USA): 2 x 1.6 kg ae/ha, PHI 14 days. Three trials each on cherries, peaches and plums were conducted in three US states. 2,4-D DMA was applied twice at 1.6 kg ae/ha with retreatment intervals of 7 to 28 (cherries), 35 to 78 days (peaches) and 77 to 93 days (plums) (Barney and Kunkel, 1995c,d,f).

Samples were harvested 12-14 days after the second application. Residues were below the LODs (<0.05 mg/kg cherries, <0.01 mg/kg peaches, plums) in control and in treated samples.

In an additional trial on fresh plums in Idaho, two directed applications of 2,4-D were made at 6.4 kg ae/ha/application. Fresh prunes from the fourfold treatment were processed to dried prunes.

Table 30. Residues of 2,4-D in cherries, peach, plums and prunes.

Crop/Reference Report no. Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		kg ae/ha	water l/ha				
Cherries (Barney and Kunkel, 1995c							
4254.94-CA49	Bing	1.6 + 1.6	468	5/2/94 + 5/9/94	Fruit	<0.05 (2)	14
4254-92-MI10	Montmorency	1.6 + 1.6	187	6/12/92 + 6/26/92	Fruit	<0.05 (4)	14
4254.92-WA15	Chinook	1.6 + 1.6	281	5/4/92 + 6/1/92	Fruit	<0.05 (4)	12
Peach (Barney and Kunkel, 1995d)							
4255.93-GA08	Summer Prince	1.6 + 1.6	187	4/28/93 + 6/2/93	Fruit	<0.01 (4)	14
4255.93-NJ01	NJ 275	1.6 + 1.6	234+271	5/10/93 + 7/27/93	Fruit	<0.01 (4)	13
4255.93-CA12	Elegant lady	1.6 + 1.6	159	4/23/93 + 6/15/93	Fruit	<0.01 (4)	16
Plums/fresh prunes (Barney and Kunkel, 1995f)							
4257.93-WA01	Friar	1.6 + 1.6	281	5/18/93 + 8/5/93	Fruit	<0.01 (4)	14
4257.93-MI04	Stanley	1.6 + 1.6	187	6/9/93 + 8/24/93	Fruit	<0.01 (4)	14
4257.93-ID03	Italian	1.6 + 1.6	187	5/23/94 + 8/24/94	Fruit	<0.01 (2)	14
		6.4 + 6.4	187	5/23/94 + 8/24/94	Fresh prunes Dried prunes	<0.01 (2) <0.01 (2)	14

Blueberries. Critical GAP (USA): 2 x 1.6 kg ae/ha, PHI 30 days. In one trial on low bush blueberries, 2,4-D DMA was applied once as a solution containing 4.5 g ae/l of water to a cloth-covered stick that was wiped onto woody weeds growing above the crop during the summer. In a second trial, 2,4-D DMA in a mixture containing 12 g ae/l of oil was applied as a spot treatment to cut stems of woody weeds during the autumn. The blueberries were harvested at normal maturity the year after treatment, (55 weeks after the wipe treatment/41 weeks after the spot treatment). Samples were also collected from adjacent plants. All residues were below the LOD of <0.05 mg/kg (Kunkel, 1995b).

2,4-D was also applied twice at 1.6 and 3.1 kg ae/ha to the middle of rows of high bush blueberries. The first application was after harvest of the previous year's crop and the second in the following spring approximately 30 days before harvest. Care was taken to avoid contact of the spray solution with the crop foliage and berries. 2,4-D residues were below or at about the LOD of 0.01 mg/kg (Kunkel, 1997b).

Cranberries. Critical GAP (USA): 2 x 4.5 kg ae/ha, PHI not defined. Two trials were conducted on cranberries. In each, a broadcast application was made to dormant plants in the spring at 4.5 kg ae/ha and two further directed wipe applications were made during the summer to the weeds growing above the cranberry crop. The cranberries were harvested 30 days after the last application. Residues ranged from <0.02 to 0.11 mg/kg (Barney and Kunkel, 1995a).

Grapes. Critical GAP: 1 x 1.6 kg ae/ha, PHI 100 days. Two field trials were conducted in California on grapes and processed products. The vineyard floor was treated with one directed application of 2,4-D at 1.6 kg ae/ha about 100 days before harvest. Some grape samples were processed into raisins and juice. All residues were below the LOD of 0.05 mg/kg (Kunkel, 1996b).

Raspberries. Critical GAP: 2 x 3.1 kg ae/ha, PHI 24 days. 2,4-D was applied twice as a directed spray away from the raspberry plants into the row centres at 1.6 and 3.1 kg ae/ha, with the second application 24 days before harvest. All residues of 2,4-D were below the LOD of 0.05 mg/kg (Baron, 1988).

Strawberries. Critical GAP: 1 x 1.7 kg ae/ha, PHI not defined (timing defined by application to dormant plants). Dormant strawberry plants received one broadcast treatment of 1.7 kg ae/ha at 129 to 59 days before harvest. This range is representative of the normal variations of local production practices. This use is needed for established perennial strawberries. All residues were below the LOD of 0.05 mg/kg (Kunkel, 1995e).

Table 31. Residues of 2,4-D in blueberries, cranberries, grapes, raspberries and strawberries.

Crop/Reference Report No., Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		kg ae/ha	water l/ha				
Blueberries[1] (Kunkel, 1997b)							
3085.93-OR18	Bluecrop	1.6 + 1.6	468	9/8/93 + 6/8/94	Fruit	<0.01 (4)	30
		3.1 + 3.1	468	9/8/93 + 6/8/94	Fruit	<0.01 (4)	30
3085.93-NC04	O'Neal	1.6 + 1.6	468	10/1/93 + 5/6/94	Fruit	<0.01 (4)	28
		3.1 + 3.1	468	10/1/93 + 5/6/94	Fruit	<0.01 (4)	28
3085.94-NJ16	Bluecrop	1.6 + 1.6	337	11/4/94 + 6/2/95	Fruit	<0.01, 0.01	31
3085.94-MI14	Jersey	1.6 + 1.6	187	8/22/94 + 6/26/95	Fruit	<0.01, 0.01	29
Low Bush Blueberry (Kunkel, 1995b)							
4295.92-ME07	Wild	4.5 g ae/l[2]		07/30/92	Fruit	<0.05 (4)	55 weeks
		12 g ae/l[3]		11/11/92	Fruit	<0.05 (2)	41 weeks
Cranberry[4] (Barney and Kunkel, 1995a)							
4297.92-MA01	Early Black	4.5		3/9/92 + 7/16/92 + 8/12/92	Fruit	0.11, 0.02, 0.05, 0.07	30
4297.92-WI07	Stevens	4.5		4/21/92 + 6/25/92 + 8/31/92	Fruit	<0.02 (4)	30
Grapes (Kunkel, 1996b)							
4298.94CA70	Thompson Seedless	1.6	449	5/14/94	Fruit	<0.05	104
					Raisin	<0.05	104
4298.94CA71	Thompson Seedless	1.6	458	5/14/94	Fruit	<0.05	101
					Juice	<0.05	101
Raspberries[5] (Baron, 1988)							
3718-MN	Red Raspberry	1.6 + 3.1	281	6/8/87 + 7/21/87	Fruit	<0.05 (4)	24
Strawberries (Kunkel, 1995e)							
4179.95-WA13	Sumas	1.7	206	1/24/95	Fruit	<0.05 (2)	129
4179.95-WA14	Red Crest	1.7	281	3/7/95	Fruit	<0.05 (2)	99
4179.95-WI17	Honey oye	1.7	187	4/17/95	Fruit	<0.05 (2)	59
4179.95-WI01	Honey oye	1.7	187	4/17/95	Fruit	<0.05 (2)	59
4179-95-NJ11	Chandler	1.7	327	3/16/95	Fruit	<0.05 (2)	75
4179-95-NH02	Earliglow	1.7	281	4/10/95	Fruit	<0.05 (2)	71

[1] Directed application to avoid plants
[2] Wipe treatment (solution containing 4.5 g ae/l)
[3] Directed spray applied to cut hardwoods (mixture containing 12 g ae/l of oil).
[4] First application was a granule followed by two wipe applications on weeds above the plants.
[5] Applications were made pre- and post-harvest

Use as herbicide on vegetables

2,4-D is directed to the ground for weed control in vegetables. Supervised residue trials were carried out on sweet corn (Table 32), potatoes (Table 33) and asparagus (Table 34).

Sweet corn. Critical GAP (USA): 1 x 1.1 + 1 x 0.56 kg ae/ha. Trials were conducted in nine US states to determine the residues in sweet corn harvested 22-48 days after the second of two applications of 2,4-D, with side-by-side comparisons of amine salt and low ester formulations. Both formulations were applied initially as pre-emergence broadcast applications at 1.1 kg ae/ha and 33-50 days later as post-emergence directed applications at 0.56 kg ae/ha before tasselling when plants were 40 to 50 cm high. The LOD for 2,4-D residues in cobs ("kernels plus cobs with husks removed") was 0.05 mg/kg (Kunkel, 1995c).

Table 32. Residues of 2,4-D in sweet corn. Kernels plus cobs with husks removed analysed. DMA and EHE formulations. Two treatments, pre-emergence and just before tasselling.

Report, no. form	Variety	Sowing date	Application		Date	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha			
(Kunkel, 1995 c)							
4183.95-WA29 DMA, EHE	Golden Jubilee	5/1/95	1.1 + 0.56	206 + 300	5/2/95 + 6/30/95	<0.05 (4)	39
4183.95-SC11 DMA, EHE	Silver Queen	4/14/95	1.1 + 0.56	196 + 196	4/15/95 + 6/1/95	<0.05 (4)	22
4183.95-WI07 DMA, EHE	Excellency Hybrid	5/17/95	1.1 + 0.56	187 + 112	5/17/95 + 6/30/95	<0.05 (4)	45
4183.95-FL45 DMA, EHE	Challenger	5/9/95	1.1 + 0.56	281 + 281	5/9/95 + 6/14/95	<0.05 (4)	23
4183.95-NY09 DMA, EHE	Callco Belle	6/1/95	1.1 + 0.56	318 + 318	6/2/95 + 7/5/95	<0.05 (4)	42
4183.95-MI03 DMA, EHE	Champ	5/18/95	1.1 + 0.56	187 + 187	5/22/95 + 6/29/95	<0.05 (4)	39
4183.95-CA38 DMA, EHE	Sweetie	3/13/95	1.1 + 0.56	542 + 1356	3/13/95 + 5/1/95	<0.05 (4)	38
4183.95-OR20 DMA, EHE	Super Sweet Jubilee	5/24/95	1.1 + 0.56	178 + 178	6/6/95 + 7/19/95	<0.05 (4)	48
4183.95-IL02 DMA, EHE			1.1 + 0.56		5/595 + 6/26/95	<0.05 (4)	37

Potatoes. Critical GAP (USA): 2 x 0.078 kg ae/ha. Eight trials were conducted in seven US states to determine the residues of 2,4-D in red potatoes after two foliar applications at 0.078 kg ae/ha/application with a retreatment interval of 9-13 days. 2,4-D was formulated as an amine salt in seven of trials in different states, and as an ester in the eighth trial. In two additional trials, amine and ester formulations were applied as above except that exaggerated rates of 0.36 g ae/ha/application were used. Potatoes were harvested after the second application as soon as tubers reached marketable size, 24-67 days after treatment. Although samples from different trials were analysed by different methods, repeated analyses from individual trials indicated that similar results were obtained by the three GLC-ECD methods (Barney and Kunkel, 1995g).

Residues were <0.05-0.13 mg/kg in 30 potato samples taken 24-67 days after the second 0.078 kg ae/ha application and <0.05-0.08 mg/kg in 8 samples harvested 50 days after the second 0.36 kg ae/ha application. Residues were highest (0.07-0.13 mg/kg) with the shortest PHI (24 days), but were also quantifiable (0.05-0.08 mg/kg) after the trial with longest PHI (67days). There was no apparent difference between the residues resulting from the use of amine salt and ester formulations.

Table 33. Residues of 2,4-D in potatoes treated at pre-bud stages. Tubers analysed

Report no.	Variety	Form	Application		Date	Residues, mg/kg	PHI, days	Analytical method
			kg ae/ha	water l/ha				
(Barney and Kunkel, 1995g)								
4302.94CA*24	Red Lasoda	DMA	0.078	598	5/23/94 + 6/3/94	0.08 (2)	45	ENC-2/93-2
4302.92ID02	Norland	DMA	0.078	187	6/17/92 + 6/30/92	0.07 (2), 0.08, 0.13	24	KANN
						0.05, 0.08 (2), 0.09	24	ENC-2/93-2
4302.92ME04	La Reuge	DMA	0.078	281	7/17/92 + 7/29/92	<0.05 (4)	59	KANN
4302.92ND02	Red Norland	DMA	0.078	187	7/6/92 + 7/16/92	<0.05 (4)	50	KAN
						<0.05 (4)	50	ENC-KAN
			0.36	187	7/6/92 + 7/16/92	0.05, 0.06, 0.07, 0.08	50	KAN
						<0.05, 0.05 (2), 0.07	50	ENC-KAN
		2-EHE	0.078	187	7/6/92 + 7/16/92	<0.05 (4),	50	ENC-KAN
			0.36	187	7/6/92 + 7/16/92	<0.05, 0.05 (2), 0.06	50	ENC-KAN
4302.93NY08	Chieftain	DMA	0.078	374	6/22/93 + 7/2/93	0.05, 0.07, 0.08 (2)	67	KAN
4302.92WA25	Red Pontiac	DMA	0.078	281	6/1/92 + 6/10/92	<0.05 (4)	44	KAN
4302.92WI06	Norland	DMA	0.078	187	6/19/92 + 7/2/92	<0.05 (4)	28	KAN

Asparagus. Critical GAP (USA): 2 x 2.2 kg ae/ha, PHI 3 days. Two trials were conducted in the USA in Washington and Michigan during 1992 and again in 1994. Two post-emergence broadcast applications of 2,4-D DMA salt were made at 2.2 kg ae/ha with 29- to 31-day retreatment intervals. In the 1992 trials, samples were harvested 24 hours after the second application. In the 1994 trials samples were taken at 24, 48 and 72 hours in WA, but only a single 72-hour sample was collected in MI owing to cool weather. The LOD was 0.05 mg/kg.

The apparent residues of 2,4-D in the 1992 trials were 10-15 mg/kg in samples from MI and 4.8-5.3 mg/kg in samples from WA. The actual residues may have been higher as fortified control samples stored with the treated samples indicated that the residues may have decreased on average by 46% during the storage period of about 20 months.

In the 1994 trials residues were 2.3 and 2.8 mg/kg in two samples at 24 hours and 1.1 and 0.97 mg/kg at 48 hours. By 72 hours the residues were 0.09 and 0.1 mg/kg in WA and 3 mg/kg in MI. The 1994 samples were analysed within 34 days of sampling, so no data on frozen storage stability are required to support the results (Kunkel, 1995a).

Table 34. Residues of 2,4-D in asparagus. Spears analysed.

Report no. Location	Variety State	Application		Date	Residue, mg/kg	PHI, hours
		kg ae/ha	water l/ha			
(Kunkel, 1995a)						
400.92-WA12	Mary WA	2.2 + 2.2	561 + 281	4/20/92 + 5/20/92	4.8, 5.1, 5.3 (2)	24
4090.92-MI06	Viking MI	2.2 + 2.2	187	5/8/92 + 6/8/92	10, 10.5, 13.5, 15	24
4090.94-WA46	Glen Smith WA	2.2 + 2.2	238 + 238	5/10/94 + 6/9/94	2.8, 2.3	24
					0.97, 1.1	48
					0.09, 0.1	72
4090.92-MI28	Martha MI	2.2 + 2.2	187	5/2/94 + 5/31/94	3	72

Use as herbicide on cereals

2,4-D is used world-wide in pre-emergence, post-emergence and pre-harvest applications to winter and summer cereals. The residue data are summarized in Tables 35-46.

Maize. Critical GAP (USA): 1.1 + 0.56 + 1.7 kg ae/ha, PHI 7 days). Seven side-by-side trials were conducted in the USA with 2,4-D DMA salt and 2-EHE. In each study two or three applications were made with a total up to about 3.4 kg ae/ha/season; these included a pre-emergence application at about 1.1 kg ae/ha, a directed post-emergence application at 0.56 kg ae/ha (except one at 1.1 kg ae/ha) when the maize was 25-41 cm high, and a pre-harvest application at 1.7 kg ae/ha 14 days before normal crop maturity. Two additional concurrent trials with the same use pattern were conducted with 2,4-D acid. Applications were made using ground equipment with intervals of 30-48 days between the first and second applications and 83-113 between the second and third applications (Carringer, 1995d,e,f).

Forage samples were collected 7 days after the second application, and silage samples at the dough-dent stage about 54-89 days after the second application (1.7-2.3 kg ae/ha total applied). Grain and fodder samples were harvested 7 days (9 days in one trial) and 14 days after the third application.

Table 35. Residues of 2,4-D in maize forage and silage.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	Water, l/ha					
DMA (Carringer, 1995e)									
AA930208.IA	Querna 7670	5/18/93	1.1	47	5/21/93	Pre-emergence			
			0.57	48	6/22/93	25-40 cm	Forage Silage	1.0 <0.01	7 70
AA930208.IL	Querna 7670	5/14/93	1.1	47	5/17/93	Pre-emergence			
			0.57	48	6/22/93	25-40 cm	Forage Silage	0.09 <0.01	7 69
AA930208.MN	Pioneer 3861	5/21/93	1.1	47	5/26/93	Pre-emergence			
			1.1	47	7/7/93	25-40 cm	Forage Silage	0.25 <0.01	7 76
AA930208.NC	Pioneer 3165	4/23/93	1.2	58	4/26/93	Pre-emergence			
			0.5	48	5/28/93	25-40 cm	Forage Silage	1.0 <0.01	7 60
AA930208.NE	Pioneer 3162	5/3/93	1.1	47	5/3/93	Pre-emergence			
			0.56	47	6/21/93	25-40 cm	Forage Silage	0.01 <0.01	7 65
AA930208.OH	GL 235	5/20/93	1.2	48	5/20/93	Pre-emergence			
			0.58	47	6/23/93	25-40 cm	Forage Silage	0.25 <0.01	7 76
AA930208.PA	Jacques 7710	5/14/93	1.1	49	5/17/93	Pre-emergence			
			0.58	47	6/22/93	25-40 cm	Forage Silage	2.7 0.01	7 89
EHE (Carringer, 1995f)									
AA930209.IA	Pioneer 3861	5/21/93	1.1	47	5/21/93	Pre-emergence			
			0.58	47	6/22/93	25-40 cm	Forage Silage	5.2 <0.01	7 70
AA930209.IL	Pioneer 3165	4/23/93	1.2	47	5/17/93	Pre-emergence			
			0.58	47	6/22/93	25-40 cm	Forage	1.1	7

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	Water, l/ha					
							Silage	<0.01	69
AA930209.MN	Pioneer 3162	5/3/93	1.1	47	5/26/93	Pre-emergence			
			1.1	47	7/7/93	25-40 cm	Forage	0.69	7
							Silage	<0.01	76
AA930209.NC	GL 235	5/20/93	1.2	58	4/26/93	Pre-emergence			
			0.52	43	5/28/93	25-40 cm	Forage	0.88	7
							Silage	<0.01	60
AA930209.NE	Jacques 7710	5/14/93	1.1	47	5/4/93	Pre-emergence			
			0.56	47	6/21/93	25-40 cm	Forage	0.03	7
							Silage	<0.01	65
AA930209.OH	GL 235	5/20/93	1.1	50	5/20/93	Pre-emergence			
			0.58	48	6/23/93	25-40 cm	Forage	0.46	7
							Silage	<0.01	76
AA930209.PA	Jacques 7710	5/14/93	1.1	50	5/17/93	Pre-emergence			
			0.57	49	6/22/93	25-40 cm	Forage	3.0	7
							Silage	<0.01	89
Acid (Carringer, 1995d)									
AA930210.IA	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence			
			0.58	49	7/8/93	25-40 cm	Forage	0.61	7
							Silage	0.03	54
AA930210.NC	Pioneer 3165	4/26/93	1.15	52	4/29/93	Pre-emergence			
			0.53	44	5/29/93	25-40 cm	Forage	0.33	7
							Silage	<0.01	59

Table 36. Residues of 2,4-D in maize fodder.

Compound (Reference) Report no.. Location	Variety	Sowing date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
DMA (Carringer, 1995e)								
AA930208.IA	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	48	10/5/93	Pre-harvest	4.4	7
							1.4	14
AA930208.IL	Querna 7670	5/14/93	1.1	48	5/17/93	Pre-emergence		
			0.57	47	6/22/93	25-40 cm		
			1.7	48	10/4/93	Pre-harvest	9.1	7
							3.8	14
AA930208.MN	Pioneer 3861	5/21/93	1.1	47	5/26/93	Pre-emergence		
			1.1	47	7/7/93	25-40 cm		
			1.7	48	9/28/93	Pre-harvest	51	7
							22	14
AA930208.NC	Pioneer 3165	4/23/93	1.2	58	4/26/93	Pre-emergence		
			0.5	43	5/28/93	25-40 cm		
			1.8	49	9/2/93	Pre-harvest	3.2	7
							9.9	14
AA930208.NE	Pioneer 3162	5/3/93	1.1	47	5/4/93	Pre-emergence		
			0.56	47	6/21/93	25-40 cm		
			1.7	47	9/17/93	Pre-harvest	4.4	7
							4.2	14

Compound (Reference) Report no.. Location	Variety	Sowing date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
AA930208.OH	GL 235	5/20/93	1.2	50	5/20/93	Pre-emergence		
			0.58	48	6/23/93	25-40 cm		
			1.7	46	9/22/93	Pre-harvest	11, 15	7
							3.6, 6.4	14
AA930208.PA	Jacques 7710	5/14/93	1.1	50	5/17/93	Pre-emergence		
			0.58	49	6/22/93	25-40 cm		
			1.7	53	10/13/93	Pre-harvest	4.2	7
							3.4	14
EHE (Carringer, 1995f)								
AA930209.IA	Querna 7670	5/18/93	1.1	47	5/21/93	Pre-emergence		
			0.58	48	6/22/93	25-40 cm		
			1.7	48	10/11/93	Pre-harvest	14	7
							30	14
AA930209.IL	Querna 7670	5/14/93	1.2	49	5/17/93	Pre-emergence		
			0.58	48	6/22/93	25-40 cm		
			1.7	48	10/4/93	Pre-harvest	3.6	7
							2.1	14
AA930209.MN	Pioneer 3861	5/21/93	1.1	47	5/26/93	Pre-emergence		
			1.1	48	7/7/93	25-40 cm		
			1.7	48	9/28/93	Pre-harvest	7.3	7
							4.3	14
AA930209.NC	Pioneer 3165	4/23/93	1.2	58	4/26/93	Pre-emergence		
			0.52	45	5/28/93	25-40 cm		
			1.75	49	9/2/93	Pre-harvest	20	7
							8.2	14
AA930209.NE	Pioneer 3162	5/3/93	1.1	47	5/4/93	Pre-emergence		
			0.56	47	6/21/93	25-40 cm		
			1.7	47	9/17/93	Pre-harvest	5	7
							5.7	14
AA930209.OH	GL 235	5/20/93	1.1	49	5/20/93	Pre-emergence		
			0.58	49	6/23/93	25-40 cm		
			1.7	47	9/22/93	Pre-harvest	6.4	7
							6.0	14
AA930209.PA	Jacques 7710	5/14/93	1.1	52	5/17/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	68	10/13/93	Pre-harvest	4.7	7
							6.4	14
Acid (Carringer, 1995d)								
AA930210.IA	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence		
			0.58	49	7/8/93	25-40 cm		
			1.7	47	10/5/93	Pre-harvest	25	7
							14	14
AA930210.NC	Pioneer 3165	4/26/93	1.15	52	4/29/93	Pre-emergence		
			0.53	44	5/29/93	25-40 cm		
			1.4	40				
			0.29	48	9/2/93	Pre-harvest	3.3	7
							1.6	14

Table 37. Residues of 2,4-D in maize grain.

Compound (Reference) Report no. Location	Variety	Sowing date	Application	Date	Growth stage	Residue, mg/kg	PHI, days

			kg ae/ha	water l/ha				
DMA (Carringer, 1995e)								
AA930208.IA	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	48	10/5/93	Pre-harvest	<0.01	7
							0.01	14
AA930208.IL	Querna 7670	5/14/93	1.1	48	5/17/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	48	10/4/93	Pre-harvest	0.01	7
							0.015	14
AA930208.MN	Pioneer 3861	5/21/93	1.1	47	5/26/93	Pre-emergence		
			1.1	47	7/7/93	25-40 cm		
			1.7	48	9/28/93	Pre-harvest	0.01	7
							<0.01	14
AA930208.NC	Pioneer 3165	4/23/93	1.2	58	4/26/93	Pre-emergence		
			0.5	43	5/28/93	25-40 cm		
			1.8	49	9/2/93	Pre-harvest	0.04	7
							<0.01	14
AA930208.NE	Pioneer 3162	5/3/93	1.1	47	5/4/93	Pre-emergence		
			0.56	47	6/21/93	25-40 cm		
			1.7	47	9/17/93	Pre-harvest	0.02	7
							0.01(2)	14
AA930208.OH	GL 235	5/20/93	1.2	50	5/20/93	Pre-emergence		
			0.58	49	6/23/93	25-40 cm		
			1.7	46	9/22/93	Pre-harvest	0.01	7
							0.01	14
AA930208.PA	Jacques 7710	5/14/93	1.1	50	5/17/93	Pre-emergence		
			0.58	49	6/22/93	25-40 cm		
			1.7	48	10/13/93	Pre-harvest	<0.01	7
							0.01	14
EHE (Carringer, 1995e)								
AA930209.IA	Pioneer 3861	5/21/93	1.1	47	5/21/93	Pre-emergence		
			0.58	48	6/22/93	25-40 cm		
			1.7	48	10/11/93	Pre-harvest	0.01	7
							0.01	14
AA930209.IL	Pioneer 3165	4/23/93	1.2	49	5/17/93	Pre-emergence		
			0.58	48	6/22/93	25-40 cm		
			1.7	48	10/4/93	Pre-harvest	0.01	7
							0.01	14
AA930209.MN	Pioneer 3162	5/3/93	1.1	47	5/26/93	Pre-emergence		
			1.1	48	7/7/93	25-40 cm		
			1.7	48	9/28/93	Pre-harvest	0.01	7
							<0.01	14
AA930209.NC	GL 235	5/20/93	1.2	58	4/26/93	Pre-emergence		
			0.52	45	5/28/93	25-40 cm		
			1.8	49	9/2/93	Pre-harvest	0.03	7
							0.01	14
AA930209.NE	Jacques 7710	5/14/93	1.1	47	5/4/93	Pre-emergence		
			0.56	47	6/21/93	25-40 cm		
			1.7	47	9/17/93	Pre-harvest	<0.01	7
							0.02	14
AA930209.OH	GL 235	5/20/93	1.1	49	5/20/93	Pre-emergence		
			0.58	49	6/23/93	25-40 cm		
			1.7	47	9/22/93	Pre-harvest	0.01	7
							<0.01	14

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
AA930209.PA	Jacques 7710	5/14/93	1.1	52	5/17/93	Pre-emergence		
			0.57	48	6/22/93	25-40 cm		
			1.7	68	10/13/93	Pre-harvest	<0.01	7
							0.01	14
Acid (Carringer, 1995d)								
AA930210.IA ACID	Querna 7670	5/18/93	1.1	48	5/21/93	Pre-emergence		
			0.58	49	7/8/93	25-40 cm		
			1.7	48	10/5/93	Pre-harvest	0.01	7
							0.01	14
AA930210.NC	Pioneer 3165	4/26/93	1.15	52	4/29/93	Pre-emergence		
			0.53	44	5/29/93	25-40 cm		
			1.4	40	5/29/93	25-40 cm		
			0.29	48	9/2/93	Pre-harvest	0.02	7
							0.01	14

Rice. Critical GAP (USA): 1 x 1.7 kg ae/ha, PHI 60 days. Ten trials were conducted, two in each of four states with the DMA salt, and one each in two of the states with the free acid. In each a post-emergence broadcast application was made at 1.6-1.8 kg ae/ha at tillering before first joint (Carringer, 1995p,q).

Samples of grain (without husk) and straw were collected at normal crop maturity, 61-104 days after treatment. The LODs were 0.01 mg/kg. Control samples of grain and straw from the CA trials showed residues of 0.11-0.13 mg/kg in grain and 0.03-0.04 mg/kg in straw, apparently from contamination when an adjacent field was sprayed with 2,4-D. Residues in treated samples were not corrected for apparent residues in the controls. The residues were <0.01-0.49 mg/kg in the grain and 0.06-8.8 mg/kg in the straw. The high residues at the LA2 trial may have been the result of drift from spraying 2,4-D on roadsides surrounding the trial site.

Table 38. Residues of 2,4-D in rice grain.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
DMA (Carringer, 1995p)									
AA930222.AR1	Newbonnet	5/9/93	1.8	99	7/19/93	1st joint	Treated	0.03	66
AA930222.AR2	Newbonnet	5/9/93	1.8	97	7/19/93	1st joint	Treated	0.01	66
AA930222.CA1	Cal Pearl	6/28/93	1.8	97	7/29/93	1st joint	Treated	0.07	104
							Control	0.12	104
AA930222.CA2	Cal Pearl	6/28/93	1.8	97	7/29/93	1st joint	Treated	0.08	104
							Control	0.11	104
AA930222.LA1	Lemont	4/29/93	1.7	95	6/26/93	1st joint	Treated	0.01	61
AA930222.LA2	RT 7015	5/28/93	1.8	95	6/26/93	1st joint	Treated	0.49[1]	62
AA930222.TX1	Katy	4/22/93	1.6	91	6/12/93	1st joint	Treated	<0.01	73
							Control	0.01, <0.01	73
AA930222.TX2	Lemont	4/25/93	1.8	95	6/21/93	1st joint	Treated	<0.01	64
Acid (Carringer, 1995q)									
AA930224.AR	Newbonnet	5/9/93	1.8	100	7/19/93	1st joint	Treated	0.05	66
AA930224.LA	Lemont	4/29/93	1.6	90	6/26/93	1st joint	Treated	0.01	61

[1] Outlier, result of drift from spraying of 2,4-D on roadsides surrounding the test site.

Table 39. Residues of 2,4-D in rice straw.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Commodity	Residue, mg/kg	PHI
			kg ae/ha	water l/ha					
DMA (Carringer, 1995p)									
AA930222.AR1	Newbonnet	5/9/93	1.8	99	7/19/93	1st joint	Treated	3.1	66
AA930222.AR2	Newbonnet	5/9/93	1.8	97	7/19/93	1st joint	Treated	1.5	66
AA930222.CA1	Cal Pearl	6/28/93	1.8	97	7/29/93	1st joint	Treated	0.34	104
							Control	0.04	104
AA930222.CA2	Cal Pearl	6/28/93	1.8	97	7/29/93	1st joint	Treated	0.06	104
							Control	0.03	104
AA930222.LA1	Lemont	4/29/93	1.7	95	6/26/93	1st joint	Treated	5.4	61
AA930222.LA2	RT 7015	5/28/93	1.8	95	6/26/93	1st joint	Treated	8.8	62
AA930222.TX1	Katy	4/22/93	1.6	91	6/12/93	1st joint	Treated	0.74	73
AA930222.TX2	Lemont	4/25/93	1.8	95	6/21/93	1st joint	Treated	1.1	64
Acid (Carringer, 1995q)									
AA930224.AR	Newbonnet	5/9/93	1.8	100	7/19/93	1st joint	Treated	2.1	66
AA930224.LA	Lemont	4/29/93	1.6	90	6/26/93	1st joint	Treated	6.4	61
							Control	0.01, <0.01	61

Wild rice. Critical GAP (USA): 1 x 0.28 kg ae/ha, PHI 60 days. A single trial was conducted with the DMA salt at 0.56 kg ae/ha. Three samples were collected from each plot after 53 days and one after 64 days. Samples were harvested by cutting heads, threshing out the seeds, and separating the grain and hulls. No 2,4-D was found in either grain or hulls. The LOD was 0.05 mg/kg (Kunkel, 1995f).

Table 40. Residues of 2,4-D in wild rice from treatments with DMA salt.

(Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
(Kunkel, 1995f)									
1015.92-MN01	Franklin (K2(2)c4)	5/19/92	0.56	45.96	7/9/92	Mid to Late Tillering	Seed	<0.05 (3)	53
								<0.05	64
							Hulls	<0.05 (3)	53
								<0.05	64

Sorghum. Critical GAP (USA): 1 x 0.56 kg ae/ha (esters), 1 x 1.1 kg ae/ha (other formulations), PHI for forage 30 days). Single post-emergence directed application of the EHE at 0.56 kg ae/ha and of the DMA salt at 1.1 kg ae/ha were made in separate trials in each of four US states. All applications were made using ground equipment when the plants were 20-25 cm tall. Forage samples were collected 26-31 days after treatment, and grain and fodder samples at maturity, 82-112 days after treatment (Carringer, 1995g,h,i).

The LOD for all samples was 0.01 mg/kg. The apparent residues of 2,4-D were <0.01-0.14 mg/kg in the forage samples, <0.01-0.01 mg/kg in the grain and <0.01- 0.04 mg/kg in the fodder samples. In most of the trials the residues in the control samples of grain and fodder were as high as or higher than those in the samples from treated plots suggesting that the results were invalid.

Table 41. Residues of 2,4-D in sorghum grain.

Compound (Reference) Report no.	Variety	Sowing date	Application		Date	Growth stage	Sample	Residues, mg/kg	PHI, days
Location			kg ae/ha	water l/ha					
DMA (Carringer, 1995i)									
AA930212.KS	NK 2030	7/11/93	1.2	48	8/2/93	20-25 cm	Treated	<0.01	110
AA930212.MO	GK 802 G	6/2/93	1.2	48	7/2/93	20-25 cm	Treated	<0.01	89
AA930212.NE	Northrup King	5/24/93	1.1	47	6/29/93	20-25 cm	Treated	0.01	99
							Control	0.01 (2)	99
AA930212.TX	GSA 1290	5/20/93	1.1	60	6/19/93	20-25 cm	Treated	<0.01	82
EHE (Carringer, 1995g)									
AA930214.KS	NK 2030	7/11/93	0.58	48	8/2/93	20-25 cm	Treated	<0.01	110
AA930214.MO	GK 802 G	6/2/93	0.57	49	7/7/93	20-25 cm	Treated	<0.01	84
AA930214.NE	Northrup King	5/24/93	0.56	47	6/29/93	20-25 cm	Treated	0.01	99
							Control	0.01 (2)	99
AA930214.TX	GSA 1290	5/20/93	0.56	58	6/16/93	20-25 cm	Treated	<0.01	82
Acid (Carringer, 1995h)									
AA930215.KS	NK 23030	7/11/93	1.1	47	8/2/93	20-25 cm	Treated	<0.01	112
AA930215.TX	GSA 1290	5/20/93	1.1	60	6/16/93	20-25 cm	Treated	<0.01	82

Table 42. Residues of 2,4-D in sorghum forage.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha				
DMA (Carringer, 1995i)								
AA930212.KS	NK 2030	7/11/93	1.2	48	8/2/93	20-25 cm	0.14	30
AA930212.MO	GK 802 G	6/2/93	1.2	48	7/2/93	20-25 cm	0.03	31
AA930212.NE	Northrup King	5/24/93	1.1	47	6/29/93	20-25 cm	0.02	30
AA930212.TX	GSA 1290	5/20/93	1.1	60	6/19/93	20-25 cm	0.08	30
EHE (Carringer, 1995g)								
AA930214.KS	NK 2030	7/11/93	0.58	48	8/2/93	20-25 cm	0.04	30
AA930214.MO	GK 802 G	6/2/93	0.57	49	7/7/93	20-25 cm	0.02	26
AA930214.NE	Northrup King	5/24/93	0.56	47	6/29/93	20-25 cm	<0.01	30
AA930214.TX	GSA 1290	5/20/93	0.56	47	6/16/93	20-25 cm	0.03	30
Acid (Carringer, 1995h)								
AA930215.KS	NK 23030	7/11/93	1.1	47	8/2/93	20-25 cm	0.06	30
AA930215.TX	GSA 1290	5/20/93	1.1	60	6/16/93	20-25 cm	0.13	30

Table 43. Residues of 2,4-D in sorghum fodder.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Growth stage	Sample	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha					
DMA (Carringer, 1995i)									
AA930212.KS	NK 2030	7/11/93	1.2	48	8/2/93	20-25 cm	Treated	0.04	110
							Control	0.02, 0.03	110
AA930212.MO	GK 802 G	6/2/93	1.2	48	7/2/93	20-25 cm	Treated	0.02	89
							Control	0.02	89

AA930212.NE	Northrup King	5/24/93	1.1	47	6/29/93	20-25 cm	Treated	0.01	99
							Control	0.02	99
AA930212.TX	GSA 1290	5/20/93	1.1	60	6/19/93	20-25 cm	Treated	0.03	82
							Control	0.03	82
EHE (Carringer, 1995g)									
AA930214.KS	NK 2030	7/11/93	0.58	48	8/2/93	20-25 cm	Treated	0.02	110
							Control	0.015	110
AA930214.MO	GK 802 G	6/2/93	0.57	49	7/7/93	20-25 cm	Treated	0.01	84
AA930214.NE	Northrup King	5/24/93	0.56	47	6/29/93	20-25 cm	Treated	0.03	99
							Control	0.03	99
AA930214.TX	GSA 1290	5/20/93	0.56	47	6/16/93	20-25 cm	Treated	<0.01	82
							Control	0.03, 0.04	82
Acid (Carringer, 1995h)									
AA930215.KS	NK 23030	7/11/93	1.1	47	8/2/93	20-25 cm	Treated	0.03	112
							Control	0.02	112
AA930215.TX	GSA 1290	5/20/93	1.1	60	6/16/93	20-25 cm	Treated	0.02	82
							Control	0.04, 0.05,	82

Wheat. Critical GAP (USA): 1 x 1.4 + 1 x 0.56 kg ae/ha, PHI 14 days. In 1993 19 trials were conducted in seven US states to determine residues of 2,4-D in wheat forage, grain and straw. One or two applications of either the EHE or the DMA salt were made at 1.4 kg ae/ha/application, except in two states where two applications of 2,4-D acid were made at 1.4 kg ae/ha/application, with ground equipment at retreatment intervals from 61-90 days. In all trials, samples of forage and hay were taken 7 and 14 days after the first application, and of grain and straw 7 and 14 days after the second application (Carringer, 1995a,b,t).

In 1994 there were 16 trials in seven US states. Half of the trials were with the EHE and the other half with the DMA salt. Applications were (i) a single at-tillering at a nominal 1.4 kg ae/ha, or (ii) a single at-tillering at 1.4 kg ae/ha followed at the hard dough stage by either a nominal 0.56 or 0.84 kg ae/ha about 7 or 14 days pre-harvest. The interval between the first and second treatments was 37-98 days (Carringer, 1995y,z). Residues in the control samples ranged from <0.01 to 0.09 mg/kg in the forage and <0.01 to 0.05 mg/kg in the grain. The application of EHE and DMA salt to the GA site was made after the tillering stage which gave abnormally high residues in the grain, forage and straw and was not representative of the use pattern.

In 1996, 12 trials were carried out repeating the use pattern of 1994, with an interval between the first and second treatments of 54-101 days (Carringer, 1996a,b).

Table 44. Residues of 2,4-D in wheat forage. All single applications at tillering.

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha			
EHE (Carringer, 1995b)							
AA930204.CA1	Yecora Rojo	2/12/93	1.4	47	4/10/93	33 19	7 14
AA930204.CA2	Yecora Rojo	4/8/93	1.4	45	5/18/93	18 16	7 14
AA930204.GA	Coker 9766	11/18/92	1.4	47	2/23/93	50 19	7 14
AA930204.KS	TAM 107	9/10/92	1.4	47	4/16/93	58 18	7 14
AA930204.MN	Hard Red Spring	5/13/93	1.4	47	6/19/93	23 10	7 14
AA930204.ND	Hard Red Spring	4/26/93	1.3	43	5/26/93	18 6	7 14
AA930204.OK	McNair	10/1/92	1.4	53	3/16/93	42 13	7 14
AA930204.WA	Stephens	10/11/92	1.5	50	4/27/93	41 19	7 14
Acid (Carringer, 1995t)							
AA930205.KS	TAM 107	9/10/92	1.5	49	4/16/93	35 6	7 14
AA930205.ND	Grandin	4/26/93	1.4	45	5/26/93	34 0.3	7 14
DMA (Carringer, 1995a)							
AA930207.CA1	Yecora Rojo	2/12/93	1.4	47	4/14/93	8.5 5	7 14
AA930207.CA2	Yecora Rojo	4/8/93	1.4	46	5/19/93	112 6	7 14
AA930207.GA	Coker 9766	11/18/92	1.4	47	2/23/93	16 4	7 14
AA930207.KS	TAM 107	9/10/92	1.4	48	4/16/93	26 9	7 14
AA930207.MN	Butte 86	5/13/93	1.4	48	6/29/93	17 6	7 14
AA930207.ND	Grandin	4/26/93	1.6	53	5/26/93	7 1	7 14
AA930207.OK	McNair 1003	10/1/92	1.4	53	3/16/93	6 4	7 14
AA930207.WA	Stephens	10/10/92	1.4	48	4/27/93	8 4	7 14
DMA (Carringer, 1995z)							
AA940502.CA1	Yecora Rojo	4/15/94	1.5	51	5/20/94	15 6	7 14
AA940502.CA2	Yecora Rojo	4/15/94	1.5	42	5/25/94	11 7.6	7 14
AA940502.GA	Andy	12/20/93	1.4	47	4/7/94	20 17	7 14
AA940502.KS	Karl	10/6/93	1.4	45	4/7/94	23, 30	7
						11	14
AA940502.MN	Stoa	5/9/94	1.4	47	6/11/94	6	7

Compound (Reference) Report no. Location	Variety	Sowing date	Application		Date	Residues, mg/kg	PHI, days
			kg ae/ha	water l/ha			
						2	14
AA940502.ND	Grandin	5/11/94	1.4	48	6/4/94	6 2	7 14
AA940502.OK	McNair	11/01/93	1.4	46	4/6/94	14, 22 5.5	7 14
AA940502.WA	MAC-1	10/18/93	1.4	47	4/18/94	5 3	7 14
EHE (Carringer, 1995y)							
AA940501.CA1	Yecora Rojo	4/15/94	1.4	45	5/21/94	20 11	7 14
AA940501.CA2	Yecora Rojo	4/15/94	1.4	45	5/26/94	22 17	7 14
AA940501.GA	Andy	12/20/93	1.4	47	4/7/94	9 11	7 14
AA940501.KS	Karl	10/6/93	1.4	45	4/7/94	54 22	7 14
AA940501.MN	Stoa	5/9/94	1.5	49	6/11/94	8 6	7 14
AA940501.ND	Grandin	5/11/94	1.4	48	6/4/94	19 4	7 14
AA940501.OK	McNair	11/10/93	1.4	46	4/6/94	30 17	7 14
AA940501.WA	Stephens	10/6/93	1.4	49	4/18/94	14 12	7 14
EHE (Carringer, 1996a)							
AA960501.CO	Tam 107	9/15/95	1.4	51	4/10/96	29 18	7 14
AA960501.GA	Coker 9835	12/5/95	1.4	49	3/13/96	33 21	7 14
AA960501.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	47	6/26/96	23 2.9	7 14
AA960501.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	48	6/21/96	14 1.5	7 14
AA960501.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	55 22	7 14
AA960501.WA	Madsen	11/6/95	1.4	47	4/25/96	33 17	7 14
DMA (Carringer, 1996b)							
AA960502.CO	Tam 107	9/15/95	1.4	51	4/10/96	9 3.7	7 14
AA960502.GA	Coker 9835	12/5/95	1.4	49	3/13/96	18, 24 12, 18	7 14
AA960502.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	46	6/26/96	14 7.6	7 14
AA960502.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	46	6/20/96	4.6, 6.3 0.62	7 14
AA960502.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	25 6.1, 9.4	7 14
AA960502.WA	Madsen	11/6/95	1.4	47	4/25/96	15	7
						7.7	14

Table 45. Residues of 2,4-D in wheat grain. CLICK HERE for continue

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
EHE (Carringer, 1995b)									
AA930204.CA1	Yecora Rojo	2/12/93	1.4	47	4/10/93	Tillering			
			1.4	45	6/15/93	Pre-harvest	Treated	0.85	7
							Treated	0.49	14
AA930204.CA2	Yecora Rojo	4/8/93	1.4	45	5/18/93	Tillering			
			1.45	48	7/19/93	Pre-harvest	Treated	0.87	7
							Treated	1.3	14
							Control	0.02	7
							Control	0.04	14
AA930204.GA	Coker 9766	11/18/92	1.4	47	2/23/93	Tillering			
			1.4	46	5/14/93	Pre-harvest	Treated	1.6	7
								0.69	14
AA930204.KS	TAM 107	9/10/92	1.4	47	4/16/93	Tillering			
			1.4	47	6/25/93	Pre-harvest	Treated	0.39, 0.5	7
							Treated	3.2	14
AA930204.MN	Hard Red Spring	5/13/93	1.4	47	6/19/93	Tillering			
			1.45	48	8/19/93	Pre-harvest	Treated	0.41	7
							Treated	0.29	14
AA930204.ND	Hard Red Spring	4/26/93	1.3	43	5/26/93	Tillering			
			1.4	48	8/13/93	Pre-harvest	Treated	0.68	7
							Treated	0.85	14
							Control	0.02	7
AA930204.OK	McNair	10/1/92	1.4	53	3/16/93	Tillering			
			1.45	57	5/28/93	Pre-harvest	Treated	3.4	7
							Treated	1.2 1.3	14
AA930204.WA	Stephens	10/11/92	1.45	50	4/27/93	Tillering			
			1.4	47	7/26/93	Pre-harvest	Treated	2.5	7
							Treated	0.86	14
Acid (Carringer, 1995t)									
AA930205.KS	TAM 107	9/10/92	1.5	49	4/16/93	Tillering			
			1.5	48	6/25/93	Pre-harvest	Treated	0.09	7
AA930205.ND	Grandin	4/26/93	1.4	45	5/26/93	Tillering			
			1.4	48	8/11/93	Pre-harvest	Treated	0.31	7
							Treated	0.39	14
							Control	<0.01	7
							Control	0.02	14
DMA (Carringer, 1995a)									
AA930207.CA1	Yecora Rojo	2/12/93	1.4	47	4/14/93	Tillering			
			1.4	45	6/23/93	Pre-harvest	Treated	2.9	7
							Treated	2.4	14
							Control	0.02	7
AA930207.CA2	Yecora Rojo	4/8/93	1.4	46	5/19/93	Tillering			
			1.4	48	7/21/93	Pre-harvest	Treated	1.9	7
							Treated	1.8	14
AA930207.GA	Coker 9766	11/18/92	1.4	47	2/23/93	Tillering			
			1.4	46	5/14/93	Pre-harvest	Treated	1.4	7
							Treated	0.84	14

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
AA930207.KS	TAM 107	9/10/92	1.4	48	4/16/93	Tillering			
			1.7	55	6/25/93	Pre-harvest	Treated	0.86	7
AA930207.MN	Butte 86	5/13/93	1.4	48	6/29/93	Tillering			
			1.4	55	8/19/93	Pre-harvest	Treated	0.79	7
							Treated	0.47	14
							Control	0.02	7
							Control	0.12	14
AA930207.ND	Grandin	4/26/93	1.4	48	5/26/93	Tillering			
			1.5	48	8/13/93	Pre-harvest	Treated	1.0	7
							Treated	1.2	14
							Control	0.04	14
AA930207.OK	McNair 1003	10/1/92	1.4	53	3/16/93	Tillering			
			1.4	56	5/28/93	Pre-harvest	Treated	6.2	7
							Treated	2.3	14
AA930207.WA	Stephens	10/10/92	1.4	48	4/27/93	Tillering			
			1.4	49	7/26/93	Pre-harvest	Treated	2.5	7
							Treated	1.0	14
DMA (Carringer, 1995z)									
AA940502.CA1	Yecora Rojo	4/15/94	1.5	51	5/20/94	Tillering	Treated	0.01	53
			1.4	47	5/20/94	Tillering			
			0.82	46	7/5/94	Pre-harvest	Treated	0.32	7
							Treated	0.28	15
			1.4	46	5/20/94	Tillering			
			0.54	45	7/5/94	Pre-harvest	Treated	0.18	7
							Treated	0.12	15
AA940502.CA2	Yecora Rojo	4/15/94	1.5	42	5/25/94	Tillering	Treated	0.03	45
			1.5	49	5/25/94	Tillering			
			0.87	49	7/2/94	Pre-harvest	Treated	0.71	7
							Treated	0.33	13
			1.3	48	5/25/94	Tillering			
			0.55	46	7/2/94	Pre-harvest	Treated	0.25	7
							Treated	0.31	13
AA940502.GA	Andy	12/20/93	1.4	46	4/7/94	Tillering	Treated	0.76, 0.84	46
			1.4	46	4/7/94	Tillering			
			0.84	46	5/16/94	Pre-harvest	Treated	1.4, 0.96	7
							Treated	1.1, 2.0	14
			1.4	46	4/7/94	Tillering			
			0.56	46	5/16/94	Pre-harvest	Treated	1.5, 1.3	7
							Treated	0.94, 0.69	14
AA940502.KS	Karl	10/6/93	1.4	45	4/7/94	Tillering	Treated	<0.01	69
			1.4	45	4/7/94	Tillering			
			0.87	48	6/8/94	Pre-harvest	Treated	2.5	7
							Treated	3.1, 4.3	14
			1.4	45	4/7/94	Tillering			
			0.57	48	6/8/94	Pre-harvest	Treated	0.3	7
							Treated	0.71, 0.87	14
AA940502.MN	Stoa	5/9/94	1.4	47	6/11/94	Tillering	Treated	0.03	73

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
			1.4	45	6/11/94	Tillering			
			0.85	47	8/16/94	Pre-harvest	Treated	0.72, 3.3	7
							Treated	1.2	14
			1.4	47	6/11/94	Tillering			
			0.57	48	8/16/94	Pre-harvest	Treated	1.2, 1.9	7
							Treated	0.78, 1.4	14
AA940502.ND	Grandin	5/11/94	1.4	48	6/4/94	Tillering	Treated	<0.01	82
			1.4	48	6/4/94	Tillering			
			0.84	46	8/18/94	Pre-harvest	Treated	0.41	7
							Treated	0.22	14
			1.4	48	6/4/94	Tillering			
			0.56	46	8/18/94	Pre-harvest	Treated	0.12	7
							Treated	0.22	14
AA940502.OK	McNair	11/01/93	1.4	46	4/6/94	Tillering	Treated	<0.01	72
			1.4	45	4/6/94	Tillering			
			0.84	50	6/10/94	Pre-harvest	Treated	0.31	7
			1.4	44	4/6/94	Tillering			
			0.55	49	6/10/94	Pre-harvest	Treated	0.19	7
AA940502.WA	MAC-1	10/18/93	1.4	47	4/18/94	Tillering	Treated	<0.01	106
			1.4	47	4/18/94	Tillering			
			0.86	47	7/25/94	Pre-harvest	Treated	0.38	7
							Treated	0.05	14
			1.4	47	4/18/94	Tillering			
			0.56	46	7/25/94	Pre-harvest	Treated	0.17	7
							Treated	0.11	14
							Control	0.02	7
EHE (Carringer, 1995y)									
AA940501.CA1	Yecora Rojo	4/15/94	1.4	45	5/21/94	Tillering	Treated	0.03	52
			1.4	45	5/21/94	Tillering			
			0.83	46	7/5/94	Pre-harvest	Treated	0.15	7
							Treated	0.26	15
			1.4	46	5/21/94	Tillering			
			0.56	47	7/5/94	Pre-harvest	Treated	0.13	7
							Treated	0.11	15
AA940501.CA2	Yecora Rojo	4/15/94	1.4	45	5/26/94	Tillering	Treated	0.18	44
			1.4	46	5/26/94	Tillering			
			0.83	46	7/2/94	Pre-harvest	Treated	0.33	7
							Treated	0.2, 0.56	13
			1.4	46	5/26/94	Tillering			
			0.54	45	7/2/94	Pre-harvest	Treated	0.33	7
							Treated	0.24	13
AA940501.GA	Andy	12/20/93	1.4	46	4/7/94	Tillering	Treated	0.26	46
			1.4	46	4/7/94	Tillering			
			0.84	46	5/16/94	Pre-harvest	Treated	0.28, 0.53	7
							Treated	0.76, 0.5	14
			1.4	46	4/7/94	Tillering			
			0.56	46	5/16/94	Pre-harvest	Treated	0.49	7
							Treated	0.75, 0.95	14

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
AA940501.KS	Karl	10/6/93	1.4	45	4/7/94	Tillering	Treated	0.01	69
			1.4	45	4/7/94	Tillering			
			0.83	45	6/8/94	Pre-harvest	Treated	0.38	7
							Treated	0.31	14
			1.4	45	4/7/94	Tillering			
			0.57	48	6/8/94	Pre-harvest	Treated	0.16	7
							Treated	0.17	14
AA940501.MN	Stoa	5/9/94	1.5	49	6/11/94	Tillering	Treated	0.01	94
			1.4	46	6/11/94	Tillering			
			0.85	47	9/6/94	Pre-harvest	Treated	0.78, 1.2	9
							Treated	0.46	16
			1.4	48	6/11/94	Tillering			
			0.57	48	9/6/94	Pre-harvest	Treated	0.41	8
							Treated	0.4, 0.63	14
							Control	0.015	7
AA940501.ND	Grandin	5/11/94	1.4	48	6/4/94	Tillering	Treated	<0.01	82
			1.4	48	6/4/94	Tillering			
			0.84	46	8/18/94	Pre-harvest	Treated	0.25	7
							Treated	0.27	14
			1.4	48	6/4/94	Tillering			
			0.56	47	8/18/94	Pre-harvest	Treated	0.08	7
							Treated	0.17	14
AA940501.OK	McNair	11/10/93	1.4	46	4/6/94	Tillering	Treated	<0.01	72
			1.4	46	4/6/94	Tillering			
			0.85	50	6/10/94	Pre-harvest	Treated	0.57, 0.96	7
			1.4	46	4/6/94	Tillering			
			0.56	49	6/10/94	Pre-harvest	Treated	0.23	7
							Control	0.02	7
AA940501.WA	Stephens	10/6/93	1.4	49	4/18/94	Tillering	Treated	0.02	105
			1.4	49	4/18/94	Tillering			
			0.85	47	7/25/94	Pre-harvest	Treated	0.22	7
							Treated	0.16	14
			1.4	45	4/18/94	Tillering			
			0.57	47	7/25/94	Pre-harvest	Treated	0.11	7
							Treated	0.06	14
							Control	0.03, 0.04 (2), 0.05	7
EHE (Carringer, 1996a)									
AA960501.CO	TAM 107	~9/15/95	1.4	51	4/10/96	Tillering	Treated	0.03	98
			1.4	51	4/10/96	Tillering			
			0.58	47	7/10/96	Pre-harvest	Treated	0.42	7
			1.4	51	4/10/96	Tillering			
			0.58	48	7/3/96	Pre-harvest	Treated	0.21	14
AA960501.GA	Coker 9835	12/5/95	1.4	49	3/13/96	Tillering	Treated	0.02, <0.01	75
			1.4	49	3/13/96	Tillering			
			0.57	47	5/20/96	Pre-harvest	Treated	0.05, 0.08	7
			1.4	49	3/13/96	Tillering			

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
			0.57	47	5/13/96	Pre-harvest	Treated	0.09, 0.13	14
							Control	0.01	
AA960501.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	47	6/26/96	Tillering	Treated	<0.01	69
			1.4	46	6/26/96	Tillering			
			0.56	48	8/20/96	Pre-harvest	Treated	0.19	7
			1.4	48	6/26/96	Tillering			
			0.56	48	8/13/96	Pre-harvest	Treated	0.2, 0.23	14
AA960501.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	48	6/21/96	Tillering	Treated	<0.01	68
			1.45	47	6/21/96	Tillering			
			0.57	48	8/21/96	Pre-harvest	Treated	0.03, 0.39	7
			1.4	47	6/21/96	Tillering			
			0.56	47	8/14/96	Pre-harvest	Treated	0.21, 0.22	14
AA960501.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	Tillering	Treated	<0.01, 0.03	84
			1.4	50	3/13/96	Tillering			
			0.56	50	5/25/96	Pre-harvest	Treated	0.08, 0.09	11
			1.4	50	3/13/96	Tillering			
			0.57	50	5/21/96	Pre-harvest	Treated	0.14, 0.16	15
AA960501.WA	Madsen	11/6/95	1.4	47	4/25/96	Tillering	Treated	<0.01 (2)	105
			1.4	47	4/25/96	Tillering			
			0.55	48	8/1/96	Pre-harvest	Treated	0.16, 0.17	7
			1.4	47	4/25/96	Tillering			
			0.57	47	7/25/96	Pre-harvest	Treated	0.16, 0.17	14
DMA (Carringer, 1996b)									
AA960502.CO	TAM 107	9/15/95	1.4	51	4/10/96	Tillering	Treated	<0.01 (2)	98
			1.3	51	4/10/96	Tillering			
			0.58	47	7/10/96	Pre-harvest	Treated	0.75, 0.9	7
			1.3	51	4/13/96	Tillering			
			0.58	48	7/3/96	Pre-harvest	Treated	0.01, 0.25	14
AA960502.GA	Coker 9835	12/5/95	1.4	49	3/13/96	Tillering	Treated	<0.01 (2)	75
			1.4	49	3/13/96	Tillering			
			0.57	47	5/20/96	Pre-harvest	Treated	0.14, 0.16	7
			1.4	49	3/13/96	Tillering			
			0.57	47	5/13/96	Pre-harvest	Treated	0.27, 0.34	14
AA960502.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	46	6/26/96	Tillering	Treated	<0.01 (2)	69

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha					
			1.4	46	6/26/96	Tillering			
			0.56	48	8/27/96	Pre-harvest	Treated	0.25, 0.36	7
			1.4	47	6/26/96	Tillering			
			0.54	46	8/20/96	Pre-harvest	Treated	0.15, 0.17	14
AA960502.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	46	6/20/96	Tillering	Treated	<0.01 (2)	69
			1.4	47	6/20/96	Tillering			
			0.56	46	8/21/96	Pre-harvest	Treated	0.57 (2)	7
			1.4	47	6/20/96	Tillering			
			0.56	47	8/14/06	Pre-harvest	Treated	0.44, 0.46	14
AA960502.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	Tillering	Treated	<0.01 (2)	84
			1.4	50	3/13/96	Tillering			
			0.57	50	5/20/96	Pre-harvest	Treated	0.08, 0.03	11
			1.4	50	3/13/96	Tillering			
			0.57	50	5/21/96	Pre-harvest	Treated	0.1, 0.24	15
AA960502.WA	Madsen	11/6/95	1.4	47	4/25/96	Tillering	Treated	<0.01	105
			1.4	47	4/25/96	Tillering			
			0.56	48	8/1/96	Pre-harvest	Treated	0.12, 0.22	7
			1.4	47	4/25/96	Tillering			
			0.56	47	7/25/96	Pre-harvest	Treated	0.08, 0.16	14

Table 46. Residues of 2,4-D in wheat straw.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
EHE (Carringer, 1995b)								
AA930204.CA1	Yecora Rojo	2/12/93	1.4	47	4/10/93	Tillering		
			1.4	46	6/15/93	Pre-harvest	73	7
							52	14
AA930204.CA2	Yecora Rojo	4/8/93	1.4	46	5/18/93	Tillering		
			1.4	48	7/19/93	Pre-harvest	76	7
							65	14
AA930204.GA	Coker 9766	11/18/92	1.4	47	2/23/93	Tillering		
			1.4	47	5/14/93	Pre-harvest	22 20	7
							17	14
AA930204.KS	TAM 107	9/10/92	1.4	47	4/16/93	Tillering		
			1.4	47	6/25/93	Pre-harvest	26	7
							17	14
AA930204.MN	Hard Red Spring	5/13/93	1.4	47	6/19/93	Tillering		
			1.5	48	8/19/93	Pre-harvest	66	7

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
							16	14
AA930204.ND	Hard Red Spring	4/26/93	1.3	43	5/26/93	Tillering		
			1.4	48	8/13/93	Pre-harvest	17	7
							17	14
AA930204.OK	McNair	10/1/92	1.4	53	3/16/93	Tillering		
			1.5	57	5/28/93	Pre-harvest	23	7
							14	14
AA930204.WA	Stephens	10/11/92	1.5	50	4/27/93	Tillering		
			1.4	47	7/26/93	Pre-harvest	19	7
							8	14
Acid (Carringer, 1995t)								
AA930205.KS	TAM 107	9/10/92	1.5	50	4/16/93	Tillering		
			1.5	49	6/25/93	Pre-harvest	7	7
AA930205.ND	Grandin	4/26/93	1.4	45	5/26/93	Tillering		
			1.4	48	8/11/93	Pre-harvest	6	7
							5	14
DMA (Carringer, 1995a)								
AA930207.CA1	Yecora Rojo	2/12/93	1.4	47	4/14/93	Tillering		
			1.4	46	6/23/93	Pre-harvest	80	7
							65	14
AA930207.CA2	Yecora Rojo	4/8/93	1.4	46	5/19/93	Tillering		
			1.4	48	7/21/93	Pre-harvest	94	7
							102	14
AA930207.GA	Coker 9766	11/18/92	1.4	47	2/23/93	Tillering		
			1.4	47	5/14/93	Pre-harvest	53	7
							5	14
AA930207.KS	TAM 107	9/10/92	1.4	55	4/16/93	Tillering		
			1.7	48	6/25/93	Pre-harvest	8	7
AA930207.MN	Butte 86	5/13/93	1.4	47	6/29/93	Tillering		
			1.4	48	8/19/93	Pre-harvest	77	7
							34	14
AA930207.ND	Grandin	4/26/93	1.4	47	5/26/93	Tillering		
			1.4	53	8/13/93	Pre-harvest	30	7
							21	14
AA930207.OK	McNair 1003	10/1/92	1.4	53	3/16/93	Tillering		
			1.4	56	5/28/93	Pre-harvest	11	7
							12	14
AA930207.WA	Stephens	10/10/92	1.4	48	4/27/93	Tillering		
			1.4	49	7/26/93	Pre-harvest	60, 63	7
							33	14
DMA (Carringer, 1995z)								
AA940502.CA1	Yecora Rojo	4/15/94	1.5	51	5/20/94	Tillering	8	53
			1.4	47	5/20/94	Tillering		
			0.82	46	7/5/94	Pre-harvest	17	7
							12	15
			1.4	46	5/20/94	Tillering		
			0.54	45	7/5/94	Pre-harvest	14	7
							15	15
AA940502.CA2	Yecora Rojo	4/15/94	1.5	42	5/25/94	Tillering	8	45

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			1.5	49	5/25/94	Tillering		
			0.87	49	7/2/94	Pre-harvest	36	7
							51	13
			1.3	49	5/25/94	Tillering		
			0.55	46	7/2/94	Pre-harvest	6	7
							41	13
AA940502.GA	Andy	12/20/93	1.4	47	4/7/94	Tillering	51	46
			1.4	47	4/7/94	Tillering		
			0.84	47	5/16/94	Pre-harvest	84	7
							91	14
			1.4	47	4/7/94	Tillering		
			0.56	47	5/16/94	Pre-harvest	82	7
							85	14
AA940502.KS	Karl	10/6/93	1.4	45	4/7/94	Tillering	1	69
			1.4	45	4/7/94	Tillering		
			0.87	48	6/8/94	Pre-harvest	32	7
							27	14
			1.4	45	4/7/94	Tillering		
			0.57	48	6/8/94	Pre-harvest	32	7
							15	14
AA940502.MN	Stoa	5/9/94	1.4	47	6/11/94	Tillering	0.2	73
			1.4	45	6/11/94	Tillering		
			0.85	48	8/16/94	Pre-harvest	5	7
							11	14
			1.4	48	6/11/94	Tillering		
			0.57	48	8/16/94	Pre-harvest	5	7
							5	14
AA940502.ND	Grandin	5/11/94	1.4	48	6/4/94	Tillering	0.01	82
			1.4	48	6/4/94	Tillering		
			0.84	47	8/18/94	Pre-harvest	8	7
							4	14
			1.4	48	6/4/94	Tillering		
			0.56	47	8/18/94	Pre-harvest	4	7
							4	14
AA940502.OK	McNair	11/01/93	1.4	46	4/6/94	Tillering	0.32	72
			1.4	45	4/6/94	Tillering		
			0.84	50	6/10/94	Pre-harvest	23	7
			1.4	44	4/6/94	Tillering		
			0.55	49	6/10/94	Pre-harvest	14	7
AA940502.WA	MAC-1	10/18/93	1.4	47	4/18/94	Tillering	0.02	106
			1.4	48	4/18/94	Tillering		
			0.86	48	7/25/94	Pre-harvest	8	7
							7	14
			1.4	47	4/18/94	Tillering		
			0.56	46	7/25/94	Pre-harvest	11	7
							6	14
EHE (Carringer, 1995y)								
AA940501.CA1	Yecora Rojo	4/15/94	1.4	45	5/21/94	Tillering	21	52
			1.4	45	5/21/94	Tillering		

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			0.83	46	7/5/94	Pre-harvest	32	7
							25	15
			1.4	46	5/21/94	Tillering		
			0.56	47	7/5/94	Pre-harvest	15	7
							15	15
AA940501.CA2	Yecora Rojo	4/15/94	1.4	46	5/26/94	Tillering	21	44
			1.4	46	5/26/94	Tillering		
			0.83	46	7/2/94	Pre-harvest	19	7
							22	13
			1.4	47	5/26/94	Tillering		
			0.54	45	7/2/94	Pre-harvest	18	7
							18	13
AA940501.GA	Andy	12/20/93	1.4	47	4/7/94	Tillering	24	46
			1.4	47	4/7/94	Tillering		
			0.84	47	5/16/94	Pre-harvest	30	7
							25	14
			1.4	47	4/7/94	Tillering		
			0.56	47	5/16/94	Pre-harvest	26	7
							22	14
AA940501.KS	Karl	10/6/93	1.4	45	4/7/94	Tillering	1	69
			1.4	45	4/7/94	Tillering		
			0.83	45	6/8/94	Pre-harvest	18	7
							12	14
			1.4	45	4/7/94	Tillering		
			0.57	48	6/8/94	Pre-harvest	11	7
							8	14
AA940501.MN	Stoa	5/9/94	1.5	50	6/11/94	Tillering	0.28	94
			1.4	46	6/11/94	Tillering		
			0.85	47	9/6/94	Pre-harvest	15	9
							14	16
			1.4	48	6/11/94	Tillering		
			0.57	48	9/6/94	Pre-harvest	6	8
							8	14
AA940501.ND	Grandin	5/11/94	1.4	48	6/4/94	Tillering	<0.01	82
			1.4	48	6/4/94	Tillering		
			0.84	47	8/18/94	Pre-harvest	6	7
							7	14
			1.4	48	6/4/94	Tillering		
			0.56	47	8/18/94	Pre-harvest	3	7
							4	14
AA940501.OK	McNair	~11/10/93	1.4	46	4/6/94	Tillering	0.27	72
			1.4	46	4/6/94	Tillering		
			0.85	50	6/10/94	Pre-harvest	14	7
			1.4	46	4/6/94	Tillering		
			0.56	49	6/10/94	Pre-harvest	9	7
AA940501.WA	Stephens	10/6/93	1.4	49	4/18/94	Tillering	0.35	105
			1.4	49	4/18/94	Tillering		
			0.85	47	7/25/94	Tillering	8	7
							6	14

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			1.4	45	4/18/94	Tillering		
			0.57	47	7/25/94	Pre-harvest	7	7
							2	14
EHE (Carringer, 1996a)								
AA960501.CO	TAM 107	~9/15/95	1.4	51	4/10/96	Tillering	0.07, 0.11	98
			1.4	51	4/10/96	Tillering		
			0.58	47	7/10/96	Pre-harvest	13	7
			1.4	51	4/10/96	Tillering		
			0.58	48	7/3/96	Pre-harvest	4	14
AA960501.GA	Coker 9835	12/5/95	1.4	47	3/13/96	Tillering	0.28, 0.46	75
			1.4	49	3/13/96	Tillering		
			0.57	47	5/20/96	Pre-harvest	10, 13	7
			1.4	49	3/13/96	Tillering		
			0.57	47	5/13/96	Pre-harvest	11	14
AA960501.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	47	6/26/96	Tillering	<0.01	69
			1.4	46	6/26/96	Tillering		
			0.56	48	8/20/96	Pre-harvest	7, 3	7
			1.4	46	6/26/96	Tillering		
			0.56	46	8/13/96	Pre-harvest	3	14
AA960501.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	48	6/21/96	Tillering	0.01	68
			1.5	47	6/21/96	Tillering		
			0.57	48	8/21/96	Pre-harvest	11, 14	7
			1.4	47	6/21/96	Tillering		
			0.56	47	8/14/96	Pre-harvest	6, 7	14
AA960501.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	Tillering	0.04	84
			1.4	50	3/13/96	Tillering		
			0.56	50	5/25/96	Pre-harvest	5	11
			1.4	50	3/13/96	Tillering		
			0.57	50	5/21/96	Pre-harvest	5	15
AA960501.WA	Madsen	11/6/95	1.4	47	4/25/96	Tillering	0.05	105
			1.4	47	4/25/96	Tillering		
			0.55	48	8/1/96	Pre-harvest	2, 6	7
			1.4	47	4/25/96	Tillering		
			0.57	47	7/25/96	Pre-harvest	17 (2)	14
DMA (Carringer, 1996b)								
AA960502.CO	TAM 107	9/15/95	1.4	51	4/10/96	Tillering	0.1, 3	98
			1.3	51	4/10/96	Tillering		
			0.58	47	7/10/96	Pre-harvest	14, 23	7
			1.3	51	4/13/96	Tillering		
			0.58	48	7/3/96	Pre-harvest	3, 4	14
AA960502.GA	Coker 9835	12/5/95	1.4	49	3/13/96	Tillering	0.52, 0.58	75
			1.4	49	3/13/96	Tillering		
			0.57	47	5/20/96	Pre-harvest	15, 21	7

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			1.4	49	3/13/96	Tillering		
			0.57	46	5/13/96	Pre-harvest	11, 15	14
AA960502.ND1	Northwood Equity Elevator 2375	5/29/96	1.4	46	6/26/96	Tillering	<0.01, 0.01	69
			1.4	46	6/26/96	Tillering		
			0.56	48	8/27/96	Pre-harvest	10, 15	7
			1.4	47	6/26/96	Tillering		
			0.54	46	8/20/96	Pre-harvest	3, 4	14
AA960502.ND2	Northwood Equity Elevator 2375	5/24/96	1.4	46	6/20/96	Tillering	<0.01	69
			1.4	47	6/20/96	Tillering		
			0.56	46	8/21/96	Pre-harvest	21, 23	7
			1.4	47	6/20/96			
			0.56	47	8/14/06	Pre-harvest	5, 6	14
AA960502.OK	Pioneer 2180	10/9/95	1.4	50	3/13/96	Tillering	0.05	84
			1.4	50	3/13/96	Tillering		
			0.57	50	5/20/96	Pre-harvest	2	7
			1.4	50	3/13/96	Tillering		
			0.57	50	5/21/96	Pre-harvest	5, 7	14
AA960502.WA	Madsen	11/6/95	1.4	47	4/25/96	Tillering	<0.01	105
			1.4	47	4/25/96	Tillering		
			0.56	48	8/1/96	Pre-harvest	2	7
			1.4	47	4/25/96	Tillering		
			0.56	47	7/25/96	Pre-harvest	6, 7	14

Use as herbicide on grasses for sugar or syrup production

Residues of 2,4-D in sugar cane are shown in Tables 47 (forage) and 48 (cane).

Sugar cane. Critical GAP (USA): 2 x 2.2 kg ae/ha, PHI not defined. Two trials each were conducted in Florida, Hawaii and Louisiana with the DMA salt and two additional trials in Florida and Louisiana with the acid. In all the trials the applications were broadcast with ground equipment at 2.2-2.6 kg ae/ha, pre-emergence and post-emergence 106-175 days later, at a total seasonal rate of 4.4-4.8 kg ae/ha (Carringer, 1995r,s).

Forage samples were collected 88-92 days after the second application and cane samples at maturity after 137-214 days. The LOD for cane and forage was 0.01 mg/kg. Residues of 2,4-D were undetectable (<0.01 mg/kg) in seven forage controls and eight cane controls; one forage control showed residues of 0.12 mg/kg. Residues in treated forage and cane samples were not corrected against the controls.

Table 47. Residues of 2,4-D in sugar cane forage.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
DMA (Carringer, 1995s)								
AA930201.FL1	CP-78-2114	12/4/92	2.3	91	12/9/93	Pre-emergence		

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
			2.4	102	6/3/93	Post-emergence	0.03	90
AA930201.FL2	CP-70-1133	2/6/93	2.2	94	2/4/93	Pre-emergence		
			2.3	100	7/2/93	Post-emergence	0.08	90
AA930201.HI1	73-6110	3/25/93-4/25/93	2.2	93	4/22/93	Pre-emergence		
			2.6	108	9/13/93	Post-emergence	0.04	88
AA930201.HI2	73-6110	4/8/93-4/16/93	2.2	93	4/22/93	Pre-emergence		
			2.3	96	2/24/93	Post-emergence	0.14	88
AA930201.LA1	321	9/30/92	2.3	94	2/24/93	Pre-emergence		
			2.2	93	6/10/93	Post-emergence	<0.01	92
AA930201.LA2	321	9/10/92	2.2	93	2/24/93	Pre-emergence		
			2.2	92	6/10/93	Post-emergence	0.01	92
Acid (Carringer, 1995r)								
AA930202.FL	CP70-1133	2/6/93	2.3	93	2/10/93	Pre-emergence		
			2.2	93	7/2/93	Post-emergence	<0.01	90
						(Control)	0.12	90
AA930202.LA	321	9/30/92	2.2	93	2/24/93	Pre-emergence		
			2.2	93	6/25/93	Post-emergence	<0.01	92

Table 48. Residues of 2,4-D in mature cane.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Growth stage	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha				
DMA (Carringer, 1995s)								
AA930201.FL1	CP-78-2114	12/4/92	2.3	91	12/9/92	Pre-emergence		
			2.4	102	6/3/93	Post-emergence	<0.01	188
AA930201.FL2	CP-70-1133	2/6/93	2.2	94	2/4/93	Pre-emergence		
			2.3	100	7/2/93	Post-emergence	<0.01	140
AA930201.HI1	73-6110	3/25/93-4/25/93	2.2	93	4/22/93	Pre-emergence		
			2.6	108	9/13/93	Post-emergence	<0.01	214
AA930201.HI2	73-6110	4/8/93-4/16/93	2.2	93	4/22/93	Pre-emergence		
			2.3	96	2/24/93	Post-emergence	<0.01	214
AA930201.LA1	321	9/30/92	2.3	94	2/24/93	Pre-emergence		
			2.2	93	6/10/93	Post-emergence	<0.01	151
AA930201.LA2	321	9/10/92	2.2	93	2/24/93	Pre-emergence		
			2.2	92	6/10/93	Post-emergence	<0.01	151
DMA (Carringer, 1995s)								
AA930202.FL	CP70-1133	2/6/93	2.3	93	2/10/93	Pre-emergence		
			2.2	93	7/2/93	Post-emergence	0.02	140
AA930202.LA	321	9/30/92	2.2	93	2/24/93	Pre-emergence		
			2.2	93	6/25/93	Post-emergence	<0.01	137

Use as herbicide on nut trees

2,4-D is directed to the ground around trees. Residue trials were carried out on almonds, hazelnuts, pecans and pistachio nuts (Table 49).

Critical GAP for tree nuts (USA): 2 x 1.6 kg ae/ha, PHI 60 days (pistachio nuts 50 days). In hazelnuts, 4 x 0.12 kg ae/hl are used as spray to wet leaves and stems of suckers that are 15 to 20 cm in height (PHI 45 days).

Almonds. The LOD for 2,4-D residues in almonds is 0.05 mg/kg. No 2,4-D was detectable in the almond kernels except in one of the five trials in which a mechanical rake was used to gather the nuts from the orchard floor. Residues of 2,4-D in these samples ranged from <0.05 to 0.16 mg/kg (Kunkel, 1997a).

Hazelnuts. Three trials were conducted in Oregon to determine the residues of 2,4-D in hazelnuts harvested 49 days after four directed applications of 2,4-D. Each trial involved a control and side-by-side treatments of 2,4-D formulated as the DMA salt and the EHE to suckers at a rate of 0.11 kg ae/hl at retreatment intervals of 28-31 days. Solutions were applied until run-off and included a sticker/spreader (Kunkel, 1996a).

Nut samples were stored at 4°C for 4-9 days before oven drying at 40-65°C for 18 hours as in commercial practice, then hulled and shelled. The residues of 2,4-D were below the LOD (<0.05 mg/kg) in four control samples; two control samples contained 0.06 and 0.07 mg/kg. The residues in 12 treated samples were <0.05-0.1 mg/kg.

Pecans. In five trials in four states side-by-side treatments with the DMA salt and EHE were applied twice at intervals of 27-34 days (Kunkel, 1996c).

Samples were collected after about 60 days and shelled immediately. The residues were below the LOD (<0.05 mg/kg) in all samples.

Pistachio nuts. In two trials in California, the DMA salt was applied twice as a directed application at 1.6 kg ae/ha, using ground equipment, at a 22-day interval (Barney, 1995e).

Treated and control nut samples were collected 50 days after the second application and shelled. The residues of 2,4-D were below the LOD (<0.05 mg/kg) in all the samples.

Table 49. Residues in almonds, hazelnuts, pecans and pistachio nuts treated with 2,4-D.

Crop/ Reference Report no. Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		rate[1]	water l/ha				
Almonds (Kunkel, 1997a)							
4306.96-CA16	Nonpareil	1.6 + 1.6 DMA	51	5/21/96 + 6/20/96	Kernels	<0.05 (2)	57
		EHE			Kernels	<0.05 (2)	57
		DMA			Hulls	<0.05 (2)	57
		EHE			Hulls	<0.05 (2)	57
4306.96-CA17	Carmel	1.6 + 1.6 DMA	51	5/21/96 + 6/20/96	Kernels	<0.05 (2)	57
		EHE			Kernels	<0.05 (2)	57
		DMA			Hulls	<0.05 (2)	57
		EHE			Hulls	<0.05 (2)	57
4306.96-CA18	Carmel	1.6 + 1.6 DMA	51	5/21/96 + 6/20/96	Kernels	<0.05 (2)	57
		EHE			Kernels	<0.05 (2)	57
		DMA			Hulls	<0.05 (2)	57
		EHE			Hulls	<0.05 (2)	57
4306.96-CA19	Nonpareil	1.8 + 1.6 DMA	61	5/14/96 + 6/7/96	Kernels	0.11, 0.16	57
		EHE			Kernels	<0.05, 0.08	57
		1.8 + 1.6 DMA	61	5/14/96 + 6/7/96	Hulls	0.05, 0.1	57
		EHE			Hulls	<0.05, 0.07	57
4306.96-CA20	Nonpareil	1.8 + 1.6 DMA	61	5/14/96 + 6/7/96	Kernels	<0.05 (2)	57
		EHE			Kernels	<0.05 (2)	57
		1.8 + 1.6 DMA	61	5/14/96 + 6/7/96	Hulls	<0.05 (2)	57
		EHE			Hulls	<0.05 (2)	57
Hazelnuts (Kunkel, 1996a)							
6106.95-OR16	Barcelona	0.11 kg ea/hl DMA		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels	<0.05, 0.1	49
		0.11 kg ea/hl EHE		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels	<0.05 (2)	49
6106.95-OR17	Barcelona	0.11 kg ea/hl DMA		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels Control	<0.05 (2) 0.07	49
		0.11 kg ea/hl EHE		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels	<0.05, 0.05	49
6106.95-OR18	Barcelona	0.11 kg ea/hl DMA		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels	<0.05 (2)	49
		0.11 kg ea/hl EHE		5/2/95 + 5/30/95 + 6/30/95 + 7/28/95	Kernels Control	<0.05 (2) 0.06	49
Pecans (Kunkel, 1996c)							
6125.95-NC11	Unknown	1.6 + 1.6 amine	31	9/12/95 + 10/10/95	Kernels	<0.05 (2)	52

Crop/ Reference Report no. Location	Variety	Application		Date	Sample	Residues, mg/kg	PHI, days
		rate[1]	water l/ha				
		1.6 + 1.6 ester	31	9/12/95 + 10/10/95	Kernels	<0.05 (2)	52
6125.95-NC12	Unknown	1.6 + 1.6 amine	31	9/15/95 + 10/12/95	Kernels	<0.05 (2)	56
		1.6 + 1.6 ester	31	9/15/95 + 10/12/95	Kernels	<0.05 (2)	56
6125.95-NM03	Western Scitley	1.6 + 1.6 amine	23	9/1/95 + 9/29/95	Kernels	<0.05 (2)	59
		1.6 + 1.6 ester	23	9/1/95 + 9/29/95	Kernels	<0.05 (2)	59
6125.95-AR04	Moore	1.6 + 1.6 amine	12	8/10/95 + 9/7/95	Kernels	<0.05 (2)	65
		1.6 + 1.6 ester	12	8/10/95 + 9/7/95	Kernels	<0.05 (2)	65
6125.95-TX32	55-17-3 and Cheyenne	1.6 + 1.6 amine	46	7/13/95 + 8/16/95	Kernels	<0.05 (2)	61
		1.6 + 1.6 ester	46	7/13/95 + 8/16/95	Kernels	<0.05 (2)	61
Pistachio (Barney, 1995e)							
4301.94-CA99	Kerman	1.6 + 1.6	49	7/12/94 + 8/3/94	Kernels	<0.05 (2)	50
4301.94-CA08	Kerman	1.6 + 1.6	57	7/12/94 + 8/3/94	Kernels	<0.05 (2)	50

[1] kg ae/ha unless otherwise stated

Use as herbicide on soya beans

2,4-D is applied in the field not less than 7 days (esters) or 15 days (other formulations) before planting. The results are summarized in Tables 50-52. Critical GAP (USA): 1 x 0.56 (esters) or 1 x 1.1 (others) kg ae/ha.

In trials in five US states single applications of the EHE were made 7-9 days before planting at 0.56-0.57, 1.4-1.5 and 3-3.2 kg ae/ha. In two of the states the DMA and the free acid were also applied at the same rates (Carringer, 1994a-d).

Fresh forage and hay samples were collected 67 to 85 days after treatment. Hay samples were air-dried for 1.5 to 7 days after cutting. Seed samples were collected at maturity 124-157 days after treatment.

The LOD for all analyses was 0.01 mg/kg.

Table 50. Residues of 2,4-D in soya bean forage from pre-plant applications.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
DMA (Carringer, 1994d)							
AA930225.IL	Kennedy IV	6/10/93	0.56	140	5/25/93	<0.01	76
			1.4	143	5/25/93	<0.01	76
			3.1	149	5/25/93	<0.01	76
AA930225.LA	Hartz 6200	6/8/93	0.56	95	5/24/93	<0.01	85
			1.4	97	5/24/93	<0.01	85
			3.1	93	5/24/93	<0.01	85

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
EHE (Carringer, 1994b)							
AA930226.AR	Tracy M	7/9/93	0.57	94	7/2/93	<0.01	73
			1.4	94	7/2/93	<0.01	73
			3.1	93	7/2/93	<0.01	73
AA930226.IL	Kennedy IV	6/10/93	0.57	96	6/3/93	<0.01	67
			1.4	93	6/3/93	<0.01	67
			3.1	96	6/3/93	<0.01	67
AA930226.LA	Hartz 6200	5/31/93	0.56	93	5/24/93	<0.01	74
			1.4	94	5/24/93	<0.01	74
			3.1	94	5/24/93	<0.01	74
AA930226.MO	Avery	7/2/93	0.56	94	6/23/93	<0.01	69
			1.4	94	6/23/93	<0.01	69
			3.1	94	6/23/93	<0.01	69
AA930226.TN	Avery	6/29/93	0.57	95	6/22/93	<0.01	70
			1.5	99	6/22/93	<0.01	70
			3.2	99	6/22/93	<0.01	70
Acid (Carringer, 1994c)							
AA930227.IL	Kennedy IV	6/10/93	0.57	95	6/3/93	<0.01	67
			1.4	94	6/3/93	<0.01	67
			3	90	6/3/93	<0.01	67
AA930227.LA	Hartz 6200	5/31/93	0.56	94	5/24/93	<0.01	74
			1.4	93	5/24/93	<0.01	74
			3.1	94	5/24/93	<0.01	74

Table 51. Residues of 2,4-D in soya bean hay from pre-plant applications.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
DMA (Carringer, 1994d)							
AA930225.IL	Kennedy IV	6/10/93	0.56	140	5/25/93	<0.01	76
			1.4	143	5/25/93	<0.01	76
			3.1	149	5/25/93	<0.01	76
AA930225.LA	Hartz 6200	6/8/93	0.56	95	5/24/93	<0.01	85
			1.4	97	5/24/93	<0.01	85
			3.1	93	5/24/93	<0.01	85
EHE (Carringer, 1994b)							
AA930226.AR	Tracy M	7/9/93	0.57	94	7/2/93	<0.01	74
			1.4	94	7/2/93	0.01	74
			3.1	93	7/2/93	0.01	74
AA930226.IL	Kennedy IV	6/10/93	0.57	96	6/3/93	<0.01	69
			1.4	93	6/3/93	0.04	69
			3.2	96	6/3/93	<0.01	69
AA930226.LA	Hartz 6200	5/31/93	0.56	93	5/24/93	<0.01	81
			1.4	94	5/24/93	<0.01	81
			3.1	94	5/24/93	<0.01	81
AA930226.MO	Avery	7/2/93	0.56	94	6/23/93	<0.01, (0.77,1.1)[1]	71
			1.4	94	6/23/93	<0.01	69

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
			3.1	94	6/23/93	<0.01, (0.25, 0.26)[1]	71
AA930226.TN	Avery	6/29/93	0.57	95	6/22/93	<0.01	72
			1.5	99	6/22/93	<0.01	72
			3.3	99	6/22/93	0.02	72
Acid (Carringer, 1994c)							
AA930227.IL	Kennedy IV	6/10/93	0.57	95	6/3/93	<0.01	69
			1.4	94	6/3/93	<0.01	69
			3	90	6/3/93	<0.01	69
AA930227.LA	Hartz 6200	5/31/93	0.56	94	5/24/93	<0.01	81
			1.4	93	5/24/93	<0.01	81
			3.1	94	5/24/93	<0.01	81

[1] Contaminated sample, analysed twice. Analysis of a further sample showed residues <0.01 mg/kg.

Table 52. Residues of 2,4-D in soya bean seed from pre-plant applications.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
DMA (Carringer, 1994d)							
AA930225.IL	Kennedy IV	6/10/93	0.56	140	5/25/93	<0.01	149
			1.4	143	5/25/93	<0.01	149
			3.1	149	5/25/93	<0.01	149
AA930225.LA	Hartz 6200	6/8/93	0.56	95	5/24/93	<0.01	157
			1.4	97	5/24/93	<0.01	157
			3.1	93	5/24/93	<0.01	157
EHE (Carringer, 1994b)							
AA930226.AR	Tracy M	7/9/93	0.57	94	7/2/93	<0.01	129
			1.4	94	7/2/93	<0.01	129
			3.1	93	7/2/93	<0.01	129
AA930226.IL	Kennedy IV	6/10/93	0.57	96	6/3/93	<0.01	140
			1.4	93	6/3/93	<0.01	140
			3.2	96	6/3/93	<0.01	140
AA930226.LA	Hartz 6200	5/31/93	0.56	93	5/24/93	<0.01	144
			1.4	94	5/24/93	<0.01	144
			3.1	94	5/24/93	<0.01	144
AA930226.MO	Avery	7/2/93	0.56	94	6/23/93	<0.01	124
			1.4	94	6/23/93	<0.01	124
			3.1	94	6/23/93	<0.01	124
AA930226.TN	Avery	6/29/93	0.57	95	6/22/93	<0.01	129
			1.5	99	6/22/93	<0.01	129
			3.3	99	6/22/93	<0.01	129
Acid (Carringer, 1994c)							
AA930227.IL	Kennedy IV	6/10/93	0.57	95	6/3/93	<0.01	140
			1.4	94	6/3/93	<0.01	140
			3	90	6/3/93	<0.01	140
AA930227.LA	Hartz 6200	5/31/93	0.56	94	5/24/93	<0.01	144
			1.4	93	5/24/93	<0.01	144

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg	PHI, days
			kg ae/ha	water l/ha			
			3.1	94	5/24/93	<0.01	144

Use as herbicide on animal feed commodities

2,4-D is used world-wide to control broad-leaved weeds in grass and pastures.

Grass and hay. Critical GAP (USA): 2 x 2.2 kg ae/ha, PHI not defined. 32 trials were conducted in 16 US states. Two post-emergence broadcast applications of the free acid, the DMA salt or the EHE were made with ground equipment at intervals of 29-33 days at about 2.2 kg ae/ha, giving a total of 4.3-4.7 kg ae/ha. Cut hay was dried for periods ranging from 10 hours to 7 days before sampling (Carringer, 1995j,k,o,u,v,w,x; Rosemond, 1995a,b,c).

The LOD for all analyses was 1 mg/kg. Residues of 2,4-D were undetectable (<1 mg/kg) in 69 forage and 70 hay controls. One forage control showed residues of 1.1 mg/kg.

Table 53. Residues of 2,4-D in rangeland and pasture grass (forage and hay). Growth stage at first treatment 20-25 cm in all trials.

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg		PHI, days
			kg ae/ha	water l/ha		Hay	Forage	
DMA (Carringer, 1995k)								
AA930216.AR	Common Bermuda grass	~ 25 years	2.2	47	7/29/93			
			2.2	45	8/22/93	501 109	173 87	0 7
AA930216.KS	Tall grass prairie		2.3	49	5/25/93			
			2.3	48	6/25/93	402 155	169 117	0 7
AA930216.MO	Fescue	~1970	2.3	48	6/16/93			
			2.2	47	7/16/93	378 236	172 122	0 7
AA930216.NY	Pasture grasses	4 years old	2.3	48	5/6/93			
			2.3	49	6/6/93	111 149	92 61	0 7
AA930216.OK	Bermuda grass	5 years old	2.3	49	6/3/93			
			2.3	51	7/5/93	388 94	236 46	0 8
AA930216.PA	Kentucky bluegrass	10/8/91	2.2	50	5/17/93			
			2.3	50	6/17/93	451 145	233 41	0 7
AA930216.TN	Fescue	~1973	2.3	47	6/1/93			
			2.3	48	7/1/93	719 279	198 107	0 7
EHE (Rosemond, 1995b)								
AA930217.KS	Mixed grass	Unknown	2.3	48	5/25/93			
			2.2	46	6/25/93	142 330	223 103	0 7
AA930217.KY	Fescue/bluegrass	1978	2.3	48	6/16/93			

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg		PHI, days
			kg ae/ha	water l/ha		Hay	Forage	
			2.3	48	7/16/93	575 216	90 103	0 7
AA930217.OK	Unknown	5 years old	2.3	50	6/3/93			
			2.3	51	7/5/93	526 126	311 41	0 7
AA930217.PA	Kentucky bluegrass	10/8/91	2.2	49	5/17/93			
			2.3	50	6/17/93	457 182	358 125	0 7
AA930217.TX	Native	Native	2.3	54	1/1/00			
			2.2	46	6/27/93	477 147	192 82	0 7
AA930217.VA	Tall Fescue - Kentucky 31	~ 20 years	2.1	50	5/12/93			
			2.3	50	6/11/93	365 231	183 120	0 7
Acid (Carringer, 1995j)								
AA930218.KS	Native grass	Native	2.3	49	5/25/93			
			2.3	49	6/25/93	478 218	135 93	0 7
AA930218.PA	Tall Fescue	10/8/91	2.2	49	5/17/93			
			2.3	51	6/17/93	572 74	153 39	0 7
DMA (Rosemond, 1995c)								
AA930219.KS	Mixed grass	April 1989	2.2	47	5/15/93			
			2.5	52	6/14/93	183 61	241 23	0 7
AA930219.ND	Mixed grass	May 1957	2.3	47	5/18/93			
			2.3	46	6/17/93	402 39	314 34	0 7
AA930219.OK	Rangeland grass	> 10 years	2.3	49	5/15/93			
			2.3	50	6/15/93	229 101	280 49	0 7
AA930219.WY	Rangeland grass	Native	2.1	50	5/12/93			
			2.2	48	6/11/93	161 19	194 20	0 7
EHE (Rosemond, 1995a)								
AA930220.KS	Mixed grass	April 1989	2.4	49	5/15/93			
			2.2	47	6/14/93	114 68	177 45	0 7
AA930220.MT	Native	Native	2.2	47	5/17/93			
			2.2	49	6/19/93	244 180	285 170	0 7
AA930220.NE	Tall Fescue - Kentucky 31		2.2	48	4/17/93			
			2.2	48	5/17/93	275 65	154 20	0 7
AA930220.OK	Native Range	> 10 years	2.2	49	5/15/93			
			2.2	49	6/15/93	153 86	258 74	0 7
AA930220.SD	Western wheat grass	1987	2.2	49	5/12/93			
			2.2	44	6/11/93	239	182	0

Compound (Reference) Report no. Location	Variety	Planting date	Application		Date	Residue, mg/kg		PHI, days
			kg ae/ha	water l/ha		Hay	Forage	
						96	32	7
Acid (Carringer, 1995o)								
AA930221.KS	Mixed Perennial	April 1989	2.2	47	5/15/93			
			2.3	48	6/14/93	170 40	162 19	0 7
AA930221.OK	Native stand	> 10 years	2.4	50	5/15/93			
			2.3	49	6/15/93	176 68	271 41	0 7
EHE (Carringer, 1995u)								
AA940503.MI	Perennial Ryegrass	5/93	2.3	48	6/16/94			
			2.3	46	7/15/94	103 65 47	155 116 74	14 21 30
AA940503.MO	Timothy	5 years	2.2	47	6/27/94			
			2.2	47	7/27/94	142 96 61	87 85 45	14 21 30
EHE (Carringer, 1995w)								
AA940505.OK	Native Rangelands	~ 10 years	2.3	53	6/8/94			
			2.2	47	7/8/94	115 124 150	62 71 44	14 21 30
DMA (Carringer, 1995v)								
AA940504.MI	Perennial Ryegrass	8/91	2.3	48	6/16/94			
			2.3	47	7/15/94	50 45 50	53 25 34	14 21 30
AA940504.MO	Timothy	5 years	2.2	47	6/27/94			
			2.2	47	7/27/94	206 156 107	121 139 68	14 21 30
DMA (Carringer, 1995x)								
AA940506.OK	Native Rangelands	~ 10 years	2.3	53	6/8/94			
			2.2	47	7/8/94	43 82 68	36 46 42	14 21 30

Mammalian products

(Krautter and Downs, 1996). Groups of 3 Holstein dairy cows were dosed twice daily with gelatine capsules containing 2,4-D for 28 to 30 consecutive days at levels equivalent to 1446, 2890, 5779 and 8585 ppm in the diet (dry-weight basis) with a single control. These doses corresponded to mean rates of about 50.6, 100, 190 and 280 mg 2,4-D/kg body weight/day. The cows were slaughtered over a 3-day period, within 12-18 hours after their last doses.

Two further groups of 3 cows were treated at the high-dose level for 28 consecutive days and slaughtered 3 or 7 days after their last doses. The cows were milked twice daily in the mornings and evenings. Proportional daily composites were prepared for individual cows in the four dose groups from milk taken on dose days 0 (pre-dose), 1, 3, 7, 11, 14, 18, 21, 24 and 28. Samples from cows in the recovery groups were prepared from milk taken on days 0, 24 and 28, and 3 or 7 days after the last dose.

During necropsy, animals were examined for gross tissue abnormalities. Samples of liver, kidneys, composite muscle (round and tenderloin) and composite fat (perirenal and omental) were homogenized in a frozen state with dry ice and stored frozen until analysis.

Mean daily feed consumption and milk production levels during the acclimatization period were similar to those during treatment in all groups. Mean body weight changes during the treatment period were also comparable among the groups. Since there were no unusual or adverse treatment-related effects, it is concluded that the tissue and milk samples were appropriate for analysis.

Residue samples were analysed according to the methods described in Howard, 1996a. The LODs were 0.05 mg/kg for liver, kidney, muscle and fat, and 0.01 mg/kg for milk. The results are shown in Table 54.

Table 54. The mean and range of 2,4-D residues in milk and tissues from dosed cows (Krautter, 1996).

Dose, mg/kg bw	Residue, mg/kg, mean and (range)				
	Milk	Liver	Kidney	Muscle	Fat
0	<0.01	<0.05	<0.05	<0.05	<0.05
50	0.04 (0.02-0.07)[1]	0.12 (0.07-0.20)	3.8 (1.6-6.5)	0.21 (0.16-0.24)	0.42 (0.33-0.51)
100	0.12 (0.05-0.18)[2]	1.9 (1.2-2.4)	14 (8.8-18)	0.41 (0.28-0.51)	0.59 (0.45-0.75)
190	0.29 (0.08-0.59)[1]	3.0 (2.1-3.5)	17 (9.7-29)	0.76 (0.49-1.1)	2.5 (1.3-3.6)
280	0.47 (0.15-0.87)[1]	3.1 (2.3-3.8)	24 (24-24)	1.0 (0.98-1.0)	2.2 (2.0-2.3)
3-day recovery	0.01 (0.01-0.02)[3]	0.45 (0.12-0.67)	0.06 (<0.05-0.10)	0.06 (0.05-0.06)	0.07 (<0.05-0.12)
7-day recovery	0.01 (<0.01-0.02)[4]	0.39 (0.26-0.51)	<0.05	<0.05	<0.05

[1] Samples collected from day 7 to day 28

[2] Samples collected from day 1 to day 28

[3] Samples collected 3 days after the last dose

[4] Samples collected 7 days after the last dose

Fish and shellfish

(Biever, 1996). Channel catfish, bluegill sunfish, northern crayfish and freshwater clams were exposed to 6 mg 2,4-D ae/l as the DMA salt in static aquatic systems with a soil substrate for periods of 3 hours to 15 days. The edible tissues of the bluegills, crayfish and clams were collected after 3, 6 and 12 hours, and 1, 2, 8 and 15 days, and those of the channel catfish at the same intervals up to 8 days only, owing to mortality in both treated and control systems (cause unknown).

The results are shown in Table 55. The maximum mean 2,4-D concentration in the catfish edible tissue was 0.07 mg/kg, 6 hours after exposure and decreased to day 8. The maximum mean residue in bluegill sunfish edible tissue was 0.06 mg/kg after 6 hours, and decreased to near the LOD (0.01 mg/kg) on days 8 and 15. The maximum residue in crayfish edible tissue was 1.1 mg/kg after 8 days and did not decrease appreciably between days 8 and 15. The 2,4-D concentration in the edible tissue from the freshwater clams was not reported because the quality control sample recoveries run with the initial sample analyses were outside the recovery range of 70 to 120% and repeat analyses were impracticable because there was not sufficient tissue remaining in some samples to achieve an LOD of 0.01 mg/kg.

Table 55. 2,4-D residues in edible tissues of channel catfish, bluegill sunfish and crayfish (Biever, 1996).

Species	Residue, mg/kg							
	3 h	6 h	12 h	Day 1	Day 2	Day 8	Day 15	Control
Catfish	0.045 [1]	0.063 [1]	0.056 [1]	0.036	0.027	0.02	[2]	[2]
	0.039	0.07	0.049	0.058	0.051	[3]	[2]	[2]
Mean	0.04	0.07	0.05	0.05	0.04			
Bluegill	0.043 [1]	0.067 [1]	0.055 [1]	0.048	0.028	0.012	0.017	<0.01
	0.045	0.054	0.029	0.052	0.042	0.01	0.013	[4]
Mean	0.04	0.06	0.04	0.05	0.04	0.01	0.02	
Crayfish	0.12 [1]	0.072 [1]	0.23 [1]	0.47	0.35	1.1	1.00	<0.01
	0.061	0.06	0.077	[3]	[3]	[3]	[3]	[3]
Mean	0.09	0.07	0.15					

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[1] The tissue sample was not composited before the initial analysis, the remaining tissue was composited before the second analysis

[2] No tissue was available for analysis owing to death of the catfish

[3] Analytical recoveries outside the 70% to 120% acceptance limits and results not reported

[4] No duplicate analysis of control tissue

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

(Johnson and Strickland, 1995a). In two trials in California on lemons treated pre- and post-harvest with 2,4-D IPE, lemon samples were stored at a commercial storage facility at 6-16°C for 28-112 days. The results are shown in Table 28.

In processing

Lemons (Johnson and Strickland, 1995b). Whole lemons from the above trials were processed into juice, wet and dry pulp, molasses, and oil using simulated commercial procedures. A single sample of each processed fraction was collected from each sample of whole fruit.

The LOD was 0.05 mg/kg for juice and wet pulp, 0.2 mg/kg for dry pulp and molasses and 0.5 mg/kg for oil. The residues of 2,4-D were below the LODs in two control samples of each processed fraction.

The processing study was adequate and indicates that residues of 2,4-D are concentrated in molasses and dry pulp, but not in juice, wet pulp or oil. The average concentration factors were 4.3 in molasses and 4.6 in dried pulp.

Table 56. Residues of 2,4-D in lemons and their processed commodities (Johnson and Strickland, 1995b).

Location	Storage, days	Residues, mg/kg/processing factor (PF)										
		RAC	Juice	PF	Wet pulp	PF	Dry pulp	PF	Molasses	PF	Oil	PF
Tulare County, CA	0	0.42	<0.05	(<0.12)[1]	0.42	1	1.8	4.3	1.9	4.5	<0.5	<1.2
	56	0.61	0.05	0.08	0.47	0.77	1.8	3	3	4.9	<0.5	<0.82
	112	0.41	0.05	0.12	0.5	1.2	3.2	7.8	2.1	5.1	<0.5	<1.2
Ventura County, CA	0	0.54	<0.05	(<0.09)[1]	0.37	0.69	2	3.7	1.6	3	<0.5	<0.93
	56	0.52	0.05	0.1	0.34	0.65	1.8	3.5	2.5	4.8	<0.5	<0.96
	112	0.5	0.05	0.1	0.49	0.98	2.8	5.6	1.8	3.6	<0.5	<1
Mean				0.1		0.88		4.7		4.3		<1
Median		0.51	0.05		0.45	0.875	1.9	4	2.0	4.7	<0.5	<1

[1] Not included in calculation of the mean

Maize (Carringer, 1995c). In two trials in Iowa and Nebraska, maize was treated three times with 2,4-D EHE as a pre-emergence application at 1.7 kg ae/ha, a post-emergence directed application at 0.83 kg ae/ha and a broadcast pre-harvest application 2.5 kg ae/ha, with ground equipment at intervals of 32- 49 days between the first and second applications and 88-111 days between the second and third applications. Grain samples were collected 7 and 14 days after the final (pre-harvest) application (Table 57).

Two treated and control samples of grain were collected from each trial at each PHI but only single samples collected at the 7-day PHI in Nebraska were processed, by simulated commercial procedures, into starch, grits, meal, flour, crude oil (wet and dry milling) and refined oil (wet and dry milling).

The LOD for all samples was 0.01 mg/kg. Residues of 2,4-D were undetectable in all the control samples.

Table 57. Residues of 2,4-D in commodities processed from maize grain (Carringer, 1995c).

Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
		kg ae/ha	water l/ha					
Quena 7670	5/18/93	1.7	47	5/21/93	Pre-emergence	grain	0.03	7
		0.83	48	6/22/93	10-16 in.			
		2.5	47	10/11/93	Pre-harvest			
Pioneer	5/3/93	1.7	47	5/3/93	Pre-emergence			
3162		0.83	47	6/21/93	10-16 in.			

Variety	Planting date	Application		Date	Growth stage	Sample	Residue, mg/kg	PHI, days
		kg ae/ha	water l/ha					
		2.5	47	9/17/93	Pre-harvest	grain	0.06	7
						starch	<0.01	
						grits	0.04	
						meal	0.05	
						flour	0.05	
						crude oil - wet milling	<0.01	
						crude oil - dry milling	<0.01	
						refined oil - wet milling	<0.01	
						refined oil - dry milling	<0.01	
						Aspirated grain fractions	2.2	

Rice (Carringer, 1995n). In two trials in Arkansas and Louisiana, 2,4-D DMA was applied to rice at about 2.5 kg ae/ha (1.5 times the GAP rate) at late tillering using ground equipment (Table 58).

Two grain samples were collected 61-66 days after treatment from treated and control plots at each site and processed into hulls, bran and milled white rice by simulated commercial procedures. Only the processed samples from Arkansas were analysed. The residues of 2,4-D were below the LOD (<0.01 mg/kg) in all the control samples.

Table 58. Residues of 2,4-D in rice and its processed fractions (Carringer, 1995n).

Sample	Location	Application, kg ae/ha	Residues, mg/kg	Processing factor
Rice, husked	AR LA	2.4 2.5	0.03 0.02	
Hulls	AR	-	0.09	3
Bran	AR	-	0.01	0.33
Milled white rice	AR	-	<0.01	indeterminate

Sorghum (Carringer, 1995m). In trials in Kansas and Texas, two sorghum grain samples were collected 81-112 days after single applications of 2,4-D DMA at 1.7 kg ae/ha with ground equipment (Table 59).

Samples from Texas were processed by simulated commercial procedures into starch and flour. The residues of 2,4-D were undetectable (<0.01 mg/kg) in the grain from both trial sites and in processed commodities from the Texas trial.

Table 59. Residues of 2,4-D in sorghum and its processed fractions (Carringer, 1995 m).

Sample	Location	Application, kg ae/ha	Residues, mg/kg	Processing factor
Sorghum	KS TX	1.8 1.7	<0.01 <0.01	
Starch	TX	-	<0.01	indeterminate
Flour	TX	-	<0.01	indeterminate

Wheat (Carringer, 1995a). In two trials each in North Dakota and Kansas, two broadcast applications of 2,4-D EHE were made at either 1.4 or 2.1 kg ae/ha, totalling 1.4 or 2.1 times the seasonal GAP rate using ground equipment with an 82-day retreatment interval. Samples were collected after 7 and 14 days in North Dakota but only after 7 days in Kansas as the 14-day sample plots were inadvertently destroyed. The Kansas grain samples were not processed.

Two treated and control grain samples were collected at each PHI in North Dakota. The 7-day samples were processed by simulated commercial procedures into bran, low grade wheat flour, patent flour, middlings, shorts and aspirated grain fractions, and the 14-day samples into aspirated grain fractions. The LOD was 0.01 mg/kg for all samples except aspirated grain fractions which had an LOD of 0.1 mg/kg. One grain control had apparent residues of 2,4-D of 0.01 mg/kg. The results are shown in Table 60.

Table 60. Residues of 2,4-D in wheat and its processed fractions (Carringer, 1995aa).

Variety	Planting date	Application		Date	Growth Stage	Sample	Residue, mg/kg	PF[1]	PHI, days
		kg ae/ha	water l/ha						
TAM 107	9/10/92	1.4	45	4/16/93	Tillering				
		1.4	47	6/25/93	Pre-harvest	Grain	0.26		7
		2.2	48	4/16/93	Tillering				
		2.1	47	6/25/93	Pre-harvest	Grain	0.56		7
Grandin	4/26/93	1.4	48	5/26/93	Tillering				
		1.4	47	8/16/93	Pre-harvest	Grain	1.5		7
						Bran	5.7	3.8	
						Low grade flour	0.21	0.14	
						Patent flour	0.19	0.13	
						Middlings	0.63	0.42	
						Shorts	0.81	0.54	
						Dust	47	31	
		2.1	47	5/26/93	Tillering				
		2.1	47	8/16/93	Pre-harvest	Grain	2.4		7
						Bran	8.3	3.5	
						Low grade flour	0.23	0.096	
						Patent flour	0.16	0.067	
						Middlings	1.1	0.46	
						Shorts	3.7	1.5	
						Dust	80	33	
		1.4	48	5/26/93	Tillering				
		1.4	47	8/16/93	Pre-harvest	Grain	0.41		14
						Dust	3.8	9.3	
		2.1	47	5/26/93	Tillering				
		2.1	47	8/16/93	Pre-harvest	Grain	0.76		14
						Dust	10	13	

[1] Processing factor

Sugar cane (Carringer, 1995l). In two trials in Florida and Louisiana, 2,4-D DMA was applied to sugar cane at 4.5 kg ae/ha with ground equipment at pre-emergence and again 110-176 days later at layby, giving a total of 9 kg ae/ha/season (4 times the GAP rate).

Single samples of cane were collected 166 or 188 days after the second application and processed into bagasse, molasses (first and final strike) and sugar by simulated commercial procedures but only the samples from Florida were analysed. The residues of 2,4-D were below the

LOD (<0.01 mg/kg) in two control cane samples and in one control sample of each processed commodity. The residues were also <0.01 mg/kg in cane samples from Florida and Louisiana and in bagasse, molasses (first strike) and sugar. The residue was 0.01 mg/kg in one sample of molasses (final strike) but a duplicate re-analysis showed <0.01 ,g/kg. The results are shown in Table 61.

Table 61. Residues of 2,4-D in sugar cane and its processed fractions (Carringer, 1995l).

Sample	Location	Total application, kg ae/ha	Residues, mg/kg
Sugar cane	FL LA	9.1 9	<0.01 <0.01
Bagasse	FL	-	<0.01
Molasses (first strike)	FL	-	<0.01
Molasses (final strike)	FL	-	0.01 <0.01
Sugar	Fl	-	<0.01

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

In a review of the US Food and Drug Administration Pesticide Monitoring Database for Fiscal Years 1992, 1993, 1994 and 1995 the only reported residues were from four samples of lemons obtained in California in 1992. The residues were 0.05, 0.06, 0.06 and 0.11 mg/kg. Table 62 shows the results from the USDA Pesticide Data Program for 1992, 1993 and 1994.

Table 62. Summary of US monitoring data for 2,4-D residues in 1992-1995.

Crop Year	Samples analysed	Samples with residues	Residues <LOD	Number of samples in residue range, mg/kg										
				≤0.01	>0.01, ≤0.02	>0.02, ≤0.03	>0.03, ≤0.04	>0.04, ≤0.05	>0.05, ≤0.06	>0.06, ≤0.07	>0.06, ≤0.07	>0.08, ≤0.09	>0.09, ≤0.10	>0.10, ≤0.15
Apples														
1992	252	0												
1993	622	7	4	4	1			1					1	
1994	683	683	239	646	36		1							
Bananas														
1992	2	0												
1993	1	1	1	1										
1994	17	17	16	17										
Broccoli														
1994	29	29	16	29										
Carrots														
1994	13	13	12	13										
Celery														
1994	17	17	17	17										

Crop Year	Samples analysed	Samples with residues	Residues <LOD	Number of samples in residue range, mg/kg										
				≤0.01	>0.01, ≤0.02	>0.02, ≤0.03	>0.03, ≤0.04	>0.04, ≤0.05	>0.05, ≤0.06	>0.06, ≤0.07	>0.06, ≤0.07	>0.08, ≤0.09	>0.09, ≤0.10	>0.10, ≤0.15
Grapefruit														
1992	256	5	5	5										
1993	630	12	2	8	2	1	1							
Grapes														
1992	261	0												
1993	621	2		1			1							
1994	658	658	202	589	69									
Green beans														
1993	1	0												
1994	3	3	3	3										
Lettuce														
1994	30	30	20	23	7									
Oranges														
1992	266	2		2										
1993	634	23		19	2	1	1							
1994	682	682	227	636	46									
Peaches														
1993	132	4		4										
1994	396	396	168	369	27									
Potatoes														
1992	243	6				2		2	2					
1993	636	28	1	9		7	2	4	2	1	1	1	1	
1994	677	677	186	583	80	5	2	2	2			1	1	1
Sweet corn														
1994	459	459	99	389	70									
Sweet peas														
1994	431	431	139	395	35	1								

NATIONAL MAXIMUM RESIDUE LIMITS

The following is a list of the national MRLs obtained from the internet site in Canada (http://www.hc-sc.gc.ca/pmra/indimrle.html).

Country	Commodity	MRL, mg/kg
Australia	citrus	5
	sugar cane	5
	edible offal (mammalian)	2
	cereal grains	0.2
	meat (mammalian)	0.2
	potato	0.1
	eggs	0.05*
	milk	0.05*
	legume vegetables	0.05*
	lupin (dry)	0.05*
	oilseed	0.05*
	poultry	0.05*
	edible offal of poultry meat	0.05*
	pulses	0.05*
Austria	all foods of vegetable origin	0.1
Belgium	citrus fruit	2
	others	0.05*
Brazil	rice, oats, rye, corn, sorghum, wheat, barley (all unprocessed)	0.2
	citrus fruits	2
	meat, milk and milk products, eggs	0.05
	grasses	P 1000
	apples, pears, quince	P 5
	sugar cane	P 2
	flax	P 1
	coffee	0.1
	soya beans	0.1
Canada	asparagus	5
	citrus fruit	2
Chile	citrus fruit	2
	potatoes	0.2
	raw cereals	0.2
	milk and dairy products, carcases, eggs	0.05*
Czech Republic	maize	0.05
	cereals (except oat)	0.1
	sorghum	0.05

Country	Commodity	MRL, mg/kg
	maize	0.05
	rice	0.05
	butcher’s meat, milk, dairy products, eggs	0.05
	baccate fruits	0.1
	potatoes	0.2
	cereals	0.5
	citrus fruits	2
Finland	citrus	2
	others	0.1
Germany	citrus fruit	2
	citrus juices	0.1
	other foods of plant origin	0.1
Hungary	all food crops (a 14 day ban on grazing)	0.1
Israel	citrus fruit	2
	eggplant	0.2
Italy	citrus fruit	0.1
	hazelnuts	0.1
	potatoes	0.1
	cereals	0.1
	forage, clover	0.1
	milk, egg, meat	0.05
Japan	rice	0.2
Kenya	citrus fruits	2
	barley, oats, rye. wheat	0.5
	potato	0.2
	blackberries, raspberries, red-black, vaccinium berries, including bearberry	0.1
	maize, rice, sorghum	0.05
	eggs, meat, milk products, milks	0.05
Korea	grapefruit	0.5
	oranges, lemons	2
	other citrus fruits	0.1
	radishes (roots)	0.1
	eggplant	0.1
	celery	0.1
	cherries	0.1

Country	Commodity	MRL, mg/kg
	cotton seed	0.1
	soya beans	0.1
	carrots	0.1
	tomatoes	0.1
	asparagus	0.1
	spinach	0.1
	red peppers	0.1
	iceberg lettuce	0.1
	ginger	0.1
	Korean plums	0.1
	wheat, oats, barley, rye	0.5
	grapes	0.5
	apples, pears	2
	apricots	2
	corn (maize), African millet, rice	0.05
	strawberries	0.05
	chestnuts, walnuts, almonds, pecans	0.2
	potatoes	0.2
	beef, goat meat, pork, horsemeat, mutton or lamb	0.05
Malaysia	meat, egg, milk and milk products	0.05
	potatoes	0.2
	cereal grains	0.2
	fruits	2
	sugar cane	3
Mexico	rice (straw), wheat (forage), sugar cane (forage), corn (forage), sorghum (forage)	20
	sugar cane (pomace and molasses)	5 FA
	citrus fruit	5 PH
	asparagus	5
	apples, pears	5
	sugar cane	2
	corn (fresh & grain), sorghum, wheat (grain)	0.5
	grapes	0.5
	potatoes	0.2
	nuts	0.1*
	melon	0.1*

Country	Commodity	MRL, mg/kg
	tomato	0.1*
	chilli pepper	0.1*
	avocado	0.1*
	cotton (seed)	0.1*
	cucumber	0.1*
	watermelon	0.1*
	citrus fruit	0.1*
	pecans	0.1*
	strawberries	0.1*
	eggplant	0.1*
	squash	0.1*
	rice	0.1
	strawberries	0.05
Netherlands	citrus fruit	2
	blueberry, blackberry, raspberry	0.1
	other fruit	0.05*
	vegetables	0.05*
	cereal	0.05*
	others	0.05*
New Zealand	stone fruit	1
	citrus fruit	5
Romania	eggs without shell, whole milk and milk products, meat	0.05
Republic of Singapore	citrus fruit	2
	edible offal of cattle, pigs, sheep and goats	2
	barley, rye, wheat	0.5
	other cereal grains	0.2
	potatoes	0.2
	blackberries, raspberries and other berries	0.1
	eggs, meat, milk and milk products	0.05
Slovak Republic	maize, rye	0.05
	raw meat, milk products, milk, eggs	0.05
	blackberries, blueberries, raspberries	0.1
	cereal	0.2
	potatoes	0.2
	citrus fruit	2

Country	Commodity	MRL, mg/kg
South Africa	citrus	2
	barley, mealies, rye, sorghum, wheat	0.5
	sugar cane	0.5
	potatoes	0.1
Spain	citrus fruits	0.1
	fruits with or without shell	0.1
	seed fruits	0.1
	stone fruits	0.1
	berries and small fruits	0.1
	other fruits	0.1
	root and tuber vegetables	0.1
	bulb vegetables	0.1
	fruits and peponides	0.1
	vegetables of the genus Brassica	0.1
	fresh aromatic herbs and leaf vegetables	0.1
	young stalks	0.1
	fungi	0.1
	legumes	0.1
	oilseeds	0.1
	other edible seeds	0.1
	potatoes	0.1
	tea and other infusions	0.1
	hops	0.1
	spices	0.1
	grains	0.1
	other products for consumption (tobacco, sugar beets, sugar cane other)	0.1
	hay and forage crops except Gramineae forage and cereal straw	0.1
	dried products	0.1
	Gramineae forage	0.2
	cereal straw	0.2
Sweden	citrus fruits	2
	fruits and vegetables (fresh and dried fruits, fresh and deep-frozen berries and green vegetables and also root vegetables)	0.1
	cereals (ripe fruits of wheat, rye, barley, oats, rice, maize, millet and buckwheat) and hulled grain, flakes and flour made from cereals	0.1
Switzerland	cereal	0.05

Country	Commodity	MRL, mg/kg
	stone fruit	0.05
	pip fruit	0.05
Taiwan	sugar cane	0.05
	citrus fruits	2
USA	asparagus	5
	apples	5
	apricots	5
	barley, grain	0.5
	barley, forage	20
	blueberries	0.1
	citrus fruit	5
	corn, grain	0.5
	corn, fresh (sweet)	0.5
	corn, fodder	20
	corn, forage	20
	cranberries	0.5
	grapes	0.5
	grass, hay	300
	grass, pasture	1000
	grass, rangeland	1000
	milled fractions (except flour) derived from barley, oats, rye and wheat	2
	millet, grain	0.5
	millet, fodder	20
	millet, forage	20
	nuts	0.2
	oats, grain	0.5
	oats, forage	20
	pears	5
	pistachios	0.2
	potable water	0.1
	potatoes	0.2
	quinces	5
	rice, grain	0.1
	rice, straw	20
	rye, grain	0.5

Country	Commodity	MRL, mg/kg
	rye, forage	20
	sorghum, grain	0.5
	sorghum, fodder	20
	sorghum, forage	20
	soya bean, grain	0.1
	stone fruits	0.2
	strawberries	0.05
	sugar cane	2
	sugar cane, forage	20
	sugar cane molasses	5
	wheat, forage	20
	wheat, grain	0.5
	raspberries	0.1
	fish	1
	shellfish	1
	cattle, fat	0.2
	cattle, kidney	2
	cattle, meat	0.2
	cattle, meat by-products (except kidney)	0.2
	eggs	0.05
	goats, fat	0.2
	goats, kidney	2
	goats, meat	0.2
	goats, meat by-products (except kidney)	0.2
	hogs, fat	0.2
	hogs, kidney	2
	hogs, meat	0.2
	hogs, meat by-products (except kidney)	0.2
	horses, fat	0.2
	horses, kidney	2
	horses, meat	0.2
	horses, meat by-products (except kidney)	0.2
	milk	0.1
	poultry	0.05
	sheep, fat	0.2

Country	Commodity	MRL, mg/kg
	sheep, kidney	2
	sheep, meat	0.2
	sheep, meat by-products (except kidney)	0.2

* MRL at the LOD P: provisional tolerance FA: tolerance for processed food PH: post harvest application

APPRAISAL

2,4-D, 2,4-dichlorophenoxyacetic acid was evaluated for residues at several Joint Meetings between 1970 and 1987, when MRLs were recommended for a number of commodities, and for its effects on the environment in 1997. The compound was evaluated by the present Meeting in the CCPR Periodic Review Programme.

The Meeting received information on animal and plant metabolism, environmental fate, analytical methods, updated GAP, supervised residue trials on crops, animal feeding studies, and residues after processing.

2,4-D is formulated as salts (diethanolamine, DEA; dimethylamine, DMA; tri-isopropanolamine, TIPA; isopropylamine, IPA) or esters (2-butoxyethyl, BEE; isopropyl, IPE; 2-ethylhexyl, EHE). It is a selective, systemic foliar-applied hormone herbicide, readily absorbed by leaves and roots, which acts as a growth regulator to control broad-leaved weeds.

The absorption, distribution, metabolism and excretion of [^{14}C]2,4-D have been studied in mice, rats, a goat, hens and fish.

Studies on rats and mice show that the absorption of 2,4-D after oral administration is rapid and almost complete: peak plasma levels were reached about 4 hours after dosing.

After oral administration of the 2-ethylhexyl ester to rats the test substance could not be detected in blood, indicating that it was rapidly hydrolyzed to 2,4-D acid whose concentration peaked in plasma 2 to 4 hours after administration and then decreased with an apparent half-life of about 9 hours.

When rats were dosed orally with 1 or 100 mg/kg bw of [^{14}C]2,4-D the excretion of radioactivity was rapid: over 94% of the administered dose was recovered by 48 hours after dosing and the half-life for urinary excretion was about 5 hours. Urine was the main route of excretion (85-94%), while faeces represented a minor excretory pathway (2-11%). At the high dose of 100 mg/kg bw 2,4-D elimination was saturated during the first hours after dosing. Its rapid clearance from plasma and rapid excretion in the urine show that its potential to accumulate is low.

In rats, [^{14}C]2,4-D was eliminated primarily unchanged in the urine (>97%). Two minor metabolites, probably 2,4-D conjugates, were detected.

The 2-ethylhexyl ester was rapidly absorbed and hydrolysed to 2,4-D and 2-ethylhexanol. No 2,4-D 2-ethylhexyl ester was found in the blood, urine or faeces 72 hours after oral administration. The 2,4-D acid produced was rapidly excreted unchanged in the urine, and the 2-ethylhexanol was further metabolized to 2-ethyl-hexanoic acid, 2-ethyl-1,6-hexanedioic acid, 2-ethyl-5-oxohexanoic acid, 2-ethyl-5-hydroxyhexanoic acid, 2-heptanone and 4-heptanone, which were and rapidly excreted in the urine, faeces and expired air. CLICK HERE for continue

The distribution pattern of the ^{14}C in the organs, tissues milk and urine of a lactating goat dosed orally with [^{14}C]2,4-D showed that the kidney (which contained 0.45% of the dose) is the main target organ. Lower proportions were found in the liver (0.07 %), milk (0.06%), fat (0.03 %) and muscle (0.01 %), whereas the total ^{14}C in the urine was 99.4 % (97.9% identified as 2,4-D). The metabolites found at lower levels were 2- or 4-chlorophenoxyacetic acid (2- or 4-CPAA) and 2,4-dichlorophenol (2,4-DCP).

In hens dosed orally with [^{14}C]2,4-D, about 90% of the dose was recovered from the excreta. The edible tissues and eggs each contained <0.1% of the total dose.

Bluegill sunfish were exposed to 11 mg/l [^{14}C]2,4-D in their water under static conditions for four consecutive days. The total ^{14}C (as 2,4-D) in the day-4 viscera (inedible) and fillet (edible) represented 1.9 and 0.41 mg/kg respectively. 2,4-D (80% of the ^{14}C, 0.33 mg/kg) and 2,4-DCP (7.9% of the total ^{14}C, 0.03 mg/kg) were present in the edible portion.

Information on the metabolism of 2,4-D in plants was provided for apples, lemons, potatoes and wheat.

After application of the 2-ethylhexyl ester to a potato crop at a rate of 0.35 kg acid equivalent per hectare (ae/ha), the residues in the tubers were 0.24 mg/kg 2,4-D (42% of the total ^{14}C), 0.15 mg/kg 4-CPAA (26% of the total ^{14}C) and 0.09 mg/kg 4-hydroxy-2,5-D (15.5% of the total ^{14}C).

In apples after the spray application of [^{14}C]2,4-D to the turf beneath the canopy of a dwarf apple tree according to label instructions, the residues were too low to be identified (total ^{14}C 0.009 mg/kg as 2,4-D).

In the forage and straw of wheat treated with 2,4-D-EME 74 and 70% of the total ^{14}C was recovered as free or conjugated 2,4-D. The rest consisted of a large number of distinct metabolites, of which 4-hydroxy-2,5-D was the major compound (8% of the total ^{14}C). In wheat grain about half the total ^{14}C was associated with natural products (protein, starch and cellulose). The remainder consisted mainly of unidentified polar and unextractable compounds. 2,4-D accounted for 6% of the total ^{14}C and was the only component identified.

[^{14}C]2,4-D IPE applied to lemons post-harvest resulted in residues of 2.4 mg/kg as 2,4-D. The fruits were stored at 5-6°C up to 16 weeks. Most of the total ^{14}C was found in the peel, with very small amounts in the pulp and juice. Lemon peel at 20 weeks contained 93.5% of the total ^{14}C (2.1 mg/kg). These residues were mainly free and conjugated forms of 2,4-D (64% of the total ^{14}C, 1.5 mg/kg). Other compounds found in minor quantities were free and bound 2,4-D IPE (0.73 % of the total ^{14}C, 0.017 mg/kg), 4-hydroxy-2,3-D or 5-hydroxy-2,4-D (0.58%, 0.013 mg/kg), 4-hydroxy-2,5-D (0.44%, 0.01 mg/kg) and 2,4-DCP (0.72%, 0.016 mg/kg). The main metabolites found in the pulp and juice were also free and conjugated 2,4-D (2.9% of the total ^{14}C, 0.07 mg/kg in the pulp; 0.99% of the total ^{14}C, 0.023 mg/kg in the juice).

The degradation of 2,4-D does not lead to environmentally significant levels of degradation products in soil or water.

Under aerobic incubation conditions, 2,4-D is rapidly degraded in soil (half-life in silty clay soil 1.7 days at 25°C). The final degradation products are CO_2 and soil-bound residues, which are mostly distributed in the fulvic acid and huminic acid fractions of the soil.

Further information was received on the fate of the 2-ethylhexyl and isopropyl moieties of the 2,4-D esters and the dimethylamine and diethanolamine of the salts.

The K_{OC} values of [^{14}C]2,4-D ranged from 59 to 117, indicating a fairly high potential for 2,4-D to be leached through the tested soils (Arizona clay loam, Mississippi loam, California sandy loam, Plainfield sand), whereas the leaching potential of the degradation products 2,4-dichloroanisole (K_{OC}: 436-1442) and 2,4-dichlorophenol (K_{OC}: 368-1204) is medium to low. In contrast to that, the results of two field lysimeter studies show that 2,4-D and its degradation products are not mobile in sandy soils (pH 5.7 in the first 30 cm, 4.8-5.0 in the next soil horizons). This indicates that 2,4-D, in spite of its high potential to be leached, is not expected to be found in groundwater (owing to its rapid degradation in the soil) when the product has been used in compliance with GAP.

Terrestrial field dissipation studies with the dimethylamine salt and 2-ethylhexyl ester over a 2-year period showed similar rates of dissipation of 2,4-D when applied as either the salt or ester because both formulations are converted rapidly to the same anionic form.

Residues in rotational crops were determined in radishes, lettuce and wheat planted 30 and 139 days after the treatment of the soil with [^{14}C]2,4-D at a rate of 2.2 kg ae/ha (acid equivalent/ha). The total radioactive residues in the 30-day crops were <0.001 mg/kg in wheat forage, 0.01 mg/kg in radish roots and 0.06 mg/kg in wheat straw. No ether-soluble residues from free or conjugated 2,4-D or its metabolites were present at levels above 0.01 mg/kg after a 30-day planting interval. The ^{14}C residues observed in the rotational crops planted after both 30 and 139 days were due to incorporation into natural products.

An aerobic aquatic degradation study of [^{14}C]2,4-D was conducted at a concentration of 5 mg/l for up to 46 days. 2,4-D acid was degraded slowly at first and represented $\leq$75% of the applied dose after 25 days. The rate of degradation then increased sharply and at day 46 2,4-D represented only 0.5% of the applied radioactivity. The major product was CO_2, which accounted for 64% of the applied ^{14}C at the end of the study period. The highest levels of the other identified residues (expressed as % of applied ^{14}C) were 1.1% 2,4-dichlorophenol at day 35, 1.1% 4-chlorophenoxyacetic acid at day 14 and 1.4 % 4-chlorophenol at day 20.

2,4-D is not likely to remain long in the environment under anaerobic aquatic conditions, in which it was degraded with a half-life of 41 days.

Further information was received on the aquatic field and pond dissipation of the dimethylamine salt and its major degradation products 2,4-D, 2,4-dichlorophenol, 2,4-dichloroanisole, 4-chlorophenoxyacetic acid and 4-chlorophenol.

The current residue analytical methods are based on extraction with a basic aqueous solution before clean-up by solid phase extraction on a C18-bonded silica cartridge and solvent partitioning. After methylation and further clean-up of the ester, the 2,4-D residues are determined as 2,4-D methyl ester by GLC with an ECD. The method was validated for plant and animal commodities with recoveries above 70%. The typical limits of determination in plant materials, milk and animal tissues are 0.01- 0.05 mg/kg. For most of the supervised trials the reported LOD was 0.01 mg/kg. Residues were determined in water, soil and sediment by GLC with mass-selective detection with LODs of 0.001 mg/l in water and 0.01 mg/kg in soil and sediment.

The analytical method provided by The Netherlands is based on similar extraction and clean-up procedures but the SPE extracts are further processed by column-switched HPLC on a pre-column packed with internal surface reversed-phase (ISRP) material and a bonded C-18 analytical column with UV detection at 118 nm. The LOD was reported to be 0.02 mg/kg for meat and 0.05-0.1 mg/kg for cereals and vegetables.

Information was submitted on the stability of 2,4-D residues in various stored analytical samples. The Meeting concluded that the compound was stable for the duration of the studies (at least two years in potatoes, cherries and cranberries and for one year in the raw agricultural commodities and processed products of cereal grains, fodder and forage, oil seed, sugar cane, grapes and pears, and for seven months in citrus fruits, plums and peaches).

The nature of the 2,4-D residues in plants is adequately understood from the apple, lemon, potato and wheat metabolism studies, and the residues in animals are known from the mouse, rat, goat, poultry and fish metabolism studies.

The Meeting concluded that the definition of the residue in plants and animals should be defined as 2,4-D *per se* for compliance with MRLs and for the estimation of the dietary intake.

The value of the partition coefficient of 2,4-D at natural pH values (log P_{OW} = 0.18 and –0.83 at pH 5 and 7 respectively) indicates that the compound is not fat-soluble.

Plant metabolism studies on wheat and potatoes treated with the 2-ethylhexyl ester and on lemon treated with the isopropyl ester indicate nearly complete hydrolysis of the esters by about 10 days after treatment with 2,4-D as the terminal residue of importance. Mammalian pharmacokinetic and metabolism studies in rats and mice indicate that the 2-ethylhexyl ester is rapidly converted to 2,4-D acid and its metabolism can be considered to be equivalent to that of 2,4-D. For these reasons, the definition of the residue arising from the application of the ethylhexyl ester or other esters should be the same as that for the residue from the free acid.

Supervised residue trials on numerous crops were carried out all in the USA and evaluated against US GAP. Because no significant difference was observed between the residues left by the acid, esters and salts, the trials in which 2,4-D acid, the ethylhexyl ester and 2,4-D dimethylamine salt were applied were combined for evaluation.

Citrus fruits. 2,4-D is used as a plant growth regulator pre-harvest on grapefruit and oranges (US GAP 1 x 0.0024 kg ae/hl, PHI 7 days), and post-harvest on lemons (US GAP 1 x 0.05 kg ae/hl). The Meeting was informed that foliar spraying of grapefruit and oranges with 2,4-D is a minor use.

Two trials according to US GAP were carried out on grapefruit. Because one year passed between the first and the last application, the samples of mature fruits from 1994 and 1995 are used for evaluation. The residues in the whole fruit were <0.05 (2), 0.07 and 0.08 mg/kg. Two further trials complying with GAP on oranges both resulted in residues in the whole fruit below the LOD: <0.05 mg/kg. All the residues in rank order were <0.05 (4), 0.07 and 0.08 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg for grapefruit and oranges, and recommended withdrawal of the current CXL of 2 mg/kg for citrus fruit. As no residue data were submitted for the edible pulp the Meeting estimated an STMR of 0.05 mg/kg, based on the residues in the whole fruit.

Two supervised residue trials of post-harvest use on lemons were carried out in California. No decrease of the residue level during storage (0-112 days at 6-16°C) was observed (range from 0.29 to 0.61 mg/kg). The Meeting could not estimate a maximum residue level owing to the small number of trials.

Use as herbicide in orchards and vineyards

A further use of 2,4-D in fruits is for weed control with applications directed to the orchard or vineyard floor. The apple metabolism study indicates that no residues are to be expected in the fruits after application directed to the orchard floor and is supporting the interpretation of the supervised trial residue data.

Pome fruits. A number of trials on apples and pears in the USA complied with current GAP (2 x 2.2 kg ae/ha, directed application, PHI 14 days). The residues in the fruits from all the 10 trials available were below the LOD of 0.01 mg/kg at 13-15 days PHI. The Meeting estimated a maximum residue level for pome fruits of 0.01* mg/kg as being a practical limit of determination. Because the residues were below the LOD in all samples, including fruit from one trial at a fivefold rate, an STMR level of 0 was estimated.

Stone fruits. Three trials each on cherries, peaches and plums (one on fresh prunes) treated at rates up to the maximum US GAP (2 x 1.6 kg ae/ha, directed application, PHI 14 days) resulted in residues below the LODs of 0.05 mg/kg (cherries) or 0.01 mg/kg (peaches and plums) at 14 days PHI. The Meeting estimated a maximum residue level for stone fruits of 0.05* mg/kg as being a practical limit of determination. Because the residues were below the LOD in all samples including fruit from one trial at a fourfold rate an STMR level of 0 was estimated.

Berries and other small fruits. In four blueberry trials at rates of 2 x 1.6 kg ae/ha as a directed application which complies with GAP in the USA, residues up to 0.01 mg/kg were found about 30 days after the last application. The residues were <0.01 (2) and 0.01 (2) mg/kg.

In six residue trials on strawberries according to US GAP (1 x 1.7 kg ae/ha, before blossom), no residues (<0.05 mg/kg) were found 59-129 days after treatment.

Two US trials on cranberries with 3 x 4.5 kg ae/ha were reported. US GAP specifies 2 x 4.5 kg ae/ha, directed application. At a PHI of 30 days, no residues above the LOD of 0.02 mg/kg were found in samples from the first trial but up to 0.11 mg/kg in those from the second trial.

Only one trial was carried out on raspberries (1 x 1.6 + 1 x 3.1 kg ae/ha). No residues above the LOD of 0.05 mg/kg were found. No residue data were reported for blackberries.

Two residue trials were carried out on grapes according to current US GAP (1 x 1.6 kg ae/ha, directed application). No residues above the LOD of 0.05 mg/kg were found at the recommended PHI of 100 days.

All the residues from trials complying with US GAP for berries in rank order were <0.01 (2), 0.01 (2), <0.05 (9) and 0.11 mg/kg.

The Meeting estimated a maximum residue level of 0.1 mg/kg for berries and other small fruits (including grapes) and recommended withdrawal of the CXLs for blackberries, raspberries, and vaccinium berries (including bearberry).

The Meeting estimated an STMR of 0.05 mg/kg for berries except grapes, and an STMR of 0 mg/kg for grapes because of their special use pattern (100 days PHI and high phytotoxicity).

Use as herbicide on vegetables

2,4-D is directed to the ground for weed control in vegetables. Supervised trials on sweet corn, potatoes and asparagus were reported.

Sweet corn (corn-on-the-cob). Nine supervised trials at US application rates were reported. Only two of them included the recommended PHI of 21 days but the treatment in all the trials was carried out at the registered plant growth stage. The residues were at or below the LOD of 0.05 mg/kg in all samples of kernels plus cob with husks removed. The Meeting estimated a maximum residue level for sweet corn of 0.05* mg/kg as being a practical limit of determination, and an STMR of 0.05 mg/kg.

Potatoes. Eight of ten trials in the USA complied with US GAP (2 x 0.078 kg ae/ha). The treatments were carried out at the registered plant growth stage. At harvest, the residues were <0.05 (5), 0.08 (2) and 0.13 mg/kg. The Meeting confirmed the current CXL of 0.2 mg/kg and estimated an STMR of 0.05 mg/kg.

Asparagus. Four trials covering the US application rate were reported but only two included the specified PHI of 3 days (the residues were 0.1 and 3 mg/kg). Two trials are not enough to estimate a maximum residue level.

Use as herbicide on cereals

2,4-D is used world-wide for the pre- or post-emergence or pre-harvest treatment of winter and summer cereals.

Maize. After three applications of the dimethylamine salt (7 trials), 2-ethylhexyl ester (6 trials), or free acid (1 trial) totalling 3.4 kg ae/ha, the residues of 2,4-D in grain after 7 days (US GAP) or 14 days were <0.01, 0.01 (8), 0.015, 0.02 (2), 0.03 and 0.04 mg/kg (4 residues at 14 days were higher than the corresponding 7-day residues). The Meeting estimated a maximum residue level of 0.05 mg/kg to replace the current CXL (0.05* mg/kg) and an STMR of 0.01 mg/kg.

Rice. Seven of ten supervised US trials complied with GAP (1 x 1.7 kg ae/ha, PHI 60 days). The residues in the rice grain without husk in rank order were <0.01(2), 0.01 (3), 0.03 and 0.05 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg for husked rice to replace the current CXL of 0.05* mg/kg for rice and an STMR of 0.01 mg/kg.

Wild rice. Only one overdosed trial (4 replicates) was reported. No residues were found after treatment with 0.56 kg ae/ha at day 53 or 64. One trial is not enough to estimate a maximum residue level.

Sorghum. 2,4-D is registered in the USA for applications of 0.56 kg ae/ha of esters or 1.1 kg ae/ha of the acid or salts. In a total of ten trials in four US states the recommended rates were applied at the registered plant growth stage.

No residues above the LOD of 0.01 mg/kg were found in the grain at harvest. The Meeting estimated a maximum residue level for sorghum of 0.01* mg/kg as being a practical limit of determination to replace the current CXL of 0.05* mg/kg, and an STMR of 0.01 mg/kg.

Wheat and rye. Many field trials were carried out on wheat in the USA, 24 of them according to US GAP (1.4 + 0.56 kg ae/ha, PHI 14 days). The residues in wheat grain in rank order were 0.11 (2), 0.12, 0.13, 0.16 (2), 0.17 (4), 0.21, 0.22 (2), 0.23, 0.24 (2), 0.31, 0.34, 0.46, 0.63, 0.87, 0.94, 0.95 and 1.4 mg/kg. The Meeting agreed to extrapolate the residue data from wheat to rye because GAP is identical and estimated maximum residue levels of 2 mg/kg to replace the current CXLs of 0.5 mg/kg with STMRs of 0.22 mg/kg.

Other cereals. 2,4-D is registered world-wide for use on barley, millet, oats and triticale. Although the US GAP for barley, oats and millet is the same as for wheat the Meeting agreed that extrapolation from wheat to barley, oats and millet could be recommended because the residue could be considerably higher from the use after blossom at the dough stage.

2,4-D is registered on triticale in Australia (1 x 1.6 kg ae/ha, PHI 7 days). Many US trials on wheat complied with Australian GAP but the Meeting did not support extrapolation of the US data as the climatic conditions are different.

The Meeting agreed to recommend the withdrawal of the current CXLs for barley and oats of 0.5 mg/kg and could not estimate a maximum residue level for millet or triticale.

Sugar cane. Eight US supervised trials according to GAP with one pre-emergence and one post-emergence treatment of 2.2 kg ae/ha were reported. The residues in mature cane at PHIs of 137-214 days were <0.01 (7) and 0.02 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.01 mg/kg.

Tree nuts. Ten trials each on almonds and pecans were carried out in the USA, five with directed applications of the dimethylamine salt and five with the 2-ethylhexyl ester, according to US GAP (2 x 1.6 kg ae/ha, PHI 60 days).

Two trials with directed applications on pistachio nuts were also according to US GAP (2 x 1.6 kg ae/ha, PHI 50 days).

Three trials each with the dimethylamine salt and the 2-ethylhexyl ester complied with the critical US GAP on hazelnuts, where 4 x 0.12 kg ae/hl are used as a spray to the stems of suckers with a PHI of 45 days.

The residues were <0.05 (8), 0.08 and 0.16 mg/kg in almond kernels, below the LOD of 0.05 mg/kg in all the samples of pecans and pistachio nuts and <0.05 (2), 0.05 and 0.1 mg/kg in hazelnuts. All residues in rank order were <0.05 (22), 0.05, 0.08, 0.1 and 0.16 mg/kg.

The Meeting estimated a maximum residue level for tree nuts of 0.2 mg/kg and an STMR of 0.05 mg/kg.

Soya bean seed, fodder and forage. The use of 2,4-D is registered in the USA for pre-planting applications of 1 x 0.56 kg ae/ha of esters or 1 x 1.1 kg ae/ha of free acid or salts. Twenty seven supervised trials were reported, with treatments of 0.56, 1.4 or 3.2 kg ae/ha. The residues in all samples of beans were lower than the LOD of 0.01 mg/kg. The Meeting concluded that no detectable residue is likely to occur in soya beans, and estimated a maximum residue level of 0.01* mg/kg and an STMR of 0 mg/kg.

No residues were detected in any of the 27 samples of fresh forage.

The fodder samples were analysed after air-drying forage for 1.5-7 days after cutting. No residues above the LOD of 0.01 mg/kg were found in the nine trials according to GAP. Residues up to 0.04 mg/kg were found after the treatments at higher rates.

The Meeting concluded that no detectable residue is to be expected in soya bean forage (green) or fodder, and estimated maximum residue levels of 0.01* mg/kg as a practical limit of determination. STMRs of 0 for soya bean forage (green) and 0.01 mg/kg for fodder were estimated.

Animal feedstuffs

Forage, hay or fodder of grasses. Supervised trials according to US GAP (2 x 2.2 kg ae/ha) were reported on rangeland and pasture grass used for animal feed. The Meeting was informed that a PHI of 0 days has to taken into account for the estimation of a maximum residue level for rangeland. The residues in the forage on the day of treatment in rank order were 90, 92, 135, 153, 154, 162, 169, 172, 173, 177, 182, 183, 192, 194, 198, 223, 233, 236, 241, 258, 271, 280, 285, 31, 314 and 358 mg/kg. The Meeting estimated an STMR of 193 mg/kg for grass forage.

The highest residues from each trial on hay (PHI of fresh forage 7-30 days) were 19, 39, 40, 50, 61, 65, 68 (2), 74, 82, 86, 94, 96, 101, 103, 109, 126, 142, 145, 147, 149, 150, 155, 180, 182, 206, 216, 218, 231, 236, 279 and 330 mg/kg. The Meeting estimated a maximum residue level of 400 mg/kg and an STMR of 117.5 mg/kg for the hay or fodder (dry) of grasses.

Maize forage and fodder. US GAP allows pre-emergence application at 1.1 kg ae/ha, a directed post-emergence application at 0.56 kg ae/ha when the maize is 25-41 cm high, and a pre-harvest application at 1.7 kg ae/ha (PHI for grain 7 days).

After two applications of 2,4-D at rates totalling 1.7-2.2 kg ae/ha, the residues in rank order were 0.01, 0.03, 0.09, 0.25 (2), 0.33, 0.46, 0.61, 0.69, 0.88, 1.0 (2), 1.1, 2.7, 3.0 and 5.2 mg/kg in 16 forage samples collected at a 7-day PHI and <0.01 (14), 0.01, 0.03 mg/kg in 16 samples for silage use collected after 54-89 days.

After three applications of 2,4-D totalling approximately 3.4 kg ae/ha, the residues in fodder were 3.6, 4.2, 4.4 (2), 5.7, 6.4 (2), 9.1, 9.9, 15, 20, 25 and 30 mg/kg at 7 or 14 days after treatment.

The Meeting estimated a maximum residue level of 10 mg/kg for maize forage and 40 mg/kg for maize fodder. STMRs of 0.65 and 6.4 mg/kg were estimated for maize forage and fodder respectively.

Rice straw and fodder. The residues of 2,4-D after treatments according to GAP at 61-66 days were 1.1, 1.5, 2.1, 3.1, 5.4, 6.4 and 8.8 mg/kg. The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 3.1 mg/kg for rice straw and fodder, dry.

Sorghum, straw and fodder. The residues in the green forage in the 10 US trials described above in rank order were <0.01, 0.02 (2), 0.03 (2), 0.04, 0.06, 0.08, 0.13 and 0.14 mg/kg 30 days after treatment. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.035 mg/kg for sorghum forage (green).

Fodder samples were harvested at maturity, approximately 82-112 days after treatment. The residues in the untreated control samples were of the same order as those in the supervised trials. The Meeting therefore concluded that the submitted data could not be used to estimate a maximum residue level for sorghum straw and fodder.

Wheat forage, straw and fodder. In the USA the first application of 2,4-D is recommended after the plant is fully tillered but before joints are formed in the stems, and the second when the grain is at the dough stage.

The wheat can be cut before the pre-harvest application and used as forage, so the forage samples were taken 7 days after the first treatment. The residues in rank order were 5, 6 (3), 6.3, 7, 8 (2), 8.5, 9 (2), 11, 14 (3), 15 (2), 16, 17, 18 (2), 19, 20 (2), 22 (2), 23 (2), 24, 25, 26, 29, 30 (2), 33 (3), 34, 35, 41, 42, 50, 54, 55, 58 and 112 mg/kg.

The residues in straw from treatments according to GAP were 2, 3, 4 (5), 5 (3), 6 (2), 7 (3), 8 (2), 11, 15 (4), 17, 18, 22, 41 and 85 mg/kg 13-15 days after pre-harvest treatment.

The Meeting estimated a maximum residue level of 100 mg/kg and an STMR of 7 mg/kg for wheat straw and fodder, dry, and an STMR of 20 mg/kg for wheat forage.

Sugar cane forage. After applying 2,4-D pre-emergence and post-emergence (at layby) to sugar cane at 2.2 kg ae/ha, the residues were <0.01(2), 0.01, 0.03, 0.04, 0.08 and 0.14 mg/kg in forage samples collected 88-92 days after the second application. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.03 mg/kg.

Animal transfer studies

Groups of 3 cows were dosed at four dose levels equal to 1446, 2890, 5779 and 8585 ppm 2,4-D ae in the diet on a dry weight basis for 28 to 30 consecutive days. Two further groups were treated at the high dose level for 28 days and slaughtered 3 or 7 days after the last dose.

Residues of 2,4-D were detected in most of the milk samples analysed. The mean residue levels in the samples from the high-dose group reached a plateau after 7 days of treatment, showing a residue level of 0.47 mg/l throughout the remaining treatment period. The mean residues in the groups allowed 3 and 7 days of recovery decreased from the levels of 0.46 and 0.47 mg/kg at 28 days to 0.01 mg/l.

The residues in the milk from the medium-high dose groups also reached a plateau after 7 days at mean levels of 0.29 and 0.04 mg/kg respectively. The residues from the medium-low dose group became steady after the first day of treatment, having a mean level of 0.12 mg/kg throughout the remaining treatment period.

Residues of 2,4-D were also detected in most of the tissue samples analysed. The mean liver residue levels in the high, medium-high, medium-low and low dose groups were 3.1, 3.0, 1.9 and 0.12 mg/kg respectively, decreasing to 0.45 and 0.39 mg/kg after 3 and 7 days recovery respectively.

The mean residues in the kidneys from the four groups were 24, 17, 14 and 3.8 mg/kg respectively, decreasing to 0.06 and <0.05 mg/kg after 3 and 7 days recovery. The mean residues in the muscles from the four groups were 1.0, 0.76, 0.41 and 0.21 mg/kg, decreasing to 0.06 and <0.05 mg/kg after 3 and 7 days recovery, and those in the fat were 2.2, 2.5, 0.59 and 0.42 (those in the medium-high group being highest), and were 0.07 and <0.05 mg/kg after 3- and 7-day recovery periods.

Thus the highest residues were in the kidneys, followed in decreasing order by liver, fat, muscle and milk. This relationship was generally consistent in all four dose groups. The residue levels were generally dose-dependent, except in fat where the mean residue in the high dose group was slightly lower than that in the medium-high group, indicating that a plateau level had been reached in fat.

The highest exposure to 2,4-D residues will arise from the use of the herbicide on pasture, where the highest residues were 358 mg/kg in grass forage. With the assumption that the maximum daily feed consumption of a dairy cow (body weight 550 kg) is 20 kg on a dry matter basis, of which 60% is grass forage containing 25% dry matter, the intake may be calculated as follows.

358 mg/kg on a wet weight basis is equivalent to 1432 mg/kg on a dry matter basis (358 + 0.25).

Grass forage forms 60% of the diet and therefore contributes 859.2 ppm total feed on dry matter basis (1432 x 0.6).

Hence the dietary intake is 859.2 x 20 / 550 = 31 mg/kg bw/day.

The lowest dose in the feeding study was 50.6 mg/kg bw/day but, as a nearly linear relation between dose and residue level with its graph passing through the origin was established, the Meeting concluded that an extrapolation downwards to the estimated actual intake was justified in this case. The following Table shows the highest and the mean measured and extrapolated residues. Maximum residue levels were estimated from the highest extrapolated residue, and STMRs from the medians of the mean extrapolated residues for estimation of the maximum residue level and the STMR respectively.

Dose, group	Residues, mg/kg									
mg/kg bw/day	Milk		Liver		Kidney		Muscle		Fat	
	highest	mean	highest	mean	highest	mean	highest	mean	highest	mean
(50.6) Actual	(0.07)	(0.04)	(0.2)	(0.12)	(6.5)	(3.8)	(0.24)	(0.21)	(0.51)	(0.42)
31 Extrapolated	0.043	0.025	0.12	0.074	3.98	2.33	0.15	0.13	0.31	0.26
(99) Actual	(0.18)	(0.12)	(2.4)	(1.9)	(18)	(14)	(0.51)	(0.41)	(0.75)	(0.59)
31 Extrapolated	0.056	0.038	0.75	0.59	5.64	4.38	0.16	0.13	0.23	0.18
(189) Actual	(0.59)	(0.29)	(3.5)	(3.0)	(29)	(17)	(1.1)	(0.76)	(3.6)	(2.5)
31 Extrapolated	0.097	0.048	0.57	0.49	4.76	2.79	0.18	0.12	0.59	0.41
(276) Actual	(0.87)	(0.47)	(3.8)	(3.1)	(24)	(24)	(1.0)	(1.0)	(2.3)	(2.2)
31 Extrapolated	0.098	0.053	0.43	0.35	2.7	2.7	0.11	0.11	0.26	0.25

[1] Residues found in the feeding study are in parentheses

The Meeting considered that liver and kidney should by combined as "edible offal", with the residues found in kidney, and estimated maximum residue levels of 0.1 mg/kg for milk, 5 mg/kg for edible offal and 0.2 mg/kg for meat and STMRs of 0.043 mg/kg for milk, 2.745 mg/kg for edible offal and 0.125 mg/kg for meat, and recommended the withdrawal of the CXLs for milks and milk products (0.05* mg/kg). No maximum residue level or STMR was estimated for fat as the results appeared to be atypical.

A metabolism study in hens showed that about 90% of the dose was recovered in the excreta. The edible tissues and eggs contained <0.1% of the total dose. The highest exposure to 2,4-D residues will arise from wheat and rye grain in which the highest residue found in the supervised trials was 1.4 mg/kg and maximum residue levels of 2 mg/kg and STMRs of 0.22 mg/kg were estimated. With the assumption that the daily maximum feed consumption of a chicken (bw 1.9 kg) is 0.12 kg on a dry matter basis, consisting of 80% wheat grain (89% dry matter) and 20% rye grain (88% dry matter), an intake of 2.25 ppm can be calculated from the maximum residue level. Therefore, no residues higher than 0.002 mg/kg (0.1%) could be expected theoretically in edible tissues and eggs. The Meeting estimated STMRs of 0 for poultry meat, edible offal and eggs, and maximum residue levels for poultry meat and edible offal of 0.05* mg/kg as a practical limit of determination. The Meeting estimated a maximum residue level for eggs at the LOD of 0.01* mg/kg to replace the CXL of 0.05* mg/kg.

Processing

Studies have been carried out to determine the effect of processing on residues of 2,4-D in lemons, maize, rice, sorghum, wheat and sugar cane.

Lemons containing 0.51 mg/kg 2,4-D (median) were processed to juice, wet and dry pulp, molasses and oil, which contained median residues of 0.05, 0.45, 1.9, 2.0 and <0.5 mg/kg respectively. The corresponding mean processing factors were 0.1, 0.88, 4.7, 4.3 and <1. The Meeting applied these factors to the STMRs of 0.05 mg/kg for oranges and grapefruit, and estimated STMR-Ps of 0.005 mg/kg for juice, 0.044 mg/kg for wet pulp, 0.235 mg/kg for dried pulp, 0.215 mg/kg for molasses and 0.05 mg/kg for oil.

The processing data on maize indicate that residues of 2,4-D do not concentrate in any of its processed commodities used for food or feed. In grits, meal and flour, the 2,4-D residues (0.04, 0.05 and 0.05 mg/kg respectively) were of the same order as in the grain (0.06 mg/kg). In aspirated maize grain fractions the residues of 2,4-D were approximately 37 times those in the grain. In view of the chemical nature of the compound, the residues in maize oil would be lower than the LOD of 0.01 mg/kg.

Because an STMR of 0.01 mg/kg was estimated for maize grain and the residues in the processed commodities were similar to those in the raw commodity, the Meeting estimated STMR-Ps of 0.01 mg/kg for maize grits, meal and flour.

One processing study on rice was reported. Residues of 2,4-D were not concentrated in rice bran or milled white rice but were concentrated by a factor of 3 in rice hulls. No STMR-P could be estimated for milled white rice because no data were reported for the unprocessed commodity (rice with husk).

As residues of 2,4-D were not detectable in sorghum grain or its processed commodities the processing trials could not be evaluated.

Wheat was treated with excessive amounts of 2,4-D to obtain high residues (1.5 and 2.4 mg/kg) and processed to produce bran, flour, middlings and shorts. The residues were concentrated in the bran and reduced in the flour by mean processing factors of 3.65 and 0.11 respectively. From the STMR for wheat grain of 0.22 mg/kg and these factors the Meeting estimated STMR-Ps of 0.803 mg/kg and 0.024 mg/kg for wheat bran and flour respectively.

Residues from two supervised trials on sugar cane with treatment at four times the GAP rate were below the limit of determination (0.01 mg/kg). The cane from one trial was processed into molasses and sugar with residues of $\leq$0.01 mg/kg in molasses and <0.01 mg/kg in sugar. No STMR-Ps were estimated.

RECOMMENDATIONS

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

Definition of the residue for compliance with MRLs and for the estimation dietary intake: 2,4-D.

Commodity		Recommendation		
		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
GC 0640	Barley	W	0.5	
FB 0018	Berries and other small fruits	0.1	-	
	Berries, except grapes			0.05
FB 0264	Blackberries	W[1]	0.1	
FC 0001	Citrus fruits	W	2	
MO 0105	Edible offal (Mammalian)	5	-	2.745
PE 0112	Eggs	0.01*	0.05*	0
FC 0203	Grapefruit	0.1	2[2]	0.05
JF 0203	Grapefruit juice			0.005
	Grapefruit molasses			0.215
	Grapefruit oil			0.05
	Grapefruit pulp, dry			0.235
	Grapefruit pulp, wet			0.044
FB 0269	Grapes			0
	Grass forage (green)			193
AS 0162	Hay or fodder (dry) of grasses	400	-	117.5
GC 0645	Maize	0.05	0.05*	0.01
CF 1255	Maize flour			0.01
AS 0645	Maize fodder	40	-	6.4
AF 0645	Maize forage	10	-	0.65
	Maize grits			0.01
CF 0645	Maize meal			0.01
MM 0095	Meat (from mammals other than marine mammals)	0.2	0.05*	0.125
	Milk products	W	0.05*	
ML 0106	Milks	0.1	0.05*	0.043
GC 0647	Oats	W	0.5	
JF 0004	Orange juice			0.005
	Orange molasses			0.215
	Orange oil			0.05
	Orange pulp, dry			0.235
	Oranges pulp, wet			0.044
FC 0004	Oranges, Sweet, Sour	0.1	2[2]	0.05
FP 0009	Pome fruits	0.01*	-	0
VR 0589	Potato	0.2	0.2	0.05
PM 0110	Poultry meat	0.05*	-	0
PO 0111	Poultry, Edible offal of	0.05*	-	0
FB 0272	Raspberries, Red, Black	W[1]	0.1	
GC 0649	Rice	W[3]	0.05*	
CM 0649	Rice, husked	0.1	-	0.01
AS 0649	Rice straw and fodder, dry	10	-	3.1
GC 0650	Rye	2	0.5	0.22

Commodity		Recommendation		
		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
GC 0651	Sorghum	0.01*	0.05*	0.01
AF 0651	Sorghum forage (green)	0.2	-	0.035
VD 0541	Soya bean (dry)	0.01*	-	0
AL 0541	Soya bean fodder	0.01*	-	0.01
AL 1265	Soya bean forage (green)	0.01*	-	0
FS 0012	Stone fruits	0.05*	-	0
GS 0659	Sugar cane	0.05	-	0.01
AV 0659	Sugar cane forage	0.2	-	0.03
VO 0447	Sweet corn (corn-on-the-cob)	0.05*	-	0.05
TN 0085	Tree nuts	0.2	-	0.05
FB 0019	Vaccinium berries, including Bearberry	W[1]	0.1	
GC 0654	Wheat	2	0.5	0.22
CF 0654	Wheat bran, processed	-	-	0.803
CF 1211	Wheat flour	-	-	0.024
	Wheat forage			20
AS 0654	Wheat straw and fodder, dry	100	-	7

[1] Replaced by recommendation for berries and other small fruits

[2] Included in MRL for Citrus fruits

[3] Replaced by recommendation for Rice, husked

DIETARY RISK ASSESSMENT

The International Estimated Daily Intakes of 2,4-D, based on the STMRs estimated for 26 commodities, for the five GEMS/Food regional diets were in the range of 3 to 10% of the ADI. The Meeting concluded that the intake of residues of 2,4-D resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

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