

## **ANNEX B**

### **Metalaxyl-M**

#### **B.7 Environmental fate and behaviour**



### B.7.1 Route and rate of degradation in soil (Annex IIA 7.1.1; Annex IIIA 9.1.1)

#### B.7.1.1 Route of degradation (Annex IIA 7.1.1.1)

##### B.7.1.1.1 Aerobic degradation in soil (Annex IIA 7.1.1.1.1)

Metalaxyl-M is the biologically active R-enantiomer of metalaxyl. Metalaxyl, the racemate is consisting of two enantiomers (R/S : 50/50).

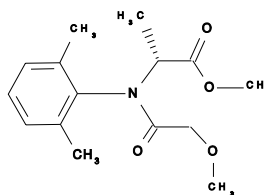
Several bridging studies comparing the degradation pathways and degradation rates of metalaxyl and metalaxyl-M were submitted. Studies with the racemic form can be used to support the assessment of the behaviour and effects of metalaxyl-M, however taking into account possible enantio-specific effects.

Numerous studies investigating the behaviour of metalaxyl in the lab and in the field were used to support the metalaxyl-M application.

The degradation studies performed with both a.s. revealed the presence of a major metabolite CGA 62826. Several specific studies investigate the behaviour of this metabolite.

The notifier submitted published articles showing the ability of soils previously treated with metalaxyl to degrade the active substance faster.

Structural formula of metalaxyl-M  
(CGA 329351)



Structural formula of metalaxyl  
(CGA 48988)



*Comparison of metalaxyl-M and metalaxyl degradation pathways and degradation rates*

Aerobic soil metabolism of  $^{14}\text{C}$ -CGA-329351 in a sandy loam soil (Fathulla, 1996a)

Guidelines :

US EPA guideline, subdivision N, series 162-1

GLP :

Yes

Material and Methods :

The aim of this study was the comparison of the degradation patterns and degradation rates of metalaxyl-M and metalaxyl under the same experimental conditions.

Test substance :

( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl, radiochemical purity : 98.4% , specific activity : (73.2  $\mu\text{Ci}/\text{mg}$ )

( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl-M, radiochemical purity : > 99% , specific activity : (81.1  $\mu\text{Ci}/\text{mg}$ )

Soil :

Table B.7.1.1.1-1 : Characteristics of the soil

Origin of soil:		California (CA0295)
Classification:		Sandy loam
Particle size distribution:	% silt	24
	% sand	68
	% clay	8
Organic matter content:	(%)	0.8
pH:		7.0
Cation exchange capacity (meq/100g soil):		7.0
Field moisture content (FMC) at 1/3 bar (%):		14.40
Microbial mass (mg microbial C/100g soil):		144.6

Test conditions :

1.5 mg a.s./kg soil was incubated under aerobic conditions at 25°C, at 75% FMC at 1/3 bar, in the dark.

Extraction methods :

3 extractions were performed with acetonitrile/ aqueous acetic acid (pH 4) (8/2), methanol/water (9/1) and dimethylformamide/ aqueous acetic acid (1/1).

Analytical methods :

Metalaxyl, metalaxyl-M and CGA 62826 were confirmed by HPLC, LC-MS and 2-dimensions TLC.

Findings :

Table B.7.1.1.1-2 : Comparison of metalaxyl and metalaxyl-M aerobic soil metabolisms - Balance and recovery of the metalaxyl experiment

Incubation time (days)	Extractable				Non-extractable	$^{14}\text{CO}_2$ ethoxyethanol-ethanolamine traps (**)	Total
	Total extractable (*)	Metalaxyl	CGA 62826	Unknown (region 2)			
0	97.6	95.1	-	-	1.3	NA	98.8
1	96.7	93.6	0.7	-	3.0	0.084	99.8
3	94.2	89.2	1.0	1.0	4.1	0.145	98.3
7	91.5	84.6	3.9	1.1	6.3	0.311	98.1
10	91.9	83.3	4.9	1.2	3.0	0.464	95.4
14	96.7	85.6	6.6	2.5	2.5	0.510	99.7
29	92.5	79.5	10.9	2.7	4.8	0.551	97.8
60	91.7	60.3	28.3	2.8	6.4	0.653	98.8

Incubation time (days)	Extractable				Non-extractable	<sup>14</sup> CO <sub>2</sub> ethoxyethanol-ethanolamine traps (**)	Total
	Total extractable (*)	Metalaxyl	CGA 62826	Unknown (region 2)			
70	91.9	50.9	37.1	2.6	6.5	0.701	99.1
99	93.6	26.5	61.9	0.6	2.9	0.954	97.5
130	91.3	12.6	71.8	4.1	5.5	1.542	98.4
160	85	6.8	69.0	2.4	7.7	2.823	95.4

(\*) : Sum of the 3 extracts

(\*\*) : Ethylene glycol trap results were not included in the table; They account for less than 0.013% of RR.

Table B.7.1.1.1-3 : Comparison of metalaxyl and metalaxyl-M aerobic soil metabolisms - Balance and recovery of the metalaxyl-M experiment

Incubation time (days)	Extractable				Non-extractable	<sup>14</sup> CO <sub>2</sub> ethoxyethanol-ethanolamine traps (**)	Total
	Total extractable (*)	Metalaxyl-M	CGA 62826	Unknown (region 2)			
0	102.4	100.0	0.4	-	1.3	NA	103.7
1	103.7	100.9	-	-	2.8	-	106.4
3	99.8	97.8	0.6	0.7	4.4	-	104.1
7	102.9	95.8	3.2	1.0	6.5	0.064	109.4
10	101.5	93.9	4.4	1.1	3.3	0.239	105.0
14	101.6	89.9	5.1	2.0	3.2	0.286	105.0
29	99.4	79.4	10.6	2.6	4.7	0.466	104.6
60	101.4	66.4	33.2	0.2	6.2	0.886	108.5
70	99.7	67.4	27.1	2.3	6.4	0.633	106.7
99	97.9	47.4	39.1	2.6	5.5	1.302	104.6
130	97.7	44.2	44.7	4.6	7.4	1.631	106.1
160	91.7	8.0	78.0	0.9	7.0	2.462	101.1

(\*) : Sum of the 3 extracts

(\*\*) : Ethylene glycol trap results were not included in the table; They account for less than 0.021% of RR.

#### Conclusions :

The experimental conditions of this study do not allow to observe the complete degradation of the a.s. : Increasing amount of metabolite CGA 62826 is observed at the end of the incubation period; mineralization is negligible (2.462% CO<sub>2</sub> after 160 days).

Similar degradation rates were observed for metalaxyl and metalaxyl-M (biphasic DT<sub>50</sub> were 58.4 and 73.5 days respectively for metalaxyl and metalaxyl-M).

Degradation pathways were similar for both compounds. The major degradation pathway involved the cleavage of the methyl ester bond to form the free acid metabolite CGA 62826. Region 2 could be a conjugate of the a.s.

Metabolism of  $^{14}\text{C}$ -CGA 329351 under aerobic conditions in two soils at 20°C. IR 95EH06 (Ellgehausen, 1996a)

**Guidelines :**

BBA Richtlinie Teil IV, 4-1

**GLP :**

Yes

**Material and Methods :**

The aim of this study was the comparison of the degradation rates of metalaxyl-M and metalaxyl in the same experimental conditions.

**Test substance :**

( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl, radiochemical purity : 98.03%, specific activity : 4.73 MBq/mg (= 127.84  $\mu\text{Ci}$ /mg) and

( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl-M, radiochemical purity : 98.8%, specific activity : 1.45 MBq/mg (= 39.3  $\mu\text{Ci}$ /mg)

**Soils :**

Table B.7.1.1.1-4 : Characteristics of the soils

Origin	Gartenacker (Switzerland)	California (US)
Classification (USDA):	sandy loam	sandy loam
Particle size distribution (%)		
Clay	9.6	10
Silt	49.0	30
Sand	41.4	60
Organic carbon content (%)	2.2	0.5
Total nitrogen (%)	0.29	-
pH	7.25	7.2
CaCO <sub>3</sub>	9.2	-
Cation exchange capacity (meq/100g soil)	8.6	7.8
Field capacity (FC; pF=2.5; g/100 g soil)	48.9	15.6
Max. water holding cap. (MWHC; g/100 g soil)	66.8	21.4
Microbial biomass (mg/100 dry soil) at start	50.6	14.3

**Test conditions :**

Incubation of metalaxyl and metalaxyl-M at the application rate of 0.2-2 mg a.s./kg, at 20°C, in the dark, at 40% MWHC and 75% FC

**Extraction methods :**

Soil: Extraction with acetone/water (4/1) followed by Soxhlet extraction with acetone.

**Analytical methods :**

Liquid scintillation counting (LSC), high performance liquid chromatography (HPLC)

**Findings :**

Table B.7.1.1.1-5 : Balance and recovery of aerobic soil metabolism study of metalaxyl-M - Comparison of 2 application rates

Incubation time (days)	Extractable					Not accounted	Non- extractable	<sup>14</sup> CO2	Total
	Metalax yl-M	CGA 62826	M2	CGA 67868	M5				
Gartenacker sandy loam, 20°C, 40% MWHC, <b>2 mg a.s./kg</b>									
0	95.86	0.00	0.00	0.00	1.56	0.00	3.45	0.00	100.83
7	42.75	29.57	0.00	2.55	1.26	1.51	20.77	0.91	99.32
14	16.74	40.36	0.00	3.72	1.00	1.35	33.95	2.82	99.94
21	6.15	38.40	1.86	0.00	0.94	0.74	47.40	4.43	99.91
28	3.47	26.04	2.06	3.18	1.09	0.62	54.43	7.94	98.83

Incubation time (days)	Extractable					Not accounted	Non-extractable	<sup>14</sup> CO <sub>2</sub>	Total
	Metalaxyl-M	CGA 62826	M2	CGA 67868	M5				
56	0.95	6.56	0.49	0.74	0.19	0.47	70.52	17.77	97.70
84	0.00	0.00	0.00	0.00	0.00	3.87	72.85	21.84	98.57
120	0.00	0.00	0.00	0.00	0.00	2.63	71.09	24.31	98.04
<b>Gartenacker sandy loam, 20°C, 40% MWHC, 0.2 mg a.s./kg</b>									
0	95.15	0.00	0.00	0.00	1.41	0.00	3.47	0.00	100.03
3	59.18	19.74	0.00	2.12	0.92	3.36	14.23	0.31	99.86
7	26.08	26.23	0.87	6.15	0.79	3.89	31.52	3.56	99.10
14	7.87	15.84	0.00	4.20	0.32	1.86	53.05	13.75	96.88
21	3.31	5.82	0.00	0.86	0.94	0.72	65.63	20.67	97.95
28	1.88	1.02	1.40	0.53	0.19	0.75	67.48	24.60	97.85
56	0.00	0.00	0.00	0.00	0.00	2.93	66.27	30.12	99.32
84	0.00	0.00	0.00	0.00	0.00	2.37	63.11	32.68	98.16
120	0.00	0.00	0.00	0.00	0.00	2.04	62.58	34.31	98.92

Table B.7.1.1.1-6 : Balance and recovery of aerobic soil metabolism study in California sandy loam - Comparison of metalaxyl-M and metalaxyl

Incubation time (days)	Extractable				not accounte d	Non- extractable	<sup>14</sup> CO2	Total
	a.s.	CGA 62826	CGA 67868	Unknow n				
Metalaxyl, California sandy loam, 20°C, 75% FC, 0.2 mg a.s./kg								
0	96.76	0.00	0.00	1.68	0.00	1.66	0.00	100.11
3	92.07	1.02	0.40	2.76	1.17	2.45	0.04	99.91
7	89.55	3.39	0.00	1.72	1.21	3.88	0.11	99.86
14	84.56	6.54	0.00	1.14	2.43	6.11	0.21	100.99
21	78.33	7.95	1.19	1.60	2.94	8.63	0.31	100.96
28	78.86	12.23	0.93	0.95	6.04	0.94	0.42	100.37
56	64.34	21.14	1.93	2.02	7.91	2.36	0.82	100.58
84	61.96	24.06	0.93	0.00	10.58	2.34	1.08	100.95
120	49.71	30.06	2.44	0.00	11.96	5.00	1.64	100.80
Metalaxyl-M, California sandy loam, 20°C, 75% FC, 0.2 mg a.s./kg								
0	97.24	0.00	0.00	1.42	0.00	1.59	0.00	100.26
3	94.07	0.00	0.00	1.37	1.27	3.11	0.11	99.93
7	91.62	1.45	0.00	0.66	1.24	4.46	0.19	99.62
14	86.68	5.51	0.00	1.04	2.70	4.57	0.31	100.81
21	80.30	6.24	1.06	0.49	3.03	8.94	0.41	100.46
28	83.27	7.85	1.12	0.76	5.78	1.61	0.55	100.94

56	71.03	16.14	1.27	0.42	7.71	3.30	1.02	100.89
84	72.47	14.93	0.00	0.00	8.09	3.72	1.12	100.32
120	55.82	22.91	1.29	0.00	14.43	3.52	2.60	100.56

Table B.7.1.1.1-7 : Comparison of metalaxyl and metalaxyl-M degradation rates.

	Gartenacker soil (0.2 mg/kg)			Gartenacker soil (2 mg/kg)	California soil (0.2 mg/kg)	
	metalaxyl-M	CGA 62826	CGA 67868	metalaxyl-M	metalaxyl-M	metalaxyl
DT <sub>50</sub>	4.0	6.9	7.1	5.7	167.9	123.4
DT <sub>90</sub>	13.2	23.0	23.4	18.9	635.8	499.5

Conclusions :

- In Gartenacker sandy loam, metalaxyl-M was degraded to two metabolites. CGA 62826 amounts account for up to 40% of the total radioactivity. CGA 67808 amounts were small (max : 6% RR). Mineralization reached 22-33% RR after 84 days. At that time 63-73% RR was recovered as unextractable.

- The behaviour of metalaxyl and metalaxyl-M was studied in California sandy loam. Degradation rates of both compounds were similar (DT<sub>50</sub> = 167.9 and 123.4 days, for metalaxyl and metalaxyl-M respectively). The degradation of both compounds was very slow in this soil. CGA 62826 amounts account for 23-30% of the total radioactivity at the end of the incubation period (120 days)

The mineralization was very limited for both compounds (1% after 84 days)

Comparison of rate of degradation of [U-<sup>14</sup>C]-phenyl CGA 48988 with CGA 329351 in soil under laboratory conditions (Ellgehausen, 1994)

Comparison of rate of degradation of [U-<sup>14</sup>C]-phenyl CGA 48988 with CGA 329351 in sandy soil Collombey under laboratory conditions (Ellgehausen, 1995a)

Guidelines :

BBA Richtlinie Teil IV, 4-1

GLP :

Yes

Material and Methods :Test substance :

(<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : 98.6%, specific activity : 4.73 MBq/mg (= 127.84 µCi/mg).

Unlabelled metalaxyl-M, chemical purity : 97.3%

Soil :

Table B.7.1.1.1-8 : Characteristics of the soils

Origin	Les Evouettes (Switzerland)	Collombey (Switzerland)
Classification (USDA):	silt loam	sand
Particle size distribution (%)		
Clay	13.9	5.1
Silt	54.3	11.4
Sand	31.8	83.5
Organic carbon content (%)	2.1	1.6
Total nitrogen (%)	0.28	0.21
pH	7.3	7.4
CaCO <sub>3</sub>	8.5	8.2
Cation exchange capacity (meq/100g soil)	14.0	11.9
Field capacity (FC; pF=2.5; g/100 g soil)	47.4	25.8



Max. water holding capac. (MWHC; g/100 g soil)	58.3	44.6
Microbial biomass (mg C/100 dry soil) at start:	65.1	51

*Test conditions :*

Two studies with similar protocol were performed to compare the degradation rate of the racemate (metalaxyl) and the R-enantiomer (metalaxyl-M). Both compounds were incubated in parallel under the same conditions, for 21 and 29 days, respectively for the 2 soils.

Aerobic incubation of 0.5 mg a.s./kg soil at 20°C, in the dark, 40% MWHC

*Extraction methods :*

Extraction of the soil samples by ethanol. The remaining water phase (soil water) was extracted with hexane.

*Analytical methods :*

Different procedures were used to determine metalaxyl-M (HPLC) and metalaxyl (HPLC and TLC) concentrations because metalaxyl-M was not radio-labelled. Corrections which were made in order to take into account the portion of a.s. present in the water extract (analyzed by TLC) allow to calculate DT<sub>50</sub> and DT<sub>90</sub> comparable for both compounds.

*Findings :*

Table B.7.1.1.1-9 : Comparison of the degradation rates of metalaxyl-M and metalaxyl at 20°C

	DT <sub>50</sub> (days)	DT <sub>90</sub> (days)
Silt loam (Les Evouettes)		
Metalaxyl-M	3.9	13.0
Metalaxyl	10.8	35.7
Sand (Collombey)		
Metalaxyl-M	8.13	27.02
Metalaxyl	13.97	46.40

*Conclusions :*

This study was performed with radiolabelled metalaxyl and unlabelled metalaxyl-M. No indications on the material balance, on the distribution pattern degradates and on the degradation pathway are provided by this study.

Under these study conditions, metalaxyl-M degraded more rapidly than metalaxyl.

CGA 329351 - Influence of Biomass on Rate of Degradation of CGA 329351 and CGA 48988 at 20°C and a Dose Rate of 0.2 kg/ha and Rate of Degradation of CGA 329351 at 30°C and a Dose Rate of 1 kg/ha. (Ellgehausen, 1998)

“ The objectives of the study were to provide information on the rate of degradation of metalaxyl-M, i.e. (R)-2-(N-(2,6-dimethyl-phenyl)-methoxyacetyl-amino)-propionic acid methyl ester (R-enantiomer) and Metalaxyl (racemate) in one soil at 20°C with different initial biomass. For this purpose, fresh soil high in microbial biomass was mixed with the same soil but low in biomass (stored soil) in varying amounts thus giving soil batches with decreasing biomass. Special attention was given to the formation and decline of its major soil degradate CGA 62826 (1). In addition the rate of degradation of Metalaxyl-M and its degradate CGA 62826 was followed at 30°C and a treatment rate corresponding to 1 kg/ha.

Table B.7.1.1.1-10 : Disappearance times for 50 (DT50) and 90 % (DT90) of the parent molecules (dose rate 0.2 mg/kg; 20°C)

Initial Biomass	Metalaxyl-M	Metalaxyl	Factor in	Factor in
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(mg mic. C/100 g Soil)	DT50 (d)	DT90 (d)	DT50 (d)	DT90 (d)	DT50	DT90
70.1	2.3	7.7	5.1	69.1	2.2	9.0
47.3	5.0	16.6	11.6	118.9	2.3	7.2
38.2	6.0	19.8	16.1	125.4	2.7	6.3
23.1	146.5	486.6	362.9	1205.5	2.5	2.5

Table B.7.1.1.1-11 : Disappearance times for 50 (DT50) and 90 % (DT90) of metalaxyl-M and the metabolite CGA 62826 (dose rate 1 mg/kg; 30°C)

Initial Biomass (mg mic. C/100 g Soil)	R-Enantiomer	DT50 (d)	DT90 (d)
70.1	Metalaxyl-M	1.6	5.2
	CGA 62826	2.8	9.3

The data clearly show an increase in half-life and in the DT-90-values with decreasing biomass. When compared with Metalaxyl the half-lives of Metalaxyl-M were, on average, 2.4 times lower. For the DT-90-values the difference was even more pronounced, i.e. they were, on average, 6.1 times shorter for Metalaxyl-M than for Metalaxyl. Metalaxyl-M showed clear exponential degradation kinetics (amounts going asymptotically versus zero).

Contrary, Metalaxyl showed distinct (rapid degradation at the beginning : r-enantiomer and slow degradation later : l-enantiomer). Thus the behaviour of Metalaxyl could be described best by a two compartment model. Based on these findings it can be assumed that at the beginning of the incubation mainly the re-enantiomer (CGA 62826\*) is formed during degradation of Metalaxyl. Thus a higher proportion of CGA 62826\* would result.

The half-life times and DT90-values of CGA 62826 (racemat, originating from Metalaxyl) and of CGA 62826\* (r-enantiomer, originating from metalaxyl-M) are presented below. Here again, the half-life of CGA 62826\* was significantly shorter than for CGA 62826. At the highest biomass the factor in half-life and DT90 was 1.8. At the medium half-life it was still 1.3. Only at the low biomass no significant difference was seen.

However the less pronounced difference in observed half-lives is for reasons discussed above most probably due to the higher proportion of CGA 62826\* built-up from metalaxyl.

Table B.7.1.1.1-12 : Disappearance times for 50 (DT50) and 90 % (DT90) of CGA 62826 (dose rate 0.2 mg/kg; 20°C)

Initial Biomass (mg mic. C/100 g Soil)	CGA 62826 (R-enantiomer)		CGA 62826 (racemate)		Factor in DT50	Factor in DT90
	DT50 (d)	DT90 (d)	DT50 (d)	DT90 (d)		
70.1	4.1	13.5	7.3	24.1	1.8	1.8
47.3	66.9	222.1	84.3	280.1	1.3	1.3
38.2	91.7	304.6	92.8	308.2	1.0	1.0
23.1	No decline observed					

#### Conclusions :

The study was designed in order to measure the degradation rates of metalaxyl-M (R-enantiomer) and metalaxyl (racemate) under different initial soil biomass. Soils with different biomass were obtained by mixing 'biologically inactive' soil (stored soil) and active soil (fresh soil) in different proportions. This procedure is unacceptable and does

not allow to extrapolate that metalaxyl-M will always degrade more rapidly than metalaxyl under the field conditions.

- Soils with more than 10 mg microbial C /100 g soil have however to be considered as biologically active soils.
- It possible that the differences in degradation rates of the soil mixtures reflect the normal distribution of DT50 in various soils.

*Degradation pathways of metalaxyl*

Degradation of CGA 48988 (Ridomil®) in soil under aerobic, aerobic/anaerobic and sterile/aerobic conditions. (Ellgehausen, 1978)

Guidelines :

Not specified

GLP :

No

Material and Methods :

*Test substance :* ( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl, specific activity : 0.9 Mbq/mg (24.25  $\mu\text{Ci}$ /mg), radiochemical purity : 99% %

*Soil :*

Table B.7.1.1.1-10 : Characteristics of the soil

Origin of soil:		Neuhofen, Germany
Classification:		Loamy sand
Particle size distribution:	% silt	7.3
	% sand	83.8
	% clay	8.9
Organic carbon content:	(%)	2.2
pH:		6.5
Cation exchange capacity (meq/100g soil):		11.3
Field capacity (g water/100 g soil):		34.0

*Test conditions :*

- Aerobic incubation of 10 mg a.s./kg dry soil in the dark at 25°C, 75% FC
- Aerobic incubation of 10 mg a.s./kg dry soil for 30 days followed by anaerobic conditions during 60 days (incubation under 2-3 cm water ventilated four times a day by a nitrogen flow)
- Sterile aerobic incubation of 10 mg a.s./kg dry soil in the dark at 25°C, 75% FC (sterilized by autoclaving)

*Extraction methods :*

Soil: Extraction with dichloromethane and methanol:water (8:2) followed by Soxhlet extraction with methanol and subsequent partitioning with dichloromethane

Residual water: Partitioned with dichloromethane.

*Analytical methods :*

Soil and water extracts: Liquid scintillation counting (LSC), preparative liquid chromatography (LC), thin layer chromatography (TLC), high performance liquid chromatography (HPLC), gas-liquid chromatography (GLC), gas-liquid chromatography/mass spectrometry (GC/MS) and high voltage electrophoresis (HVE).

Findings :

Table B.7.1.1.1-11 : Balance and recovery of aerobic/ anaerobic/sterile soil metabolism study of metalaxyl

Incubation time (days)	Extractable residues				Non-extractable	<sup>14</sup> CO <sub>2</sub> 2-methoxyethanol, NaOH and H <sub>2</sub> SO <sub>4</sub> traps	Total
	Metalaxyl	CGA 42447	CGA 62826	Polar residues			
aerobic conditions							
0	97.9	-	-	-	2.1	-	100.0
14	82.0	-	15.6	-	3.7	0.4	101.7
31	59.9	-	29.5	-	6.3	0.9	96.6
66	25.7	-	53.6	-	14.1	2.9	96.3
89	19.1	-	47.9	-	19.8	5.4	92.2

Incubation time (days)	Extractable residues				Non-extractable	<sup>14</sup> CO <sub>2</sub> 2-methoxyethanol, NaOH and H <sub>2</sub> SO <sub>4</sub> traps	Total
	Metalaxyl	CGA 42447	CGA 62826	Polar residues			
181	4.8	-	32.9	3.7	37.3	15.2	93.9
360	<2.0	0.5	23.0	4.8	38.3	25.3	93.9
Aerobic/anaerobic conditions							
66	49.4	-	42.0	-	9.3	0.8	101.5
89	32.5	-	52.4	-	8.4	0.9	94.2
Sterile aerobic conditions							
31	94.0	-	0.6	0.5	3.2	0.1	98.4
66	90.6	-	2.7	1.0	4.7	0.1	99.1
89	91.7	-	0.5	-	4.3	0.2	96.7

Conclusions :

Under aerobic conditions metalaxyl is degraded to a major metabolite CGA 62826 which reaches a maximum of 53.6 % RR after 66 days. The mineralization reached 5.4 % after 89 days. At that time, 19.8% RR was recovered as non extractable residue. (DT<sub>50</sub> ~ 40 days, DT<sub>90</sub> ~ 140 days).

Under anaerobic conditions, degradation of metalaxyl is slower. The information on the anaerobic degradation is scarce (2 incubation times, no data on the previous aerobic incubation) and does not allow to calculate DT<sub>50</sub> and DT<sub>90</sub>.

Under sterile conditions, almost no degradation of the a.s. occurs.

Degradation of <sup>14</sup>C-labelled metalaxyl (CGA 48988) in one soil incubated under various experimental conditions. (Schanné, 1991)

Guidelines :

BBA Richtlinie Teil IV, 4-1

Statutory Order from the Ministry of the Environment No. 791 of December 10, 1987 on Chemical Pesticides (Danish EPA)

GLP :

Yes

Material and Methods :

*Test substance :* (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : 98.9 %, specific activity : 3.3 Mbq/mg  
*Soil :*

Table B.7.1.1.1-12 : Characteristics of the soil

Origin of soil:		Les Evouettes (Switzerland)
Classification:		Silt Loam (USDA)
Particle size distribution:	% silt	50.7
	% sand	38.0
	% clay	11.3
Organic carbon content (%)		1.4
pH:		6.1
Cation exchange capacity (meq/100g soil):		15.5
Maximum water holding capacity (g/100 g soil):		55.3
Field capacity (g water/100 g soil):		40.2
Microbial biomass (prior to the test) (mg C/100 g dry soil)		31.5

Test conditions :

- aerobic incubation of 1.348 and 0.134 mg a.s./kg dry soil in the dark, at 10 and 20°C, 30 and 60% FC

*Extraction methods :*

Soil: Extractions with methanol:water (8:2), water, methanol, followed by Soxhlet extraction with methanol .

*Analytical methods :*

Soil extracts (all except water extract) were pooled and analyzed by liquid scintillation counting (LSC), thin layer chromatography (TLC).

Traps: Liquid scintillation counting

Findings :

Table B.7.1.1.1-13 : Balance and recovery of aerobic soil metabolism study of metalaxyl under various temperature and moisture conditions

Incubation time (days)	Extractable residue					Non-extractable	Volatiles (NaOH)	Volatiles (ethylene glycol)	Total
	Metalaxyl	CGA 62826	CGA 67868	Polar residues	Water extract				
1.348 mg/kg, 60% FC, 20°C									
0	101.47	-	-	-	-	0.90	nd	0.00	102.37
7	71.47	12.96	-	0.93	1.82	6.96	1.80	<0.01	95.94
14	48.02	22.31	-	-	2.33	16.36	3.59	<0.01	92.61
28	20.37	8.88	0.77	4.22	2.30	38.89	13.06	<0.01	88.49
49	8.65	3.20	-	3.66	1.94	46.09	25.30	<0.01	88.84
70	2.87	2.26	-	3.35	1.74	50.05	25.03	<0.01	85.30
113	1.30	1.05	-	2.53	1.15	50.01	26.64	0.01	82.69
167	2.32	-	-	0.99	1.15	42.99	35.28	0.02	82.75
1.348 mg/kg, 30% FC, 20°C									
0	102.98	0.86	-	-	-	0.76	nd	nd	104.60
7	79.76	9.95	-	-	1.62	3.28	0.65	<0.01	95.25
14	64.24	20.99	-	-	2.28	6.65	0.24	<0.01	94.40
28	38.43	34.10	-	-	3.79	12.88	3.68	<0.01	92.88
49	23.46	31.38	-	3.17	3.79	22.84	8.03	<0.01	92.67
70	14.53	22.82	-	2.50	3.51	35.65	12.84	<0.01	91.85
113	4.93	7.89	-	3.94	2.14	48.40	23.42	0.02	90.74
167	2.52	5.53	-	2.36	1.99	46.08	25.01	0.02	83.25
246	1.05	2.92	-	2.91	1.71	46.75	31.93	0.05	87.32
1.348 mg/kg, 60% FC, 10°C									
0	95.17	-	-	-	-	1.01	0.00	nd	96.18
7	89.08	4.32	-	-	1.10	2.06	0.19	<0.01	96.75
14	83.87	9.80	-	-	1.13	3.24	0.43	<0.01	95.84
28	77.61	17.56	-	-	1.83	6.39	0.34	<0.01	91.09
49	57.62	33.51	2.27	-	2.77	13.43	3.01	<0.01	91.36
70	26.27	20.11	2.28	5.56	2.94	24.70	5.67	<0.01	87.53
113	19.08	14.47	0.86	4.69	2.72	35.83	5.75	0.02	86.18
167	6.95	19.22	0.73	4.14	4.49	38.87	15.45	0.02	89.87
246	10.97	9.48	0.51	4.32	2.65	43.46	12.37	0.02	83.76
422	1.89	1.97	-	4.06	2.34	49.01	23.07	0.02	82.37
0.134 mg/kg, 60% FC, 20°C									
0	101.08	1.87	-	-	-	1.14	nd	nd	104.07
7	48.77	26.06	2.75	-	3.52	15.50	4.28	<0.01	100.88
14	34.22	18.57	-	-	3.00	31.72	7.21	<0.01	94.72
28	16.34	6.35	-	2.45	2.47	48.54	22.58	<0.01	98.73
49	6.75	4.20	-	2.06	2.02	53.79	28.94	<0.01	97.76
70	3.05	0.59	-	3.14	1.79	56.17	32.12	0.01	96.87
113	2.15	0.85	-	2.60	1.45	55.91	38.07	0.13	101.16

Incubation time (days)	Extractable residue					Non-extractable	Volatiles (NaOH)	Volatiles (ethylene glycol)	Total
	Metalaxyl	CGA 62826	CGA 67868	Polar residues	Water extract				
167	3.88	-	-	2.98	2.24	50.15	33.04	0.12	92.95

nd : not detected

Table B.7.1.1.1-14 : Degradation rate of metalaxyl under various temperature and moisture conditions

Application rate (mg a.s./kg soil)	Temperature (°C)	% MWHC	DT <sub>50</sub> (days)	DT <sub>90</sub> (days)
1.348	20	60	14	45
1.348	20	30	26	87
1.348	10	60	43	144
0.134	20	60	7	36

Conclusions :

Under aerobic conditions, metalaxyl is degraded to a major metabolite CGA 62826. Another metabolite CGA 67868 was found at levels < 2.75%. This metabolite was found the most frequently in the test at 10°C. Polar residues were found at levels < 5.56%

The mineralization reaches 23-38% after 113 days at 20°C; The mineralization reaches 5.75 % after 113 days at 10°C.

After 113 days, non extractable residues accounts for 36% and 48-56 % RR at 10 and 20°C respectively.

DT<sub>50</sub> and DT<sub>90</sub> were determined for various temperature and moisture conditions.

CGA 48988: Degradation of the fungicide CGA 48988 in two German standard soils under laboratory conditions. (Ellgehausen, 1977a)

Guidelines :

Not specified

GLP :

no

Material and Methods :

*Test substance :* (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : not specified , specific activity : 0.9 Mbq/mg (24.25 µCi/mg) (specified in the Tier I)

*Soil :*

Table B.7.1.1.1-15 : Characteristics of the soils

Origin of soil:		Neuhofen, Germany	Hatzenbühl Germany
Classification:		Loamy sand	Sandy loam
Particle size distribution:	% silt	7.3	12.4
	% sand	83.8	77.1
	% clay	8.9	10.5
Organic carbon content:	(%)	2.2	1.1
pH:		6.5	4.8

*Test conditions :*

Aerobic incubation of 10 mg a.s./kg soil in the dark at 22°C, 40% MWHC

*Extraction methods :*

Extraction with dichloromethane, methanol:water (8:2)

*Analytical methods :*

Gas chromatography (according to Tier I) no description of the method in the report

Findings :

DT<sub>50</sub> of 5 and 26 weeks were determined

Conclusions :

The quality of the study is very poor. The results are not taken into account in the final evaluation.

Degradation of metalaxyl (CGA 48988) in aerobic soils at a temperature of 15°C. (Guth, 1985a)

Guidelines :

Not specified

GLP :

No

Material and Methods :

*Test substance :* (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : > 99% , specific activity : 1.0 Mbq/mg (27.13 µCi/mg)

*Soil :*

Table B.7.1.1.1-16 : Characteristics of the soils

Origin of soil:		Strassenacker, Switzerland	Collombey, Switzerland
Classification:		Silt loam	Sand
Particle size distribution:	% silt	75	4.3
	% sand	16.3	93.3
	% clay	8.8	2.3
Organic carbon content:	(%)	1.4	0.6
pH:		8.1	7.7
Cation exchange capacity (meq/100g soil):		11.2	5.4
Field capacity (g water/100 g soil):		38.8	13.6
Microbial mass (mg microbial C/100g soil):		200.3	56.3

*Test conditions :*

Aerobic incubation of 10 mg a.s./kg dry soil, in the dark, at 15°C, 70% FC

*Extraction methods :*

Soil: Extraction with methanol:water (8:2) followed by Soxhlet extraction with methanol



Analytical methods :

Methanol/water and soxhlet extracts were pooled and analyzed by liquid scintillation counting (LSC) and thin layer chromatography (TLC).

Total radioactivity in soil prior to extraction was determined by LSC following combustion. (results not reported in the original study)

Findings :

Table B.7.1.1.1-17 : Balance and recovery of radioactivity - aerobic soil metabolism study of metalaxyl at 15°C

Incubation time (days)	Extractable				Non- extractable	<sup>14</sup> CO2	Total
	Metalaxyl	CGA 62826	Metabolite I (unknown)	Polar residues			
Strassenacker silt loam							
0	91.0	-	-	-	12.0	-	103.0
28	53.6	21.7	-	6.4	14.0	1.8	97.5
56	36.4	34.2	-	8.1	17.9	3.0	99.6
84	33.1	34.3	-	8.8	19.0	3.6	98.8
168	22.2	31.8	2.5	7.5	26.2	8.9	99.1
252	12.3	14.4	2.7	14.5	36.7	15.7	96.2
Collombey sand							
0	96.4	-	-	0.2	2.2	-	98.8
28	54.3	18.3	-	7.3	14.4	3.6	97.9
56	29.8	31.2	-	9.7	17.7	5.8	94.2
84	26.2	31.7	-	9.8	19.2	6.0	92.9
168	12.0	29.4	2.0	10.6	32.0	9.6	95.6
252	1.9	9.8	1.0	12.0	44.2	19.5	88.4

Conclusions :

Under aerobic conditions metalaxyl was degraded to a major metabolite CGA 62826 which reached a maximum of 31-34% after 56-84 days. Polar residues were continuously increasing during the incubation period and reach 12-14. % RR at day 252. The mineralization reached 3.6-6.0% after 84 days. At that time 19.0-19.2% RR was recovered as non extractable residue. (DT<sub>50</sub> = 42 and 33 days in silt loam and sand soils, respectively)

Distribution and degradation of CGA 48988 ('Ridomil') in a field soil (Ellgehausen, 1977b)

GLP :

no

Material and Methods :

*Test substance :* (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : not mentioned , specific activity : 4.944 µCi/mg

*Soil :*

Table B.7.1.1.1- 18 : Characteristics of the soil

Origin of soil:		Sisseln, Switzerland
Classification:		Silt loam
Particle size distribution:	% silt	17.3
	% sand	65.8
	% clay	16.9

Organic matter content:	(%)	2.5
pH:		7.5

*Test conditions :*

Application of 4090 g a.s./ha in the field equivalent to 5.6 ppm in the 0-7.5 cm soil layer. Examination of 30 cm soil cores at 33, 54, 81, 103 and 355 days after application.

*Extraction methods :*

Extraction of soil samples with dichloromethane, methanol/water (80/20) followed by Soxhlet extraction with methanol.

*Analytical methods :*

Liquid scintillation counting (LSC), thin layer chromatography (TLC), Liquid Chromatography (LC) high performance liquid chromatography (HPLC), gas chromatography (GC), mass spectrometry (MS), GC-MS, high voltage electrophoresis.

Findings :

Table B.7.1.1.1-19 : % recovery of radioactivity in a field experiment (soil cores)

Incubation time (days)		0 - 7.5 cm	7.5 - 15 cm	15 - 30 cm
0	metalaxyl	98.6	6.0	8.2
33	metalaxyl	16.0	7.0	5.1
	CGA 62826	6.3	3.9	3.8
	polar, non-polar, non extractable residues	5.7	3.2	6.2
54	metalaxyl	7.3	4.4	1.7
	CGA 62826	2.4	2.6	1.4
	polar, non-polar, non extractable residues	9.8	5.3	3.1
81	metalaxyl	4.8	4.1	2.7
	CGA 62826	0.2	1.1	1.0
	polar, non-polar, non extractable residues	8.3	7.0	5.3
103	metalaxyl	3.5	2.1	1.8
	CGA 62826	0.2	0.4	0.5
	polar, non-polar, non extractable residues	9.0	7.5	5.5
355	metalaxyl	0.8	0.4	0.3
	CGA 62826	0.3	0.1	0.1
	polar, non-polar, non extractable residues	3.8	4.1	3.1

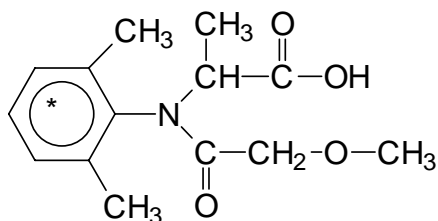
Conclusions :

This experiment performed in the field (soil cores) showed that metalaxyl disappears rapidly from the soil (28% radioactivity as metalaxyl after 33 days). Metalaxyl is found up to a depth of 30 cm.

The main metabolite found in the soil is CGA 62826. This metabolite is found at all the sampling depths. Amounts of other residues are very limited.

*Degradation pathway of the free acid metabolite CGA 62826*

Structural formula of metabolite CGA 62826



Degradation of CGA 62826 in soil under aerobic conditions. (Suter, 1982)

Guidelines : Not specifiedGLP : NoMaterial and Methods :*Test substance* : ( $^{14}\text{C}$ -phenyl ring) labelled metabolite CGA 62826, radiochemical purity : not specified, specific activity : 0.84 Mbq/mg (22.7  $\mu\text{Ci/mg}$ )*Soil* :

Table B.7.1.1.1-20 : Characteristics of the soil

Origin of soil:		Strassenacker, Switzerland
Classification:		Silt loam
Particle size distribution:	% silt	49.1
	% sand	47.0
	% clay	3.9
Organic matter content:	(%)	1.1
Calcium carbonate content:	(%)	10.0
pH:		7.5
Cation exchange capacity (meq/100 g soil)		7.3

*Test conditions* :

aerobic incubation of 10 mg metabolite/kg soil in the dark, at 25°C, 70% FC

*Extraction methods* :

Extraction of soil samples with acetonitrile/water (80/20) followed by Soxhlet extraction with acetone

*Analytical methods* :

Liquid scintillation counting (LSC), high performance liquid chromatography (HPLC) and mass spectrometry (MS).

Findings :

Table B.7.1.1.1-21 : Balance and recovery of radioactivity - aerobic soil metabolism study of metabolite CGA 62826 at 25°C

Incubation time (months)	Extractable				Non-extractable	$^{14}\text{CO}_2$	Total
	CGA 62826	CGA 67868	M 3.5 (unknown)	M 5.5 (unknown)			
0	95.6	-	1.5	-	1.9	-	99.0
0.5	88.5	2.2	1.9	-	6.3	1.8	100.8
1	80.2	5.8	2.4	-	10.4	3.6	102.4
2	64.5	8.4	1.2	-	14.4	6.3	95.0
3	59.1	12.5	2.8	-	17.5	8.3	100.5
6	37.1	15.3	2.8	-	25.8	14.3	95.4
7	24.5	0.5	3.8	0.8	36.0	28.9	94.5
9	15.3	0.2	5.0	1.3	37.1	35.0	93.9

Incubation time (months)	Extractable				Non-extractable	<sup>14</sup> CO <sub>2</sub>	Total
	CGA 62826	CGA 67868	M 3.5 (unknown)	M 5.5 (unknown)			
12	7.3	0.1	2.5	2.1	42.3	41.6	95.9

Conclusions :

The major metabolite of metalaxyl, CGA 62826, is degraded by deamidation to CGA 67868.

The metabolite CGA 67868 reached a maximum of 15% after 6 months.

After 3 months, mineralization accounted for 8.3% RR and increased up to 41.6% at the end of the incubation period.

After 3 months 17.5% RR was recovered as non extractable residue.

DT<sub>50</sub> (CGA 62826) = 102 days

Degradation of CGA 62826 in aerobic soils at a temperature of 15°C. (Guth, 1985b)

Guidelines :

Not specified

GLP :

No

Material and Methods :

*Test substance :* (<sup>14</sup>C-phenyl ring) labelled metabolite CGA 62826, radiochemical purity : 83 %, specific activity : 0.48 Mbq/mg (12.87 µCi/mg)

*Soil :*

Table B.7.1.1.1-22 : Characteristics of the soils

Origin of soil:		Strassenacker, Switzerland	Collombey, Switzerland
Classification:		Silt loam	Sand
Particle size distribution:	% silt	75	4.3
	% sand	16.3	93.3
	% clay	8.8	2.3
Organic carbon content:	(%)	1.4	0.6
pH:		8.1	7.7
Cation exchange capacity (meq/100g soil):		11.2	5.4
Field capacity (g water/100 g soil):		38.8	13.6
Microbial mass (mg microbial C/100g soil):		200.3	56.3

*Test conditions :*

Aerobic incubation of 10 mg a.s./kg dry soil, in the dark, at 15°C, 70% FC

*Extraction methods :*

Soil: Extraction with methanol:water (8:2) followed by Soxhlet extraction with methanol

*Analytical methods :*

Methanol/water and soxhlet extracts were pooled and analyzed by liquid scintillation counting (LSC) and thin layer chromatography (TLC).

Total radioactivity in soil prior to extraction was determined by LSC following combustion. (results not reported in the original study)

Findings :

Table B.7.1.1.1-23 : Balance and recovery of radioactivity - aerobic soil metabolism study of metabolite CGA 62826 at 15°C

Incubation time (days)	Extractable				Non- extractable	<sup>14</sup> CO <sub>2</sub>	Total
	CGA 62826	Metalaxyl (*)	Metabolite I (unknown)	Polar residues			
Strassenacker silt loam							
0	71.7	4.5	2.9	9.4	14.4	-	102.9
28	45.6	6.0	1.7	10.6	26.0	4.8	94.7
56	35.0	3.3	2.7	6.1	36.0	9.2	92.3
84	29.8	3.2	2.2	6.6	43.6	14.3	99.7
168	16.0	1.4	1.3	6.3	50.2	20.2	95.4
238	6.9	-	0.8	11.3	56.9	27.3	103.2
Collombey sand							
0	72.3	4.5	2.7	15.1	7.5	-	102.1
28	48.0	-	7.1	12.0	27.4	4.9	99.4
56	37.2	3.6	3.4	10.9	32.9	8.6	96.6
84	37.1	2.7	3.7	10.0	38.0	10.9	102.4
168	10.0	3.1	7.5	15.3	43.9	17.4	97.2
238	8.6	0.9	0.6	19.3	44.7	20.1	94.2

(\*) : radiolabelled CGA 62826 was prepared by hydrolysis of metalaxyl and contained approx. 5% of the starting material as impurity.

The pattern of the different radioactivity fractions recovered at day 0 shows that 25% of the radioactivity is found as unknown metabolites (M I, polar metabolite, bound residue). It seems therefore that a large part of the CGA 62826 total amount is misidentified.

#### Conclusions :

The quality of this study is not satisfying since the purity of the initial solution is questionable.

*Biological degradation in activated soils*

Several studies and published articles deal with the the biological degradation in activated soil (soils with a history of prior metalaxyl treatment where the microbial populations degraded the a.s. more easily).

These studies showed that the phenomenon of accelerated degradation could exist under some environmental conditions (but not always). These effects were not considered in the final assessment of the behaviour of the a.s.

Rate of degradation of metalaxyl (Ridomil®) in South African and Swiss soils; The influence of soil pretreatments (Guth, 1981)

Guidelines :

Not specified in the report

GLP :

No

Material and Methods :

*Test substance :*

unlabelled metalaxyl, no indication of the purity

*Soil :*

Table B.7.1.1.1-24 : Characteristics of the soils

	Evenrond, South Africa	Stein AG, Switzerland	Strassenacker VS, Switzerland
pH	5.4	7.1	7.5
Organic Matter (%)	2.3	5.0	1.9
Cation exchange capacity (meq/100 g soil)	n.d.	25.0	7.3
Clay content (%)	31	34.6	3.9
Silt content (%)	13	17.4	49.1
Sand content (%)	56	43.0	47.0

*Test conditions :*

South African soil was pre-treated with 2.5 g a.s./m<sup>2</sup>. No other information is given about the pre-treatment (climatic conditions, interval between pre-treatment and collection of the soil sample,...)

Soil samples fortified with 10 mg a.s. /kg were stored in darkness, at 25 ± 1°C, 75% FC in Erlenmeyer flasks closed with cotton wool plugs to allow air exchange.

*Extraction methods :*

Three extractions with methanol:water (8:2) followed by Soxhlet extraction with methanol. Extracts were combined, concentrated and partitioned with dichloromethane and subsequent concentration and clean-up by column chromatography.

*Analytical methods :*

Gas chromatography (GC) with nitrogen-phosphorus (NP) detection

Findings :

Table B.7.1.1.1-25 : Degradation rates of metalaxyl and metalaxyl-M in untreated and pretreated soils

	Evenrond (untreated)	Evenrond (pretreated)	Stein (untreated)	Strassenacker (untreated)
DT <sub>50</sub> (days)	40	21	20	50

Conclusions :

The rate of degradation of metalaxyl could neither be correlated with the total number of micro-organisms nor with the number of fungi, yeasts and actinomycetes.

The only significant observable effect of soil micro-organisms was the almost complete elimination of the yeast population.

The rate of degradation of metalaxyl was increased by a factor of two in the pretreated South African soil (DT<sub>50</sub> = 40 d) compared with the untreated one (DT<sub>50</sub> = 21 d). It was concluded that differences correspond to natural variation from one soil to another (DT<sub>50</sub> of untreated soils = 20, 40, 50 days). The study is inconclusive.

Biodegradation of Metalaxyl in Avocado Soils (Bailey et al., 1985) (published literature)

Using a sensitive bioassay involving *Phytophthora boehmeriae* as the test organism, biodegradation of metalaxyl was compared in five avocado soils that had received repeated applications of the fungicide over a period of 2-5 yr and control soils that had not received the fungicide. Treated soils and control soils were collected in the same groves.

- In 2 of 5 soils with a history of metalaxyl treatment there was much more rapid degradation of the fungicide compared with similar soils that had not received the chemical. The average half-life of metalaxyl in these soils was 28 days, and in the most active soils the half-life was 14 days.

- In 2 of 5 soils, metalaxyl degradation rates were similar in the soils with history of metalaxyl treatment and the untreated soil.

- In one soil, both untreated and 'activated' soils showed rapid degradation of metalaxyl.

In conclusion, this study revealed that in some circumstances, biodegradation of metalaxyl is enhanced by prior treatment of the soil with the compound, while in other cases this phenomenon did not occur.

Characterization of microorganisms involved in accelerated biodegradation of metalaxyl and metolachlor in soils (Bailey et al., 1986) (published literature)

Study investigating the degradation of metalaxyl by a wide range of soil-microorganisms in 'adapted' soil. The article was not taken into account in the monograph.

Transformation of Metalaxyl by the Fungus *Syncephalastrum racemosum* (Zheng, et al., 1988) (published literature)  
The article was not taken into account in the monograph.

Studies of the rates of degradation of metalaxyl in different soils (Il, et al., 1994) (poster presentation on a IUPAC congress - The article was not taken into account in the monograph)

Environmental Behavior of Acetamide Pesticide Stereoisomers. 2. Stereo- and Enantioselective Degradation in Sewage Sludge and Soil (Muller et al., 1995) (published literature)

The degradation of five acetamide pesticides (alachlor, acetochlor, metalaxyl, metolachlor and dimethenamid) with different types of stereoisomerism (axial and/or C-chirality) was studied in soil and sewage sludge using chiral high-resolution gas chromatography/mass spectrometry. Metalaxyl showed different enantioselectivity in the two media with the 1'S-(+)-enantiomer faster degraded in sewage sludge and the fungicidal more active 1'R-(+)-enantiomer (= metalaxyl-M) faster degraded in soil.

#### **B.7.1.1.2 Anaerobic degradation in soil (Annex IIA 7.1.1.1.2)**

See point B.7.1.1.1

**B.7.1.1.3 Soil photolysis (Annex IIA 7.1.1.1.2)**

Photodegradation of  $^{14}\text{C}$ -CGA 329351 on soil under artificial light (Sparrow, 1995)

Guidelines :

US EPA , Subdivision N,161-3

GLP :

Yes

Material and Methods :*Test substance :*

( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl, radiochemical purity : 98.4%, specific activity : 2.7 MBq/mg (= 73.2  $\mu\text{Ci/mg}$ ) and

( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl-M, radiochemical purity : 99.1%, specific activity : 3 MBq/mg (= 81.1  $\mu\text{Ci/mg}$ )

*Soil :*

The Agvise Soil Characterization Report was not included in the dossier

*Test conditions :*

Irradiation: Suntest apparatus: Xenon arc lamp with filter to exclude wavelength < 290 nm.

Test duration: 30 days (12 hrs. irradiation per day)

Sterilisation: The soil was not sterilized

Treatment: 1.5  $\mu\text{g}$  per g soil

Temperature: approx.  $25 \pm 1^\circ\text{C}$

Soil moisture  $6.23 \pm 0.75\%$  (75% of FC at 1/3 bar)

*Extraction methods :*

Extraction of the soil plates by acetonitrile/water (8/2) followed by methanol/water (8/2)

*Analytical methods :*

Liquid scintillation counting (LSC), Thin layer chromatography (TLC), identification by high performance liquid chromatography (HPLC)

Findings :

Table B.7.1.1.3-1 : Balance and radioactivity recovery of the photolysis study of metalaxyl-M (\*)

Incubation time (days)	Extractable					Non-extractable	<sup>14</sup> CO <sub>2</sub>	Total
	Metalaxyl-M	CGA 42447	CGA 37734	CGA 62826	Total extractable			
irradiated samples								
0	92.70	-	-	-	99.10	1.48	-	100.57
30	86.41	0.83	0.01	0.67	99.10	4.11	1.00	103.70
dark samples								
0	93.21	-	-	-	100.06	1.41	-	101.48
30	88.54	-	-	2.23	99.56	2.64	0.06	102.25



Table B.7.1.1.3-2 : Balance and radioactivity recovery of the photolysis study of metalaxyl (\*)

Incubation time (days)	Extractable					Non-extractable	<sup>14</sup> CO <sub>2</sub>	Total
	Metalaxyl	CGA 42447	CGA 37734	CGA 62826	Total extractable			
irradiated samples								
0	89.39	-	-	-	98.16	7.07	-	101.69
30	83.69	0.60	0.27	0.61	94.76	5.79	0.81	101.37
dark samples								
0	91.98	-	-	-	98.18	2.44	-	100.62
30	86.48	0.66	0.34	0.62	99.19	4.03	0.09	103.30

(\*) : % total radioactivity recovered. The figures are the mean of two duplicates. Unknown minor metabolites were not included in these tables. Intermediate incubation time results (3, 7, 14, 21 days) were not included in the monograph because their radioactivity pattern is similar to the last one (after 30 days)

#### Conclusions :

Irradiation resulted in half-life times of 248 days (metalaxyl-M) and 303 days (metalaxyl) which was comparable to the non-irradiated control samples.

Based on the results of this study, it can be concluded that neither metalaxyl-M nor metalaxyl is photodegraded on soil films.

Three other studies performed with metalaxyl were submitted.

Photolysis of CGA-48988 (Ridomil) on soil surfaces under artificial sunlight conditions (Burkhard, 1978)

The study was not taken into consideration in the final evaluation because the exposure duration was too short (3 days)

Soil photolysis of metalaxyl under natural sunlight (Spare, 1988a)

Soil photolysis of metalaxyl by artificial light (Spare, 1988b)

Two additional photolysis studies were performed on a sand loam soil, using either artificial and natural sunlight as radiation source. After an exposure of 14 days, calculations yielded a half-life of 14, respective 16 days for the natural and artificial sunlight. The only photolysis product detected in both experiments was CGA 62826, which was present at 10-15% of the initial dose applied. Results of both studies are contradictory with the results of the metalaxyl/metalaxyl-M study (Sparrow, 1995). Nevertheless, The RMS considers that soil photolysis is not expected to play an important role for the dissipation of the compound. 'This assumption is supported by the fact that the UV-absorption of metalaxyl shows no spectral overlap upon 290 nm, the cut-off region for sunlight (Phaff 1995). However, heterogeneous photolytic reactions in the presence of photo sensitizers such as humic acids might occur to some extent under field conditions.'

### B.7.1.2 Rate of degradation (Annex IIA 7.1.1.2.1; Annex IIIA 9.1.1.1.1)

#### B.7.1.2.1 Aerobic degradation

See point B.7.1.1

#### B.7.1.2.2 Anaerobic degradation

See point B.7.1.1

### **B.7.1.3 Field studies (Annex IIA 7.1.1.2.2; Annex IIIA 9.1.1.2)**

#### **B.7.1.3.1 Soil dissipation testing**

Several field studies were performed with metalaxyl. Summary tables of each individual test are presented in the appendix to this section.

The notifier (Plücken, U. 1997) recalculates dissipation rates for the a.s. and the metabolite CGA 62826 on the basis of the field dissipation studies containing information on the metabolite CGA 62826. The results of this recalculation are presented in the table B.7.3-2 (results between brackets). The original results from the studies are also presented in the same table (without brackets).

#### **B.7.1.3.2 Soil residue testing - soil accumulation testing**

Several field studies were performed with metalaxyl. Summary tables of each individual test are presented in the appendix to this section.

**B.7.2 Adsorption, desorption and mobility in soil (Annex IIA 7.1.2 and 7.1.3; Annex IIIA 9.1.2)****B.7.2.1 Adsorption and desorption of the active substance and relevant metabolites (Annex IIA 7.1.2)**

The adsorption/desorption properties of metalaxyl-M, metalaxyl and metabolite CGA 62826 were determined.

*Adsorption/desorption of metalaxyl-M*

Adsorption/desorption of  $^{14}\text{C}$ -CGA 329351 by the batch equilibrium method on representative agricultural soils (Spare, 1995)

Guidelines :

US EPA guideline, Subdivision N, Series 163-1

GLP :

Yes

Material and Methods :

*Test substance :* ( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl-M, radiochemical purity : 98.8%, specific activity : 3 MBq/mg (= 81.1  $\mu\text{Ci/mg}$ )

*Soils :*

Table B.7.2.1-1 : Characteristics of the soils

Origin of soil:		Mississippi	Maryland	California	Washington	Arizona
Classification		Clay	Sand	Sandy Loam	Loam	Silty Clay Loam
Particle size distribution:	% sand	23	91	65	49	17
	% silt	26	6	30	42	52
	% clay	51	3	5	9	31
Organic matter content (%)		2.3	0.6	0.4	2.6	0.3
Organic carbon content (%)		1.33	0.35	0.23	1.51	0.17
pH:		7.0	5.4	6.3	7.0	7.9
Cation exchange capacity (meq/100 g soil)		37.8	4.1	8.0	22.7	50.4
Bulk density (air dried and sieved (2 mm) soil) (g/ml)		1.20	1.52	1.41	1.14	1.18
Field capacity at 1/3 bar (ml H <sub>2</sub> O/100 g dry soil)		41.8	11.5	18.2	35.0	34.1

*Tests conditions :*

- soil samples (10 g : sand and sandy loam soils, 4 g : loam and silty clay loam soils, 1 g : clay soil) were shaken with 20 ml 0.01 M  $\text{CaCl}_2$  solution at 25°C for 4 hours in the adsorption isotherm determination .

- Dilution series from a stock solution with four different concentrations: 0.0; 0.206; 0.513; 1.028; 5.145 and 10.217 mg a.s./l aqueous 0.01 M  $\text{CaCl}_2$  solution were made.

*Analytical methods :*

A material balance of the test substance recovered in the supernatant and in the soil was performed (98.2 to 101.4 % recovery)

Concentrations in the clear equilibrium supernatants and in the soils after extraction were determined by LSC measurement.

TLC measurements confirmed that metalaxyl-M was stable during the experiment (97.7% RR or greater was quantitated as metalaxyl-M)

Findings :

Table B.7.2.1-2 : Adsorption/desorption constants of metalaxyl-M

		Mississippi	Maryland	California	Washington	Arizona
		Clay	Sand	Sandy Loam	Loam	Silty Clay Loam
Adsorption	k	7.6	0.1	0.2	1.3	2.3
	n	0.69	1.12	1.03	0.957	0.862
	K <sub>oc</sub>	570	20	68	86	1299
Desorption	k	18.4	2.8	1.8	2.9	6.2
	n	0.832	1.009	1.06	1.05	0.963
	K <sub>oc</sub>	1376	790	785	195	3539

Conclusions :

Metalaxyl-M shows a very large range of K<sub>oc</sub> (20-1299). It is classified in a low to very high mobility class, according to Mc Call (1988).

*Adsorption/desorption of metalaxyl*

Adsorption/desorption of  $^{14}\text{C}$ -metalaxyl (Spare, 1987)

Guidelines :

US EPA guideline, Subdivision N, Series 163-1

GLP :

Yes

Material and Methods :

*Test substance :* ( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl, radiochemical purity : 99.1%, specific activity : 0.65 MBq/mg (17.5  $\mu\text{Ci/mg}$ )

*Soils :*

Table B.7.2.1-3 : Characteristics of the soils

Origin of soil:		Maryland	Maryland	Mississippi	California
Classification		Clay	Sand	Loam	Sandy Loam
Particle size distribution:	% sand	25.2	95.6	49.6	74.0
	% silt	32.8	2.2	39.2	19.6
	% clay	42.0	2.2	11.2	6.4
Organic matter content (%)		4.8	0.9	1.2	0.5
Organic carbon content (%)		2.8	0.5	0.7	0.3
pH:		5.9	6.5	7.6	6.5
Cation exchange capacity (meq/100 g soil)		24.3	1.8	8.0	4.7
Bulk density (air dried and sieved (2 mm) soil) (g/ml)		1.21	1.64	1.23	1.51
Field capacity at 1/3 bar (ml H <sub>2</sub> O/100 g dry soil)		35.9	3.8	13.3	6.1

*Tests conditions :*

- 5 g soil samples were shaken with 25 ml 0.01 M  $\text{CaCl}_2$  solution at 25°C for 6 hours in the adsorption isotherm determination .

- Dilution series from a stock solution with four different concentrations: 0.0; 0.21; 0.52; 1.03; 5.13 and 10.16 mg a.s./l aqueous 0.01 M  $\text{CaCl}_2$  solution were made.

*Analytical methods :*

Concentrations in the clear equilibrium supernatants after extraction were determined by LSC measurement.

TLC measurements confirmed that metalaxyl was stable during the experiment (These data were not provided)

Findings :

Table B.7.2.1-4 : Adsorption/desorption constants of metalaxyl

		Maryland	Maryland	Mississippi	California
		clay	sand	loam	sandy loam
Adsorption	k	8.012	0.157	1.401	0.400
	n	0.864	1.257	0.766	1.033
	K <sub>oc</sub>	283.8	29.6	199.8	136.1
Desorption	k	11.346	2.482	2.975	2.064
	n	0.936	1.386	1.070	1.282
	K <sub>oc</sub>	401.9	469.2	421.4	702.0

Conclusions :

Metalaxyl is classified in very high to medium mobility class, according to Mc Call (1988).

Adsorption and desorption of CGA 48988 (RIDOMIL<sup>®</sup>) in various soil types (Guth, 1978a)

Guidelines :

Not specified.

GLP :

No

Material and Methods :

*Test substance* : (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : not specified, specific activity : 1.6 MBq (43.2 µCi/mg)

*Soils :*

Table B.7.2.1-5 : Characteristics of the soils

Origin of soil:		Collombey, VS, Switzerland	Lakeland, Florida, USA	Les Evouettes, VS, Switzerland	Vetroz, VS, Switzerland
Classification		Sand	Sand	Silty Loam	Sandy Loam
Particle size distribution:	% sand	87	96.4	38.4	57.8
	% silt	10.2	2.1	49.4	19.6
	% clay	2.8	1.5	12.2	22.6
Organic matter content (%)		2.2	1.2	3.6	5.6
Organic carbon content (%)		1.3	0.7	2.1	3.3
pH:		7.8	6.3	6.1	6.7
CaCO <sub>3</sub> (%)		11.5	0.1	0	15
Cation exchange capacity (meq/100 g soil)		14.0	3.7	9.0	29.4

*Tests conditions :*

- 25-50 g soil samples were shaken with 100 ml aqueous solution at 20°C for 24 hours in the adsorption isotherm determination .

- Dilution series from a stock solution with four different concentrations: 1.0; 2.5; 5.0 and 10.0 mg a.s./l aqueous solution were made.

*Analytical methods :*

Concentrations in the clear equilibrium supernatants after extraction were determined by LSC measurement.

Findings :

Table B.7.2.1-6 : Adsorption/desorption constants of metalaxyl

		Collombey, VS, Switzerland	Lakeland, Florida, USA	Les Evouettes, VS, Switzerland	Vetroz, VS, Switzerland
		Sand	Sand	Silty Loam	Sandy Loam
Adsorption	k	0.43	0.48	0.87	1.40
	K <sub>om</sub>	20	40	24	25
	K <sub>oc</sub>	33	69	41	42

Conclusions :

This study confirms the very high mobility of metalaxyl.

*Adsorption/desorption of the free acid metabolite CGA 62826*

Adsorption/desorption of  $^{14}\text{C}$ -CGA 62826 by the batch equilibrium method on representative agricultural soils (Spare, 1996)

Guidelines :

US EPA guideline, Subdivision N, Series 163-1

GLP :

Yes

Material and Methods :

*Test substance :* ( $^{14}\text{C}$ -phenyl ring) labelled metabolite CGA 62826, radiochemical purity : 98.2%, specific activity : 40.41  $\mu\text{Ci/mg}$ )

*Soils :*

Table B.7.2.1-7 : Characteristics of the soils

Origin of soil:		Mississippi	Maryland	California	Washington	Arizona
Classification		clay	sand	sandy loam	loam	clay loam
Particle size distribution:	% sand	12	91	63	47	35
	% silt	25	3	29	36	35
	% clay	63	6	8	17	30
Organic matter content (%)		2.1	0.6	1.0	2.2	1.0
Organic carbon content (%)		1.218	0.348	0.580	1.276	0.580
pH:		6.1	5.4	6.9	7.0	7.9
Cation exchange capacity (meq/100 g soil)		38.5	3.4	5.4	19.1	40.6
Bulk density (air dried and sieved (2 mm) soil) (g/ml)		1.08	1.47	1.13	1.05	1.06
Field capacity at 1/3 bar (ml $\text{H}_2\text{O}$ /100 g dry soil)		42.0	5.0	11.8	21.4	26.5

*Tests conditions :*

- 10 g soil samples were shaken with 20 ml 0.01 M  $\text{CaCl}_2$  solution at 25°C for 3 hours in the adsorption isotherm determination .

- Dilution series from a stock solution with four different concentrations: 0.0; 0.204; 0.502; 1.005; 4.966 and 10.077 mg a.s./l aqueous 0.01 M  $\text{CaCl}_2$  solution were made.

*Analytical methods :*

A material balance of the test substance recovered in the supernatant and in the soil was performed (95 to 101 % recovery)

Concentrations in the clear equilibrium supernatants and in the soils after extraction were determined by LSC measurement.

TLC measurements confirmed that metabolite CGA 62826 was stable during the experiment (98.6% RR or greater was quantitated as CGA 62826)



Findings :

Table B.7.2.1-8 : Adsorption/desorption constants of metabolite CGA 62826

		Mississippi	Maryland	California	Washington	Arizona
		clay	sand	sandy loam	loam	clay loam
Adsorption	k	0.9	0.1	0.02	0.1	0.1
	n	1.056	1.078	1.154	1.100	1.077
	K <sub>oc</sub>	72	36	3	8	17
Desorption	k	3.8	1.6	> 1	11.4	> 1
	n	1.031	1.089	-	0.877	-
	K <sub>oc</sub>	311	473	172	895	172

Conclusions :

The metabolite CGA 62826 is classified as highly to very high mobile, according to Mc Call (1988).

Soil Adsorption CGA 62826 (Heinis, 1994a)

Guidelines :

Not specified.

GLP :

No

Material and Methods :

*Test substance* : unlabelled metabolite CGA 62826 , purity 99.6%

*Soil* :

Table B.7.2.1-9 : Characteristics of the soil

Origin of soil:		'Les Evouettes', Switzerland
Classification (USDA):		Loam
Particle size distribution:	% silt	45.6
	% sand	39.5
	% clay	14.9
Organic matter content:	(%)	2.41
Organic carbon content: **)	(%)	1.40
Total nitrogen:	(%)	n.a.
pH:		5.5
CaCO <sub>3</sub> :	(%)	n.a.
Cation exchange capacity:	(meq/100 g soil)	11.6
Bulk density (air dried and sieved (2 mm ) soil)	(g/ml)	n.a.
Maximum water holding capacity (MWC; pF<0.3):	(ml H <sub>2</sub> O/100 g dry soil)	n.a.
Field capacity (FC; pF=2.5):	(ml H <sub>2</sub> O/100 g dry soil)	n.a.

Tests conditions :

- 10 g soil samples were shaken with 25 ml 0.01 M CaCl<sub>2</sub> solution at 22°C for 8 hours in the adsorption isotherm determination .

- Dilution series from a stock solution with four different concentrations: 0.625; 1.25; 2.5; 5 and 10 mg a.s./l aqueous 0.01 M CaCl<sub>2</sub> solution were made.

Analytical methods :

Concentrations in the clear equilibrium supernatants were determined by HPLC.

Findings :

Table B.7.2.1-10 : Adsorption/desorption constants of metabolite CGA 62826

		'Les Evouettes', Switzerland
		Loam
Adsorption	k	0.3
	n	1.099
	K <sub>oc</sub>	22

Conclusions :

The determination of the adsorption constant was performed only for one soil. This study confirms the results of the previous study (Spare, 1995) : The metabolite CGA 62826 is classified in very high mobility class, according to Mc Call (1988).

Additional information from the literature was provided by the notifier.

The adsorption, mobility, and persistence of metalaxyl in soil and aqueous systems (Sharom et al., 1982)

This article deals with the adsorption, the leaching and the degradation properties of metalaxyl. The observations which were made confirm the high mobility of the a.s.

Adsorption of carbofuran, metalaxyl, and simazine: Koc evaluation and relation to soil transport (Sukop et al., 1992)

This article deals with a comparison of adsorption parameters of several pesticides. Koc of 204-3490 were determined for metalaxyl.

**B.7.2.2 Column leaching studies with the active substance and relevant metabolites (Annex IIA 7.1.3.1; Annex IIIA 9.1.2.1)**

Leaching model study with the fungicide CGA-48988 in four standard soils (Guth, 1976a)

Guidelines :

Not specified

GLP : No

Material and Methods :

*Test substance :* (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : not specified, specific activity : 1.6 MBq (43.2 µCi/mg)

*Soil :*

Table B.7.2.2-1 : Characteristics of the soils

Origin of soil:		Collombey, VS, Switzerland	Lakeland, Florida, USA	Les Evouettes, VS, Switzerland	Vetroz, VS, Switzerland
Classification		Sand	Sand	Silty Loam	Sandy Loam
Particle size	% sand	87	99.1	38.4	57.8
distribution:	% silt	10.2	0.5	49.4	19.6
	% clay	2.8	0.4	12.2	22.6
Organic matter content:	(%)	2.2	0.4	3.6	5.6
pH:		7.8	6.6	6.1	6.7
CaCO <sub>3</sub>	(%)	11.5	0	0	15

*Test conditions :*

630 µg a.s. were put on top of the column (length : 30 cm; diameter : 4 cm) and eluted by 251 ml water, equivalent to

200 mm rainfall. Duration of the elution was 2 days.

*Extraction - analytical methods :*

Extraction of the soil samples with acetone in soxhlet; determination by LSC

Findings :

Table B.7.2.2-2 : Vertical distribution of metalaxyl (fresh residue) in columns segments and percolate - Data in % applied radioactivity applied onto the column

Depth of soil layer	Collombey, VS, Switzerland	Lakeland, Florida, USA	Les Evouettes, VS, Switzerland	Vetroz, VS, Switzerland
0 - 2 cm	0.6	1.0	1.4	3.2
2 - 4 cm	0.4	0.4	0.8	5.6
4- 6 cm	0.4	< 0.4	1.0	8.3
6 - 8 cm	0.5	0.4	1.9	17.0
8 - 10 cm	0.5	0.4	2.6	44.5
10 - 12 cm	0.7	< 0.4	2.6	16.5
12 - 14 cm	0.7	< 0.4	6.8	1.1
14 - 16 cm	1.3	< 0.4	4.7	< 0.4
16 - 18 cm	1.5	< 0.4	19.0	< 0.4
18 - 20 cm	2.1	< 0.4	17.7	< 0.4
20 - 22 cm	2.7	< 0.4	17.6	< 0.4
22 - 24 cm	4.0	< 0.4	10.9	< 0.4
24 - 26 cm	5.4	0.5	2.7	< 0.4
26 - 28 cm	7.7	0.5	< 0.4	< 0.4
28 - 30 cm	12.1	0.8	< 0.4	< 0.4
Leachate	57.7	92.0	0.6	< 0.4
Total Percentage Recovered	98.3	96.0	90.3	96.2

Conclusions :

This study confirms the high leaching potential of metalaxyl. Leaching is particularly important in sand soils.

Column leaching of CGA 48988 and CGA 329351 (Heinis, 1994b)

The study is not acceptable. Very poor quality of the test description and the data reporting.

Leaching behaviour of the fungicide CGA 48988 in three German standard soils (Guth, 1976b)

The study is not acceptable. Very poor quality of the test description and the data reporting.

### **B.7.2.3 Aged residue column leaching (Annex IIA 7.1.3.2; Annex IIIA 9.1.2.1)**

Column leaching characteristics of aged <sup>14</sup>C-CGA 329351 in four soil types (Fathulla, 1996b)

Guidelines :

EPA Guidelines (Subdivision N, Section 162-1), (EPA 738-R-93-010)

GLP :

Yes

Material and Methods :

*Test substance :*

*Test substance :*

(<sup>14</sup>C-phenyl ring) labelled metalaxyl-M, radiochemical purity : 99.1 %, specific activity : 3 MBq/mg (= 81.1 µCi/mg), chemical purity : 99.9%

(<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : 98.4 %, specific activity : 2.7 MBq/mg (= 73.2 μCi/mg), chemical purity : 99.2%

*Soils :*

Table B.7.2.3-1 : Characteristics of the soils

Origin of soil:		California	Mississippi	Wisconsin	Arizona
Classification:		sandy loam	loam	sand	silty clay loam
Particle size distribution:	% sand	60	44	91	12
	% silt	32	48	5	58
	% clay	8	8	4	30
FMC (1/3 bar) %		16.4	22.21	7.57	33.39
OC content: (%)		0.65	0.24	0.47	0.88
biomass: (mg C/kg)		144.627	333.829	77.274	103.79
pH:		7.1	7.0	5.6	7.9
CEC (meq/100 g)		5.8	9.3	3.5	44.3

*Test conditions :*

- Soils containing respectively metalaxyl (1.5 and 2.9 mg a.s./kg) and metalaxyl-M (1.5 mg a.s./kg) were aged for 30 days at 25°C and 75% of the field moisture content at 1/3 bar. Active substance and metabolite concentrations were monitored during the aging time. Degradation half-lives were determined.

- Columns were filled with 30.48 cm of fresh soil; 40 g of 'aged' soil at surface, topped with 10 g of fresh soil. The columns (diameter : 5 cm) were eluted by 1030 ml 0.01 M  $\text{CaCl}_2$  solution , equivalent to 508 mm rainfall .

*Extraction - analytical methods :*

Total radioactivity was measured by LSC. The soil layers and leachate were analyzed by HPLC, 2D TLC and LC/MS.

**Findings :**

Table B.7.2.3-2 : Vertical distribution of metalaxyl (aged residue) in columns segments and percolate - Data in % applied radioactivity applied onto the column

[illegible]

<b>Total</b>	95.8	102.8	101.0	93.7	99.3	98.4	100.2	92.8	97.6	97.7	89.8	96.8
<b>Koc (**)</b>	106	67	100	410	348	438	123	139	128	726	874	580

(\*) : The two-dimensional TLC results for the a.s. and the major metabolites are reported in this table.

(\*\*) : based on the volume of water required to leach one-half of the total radioactivity through the soil column.

#### Conclusions :

No significant differences were observed in the leaching potential of metalaxyl-M and metalaxyl . This study confirms the high to medium mobility of the the a.s. (Koc = 100-580) This study confirms the higher mobility of the metabolite CGA 62826 as compared to the a.s. (In the Arizona silty clay loam the metabolite is recovered in the leachate while the a.s. front reached the fourth soil section)

Leaching characteristics of aged <sup>14</sup>CGA-48988 (RIDOMIL) residues in two standard soils (Guth, 1978b)

#### Guidelines :

Not specified

#### GLP :

No

#### Material and Methods :

*Test substance :* (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : not specified, specific activity : 1.6 MBq (43.2 µCi/mg)

#### *Soils :*

Table B.7.2.3-3 : Characteristics of the soils

Origin of soil:		Collombey, VS, Switzerland	Les Evouettes, VS, Switzerland
Classification		Sand	Silty Loam
Particle size distribution:	% sand	87	38.4
	% silt	10.2	49.4
	% clay	2.8	12.2
Organic matter content:	(%)	2.2	3.6
pH:		7.8	6.1
CaCO <sub>3</sub>	(%)	11.5	0

#### *Test conditions :*

- Soils containing respectively 5.6 and 8.4 mg a.s./kg were aged for 30 days at 25°C and +/- 55% relative humidity. After aging 100.3 and 100.7% radioactivity were recovered by LSC. 97.4 and 99.2% radioactivity were extractable by methanol/water (8/2). The identification of the extracted substances was not performed.

- Columns were filled with 28 cm untreated soil and 2 cm aged soil (=252 µg metalaxyl eq/column). The columns (length : 30 cm; diameter : 4 cm) were eluted by 720 ml water, equivalent to 572 mm rainfall . Duration of the elution was 45 days.

#### *Extraction - analytical methods :*

- Soil layers were extracted with methanol:water (8:2) and with methanol alone by Soxhlet extraction.

- Leachate was extracted with acidified dichloromethane. Dichloromethane extracts were then extracted with diethyl ether. Radioactivity associated with extracts was then determined by liquid scintillation counting (LSC). Non-extractable radioactivity was determined by LSC following combustion. Radioactivity in extracts was characterised by thin layer chromatography (TLC).

#### Findings :

Table B.7.2.3-4 : Vertical distribution of metalaxyl (aged residue) in columns segments and percolate - Data in % applied radioactivity applied onto the column

Depth of soil layer	Collombey, VS, Switzerland			Les Evouettes, VS, Switzerland		
	extractable	non extractable	total	extractable	non extractable	total
0 - 2 cm	2.5	1.3	3.8	2.5	2.5	5.0
2 - 4 cm	0.4	0.3	0.7	0.6	1.4	2.0
4 - 6 cm	0.3	0.2	0.5	1.0	0.3	1.3
6 - 8 cm	0.3	0.2	0.5	0.7	0.9	1.6
8 - 10 cm	0.3	0.1	0.4	0.9	0.5	1.4
10 - 12 cm	0.3	0.1	0.4	1.0	0.6	1.6
12 - 14 cm	0.5	0.2	0.7	0.4	0.3	0.7
14 - 16 cm	0.5	0.2	0.7	1.3	0.5	1.8
16 - 18 cm	0.6	0.1	0.7	1.3	0.3	1.6
18 - 20 cm	0.6	0.2	0.8	1.8	0.5	2.3
20 - 22 cm	0.8	0.2	1.0	1.9	0.3	2.2
22 - 24 cm	0.7	0.3	1.0	2.0	0.2	2.2
24 - 26 cm	0.8	0.2	1.0	2.3	0.3	2.6
26 - 28 cm	0.9	0.3	1.2	3.0	0.4	3.4
28 - 30 cm	2.2	0.5	2.7	4.7	0.5	5.2
<u>Total soil layers</u>	11.7	4.4	16.1	25.4	9.5	34.9
<u>Leachate</u>	69.4			43.1		
Metalaxyl	44.5			34.0		
CGA 62826	22.5			7.8		
<b>Total Percentage Recovered</b>	85.5			78.0		

Conclusions :

This aged residue leaching study reveals the high leaching potential of metalaxyl and its main metabolite CGA 62826.

Leaching characteristics of aged residues of  $^{14}\text{C}$ -metalaxyl (RIDOMIL<sup>®</sup>) residues in Speyer soil (Suter, 1985)

Guidelines :

Not specified

GLP :

No

Material and Methods :

*Test substance :* ( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl, radiochemical purity : not specified, specific activity : 1.72 MBq (46.5 $\mu\text{Ci/mg}$ )

*Soil :*

Table B.7.2.3-5 : Characteristics of the soil

Origin of soil:		Speyer 2.1
Classification		Sand
Particle size	% sand	94.5 (>20 $\mu\text{m}$ )
distribution:	% silt	2.8 (2 - 20 $\mu\text{m}$ )

	% clay	2.7 (< 2 µm)
Organic matter content:	(%)	0.86
pH:		6.6

*Test conditions :*

- Soil containing 6.9 mg a.s./kg was aged for 5 months at 25°C and 70% of field capacity. After aging 101.6% radioactivity was recovered by LSC. The radioactivity was identified as 38.6% metalaxyl, 33.2% CGA 62826, 7.0% CGA67868, 8.2% non extractable.

- Columns were filled with 28 cm untreated soil and 2 cm aged soil. The columns (length : 30 cm; diameter : 5 cm) were eluted by 393 ml water, equivalent to 200 mm rainfall . Duration of the elution was 2 days.

*Extraction - analytical methods :*

Soil layers and leachate were extracted with acetonitrile:water (8:2) and with acetone alone by Soxhlet extraction. Radioactivity associated with extracts was then determined by liquid scintillation counting (LSC). Non-extractable radioactivity was determined by LSC following combustion. Radioactivity in extracts was characterised by high performance liquid chromatography (HPLC).

*Findings :*

Table B.7.2.3-6 : Vertical distribution of metalaxyl (aged residue) in columns segments and percolate - Data in % applied radioactivity applied onto the column

	Extractable				Non extractable	Total
	Metalaxyl	CGA 62826	CGA 67868	Sum of Unidentified		
0 - 2 cm	4.98	0.68	0.14	0.07	4.65	10.48
2 - 4 cm	0.60	0.02	0.00	0.01	1.22	1.85
4 - 6 cm	n.d.	n.d.	n.d.	n.d.	0.40	0.62
6 - 8 cm	n.d.	n.d.	n.d.	n.d.	0.16	0.48
8 - 10 cm	n.d.	n.d.	n.d.	n.d.	0.05	0.34
10 - 12 cm	n.d.	n.d.	n.d.	n.d.	< 0.01	0.39
12 - 14 cm	n.d.	n.d.	n.d.	n.d.	< 0.01	0.30
14 - 16 cm	n.d.	n.d.	n.d.	n.d.	< 0.01	0.40
16 - 18 cm	n.d.	n.d.	n.d.	n.d.	< 0.01	0.71
18 - 20 cm	n.d.	n.d.	n.d.	n.d.	< 0.01	0.42
20 - 22 cm	n.d.	n.d.	n.d.	n.d.	< 0.01	0.46
22 - 24 cm	0.98	0.07	0.00	0.01	< 0.01	1.06
24 - 26 cm	3.77	0.37	0.12	0.00	< 0.01	4.25
26 - 28 cm	3.81	0.27	0.15	0.03	< 0.01	4.26
28 - 30 cm	5.38	0.66	0.30	0.03	< 0.01	6.37
Total Percentage Recovered	-	-	-	-	6.43	32.37
Leachate	11.02	45.20	6.34	6.34	-	68.90
Recovery	-	-	-	-	-	101.3

*Conclusions :*

This aged residue leaching study shows the high leaching potential of metalaxyl and the even higher mobility of metabolites CGA62826 and CGA 67868.

**B.7.2.4 Lysimeter and field leaching studies (Annex IIA 7.1.3.3; Annex IIIA 9.1.2.2)**

Degradation and leaching of <sup>14</sup>C-metalaxyl in two sand lysimeters under outdoor conditions after application to potatoes. (Kubiak, 1995a)

*Guidelines :*

BBA Richtlinien Teil IV, 4-3

GLP :

Yes

Material and Methods :

*Test substance* : EC formulation containing 240 g a.s./l. ( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl, radiochemical purity : 97%, specific activity : 2010 kBq/mg

*Soil* :



Table B.7.2.4-1 : Characteristics of the soil

Origin of soil:	Birkenheide, Rhineland Palatinate, Germany.		
Classification:	Sandy soil		
Depth (cm):	0-30	30-60	60-120
Particle size distribution:			
% silt	15.6	15.6	12.5
% sand	80.8	79.8	81.9
% clay	3.6	4.6	5.6
% Organic carbon:	1.0	0.2	0.1

pH of each 10 cm soil layer was measured at the termination of the study. pH were in the range 5.5-6.7 and 6.2-7.3 for lysimeters 19 and 20 respectively.

*Test conditions :*

- The product was applied to both lysimeters (0.8 m<sup>2</sup> surface area and 1.3 m depth) filled with an undisturbed sandy soil monolith.
- A total amount of 26.2 and 28.4 mg a.s. was applied to each of the lysimeters, equivalent to 328 and 355 g a.s./ha.
- The total amounts leachate were 310.3 and 284.5 l for lysimeters 19 and 20 during the first year of the study. They were 632.8 and 604.5 l during the second year of the study.

Table B.7.2.4-2 : Lysimeter study - Experimental design

Total precipitation	
	Potatoes sown in April 92
July 92 - June 93 761 mm (including 339 mm irrigation)	29/06/92 : 80 g a.s./ha (nominal) 14/07/92 : 80 g a.s./ha (nominal)
	27/07/92 : 240 g a.s./ha (nominal)
	- Rape as intermediate crop sown after harvesting potatoes - Winter wheat sown in autumn 92
July 93 - June 94 878.5 mm (including 252.5 mm irrigation)	- Rape as intermediate crop sown after harvesting wheat - Winter barley sown in autumn 93

*Analytical methods :*

Leachates : Total radioactivity and dissolved <sup>14</sup>CO<sub>2</sub> were determined by liquid scintillation counting (LSC). The leachates were acidified, extracted with methanol/water then analysed for metalaxyl, CGA 62826 and CGA 108906 by thin layer chromatography (TLC), high performance liquid chromatography (HPLC) and mass spectroscopy (MS).

Soil : Samples taken from the top 10 cm of soil 91 and 373 days after the first application and the whole soil profile (0 - 130 cm) at the end of the study were analysed for total radioactivity by combustion and LSC. Samples extracted with acetonitrile/water (80:20 v/v) were analysed by TLC and HPLC.

Crop : Total radioactivity in the crops was analysed by combustion and LSC.

Findings :

Table B.7.2.4-3 : Radioactivity recovered in the leachates of the lysimeters - concentrations expressed in µg/l for the total leachate of one year

Period	TRR <sup>1</sup>		metalaxyl		CGA 62826		CGA 108906	
	µg/l <sup>2</sup>	% of applied radioactivity	µg/l <sup>2</sup>	% of applied radioactivity	µg/l <sup>2</sup>	% of applied radioactivity	µg/l <sup>2</sup>	% of applied radioactivity
Lysimeter 19								
1 <sup>st</sup> year of study July 92 - June 93	5.31	6.29	0.05	0.06	4.12	4.88	0.71	0.74
2 <sup>nd</sup> year of study July 93 - June 94	1.62	2.00	0.05	0.06	0.82	1.01	0.52	0.65
Sum of 2 years July 92 - June 94	3.43	8.29	0.05	0.12	2.44	5.89	0.61	1.49
Lysimeter 20								
1 <sup>st</sup> year of study July 92 - June 93	4.23	4.24	0.01	0.01	2.48	2.48	1.11	1.11
2 <sup>nd</sup> year of study July 93 - June 94	1.11	1.25	<0.01	< 0.01	0.25	0.28	0.52	0.5
Sum of 2 years July 92 - June 94	2.58	5.49	<0.01	0.01	1.30	2.76	0.80	1.70

1: TRR = total radioactive residues, determined by LSC measurement of leachate samples. TRR contains all radioactivity associated e.g. with carbonate, a.s., metabolites, water soluble humic matter (-conjugates).

2 : calculated as a.s. equivalents

The leachate concentrations were determined, roughly, twice a month. These series of values give a view of the evolution of the leaching.

- Metalaxyl was recovered in the leachates during the autumn of both sampling years (maximum concentration = 0.36 µg/l).

- The TRR reached a plateau of 8-10.5 µg/l from December 92 to May 93. The RR is mainly metabolite CGA 62826 (7 to 9 µg/l) and metabolite CGA 108906 (1-2 µg/l). No radioactivity is recovered as metalaxyl during this period.

Two soil samplings were performed at days 91 and 373 after the last application.

At the end of the study both lysimeters were dismantled and the radioactivity of the soil layers was determined.

Table B.7.2.4-4 : Radioactivity recovered in the different soil layers of the lysimeters (in % of the total dose applied)

	Lysimeter 19	Lysimeter 20
91 days (0 - 10 cm)	18.82	19.47
373 days (0 - 10 cm)	3.42	6.57
731 days		
0 - 10 cm	2.73	5.09
10 - 20 cm	2.71	5.27
20 - 30 cm	1.87	1.99
30 - 40 cm	1.30	0.84
40 - 50 cm	0.63	0.27
50 - 60 cm	0.70	0.22
60 - 70 cm	0.54	0.18
70 - 80 cm	0.54	0.27
80 - 90 cm	0.52	0.17
90 - 100 cm	0.38	0.18
100 - 110 cm	0.32	0.23
110 - 120 cm	0.37	0.26
120 - 130 cm	0.92	0.50
Total (0 - 130 cm)	13.50	15.49

The radioactivity recovered after 731 days accounts for 13.5-15.49 % of the applied amount. The RR was identified as bound residue.

Conclusions :

A total amount of metalaxyl equivalent to 328-355 g a.s./ha was applied to sand lysimeters.

- Metalaxyl was recovered transiently in the leachates during the autumn of both sampling years (maximum concentration = 0.36 µg/l). This presence of the a.s. should be due to preferential flow through cracks in the soil.
- The radioactivity recovered in the combined leachates of one year was identified as CGA 62826 (0.25 - 4.12 µg/l) and CGA 108906 (0.52-1.12 µg/l)

Degradation and leaching of <sup>14</sup>C-metalaxyl in two sand lysimeters under outdoor conditions after application to vine  
- Results from 1st experimental year (Kubiak, 1995b)

Guidelines :

BBA Richtlinien Teil IV, 4-3

GLP :

Yes

Material and Methods :

*Test substance :* EC formulation containing 240 g a.s./l. (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : 97%, specific activity : 2010 kBq/mg

*Soil :*

Table B.7.2.4-5 : Characteristics of the soil

Origin of soil:	Birkenheide, Rhineland Palatinate, Germany.		
Classification:	Sandy soil		
Depth (cm):	0-30	30-60	60-120
Particle size distribution:			
% silt	15.6	15.6	12.5
% sand	80.8	79.8	81.9
% clay	3.6	4.6	5.6
% Organic carbon:	1.0	0.2	0.1

*Test conditions :*

- The product was applied to both lysimeters (0.8 m<sup>2</sup> surface area and 1.3 m depth) filled with an undisturbed sandy soil monolith.

- A total amount of 29.2 and 26.4 mg a.s. was applied to each of the lysimeters, equivalent to 365 and 330 g a.s./ha
- The results of the second year of the experiment were not provided. No information on the soil recoveries.

Table B.7.2.4-6 : Lysimeter study - Experimental design

Total precipitation	
	one vine in each lysimeter
July 92 - June 93 761 mm (including 339 mm irrigation)	29/06/92 : 80 g a.s./ha (nominal) 14/07/92 : 80 g a.s./ha (nominal) 27/07/92 : 240 g a.s./ha (nominal)

Analytical methods :

Leachate was acidified with 6 N H<sub>2</sub>SO<sub>4</sub> to pH 2 before clean-up with a C<sub>18</sub> cartridge. The cartridge was then desiccated and eluted with methanol. The eluates were then analysed by thin layer chromatography (TLC), high performance liquid chromatography (HPLC) and mass spectroscopy (MS).

Grapes were extracted in acetonitrile:water (8:2) followed by centrifugation before cleanup. same cleanup and determination were used.

Findings :

Table B.7.2.4-7 : Radioactivity recovered in the leachates of the lysimeters - concentrations expressed in µg/l for the total leachate of one year

Period	TRR <sup>1</sup>		metalaxyl		CGA 62826		CGA 108906	
	µg/l <sup>2</sup>	% of applied radioactivity	µg/l <sup>2</sup>	% of applied radioactivity	µg/l <sup>2</sup>	% of applied radioactivity	µg/l <sup>2</sup>	% of applied radioactivity
Lysimeter 15								
1 <sup>st</sup> year of study July 92 - June 93	4.65	3.73	0.01	<0.01	3.86	3.11	0.48	0.38
Lysimeter 16								
1 <sup>st</sup> year of study July 92 - June 93	3.44	3.15	-	-	2.42	2.22	0.76	0.69

1: TRR = total radioactive residues, determined by LSC measurement of leachate samples. TRR contains all radioactivity associated e.g. with carbonate, a.s., metabolites, water soluble humic matter (-conjugates).

2 : calculated as a.s. equivalents

The leachate concentrations were determined, roughly, twice a month. These series of values give a view of the evolution of the leaching.

- Metalaxyl is generally not present in the leachates during whole study (maximum of 0.03-0.05 µg/l found in the leachate of one of the lysimeters at two successive sampling dates).
- The TRR reached a plateau in December 92 and then decreased slowly. The RR is mainly metabolite CGA 62826 (maximum of 6.64 µg/l) and metabolite CGA 108906 (maximum of 1.89 µg/l).

Conclusions :

A total amount of metalaxyl equivalent to 330-365 g a.s./ha was applied to sand lysimeters.

- Metalaxyl is generally not present in the leachates during whole study (maximum of 0.03-0.05 µg/l found in the leachate of one of the lysimeters at two successive sampling dates).
- The radioactivity recovered in the combined leachates of one year was identified as CGA 62826 (2.42-3.86 µg/l)

and CGA 108906 (0.48-0.76 µg/l)

3 field leaching studies were provided.

CGA 48988 - Leaching study report - F30 Aigues-Mortes (Tournayre, 1983a)

CGA 48988 - Leaching study report - F84 Camaret (Tournayre, 1983b)

metalaxyl (CGA 48988) - Determination of residues in groundwater resulting from treatment of vineyards under practical conditions (Bütler, 1982)

Material and methods :

3 leaching studies were realized with metalaxyl formulations. The quality of the reports of both studies of Tournayre; 1983 is poor (experimental conditions and analytical methods are not properly described)

The detection limits of the analytical methods for the 3 studies is higher than the limit of 0.1 µg/l.

Summary tables of the trials are submitted in the appendix to this section.

Table B.7.2.4-8 : Field leaching studies - Characteristics of the soils and main results

Crop	Soil	Groundwater level	Sampling period	Leachate concentrations	References
Barley, 1 application of 0.225 kg a.s./ha	Sand (98.4% sand)	upper level of groundwater 10-40 cm	63 to 411 days after treatment	1 to 2000 µg a.s. /l (LOD not specified)	Tournayre, 1983a
Vine, 1st year : 5 applications corresponding to a total application rate of 1.250 kg a.s./ha 2nd year : 2 applications corresponding to a total application rate of 0.450 kg a.s./ha	Silt loam	upper level of groundwater 10-70 cm	up to 6 months after the last application. (3 years observation)	<4 µg a.s. /l (LOD = 4 µg/l)	Tournayre, 1983b
Vine, 4-5 applications, corresponding to a total application rate of 0.66 to 1.3 kg a.s./ha	Soil with low clay content 0-9%	sampling depth : 200-250 cm	up to 70 days after last application	<1 µg/l to 24.4 µg a.s. /l depending on the sampling points and dates (LOD = 1 µg/l) (some concern about the quality of the analytical method since high concentration was recovered at the first application date; possible preferential flow)	Bütler, 1982

Conclusions :

The quality of the 3 studies is poor (experimental design, analytical methods)

The monitoring of groundwater (depth 10-250 cm ) for 3 different scenarios revealed that the concentrations recovered vary greatly in relation with the nature of soil, the sampling dates...

#### **B.7.2.5 Monitoring data (Annex IIA 7.4)**

2 monitoring studies dealing with the contamination of surface water (Sacramento River, California) and groundwater (existing wells in 3 locations in Florida, North Carolina and Oregon) were submitted. Summary tables of the trials are presented in the appendix to this section.

Data on groundwater monitoring in several European countries, Canada and the United States are also available.

Summary of the metalaxyl surface water monitoring for 1983-1985 (Balu, 1985a)

Material and methods :

- River water samples have been collected twice monthly from the Sacramento River. Samples were taken from the river near the bank where the water was free-flowing. Tap water of river origin was sampled from a residence nearby.

- See summary table in appendix

*Analytical methods :*

The water after filtration and cartridges elution is extracted by ethyl acetate and analyzed by GC. The detection limit of the method was 1 µg/l which was decreased to 0.25 µg/l during the later periods.

Findings and conclusion:

No information is provided on the extent of the use of metalaxyl in the Sacramento basin and on the soil properties of the region. No information is provided on the method of production of the tap water : Purification,...

No residues were observed during the first year of the study.

Metalaxyl residues exhibited transient peaks of 0.97 to 3.5 µg/l on approximately a monthly basis in March through September, 1984, and also in 1985 at levels of 0.25-0.43 µg/l in February through the most recent samplings in July;

No residues were detected in any of the tap water samples.

Ridomil groundwater monitoring study results during 1983-1984 (Balu, 1985b)

Material and methods :

Water samples were collected monthly from wells in three locations - Florida, North Carolina and Oregon. The following criteria were used in the selection of the test sites :

1. High metalaxyl use area.
2. Established wells used for either drinking or irrigation.
3. Near the treatment area (preferably 30-90 m from plot perimeter).
4. Minimum of three wells at each location.

Groundwater samples were collected during the period May 1983 to May 1985 at regular monthly intervals.

See summary in appendix

*Analytical methods :*

The water after filtration is extracted by ethyl acetate and analyzed by GC. The detection limit of the method was 1 µg/l which was decreased to 0.25 µg/l during the later periods. Recoveries were between 61 and 138%

Findings :

Table B.7.2.5-1 : Monitoring of groundwater - Characteristics of the areas and main results

Location	Soil	Crop	Groundwater table	Results
Florida wells	Sandy soil	Citrus  typical treatment rate is 1.12 to 2.24 kg a.s./ha applied at three-month intervals (as ground application as well as for the seebed treatment)	- groundwater table 12.2-15.2 m	residues < 1 µg/l (later < 0.25 µg/l) - Only one sample, sampled on 9/12/84 showed detectable residue of 3.1 µg/l.  Unusually high residues in the range of 29-226 µg/l were found in one well. It was confirmed that the contamination was due to a malfunctionment of the pumping system
North Carolina wells	Gravelly sandy loam	Tobacco  typical treatment rate is 2.24 kg a.s./ha as a single application	- groundwater table 12.2-15.2 m	residues < 1 µg/l (later < 0.25 µg/l)
Oregon wells	Sandy loam and silt loam	Hops  0.56 kg a.s./ha as a single application	- groundwater table 12.2-15.2, 18.3, 36.6-42.6 m	residues < 1 µg/l (later < 0.25 µg/l)

Conclusions :

This monitoring of wells situated in regions where metalaxyl was intensively used showed that the concentrations of a.s. in the groundwater (depth 12.2-15.2 m) were generally below the detection limit (< 1 and later < 0.25 µg/l)

## Metalaxyl in Monitoring Studies (Egli, 1998a)

The following overview covering the literature from 1985 to 1997 was prepared by the notifier. The complete reference list is provided in the overview of Egli.

“Although there are relatively few report to have included metalaxyl in monitoring studies, it is assumed to be comprehensive. Since most of the papers provide overviews of the situation in sometimes overlapping regions, the same detections may have been published repeatedly.

**Europe before 1990** (Fielding *et al.*, 1991)

This review, initiated by COST 64, contains the available data from several European countries. The intention was “to achieve a general picture of the current situation”. In *Germany* 37 pesticides were detected in groundwater; among these, metalaxyl was detected in 3 out of 55 measurements (the number of water sources is reported to be not available). All detections were <0.1 µg/l. No detections are reported from *Italy*, *Denmark*, *United Kingdom*, *Sweden*.

**Europe before 1995** (Carter and Heather, 1995)

Detections of pesticides in groundwater in selected European countries, viz. Austria, Denmark, France, Italy, The Netherlands, Sweden, Switzerland, UK, are listed. The list contains 70 pesticides that have been detected in groundwater. Findings of metalaxyl have been reported for The Netherlands only. No details about frequency or the concentration range are given.



***The Netherlands before 1990 (Hopman et al., 1990)***

The study lists numerous pesticides detected in groundwater, bank water and some surface waters, particularly in the Netherlands but also elsewhere in Europe and in USA. Mention is made of a study concentrating on small surface water bodies: in 1984 residues of up to 12 µg/l metalaxyl were found. No detections of metalaxyl are reported in groundwater. The authors concluded, however, a considerable need for further research into metalaxyl.

***The Netherlands before 1992 (Hopman et al., 1992)***

Despite occasional detections of metalaxyl in the river Rhine, it was never detected in bank water (18 wells close to the river). In groundwater, metalaxyl was occasionally found at 1-3 sites, no further details are presented.

***Sweden 1985-87 (Torstensson, 1990)***

An overview without details is given of the occurrences of pesticides in groundwater and surface water. Besides detections of herbicides, minor findings of other pesticides including metalaxyl are reported for surface water. No metalaxyl occurred, however, in groundwater.

***Switzerland 1988 (Walter et al., 1991)***

In the State of Bern, 300 drinking water supplies were analyzed for a series of pesticides including metalaxyl. In this region, drinking water is almost exclusively produced from groundwater. Unlike some herbicides, metalaxyl could never be detected. The limit of detection was between 0.01 and 0.05 µg/l.

***Germany before 1989 (Schmidt and Zullei-Seibert, 1989; Zullei-Seibert, 1990)***

The paper presents the results of an inquiry among German water supply companies with regard to the results of routine analysis of drinking water, groundwater and surface water. The 300 companies that have routinely analysed the water for pesticides and have participated in the inquiry, produce 55.5% of the drinking water in Germany. In none of the drinking water samples, nor in groundwater, metalaxyl was detected. Only detections in surface water in the states Baden-Württemberg and Nordrhein-Westfalen were reported. No quantitative results are given.

***Germany 1986-1990 (Rogg, 1991)***

The monitoring study by a large water works covers the entire catchment area of an alluvial groundwater aquifer in the Rhine valley in southern Germany that is exploited for the production of drinking water. It includes groundwater and surface water infiltrating into the groundwater. In 9 out of 456 samples (= 2%) of groundwater and surface water, metalaxyl was detected. Concentrations ranged from 0.05 to 0.22 with a mean of 0.10 µg/l. Most of the findings come from surface water (approx. 5% of samples) whereas only 1 or 2 detections (<1%) were made in groundwater. No more quantitative information is given about the proportion of findings in groundwater and in surface water. No detections of metalaxyl were observed in drinking water.

These results may be those reported by Zullei-Seibert, 1990.

***Germany 1991-93 (Amann et al., 1996)***

In a monitoring program in Bavaria, 23 sites were sampled. The selection of the sites was based on the use of pesticides and the situation in the protective area (agricultural intensity, main crops, railways, bank filtration). Metalaxyl was found 3 times in "very low amounts" (no further details are provided).

***Germany 1990-94 (Arbeitskreis "Grundwassergüte", 1997)***

This account about the state of the groundwater in Germany contains sub-chapters from all German States. Metalaxyl results are reported only from the State Baden-Württemberg, where from 1990 until 1994 as much as 2523 groundwater sampling sites were monitored. Metalaxyl was detected at only 13 sites (= 0.5%), of these the concentration exceeded 0.1 µg/l at only 7 sites. From the other States no detections of metalaxyl are reported; however, no information whether or not metalaxyl was looked for, was included in this report.

*Poland 1993-94 (Dabrowski et al. 1996)*

In this paper, a progress report on an ongoing investigation of the groundwater situation in Posnania is presented. The sampling from 24 wells took place monthly from May 1993 until October 1994. Of 50 pesticides looked for, 26 were detected. Metalaxyl was found only in 3 times out of 225 samples at concentrations of 0.08 - 0.09 µg/l.

*England and Wales 1992-94 (Anonymous, 1996)*

The report contains the results of surface and ground water monitoring studies in 1992, 1993, and 1994 in England and Wales. Metalaxyl exceeding 0.1 µg/l was detected in surface water in 1993 (4 out of 197 samples) and 1994 (1 out of 168 samples). In groundwater, metalaxyl was monitored in 1993 only; it could not be detected in all 25 samples analyzed.

***Further data***

In addition to these published data, a series of analytical results of metalaxyl in German well water may be mentioned here that has been generated by the then Ciba-Geigy Ltd in the years 1986-87 (Giannone and Formica, 1988). Samples were taken in July, August and September at 22 sites in the wine-producing State of Rheinland-Pfalz. No residues were found of metalaxyl nor of the acid metabolite (<0.05 µg/l)

. Although this early monitoring study does not suffice modern requirements (no sampling protocol was recorded), the results demonstrate that there were no reasons for concerns.

Moreover, there are many overview articles which do not contain any information about metalaxyl detections, without mentioning, however, whether metalaxyl has been looked for and not detected, or whether and why it has not been included into the monitoring at all. The overview of the European situation by the French Ministry of Agriculture and Fishery (Dabène and Marié, 1993) or the comprehensive report with a similar objective by Isenbeck-Schröter et al. 1997 are examples of such studies."

Conclusions

Detailed evaluation of these data on metalaxyl should be performed at Member State level in order to assess whether the proposed uses of metalaxyl-M would lead to unacceptable water contamination in the future.

"In the studies that did include metalaxyl, no or only few detections of this compound were made. Where quantitatively reported, the concentrations found were <0.1 µg/l. On the whole, the conclusion can be drawn that the uses of metalaxyl over the past 20 years have not led to more than occasional detections of metalaxyl in groundwater. Hardly ever did residues exceed 0.1 µg/l."

'Risk assessment example for Schmollenberg conference : Metalaxyl (Behl, 1995)

In January, 1995, the US EPA issued a Reregistration Eligibility Document (RED) for metalaxyl. The document presents the US EPA's evaluation of the database for the a.s., conclusions on the potential human health and environmental risks of the current product uses, and the conditions under which these uses and products will be eligible for reregistration. Information on water monitoring performed in the USA and Canada are summarized in the table herbelow.

Table B.7.2.5-2 : Ground water monitoring data from USA and Canada

Crop	Study	Wells with Detections/Wells Sampled	Sample Concentration (ppb)	Study Quality
United States of America				
Citrus	1980 Florida	0/3	N.D.	poor
	1983-85 Florida	2/4	3.1 - 4.7	marginal
	Ongoing Florida (1995)	5/495 wells with detection	0.6 - 1.5 in deeper aquifer 6.8-33 in shallow surficial aquifer	good- excellent
Tobacco	1981 Maryland	1/6	1.2 - 2.1	poor
	1986-88 North Carolina, Tennessee	5/12 (4 North Carolina; 1 Tennessee)	0.27 - 3.0	poor-good
Canada				
Potatoes	1994-95 New Brunswick	8/22	0.1 - 1.1	good
	1994-95 Prince Edward Island	2/20	0.07 - 0.25	good
	1994-95 Piezometer Study Prince Edward Island	ELISA : 45/99  GC/MS confirmation 22/99  (difference attributed to method sensitivity)	0.1 - 0.65 --ELISA  0.04 - 1.4 --GC	good
	1994-95 Tile Drainage Study Prince Edward Island		1.1 - 4.7 -- drains; first event post- application  0.1 - 0.3 -- drains; 10 months post-application  1.6 - 4.5 -- runoff	good

#### Conclusions :

Data from the United States were collected in areas with very high application rates of metalaxyl which are not representative of the intended uses of metalaxyl-M.

The original study concerning the monitoring in Canada is briefly described herebelow

Metalaxyl Ground Water Study - 1994-95 (Environment Canada Atlantic Region)

Study already mentioned in the review of Behl (1995)

The leaching and ground water contamination potential of metalaxyl was studied using 3 approaches : 1- sampling domestic wells situated on or near potato farms where the pesticide is used, 2 - by sampling piezometer wells, located within potato fields with metalaxyl history, 3- by sampling surface and sub-surface drainage water from a tiled commercial potato field during precipitation events. The study was located in New Brunswick and Prince Edward Island ( Canada).

Well depths were ranging from 10 to 40 m. Soils were predominantly sandy loam, but also include loamy sands, loam and clay loams. Mean precipitations were 1050-1150 mm/year, mean monthly temperatures from -6.8 in February to 19.1 °C in July. The metalaxyl application rate in potato is not well defined in the study.

The notifier comments this study extensively in 'comments on Canadian metalaxyl water monitoring report' (Egli et al., 1998b)

#### Findings :

All the metalaxyl concentrations considered below should be regarded as meaning "metalaxyl + CGA 62826 as metalaxyl".

*1- Wells :* Metalaxyl was consistently detected over the 10 month sampling period, both by immunoassay and by GC-MS, in 8 of the 22 New Brunswick wells and in 2 of the 21 Prince Edward Island wells. The concentrations ranged from 0.1 to 168 µg/L. However, excluding instances where well contamination could be attributed to accidental releases, concentrations did not exceed 1.1 µg/L.

*2 - Piezometers :* Metalaxyl was detected by immunoassay in 45 of the 99 piezometer water samples at concentrations ranging from 0.1 to 0.65 µg/L. The concentrations detected by GC-MS ranged from trace amounts of 0.04 up to 1.4 µg/L.

*3 - Tile drainage water :* Metalaxyl concentrations in tile drainage water were highest in samples from the first post-application rain event (1.1 - 4.7 µg/L, November 1994). Samples taken in May of 1995, about 10 months after application, showed concentrations of 0.1 to 0.3 µg/L. Likewise, concentrations in surface runoff were highest in samples from the first post-application rain event (1.6 - 4.5 µg/L, November 1994) but declined sharply afterwards.

#### Conclusions :

The concentrations of metalaxyl + its metabolite CGA62826 found in this study are generally in accordance with data found in the lysimeter. However the study does not allow to distinguish between the a.s. and other metabolites with the same moiety.

### B.7.3 Summary of behaviour in soil and predicted environmental concentration in soil (PECs) Annex IIIA 9.1.3)

#### *Route of degradation*

Under aerobic conditions, the main degradation proceeds via ester cleavage yielding the free acid metabolite CGA 62826. The metabolite was found in all the soil metabolism studies at high levels (maximum 22, 26.23, 40.36 % RR in Ellgehausen, 1996).

The degradation of CGA 62826 further proceeds with the formation of metabolite CGA 67868 and polar residues. The metabolite CGA 67868 was found in several studies at low levels (max 2.28-2.75, 3.72-6.15 % RR in Ellgehausen, 1996 and Schanné, 1991). It was also the main degradate recovered in the metabolism studies performed with CGA 62826 (Suter, 1982).

Several minor metabolites were also detected.

- Beside the a.s. and the major metabolites also found in the other soil studies, several minor metabolites were detected in the rotational crop study (CGA 108905, CGA 108906, CGA 107955, CGA 37734, CGA 79353, CGA 78532). The objective of the study (Mac Farland, 1992, described under point B.6) was to investigate the uptake and metabolism of metalaxyl in several rotational crops grown in the greenhouse following a target crop of tobacco. The tobacco was grown in soil treated with 3.36 kg a.s./ha preemergent application.
- The metabolite CGA 42447 was found at very low level (0.5% RR) in a soil metabolism study (Elgehausen, 1978).
- Some polar compounds were found in different studies at very low amounts, and therefore not further characterized.

The final degradation occurred via mineralization and formation of bound residues. Mineralization reached 22-33% RR after 84 days. At that time 63-73% RR was recovered as unextractable (Ellgehausen, 1996)

A study evaluating the degradation of metalaxyl under anaerobic and sterile conditions was provided. This study, although of poor quality, showed that degradation is low under anaerobic conditions. Under sterile conditions no degradation occurred indicating that the a.s. degradation is mainly biotic.

A study of good quality evaluating the photolysis of metalaxyl-M and metalaxyl in parallel showed that both compounds are photolytically stable ( $DT_{50}$  = 248 and 303 days respectively for metalaxyl-M and metalaxyl).

Some additional information was provided on the possible adaptation of the soil microflora leading to an accelerated degradation on soils repeatedly treated with the a.s. This phenomenon of adaptation is not observed in all the soil conditions.

#### *Laboratory degradation*

Several studies were realized under different conditions with metalaxyl and metalaxyl-M. (Table B.7.3-1)

- The comparison of the 4 studies where the degradation of metalaxyl-M and metalaxyl were followed in parallel reveal that the degradation of both compounds are similar :

		median
$DT_{50}$ metalaxyl-M	3.9, 8.13, 73.5, 167.9	40.8 d
$DT_{50}$ metalaxyl	10.8, 13.97, 58.4, 123.4	36.2 d

The notifier argues that metalaxyl-M degraded more rapidly than the racemate metalaxyl particularly under environmental conditions enhancing the biological processes. The notifier proposes therefore to apply a correction factor of 1.4 for the extrapolation from metalaxyl to metalaxyl-M. Under conditions of low biological activity, abiotic chemical processes would be involved, leading to slower, not enantiospecific processes. (Ellgehausen, 1998)

The RMS did not follow this statement and considers that degradation rates of metalaxyl should be extrapolated to metalaxyl-M without conversion factor because the examination of studies realized in parallel with both a.s. did not lead to the unequivocal conclusion of a more rapid degradation of metalaxyl-M.

The metalaxyl values were used to extrapolate to metalaxyl-M since numerous data at several temperatures are available for the racemate.

The values of the California sandy loam study ( $DT_{50} = 167.9, 123.4$ ) were not taken into account in the determination of the typical  $DT_{50}$  because the goal of this study was the identification of the metabolic pathway with less emphasis on the degradation rate.

		median
$DT_{50}$ metalaxyl, 20-25°C	7, 10.8, 13.97, 14, 20, 40, 40, 50, 58.4	<b>20 d</b>
$DT_{50}$ metalaxyl, 15°C	33, 42	38 d
$DT_{50}$ metalaxyl, 10°C	43	43 d
$DT_{90}$ metalaxyl, 20-25°C	35.7, 36, 45, 46.4, 140	45 d
$DT_{50}$ CGA 62826, 20°C	4.2, 5.3, 14.9, 25.3, 102, nd	14.9 d
$DT_{50}$ CGA 62826, 10°C	62.1	62 d

#### *Field dissipation*

The notifier recalculates dissipation rates for the a.s. and the metabolite CGA 62826 on the basis of the field dissipation studies containing information on the metabolite CGA 62826. The results of this recalculation are presented in the table B.7.3-2 (results between brackets). The original results from the studies are also presented in the same table (without brackets). The median of the original a.s. data and the recalculated data are similar :  $DT_{50} = 36$ ,  $DT_{90} = 157$ .

The examination of individual results shown below reveal that the median is a good approximation of the realistic worst case for the  $DT_{50}$  and  $DT_{90}$  field for metalaxyl as well as for metalaxyl-M.

		median
$DT_{50}$ metalaxyl, field	39.4, 20.4, 19.5, 86.9, 38.8, 38.5	<b>38.7 d</b>
$DT_{90}$ metalaxyl, field	132, 67.8, 64.7, 288.7, 128.8, 127.8	128.3 d
$DT_{50}$ CGA 62826, field	nd, nd, 10.4, 36.4, 27.9, 36.4	31.2 d

Residue testing studies were performed with metalaxyl at an application rate (200-250 g/ha) and a number of applications (3-13) slightly higher than the major intended uses (110-150 g/ha; 2-5 applications). These studies show that the maximum concentrations are found in the top soil just after application. The a.s. degraded rapidly between the applications. Soil concentrations did not increase with the number of applications. The maximum concentrations observed just after the applications were in the range 0.13- 0.20 - 0.44 mg a.s./kg soil. (Table B.7.3-3).

#### *Adsorption/desorption*

Several adsorption/desorption studies were performed (Table B.7.3-4).

Metalaxyl-M is classified in the low to very high mobility classes :  $K_{oc} = 20-1299$

Metalaxyl is classified in the medium medium to very high mobility classes :  $K_{oc} = 29-283.8$

The major metabolite CGA 62826 is classified in the high to very high mobility classes :  $K_{oc} = 3-72$

The wide  $K_{oc}$  ranges could indicate different adsorption behaviours in function of the soil types (clay or sand).

### *Column leaching*

The columns leaching studies confirm the adsorption/desorption results. They indicate the high mobility of both metalaxyl-M and metalaxyl. The mobility of the metabolite CGA 62826 is even higher. (Table B.7.3-5)

### *Lysimeter studies*

2 lysimeter studies were performed with metalaxyl. Metalaxyl was applied at the rate of 330-365 g a.s./ha/season on 4 sandy soil monoliths. Crops were potatoes and vines. Metalaxyl was recovered in the combined leachate of one year at concentrations of <0.01 to 0.05 µg/l. The metabolite CGA 62826 was recovered at the concentration of 0.25-4.12 µg/l. The metabolite CGA 108906 was recovered at the concentration of 0.16-1.11 µg/l. (Table B.7.3-6)

### *Field leaching data*

3 field leaching studies were submitted. The quality of the studies is questionable and no real conclusion can be taken from these data. Leachate concentrations of <1 to 2000 µg a.s./l were recovered. (Table B.7.3-7)

Drain water concentrations were measured in two studies of dissipation. (Table B.7.3-2) Drain systems were at 0.8 and 1.2 m depth. Water concentrations were generally measured after heavy rainfall. The maximum concentrations were 17-87 µg a.s./l. Levels of CGA 62826 in the range <10-32 µg/l were measured in one of the studies

### *Groundwater monitoring*

Data on groundwater monitoring in several European countries, Canada and the United States are also available. Detailed evaluation of these data on metalaxyl should be performed at Member State level in order to assess whether the proposed uses of metalaxyl-M would lead to unacceptable water contamination in the future.

“In the studies performed in Europe that did include metalaxyl, no or only few detections of this compound were made. Where quantitatively reported, the concentrations found were <0.1 µg/l. On the whole, the conclusion can be drawn that the uses of metalaxyl over the past 20 years have not led to more than occasional detections of metalaxyl in groundwater. Hardly ever did residues exceed 0.1 µg/l.”

Data from USA and Canada show that metalaxyl is detected in a limited number of wells at levels >0.1 µg/l. These data reveal that applications at high rates are susceptible to contaminate groundwater.

Figure B.7.3-1 : Proposed metabolic pathway of metalaxyl-M (CGA 329351)

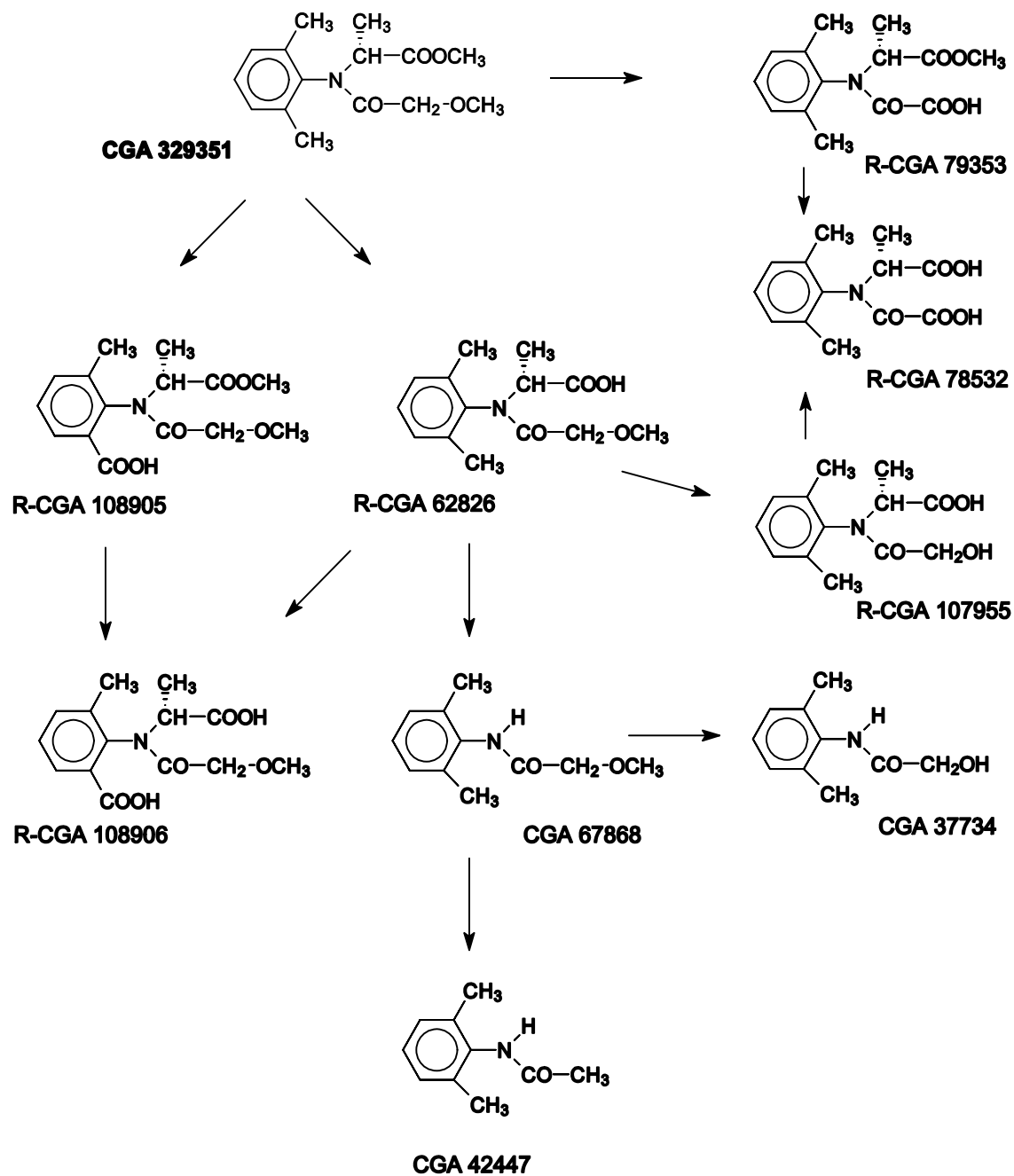




Table B.7.3-1 : Summary of behaviour in soil - laboratory degradation of metalaxyl-M and metalaxyl

Test soil				Test system	Results			References
Soil type	Soil pH <sub>(KCl)</sub>	CEC	OC (%)		metalaxyl-M DT <sub>50</sub> DT <sub>90</sub> (in days)	metalaxyl DT <sub>50</sub> DT <sub>90</sub> (in days)	CGA 62826 DT <sub>50</sub> (in days)	
Sandy loam (California)	7.0	7.0	0.46	aerobic, 25°C, 75% FMC	73.5	58.4		Fathulla, 1996a
Sandy loam (Gartenacker)	7.25	8.6	2.2	aerobic, 20°C, 40% MWHC	4.0-5.7 13.2-18.9		(4.2-14.9)	Ellgehausen, 1996
Sandy loam (California)	7.2	7.8	0.5	aerobic, 20°C, 75% FC	167.9 635.8	123.4 499.5	(131.5-133.6)	
Silt loam (Les Evouettes)	7.3	14.0	2.1	aerobic, 20°C, 40% MWHC	3.9 13.0	10.8 35.7		Ellgehausen, 1994
Sand (Collombey)	7.4	11.9	1.6	aerobic, 20°C, 40% MWHC	8.13 27.02	13.97 46.4		Ellgehausen, 1995
Loamy sand (Neuhofen)	6.5	11.3	2.2	aerobic, 25°C, 75% MWHC		~ 40 140		Ellgehausen, 1978
Silt loam (Les Evouettes)	6.1	15.5	1.4	Aerobic 20°C, 60% MWHC		7- 14 36-45	(5.3 - nd)	Schanné, 1991
				20°C, 30% MWHC		26 87	(25.3)	
				10°C, 60% MWHC		43 144	(62.1)	
Silt loam (Strassenacker)	8.1	11.2	1.4	aerobic, 15°C, 70% FC		42		Guth, 1985
Sand (Collombey)	7.7	5.4	0.6	aerobic, 15°C, 70% FC		33		
Silt loam (Strassenacker)	7.5	7.3	0.64	aerobic, 25°C, 75% FC			102	Suter, 1982
Sandy clay loam (Evenrond)	5.4	-	1.3	aerobic, 25°C, 75% FC		40-21 (untreated and pretreated)		Guth, 1981
Sandy clay loam (Stein)	7.1	25.0	2.9			20		
Sandy loam (Strassenacker)	7.5	7.3	1.1			50		
Soil	-	-	-	photolysis of metalaxyl-M and metalaxyl at 25°C	248	303	-	Sparrow, 1995

(\*) The notifier recalculates degradation rates for the a.s. and the metabolite CGA 62826 on the basis of the degradation studies containing information on the metabolite CGA 62826. The results of this recalculation are

presented between brackets. (Egli et al., 1997)

Table B.7.3-2 : Summary of behaviour in soil - Metalaxyl field dissipation studies

Test soil				Test system : - appl. rate - n° of appl. - crop	Results			Ref
- Soil type - Location	Soil pH <sub>(KCl)</sub>	CEC	Organic Carbon content (%)		metalaxyl		CGA 62826	
					DT <sub>50</sub>	DT <sub>90</sub>	DT <sub>50</sub>	
- loamy sand (Ger)  - Altrajensdorf Schlewig-Holstein (Germany)	6.0	-	1.41	- 2000 g a.s./ha - 1appl. - bare ground	18  (39.4)	196  (132)	  (-)	1
- loamy sand (Ger)  - Lorsch-Wahlig Rheinhessen (Germany)	6.2	-	1.05	- 2000 g a.s./ha - 1appl. - bare ground	11  (20.4)	118  (67.8)	  (-)	2
- clayey silt (Ger)  - Plattling-See Lower Bavaria (Germany)	6.8	-	1.35	- 2000 g a.s./ha - 1appl. - bare ground	23  (19.5)	76  (64.7)	  (10.4)	3
- Silty clay loam (Ger)  - Keeken Lower Rhine (Germany)	6.1	-	4.4	- 2000 g a.s./ha - 1appl. - bare ground	79  (86.9)	263  (288.7)	  (36.4)	4
- Silt loam (USDA)  - Les Barges (Switzerland)	7.7	-	4.29	- 2000 g a.s./ha - 1appl. - bare ground - drainage system at 1.2 m depth. LOD = 10 µg/l	No accurate DT <sub>50</sub> calculation was possible  < 10 to 17 µg a.s. /l in drain water < 10 µg CGA 62826 /l in drain water			5
- Sandy loam (USDA)  St Aubain (Switzerland)	8.1	-	1.45	-2000 g a.s./ha - 1 appl. - bare ground - drainage system at 0.8 m depth. LOD = 10 µg/l	No accurate DT <sub>50</sub> calculation was possible  < 10 to 87 µg a.s. /l in drain water < 10 to 32 µg CGA 62826 /l in drain water			6
- Sandy loam (USDA)  Madera (California)	6.3	4.4	0.52	-3360 g a.s./ha - 1 appl. - bare ground	36  (38.8)	  (128.8)	  (27.9)	7
				-3360 g a.s./ha - 1 appl. on sowing - tomatoes were sown on the field.	27  (38.5)	  (127.8)	  (34.6)	8

Test soil				Test system : - appl. rate - n° of appl. - crop	Results			Ref
- Soil type - Location	Soil pH <sub>(KCl)</sub>	CEC	Organic Carbon content (%)		metalaxyl		CGA 62826	
					DT <sub>50</sub>	DT <sub>90</sub>	DT <sub>50</sub>	
- Loam (USDA)  Hollandale (Minnesota)	7.9	17.1	2.1	-3360 g a.s./ha - 1 appl. - bare ground	113	-	-	9
- Loamy sand (USDA)  Maxton (North Carolina)	5.4	1.5	0.46	- 4800 g a.s./ha - 1 appl. - tobacco plot	39.1	-	142	11
				- 4800 g a.s./ha - 1 appl. - bare ground	38.3	-	128	

(\*) The notifier recalculates dissipation rates for the a.s. and the metabolite CGA 62826 on the basis of the field dissipation studies containing information on the metabolite CGA 62826. The results of this recalculation are presented between brackets. (Egli et al., 1997)

Table B.7.3-3 : Summary of behaviour in soil - Soil residue testing, soil accumulation testing with metalaxyl

Test soil				Test system : - appl. rate - n° of appl. - crop	Results		Ref
- Soil type - Location	Soil pH <sub>(KCl)</sub>	CEC	Organic Carbon content (%)		metalaxyl	CGA 62826	
- Loam (USDA)  Plattsville Ontario, Canada	6.9	9.1	1.16	- 200 g a.s./ha - 3 appl. - bare ground	max = 0.18 mg/kg (after last application)  DT <sub>50</sub> ~ 40d	max = 0.06 mg/kg	12
- Silt loam (USDA)  Milverton Ontario, Canada	7.3	30.1	2.55	- 200 g a.s./ha - 3 appl. - bare ground	max = 0.23 mg/kg (after last application)  DT <sub>50</sub> ~ 40d	max = 0.06 mg/kg	13
- Luvisol  Fredericton, New Brunswick, Canada	-	-	-	- 200 g a.s./ha - 3 appl. - bare ground	max = 0.21 mg/kg 'Accumulation' between applications	max = 0.09 mg/kg	14
Sandy loam (USDA) Truro, Nova Scotia, Canada	5.9	-	3.48	- 200 g a.s./ha - 3 appl. - bare ground	max = 0.13 mg/kg (after last application)	max = 0.03 mg/kg	15
- Silt loam (USDA)  - Les Barges (Switzerland)	7.7	-	4.29	- 250 g a.s./ha - 5 appl. - bare ground	max = 0.20 mg/kg (21 d after last application)  (Bad quality)	-	18
- Silt loam (USDA)  - Les Barges (Switzerland)	7.7	-	4.29	- 250 g a.s./ha - 5 appl. - bare ground	max = 0.20 mg/kg (22 d after last application)  (Bad quality)	-	19
- Loamy sand (USDA) Ottersum The Netherlands	5.4	-	0.52	- 200 g a.s./ha -13 appl. - potato plot - first sampling occurs after last application.	> 0.44 to 0.27 mg a.s./kg in top soil (from d 0 to d 60)  < 0.02 at d 90	not measure d	21
- 'Sea clay' Klaaswaal The Netherlands	7.9	-	1.8	- 200 g a.s./ha -13 appl. - potato plot - first sampling occurs after last application.	0.31 to 0.33 mg a.s./kg in top soil (from d 0 to d 14)  0.05 to 0.03 mg/kg in top soil (from d 28 to d 120)	Not measure d	21

Table B.7.3-4 : Summary of behaviour in soil - Koc of metalaxyl-M and metalaxyl

Test soil				Test system	Results	References
Soil type	Soil pH <sub>(KCl)</sub>	CEC	OC (%)		Koc	
Clay	7.0	37.8	1.33	metalaxyl-M	570	Spare, 1995
Sand	5.4	4.1	0.35		20	
Sandy loam	6.3	8.0	0.23		68	
Loam	7.0	22.7	1.51		86	
Silty clay loam	7.9	50.4	0.17		1299	
Clay	5.9	24.3	2.8	metalaxyl	283.8	Spare, 1987
Sand	6.5	1.8	0.5		29.6	
Loam	7.6	8.0	0.7		199.8	
Sandy loam	6.5	4.7	0.3		136.1	
Sand	7.8	14.0	1.3	metalaxyl (Bad quality)	33	Guth, 1978
Sand	6.3	3.7	0.7		69	
Silty loam	6.1	9.0	2.1		41	
Sandy loam	6.7	29.4	3.3		42	
Clay	6.1	38.5	1.22	CGA 62826	72	Spare, 1995
Sand	5.4	3.4	0.35		36	
Sandy loam	6.9	5.4	0.58		3	
Loam	7.0	19.1	1.28		8	
Clay loam	7.9	40.6	0.58		17	
Loam	5.5	11.6	1.40	CGA 62826	22	Heinis, 1994

Table B.7.3-5 : Summary of behaviour in soil - Column leaching of metalaxyl-M and metalaxyl

Test soil				Test system	Results	References
Soil type	Soil pH <sub>(KCl)</sub>	CEC	OC (%)			
Sand	7.8	-	1.28	metalaxyl 30 cm length, 2 days elution equivalent to 200 mm rainfall	57.7% RR in the leachate	Guth , 1976
Sand	6.6	-	0.30		92.0% RR in the leachate	
Silty loam	6.1	-	2.09		50% depth : 20cm 0.6% RR in the leachate	
Sandy loam	6.7	-	3.25		50% depth : 10cm < 0.4% RR in the leachate	
Sandy loam	7.1	5.8	0.65	metalaxyl-M (aged residue) 30 cm length, elution	Koc = 100	Fathulla, 1996
Loam	7.0	9.3	0.24		Koc = 438	
Sand	5.6	3.5	0.47		Koc = 128	

Test soil				Test system	Results	References
Soil type	Soil pH <sub>(KCl)</sub>	CEC	OC (%)			
Silty clay loam	7.9	44.3	0.88	equivalent to 508 mm rainfall	Koc = 580	
Sandy loam	7.1	5.8	0.65	metalaxyl (aged residue) 30 cm length, elution equivalent to 508 mm rainfall	Koc = 67-106	
Loam	7.0	9.3	0.24		Koc = 348-410	
Sand	5.6	3.5	0.47		Koc = 123-139	
Silty clay loam	7.9	44.3	0.88		Koc = 726-874	
Sand	7.8	-	1.28	metalaxyl (aged residue) 30 cm length, 45 days elution equivalent to 572 mm rainfall	69.4 % RR in the leachate as metalaxyl and CGA 62826	Guth, 1978
Silty loam	6.1	-	1.91		43.1 % RR in the leachate as metalaxyl and CGA 62826	
Sand (Speyer 2.1)	6.6	-	0.50	metalaxyl (aged residue) 30 cm length, 2 days elution equivalent to 200 mm rainfall	68.9 % RR in the leachate as metalaxyl, CGA 62826 and CGA 67868	Suter, 1985

Table B.7.3-6 : Summary of behaviour in soil - Lysimeter studies with metalaxyl

Test soil				Test system	Results	References
Soil type	Soil pH <sub>(KCl)</sub>	CEC	OC (%)			
Sandy soil	5.5-6.7 and 6.2-7.3	-	0-30 cm : 1.0%; 30-60 cm : 0.2% 60-120 cm : 0.1%	3 applications in potatoes, corresponding to 400 g a.s./ha during the first year ; Study duration : 2 years	Concentrations in the combined leachates of 1 year  metalaxyl : <0.01-0.05 µg/l CGA 62826 : 0.25 - 4.12 µg/l CGA 108906 : 0.52-1.11 µg/l	Kubiak, 1995a
Sandy soil	-	-	0-30 cm : 1.0%; 30-60 cm : 0.2% 60-120 cm : 0.1%	3 applications in vine, corresponding to 400 g a.s./ha during the first year ; Study duration : 1 year	Concentrations in the combined leachates of 1 year  metalaxyl : <0.01-0.01 µg/l CGA 62826 : 2.42 - 3.86 µg/l CGA 108906 : 0.48-0.76 µg/l	Kubiak, 1995b

Table B.7.3-7 : Summary of behaviour in soil - Field leaching studies with metalaxyl

Crop	Soil	Groundwater level	Sampling period	Leachate concentrations	References
Barley, 1 application of 0.225 kg a.s./ha	Sand (98.4% sand)	upper level of groundwater 10-40 cm	63 to 411 days after treatment	1 to 2000 µg a.s. /l (LOD not specified)	Tournayre, 1983a
Vine, 1st year : 5 applications corresponding to a total application rate of 1.250 kg a.s./ha 2nd year : 2 applications corresponding to a total application rate of 0.450 kg a.s./ha	Silt loam	upper level of groundwater 10-70 cm	up to 6 months after the last application. (3 years observation)	<4 µg a.s. /l (LOD = 4 µg/l)	Tournayre, 1983b
Vine, 4-5 applications, corresponding to a total application rate of 0.66 to 1.3 kg a.s./ha	Soil with low clay content 0-9%	sampling depth : 200-250 cm	up to 70 days after last application	<1 µg/l to 24.4 µg a.s. /l depending on the sampling points and dates (LOD = 1 µg/l) (some concern about the quality of the analytical method since high concentration was recovered at the first application date)	Bütler, 1982



Table B.7.3-8 : Summary of behaviour in soil - Groundwater monitoring data on metalaxyl (Balu, 1985)

Location	Soil	Crop	Groundwater table	Results
Florida wells	Sandy soil	Citrus  typical treatment rate is 1.12 to 2.24 kg a.s./ha applied at three-month intervals (as ground application as well as for the seedbed treatment)	- groundwater table 12.2-15.2 m	residues < 1 µg/l (later < 0.25 µg/l) - Only one sample, sampled on 9/12/84 showed detectable residue of 3.1 µg/l.  Unusually high residues in the range of 29-226 µg/l were found in one well. It was confirmed that the contamination was due to a malfunctionment of the pumping system
North Carolina wells	Gravelly sandy loam	Tobacco  typical treatment rate is 2.24 kg a.s./ha as a single application	- groundwater table 12.2-15.2 m	residues < 1 µg/l (later < 0.25 µg/l)
Oregon wells	Sandy loam and silt loam	Hops  0.56 kg a.s./ha as a single application	- groundwater table 12.2-15.2, 18.3, 36.6-42.6 m	residues < 1 µg/l (later < 0.25 µg/l)

*Predicted Environmental Concentrations in soil (Foliar uses)*

The estimations of the PECs were calculated assuming that :

- Metalaxyl-M has a  $DT_{50}$  (soil) = 38.5 days (= median field  $DT_{50}$  of metalaxyl  $\approx$  maximum  $DT_{50}$ )
- Equal distribution in the top 5 cm of the soil with a bulk density of  $1.5 \text{ g/cm}^3$
- Major uses of metalaxyl-M are

Crop	Application rate	Number of applications/season
grapes (foliar use)	120 g a.s./ha	2-4
potatoes (foliar use)	110 g a.s./ha	2-5

Table B.7.3-9 : PEC soil - Foliar spray to control airborne diseases (formulation RIDOMIL GOLD MZ 68 WP)

Time after applications (days)	Grapes 120 g a.s./ha 4 applications with 7 d interval 70% of applied dose reaching the soil	Potatoes 110 g a.s./ha 5 applications with 7 d interval 50% of applied dose reaching the soil
	Actual concentration (mg a.s./kg soil)	Actual concentration (mg a.s./kg soil)
0	0.112	0.073
1	0.110	0.072
2	0.108	0.071
4	0.104	0.068
7	0.099	0.065
7	(2nd appl) 0.210	(2nd appl.) 0.138
14	(3rd appl) 0.298	(3rd appl.) 0.195
21	(4th appl) 0.374	(4th appl.) 0.245
28	0.330	(5th appl.) 0.290
50	0.222	0.195
100	0.090	0.079

PEC for the major metabolite CGA 62826 could be considered as equivalent to the PEC of the a.s. (field  $DT_{50}$  of the a.s. and its metabolite are quite similar.). Soil accumulation studies were provided which give measured concentrations for metalaxyl and its metabolite (table B.7.3-3) . These data are in good accordance with the PEC which were calculated (table B.7.3-9). Moreover the (eco)toxicity data showed that the metabolite is less toxic than the parent.

*Predicted Environmental Concentrations in soil (Soil uses)*

The estimations of the PECs were calculated assuming that :

- Metalaxyl-M has a  $DT_{50}$  (soil) = 38.5 days (= median field  $DT_{50}$  of metalaxyl  $\approx$  maximum  $DT_{50}$ )
- Equal distribution in the top 5 cm of the soil with a bulk density of  $1.5 \text{ g/cm}^3$
- The following scenarios were followed :

Crop	Application rate	Number of applications/season
orchard and ornamental crops	1000 g a.s./ha (typical high dose rate)	1
annual field crops		
orchard crops and ornamentals	1 g a.s./ $\text{m}^2$ in root zone	1-2

Table B.7.3-10 : PECsoil - Soil treatment against soilborne diseases (formulation RIDOMIL GOLD 480EC)

Time after applications (days)	orchard and ornamental crops annual field crops 1000 g a.s./ha 1 application 100 % of applied dose reaching the soil		Root zones in plantation 1 $\text{g/m}^2$ 1 application 100 % of applied dose reaching the soil	
	Actual concentration (mg/kg soil)	Time weighed average (mg/kg soil)	Actual concentration (mg/kg soil)	Time weighed average (mg/kg soil)
0	1.33	1.33	13.33	13.33
1	1.31	1.32	13.10	13.21
2	1.29	1.31	12.86	13.10
4	1.24	1.29	12.40	12.86
7	1.18	1.25	11.75	12.53
14	1.04	1.18	10.36	11.79
21	0.91	1.11	9.14	11.10
28	0.81	1.05	8.05	10.47
50	0.54	0.88	5.42	8.79
100	0.22	0.62	2.20	6.18

#### **B.7.4 Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2)**

##### **B.7.4.1 Hydrolysis rate of relevant metabolites, degradation and reaction products (Annex IIA 7.2.1.1)**

The hydrolysis rate of metalaxyl-M was determined according to OECD guideline 111. Hydrolysis was measured at different temperatures and pH conditions (Ellgehausen, 1996b)

pre-test at 50 °C at pH 1, 5, 7 and 9 : hydrolytical stability up to pH 7 (= less than 10 % of degradation after 5 days)  
further tests at pH 9 :

60 °C :  $k = 2.97 \cdot 10^{-6} \text{ s}^{-1}$ ;  $t_{1/2} = 2.7 \text{ d}$

50 °C :  $k = 1.04 \cdot 10^{-6} \text{ s}^{-1}$ ;  $t_{1/2} = 7.7 \text{ d}$

25 °C :  $k = 6.89 \cdot 10^{-8} \text{ s}^{-1}$ ;  $t_{1/2} = 116.4 \text{ d}$

20 °C :  $k = 3.72 \cdot 10^{-8} \text{ s}^{-1}$ ;  $t_{1/2} = 215.8 \text{ d}$  (calculated)

Hydrolysis proceeds via cleavage of the methylester bond, leaving (R)-2-[N-(2,6-dimethylphenyl)-methoxyacetyl-amino]-propionic acid (CGA 62826)

It was shown that the a.s. is very slightly hydrolyzed. CGA 62826 being the sole metabolite recovered in this test, it can be expected that this major acid metabolite, also found in the soil metabolism and water/sediment study, will not be further hydrolyzed. An hydrolysis study with CGA 62826 is not required.

##### **B.7.4.2 Direct phototransformation of relevant metabolites, degradation and reactions products in water (Annex IIA 7.2.1.2)**

The phototransformation of metalaxyl-M in water was studied according to the US-EPA-161-2 guideline. (Ellgehausen, 1995c)

This study showed that no significant degradation occurred at 25°C, in water buffered at pH 7.

After 240 h continuous exposure : still 97.16 % of metalaxyl-M present (dark-control : after 240 h still 96.30-98.61 % of metalaxyl-M present). No half-life was calculated.

Only very minor amounts of degradates observed (ranging on average between 0.22 and 1.77 % of the radioactivity applied). Degradates were not further characterized.

It was shown that the phototransformation of metalaxyl-M is very limited. Only very minor amounts of degradates were observed. The metabolite CGA 62826 and the parent have the same chromophore. It can be expected that the major metabolite CGA 62826 is photolitically as stable as the parent. A phototransformation study with CGA 62826 is therefore not required.

##### **B.7.4.3 Ready biodegradability of the active substance (Annex IIA 7.2.1.3.1)**

Report on the test for ready biodegradability of CGA 329351 (Enantiomer of CGA 48988) in the carbon dioxide evolution test (Grade, 1995)

Guidelines :

Guideline OECD No. 301/B

GLP :

Yes

Material and Methods :

*Test substance* : metalaxyl-M, chemical purity : 97.1%

*Test conditions* :

The test substance was mixed with distilled water. After homogenizing the volume was adjusted to 1.5 l with test medium to produce the concentration 29.3 and 28.3 mg test substance/l (18.9 mg ThOC and 18.3 mg ThOC/l). During exposure the evolved CO<sub>2</sub> trapped by the 0.05 N NaOH solution of the blank, reference, test substance and test substance+reference was measured at 0,3, 6, 8, 10, 13, 15, 17, 20, 22, 24, 28 and 29 days. Test temperature was  $22 \pm 2^\circ\text{C}$ .

Findings and conclusions :

The test substance did not inhibit the biodegradation of the reference substance. The biodegradation of the test substance was 0% in 29 days, therefore the test substance was not biodegradable in this test.

**B.7.4.4 Water/sediment study (Annex IIA 7.2.1.3.2)**

<sup>14</sup>C-CGA 48988 (metalaxyl): Degradation and metabolism in aquatic systems (Morgenroth, 1994)

Guidelines :

BBA, part IV, 5-1

GLP :

Yes

Material and Methods :

*Test substance :* (<sup>14</sup>C-phenyl ring) labelled metalaxyl, radiochemical purity : 94.9% (HPLCcheck), specific activity : 4.73 MBq (127.84 µCi/mg)

*Waters and sediments :*

Two natural water/sediment systems collected from pond and river were used in the study.

Table B.7.4.4-1 : Characteristics of waters

Origin		Rhine river Mumpf - Zeltplatz, Aargau, Switzerland	Pond water, Ormalingen, Weiherhof-Tal, Baselland, Switzerland
Temperature (°C)	surface	11.7	10
	5 cm above sediment	11.6	9.8
pH	surface	7.89	8.23
	5 cm above sediment	7.89	8.78
Redox potential (mV)	surface	174	147
	5 cm above sediment	172	16
Oxygen content (mg/l)	surface	10.4	8.5
	5 cm above sediment	10.8	8.7
NO <sub>3</sub> -N (mg/l)		1.02	0.47
NO <sub>2</sub> -N (mg/l)		0.03	0.01
NH <sub>4</sub> -N (mg/l)		0.03	0.03
N total (mg/l)		1.08	0.51
P as ortho phosphorus (mg/l)		0.2	0.07
TOC (mg C/l)		76.0	163.0
Hardness (°dH)		13.5	21.5

Table B.7.4.4-2 : Characteristics of sediments

Origin		Rhine river Mumpf - Zeltplatz, Aargau, Switzerland	Pond water, Ormalingen, Weiherhof-Tal, Baselland, Switzerland
pH		7.49	6.88
Redox potential (mV)		-172	-136
N-total (Kjeldahl) (g/kg sediment)		0.70	4.03
P-total (g/kg sediment)		0.38	0.46
Organic carbon (%)		0.60	4.72
Biomass (mg microb. C/100 g dry sediment)		70.7	250.7
Cation exchange capacity (meq/100 g sediment)		6.1	28.2
Dry mass (kg dry sediment/kg fresh sediment)		0.70	0.34
Particle size distribution			
- % silt		16.9	60.9
- % sand		78.6	37.1

- % clay	4.5	2.0
Classification	loamy sand	Silt loam

*Test conditions :*

- Metalaxyl was applied to two water/sediment systems and incubated at 20 °C for up to 240 d. Each incubation flask contained a 2 cm sediment and a 6 cm water layer. Gentle agitation of the surface without disturbing the sediment was achieved by means of a magnetic stirrer.

- 129.47 µg metalaxyl was added to each flask which represented a concentration of 0.189-0.208 mg a.s./l water.

- pH, oxygen concentration and redox potential were monitored during the whole study.

*Extraction - analytical methods :*

- Liquid scintillation counting (LSC) of water samples, trap solutions and soil following combustion.

- Sediment was extracted three times with acetone:water (8:2), methanol:water (8:2) once for samples taken from day 14 onwards and Soxhlet extraction with acetone once overnight for samples taken on days 14, 28, 56 and 181. Radioactivity was characterised by thin layer chromatography (TLC) and high performance liquid chromatography (HPLC).

*Findings :*

Table B.7.4.4-3 : Distribution of radioactivity and balance in river water/sediment system (data in % applied radioactivity)

	(Days)							
	0	7	14	28	56	112	181	240
<u>CO<sub>2</sub></u> <sup>1</sup>	n.p.	0.1	0.2	0.7	1.6	3.0	4.3	7.6
Volatiles	n.p.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
<u>Water (*)</u>	105.7	87.0	77.4	79.1	77.9	77.7	74.6	71.1
- metalaxyl	102.4	82.6	67.4	57.2	37.7	14.2	3.2	1.4
- CGA 62826	-	1.0	7.1	18.1	32.7	55.0	61.0	59.2
- CGA 67868	3.3	3.3	2.2	2.4	3.0	3.1	3.4	5.4
<u>Sediment</u>	1.7	20.1	26.3	24.8	26.8	23.2	24.2	25.3
<u>Extractable (*)</u>	n.p.	18.6	26.2	22.7	23.2	17.6	17.0	15.0
- metalaxyl	-	16.4	17.1	15.2	11.5	3.9	1.3	0.7
- CGA 62826	-	1.6	7.7	6.5	9.8	12.3	13.1	12.3
- CGA 67868	-	0.6	1.0	0.5	0.7	0.8	0.8	1.3
Bound residue	1.7	1.5	0.1	2.1	3.6	5.6	7.2	10.4
<u>Balance (CO<sub>2</sub> + water + sediment)</u>	107.4	107.2	103.8	104.6	106.2	103.8	103.1	104.0

Table B.7.4.4-4 : Distribution of radioactivity and balance in pond water/sediment system (data in % applied radioactivity )

	(Days)							
	0	7	14	28	56	112	181	240
<u>CO<sub>2</sub></u> <sup>1</sup>	n.p.	0.1	0.1	0.2	0.6	1.2	1.6	4.1
Volatiles	n.p.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	<0.1
<u>Water</u> (*)	104.8	76.8	72.5	67.9	73.1	72.3	69.4	65.5
- metalaxyl	100.1	69.4	56.0	35.0	8.3	0.4	0.0	0.7
- CGA 62826	-	4.8	12.9	30.2	58.7	68.8	58.1	57.2
- CGA 67868	4.7	2.6	3.2	1.8	2.2	2.2	1.6	2.0
<u>Sediment</u>	2.1	27.9	28.1	33.9	32.9	30.0	33.2	34.4
Extractable	n.p.	24.9	24.5	29.2	26.4	21.2	23.0	20.5
- metalaxyl	-	20.4	19.0	11.0	1.9	0.6	0.1	0.2
- CGA 62826	-	3.9	4.0	17.0	23.0	19.0	20.7	19.1
- CGA 67868	-	0.4	1.0	0.8	1.0	0.6	0.8	0.6
Bound residue	2.1	3.0	3.7	4.7	6.5	8.8	10.2	13.8
<u>Balance (CO<sub>2</sub> + water + sediment)</u>	106.8	104.8	100.8	102.1	106.6	103.5	104.2	104.0

(\*) : Minor unknown fractions are not included in the tables.

#### Conclusions :

Metalaxyl is distributed to both sediment and water phases. Metalaxyl is degraded to metabolite CGA 62826 (DT<sub>50</sub> whole system are 47.5 and 22.4 days for the river and pond system respectively). The metabolite CGA 62826 is a major metabolite slightly decreasing from day 112-181 to day 240 (Maximum 61.0-68.8% applied radioactivity in water after 112-181 days). DT<sub>50</sub> (CGA 62826) > 1 year. Other metabolites (CGA 67868 and 5 unknown peaks) are found at low levels (<10% radioactivity)

Mineralization is low (7.6% and 4.1% of the radioactivity are recovered as CO<sub>2</sub> after 240 days)

Amounts of bound residue are increasing slowly during the whole incubation period and are reaching 10.4 and 13.8% of the applied radioactivity after 240 days.

Metalaxyl - aerobic aquatic metabolism of <sup>14</sup>C-metalaxyl (Vithala, 1991)

This study, performed according to the US EPA guideline was not taken into consideration for the evaluation of the active substance because :

- The test soil (paddy clay soil) is not representative of those likely to be exposed,
- The test conditions (25°C, duration = 30 days, uncomplete characterization of the test soil) diverge from the SETAC recommendations

This study nevertheless confirms the results of the previous study (Morgenroth, 1994) : Distribution of the a.s. to both phases, degradation of metalaxyl to CGA 62826, similar DT<sub>50</sub> whole system (55.1 days).

Metalaxyl: Anaerobic Aquatic Metabolism of  $^{14}\text{C}$ -Metalaxyl (Vithala, 1992)

Guidelines :

EPA guideline, (Subdivision N, section 162-3)

GLP : Yes

Material and Methods :

*Test substance :* ( $^{14}\text{C}$ -phenyl ring) labelled metalaxyl, radiochemical purity : 94.13% (HPLC check), specific activity : 1.25 MBq (33.7  $\mu\text{Ci/mg}$ )

*Water and sediment :*

The water and sediment were obtained from a paddy field situated in Louisiana.

Table B.7.4.4-5 : Characteristics of the sediment

Origin:		Louisiana Rice paddy	
Texture:		Clay	
pH:		7.3	
Composition	% Organic Matter:	3.6	
	% Clay:	68	
	% Silt:	24	
	% Sand:	8	
Cation exchange capacity (meq/100 g)		28.9	

*Test conditions :*

The dosage solution was applied after 115 days preincubation to give a final concentration of 1.78 ppm. The incubation was performed at 24.6 -25.4°C in the dark with a constant flow of humidified nitrogen at 50-60 ml/minute.

*Extraction - analytical methods :*

Water : combustion and liquid scintillation counting (LSC). Extracted with 0.1% trifluoroacetic acid aqueous solution and analysed by LSC and high performance liquid chromatography (HPLC).

Sediment : combustion and LSC. Extracted with methanol, and 0.1% trifluoroacetic acid aqueous solution. Day 24 and 30 samples further extracted with 1M sodium hydroxide. Analysed by HPLC.

Findings :

Table B.7.4.4-6 : Distribution of radioactivity and balance in paddy field water/sediment system - anaerobic incubation (data in % applied radioactivity )

	(Days)											
	0	6	13	21	28	41	70	100	149	198	265	385
<u>CO<sub>2</sub></u>	-	0.01	0.01	0.02	0.02	0.03	0.08	0.15	0.18	0.23	0.75	1.35
<u>Water</u>	51.63	46.45	46.46	48.34	47.81	52.02	57.25	59.92	57.29	54.79	59.42	44.28
- metalaxyl	50.87	36.73	30.31	28.52	24.99	17.23	3.76	-	-	-	-	-
- CGA 62826	0.76	7.66	14.30	16.57	19.02	30.47	47.83	53.47	50.62	45.91	49.06	34.50
- CGA 119857	-	-	1.47	3.26	-	4.31	5.66	6.45	6.26	8.07	8.41	8.90
<u>Sediment</u>	48.83	52.08	49.79	49.51	46.86	45.64	35.68	34.07	30.98	39.09	51.50	40.19
Extractable	47.78	46.31	46.68	46.41	44.63	44.0	32.57	30.99	28.77	36.52	48.42	38.46
- metalaxyl	45.48	40.11	35.18	31.53	26.95	20.17	4.90	1.25	-	-	-	-
- CGA 62826	0.85	5.80	11.00	13.58	14.26	20.89	23.90	23.84	21.79	28.12	36.47	13.57



- CGA 119857	-	-	0.50	1.30	0.38	2.94	2.57	3.74	6.99	8.16	7.39	7.35
Bound residue	1.05	5.77	3.11	3.10	2.23	1.64	3.11	3.08	2.21	2.57	3.08	1.73
Balance (CO <sub>2</sub> + water + sediment)	100.46	98.54	96.26	97.87	94.69	97.69	93.01	94.14	88.45	94.11	111.67	85.82

**Conclusions :**

The characterization of the soil is insufficient; the water properties were not determined.

Metalaxyl is distributed to both sediment and water phases. Metalaxyl is degraded anaerobically to metabolite CGA 62826 (DT<sub>50</sub> whole system = 29.9 days). Two major metabolites were observed (CGA 62826 at 77 % applied radioactivity after 100 days, CGA 119857 at 16% radioactivity after 198 days)

Amount of bound residue is low during the whole incubation period (generally 1.0 -3.1 % applied radioactivity).

Metabolites CGA 325631 and hydroxy-metalaxyl were found only at two sampling times at very low concentrations.

Two field studies were conducted to determine the dissipation of metalaxyl in rice paddy field. These studies are not required by the directive 91/414/EEC.

Ridomil® 2E (metalaxyl): An Aquatic Dissipation Study for Water Seeded Rice in Memphis, Tennessee (Biever, 1992)

Aquatic dissipation of metalaxyl (Ridomil® 2E) in a California rice paddy (Leech, 1992)

**Guidelines :**

EPA guideline, (Subdivision N, section 164-2) for both studies

**GLP :**

Yes, for both studies

**Material and Methods :**

*Test substance* : formulation RIDOMIL 2E (formulation containing 120 g a.s./l)

**Test conditions :**

The experimental designs of both studies are rather similar: the formulation was applied at the dose rate of 0.56-0.58 kg a.s./ha to 3 test plots/study (plot size : 450 m<sup>2</sup>), a fourth plot was used as control. After the application, the plots were flooded with water . Water level was maintained at constant level during the whole study. The plots were maintained as a closed system without water discharge.

The soils were sampled to a depth of 22.5 and 60 cm respectively for the Memphis and Madera studies. Water was sampled regularly.

**Analytical methods :**

Memphis study : Soil was extracted using 50% methanol:water (v/v). Soil and water were adjusted to pH 2 using dilute sulphuric acid, Extracted with methanol using octadecyl bonded silica (C-18) solid phase (SPE) columns, derivatised and extracted with hexane. Analysis by gas chromatography (GC).

Madera study : Soil samples were extracted with methanol:water, partitioned into methylene chloride:ethyl acetate, derivatised and extracted with hexane. Analysis by gas chromatography (GC) with a nitrogen-phosphorus detector. Water samples were extracted with methylene chloride:ethyl acetate, derivatised and extracted with hexane. Analysis by gas chromatography (GC) with a nitrogen-phosphorus detector.

**Findings :**

Table B.7.4.4-7 : Test conditions and main results of two field studies investigating the dissipation of metalaxyl in rice paddy fields

Soil				Test system	Results	Reference
Soil	pH	CEC	OC %			
silt loam	6.3	4.0	0.58	Rice paddy field - Tennessee - 0.56 kg a.s./ ha was applied on bare soil. - Field was then flooded with water. - Plots were drained after 120 days	DT <sub>50</sub> water = 5 days DT <sub>50</sub> (7.5 cm top soil) = 11.5 days	Biever, 1992

Soil				Test system	Results	Reference
Soil	pH	CEC	OC %			
clay loam, clay subsoil	7.1	12.7-21.7	0.29	Rice paddy field - California - 0.58 kg a.s./ ha was applied on prepared seed bed. Rice was then sown. - Field was flooded with water (10-15 cm depth) - Plots were drained after 92 days - Soil was monitored up to 259 days	DT <sub>50</sub> water = 20 days DT <sub>50</sub> (7.5 cm top soil) = 24 days	Leech, 1992

**Conclusions :**

The degradation rates found in the laboratory water/sediment study (DT<sub>50</sub> (whole system) = 47.5, 22.4 at 20°C) are reflected correctly in the paddy field dissipation rates (DT<sub>50</sub> soil = 11.5, 24 days). However, it can be expected that factors such as high water temperature, light, volatilization, etc are explaining the lower DT<sub>50</sub> in the field.

**B.7.4.5 Degradation in the saturated zone of active substance, metabolites, degradation and reaction products (Annex IIA 7.2.1.4)**

“From studies such as aqueous hydrolysis, degradation in sterile and anaerobic soil it is concluded that metalaxyl-M would slowly degraded in the saturated zone. The metabolite CGA 62826 would dissipate only by dilution under such conditions.”

No studies are required under this point. It should be concluded that no degradation of metalaxyl-M and its metabolite occur in the saturated zone.

**B.7.5 Impact on water treatment procedures (Annex IIIA 9.2.2)**

No guidance, no study is required.

**B.7.6 Summary of behaviour in water and predicted environmental concentrations in surface water and in ground water (PEC<sub>sw</sub>, PEC<sub>gw</sub>) (Annex IIIA 9.21, 9.2.3)**

*Physico-chemical properties*

Metalaxyl-M is not photodegradable in water. The a.s. is not hydrolyzed at any pH. The a.s. is not readily biodegradable

*Water/sediment studies*

In water/sediment study under aerobic conditions, metalaxyl is distributed to both sediment and water phases. Metalaxyl is degraded to metabolite CGA 62826 (DT<sub>50</sub> whole system are 47.5 and 22.4 days for the river and pond system respectively). The metabolite CGA 62826 is a major metabolite slightly decreasing from day 112-181 to day 240 (Maximum 61.0-68.8% applied radioactivity in water after 112-181 days). DT<sub>50</sub> (CGA 62826) > 1 year. Other metabolites (CGA 67868 and 5 unknown peaks) are found at low levels (<10% radioactivity). Mineralization is low (7.6% and 4.1% of the radioactivity are recovered as CO<sub>2</sub> after 240 days). Amounts of bound residue are increasing slowly during the whole incubation period and are reaching 10.4 and 13.8% of the applied radioactivity after 240 days.

In water/sediment study under anaerobic conditions, metalaxyl is distributed to both sediment and water phases. Metalaxyl is degraded anaerobically to metabolite CGA 62826 (DT<sub>50</sub> whole system = 29.9 days). Two major metabolites were observed (CGA 62826 at 77 % applied radioactivity after 100 days, CGA 119857 at 16% radioactivity after 198 days)

Amount of bound residue is low during the whole incubation period (generally 1.0 -3.1 % applied radioactivity). Metabolites CGA 325631 and hydroxy-metalaxyl were found only at two sampling times at very low concentrations.

*Rice paddy field studies*

Results of two rice paddy field studies performed with metalaxyl were submitted. They reveal that the a.s. has a DT<sub>50</sub> of 5-20 days in water while the DT<sub>50</sub> in the top soil is 11-24 d

*Degradation in the saturated zone*

Due to the very low degradation of metalaxyl-M under abiotic conditions, it should be concluded that no degradation of metalaxyl-M and its metabolite occur in the saturated zone.

Figure B.7.6-1 : Proposed metabolism pathway of metalaxyl-M in water

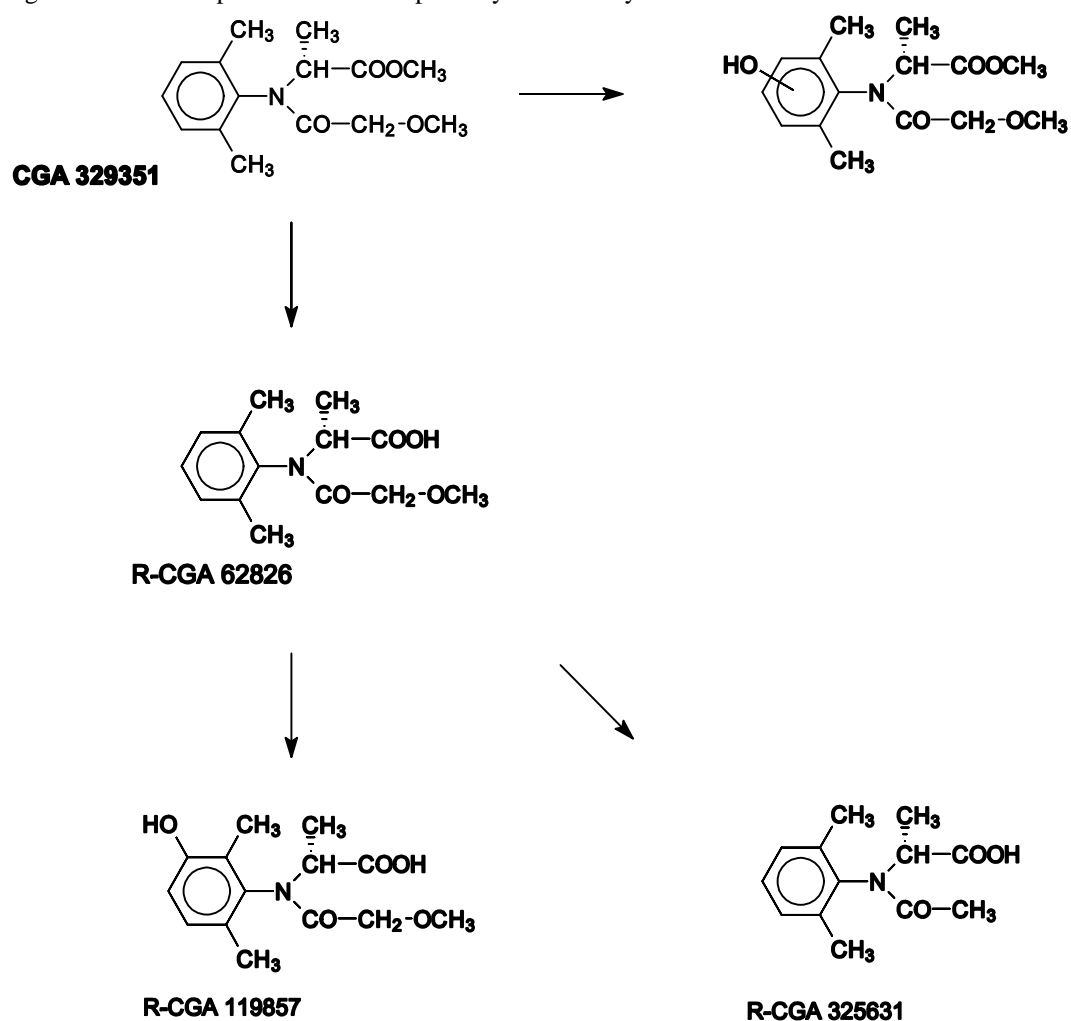


Table B.7.6-1 : Summary of behaviour in water

Test medium (soil, sediment, water)				Test system	Results	References
Medium type	pH	CE C	OC %			
Water	1, 5, 7, 9	-	-	Metalaxyl-M Hydrolysis	No hydrolysis at pH 1, 5, 7 $t_{1/2} = 215.8$ d, at 20 °C, pH 9  Hydrolysis of CGA 62826 is not expected	Ellgehausen, 1996
Water	7	-	-	Metalaxyl-M Photolysis at 25°C	No photolysis of the a.s.  Photolysis of CGA 62826 is not expected	Ellgehausen, 1995
Water	-	-	-	Metalaxyl-M Ready biodegradability	Metalaxyl-M is not ready biodegradable (0% after 29 d)	Grade, 1996
Loamy sand	7.4 9	6.1	0.6 0	Metalaxyl, aerobic water/sediment study at 20°C (Rhine river sediment)	DT <sub>50</sub> (whole system, river) = 47.5 d DT <sub>50</sub> (CGA 62826) > 1 year	Morgenroth, 1994
Silt loam	6.8 8	28.2	4.7 2	Metalaxyl, aerobic water/sediment study at 20°C (Pond sediment)	DT <sub>50</sub> (whole system, pond) = 22.4 d DT <sub>50</sub> (CGA 62826) > 1 year	
Clay	7.3	28.9	2.0 9	Metalaxyl, anaerobic water/sediment study at 25°C (Paddy field soil)	DT <sub>50</sub> (whole system) = 29.9 d	Vithala, 1992
Silt loam	6.3	4.0	0.5 8	Metalaxyl - Rice paddy field - Tennessee - 0.56 kg a.s./ ha was applied on bare soil. - Field was then flooded with water. - Plots were drained after 120 days	DT <sub>50</sub> water = 5 days DT <sub>50</sub> (7.5 cm top soil) = 11.5 d	Biever, 1992
Clay loam, clay subsoil	7.1	12.7 -21.7	0.2 9	Metalaxyl - Rice paddy field - California - 0.58 kg a.s./ ha was applied on prepared seed bed. Rice was then sown. - Field was flooded with water (10-15 cm depth) - Plots were drained after 92 days - Soil was monitored up to 259 days	DT <sub>50</sub> water = 20 days DT <sub>50</sub> (7.5 cm top soil) = 24 d	Leech, 1992

*Predicted Environmental Concentrations in surface water (Foliar uses)*

To estimate the PEC<sub>sw</sub> several routes have to be considered : direct overspray, spray drift, run off, discharge via drainage.

1- Direct overspray would not correspond to good agricultural practice and is not further considered

2 - Run off. The estimation of the PEC surface water resulting from runoff is based on the following assumptions  
 - 0.5% a.s. applied runoff from a 1 ha field into a 0.2 ha pond of 1 m depth  
 - 120 g a.s./ha applied.

The concentration in water is estimated to 0.3 µg/l.

3 - Drain discharge. Drain water concentrations were measured in two studies of dissipation. (Table B.7.3-2) Drain systems were at 0.8 and 1.2 m depth. Water concentrations were generally measured after heavy rainfall. The maximum concentrations were 17-87 µg a.s./l. Levels of CGA 62826 in the range <10-32 µg/l were measured in one of the studies

4 - Spray drift

The estimations of the PEC surface water were calculated assuming that :

- Metalaxyl-M has a DT<sub>50</sub> (whole system) = 47.5 days
- Distribution to a 30 cm deep waterbody
- Major foliar uses of metalaxyl-M are

Crop	Application rate	Number of applications/season
grapes (foliar use)	120 g a.s./ha	2-4
potatoes (foliar use)	110 g a.s./ha	2-5

Table B.7.6-2 : PEC surface water - Foliar spray to control airborne diseases (formulation RIDOMIL GOLD MZ 68 WP)

Time after applications (days)	Grapes 120 g a.s./ha 4 applications with 7 d interval 5 m drift , 5 % of applied dose reaching the water body	Potatoes 110 g a.s./ha 5 applications with 7 d interval 1 m drift, 5% of applied dose reaching the water body
	actual concentration (mg a.s./l)	actual concentration (mg a.s./l)
0	0.0020	0.0018
1	0.0019	0.0018
2	0.0019	0.0018
4	0.0019	0.0017
7	0.0018	0.0017
7	(2nd appl.) 0.0038	(2nd appl.) 0.0035
14	(3rd appl.) 0.0054	(3rd appl.) 0.0050
21	(4th appl.) 0.0069	(4th appl.) 0.0063
28	0.0062	(5th appl.) 0.0076
42	0.0051	0.0061
100	0.0022	0.0026

*Predicted Environmental Concentrations in surface water (Soil uses)*

The estimations of the PEC<sub>surface water</sub> were calculated assuming that :

- Metalaxyl-M has a DT<sub>50</sub> (whole system) = 47.5 days
- Distribution to a 30 cm deep waterbody
- The following scenario was followed :

Crop	Application rate	Number of applications/season
orchard and ornamental crops	1000 g a.s./ha (typical high dose rate)	1
annual field crops		

Table B.7.6-3 : PEC<sub>surface water</sub> - Soil treatment against soilborne diseases (formulation RIDOMIL GOLD 480EC)

Time after applications (days)	perennial crops and ornamentals, annual crops, application on the soil 1000 g a.s./ha 1 application 1 m drift , 5% of applied dose reaching the water body	
	Actual concentration (mg/l water)	Time weighed average (mg/l water)
0	0.017	0.017
1	0.016	0.016
2	0.016	0.016
4	0.016	0.016
7	0.015	0.016
14	0.014	0.015
21	0.012	0.014
28	0.011	0.014
50	0.008	0.012
100	0.004	0.009

*PEC surface water for the metabolite CGA 62826*

The DT<sub>50</sub> of CGA62826 in water is more than 1 year. It seems therefore more appropriate to take the initial actual concentration calculated for the a.s. as a good approximation of the PEC of CGA 62826

*PEC ground water*

Input parameters

<b>Crop</b>	<b>Application rate</b>	<b>Number of applications/season</b>
grapes (foliar use)	120 g a.s./ha	2-4
potatoes (foliar use)	110 g a.s./ha	2-5

Median DT50 of metalaxyl under laboratory conditions at 20°C is 20 days.

The notifier considers that the DT50 of metalaxyl-M is 1.4-2 times shorter than the DT50 of metalaxyl. This difference should be more marked in biologically active soils.

The rapporteur MS considers that metalaxyl-M and metalaxyl have similar DT50. Studies performed with mixtures of biologically active soil and inactive soil are not considered as representative and could simply reveal the normal distribution of degradation rates in different soils.

DT50 of CGA62826 of 5 to 100 days were reported in several laboratory studies performed at 20°C

Koc values of metalaxyl-M of 20 to 570 (1299) were reported in the adsorption study

Koc values of CGA 62826 of 3 to 72 were reported in the adsorption study



Modelling studies

Leaching behaviour of CGA 329351 and CGA 62826 - Modelling study for Italian, Belgian and Norwegian conditions (Hosang, 1997a)

Computer simulations were conducted to assess the leaching potential of the fungicide metalaxyl-M and its acid metabolite CGA 62826. The calculations are based on three scenarios which are to represent the soil and climate conditions typically encountered in the Northern, the Central and the Southern part of the EU.

All calculations were performed with the LEACHP model (Hutson & Wagenet 1992).

*Parameters settings :*

Table B.7.6-4 : LEACHP parameter settings used for the simulations

Simulation period	10 years (1/1/1 to 12/31/10)
Time step	0.01 days
Soil layer thickness	50 mm
Lower boundary condition	free drainage
Soil temperature	calculated
Plant growth	calculated
Chemical and environmental parameters	see below

*Substances properties :*

Table B.7.6-5 : Properties of metalaxyl-M and CGA 62826 used for the calculations

		Parent CGA 329351	Metabolite CGA 62826
Molecular Weight		279.34	265.31
Solubility (25°C) mg/L		2.60 10 <sup>4</sup>	2.65 10 <sup>5</sup> (pH 7.27)
Vapor density (mg/L)		3.78 10 <sup>-4</sup> (25° C)	1.09 10 <sup>-6</sup> (20° C)
K <sub>oc</sub> (mL/g)	“very low”	25	10
	“low”	50	27
	“medium”	200	70
	“high”	500	100
Half-Life (d) (20°C)	“low”	5 (75 % to 62826)	5
	“medium”	7 (75 % to 62826)	10
	“high”	10 (75 % to 62826)	15

*Applications :*

the scenario which was used is the potato crop encountered in the European different countries.

Four applications per year at 100 g a.s./ha were assumed during the first 8 years of the simulation and no use in the 2 following years. Full amount reaching the soil

*Soils :*

sandy soil for the Norway situation , OC 2.% in the 0-20 cm horizon, 1.3 % in the 20-40 cm horizon, 0.4% in the 40-80 cm horizon, 0.1% in the 80-100 cm horizon

clay loam soil for the Belgian and Italian situations , OC 2.% in the 0-20 cm horizon, 1.3 % in the 20-40 cm horizon, 0.4% in the 40-80 cm horizon, 0.1% in the 80-100 cm horizon. All soil details are reported in the study.

*Weather conditions :*

Precipitation, potential evapotranspiration and air temperatures were reported for the 3 climate scenarios of Norway, Brussels and Florence.

Rainfall amount was 861 mm/year for Norway, 785 mm/year for Brussels, 816 mm/year for Florence.

**Findings :**

Table B.7.6-6 : Predicted concentrations in ground water at 100 cm soil depth over 9 years under the conditions of Norway

Concentrations (µg/L)	metalaxyl-M			Concentrations (µg/L)	CGA 62826		
	short half-life 5 d	medium half-life 7 d	long half-life 10 d		short half-life 5 d	medium half-life 10 d	long half-life 15 d
very low K <sub>oc</sub> 25	0.0859	0.336	1.10	very low K <sub>oc</sub> 10	0.0897	0.684	2.06
low K <sub>oc</sub> 50	0.0139	0.0744	0.3198	low K <sub>oc</sub> 27	0.0158	0.192	0.789
medium low K <sub>oc</sub> 200	3.0 10 <sup>-5</sup>	0.00021	0.00192	medium low K <sub>oc</sub> 70	0.0002	0.00877	0.0637
high K <sub>oc</sub> 500	0	0	0	high K <sub>oc</sub> 100	2.8 10 <sup>-5</sup>	0.0014	0.0133

Table B.7.6-7 : Predicted concentrations in ground water at 100 cm soil depth over 9 years under conditions of Belgium

Concentrations (µg/L)	metalaxyl-M			Concentrations (µg/L)	CGA 62826		
	short half-life 5 d	medium half-life 7 d	long half-life 10 d		short half-life 5 d	medium half-life 10 d	long half-life 15 d
very low K <sub>oc</sub> 25	0.0065	0.0409	0.205	very low K <sub>oc</sub> 10	0.0063	0.0842	0.437
low K <sub>oc</sub> 50	0.0010	0.0088	0.0572	low K <sub>oc</sub> 27	0.00118	0.0225	0.158
medium low K <sub>oc</sub> 200	0	3.9 10 <sup>-5</sup>	0.00031	medium low K <sub>oc</sub> 70	0	0.00074	0.0101
high K <sub>oc</sub> 500	0	0	0	high K <sub>oc</sub> 100	2.8 10 <sup>-5</sup>	0.0014	0.0133

Table B.7.6-8 : Predicted concentrations in ground water at 100 cm soil depth over 9 years under the conditions of Italy

Concentrations (µg/L)	metalaxyl-M			Concentrations (µg/L)	CGA 62826		
	short half-life 5 d	medium half-life 7 d	long half-life 10 d		short half-life 5 d	medium half-life 10 d	long half-life 15 d
very low K <sub>oc</sub> 25	0.0059	0.0382	0.196	very low K <sub>oc</sub> 10	0.00866	0.114	0.59
low K <sub>oc</sub> 50	0.00086	0.0074	0.0493	low K <sub>oc</sub> 27	0.00159	0.0315	0.21
medium low K <sub>oc</sub> 200	0	0	0.000216	medium low K <sub>oc</sub> 70	0	0.00143	0.016
high K <sub>oc</sub> 500	0	0	0	high K <sub>oc</sub> 100	0	0.00026	0.0034

Leaching and Accumulation Potential of CGA 329351 and CGA 62826 in Soil - Computer Simulations in Compliance with the Dutch Registration Guideline (Hosang, 1997b)

The simulations were to comply with the Dutch registration requirements for pesticides and therefore were based on the PESTLA model and the Dutch standard weather and soil scenarios. As for farming conditions, spring and autumn applications were considered.

*Application :*

A single application of the product is assumed at a rate of 1 kg a.s./ha on 25 May (spring application scenario) or on 1 November (autumn application scenario) in the first year of the simulation. Throughout the simulation period the soil is cropped with corn. Since PESTLA is not capable of describing the formation of metabolites in soil, a surface application rate of 1 kg a.s./ha is assumed for each substance. Corrections for the actual use rates (0.4 and 0.6 kg a.s./ha for CGA 329351), losses during application (20 %) and the actual amounts of CGA 62826 formed (60 % of the applied parent) are only made at a later stage.

*Soil :* sandy soil Landhorst, Noord Brabant, % OM = 4.7 % in the 0-30 cm plough layer, 0.8% in the 30-50 cm layer, 0.2% in the 50-60 cm layer and <0.1% below.

*Weather conditions :*

Meteorological conditions were those recorded in de Bilt (Utrecht) in 1980. Rainfall amount was 860 mm.

Findings :

Table B.7.6-9 : Maximum concentration of metalaxyl-M in the top meter of the groundwater [ $\mu\text{g/L}$ ] - spring application

	$K_{oc}$ : 25 mL/g	$K_{oc}$ : 50 mL/g	$K_{oc}$ : 200 mL/g	$K_{oc}$ : 500 mL/g
DT <sub>50</sub> : 5 days	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$
DT <sub>50</sub> : 7 days	1.30 $10^{-3}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$
DT <sub>50</sub> : 10 days	8.58 $10^{-4}$	1.78 $10^{-5}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$

Table B.7.6-10 : Maximum concentration of metalaxyl-M in the top meter of the groundwater [ $\mu\text{g/L}$ ] - autumn application

	$K_{oc}$ : 25 mL/g	$K_{oc}$ : 50 mL/g	$K_{oc}$ : 200 mL/g	$K_{oc}$ : 500 mL/g
DT <sub>50</sub> : 5 days	4.80 $10^{-2}$	2.06 $10^{-4}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$
DT <sub>50</sub> : 7 days	1.93 $10^{-1}$	1.94 $10^{-3}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$
DT <sub>50</sub> : 10 days	6.53 $10^{-1}$	1.16 $10^{-2}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$

Cases where the EU limit for pesticides in groundwater is exceeded are shaded.

Table B.7.6-11 : Maximum concentration of CGA 62826 in the top meter of the groundwater [ $\mu\text{g/L}$ ] - spring application

	$K_{oc}$ : 10 mL/g	$K_{oc}$ : 27 mL/g	$K_{oc}$ : 70 mL/g	$K_{oc}$ : 100 mL/g
DT <sub>50</sub> : 5 days	4.54 $10^{-5}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$
DT <sub>50</sub> : 10 days	7.52 $10^{-3}$	4.54 $10^{-4}$	< 1.00 $10^{-6}$	< 1.00 $10^{-6}$
DT <sub>50</sub> : 15 days	8.30 $10^{-2}$	1.55 $10^{-2}$	1.06 $10^{-4}$	1.65 $10^{-6}$

Table B.7.6-12 : Maximum concentration of CGA 62826 in the top meter of the groundwater [ $\mu\text{g/L}$ ] - autumn application

	$K_{oc}$ : 10 mL/g	$K_{oc}$ : 27 mL/g	$K_{oc}$ : 70 mL/g	$K_{oc}$ : 100 mL/g
DT <sub>50</sub> : 5 days	6.91 $10^{-1}$	2.22 $10^{-2}$	2.58 $10^{-6}$	< 1.00 $10^{-6}$
DT <sub>50</sub> : 10 days	4.41 $10^{-1}$	3.37 $10^{-1}$	2.83 $10^{-4}$	2.04 $10^{-6}$

DT <sub>50</sub> : 15 days	8.99	9.78	10 <sup>-1</sup>	2.30	10 <sup>-3</sup>	<del>6.91</del>	<del>10<sup>-5</sup></del>
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Cases where the EU limit for pesticides in Groundwater is exceeded are shaded.

Conclusions on the groundwater modelling studies:

- The notifier presents a wide range of DT50/Koc/pedo-climatic scenarios for the a.s. and its metabolite CGA62826.
- The assumptions taken into account in these two modelling studies reflect partially the actual properties of the a.s. and its metabolite. (DT<sub>50</sub> are too short, Koc too high for the a.s. and the metabolite). It is therefore necessary to consider these models calculations in some ways as 'best cases' situations.
- In some scenarios, however not unrealistic, groundwater contamination by the active substance is observed.
- The water contamination by the metabolite CGA 62826 is possible in a large number of scenarios

**B.7.7 Fate and behaviour in air (Annex IIA, 7.2.2; Annex IIIA 9.3)**

Volatilization of CGA 48988 from soil under laboratory conditions (Burkhard, 1977)

Guidelines :

Not specified

GLP :

No

Material and Methods :

*Test substance* : unlabelled metalaxyl,

*soil* :

Table B.7.7-1 : Characteristics of the soils

Origin	Collombey	Les Evouettes
Classification	Sand	Silty Loam
pH	7.8	6.1
Organic Matter (%)	2.2	3.6
Particle size:		
Clay (%)	2.8	12.2
Silt (%)	10.2	49.4
Sand (%)	87.0	38.4
Maximum Water Content (g water/100 g soil)	22	38

Experimental conditions :

Soils samples at the concentration of 40-120 µg a.s. /g (12% soil moisture) were placed in volatilisation chambers (glass, 7.8 cm diameter, surface area 48 cm<sup>2</sup>, height 7.0 cm, volume 340 cm<sup>3</sup>) for 48 hours. The volatilisation was measured under different temperatures and air flow rates.

Analytical methods :

The evaporated metalaxyl was trapped in ethylene glycol. Extraction with methylene chloride and water containing sodium chloride. The extracts were then analysed by gas chromatography (GC). The radioactivity content of the extracts was determined by liquid scintillation counting (LSC)

Findings :

Table B.7.7-2 : Volatilisation of metalaxyl from soil under different environmental conditions

Soil Type	Temperature (°C)	Air Flow Rate (l/h)	Initial Soil Concentration (µg/g)	Amount Volatilised After 48 hours (µg/cm <sup>2</sup> )	Volatilisation Rate (ng/cm/h)
Collombey sand	35	30	40	0.16	3.3
	35	30	80	0.29	5.9
	35	30	120	0.38	8.0
	35	30	160	0.52	10.8
	45	30	120	-	-
	55	30	120	-	-
	35	15	120	-	-
	35	60	120	-	-
Les Evouettes Silty Loam	35	30	120	0.24	5.1

Conclusions :

- The rate of volatilization of metalaxyl from soil increased with increasing pesticide concentration in soil. At 35 °C, an air flow rate of 30 l/h, an initial concentration of 120 µg/g metalaxyl and a soil-water content of 12 %, the volatilization rate was determined to be 0.010 kg·ha<sup>-1</sup>·day<sup>-1</sup> from Collombey sand, and 0.006 kg·ha<sup>-1</sup>·day<sup>-1</sup> from Les Evouettes silty loam, respectively. This difference was due to the different adsorptive capacities of the test soils.

- From both soil types, only 49 ± 6 % of the volatilized radioactivity was determined as metalaxyl. The other half of the volatilized radioactivity could not be identified or characterized since even at the highest rate of application only very small amounts volatilized from the soils.

Volatilisation of CGA 48988 from bean leaves under indoor conditions after spray application of [<sup>14</sup>C-phenyl] labelled material (Krauss, 1992)

**Guidelines :**

Richtlinien für die Prüfung von Pflanzenschutzmitteln im Zulassungsverfahren, Teil IV, 6-1, Biologische Bundesanstalt für Land- und Forstwirtschaft, Bundesrepublik Deutschland, Juli, 1990

**GLP :**

Yes

**Material and Methods :**

Bean plants (*Phaseolus vulgaris nana* var. *Autan*) were cultivated in 17 x 17 cm pots under greenhouse conditions. Seven week old plants (stage of growth: flowering/first fruits) were used for the volatilisation experiment. Before application each plant was thinned to 6 leaves.

Relative humidity: : 36 - 44 % (day) 38 - 44% (night)

Temperature (°C): 20 - 21 (day) 19 (night)

Lighting conditions: 11 h illumination, 10 h dark, 3 h illumination (5000 lux)

Sample area (cm<sup>2</sup>): Total treated surface was 85 x 60 cm

Test substance preparation: 2.1 mg [<sup>14</sup>C] metalaxyl and 36.9 mg unlabelled metalaxyl were ground with 218.2 mg of the blank formulation A-5715 A to obtain the WP 15 formulation. Before application the formulation was diluted to 17 cm<sup>3</sup> with water.

Application rate : 635 g a.s./ha in 333 l

Application technique: Tee-Jee flatjet nozzle 8001E at 3.0 bar overpressure, moving at a speed 0.4 m/s. The distance from the nozzle to the soil surface was 43 cm.

Number of samples: 10 bean plants

Sampling intervals: Two pots were analysed separately at intervals of 15 minutes, 1, 3, 6 and 24 hours after treatment.

Analysis: Plants rinsed with methanol and washed leaf samples were extracted with methanol and combusted.

Radioactivity was measured by liquid scintillation counting (LSC) and the washings and extracts were analysed by thin layer chromatography (TLC).

**Findings :**

Table B.7.7-3 : Volatilisation of metalaxyl from bean leaves

Exposure Time	15 min	1 hr	3 hr	6 hr	24 hr
Surface Radioactivity	95.2	92.9	90.4	90.1	80.2
(% of surface radioactivity as metalaxyl)	(94.7)	(95.3)	(95.3)	(95.8)	(94.2)
Penetrated Radioactivity	4.8	7.1	9.6	9.9	-
Percent Remaining Relative to Amount at t = 15 min	100	92.8	89.3	85.4	65.6

**Conclusions :**

This study shows that volatilisation from the leaves occur. (35% of RR volatilized after 24 h). This study was performed under glasshouses conditions. It is difficult to interpret the results and their relevance in the evaluation of the general behaviour of metalaxyl in the air.

**B.7.8 Summary of behaviour in air and predicted environmental concentrations in air (PECa) (Annex IIIA 9.3)**

The volatility of metalaxyl from soil and from leaves surface were determined. It is difficult to determine the relevance of these results in the evaluation of the general behaviour of metalaxyl in the air.

It is not expected that metalaxyl-M would be present in air for extended time periods or be transported over long distances or even into the stratosphere because :

- Metalaxyl-M is slightly volatile ( $3.3 \cdot 10^{-3}$  Pa at 25°C) (Geoffroy, 1994b)
- The estimated half-life of metalaxyl-M in the atmosphere (by hydroxyl radical oxidation) is between 4 and 6 hours (Stamm, 1995)

#### **B.7.9 Definition of the residue (Annex IIA 7.3)**

##### *Definition of the residue in soil*

Metalaxyl-M was shown to be degraded in all aerobic laboratory and field studies to metabolite CGA 62826, the free acid. This metabolite has only a low biological activity. Nevertheless, it has to be considered a relevant soil metabolite due to the significant amounts in soil during months after application.

Further degradation results in bound residues and carbon dioxide. Besides these, only minor metabolites occur, accounting for a few % of the applied radioactivity. These compounds have no toxicological or environmental significance.

Relevant residue in soil is metalaxyl-M and CGA 62826.

##### *Definition of the residue in water*

Metalaxyl-M was shown to be degraded in water/sediment and paddy field studies to metabolite CGA 62826, the free acid. This metabolite has to be considered a significant metabolite due to the significant amounts found in water (surface water, ground water), its low degradation rate, its high leaching potential. Nevertheless, it must be added that this metabolite has only a low biological activity.

Further degradation results in bound residues and carbon dioxide. Besides these, only minor metabolites occur, accounting for a few % of the applied radioactivity. These compounds have no toxicological or environmental significance.

Relevant residue in water is metalaxyl-M and CGA 62826.

**B.7.10 References relied on****Environmental fate and behaviour of the active substance (Annex IIA 7)**

Annex point(s) 91/414/EE C	Author, title, report number, test institute, date of report Owner of the report (company or organisation) Submitted by (company or organisation) For publications: reference	Ciba file N°	GLP GEP	Published Protected
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IIA 7.1.3.3	Balu, K. 1985a and b. Ridomil groundwater monitoring study results during 1983 - 1984, Ciba-Geigy Corp., USA, Rep.Nr. EIR-85023, 09.12.1985 Owned by Ciba-Geigy Ltd., Basle, Switzerland Submitted by Ciba-Geigy Ltd., Basel, Switzerland	48988/293	no	unpublished -
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## **ANNEX B**

### **Metalaxyl-M**

#### **Appendix G :**

**Soil dissipation testing (metalaxyl)**

**Soil residue testing - soil accumulation testing (metalaxyl)**

**Water monitoring data (metalaxyl)**

