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Measurements and computations on the behaviour of the insecticides azinphos-methyl and dimethoate in ditches

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Abstract

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The unintentional pollution of surface water was studied during spraying of the insecticides azinphos-methyl and dimethoate on two fruit farms. Spray drift depended closely on the local situations at the fruit farms (windbreaks, distance from trees to ditches, paths) and on way of application.

During application, the concentrations of both insecticides in water and in ditch bottoms were measured. Methods were adapted or developed for sampling, extraction, clean-up and gas-chromatography. Shortly after spraying, concentrations were several hundreds of mg m^{-3}. The half-lives of azinphos-methyl ranged from 3 to 4 d; those for dimethoate ranged from 4 to 13 d.

Water flow from and to ditch sections was estimated on both fruit farms during application. Flow through the ditch bottom was estimated as a closing item in a balance equation. All items of water balance were introduced into computation models of the behaviour of pesticides in surface water and bottom material. The set of differential equations was solved numerically after programming in the computer language CSMP III. Simulation of a trial with low discharge from a siphon-linked ditch indicated that conversion of both compounds in water was 70-90% of the material balances. Penetration into the ditch bottom was slow. During water flow through the ditches, convective transport and dispersion were predominant.

Decline of azinphos-methyl and dimethoate was also measured in outdoor tank systems with a bottom layer. Fluctuations in pH and variations in light penetration influenced decline rates. Computations for the tank system indicated that conversion in the water compartment was the major item in material balance. The computed and measured masses of the insecticides in the bottom layer were less than 10% of the amount added.

Conversion rates in surface water and in systems with anaerobic bottom material were measured in the laboratory at 10 and 20 °C. Conversion in water in the dark was slow, with half-lives of both compounds at about 100 d at 20 °C. The conversion rates of azinphos-methyl in anaerobic bottom material at 20 °C was about ten times those in surface water. Copper ions were catalytic in the conversion of both insecticides in water.

Free descriptors: adsorption coefficient, clean-up, gas--liquid chromatography, bottom material, conversion, insecticides, azinphos-methyl, dimethoate, watercourse, ditch, sampling, spray drift, diffusion, dispersion, computations, half-life, rate-constant.

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Contents

List of symbols and units

a = dispersion constant (Equation 40) (1)

$\bar{A}$ = average wetted cross-sectional area of ditch (m^2)

$(A_{\mathrm{b}})_{z=0}$ = surface area of first bottom compartment at sediment--water interface (m^2)

b_1 = width at bottom of ditch; width of compartment 1 (m)

c_{a} = mass concentration of substance in free air ($\mathrm{mg\ m^{-3}}$)

c_{b} = mass concentration of substance in bottom material: mass of substance divided by volume of bottom material ($\mathrm{mg\ m^{-3}}$)

$c_{\mathrm{i,a}}$ = equilibrium mass concentration of substance at gas--liquid interface: mass of substance divided by volume of air ($\mathrm{mg\ m^{-3}}$)

$c_{\mathrm{i,w}}$ = equilibrium mass concentration of substance at gas--liquid interface: mass of substance divided by volume of water ($\mathrm{mg\ m^{-3}}$)

c_{lb} = mass concentration of substance in liquid phase of bottom material: mass of substance divided by volume of liquid phase ($\mathrm{mg\ m^{-3}}$)

c_{w} = mass concentration of substance in water or water compartment ($\mathrm{mg\ m^{-3}}$)

$c_{\mathrm{w,i}}$ = mass concentration of substance in intake water ($\mathrm{mg\ m^{-3}}$)

$c_{\mathrm{w,max}}$ = maximum mass concentration at a sampling point ($\mathrm{mg\ m^{-3}}$)

$c_{\mathrm{w,u}}$ = mass concentration of substance in upstream ditch section ($\mathrm{mg\ m^{-3}}$)

d_2 = depth of upper surface of second bottom compartment (m)

$D_{\mathrm{dif,lb}}$ = diffusion coefficient of substance in liquid phase of bottom material (in terms of volume of liquid phase and depth in bottom material) ($\mathrm{m^2\ d^{-1}}$)

$D_{\mathrm{dif,w}}$ = diffusion coefficient of substance in water ($\mathrm{m^2\ d^{-1}}$)

D_{l} = longitudinal dispersion coefficient ($\mathrm{m^2\ d^{-1}}$)

f_{l} = labyrinth or tortuosity factor: ratio of surface area of bottom material to liquid phase (1)

$F_{\mathrm{s,wd}}$ = flow rate of substance into downstream ditch section during intake period ($\mathrm{mg\ d^{-1}}$)

$F_{\mathrm{s,wi}}$ = flow rate of substance into water compartment during intake period ($\mathrm{mg\ d^{-1}}$)

$F_{\mathrm{s,wo}}$ = flow rate of substance out of water compartment during pumping period ($\mathrm{mg\ d^{-1}}$)

$F_{\mathrm{s,wu}}$ = flow rate of substance into water compartment from upstream ditch section during pumping period ($\mathrm{mg\ d^{-1}}$)

F_{v} = areic mass flux across gas--liquid interface by volatilization ($\mathrm{mg\ m^{-2}\ d^{-1}}$)

g = acceleration due to gravity ($\mathrm{m\ d^{-2}}$)

H = Henry's constant (Equation 5) (1)

h_g = height of groundwater level above ditch bottom (m)

h_w = height of water level above ditch bottom (m)

$\bar{h}_w$ = average water depth (m)

j = index number of bottom compartment (1)

$J_{conv,lb}$ = areic mass flux by convection into bottom material: mass flux divided by area of bottom material ($mg\ m^{-2}\ d^{-1}$)

$J_{conv,w}$ = areic mass flux by convection in water: mass flux divided by wetted cross-sectional area of ditch ($mg\ m^{-2}\ d^{-1}$)

$J_{dif,lb}$ = areic mass flux by diffusion in bottom material: mass flux divided by area of bottom material ($mg\ m^{-2}\ d^{-1}$)

$J_{dif,w}$ = areic mass flux by diffusion in water: mass flux divided by wetted cross-sectional area of ditch ($mg\ m^{-2}\ d^{-1}$)

$J_{disp,lb}$ = areic mass flux by convective dispersion into bottom material: mass flux divided by area of bottom material ($mg\ m^{-2}\ d^{-1}$)

$J_{disp,w}$ = areic mass flux by convective dispersion in water: mass flux divided by wetted cross-sectional area of ditch ($mg\ m^{-2}\ d^{-1}$)

$J_{s,lb}$ = total areic mass flux into bottom material: mass flux divided by area of bottom material ($mg\ m^{-2}\ d^{-1}$)

$J_{s,w}$ = total areic mass flux in water: mass flux divided by wetted cross-sectional area of ditch ($mg\ m^{-2}\ d^{-1}$)

k = dispersion constant (Equation 41) (1)

$k_{c,b}$ = rate coefficient for conversion of substance in bottom material (d^{-1})

$k_{c,w}$ = rate coefficient for conversion of substance in water (d^{-1})

k_g = exchange coefficient for gas phase ($m\ d^{-1}$)

k_l = exchange coefficient for liquid phase ($m\ d^{-1}$)

K_M = Mannings coefficient for bottom roughness ($m^{1/3}\ d^{-1}$)

k_r = first-order rate coefficient for decline (d^{-1})

$K_{s/l}$ = distribution quotient solid/liquid phase = adsorption coefficient (in terms of volume of liquid phase and mass of solid phase) ($m^3\ kg^{-1}$)

$k_{t,l}$ = overall liquid phase transfer coefficient ($m\ d^{-1}$)

l_{com} = length of ditch compartment (m)

l_d = dispersion distance (m)

m = initial injected mass of substance (mg)

M_1 = first moment (Equation 51) (d)

m_b = mass of slice of wet bottom material (kg)

m_d = mass of slice of dry bottom material (kg)

m_f = multiplication factor for downward increase in thickness of bottom compartments (1)

m_n = measured mass of pesticide in water compartment before Sampling n (mg)

m'_n = mass of pesticide in water compartment corrected for (mg) volume of samples withdrawn

$m_{r,A}$ = areic ratio of contamination of water: ratio of mass of substance introduced into water divided by area of water to mass of substance applied to land divided by land area (1)

n = integer, Sampling No (in time series) (1)

P_1 = wetted perimeter of ditch (m)

q_b = rate of flow through wetted perimeter of ditch (m^3 d^{-1})

q_d = rate of discharge from water compartment (m^3 d^{-1})

$q_{d,u}$ = rate of discharge from upstream ditch section (m^3 d^{-1})

q_{dr} = flow rate through drains (m^3 d^{-1})

q_e = rate of evaporation from water compartment (m^3 d^{-1})

q_i = rate of intake into water compartment (m^3 d^{-1})

$q_{i,d}$ = rate of intake into downstream ditch section (m^3 d^{-1})

q_p = rate of precipitation into water compartment (m^3 d^{-1})

R = hydraulic radius (m)

$R_{c,b}$ = rate of conversion in bottom material (mg m^{-3} d^{-1})

$R_{c,w}$ = rate of conversion in water (mg m^{-3} d^{-1})

s_1 = slope of lower part of ditch walls (tg α = horiz./vert.) (1)

t = time (d)

Δt = time step (in simulation experiments) (d)

$t_{\frac{1}{2}}$ = half-life (d)

$t_{\frac{1}{2},v}$ = volatilization half-life (d)

t_{max} = time at which the maximum mass concentration is reached at a sampling point (d)

$\bar{u}$ = average flow velocity of water (m d^{-1})

u_* = shear velocity (m d^{-1})

V_b = volume of slice of wet bottom material (m^3)

V_{1b} = filtration velocity through bottom compartments (in terms of volume of water and area of bottom material) (m d^{-1})

V_{1b} (1) = filtration velocity through the first bottom compartment (in terms of volume of water and area of bottom material) (m d^{-1})

$V_{s,n}$ = volume of water sample (in time series) (m^3)

V_w = volume of water compartment (m^3)

dV_w/dt = change in storage of water compartment (m^3 d^{-1})

x = downstream distance along ditch axis (m)

z = depth in bottom (m)

α = arctg s_1 (1)

β = arctg $(1/s_1)$ (1)

γ = drainage resistance (kg m^{-2} d^{-1})

ϵ_1 = volume fraction of liquid: volume of liquid phase divided by volume of bottom material (1)

ρ_b = (dry) bulk density of bottom material: mass of solid phase divided by volume of bottom material (kg m^{-3})

ρ_s = density of solid phase of bottom material: mass of solid phase divided by volume of solid phase ($kg\ m^{-3}$)

ρ_w = density of water ($kg\ m^{-3}$)

τ_0 = shear stress at ditch walls ($kg\ m^{-1}\ d^{-2}$)

1 Occurrence and origin of pesticides and herbicides in the aquatic environment

The problem of the occurrence of pesticides and herbicides in surface water has so many aspects that a research program in this field must needs be restricted to part of it. To set the present research program in context and to allow a better evaluation of the results, Chapter 1 gives a general sketch of the problem sphere before the research approach is described in Chapter 2. For the description of concentrations that can occur in surface water (mainly in the larger watercourses), the results of extensive monitoring research could be used. Only a few data have been published on the size of the source of specified contamination. In several cases, an emission to surface water could well occur, however little is known about the size of the source. Some possible sources of pesticides and herbicides in surface waters are discussed in Section 1.5.

1.1 CHLORINATED HYDROCARBON PESTICIDES AND RELATED COMPOUNDS

Monitoring of surface waters and bottom sediments started in the United States about ten years after the introduction of the organochlorine insecticides. It soon became evident that small amounts of these insecticides were present in many surface waters. Since then, extensive surveys have been made in several countries. Most attention was paid to the chlorinated hydrocarbons, since these were widely used and could be rather easily measured with gas chromatographs equipped with an electron-capture detector. Several chlorinated hydrocarbons are only slowly degraded in water. Reviews of organochlorine residues in water were given, for instance, by Westlake & Gunther (1966), Nicholson (1969) and Edwards (1973). Their summarized data show that the residue levels in water are relatively low, ranging from a few micrograms to a few milligrams per cubic metre, except near point sources like discharge of industrial effluent, direct application or accidental contamination.

Chlorinated hydrocarbons were detected in water samples in many European countries (Greve, 1972; Herzel, 1972; Lowden et al., 1969; Sörensen, 1973). These measurements show that lindane, having the highest water solubility of the general chlorinated hydrocarbon insecticides (King et al., 1969), was most commonly found in Europe.

Most chlorinated hydrocarbons show a low solubility in pure water and they may be readily adsorbed to humic substances, organo-clay complexes and other particulate matter in suspension. In laboratory experiments, the release of these compounds from sediments into water was found to be slow (Choi & Chen, 1976). Chlorinated hydrocarbon residues may long persist in the bottom material. For instance, Dimond et al. (1971) showed that the average content of DDT and its metabolites in dry mud from the bottom of small streams decreased from 1.08 mg kg^{-1}, one year after a single application to 0.59 mg kg^{-1} after five years. After ten years, the content had declined to 0.07 mg kg^{-1}. The bottom sediment may be stirred up by strong currents and the transport of DDT in water may thus occur while still largely adsorbed on suspended material (Nicholson, 1969).

Since some organochlorine insecticides are known to be persistent and tend to accumulate in organisms, especially in adipose tissue of animals, their use has been restricted or banned in several countries. In the Netherlands, the last applications of DDT were banned on 1 July 1973.

Monitoring of chlorinated hydrocarbons in Dutch surface waters

The first monitoring in the Netherlands dates back to 1967 and since May 1969, water has been sampled at many points. These sampling points were distributed over the River Rhine with its tributaries, intakes for drinking water supplies and large agricultural areas (Greve, 1971).

Greve (1972) and Meijers (1973) found that α-hexachlorocyclohexane (α-HCH), lindane (γ-HCH) and hexachlorobenzene (HCB) were nearly always present in Rhine water. The insecticide endosulfan had been found in that river in several waves during the years 1969 and 1970, but was rarely found after July 1970. Other organochlorine pesticides and their conversion products (heptachlor, its epoxide, aldrin, dieldrin, endrin and DDT plus related compounds) were occasionally detected in rather low concentrations. The average concentration over the period 1 September 1969 to 1 April 1972, amounted to 0.15 mg m^{-3} for α-hexachlorocyclohexane, 0.10 mg m^{-3} for lindane and 0.13 mg m^{-3} for hexachlorobenzene (Greve, 1972). The concentrations of the by-product α-hexachlorocyclohexane were thus found to be higher than those of the pesticide lindane itself. In view of the limited use of pesticides containing α-hexachlorocyclohexane in agriculture along the Rhine, industry has probably been the main source of pollution. The high concentrations of hexachlorobenzene could not be explained by the limited use of this compound as an agricultural fungicide or by its presence as an impurity in a fungicide like quintozene. Hexachlorobenzene is an intermediate compound of frequent occurrence in industrial syntheses. This compound is also used as a flame retardant.

Since 1972, all monitoring data measured for the larger Dutch waterways administered by national authorities have been tabulated in the quarterly surveys of Rijkswaterstaat (1973-1978). These newer data (Table 1) show that the concentrations of α-HCH and of lindane decreased considerably. As there was no systematic trend in the discharge of the river, which averaged 1890 m^3 s^{-1} over this 5 year period, the discharge of the latter two chlorinated hydrocarbons must have actually decreased.

1.2 CHOLINESTERASE INHIBITORS

The monitoring program started in the Netherlands in 1967 and also included the measurement of cholinesterase inhibitors (mainly organophosphorus and carbamate pesticides) in surface waters. Greve et al. (1972) showed that rather high concentrations of cholinesterase inhibitors were present in the Rhine and its distributaries. They analysed some water samples from this river system in more detail. Five insecticides were detected by thin-layer chromatography (TLC) and gas--liquid chromatography (GLC), while their presence

Table 1. Average mass concentrations of a few chlorinated hydrocarbons in Rhine water sampled near Lobith, the Netherlands. (After Rijkswaterstaat, 1973-1978).

Compound	Quarter	Mass concentrations (mg m^{-3}) in different years				
		1973	1974	1975	1976	1977
Hexachlorobenzene (HCB)	1st	0.18	0.11	0.04	0.10	0.07
	2nd	0.11	0.12	0.07	0.12	0.07
	3rd	0.08	0.17	0.08	0.16	0.14
	4th	0.09	0.06	0.10	0.13	0.04
α-Hexachlorocyclohexane (α-HCH)	1st	0.28	0.25	0.06	0.04	0.02
	2nd	0.13	0.35	0.10	0.06	0.02
	3rd	0.15	0.21	0.05	0.06	0.03
	4th	0.22	0.04	0.04	0.04	0.01
Lindane (γ-HCH)	1st	0.26	0.13	0.04	0.03	0.02
	2nd	0.10	0.17	0.05	0.04	0.03
	3rd	0.09	0.13	0.03	0.03	0.03
	4th	0.14	0.02	0.03	0.02	0.04

was confirmed with a mass spectrometer (MS) (Table 2). The presence of cholinesterase inhibitors in surface water is unfavourable, because cholinesterase activity is intimately related to life in the aquatic environment. Little is known about the significance of sub-lethal concentrations for aquatic organisms.

The average concentration of cholinesterase inhibitors, expressed in paraoxon equivalent, measured during 1970, 1971 and 1972 was below 1 mg m^{-3} (Greve et al., 1972). However, the concentrations in the Rhine near Lobith increased from the first quarter of 1973 onwards. Occasionally the concentrations were fairly high in 1976, which could not be explained by the relatively low discharge of water in the Rhine in that year (Table 3; Figure 1).

In 1976, an important industrial effluent source was traced by the Institut für Wasser, Boden- und Lufthygiene des Bundesgesundheitsamtes (BGA) in the River Main. After the complaints of the BGA and the National Institute of Public Health in the Netherlands, the concentration of paraoxon equivalent near this source diminished within a few weeks from a maximum of 3000 mg m^{-3} to about 10 mg m^{-3} (Fritschi et al., 1978).

In other surface waters in the Netherlands, the level of cholinesterase inhibitors was found to be substantially lower than that in the River Rhine, even below the detection limit of 0.05 mg m^{-3} (Wegman & Greve, 1978).

In other countries too, small amounts of organophosphorus pesticides were found in

Table 2. Mass concentration of a few cholinesterase inhibitors in Rhine water. (After Greve et al., 1972).

Cholinesterase inhibitor	Mass concentration (mg m^{-3})	
	November 1971	January 1972
Dimethoate	0.07	0.08
Malathion	0.01	0.01
Diazinon	0.02	0.05
Parathion	0.03	0.07
Carbaryl	0.40	0.20

Table 3. Average mass concentration of cholinesterase inhibitors in Rhine water sampled near Lobith. Concentrations expressed in mg paraoxon equivalent per m^3 water. (After Rijkswaterstaat, 1973-1978).

Quarter	Mass concentration (mg m^{-3}) in different years				
	1973	1974	1975	1976	1977
1st	5.73	0.92	4.5	31.0	5.9
2nd	1.52	0.95	2.9	21.0	5.4
3rd	2.42	2.74	10.1	2.2	3.8
4th	3.27	1.64	12.1	3.8	1.9
Annual average	3.24	1.56	7.4	14.5	4.3

surface water. For example in British rivers, Lowden et al. (1969) found carbophenothion 0.01-1, diazinon 0.01-0.03, demeton or demeton-S 0.01, malathion 0.01 and phorate 0.01 mg m^{-3}. In West Germany, Sörensen (1973) found several organophosphorus pesticides in surface waters, with a strong variation in concentration dependent on the sampling points. His results are represented in Table 4. In the River Main, dimethoate was regularly present in concentrations between 1 and 10 mg m^{-3} (Kussmaul, 1978).

Extensive reports on cholinesterase inhibitors in surface waters in Italy were given by Del Vecchio et al. (1970), who measured chlorpyriphos, diazinon, fenchlorphos, malathion, methyl-parathion and parathion in a range from less than 0.01 mg m^{-3} to about 0.70 mg m^{-3}.

1.3 HERBICIDES

Monitoring studies in various areas of the United States showed that unintentional presence of herbicides in natural waters was infrequent and at low levels (Frank, 1972). During extensive monitoring of streams in the western United States, concentrations of

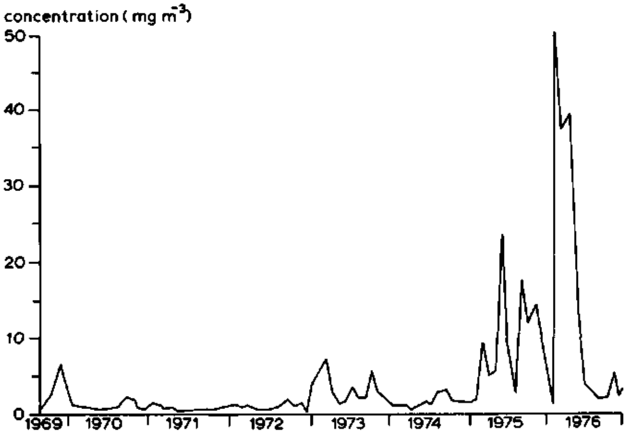


Figure 1. Cholinesterase inhibitors in Rhine water (Lobith) in mg paraoxon equivalent per m^3. (After Fritschi et al., 1978).

Table 4. Organophosphorus pesticides in surface water in West Germany. (After Sörensen, 1973). N.A. = not analysed; - = ≤ 0.01 mg m^{-3}.

Sampling point	Mass concentration (mg m^{-3})					
	bromophos	dimethoate	disulfoton	parathion	methyl-parathion	sulfotepp
Rhine near Ingelheim	0.15	N.A.	-	0.12	-	-
Wupper near Friedenstal	-	-	113	23.5	0.45	18.8
Wupper near Leverkussen	-	-	2.0	0.12	-	1.08
Rhine near Leverkusen--Hitdorf	-	N.A.	2.0	-	-	1.95
Rhine near Düsseldorf--Benrath	-	10.8	0.1	-	-	-

2,4-D were usually less than 1 mg m^{-3}. In those streams, low residues of 2,4,5-T were found too (Schulze et al., 1973). For several years, atrazine has been used on a large scale for weed control in the Corn Belt in the United States. This compound with a solubility in water of 33 g m^{-3} is most frequently detected in the recent monitoring studies. Richard et al. (1975) found that the atrazine concentrations in run-off, in drainage ditches, and in a few rivers in Iowa were more than 1 mg m^{-3} a few days after intensive rainfall.

Waldron (1974) investigated the contribution of agricultural, municipal, residential and industrial activities to pesticide pollution of Lake Erie in 1971-1972. During this study, residues of seven organochlorine insecticides, three triazine herbicides, three chlorophenoxy acid herbicides and five organophosphorus insecticides were monitored. These analyses of river water and bottom mud indicated only sporadic occurrence of minute concentrations. He found atrazine to be the most frequently detectable herbicide. In ten samples of river water with peak residue levels, the concentrations ranged from 3 to 70 mg m^{-3}. Sometimes simazine was detected.

Little information is available about unintentional occurrence of herbicides in Dutch surface waters. The application of herbicides for aquatic weed control in the Netherlands will be briefly discussed in Section 1.4.

1.4 DIRECT APPLICATION OF PESTICIDES TO SURFACE WATERS

Probably the greatest direct source of pesticides in water has been the tens of thousands of tons of DDT that were applied annually to surface water (Westlake & Gunther, 1966) and estuarine salt marshes over two decades to control mosquitoes (Butler, 1969).

Sometimes pesticides were used in programs to eradicate trash fish. For example, camphechlor (Toxaphene) was used to eliminate undesired fish species in many fresh-water fishing lakes in the United States (Veith & Lee, 1971).

A recent example of pesticide application in surface water is the use of temefos (Abate) as larvicide against *Simulium* in some areas of Africa, and South and Central America. Certain species of Simuliidae are vectors of an important filarial disease of man, onchocerciasis. DDT was formerly used as a larvicide against *Simulium*. In recent years, temefos has been recommended by the World Health Organization as a comparatively safe alternative to the chlorinated hydrocarbons (Dale et al., 1975). Another example is the promising molluscicide trifenmorph (Frescon) applied in warm, slowly moving, water for the control of snails, which are intermediate hosts of trematodes causing schistosomiasis (bilharziasis) in man (Osgerby, 1970).

In the Netherlands, no pesticide is applied in that way to surface water.

Application of herbicides

Only a few herbicides are approved in the Netherlands for the control of aquatic weeds under special conditions (Plantenziektenkundige Dienst, 1978). In this section, a short description is given of the situation in 1978. A few characteristics of the physico-chemical behaviour of these herbicides in watercourses are indicated and some remarks are made about possible side-effects.

Dalapon

This herbicide is used on a rather large scale against grassy weeds like reed (*Phragmites communis*) and float grass or reed sweetgrass (*Glyceria maxima*) in watercourses. Applications are only permitted after 15 July. Dalapon (salt) is highly soluble in water: > 800 kg m^{-3} at 25 °C. It decomposes quickly. The major degradation product of dalapon is pyruvic acid, which is ubiquitous in organisms. No significant environmental problems have been observed over many years of wide-scale use (Kenaga, 1974).

Paraquat and diquat

These herbicides are used for aquatic weed control on a fairly large scale, particularly paraquat. They show high activity against submerged weeds like water thyme or Canadian pondweed (*Elodea canadensis*) and pondweed (*Potamogeton species*). Application is only allowed after 1 June. The period with distinct herbicidal activity is comparatively short: usually a few days or less. These compounds are strongly adsorbed onto suspended particulate matter and bottom material, and they are rapidly taken up by aquatic plants and algae (Simsiman & Chesters, 1976). There may be some photochemical degradation, dependent on factors like time of application, solar radiation and exposure of the water to solar radiation. Frank & Comes (1967) showed that paraquat and diquat adsorbed to bottom muds of ponds, persisted in high concentrations for more than 85 and 160 days, respectively.

Side-effects and alternatives

The contact herbicidal activity of a compound like paraquat causes rapid death of submerged aquatic vegetation, resulting in changes in the physical, chemical and biological nature of a treated stretch of water. The removal of competition by certain weeds may result in abundant growth of algae some time after treatment. The breakdown by micro-organisms of rapidly dying plant material requires a lot of oxygen, which may decrease the concentration of dissolved oxygen to very low levels (Brooker & Edwards, 1975). Such changes in living conditions may also indirectly reduce populations of aquatic animals. In view of the side-effects of herbicides in surface water, improvements to mechanical ditch cleaning has been studied. In recent years, the practicality of some biological methods of aquatic weed control has been investigated (van Zon, 1974).

For the control of undesired plant growth of temporarily dry ditch bottoms, other herbicides like diuron, dichlobenil and simazine are approved, as long as no water flow through these ditches is to be expected during the next two months (Plantenziektenkundige Dienst, 1978). An important question with these applications is to what extent these compounds may be released into water and transported when water starts to flow through the ditch again.

1.5 ORIGIN OF UNINTENTIONAL CONTAMINATION OF SURFACE WATER WITH PESTICIDES

Industrial, domestic and agricultural waste

Point sources of contamination of surface water with pesticides outside agriculture may be the discharge of industrial or domestic waste water and sewage plant effluents.

The waste from pesticide factories may be highly contaminated. A well known incident was the general death of fish in the Rhine in June 1969 caused by large amounts of endosulfan (Greve & Wit, 1971). Recently a major industrial discharge, highly contaminated with cholinesterase inhibitors, was traced in the River Main by Fritschi et al. (1978) (Section 1.2). In the undiluted effluent of a factory for organophosphorus and carbamate pesticides in Kansas City, Coppage & Braidech (1976) found concentrations as high as 2000 to 4000 mg m^{-3} for disulfoton, fensulfothion, azinphos-methyl and propoxur. They reported that about 3.2 kg of azinphos-methyl entered the river each day (corresponding with a concentration of about 0.16 mg m^{-3} at low river flows).

Some industries use insecticides in their processes. Lowden et al. (1969) showed, for example, that the effluent from moth proofing in wool and carpet factories contained lindane 0.14, dieldrin 1.8 and DDT 0.8 mg m^{-3}.

Agricultural 'point sources of contamination' can be accidental spill from equipment, cleaning of equipment, carelessness in handling, transport and disposal of empty containers, and inadvertent disposal of remaining spray liquid or dipping baths.

Surface run-off from agricultural land

One of the two principal sources of surface water contamination by pesticides in the United States is probably run-off from agricultural land (Nicholson, 1969; Baily et al., 1974).

After treatment of a watershed in Arizona with the herbicide picloram, the concentrations in stream water at the outlet of the watershed were measured by Davis & Ingebo (1973). They found maximum concentrations of 350-370 mg m^{-3}, which occurred during the first three months after treatment and were associated with heavy rainfall.

Miles & Harris (1971) showed a correlation between rainfall rate and concentration of DDT and metabolites in creek water flowing into Lake Erie.

In a study of dieldrin movement from soil to water in two watersheds, only 0.07% of the amount applied to soil appeared in run-off water with the largest losses occurring in the first two months after application (Caro & Taylor, 1971). Many other workers reported seasonal peaks in residues that coincided with periods of extensive agricultural use.

The surface run-off from agricultural land in the flat areas of the Netherlands is likely to be of minor importance.

Control of ditchside vegetation

When herbicides are used for the control of ditchside weeds, part of the spray may reach the water. Just as for the control of aquatic weeds (Section 1.4), only a few herbicides are approved for the control of ditchside vegetation in the Netherlands. Applications of paraquat are allowed only after 1 June. In practice, these restrictive measures will partly diminish the use of herbicides for control of ditchside vegetation. Further by applications of dalapon and paraquat, there may be a risk of instability of the ditch slopes or a risk of disturbance of the competitive equilibrium between herbs and grasses. At present, mechanical weed control of ditchside vegetation is highly recommended (Plantenziektenkundige Dienst, 1978).

Leaching of pesticides through the soil

After application of pesticides to plants or to the soil surface, various decline processes will start such as volatilization and conversion, including photochemical conversion. A fraction of the amount deposited on the plants may reach the soil surface at a later stage, for example by washing off by rain. It is of interest to know what fraction of the amount reaching the soil surface is leached into the subsoil. Especially pesticides combining weak adsorption in soil with a low decomposition rate are apt to be leached from the rooting zone. Movement of such compounds to the subsoil becomes substantially greater when there is no plant growth or when they are applied in the autumn (Leistra, 1975).

A Dutch working group is concerned with systematic evaluation of pesticides and herbicides for risk of leaching to groundwater. Substances that may give rise to residues in the groundwater are not permitted in groundwater protection areas around pumping stations for domestic supply.

During movement through soil, there is usually considerable time available for conversion of the pesticides. Of course, rather persistent and mobile conversion products may also be leached. Concentrations are decreased by spreading processes like convective dispersion and diffusion, as well as by decomposition and uptake.

Few quantitative results are available on transport of pesticides through the subsoil to surface waters. Most of the groundwater has to move over considerable distances and with a range of, generally long, residence times through the subsoil to tile-drains or ditches. Basic data on movements and rates of conversion in subsoil are few. Only recently did it become possible to estimate - by computational models - the amounts that may be expected to leach from the root zone under various conditions (Leistra & Dekkers, 1976).

Drift from application by aircraft or by tractor-drawn spraying machines

Applications by aircraft mainly occur on large fields of the same crop in arable farming. The method is mainly used for fungicides, for example of the benzimidazole group, dithiocarbamates, and organotin compounds. To a lesser extent, insecticides are sprayed from aircraft, most of them being organophosphorus compounds such as fenitrothion, dimethoate, bromofos-ethyl, thiometon and fosalone. Only rarely can herbicides be applied in this way, because of the risk of damage to crops on adjacent fields. A review of possible pesticide applications by aircraft was given by the Plantenziektenkundige Dienst (1975), with advantages and disadvantages of this method. Possible undesirable consequences of spray drift from the target fields were clearly shown. With application from aircraft, it is hardly possible to avoid contamination of the watercourses bordering on the treated fields. It is thus advisable to select the compounds with the lowest toxicity to aquatic organisms. Data on the behaviour of pesticides in surface water and their toxicity to aquatic organisms are essential in selection of compounds suitable for aerial application.

When applying insecticides, acaricides or fungicides by tractor-drawn sprayers to high crops like fruit trees, spray drift may occur over considerable distances so also to neighbouring watercourses.

With careful applications of pesticides and herbicides to the soil surface or to fields with low vegetation - mainly by tractor-drawn spraying equipment with a low spray boom - and also adequate droplet size little spray will drift and thus also little contamination of water will occur.

Relative importance of the various contaminations sources

In spite of the numerous studies on the occurrence and origin of pesticides in surface waters, the relative importance of the various unintentional sources of contamination is difficult to assess. When samples are collected near known sources of pesticide pollution, the levels tend to be high. On the other hand, analysis of samples collected in monitoring programs indicate comparatively low levels of contamination because of the strong dilution that occurs after a pollutant is introduced into an aquatic system.

Unintentional introduction of pesticides from agriculture into surface water still requires considerable attention. In the present study, spray-drift from orchards to drainage ditches was investigated in more detail.

2 Introduction to the present research program

2.1 AGRICULTURAL EMISSION OF PESTICIDES TO SURFACE WATER

The literature data collected in Chapter 1 show the presence of various pesticides in surface waters. The reported concentrations vary widely, depending, for instance, on the size of the source, the distance from the source and the dilution.

One aspect of the research program of our laboratory is the contribution of agriculture to contamination of surface waters with pesticides. A number of situations with possible emission of pesticides from agriculture to surface water were described in Chapter 1.

If unintentional introduction of pesticides into surface water be expected, various questions have to be answered. These questions can be divided into three groups:

1. What are the sources? What is the extent of contamination? What is the frequency of emission? How can emissions be prevented or reduced?
2. What is the physico-chemical behaviour of specific pesticides after they have reached open water? What will be the resulting concentration-time relationships in surface waters?
3. What are the consequences of these concentrations for aquatic organisms and for the quality of the water in view of the intended use; for example as drinking water for man and animals, as irrigation water and as recreational water?

- Sources of agricultural contamination of surface water by pesticides can be characterized by inspection and by careful measurements if necessary. Local circumstances are important. Contamination of surface will depend heavily on the way pesticides are applied and on the care taken by the user.

Contaminations should be first of all be reduced by eduction, and by making the users more conscious of the problems. Preventive advisory activities should be directed to the people working with pesticides in the field. This aspect lends itself only to a limited extent for physico-chemical research.

In the present investigation, spray drift of pesticides from orchards to drainage ditches was investigated in some detail on a few fruit farms in the Lopikerwaard Polder (Chapter 9).

- Physico-chemical behaviour was the main aspect of study in surface water. Attention was paid to the adsorption of pesticides on ditch bottom material and to the penetration of pesticides into ditch bottoms. Conversion rates of pesticides were studied in surface water under different conditions and in bottom material. Transport and conversion were also investigated in field trials. Computation models were developed and used. A main object of the present study was to obtain a quantitative description of the concentration-time relationships for pesticides in watercourses.

- The consequence for aquatic organisms of the exposure to biologically active compounds is mainly a toxicological problem. This field of research is rather complex so that special research programs are required. In the present investigation, only a short compilation of literature data on the toxicity of two model pesticides for aquatic organisms was made (Section 3.6). Other potential problems associated with pesticide residues depend on the local situation and the specific use of the water.

2.2 LAY-OUT OF THE PRESENT RESEARCH PROGRAM

In view of the many questions to be answered (Section 2.1), this investigation was restricted to a few pesticides and to a few agricultural situations in which contamination of surface water by pesticides was likely.

At present, aquatic herbicides are only applied on a limited scale in the Netherlands. So model pesticides were selected which may unintentionally contaminate surface waters. Since the use of chlorinated hydrocarbon insecticides has been drastically reduced, mainly organophosphorus and carbamate insecticides are applied in horticulture and arable farming. Some of these compounds are rather toxic to various aquatic organisms. Although such compounds are generally less persistent than the chlorinated hydrocarbons, there was evidence that some of them may be rather persistent in surface waters. Conditions in aquatic media are so different from those in plants, in soil or on artificial surfaces, that special measurements on conversion rates in surface water are needed.

The important organophosphorus pesticides azinphos-methyl and dimethoate were selected as model compounds. The rates of conversion under aquatic conditions were largely lacking. A general characterization of the use and properties of azinphos-methyl and dimethoate is given in Chapter 3.

In an orientation stage of the investigation, various surface waters were sampled in the Kromme Rhine area and in the Lopikerwaard Polder (Province of Utrecht). Initially much attention was needed to the development of experimental methods and analytical procedures. Sampling of water and bottom material required special techniques (Chapter 4). Many problems had to be solved in gas chromatography at low levels of the compounds. Large amounts of interfering substances in all extracts of bottom material had to be removed (Chapter 5). The development of suitable clean-up procedures for these extracts required much attention.

Later it became evident that attention had to be focused on a few situations in which both model compounds were applied. Two fruit farms were selected for more detailed study, one near the village of Benschop and one near the village of Jaarsveld, both in the Lopikerwaard (Chapter 9). A criterion in the selection of sampling points was that on these farms the drainage ditches contained water throughout the growing season. Furthermore on both farms, the ditch systems were occasionally discharged by small pumping stations, which made it possible to estimate the water balance of the ditches (Chapter 10).

In the situations selected for the field trials, considerable drift from the orchards into ditches could be expected. The farms were traversed by several farm ditches. Several trees grow just alongside the ditches with their crowns above the water, so that inevitably a certain amount of the spray descended into the water. Although suitable objects for the present study, these situations are not common in fruit-growing areas. Local situations vary widely and should thus be considered. In most fruit-growing areas, the proportion of open water is far less; ditches may be dry during the growing season. Often fruit trees are separated from the ditches by a wind-break of trees, by a path, or by a sizable border. Thus it may be expected that contamination on the two farms would represent an upper limit of contamination rather than an average value.

At an early stage of the research, it became clear that field situations can be quite complex. So simpler trials were made in outdoor tanks, measuring the rate of decline in water and penetration into bottom material (Chapter 7). The decline trials in these outdoor systems were carried out under temperature and light conditions similar to those in the field.

In view of the large number of compounds and conditions of applications, there is a need for an initial characterization of the compounds in well defined laboratory tests. In laboratory tests, conversion rate and adsorption of azinphos-methyl and dimethoate were measured under controlled conditions (Chapter 6).

The evaluation of the behaviour of many pesticides under various conditions in surface water would require an enormous research capacity. It is not feasible to study all relevant compounds under all possible environmental conditions. Several principles in the behaviour of pesticides in surface water are of general nature; they can be applied to various contaminants under different circumstances. Therefore, computational models for the quantitative description of physico-chemical behaviour of pesticides in surface water are considered good tools in this research. These models aim at the quantitative description of concentration as a function of position and time (Chapters 8, 10 and 11). Detailed investigations for model pesticides could thus yield information of more general validity on the physico-chemical behaviour of pesticides in surface water.

In view of the complexity of aquatic systems and of the need for flexibility, the differential equations were solved numerically. The computer simulation language CSMP III (IBM, 1975) was used for programming the models.

The computation models were primarily considered to be research tools by which areas of too limited knowledge could be traced more clearly. The results of model computations provide a starting point for further investigations. Computation models may become more suitable for making predictions, starting from a limited set of basic data on the compound and from the hydrological situation.

3 Review of the use and properties of azinphos-methyl and dimethoate

3.1 APPLICATION OF AZINPHOS-METHYL AND DIMETHOATE IN FRUIT FARMING

For the control of harmful arthropods in arable farming, horticulture and landscape management, various pesticides are available (Gids voor Ziekten- en Onkruidbestrijding in Land- en Tuinbouw, 1977). The model compounds in the present study are approved for various purposes.

Azinphos-methyl can be used in apple and pear orchards, and in flower crops. The situation that received particular attention in this study was application in apple and pear orchards, where azinphos-methyl as 25% (w/w) wettable powder, may be used especially against caterpillars, and further against psyllids, apple blossom weevils, sawflies and pear blossom weevils.

Dimethoate is approved for use against harmful insects in various fruits. Further, this compound may be used on outdoor vegetables, potatoes, sugar-beet and cereals. The compound is also used to some extent on ornamentals, flower bulbs and on nursery stock. The applications of dimethoate in orchards, subject of the present investigation, are directed against aphids, psyllids, woolly aphids, capsids and sawflies. Dimethoate is used in different formulations, namely as 20% (w/w) wettable powder and as liquids of mass concentration 200 and 400 kg m^{-3}.

Combinations of azinphos-methyl and dimethoate, formulated as a wettable powder with 20% + 10% active ingredient, are approved for use against some insects on apples, pears, cabbages and potatoes. The number of applications of both insecticides or the mixture depends on the extent of occurrence of the insects, but often several applications may be necessary to control them. Nowadays sex pheromones can be used as a warning system for the presence of populations of summer fruit tortrix moths. By using this system of 'supervised control', the number of applications can sometimes be reduced (Minks & de Jong, 1975). For the wettable powder of azinphos-methyl, the recommended dose of product is 0.3 g m^{-2} (3 kg ha^{-1}) and that for 40% dimethoate is 0.1 cm^3 m^{-2} (1 litre ha^{-1}).

In the Netherlands, the maximum permitted residue of azinphos-methyl on apple and pear is 0.4 mg kg^{-1}; that for dimethoate is 0.6 mg kg^{-1}, but an increase to 1.5 mg kg^{-1} is under consideration. Safety periods between application and harvest for both insecticides on apple and pear are three weeks. Because of the toxicity of both compounds to bees, applications during flowering of fruit trees are not allowed (Gids voor Ziekten- en Onkruidbestrijding in Land- en Tuinbouw, 1977).

3.2 PHYSICO-CHEMICAL PROPERTIES OF THE COMPOUNDS

Physico-chemical properties of azinphos-methyl and dimethoate are tabulated in Table 5 and Table 6, respectively. These data show that both compounds have a rather low volatility, and that dimethoate is far more soluble in water than azinphos-methyl. Further information can be found in handbooks like that of Martin & Worthing (1977).

3.3 CONVERSION RATES AND PATHWAYS OF THE COMPOUNDS

The conversion rates of pesticides in soils and water under constant or under only slightly varying environmental circumstances can often be characterized by one rate constant. The following first-order rate equation can often be used:

$$dc/dt = -k_c\, c \qquad (1)$$

in which

c = mass concentration of substance ($mg\ m^{-3}$)

t = time (d)

k_c = rate coefficient for conversion (d^{-1})

Integration of Equation 1 yields

$$k_c = -\ln\,(c/c_0)/t \qquad (2)$$

Table 5. Physico-chemical properties of azinphos-methyl. Sources: (1) Bayer A.G. (1971); (2) Cavagnol & Talbott (1967); (3) Martin & Worthing (1977); (4) Spencer (1973); (5) Wäckers (1977).

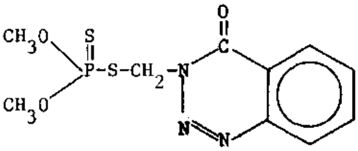
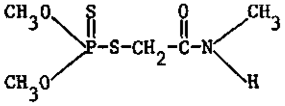
Chemical name	(3)	*O,O*-dimethyl *S*-[(4-oxo-1,2,3-benzotriazin-3-(4H)-yl)methyl] phosphorodithioate
Trade names	(3)	Gusathion (Bayer); Guthion (Chemagro)
Structural formula	(1)	
Molecular formula	(1)	$C_{10}H_{12}N_3O_3PS_2$
Molecular mass	(1)	317.3
Melting point	(1)	73-74 °C (pure compound)
	(2)	65-68 °C (technical material)
Vapour pressure	(3)	< 51 mPa at 20 °C
	(5)	ca 0.5 mPa at 25 °C
Solubility	(4)	in water about 33 $g\ m^{-3}$ at room temperature; soluble in many organic solvents

Table 6. Physico-chemical properties of dimethoate. Sources: (1) Martin & Worthing (1977); (2) Spencer (1973); (3) Wagner & Frehse (1976).

Chemical name	(1)	*O,O*-dimethyl *S*-[2-(methylamino)-2-oxoethyl] phosphorodithioate
Trade names	(1)	Cygon (American Cyanamid); Fostion MM, Rogor (Montecatini); Roxion (Cela); Perfekthion (BASF)
Structural formula	(2)	
Molecular formula	(1)	$C_5H_{12}NO_3PS_2$
Molecular mass	(1)	229.2
Melting point	(1)	51-52 °C
Boiling point	(3)	117 °C (13.3 Pa)
Vapour pressure	(3) (1)	1 mPa at 20 °C 1.1 mPa at 25 °C
Solubility	(1),(2)	in water 25 kg m^{-3} at 21 °C; most soluble in polar solvents such as methanol, ethanol and other alcohols; ketones such as acetone and cyclohexanone; lower solubility in apolar solvents such as xylene and aliphatics such as hexane

in which

c_o = concentration at time zero (mg m^{-3})

The half-life of a compound ($t_{\frac{1}{2}}$) is simply related to its rate coefficient, according the following relationship:

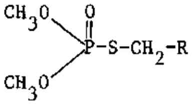
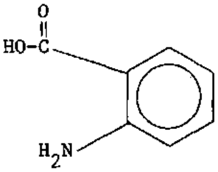
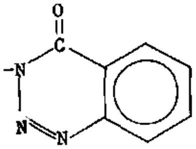
$$t_{\frac{1}{2}} = 0.693/k_c \tag{3}$$

Half-lives of azinphos-methyl and dimethoate in various media under different environmental conditions as reported in literature will be briefly discussed in the following sections. The literature data on rate coefficients of both compounds in surface water under various circumstances will be discussed in relation to our own experiments in water from outdoor tanks, which will be described in Chapter 6.

Conversion rates and pathways of azinphos-methyl

The conversion rate of azinphos-methyl on crops and tree fruits is dependent on various climatic conditions and on the nature of the plant material. On vegetables, forage crops and tree fruits grown under field conditions, the average half-life for azinphos-methyl ranges from 3 to 8 days (Chemagro Division Research Staff, 1974). However, under certain circumstances the half-life may be substantial longer. For example, Gunther et al. (1963) found that in California the half-life on and in the peel of Valencia oranges was

Table 7. Structural formulae of identified conversion products of azinphos-methyl (after Wieneke & Steffens, 1976).

(I)	Azinphos-methyl oxygen analogue	
(II)	Mercaptomethyl benzazimide	$H-S-CH_2-R$
(III)	Dimethyl benzazimide sulfide	$R-CH_2-S-CH_2-R$
(IV)	Dimethyl benzazimide disulfide	$R-CH_2-S-S-CH_2-R$
(V)	Benzazimide	$H-R$
(VI)	*N*-methyl benzazimide	CH_3-R
(VII)	Anthranilic acid	
	R =	

340-400 days.

The conversion products of [^{14}C]azinphos-methyl on bean leaves were investigated by Wieneke & Steffens (1976). They found that 16 radioactive compounds could be extracted with organic solvents. The compounds I, III or IV, and V from Table 7 were identified. Fourteen water-soluble products could not be identified. This can be seen as an indication of the difficulties in separation and analyses of polar and thus highly water-soluble conversion products of azinphos-methyl.

Studies on soil persistence of azinphos-methyl as described in the literature show that the conversion rate is dependent on many factors, such as formulation, moisture content of the soil, soil type, biological activity of the soil and various climatic conditions. Schultz et al. (1970) found that in field trials where azinphos-methyl was applied as an emulsion on a silt-loam soil 50% was lost in 12 days. Application in granular form followed by rotary tillage to a depth of 0.1 m required 28 days for a 50% loss. After 1 year, 13% of the applied granules was recovered in the form of azinphos-methyl. The conversion products II, III or IV, V and VI from Table 7 were identified. Four unidentified compounds were found. Yaron et al. (1974a) reported that in a silty loam soil (organic matter content lower than 1%, pH 8.4, cation-exchange capacity 134 mmol kg^{-1} and volume fraction of water 50%) the rate coefficient for conversion was 0.011 d^{-1} at 6 °C and 0.053 d^{-1} at 25 °C. Lower rate coefficients were found by Iwata et al. (1975) in dust from several sieved soils. The approximate rate coefficient for conversion at 30 °C with constant overhead illumination from fluorescent tubes ranged from 0.07 d^{-1} for a clay and a silt loam soil to 0.008 7 d^{-1} for a sandy loam and a loam soil. The moisture content was 40% of the maximum retentive capacity, as determined for unsieved soils.

Recently, the photodecomposition of $[^{14}C]$azinphos-methyl in a thin layer of soil (of 2 kg moist silt-loam per square metre of glass surface) was studied by Liang & Lichtenstein (1976). They found that, after 8 h exposure to sunlight, about 80% of the original dose was recovered by benzene extraction. Nearly 3.5% was converted to non-insecticidal water--soluble conversion products and approximately 16% was found as bound residue. In their control measurements in the dark, no degradation and no bound residues were found.

The effects of light and pH on the conversion of $[^{14}C]$azinphos-methyl in an aqueous solution of 2 g m^{-3} were investigated by Liang & Lichtenstein (1972). The conversion of azinphos-methyl in the aqueous solution exposed to ultraviolet light was very rapid. After two hours exposure, they found that 56% of the dose could be recovered by chloroform extraction; this phase consisted mostly of benzazimide (V) or the oxygen analogue of azinphos-methyl (I) (45% of ^{14}C applied), 4% anthranilic acid (VII) and only a few percent of compounds II, III or IV, and VI (Table 7). About 25% of the dose remained in the water phase and the missing radioactive material was assumed to be volatilized.

The conversion of azinphos-methyl in water is highly dependent on pH, as will be discussed in more detail in Chapter 6. Liang & Lichtenstein (1972) found that at pH 10 and pH 11 after 7 days at 25 °C, 18% and 97%, respectively of the dose of $[^{14}C]$azinphos-methyl was converted to water-soluble conversion products. At pH 10 the chloroform-soluble conversion products (82% of ^{14}C applied) consisted primarily of compounds III or IV, and VI, totalling 34% of the ^{14}C applied; 30% of the ^{14}C was converted to compounds V or I, and 18% of the ^{14}C was recovered as azinphos-methyl or compound II.

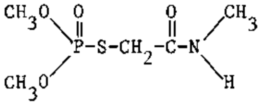
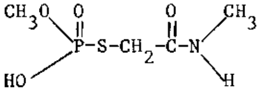
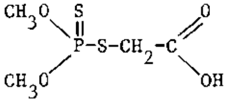
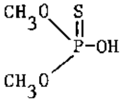
Conversion rates and pathways of dimethoate

Dimethoate shows a rather high rate of conversion in and on crops. For example, Bache & Lisk (1965) reported that the rate coefficient for conversion of dimethoate in field--sprayed lettuce was about 0.17 d^{-1}. Pree et al. (1976) found that 50% of dimethoate on apple-tree leaves disappeared in 2.3-7.2 d, dependent on time of application and formulation. Possible conversion pathways that may occur in plants were summarized by Menzie (1969; 1974).

Bohn (1964) investigated the decline rate of dimethoate in a sandy loam soil (pH 5.5) after application of 1 kg of active ingredient per hectare (0.1 g m^{-2}) as emulsifiable concentrate. The sampling depth was 7.5 cm. Under drying conditions, k_c was 0.17 d^{-1} and after 33 mm of rainfall k_c was 0.28 d^{-1}. In incubation studies, Bache & Lisk (1966) found a k_c of 0.43 d^{-1} in a moist silt-loam soil (pH 5.8). When dimethoate was mixed in a moist loam soil (2.3% organic matter, pH 5.7, 75% of field capacity) and placed in a light room at 20-30 °C, the rate coefficient for conversion was found to be 0.021 d^{-1} (Bro-Rasmussen et al., 1970). Significant conversion of dimethoate to its oxygen analogue (VIII, Table 8) was measured in different soils by Bache & Lisk (1966) and by Duff & Menzer (1973).

Radioactive $[^{32}P]$dimethoate was rapidly hydrolysed in water at pH 11. In 2 h, 87% of the dimethoate was converted to water-soluble materials, which remained in the aqueous phase upon extraction with chloroform. The water-soluble conversion products were predomi-

Table 8. Structural formulae of conversion products of dimethoate.

(VIII)	Dimethoate oxygen analogue (= omethoate, dimethoxon) Tradename Folimat	
(IX)	Des-methyl dimethoate	
(X)	Dimethoate carboxylic acid	
(XI)	Dimethyl thiophosphoric acid	

nantly des-methyl dimethoate (IX) (49.3%) dimethyl thiophosphoric acid (XI) (32.8%) and dimethoate carboxylic acid (X) (9.5%) (Table 8). More than 97% of the labelled material in the chloroform extract (about 13% of the ^{32}P) was found to be unchanged dimethoate (Brady & Arthur, 1963).

3.4 ADSORPTION AND LEACHING OF THE COMPOUNDS IN SOIL

The extent to which pesticides are leached in soils is mainly determined by adsorption coefficient, rate coefficient for conversion of the compound, characteristics of the soil, climatic conditions and plant growth. The extent of groundwater pollution through leaching under various conditions can be approximated with computational models (Leistra & Dekkers, 1976).

In Table 9, adsorption data of azinphos-methyl are reported as measured by Bayer A.G. (1978). The adsorption coefficients, determined by a batch-equilibrium technique show that azinphos-methyl will be rather strongly adsorbed on soils. This can be expected in view of its low solubility in water. Because of the relatively high adsorption coefficient and a considerable rate of conversion under some field conditions, azinphos-methyl may be transported in soils to only a small depth. For example, Yaron et al. (1974b) found that azinphos-methyl was not transported deeper than 0.3 m in a sandy loam soil (organic matter content of 0.6% and pH 8.4) after irrigation at a rate of 0.28 m irrigation water over 38 days.

The systemic insecticide dimethoate is highly soluble in water (Table 6) and is adsorbed to only a limited extent on soil material. For example, the adsorption coefficient onto a silt loam soil (organic matter content of 2.7%) is about $0.21\ 10^{-3}\ m^3\ kg^{-1}$ (Graham-Bryce, 1969). Whether groundwater pollution with dimethoate will occur depends on many factors. The leaching of dimethoate from a sandy loam field with a potato crop can be estimated from the results of the simulation experiments of Leistra & Dekkers (1976). Assuming a rate coefficient for conversion of 0.03 d^{-1} (Section 3.3), an adsorption coeffi-

Table 9. Soil characteristics and adsorption coefficients of azinphos-methyl as measured by Bayer A.G. (1978).

Soil	% Clay (<2 µm)	% Silt (2-50 µm)	% Organic matter	pH (water)	$K_{s/1}$ (m^3 kg^{-1})
Sandy loam	10.5	33.1	1.1	6.4	$3.3\ 10^{-3}$
Silt-loam	20.5	62.8	1.8	5.5	$11.0\ 10^{-3}$
Highly organic silt-loam	19.0	56.8	4.6	5.4	$28.5\ 10^{-3}$

cient zero and an annual infiltration of rainfall 0.66 m, the extent of leaching from a top layer 1 m thick was computed to be less than 0.1% of the dose.

3.5 VOLATILIZATION OF THE COMPOUNDS FROM WATER BODIES

The rate of volatilization of pesticides from water bodies to the atmosphere can be estimated by procedures of Liss & Slater (1974) and of Mackay & Leinonen (1975). They used a two-layer model, composed of a liquid film and a gas film separated by gas--liquid interface. The main body of each fluid was assumed to be well mixed. Transfer of the pesticides through the layers was by molecular diffusion, which can be described by Fick's first law. The areic mass flux F_v (mg m^{-2} d^{-1}) across the gas--liquid interface by volatilization can then be expressed as a function of the concentration difference across the layers and the exchange constants for the liquid and gas phases, respectively, as shown in Equation 4.

$$F_v = k_l(c_w - c_{i,w}) = k_g(c_{i,a} - c_a) \tag{4}$$

in which

c_w and c_a	are mass concentrations of substance in open water and in free air	(mg m^{-3})
$c_{i,w}$ and $c_{i,a}$	are equilibrium mass concentrations of substance at gas--liquid interface	(mg m^{-3})
k_l and k_g	are exchange coefficients for liquid and gas phases	(m d^{-1})

If the exchanging compound obeys Henry's law, then, at the equilibrium presumed at the interface

$$c_{i,a} = H\ c_{i,w} \tag{5}$$

in which

H = Henry's constant (1)

This constant can be estimated from the quotient of mass concentration of saturated vapour (via vapour pressure) of the compound and the solubility of the compound in water.

Elimination of $c_{i,a}$ and $c_{i,w}$ in Equations 4 and 5 yields

$$F_v = (c_w - c_a/H)/\left[1/k_l + 1/(H\,k_g)\right] \tag{6}$$

which can be written as

$$F_v = k_{t,l}(c_w - c_a/H) \tag{7}$$

and

$$1/k_{t,l} = 1/k_l + 1/(H\,k_g) \tag{8}$$

in which

$k_{t,l}$ = overall liquid phase transfer coefficient (m d^{-1})

The mass transfer coefficients can be considered to be conductivities and their reciprocals to be resistances by analogy to Ohm's law.

Combining the areic mass flux, F_v, across the interface in a balance equation in an unsteady state model (and assuming no other pathways of loss) leads to the differential Equation 9:

$$\mathrm{d}(h_w\,c_w)/\mathrm{d}t = -k_{t,l}(c_w - c_a/H) \tag{9}$$

in which

h_w = water depth (m)

If c_a is negligible, which means that the background atmospheric level of the compound is low, then Equation 9 can be simplified and a half-life $t_{\frac{1}{2},v}$ can be simply derived from Equation 9:

$$t_{\frac{1}{2},v} = 0.693\ h_w/k_{t,l} \tag{10}$$

in which

$t_{\frac{1}{2},v}$ = volatilization half-life (d)

The significance of volatilization for the model compounds was estimated by Equation 10, using the data from Tables 5 and 6. Water depth was assumed to be 0.2 m. The transfer coefficients (k_l and k_g) at 25 °C were estimated by the procedure of Liss & Slater (1974). The volatilization half-lives of azinphos-methyl and dimethoate were calculated to be 413 d and 0.17 x 10^6 d, respectively. At lower air temperature (prevailing under field conditions), the volatilization half-lives could be even longer. The volatilization of $[^{14}C]$-azinphos-methyl from tap water at 30 °C was measured by Lichtenstein & Schultz (1970). They found that after one day only traces of radioactive azinphos-methyl were found in vapour traps. The preliminary conclusion is that the rate of volatilization of the model compounds from surface waters will be of minor importance.

3.6 SOME TOXICOLOGICAL DATA OF THE COMPOUNDS

Azinphos-methyl

The acute oral LD_{50} of azinphos-methyl for female and male rats varies between 10-20 mg per kilogram liveweight (Bayer A.G., 1971). The toxicity of metabolites of azinphos-methyl has been indicated by the WHO as an area for further research (WHO/FAO, 1974).

The acute toxicity of azinphos-methyl to a variety of aquatic organisms has been reviewed by US Environmental Protection Agency (1973). However the reported American species of aquatic organisms are not fully comparable with the species occurring in Dutch surface waters. Nevertheless, some data are shown in Table 10. These date show the high acute toxicity of azinphos-methyl to crustaceans, several fish species and some salt-water organisms. The differences in the acute toxicity to aquatic organisms are first of all determined by the susceptibility of the species. However, materials and test methods may cause substantial variation in the acute toxicity. It is well known that acute toxicity can be modified by factors like formulation, temperature, water hardness, animal size and age, previous exposure, physiological condition, and occurrence of other pesticides.

More research on semi-chronic and chronic effects and no-effect levels of azinphos-

Table 10. Toxicity of azinphos-methyl to aquatic organisms. Sources: (1) References in US Environmental Protection Agency (1973); (2) Adelman et al. (1976); (3) Bayer A.G. (1971); (4) Portmann & Wilson (1971).

Organisms	Acute toxicity (LC_{50})[1]		No effect level	Source
	mass conc ($mg\ m^{-3}$)	exposure time (h)		
Crustaceans:				
Gammarus fasciatus	0.10	96		(1)
Asellus brevicaudus	21	96		(1)
Insects:				
Ophiogomphus rupinsulensis	12	96	1.73 (30 d)	(1)
Pteronarcys californica	1.5	96		(1)
Fishes:				
Perca flavescens	13	96		(1)
Ictalurus punctatus	3 290	96		(1)
Micropterus salmoides	5	96		(1)
Pimephales promelas	1 950	96	0.51 (test on fecundity)	(2)
Lebistes reticulatus	100	96		(3)
Carassius auratus	> 1 000	96		(3)
Saltwater organisms:				
Pandalus montagui	0.3-1	48		(4)
Crangon crangon	0.3-1	48		(4)
Carcinus maenas	33-100	48		(4)

1. LC_{50} is the mass concentration of toxicant that kills 50% of the organisms exposed to it during a specified exposure time.

-methyl on aquatic organisms will be necessary to recommend criteria for water quality.

Dimethoate

The acute oral LD_{50} of dimethoate for white rats is 600 mg kg^{-1} (Dauterman et al., 1959). Those for the oxygen analogue of dimethoate (omethoate), des-methyl dimethoate, and dimethoate carboxylic acid (Table 8) were found to be 55, 1500-2000 and 2500-3000 mg kg^{-1}, respectively (Dauterman et al., 1959). Thus the oxygen analogue is the most toxic compound.

Toxicity data of dimethoate to aquatic organisms are presented in Table 11. These data show that dimethoate is hardly toxic to fish, but some salt-water organisms were shown to be very sensitive to dimethoate. Omethoate appeared to be much more toxic to *Daphnia magna* than dimethoate.

Table 11. Toxicity of dimethoate to aquatic organisms. Sources: (1) Canton (1977); (2) Martin & Worthing (1977); (3) Portmann & Wilson (1971).

Organisms	Acute toxicity (LC_{50})		Source
	mass conc (mg m^{-3})	exposure time (h)	
Crustaceans:			
Daphnia magna	6 400	48	(1)
(Same species, omethoate)	31	48	(1)
Fishes:			
Gambusia affinis	40 000-50 000	96	(2)
Salmo gairdneii	10 000	48	(1)
Lebistes reticulatus	570 000	96	(1)
Saltwater organisms:			
Pandalus montagui	33	48	(3)
Crangon crangon	0.3-1	48	(3)
Carcinus maenas	> 3 300	48	(3)

4 Sampling of water and bottom material in ditches for analysis of pesticide residues

4.1 SHORT REVIEW OF DEVICES AND PROCEDURES FOR WATER SAMPLING

Various procedures have been described for the collection of samples from surface waters. As yet, methods and terminology for water sampling have not been standardized (Josephson, 1974). For pesticides, the selection of methods is determined by the objectives of the study and the sampling situation (Monitoring Panel of FWGPM, 1974; US Environmental Protection Agency, 1974).

One should always be aware of possible interactions between pesticides and sampler components. Many pesticides show strong adsorption on the surface of materials like rubber and plastics, which are commonly used for collecting water samples. Parr et al. (1974) sometimes found a considerable adsorption by sampler components. Various admixtures may be released from polymers, which interfere with chemical analysis of the pesticides. Therefore as inert a material as possible (preferably glass or stainless steel) should be used for sampling. Poly(tetrafluoroethylene) (Teflon) will presumably often not contaminate the sample (Feltz et al., 1971).

Water can be sampled by lowering some glass or stainless steel container into the water body. Filling of the container while held just beneath the water surface avoids skimming off a floating film, through which a sample would not be representative. Feltz & Culbertson (1972) pointed out that a high percentage of all water samples in pesticide monitoring programs was obtained by shallow emersion of containers. Such samples are commonly referred to as dip or grab samples.

Especially pesticides showing a hydrophobic character, for instance most of the chlorinated hydrocarbons, may not be equally distributed over the depth of a watercourse. The highest concentrations of these pesticides may occur at the surface, especially if this is covered by an oily film. If water samples need to be almost free from floating materials, bottle-samplers can be improved by constructing a spring-loaded cap. These spring-loaded caps can be opened at any desired depth by pulling on a line. A recent construction was described by Gump et al. (1975). Mitchell & Dickey (1973) developed a sampler with a spring-loaded locking unit that allowed sampling of water from small ponds or lagoons by one person standing on the bank.

Besides the dip samplers, two other groups of sampling devices are in common use, particularly in automatic water-sampling programs, namely pump and vacuum samplers. A disadvantage of these types is the risk that the orifices of the suction pipe may get plugged. Most of the automatic water samplers need electric power supply for pumping and for cooling the samples. An exception is a vacuum-type of sampler composed of bottles evacuated before sampling and equipped with pinch valves (Hergert & Gall, 1973). These valves are opened in turn by a timed trigger. This sampler has separate tubes for each sampling. A disadvantage of this sampler is again possible adsorption on and release from the PVC tubes and the rubber closing tubes. Modification will be necessary for the sampling of waters in studies on pesticides.

4.2 WATER SAMPLING IN THE PRESENT STUDY

Dip samples from the small drainage ditches were collected with a small barrel attached to a telescopic fishing rod, with a maximum length of nearly 4 m. The volume of the stainless steel barrel was 0.4 dm^3 (Figure 2b). By bulking the dip samples, average concentrations in ditches can be measured. Ten subsamples were taken and collected in a glass bottle of volume 2 dm^3 which was closed with a ground-glass stopper. Before using these bottles, they were thoroughly cleaned by alkali treatment, rinsed with distilled water and re-distilled acetone and oven-dried at 110 °C.

To collect water samples from wider and deeper watercourses, a sampling device was constructed of a telescopic fishing rod with a removable glass bottle, volume 1 dm^3, fit-

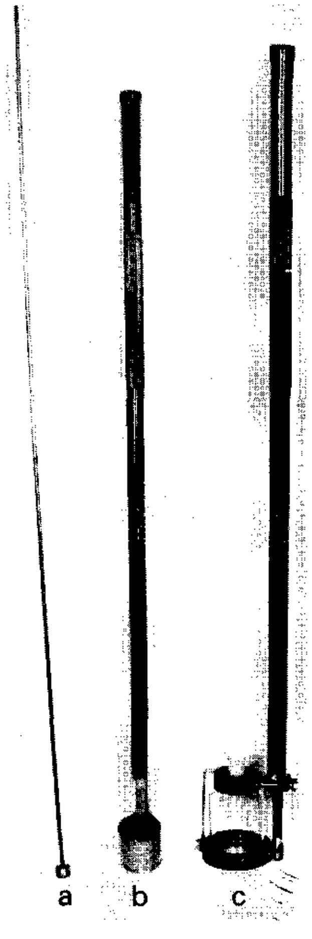


Figure 2. Water sampling devices used in the present study.
a. Stainless steel tube used for sampling of drainage ditches and groundwater.
b. Stainless steel dip sampler used for sampling of drainage ditches.
c. Glass dip sampler used for sampling of large watercourses.

ted at the end. The extended length of this fishing rod was more than 5 m (Figure 2c). From bridges over such watercourses, the glass bottle was repeatedly lowered to the bottom and slowly raised to the water surface during filling. This procedure was repeated at different places across the water body to get a sample representative for the entire cross--section.

For detailed measurement of the distribution of pesticide residues in ditches after spray-drift contamination, a simple vacuum-type sampler was developed. This sampler consisted of a stainless steel tube (inner diameter 6 mm) fitted with a copper wire netting filter at the end (openings of 0.33 mm) and connected to a glass bottle of 2 dm^3 with stopper and cock (Figure 2a). This bottle was evacuated with a hand-operated vacuum pump. The same sampling equipment was used for sucking up groundwater samples from groundwater tubes (Section 9.3.11).

This vacuum-type of water sampler was also used for taking samples during dispersion measurements in watercourses with flowing water (Chapter 11). For this purpose, the suction capacity was enlarged by adding a vacuum reservoir of glass, volume 10 dm^3. Four seperate stainless steel tubes were installed with the lower end at different positions in the wetted cross-section of the ditch and each was connected to a glass bottle of 0.25 dm^3. These small bottles were connected, by polyethylene tubes and glass cocks, to the evacuated glass reservoir. Thus four samples could be sucked up nearly simultaneously within a few seconds.

4.3 SHORT REVIEW OF DEVICES AND PROCEDURES FOR SAMPLING BOTTOM MATERIAL

Water and bottom sediment must be sampled almost simultaneously for study of the physico-chemical behaviour of pesticides in ditches. In many instances, pesticide concentrations in the ditch bottom decrease strongly with depth. For accurate sampling of bottom material, good methods are needed giving least disturbance and allowing division of the sample into thin layers.

Little progress had been made in developing equipment to collect representative samples near the liquid--solid interface, which is difficult to sample without disturbance (Monitoring Panel of FWGPM, 1974).

Sampling of the bottom material in ponds and ditches for analysis of pesticide residues usually involves dredging or coring devices. The well-known Ekman dredge (Lamotte & Bourlière, 1971), widely used for biological surveying, is also used for soft bottoms in pesticide monitoring programs. The main disadvantage of the Ekman dredge and other dredging devices is that part of the water and bottom material is squeezed out of the dredge when it is closed. Further, many grab samples are collected from unascertainable depth (Aarefjord, 1972; Larimore, 1970). To overcome this problem, Jackson (1970) constructed a controlled-depth volumetric bottom sampler. Concentrations of camphechlor (Toxaphene) in samples of lake sediments obtained with an Ekman dredge were generally much less than those in samples obtained with a corer (Veith & Lee, 1971). These authors measured contents expressed in dry mud of 6.2 mg kg^{-1} in dredge samples and of 90.0 mg kg^{-1} in the 0 to 0.05 m section of core samples.

Coring devices allow more detailed measurement of pesticide distribution with depth in mud bottoms of watercourses. However, the sediment column can easily be disturbed during sampling, for example when obstacles like twigs or leaves obstruct the cutting edge of the coring device. Moreover, most core samplers lack effective seals to hold a sample in place when the sampler leaves the water (Feltz & Culbertson, 1972). Serious disturbance can occur with some samplers, which must be turned over before lifting from the bottom surface (Thayer et al., 1975).

In relatively deep watercourses with a soft bottom, nearly undisturbed mud cores can be taken with a Jenkin mud sampler (Mortimer, 1942). This sampler consists of a removable core tube in a framework, with a spring-loaded locking system that slowly closes a bottom lid just before a top one.

4.4 SAMPLING OF BOTTOM MATERIAL IN THE PRESENT STUDY

To sample bottom material in relatively shallow ditches with little disturbance, a coring device was constructed by the Technical and Physical Engineering Research Service in Wageningen. This corer consists of a poly(methyl methacrylate) (Perspex) sample holder (inner diameter 80 mm) with a sharp stainless steel cutting edge on the lower end and a closing system on top (Figures 3 and 4). Adsorption of both model compounds on Perspex was measured to be very low.

To obtain a mud sample, the holder (with both sides open) was gently lowered vertically through the water into the ditch bottom, till the upper end of the holder nearly reached the water-sediment interface. Next, the top of the holder was tightly closed by turning a milled knob at the top of the rod (Figure 4). The holder containing the column of mud and water was slowly raised and the lower end of the holder was stoppered with a polyethylene cap, while it was still under water. After removing the rod section, the top of the holder was also stoppered with a polyethylene cap. Since the tubes were transparent, immediate visual inspection of the intact mud core was possible.

The holder stoppered at both ends was placed vertically in a crate, in which six columns could be carried to the laboratory without disturbance.

The overlying water was slowly removed and for a few days the column was placed vertically in a deep-freezer at -20 °C. By pouring warm water along the outside of the tubes, the frozen-mud column could be quickly removed. This column was again placed in the deep--freezer at -20 °C, pending division into thin slices, extraction and analysis.

Undisturbed mud cores to test for pesticide residues in tank experiments were taken with poly(methyl methacrylate) tubes (inner diam. 40 mm ; out diam. 50 mm; length 410 mm), bevelled at the lower end. During sampling, the holder was slowly pushed into the bottom material and was closed at the upper end with a stopper before lifting. After raising the holder from the bottom, another stopper was pushed into the lower end, just before lifting the tube above the water. In the laboratory, the columns were processed in the same way as the ditch-bottom columns, removing the overlying water and freezing at -20 °C.

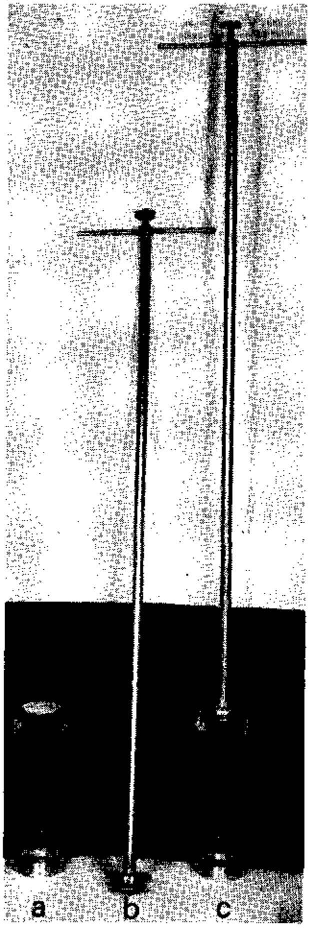


Figure 3. Sampler for bottom material.
a. Poly(methyl methacrylate) tube.
b. Stainless steel rod with closing system.
c. The tube connected to the closing system with two adjustable catches.

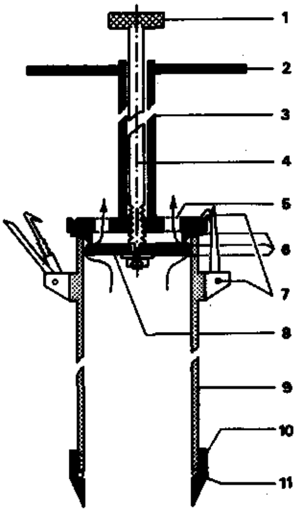


Figure 4. Cross-section of the sampler for bottom material. 1 Milled knob. 2 Handgrip. 3 Stainless steel tube, inner diam. 19 mm, outer diam. 25 mm. 4 Stainless steel rod, diam. 12 mm, with screwthread below. 5 Cover plate with six bore holes, diam. 12 mm. 6 Rubber washers. 7 Two adjustable catches. 8 Stainless steel flange. 9 Poly(methyl methacrylate) sample holder, inner diam. 80 mm, outer diam. 90 mm. 10 Stainless steel cutting ring. 11 Rubber ring. 12 Polyethylene cover.
Working principle:
Before lowering into the ditch, the flange 8 must be screwed down with the milled knob 1. When lifting, the flange 8 must be closed against the stainless steel edge of the cover plate 5.

5 Procedures for chemical analysis for azinphos-methyl and dimethoate in surface water and bottom material

5.1 INTRODUCTION

The procedure for the analysis of pesticides in samples of water and bottom material involves various stages. Firstly, the pesticide or its conversion product must be extracted as selectively and efficiently as possible from the water or mud sample into a suitable solvent. The extract will then usually be cleaned up to eliminate compounds interfering with detection. Many pesticides and sometimes also their conversion products can then be measured quantitatively by gas--liquid chromatography. Finally, an additional identification may be necessary to confirm results.

5.2 METHODS FOR EXTRACTION OF PESTICIDES FROM SURFACE WATERS

Two types of extraction methods may be used for extraction of pesticides from surface water. Over several years, mainly liquid--liquid extraction methods have been used. In recent years, techniques involving adsorption on various solid adsorbents in columns have received growing attention.

The liquid--liquid extraction methods can be divided into batch equilibration and continuous extraction procedures. A limiting factor for liquid--liquid extraction methods may be the partitioning of the pesticide between solvent and aqueous phase. Repeated extraction with comparatively large volumes of solvent may be required to get acceptable recovery of rather polar substances from water. Examples are the rather polar and thus water-soluble metabolites of various organophosphorus pesticides.

The batch equilibration/extraction technique, using a separatory funnel, often yields high recoveries of apolar to slightly polar organochlorine and organophosphorus pesticides (Konrad et al., 1969; Greve, 1972, Ripley et al., 1974). An advantage is that a large number of samples can be readily extracted. A disadvantage of the separatory funnel extraction procedure may be the limited volume of water that can be extracted at one time. Continuous liquid--liquid extraction techniques allow extraction of large volumes of water, thus in principle much lower concentrations can be measured (Goldberg et al., 1971; Meijers & van de Leer, 1976). However, most of the continuous liquid--liquid extraction procedures are too cumbersome for analysis of large numbers of samples. Further there may be chemical conversion of the pesticide during the heating of the solvent in continuous extractors with a distiller.

The other group of extraction methods is based on adsorption onto an adsorbent in a column. The extraction efficiency of pesticides from water samples with some non-ionic materials will be discussed briefly.

Activated carbon is highly suitable for adsorption of several pesticides from water, but adsorbed pesticides are difficult to elute completely. Extraction of organophosphorus pesticides from the activated carbon usually gives low recoveries (Eichelberger & Lichtenberg, 1971a).

Polymeric resin Amberlite XAD-2 (a polymer of styrene and divinyl benzene with low polarity) may be used for extraction of several organochlorine pesticides and polychlorinated biphenyls from natural waters (Coburn et al., 1977). A disadvantage of such resins is that before use, extensive cleaning of the resins with solvents is necessary to reduce the background of interfering compounds to acceptable levels.

Polyurethane foams are only adequate for adsorption of apolar organochlorine pesticides and polychlorinated biphenyls (Musty & Nickless, 1974).

Preliminary results described by Leoni et al. (1975) indicate that the use of Tenax (a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide made by AKZO, Arnhem) is promising for extraction of pesticides from water. Particularly the extraction of organophosphorus pesticides yielded reasonable results, even at low concentration (1 mg m^{-3}).

The adsorption of pesticides from surface waters may be adversely affected by the presence of other contaminants and natural substances in water (such as surfactants, fatty substances and algae). Extraction of large volumes of surface water with adsorbents may also yield high concentrations of interfering compounds. Further detailed investigations are necessary before the adsorption techniques may be utilized for extraction of organophosphorus pesticides.

5.3 EXTRACTION OF AZINPHOS-METHYL FROM WATER SAMPLES

Azinphos-methyl and its oxygen analogue were extracted from samples of surface water with a liquid--liquid extraction method (Greve, 1972). The unfiltered water samples (0.1 dm^3 from the tanks and usually 1 dm^3 from watercourses) were extracted in a separatory funnel with consecutively 100, 50 and 50 cm^3 portions of dichloromethane by handshaking each time for one minute. The combined extracts were dried on calcinated granular Na_2SO_4, concentrated to a few cubic centimetres in a Kuderna--Danish equipment and evaporated to dryness at room temperature with a gentle stream of nitrogen gas. The residue was dissolved in a known volume (0.5 cm^3 or more) of a suitable solvent (acetone, hexane or ethyl acetate) corresponding to the solvent used for the reference solution. The solutions were immediately placed in a deep-freezer to avoid chemical conversion and evaporation of the solvent, before clean-up and gas chromatography. The procedure was sufficiently rapid to allow extraction of up to 24 water samples in a day.

The mean recoveries of azinphos-methyl and its oxygen analogue from spiked water samples are presented in Table 12. The levels of spiking (in duplicate) were 1, 10 and 100 mg m^{-3} for azinphos-methyl in 6 drinking water samples and 100 mg m^{-3} for azinphos-methyl and its oxygen analogue in 12 surface water samples. At the three spiking levels, no significant differences were found in the recovery of compounds. The effects of shaking intensity was investigated because some surface waters containing many algae tended to form heavy emulsions during vigorous shaking. Nearly all surface water samples were extracted by 'normal' shaking (about 80 shakes per minute) yielding good recoveries for azinphos-methyl and its oxygen analogue.

Table 12. Recoveries of azinphos-methyl and its oxygen analogue from spiked water samples.

Compound	Type of water	Details on procedure[1]	Number of extractions	Recovery (%)	Coefficient of variation (%)
Azinphos-methyl	drinking water	normal shaking	6	100	4
		slow shaking	6	87	7
		vigorous shaking	6	96	9
		double volume of solvent	6	104	2
	surface water	normal shaking	12	99	3
Azinphos-methyl oxygen analogue	surface water	normal shaking	12	101	5

[1] The slow, normal and vigorous shaking was with about 40, 80 and 120 shakes per minute, respectively.

5.4 EXTRACTION OF DIMETHOATE FROM WATER SAMPLES

With the procedure for extraction of azinphos-methyl from surface water (Section 5.3), dimethoate could also be extracted with acceptable recoveries (Table 13). The comparatively polar dimethoate was only moderately extracted by slow shaking. The polar oxygen analogue of dimethoate was poorly extracted with the volume of dichloromethane used in the standard extraction. High recovery of the oxygen analogue could be obtained by extraction of small water samples (50 cm^3) with consecutively 100, 50, 50 and 50 cm^3 portions of chloroform, which resulted in an average recovery of 91% (coefficient of variation 5%).

5.5 METHODS FOR EXTRACTION OF PESTICIDES FROM BOTTOM MATERIAL

Pesticides can be extracted from soils and bottom material by a variety of techniques such as shaking, tumbling, blending, Soxhlet refluxing and ultrasonic vibration. The choice of the solvents or solvent combinations depends mainly on the nature of the substance

Table 13. Recoveries of dimethoate from spiked water samples.

Type of water	Details on procedure[1]	Number of extractions	Recovery (%)	Coefficient of variation (%)
Drinking water	normal shaking	6	88	7
	slow shaking	6	69	11
	vigorous shaking	6	90	8
	double volume of solvent	6	96	2
Surface water	normal shaking	12	94	3

[1] The slow, normal and vigorous shaking was with about 40, 80 and 120 shakes per minute, respectively.

to be extracted (Caro & Taylor, 1976). Little information was available on the effect of the spiking method or equilibration conditions on the extractability of pesticides from bottom materials.

In many instances, rather polar solvents have to be used, which will co-extract comparatively large amounts of interfering substances from the bottom materials. Consequently, the extraction will nearly always have to be followed by cumbersome clean-up procedures.

5.6 EXTRACTION OF AZINPHOS-METHYL FROM BOTTOM SAMPLES

Several combinations of organic solvents were tested to minimize the amount of co-extractants, which interfere in the gas chromatography of azinphos-methyl. Finally, a mixture of 200 cm^3 *n*-hexane, 25 cm^3 dichloromethane and 25 cm^3 acetonitrile proved to be suitable. Thin slices of bottom material were extracted once with this mixture of solvents by shaking mechanically for 2 h. The liquid phase of the extraction slurry was collected with a pressurized membrane filter, equipped with an inert silicate-fibre filter.

The *n*-hexane--dichloromethane fraction was separated from the water--acetonitrile layer in a separatory funnel, then dried with anhydrous sodium sulphate and filtered over a Pyrex glass-filter (average pore size 90-150 μm). The final volume of the *n*-hexane--dichloromethane fraction was noted to allow corrections for losses during the different manipulations. The latter solution was concentrated in Kuderna--Danish equipment to a few cubic centimetres and evaporated to dryness with a gently stream of nitrogen gas. Then the residue was dissolved in a small volume of hexane (0.5 cm^3) ready for further clean-up.

5.7 EXTRACTION OF DIMETHOATE FROM BOTTOM SAMPLES

Slices of bottom material from the outdoor tanks (Section 7.4) were extracted once by shaking mechanically for 2 h with 25 cm^3 of distilled water and 50 cm^3 of ethyl acetate. The liquid phase of the extraction slurry was filtered off through a Büchner funnel with 15 g of Celite Hyflo Supergel. The ethyl acetate phase was separated from the aqueous phase in a separatory funnel and dried with anhydrous sodium sulphate. The losses of ethyl acetate during the procedure were noted to allow the necessary corrections.

The extracts were concentrated in a rotary evaporator and, after clean-up, measured by gas--liquid chromatography. The method yielded a good recovery of spiked samples of bottom material (Section 5.12) but the use of Hyflo hampered rapid estimation of dry mass of the bottom material.

5.8 METHODS FOR CLEAN-UP OF EXTRACTS

Various clean-up procedures in estimating residues of pesticides in water have been described (Chesters et al., 1974; Fishbein, 1975). Co-extracted materials interfering in the analysis are usually removed by adsorption chromatography, in which the adsorbent Florisil is widely used. This material retains the polar co-extractives very well, whereas apolar chlorinated hydrocarbon pesticides may be easily eluted with an apolar solvent. With the more polar organophosphorus pesticides, such separations are more difficult.

Moreover, it seems that some insecticides may be firmly bound on Florisil (Kadoum, 1967). Another widely used adsorbent, silica gel, has been successfully used to separate chlorinated and organophosphorus pesticides from co-extractives (Kadoum, 1967; Leoni, 1971).

The interfering compounds in extracts from bottom materials are usually removed also by adsorption chromatography. For example, Law & Goerlitz (1974) separated PCBs, DDT and related compounds and chlordane in such extracts from interfering substances by using two chromatographic columns filled with aluminium oxid and silica gel, respectively. Little information is available on suitable clean-up procedures for organophosphorus pesticides in extracts from bottom material.

Clean-up procedures often need to be checked and modified for each combination of pesticide and sampling place, because bottom material may contain varying amounts of specific interfering compounds.

5.9 CLEAN-UP FOR AZINPHOS-METHYL EXTRACTS FROM WATER

The liquid-chromatographic system consisted of a glass column of length 80 mm and inner diameter 10 mm filled with 4 g dry silica gel (Kieselgel Woelm, 32-63 µm, non-activated and used as received).

The extract, dissolved in 0.5 cm^3 ethyl acetate, was applied to the column, which was eluted with ethyl acetate supplied from a glass reservoir mounted at a height of about 0.5 m above the top of the column.

The first eluate fraction of 5 cm^3 (yellow) was discarded. The second fraction (7 cm^3) of the eluate contained azinphos-methyl. The average recovery from 6 spiked extracts of water samples was 96%, with a coefficient of variation of 3%. This simple clean-up procedure allowed quick removal of many interfering substances from extracts of surface water.

5.10 CLEAN-UP FOR DIMETHOATE EXTRACTS FROM WATER

The procedure described in Section 5.9 was also used for clean-up of dimethoate in extracts of surface water. Dimethoate eluted in a fraction of 22 cm^3, immediately after the fraction containing azinphos-methyl. The average recovery of dimethoate from 7 spiked extracts was 92% with a coefficient of variation of 3%.

5.11 CLEAN-UP FOR AZINPHOS-METHYL EXTRACTS FROM BOTTOM MATERIAL

The measurement of azinphos-methyl in bottom material from the tanks and ditches required a thorough clean-up to eliminate several highly interfering substances. Various systems of liquid adsorption chromatography had to be tested before an acceptable method could be developed.

In a glass tube (200 mm long and with an inner diameter of 8 mm) 2.8 g non-activated silica gel was poured, to a height of 180 mm. The extracts of azinphos-methyl were applied to the top of the column, which was then eluted with a concave gradient of dichloromethane in *n*-hexane. This gradient was made by constructing a gravity flow system, using a measuring cylinder (with 50 cm^3 *n*-hexane) and a conical flask (with 80 cm^3 dichloromethane).

The first eluate fraction (80 cm^3) with many interfering substances was discarded; the second eluate fraction (23 cm^3) contained azinphos-methyl. The average recovery (16 runs distributed over various measuring series) from bottom material extracts spiked with azinphos-methyl was 91% with a coefficient of variation of 7%.

Sometimes air bubbles appeared in the gravity system, which influenced the elution process. Therefore this system was replaced by a pumping system. The same solvents were used, resulting in nearly the same elution pattern. This improved system was quicker, yielded somewhat higher recoveries and showed less variation then the gravity system (Section 6.4).

5.12 CLEAN-UP FOR DIMETHOATE EXTRACTS FROM BOTTOM MATERIAL

For clean-up of dimethoate extracts from bottom material from the tanks, a glass tube 200 mm long of inner diameter 20 mm was filled with 17.3 g non-activated silica gel to a height of 120 mm. The extracts of the bottom material were added on top of the silica gel column and eluted with a mixture of ethyl acetate and *n*-hexane (4:1 by volume). Dimethoate was recovered from the column in the 100-170 cm^3 fraction of the eluate. The recovery from 5 spiked extracts averaged 95%, with a coefficient of variation of 6%.

5.13 CONCENTRATION MEASUREMENTS BY GAS--LIQUID CHROMATOGRAPHY

The final assessment of pesticide concentrations in the cleaned extracts can be accomplished in different ways. However, some methods suffer from lack in sensitivity and specificity. The method usually preferred for measurement of organophosphorus pesticides is gas--liquid chromatography (GLC). The apparatus may be equipped with one of the several available selective and sensitive detectors for compounds containing P or S. Several types of column packing with different stationary (liquid) phases have been used under various chromatographic conditions, for isothermal or temperature-programmed gas chromatography of phosphorus-containing pesticides (Zweig, 1972).

Even after previous clean-up by adsorption chromatography, it is often found that peaks of co-extracted substances coincide with the peaks of pesticidal compounds in the gas chromatograms. So it is often necessary to analyse the samples with two or three gas--chromatographic columns containing stationary phases of different polarity (Cochrane, 1976).

Mass spectrometry, especially in combination with GLC, is one of the best methods for further confirmation of the identity of pesticides residues.

5.14 MEASUREMENT OF AZINPHOS-METHYL

The quantitative measurement of azinphos-methyl has been the object of some special studies. The available analytical methods were reviewed by the Chemagro Division Research Staff (1974). The best available technique for measurement of azinphos-methyl is gas--liquid chromatography (GLC). However a selective and sensitive measurement of azinphos-

-methyl can be carried out by GLC only on a few column packings (Zweig, 1972).

In the present study, the azinphos-methyl extracts were analysed with a Tracor 550 gas chromatograph equipped with a flame-photometric detector (FPD) operating in the phosphorus mode. Azinphos-methyl and its oxygen analogue were measured on two different columns. The gas-chromatographic conditions and column specifications are presented in Table 14.

The cleaned extracts of water and bottom material were evaporated and then dissolved in an appropriate volume of solvent (acetone or ethyl acetate). Reference solutions of insecticide in the corresponding solvent were made from analytical-grade azinphos-methyl (98% purity) and its oxygen analogue (99%), obtained from Chrompack & Nederland B.V., Middelburg. With a 10 mm^3 injection syringe, 5-10 mm^3 of the extracts and of reference solutions were injected alternately into the gas chromatograph. The linearity of the response of the signal with different reference solutions was quite reasonable, but after injection of some extracts with an unknown amount of co-extractives, there was some variation in response to reference solutions. For this reason, the extracts were injected two or three times, alternately with reference solutions. The concentrations of the extracts were properly diluted after a preliminary measurement so that the response of the extracts was in the range of the response of reference solutions.

The pesticide concentrations in the extracts were measured by comparing peak heights with those from the reference solutions. By using Column II, packed with 3% Apiezon-L (Table 14) azinphos-methyl and its oxygen analogue could be measured simultaneously and rather sensitively. The retention times of azinphos-methyl and its oxygen analogue were relatively small. The detection limits set at three times the noise were comparatively low for both columns (Table 14).

Table 14. Gas-chromatographic conditions for measurement of azinphos-methyl and its oxygen analogue.

Column I: glass column; 40 cm long; 0.3 cm inner diam.; packed with 4% SE-30/6% SP-2401 coated on Supelcoport 100-120 mesh, obtained from Supelco Inc. (Pleuger Nederland, Amstelveen).

Column II: glass column; 60 cm long; 0.3 cm inner diam.; packed with 3% Apiezon-L on Chromosorb W-AW-DMCS, 80-100 mesh, obtained from Chrompack Nederland B.V., Middelburg.

	Column I		Column II	
	azinphos-methyl	oxygen analogue	azinphos-methyl	oxygen analogue
Carrier gas N_2 (cm^3 min^{-1})	180	180	92	92
Detector gases				
H_2(cm^3 min^{-1})	150	150	150	150
O_2(cm^3 min^{-1})	10	10	10	10
air(cm^3 min^{-1})	30	30	30	30
Temperature (°C)				
column	180	150	200	200
injection port	210	210	210	210
detector	210	210	210	210
Detection limit (ng)	0.4	5	0.2	2
Retention time (min)	2.3	1.8	3.4	2.2

5.15 MEASUREMENT OF DIMETHOATE

Dimethoate may be measured by GLC with various column packings (Zweig, 1972). In the present study, the extracts of surface water and bottom material were analysed for dimethoate and its oxygen analogue with a Tracor 550 (containing Column I or II) and a Pye Unicam GCV gas chromatograph (containing Column III). Both gas chromatographs were equipped with flame-photometric detectors. The column specification, gas-chromatographic conditions, retention times and detection limits are tabulated in Table 15. The injection and calculation procedure was the same as for azinphos-methyl.

The diversity of the interfering substances in surface water extracts sometimes necessitated the use of three chromatographic columns with different polarity of the stationary phase to obtain certainty about the identity of dimethoate. By using Column III, dimethoate and its oxygen analogue could be measured simultaneously.

Table 15. Gas-chromatographic conditions for measurement of dimethoate and omethoate.

Column I and II are the same columns as used for azinphos-methyl, already specified in Table 14.

Column III: glass column; 95 cm long; 0.2 cm inner diam.; packed with 3% Carbowax 20M on Chromosorb W-AW-DMCS, 80-100 mesh, obtained from Chrompack Nederland B.V., Middelburg.

	Column I		Column II	Column III	
	dimethoate	omethoate	dimethoate	dimethoate	omethoate
Carrier gas N_2 (cm^3 min^{-1})	100	80	66	80	80
Detector gases					
H_2(cm^3 min^{-1})	150	150	150	40	40
O_2(cm^3 min^{-1})	10	10	10	-	-
air(cm^3 min^{-1})	30	30	30	40	40
Temperatures (°C)					
column	135	135	170	190	190
injection port	210	210	210	210	210
detector	210	210	210	210	210
Detection limit (ng)	0.1	0.3	0.01	0.2	1
Retention time (min)	2.0	1.6	0.6	3.5	2.7

6 Conversion rate and adsorption of azinphos-methyl and dimethoate in aquatic systems

6.1 INTRODUCTION

Laboratory tests were needed for the following three reasons.

-Because of the large number of pesticides and conditions of application, there is need for an initial characterization of pesticide behaviour. Attempts are needed to design quick laboratory tests, the results of which can be used to predict the behaviour of pesticides in the aquatic environment. However there is no consensus on the experimental methods to be used, and there is much discussion on the way in which such tests must be done. Consequently there is need for comparative research on the conversion rate in different aquatic systems. Persistence data obtained in the laboratory has to be compared with those obtained under field conditions. Much attention has to be paid to the characterization of aquatic systems, both in the laboratory and in the field.

-Because the conversion rate of pesticides in the field may vary considerably with place and time, data is needed on the factors involved. The effect of separate factors can often be studied only adequately under well controlled laboratory conditions. The relationships obtained can then be introduced into computer simulation models to make quantitative predictions.

-The rate of decline under outdoor conditions is the result of various processes that may occur simultaneously. In field studies, it is difficult to separate the contribution to the decline of processes like microbial, chemical and photo-chemical conversion, volatilization, adsorption and penetration. Furthermore it is difficult to extrapolate the results from one field situation to another. Relationships obtained under well controlled conditions can be introduced into computer simulation models to be checked by well defined field trials.

6.2 CONVERSION RATE OF AZINPHOS-METHYL IN AQUEOUS SOLUTIONS KEPT IN DARKNESS

Literature data

Comparative studies on the rates of hydrolysis of organophosphorus pesticides in aqueous solutions have been made by Mühlmann & Schrader (1957), Ruzicka et al. (1968), Faust & Gomaa (1972) and Grahl (1973). In general phosphoro-dithioates are more stable in aquatic media than their phosphoro-thionate analogues. Organophosphorus pesticides are in most instances comparatively persistent under acidic conditions (Faust & Gomaa, 1972).

The conversion rates of pesticides in aqueous solutions can be usually characterized by a rate coefficient ($k_{c,w}$), assuming a first-order reaction (Section 3.3, Equation 1). This rate coefficient for conversion may be composed of several partial coefficients, which represent the various catalytic and enzymic influences on the reactions (Grahl, 1973). However, the mechanisms of the reactions are mostly poorly understood and more research is required on the factors affecting decomposition rates of organophosphorus pesticides in aqueous solutions.

The conversion rates of azinphos-methyl and its oxygen analogue are highly dependent on pH. The relationships between rate of hydrolysis at 70 °C and pH obtained by Mühlmann & Schrader (1957) are shown in Figure 5. Azinphos-methyl was hydrolysed slower in aqueous solution than its oxygen analogue and both compounds were less stable with increasing pH. The temperature during these hydrolysis tests was high (70 °C); thus the rates of hydrolysis under environmental conditions may be expected to be much lower.

Rates of hydrolysis at more realistic temperatures were measured by Bayer A.G. (1978), Liang & Lichtenstein (1972) and Heuer et al. (1974). The rate coefficients for conversion at various pH values assessed in these studies are presented in Figure 6. The strong increase in the rate coefficient for hydrolysis of azinphos-methyl with increasing pH is clearly shown. The large differences between the rate coefficients found in the different studies can probably be attributed to differences in the test materials and in the chemical composition of the buffered aqueous solutions.

Obviously literature data on the rate of hydrolysis of azinphos-methyl in the pH range 7-8.5 at surface-water temperatures (10-20 °C) prevailing in the area of study are very scarce. No data could be found on the hydrolysis rate of the oxygen analogue of azinphos-methyl at such temperatures. Moreover conversion rates of azinphos-methyl and of its wettable powder in surface water were not found in the literature.

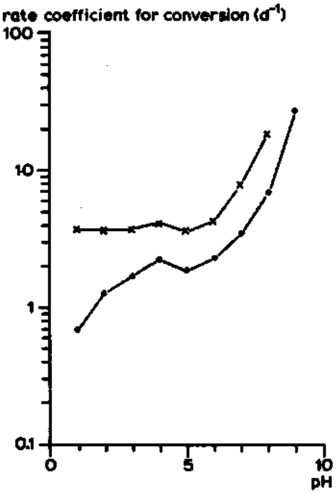


Figure 5. Effect of pH on hydrolysis rates of azinphos-methyl (●-●) and its oxygen analogue (x-x) in aqueous solution at 70 °C. (After Mühlmann & Schrader, 1957).

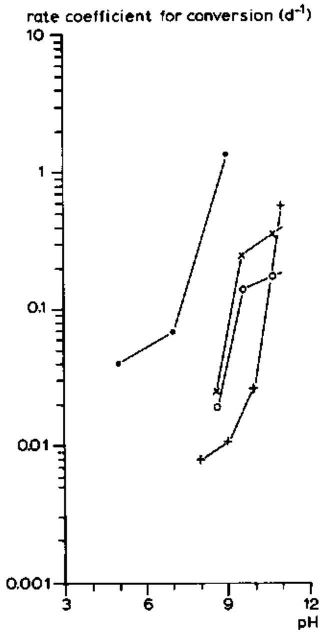


Figure 6. Effect of pH on rate coefficient for hydrolysis *of azinphos-methyl in aqueous solutions at different* temperatures. Data from ●-● (20 °C) Bayer A.G. (1978), +–+ (20 °C) Liang & Lichtenstein (1972) and x-x (25 °C), o–o (6 °C) Heuer et al. (1974).

Procedures for measuring the hydrolysis of azinphos-methyl in buffer solutions

Hydrolysis rates of azinphos-methyl as analytical grade (98% purity) were measured in aqueous solutions buffered at two pH values. A buffered aqueous solution of pH 7.7 was prepared in de-ionized water with phosphate, borate and hydrochloric acid. Another buffered aqueous solution of pH 8.9 was made in de-ionized water with boric acid, potassium chloride and sodium hydroxide. (Both buffers were prepared with Titrisol® solutions of E. Merck, Darmstadt). A volume of 5 cm^3 of the buffered aqueous solutions containing 50 μg azinphos-methyl was added to test tubes (15 cm^3) which were closed with ground-glass stoppers. All test tubes were placed in the dark in a water bath at 15 °C. After the concentrations in the tubes with pH 8.9 had decreased to half their initial value, the temperature of the water bath was raised from 15 to 20 °C. After the concentration was halved again (20 °C, pH 8.8) the temperature was raised to 25 °C. The temperature fluctuations during the tests were less than 0.5 °C.

At appropriate time intervals, two tubes of both pH values were extracted twice with 5 cm^3 of dichloromethane. The combined extracts were collected in a test tube and dried by adding a small spoon of anhydrous sodium sulphate. The dichloromethane was removed with a gentle stream of nitrogen gas, after which azinphos-methyl was dissolved in acetone. The analyses were by gas--liquid chromatography using Column I for the 15 °C series and on Column II for the other temperatures (Table 14). The average recovery was 98% with a coefficient of variation of 1%.

Procedure for measuring the conversion of azinphos-methyl in surface water

Conversion rates were measured of azinphos-methyl (98% purity), its oxygen analogue (99% purity) and azinphos-methyl w.p. (25% wettable powder) dissolved in surface water. The solutions were not buffered. The incubation jars were placed in temperature-controlled cabinets at 10 and 20 °C. In the cabinets, the fluctuation of temperature was about 1 °C.

The surface water was obtained from untreated Tank III (Chapter 7) and was filtered over an inert silicate-fibre filter (size 0) to remove suspended particles. The chemical composition of this aqueous solution is shown in Table 16. The initial pH was adjusted to 7.0 by addition of a small volume of sulphuric acid substance concentration 0.5 kmol m^{-3}. During tests, the pH was measured before the extractions.

Aqueous solutions were prepared, concentrations 10 g m^{-3} and 5 g m^{-3} of azinphos-methyl, 20 g m^{-3} of its oxygen analogue, and 20 g m^{-3} of azinphos-methyl w.p. Volumes of 50 cm^3 of these solutions were added to glass jars (250 cm^3), which were closed with poly-

Table 16. Chemical characteristics of water from untreated outdoor tank III (Chapter 7), used for the conversion tests with azinphos-methyl in the laboratory. Analyses by the Eastern Laboratory for Water Testing, Doetinchem. Sampling date: 15 August 1977. Data of analyses: 19 October 1977.

Characteristics	Mass concentration (g m^{-3})	
COD	110	
NO_3^-	< 1	
NH_4^+	< 0.05	
Total N	2.5	
Orthophosphate (as PO_4)	5.2	
Total phosphate (as PO_4)	5.5	
Cl^-	345	1)
Ca^{2+}	212	1)
HCO_3^-	77	
CO_2	3	
CO_3^{2-}	0	
SO_4^{2-}	12	
Hardness (as CaO)	301	1)
Cu^{2+}	< 5 mg m^{-3}	
Conductivity	113.4 mS m^{-1}	1)

1) For a better precipitation of suspended material during centrifuging, 555 g of calcium chloride was added per cubic metre of aqueous solution at the start of the test.

ethylene caps. For each combination of compound and concentration, 18 jars were incubated.

In outdoor trials (Chapter 7), copper sulphate was used to suppress an algal bloom in the water of the tanks. The effect of copper sulphate on the conversion rate of azinphos-methyl in water was measured in an incubation study. Copper sulphate was added to water from untreated Tank III to a mass concentration of 3.2 g m^{-3}. In that test, the aqueous solution was spiked with azinphos-methyl w.p. at 16 g m^{-3}. The glass jars were placed in the dark in two temperature-controlled cabinets at 10 and 20 °C.

Triplicate samples were extracted in a separatory funnel with consecutively 100, 50 and 50 cm^3 of dichloromethane as described in Section 5.3. Analysis was by GLC, using Column II (Table 14) for all compounds. The recoveries of azinphos-methyl and its oxygen analogue were almost 100%, with low coefficients of variation (Table 12).

Measured conversion rates of azinphos-methyl in aqueous solution

The effect of pH on the rate of hydrolysis of azinphos-methyl, as analytical grade, in buffered aqueous solutions at different temperatures is shown in Figure 7. The decline patterns were approximated with a first-order reaction rate equation. The hydrolysis rate coefficients and half-life values are tabulated in Table 17.

The rate coefficients for hydrolysis and the coefficients of determination (r^2; square of correlation coefficient) were calculated with a standard regression program on a Hewlett Packard desk calculator. Table 17 shows lower coefficients of determination at lower pH; this could have been improved by measuring concentrations over longer periods. During the hydrolysis tests, the differences between duplicate samples on the sampling dates were less than 2% of their average concentrations.

The rate coefficients were highly dependent on pH and temperature. The average rate of hydrolysis at pH 8.7 to 8.9 was about four times as fast as that at pH 7.6 to 7.7. Increasing the temperature in both buffered solutions resulted in a considerable increase in the rate coefficients for hydrolysis ($k_{c,w}$). The effect of temperature on $k_{c,w}$ in the range 15-20 °C was smaller than in the range 20-25 °C. This effect could not be described by an Arrhenius relationship, since a plot of lg $k_{c,w}$ against $1/T$ did not yield a straight line. Change in the aqueous solutions (for example a decrease in redox potential with time) might have disturbed the Arrhenius relationship.

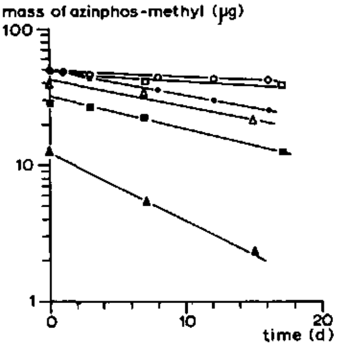


Figure 7. Effect of pH on rate of hydrolysis of azinphos-methyl, analytical grade, in buffered aqueous solutions at different temperatures. o = pH 7.7, 15 °C; □ = pH 7.6, 20 °C; Δ = pH 7.6, 25 °C; ● = pH 8.9, 15 °C; ■ = pH 8.8, 20 °C; ▲ = pH 8.7, 25 °C.

Table 17. First-order rate coefficients and half-lives for the hydrolysis of azinphos-methyl, analytical grade, in buffered aqueous solutions.

Temperature (°C)	pH	Rate coeff. (d^{-1})	Half-life (d)	Coeff. of determ.
15	8.9	0.0419	16.6	0.99
20	8.8	0.0541	12.8	0.98
25	8.7	0.114	6.1	0.95
15	7.7	0.0090	77	0.86
20	7.6	0.0126	55	0.90
25	7.6	0.0424	16	0.88

Measured conversion rates of azinphos-methyl in surface waters

The results of the conversion tests with azinphos-methyl, its oxygen analogue and azinphos-methyl w.p. in surface water are shown in Figure 8. The calculated first-order rate coefficients ($k_{c,w}$) are presented in Table 18.

Although the samples of surface water were not buffered, the variation in pH did not disturb the approximate first-order conversion patterns shown in Figure 8. No distinct trends in pH were observed during the tests. The coefficients of determination were relatively high for tests in unbuffered solutions.

The differences between the concentrations in the three samples on each of the sam-

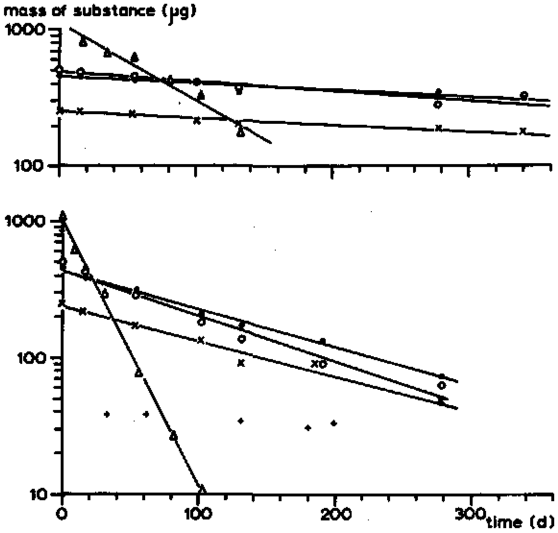


Figure 8. Mass of substance in surface water against time during laboratory incubations at 10 (above) and 20 °C (under). • = azinphos-methyl (analytical grade); x = the same, with half the initial mass; o = azinphos-methyl (25% w.p.); Δ = azinphos-methyl oxygen analogue; + = azinphos-methyl (25% w.p.) and copper sulphate added.

Table 18. First-order rate coefficients and half-lives for the conversion of azinphos-methyl and its oxygen analogue in surface water during incubation in the dark at 10 and 20 °C.

Compound	Temperature (°C)	pH, average (and range)	Rate coeff. (d^{-1})	Half life (d)	Coeff. of determ.	Averaged difference[3] (%)
Azinphos-methyl (analytical grade)	10[1]	7.5 (6.7-8.1)	0.0011	624	0.87	4
	10[2]	7.4 (6.4-7.9)	0.0011	613	0.89	3
	20[1]	6.6 (5.7-7.5)	0.0064	109	0.99	6
	20[2]	6.8 (6.4-7.6)	0.0057	122	0.97	6
Azinphos-methyl (25% w.p.)	10	7.5 (7.1-8.1)	0.0016	427	0.87	2
	20	7.6 (6.1-8.4)	0.0077	91	0.97	11
Azinphos-methyl oxygen analogue	10	7.7 (7.3-8.2)	0.013	54	0.97	12
	20	7.7 (7.4-8.3)	0.045	16	1.00	21

1. Dose 0.5 mg.
2. Dose 0.25 mg.
3. See text.

pling dates were expressed as a percentage of the average concentrations on that sampling date. After that, these percentages were averaged for all sampling times for each incubation test (Table 18). The averaged differences were relatively small, with an exception for the oxygen analogue of azinphos-methyl at 20 °C, where difference averaged 21%.

The rate coefficients for conversion of the compounds were highly dependent on temperature. At 10 °C, these coefficients were only about a third to a sixth of those at 20 °C. Halving the dose of azinphos-methyl, analytical grade, hardly affected half-lives (Table 18). With a w.p. formulation, azinphos-methyl showed a somewhat faster conversion than when applied as pure compound (Table 18).

The conversion rate of the oxygen analogue of azinphos-methyl in surface water was considerably higher than that of azinphos-methyl itself. During incubation of azinphos-methyl in surface water, the oxygen analogue could not be detected, perhaps because of the rapid conversion of the oxygen analogue.

Adding copper sulphate to the surface water (20 °C) resulted in rapid conversion of azinphos-methyl shortly after the start of the test, followed by a period with slow conversion (Figure 8). This decline pattern could not be described as a first-order reaction. An explanation for this decline pattern could possibly be found if copper ion concentrations had been followed with time.

A comparison of the results of the incubations of azinphos-methyl in surface water at 20 °C (Table 18) with those obtained in buffered aqueous solutions (Table 17) was rather difficult in view of the low coefficient of determination in the buffered tests and in view of the variations in pH in the tests with surface water. Conversion of azinphos-methyl in aqueous solutions in the dark is a rather slow process at temperatures prevailing out of doors.

6.3 CONVERSION RATE OF DIMETHOATE IN AQUEOUS SOLUTIONS KEPT IN DARKNESS

Literature data

The rates of hydrolysis of dimethoate and its oxygen analogue (omethoate) in aqueous solutions at different pH values were examined by Grimmer et al. (1968). Their results at 25 °C are presented in Figure 9. The rates of hydrolysis of dimethoate and its oxygen analogue are highly dependent on pH. The rate coefficient for hydrolysis of dimethoate increases by a factor of almost 100 when pH increases from 7.0 to 10.0. Dimethoate was found to be degraded more slowly than omethoate. Dimethoate is degraded slowly in acid aqueous solutions.

Eichelberger & Lichtenberg (1971b) incubated dimethoate in river water placed in the laboratory under sunlight and fluorescent light. The pH was 7.3 at time zero and increased to 8.0 after eight weeks. In that time, half of the initial amount was converted (on average, $k_{c,w} = 0.012\ d^{-1}$). Brady & Arthur (1963) measured the rate coefficient of hydrolysis of dimethoate in a sodium carbonate solution, substance concentration 0.05 $kmol\ m^{-3}$ (adjusted to pH 11), in flasks on a shaker. They measured a $k_{c,w}$ of 28 d^{-1}. Unfortunately, temperatures were not specified in these papers. Wagner & Frehse (1976) referred to industrial data indicating that hydrolysis rates of dimethoate and omethoate at 21 °C and pH 9 were 0.12 and 2.3 d^{-1}, respectively. These values agree fairly well with the results in Figure 9.

Conversion rates of dimethoate in surface water at lower water temperatures were not found in the literature. Further tests were done to measure conversion rates of dimethoate in surface water at lower water temperatures, and with addition of copper sulphate and calcium chloride to the aqueous solution.

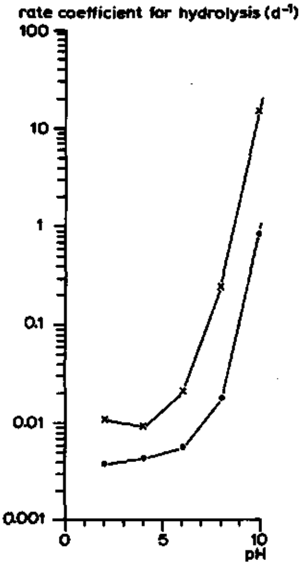


Figure 9. Effect of pH on the rate coefficient for hydrolysis of dimethoate (●-●) and omethoate (x-x), in buffered aqueous solutions at 25 °C. (After Grimmer et al., 1968).

Procedures for measuring the conversion of dimethoate in surface water

The conversion rate of dimethoate dissolved in untreated water from Tank I was studied. The water was filtered (Section 6.2) and not buffered. The chemical composition of this aqueous solution is shown in Table 19. The pH at the start of the experiment was adjusted to 7.0 by adding of a small volume of sulphuric acid 0.5 kmol m^{-3}. During the tests, pH was measured before each extraction.

Dimethoate was applied as analytical grade (98% purity). Initially the concentration in the aqueous solution was 20 g m^{-3}. Details of incubation were similar to those for azinphos-methyl (Section 6.2). The aqueous solutions were incubated at 10, 15 and 20 °C.

In a separate series of tests, the effects of adding calcium chloride or calcium chloride plus copper sulphate on the conversion rate of dimethoate were investigated. The calcium chloride, which is usually added in adsorption studies, was applied to a mass concentration of 5.55 kg m^{-3}. The concentration of copper sulphate in the relevant incubation solutions was 3.2 g m^{-3}. These latter solutions were only incubated at 20 °C.

The extraction procedures were the same as for conversion tests with azinphos-methyl. Analysis was by GLC with Column III (Table 15). Average recovery of dimethoate from 12 spiked water samples was 96%, with a coefficient of variation of 2%.

Table 19. Chemical characteristics of the water from untreated outdoor Tank I (Chapter 7) used for the conversion tests with dimethoate in the laboratory. Analyses by the Eastern Laboratory for Water Testing, Doetinchem. Sampling data: 15 March 1978. Date of analysis: 11 April 1978.

Characteristics	Mass concentration (g m^{-3})
COD	15
NO_3^-	< 1.0
NH_4^+	0.19
Total N	0.19
Orthophosphate	0.20
Total phosphate	0.30
Cl^-	11
Ca^{2+}	33
HCO_3^-	59
CO_2	2
CO_3^{2-}	0
SO_4^{2-}	57
Hardness (as CaO)	47
Cu^{2+}	< 5 mg m^{-3}
Conductivity	19 mS m^{-1}

Measured conversion rates of dimethoate in surface water

The effect of temperature on rate of conversion of dimethoate, analytical grade, in surface water is shown in Figure 10. The decline patterns at 20 °C could not be characterized for the whole period of incubation by a first-order reaction equation. Initially the decline was relatively slow, later conversion rates increased (Figure 10). The increase in conversion rates may be due to change in the chemical or microbial conditions in the surface water during incubation. There is an apparent inconsistency in the effect of temperature.

The differences between concentrations in the triplicate samples at the start of incubations were rather small (Table 20). However these differences became rather large at the end of the tests. This phenomenon could be partly related to changes in pH in the unbuffered surface water. In some samples incubated at 20 °C, relatively high pH values were measured, which corresponded to low concentrations; relatively low pH values corresponded to high concentrations. On average, pH changes did not show a clear upward of downward trend.

The first part of the decline curves for dimethoate in surface water (Figure 10) was approximated with a first-order rate equation. The rate coefficients are presented in Table 20. The rate coefficient of dimethoate for the first part of the decline curve at 15 °C was omitted in view of the few data in that part of the curve. First-order rate coefficients for the second part of the decline at 20 °C were omitted in view of the large deviations in concentrations for triplicate samples at the end of the tests (Table 20).

The decline curve of dimethoate in surface water with calcium chloride is shown in Figure 11. The conversion rates for the first period of incubation at 20 °C with and without addition of calcium chloride were nearly the same. The wide scatter of points in the second period made any comparison between conversion rates in either medium impossible.

Adding copper sulphate to the aqueous solution resulted in a great increase in the conversion rate of dimethoate. The limited number of samples did not allow assessment of the shape of the decline curve. Assuming a first-order conversion rate equation for the first four points, an average rate coefficient of 0.12 d^{-1} ($t_{\frac{1}{2}}$ = 5.9 d) was calculated (Figure 11).

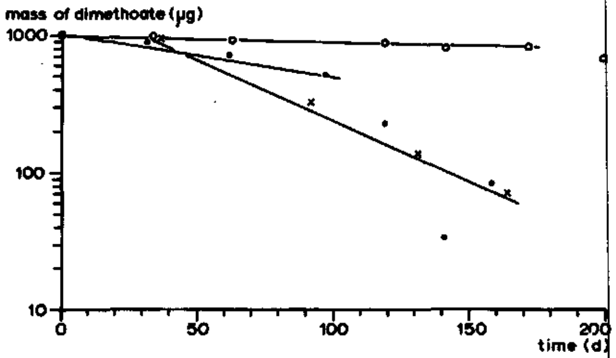


Figure 10. Mass of dimethoate in surface water against time of incubation at 10 (o), 15 (x) and 20 °C (•).

Table 20. First-order rate coefficients and half-lives for conversion of dimethoate in surface water in the dark at 10, 15 and 20 °C.

Additive	Temp. (°C)	Period[1]	pH, average (and range)	Rate coeff. (d^{-1})	Half life (d)	Coeff. of determ.	Averaged difference[2] (%)
None	10	I,II	7.4 (7.1-7.6)	0.0012	592	0.93	2
	15	I	7.1 (6.9-7.2)	-[3]	-[3]	-[3]	1
		II	6.2 (5.8-6.8)	0.020	34	0.97	30
	20	I	7.2 (6.6-7.5)	0.0071	97	0.94	13
		II	6.6 (5.8-7.6)	-[3]	-[3]	-[3]	65
$CaCl_2$	20	I	7.1 (6.6-7.4)	0.0061	113	0.95	3
		II	7.1 (6.4-7.8)	-[3]	-[3]	-[3]	13
$CaCl_2$ + $CuSO_4$	20	I,II	7.1 (6.7-7.7)	0.12	5.9	0.98	19

1. I = first period; II = second period (see text).
2. See Section 6.2.
3. Omitted values (see text).

The conversion rate of dimethoate incubated in surface water in the dark at pH around 7 was rather slow, especially at low temperatures. In general, these rates were somewhat higher than those of azinphos-methyl (Tables 20 and 18).

During incubation of dimethoate in surface water, the formation of the oxygen analogue of dimethoate (omethoate) could not be detected. This might be related to the fast conversion of omethoate in hydrolysis tests, as reported in literature (Figure 9).

6.4 CONVERSION RATE OF AZINPHOS-METHYL IN SYSTEMS OF BOTTOM MATERIAL AND SURFACE WATER

Data on the conversion rate of azinphos-methyl and its oxygen analogue under anaerobic conditions in bottom material could not be found in the literature. More research was thus needed on decomposition rates in such media. To simulate natural conditions, it was decided to investigate the conversion rate in a system of bottom material in contact with surface water.

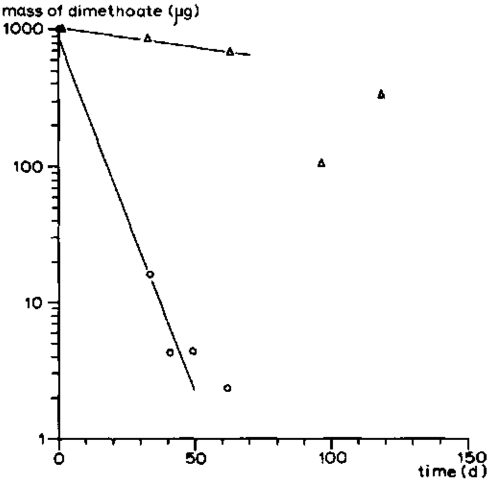


Figure 11. Mass of dimethoate in surface water against time of incubation at 20 °C. Δ = calcium chloride added; o = calcium chloride plus copper sulphate added.

Procedures for measuring the conversion of azinphos-methyl in systems with bottom material

The conversion rate of azinphos-methyl was studied in a mixture of water and bottom material from the untreated Tank III. The water was filtered as in Section 6.2 and was not buffered. The chemical composition of this aqueous solution is presented in Table 16. The pH at the start of the test was adjusted to 7.0 as described in Section 6.2. The bottom material was collected from untreated Tank III and thoroughly mixed before the start of the test.

About 25 g of fresh bottom material was introduced into a centrifuge tube (70 cm^3) equipped with a ground-glass stopper. Then 50 cm^3 of surface water spiked with azinphos--methyl (analytical grade, 0.5 or 0.25 mg), its oxygen analogue (1 mg) or azinphos-methyl w.p. (0.5 mg) was added. For each combination of compound and concentration, 18 centrifuge tubes were incubated. These tubes were placed in a controlled-temperature cabinet at 20 °C ± 1 °C. At 10 °C, only one series was set up with a dose of 0.5 mg of azinphos-methyl, analytical grade. During incubation, the tubes were placed twice a week on a shaker for 5 min. Redox potentials in the bottom material were measured at intervals of 2 weeks.

At appropriate time intervals, three tubes of each series were centrifuged for 5 min at 33 Hz (2000 min^{-1}). The supernatant liquid was measured and extracted as described in Section 6.2. The bottom material was quantitatively transferred into a glass jar and extracted as described in Section 5.6. After extraction, the dry mass of the bottom material was determined by drying to constant mass at 105 °C.

The extracts of the bottom material were cleaned up by column chromatography using the improved pumping system for the elution solvent as described in Section 5.11. The first eluate fraction (60 cm^3) could be discarded; the second eluate fraction (28 cm^3) contained azinphos-methyl. Next 20 cm^3 of a mixture of dichloromethane and acetone (2:1, v/v) was pumped through the column and was discarded. After that the oxygen analogue of azinphos-methyl could be collected in the following 20 cm^3.

The extracts of the aqueous solutions and the cleaned extracts of bottom material were analysed by gas--liquid chromatography on Column II (Table 14). The recoveries of azinphos-methyl and its oxygen analogue from the aqueous solutions were almost 100% (Table 12). The recoveries of these compounds from spiked bottom material were 103% (coefficient of variation 3%) and 59% (coefficient of variation also 3%), respectively. The relatively low recovery of the oxygen analogue was probably due to low efficiency of extraction because the recovery for the clean-up procedure alone was 96%, with a coefficient of variation of 6%. No corrections were made for recovery.

Measured conversion rates of azinphos-methyl in systems with bottom material

The concentrations of azinphos-methyl in systems with bottom material at various times during incubation at 10 and 20 °C are shown in Figures 12 and 13, respectively. The calculated first-order rate coefficients for the conversion of azinphos-methyl in this system are presented in Table 21.

The average redox potential in the bottom layer of the system was about -0.12 V.

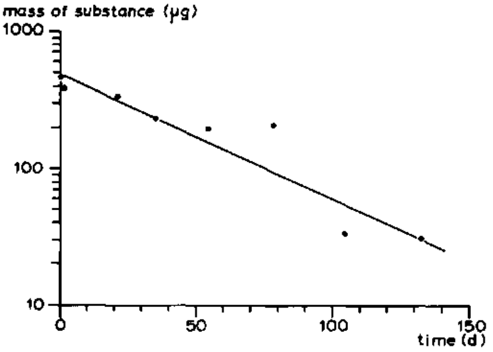


Figure 12. Mass of azinphos-methyl (analytical grade) in systems with bottom material against time of incubation at 10 °C.

During the incubation period, the standard deviation of 13 measurements was 0.04 V. The bottom material can be classified as anaerobic.

The averaged differences between triplicate samples were relatively small, except for incubation at 10 °C (Table 21). Raising the temperature from 10 to 20 °C increased the conversion rate of azinphos-methyl by a factor 3.4. Halving the amount of azinphos-methyl resulted in nearly the same conversion rates (Figure 13; Table 21).

The conversion rate of the oxygen analogue of azinphos-methyl in bottom material was slightly higher than the conversion rate of azinphos-methyl itself. During incubation of azinphos-methyl in this system with bottom material, no oxygen analogue could be found.

Although the average pH in the bottom material was slightly lower than the average pH in tests with surface water, the conversion rates of azinphos-methyl in the anaerobic bottom material were generally 10 to 20 times as fast (Tables 18 and 21). However the

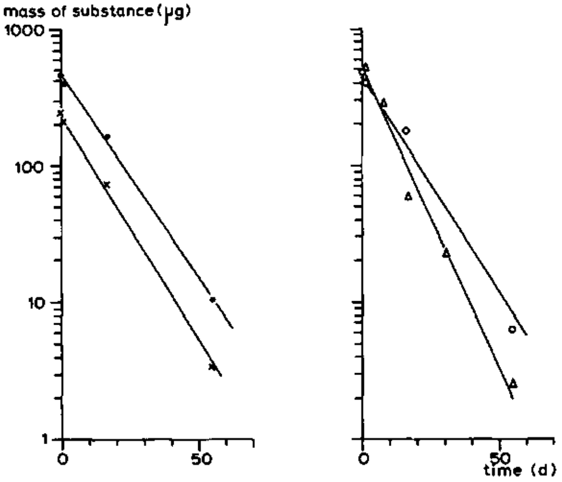


Figure 13. Mass of substance in systems with bottom material against time of incubation at 20 °C. • = azinphos-methyl (analytical grade); x = the same compound with half the initial dose; o = azinphos-methyl (25% w.p.); Δ = azinphos-methyl oxygen analogue.

Table 21. Rate coefficients and half-lives for the conversion of azinphos-methyl and its oxygen analogue incubated in systems with anaerobic bottom material at 10 and 20 °C.

Compound	Temperature (°C)	pH, average (and range)	Rate coeff. (d^{-1})	Half life (d)	Coeff. of determ.	Averaged difference[3] (%)
Azinphos-methyl (analytical grade)	10	6.9 (6.8-7.2)	0.020	34	0.88	25
	20[1]	6.8 (6.6-7.1)	0.068	10	1.00	11
	20[2]	6.8 (6.6-7.1)	0.078	8.9	1.00	5
Azinphos-methyl (25% w.p.)	20	6.8 (6.6-7.1)	0.079	8.8	0.99	14
Azinphos-methyl oxygen analogue	20	6.8 (6.6-7.1)	0.10	7.0	0.98	13

1. Dose 0.5 mg.
2. Dose 0.25 mg.
3. See text.

differences between the conversion rates of the oxygen analogue of azinphos-methyl in both media were not so large.

6.5 CONVERSION RATE OF DIMETHOATE IN SYSTEMS OF BOTTOM MATERIAL AND SURFACE WATER

No data on the conversion rate of dimethoate in anaerobic bottom material were found in the literature.

Procedures for measuring conversion of dimethoate in systems with bottom material

The incubations were carried out in centrifuge tubes with ground-glass stoppers (Section 6.4). About 25 g of fresh bottom material from untreated Tank I was introduced into the tubes. To that was added 50 cm^3 of surface water (from Tank I; for chemical characteristics see Table 19) spiked with 1 mg of dimethoate (analytical grade). These tubes were placed in three constant-temperature cabinets adjusted to 10, 15 and 20 °C. Redox potentials in the bottom material were measured monthly.

At appropriate time intervals, three tubes were centrifuged and the supernatant liquid was extracted in the same way as described for azinphos-methyl in Section 6.4. The extraction of dimethoate from the bottom material described in Section 5.7 was modified. After removing the supernatant liquid, 5 cm^3 of de-ionized water and 40 cm^3 of ethyl acetate were added to the bottom material in the centrifuge tube. The tubes were placed on a shaker for 1 h, thereafter the tubes were centrifuged and the supernatant solution was collected. The extraction procedure was repeated twice with 30 cm^3 of ethyl acetate. The combined extracts were dried with anhydrous sodium sulphate and evaporated to dryness in a rotary evaporator.

The extracts of the bottom material were cleaned up as described for extracts of water (Section 5.10). The only difference was that the elution liquid (ethyl acetate) was half-saturated with water (mass fraction of water 1.6%). The first eluate fraction of 10 cm^3 was discarded. The next 10 cm^3 of eluate contained the dimethoate. The fractions were analysed by GLC with Column III (Table 15). The average recovery of dimethoate from 25 spiked samples of bottom material was 90%, with a coefficient of variation of 4%. No corrections for recovery were made.

Measured conversion rates of dimethoate in systems with bottom material

The results of incubation of dimethoate in systems with anaerobic bottom material at 10, 15 and 25 °C are presented in Figure 14. Initially the conversion rates of dimethoate were slow, becoming considerably higher later. The decline patterns were approximated with a first-order rate equation for each of these two time periods.

The average pH and ranges of pH in the systems with bottom material were nearly the same for different temperatures. The averaged differences between the concentration of dimethoate in triplicate bottom samples were relatively small (Table 22). The increase in conversion rate for each of the incubations in the second period could be related to a change in chemical or microbial conditions. The redox potential in the bottom material dropped from -0.03 V at the start of the test to -0.12 V at the end.

As temperature increased, the duration of the first period with comparatively slow conversion decreased. As the temperature increased conversion rates considerably increased in systems with bottom material.

The conversion of dimethoate in the anaerobic bottom material system was considerably faster than in aqueous solutions (Tables 20 and 22). The conversion rates of dimethoate in the first period of incubation were slower than those of azinphos-methyl. In the second period of incubation, the rates of decline of dimethoate (Table 22) seemed to be considerably faster than those for azinphos-methyl (Table 21).

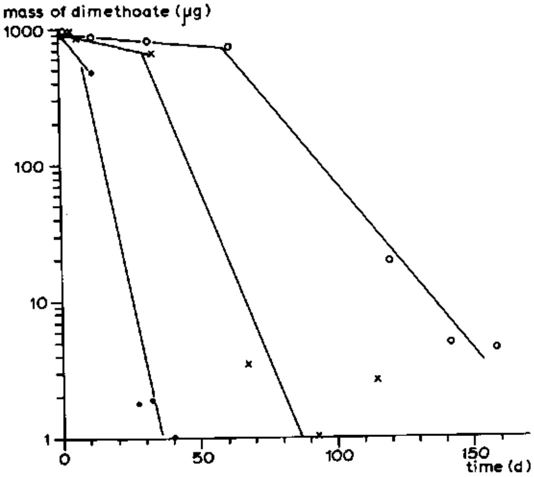


Figure 14. Mass of dimethoate (analytical grade) in systems with bottom material against time during incubation tests at 10 (o), 15 (x) and 20 °C (•).

Table 22. First-order rate coefficients and half-lives for conversion of dimethoate incubated in systems with anaerobic bottom material at 10, 15 and 20 °C.

Temp. (°C)	Period[1]	pH, average (and ranges)	Rate coeff. (d^{-1})	Half life (d)	Coeff. of determ.	Averaged difference[2] (%)
10	I	7.0 (6.9-7.0)	0.0044	157	0.99	2
	II	6.9 (6.8-6.9)	0.055	13	0.97	14
15	I	7.0 (6.9-7.1)	0.010	68	0.99	1
	II	6.9 (6.8-6.9)	0.11	6.2	0.94	7
20	I	7.1 (7.0-7.1)	0.054	13	1.0	6
	II	7.0 (6.9-7.1)	0.23	3.0	0.86	5

1. I = first period, II = second period (see text).
2. See text.

6.6 ADSORPTION OF AZINPHOS-METHYL ON BOTTOM MATERIALS

Adsorption of pesticides on agricultural soils under various conditions has been studied by many workers. These studies show that pesticide adsorption is a complex phenomenon, dependent on the chemical and physical properties of the pesticides as well as of the soil. In the field, adsorption in influenced by many environmental factors and especially by soil properties like organic matter content, clay content, cation-exchange capacity, surface area and pH. Of these partly interrelated properties, organic matter content and clay content are usually considered the most important. The composition of soils and bottom materials should therefore be specified.

Data on adsorption of azinphos-methyl onto bottom materials rich in organic matter and clay were not found in literature (Table 9).

Procedures in adsorption tests with azinphos-methyl

Adsorption of azinphos-methyl was studied by the batch-equilibration technique for bottom materials from the tanks and from the watercourses on fruit farms. For characteristics of the bottom materials see Table 23.

Solutions of azinphos-methyl (analytical grade) in de-ionized water were prepared with CaCl at 555 g m^{-3}. The concentrations of azinphos-methyl were 1, 3, 5, 7, 9 and 13.5 g m^{-3}, respectively. Of each of these solutions, 10 cm^3 were equilibrated in quadruplicate with 2 g of bottom material (air dry) in 13-cm^3 centrifuge tubes with ground-glass stoppers. The tubes were turned overnight (15 h) on an inclined turntable at a frequency of 0.22 Hz (13 min^{-1}) at room temperature (18 to 21 °C).

After centrifuging, 5 cm^3 of the supernatant aqueous phase was analysed for concentrations. In 14 tubes, the remaining bottom material was also extracted, after which the extract was cleaned up according to the improved procedure described in Section 6.4. The recovery of the amounts of azinphos-methyl supplied to water and bottom material was about 100% with a coefficient of variation of 7%. Corrections for recovery or decomposition were not made.

Table 23. Origin and characteristics of the bottom materials used in adsorption studies for azinphos-methyl and dimethoate. Bottom materials collected from the water tanks and from the watercourses on the fruit farms in the Lopikerwaard Polder. Compositional data from the Laboratory for Soil and Crop Testing, Oosterbeek.

Origin of material[1]	Loss on ignition (%)	C(element) (%)	$CaCO_3$ (%)	Clay <2 µm (%)	Silt 2-50 µm (%)	Cation[3] exchange capacity (mmol kg^{-1})	pH-KCl	Adsorption coefficient ($m^3\ kg^{-1}$)	
								azinphos-methyl	dimethoate
Tanks	8.7	5.05	11.3	53.3	32.2	389	7.2	$70\ 10^{-3}$	$0.5\ 10^{-3}$ $2.6\ 10^{-3}$ [2]
BSL front section	16.1	9.27	3.4	64.3	33.8	487	6.9	$149\ 10^{-3}$	$0.79\ 10^{-3}$
BSL back section	26.2	15.43	2.8	59.8	36.4	623	6.9	$409\ 10^{-3}$	$3.4\ 10^{-3}$
BSD back section	20.5	11.63	5.7	55.5	36.8	570	7.1	$211\ 10^{-3}$	$1.6\ 10^{-3}$
JM front section	7.4	4.04	2.1	27.7	20.5	250	7.1	$53\ 10^{-3}$	
JM back section	11.5	5.92	3.3	33.8	20.2	313	7.0	$77\ 10^{-3}$	

1. For sampling sites see Section 9.3.2.
2. Relatively high adsorption coefficient, using only the lowest two concentrations.
3. Based on the entity of cation carrying a single charge.

Checks were made on the possible effect of air-drying of bottom material before the experiment. Adsorption tests for azinphos-methyl were also done with a suspension of fresh bottom material, as used for the conversion tests (Section 6.4). These suspensions were also equilibrated in the large tubes (70 cm^3) for 15 h. The extraction procedure was the same as described in Section 6.4.

Measured adsorption coefficients of azinphos-methyl

The mass fraction of azinphos-methyl adsorbed onto the bottom material (expressed on dry matter basis) was plotted in Figure 15 against the concentration remaining in the solution. Linear adsorption isotherms were calculated with a regression program from the points for the five lowest concentrations. The adsorption coefficients ($K_{s/l}$), which represent the slope of the isotherms, are given in Table 23. At the highest concentration, a small deviation from the linear adsorption isotherm was sometimes observed, especially when adsorption was comparatively low.

The adsorption coefficients of azinphos-methyl for the various bottom materials were much higher than the coefficients reported for silt-loam soils (Section 3.4, Table 9). The adsorption coefficients of azinphos-methyl for the various bottom materials correspond well with the organic matter contents of these bottom materials (Table 23).

The averaged differences between the final concentrations of azinphos-methyl in quadruplicate samples were less than 5% of the average values for all concentrations.

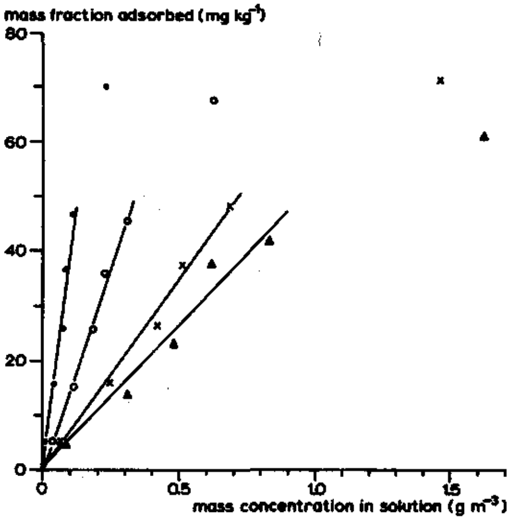


Figure 15. Adsorption of azinphos-methyl on various bottom materials. The linear adsorption isotherms were derived from the points for the lowest five concentrations. ● = Benschop, siphon-linked ditch, back section; o = Benschop, siphon-linked ditch, front section; x = Bottom material used in tank trial; ▲ = Jaarsveld, middle ditch, front section.

Adsorption of azinphos-methyl onto fresh bottom material from the outdoor tanks resulted in an adsorption coefficient of 0.073 ($m^3\ kg^{-1}$), which was only slightly higher than that for air-dried bottom material (Table 23). Thus a clear effect of air-drying of bottom material on adsorption of azinphos-methyl could not be demonstrated.

6.7 ADSORPTION OF DIMETHOATE ON BOTTOM MATERIALS

Values for the adsorption of dimethoate on bottom material were lacking in the literature.

Procedures in adsorption tests with dimethoate

Four bottom materials were used as characterized in Table 23. Solutions of dimethoate (analytical grade) in de-ionized water with $CaCl_2$ at 5550 g m^{-3} were prepared. The initial concentrations of dimethoate were 1.06, 2.25, 5.0, 10.1, and 19.5 g m^{-3}. Of each of these solutions, 10 cm^3 were added in triplicate to 2 g of bottom material (air dry) in centrifuge tubes, which were then rotated overnight as in Section 6.6.

After centrifuging, 5 cm^3 of the supernatant liquid was extracted with consecutively 10, 5 and 5 cm^3 of dichloromethane (Section 5.4). Again, the material balance was checked by extracting the bottom material (Section 6.5). The recovery of dimethoate applied to 11 adsorption systems with water and bottom material was 91%, with a coefficient of variation of 2%. Corrections for recovery or decomposition were not made.

The effect of air drying of bottom material on the adsorption isotherm was checked in the way described in Section 6.6.

Measured adsorption coefficients of dimethoate

The adsorption of dimethoate onto the bottom materials at various concentrations in solution is shown in Figure 16. Linear isotherms were calculated with a regression program using all the points. The adsorption coefficients of dimethoate onto the various bottom

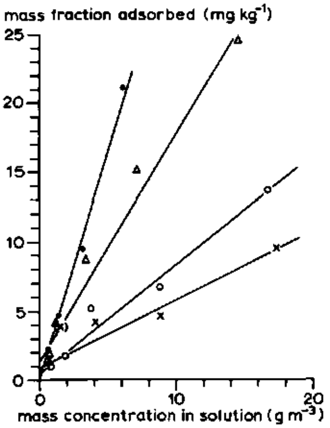


Figure 16. Adsorption of dimethoate on various bottom materials. Linear adsorption isotherms calculated using the points for all concentrations. ● = Benschop, siphon-linked ditch, back section; o = Benschop, siphon-linked ditch, front section; Δ = Benschop, supplementarily drained ditch, back section; x = Bottom material used in tank trial.

materials are given in Table 23. These coefficients are about a hundredth of those for azinphos-methyl.

The relationship between the adsorption coefficients and the organic matter contents was quite clear, just as for azinphos-methyl (Table 23). The differences between the concentrations of dimethoate in triplicate samples with the small centrifuge tubes were less than 4% of their averages. With the large centrifuge tubes (70 cm^3), the differences between triplicate samples were less than 2% of the average concentrations.

The adsorption of dimethoate at relatively low concentrations on fresh (not dried) bottom material and on previously dried bottom material is presented in Figure 17. The adsorption coefficient of dimethoate onto fresh bottom material was 0.0032 $m^3\ kg^{-1}$. That for the dried bottom material was half of that value. The reduction in adsorption due to previous drying may be caused by a partly irriversible change in the organic material during air-drying.

6.8 GENERAL DISCUSSION

The hydrolysis rates of azinphos-methyl and dimethoate at pH around 7 are rather low. These rates increase strongly with pH. This is one of the most essential characteristics of these compounds in surface water and can be seen as confirmation of earlier investigations.

Conversion rates can be studied with various types of water, including distilled water, de-ionized water, tap water, ground water and surface water. Close comparison of the results of incubation of azinphos-methyl in surface water with those obtained in buffered aqueous solutions was rather difficult in view of variations in pH in the surface water tests.

Remarkable is the catalytic effect of Cu^{2+} on conversion rates of azinphos-methyl and dimethoate in surface water. So in conversion studies, copper concentrations in surface

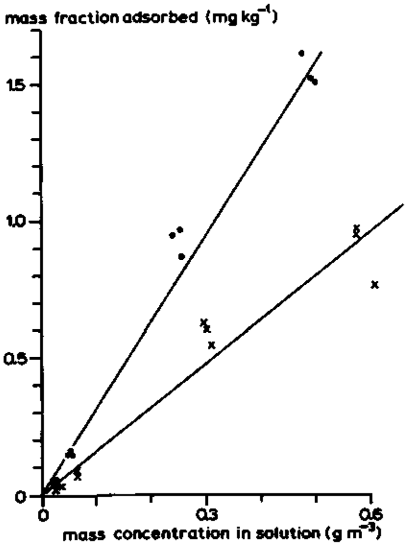


Figure 17. Adsorption of dimethoate on bottom material of outdoor tanks. Isotherms were calculated with linear regression program for all relatively low concentrations. ● = fresh (undried) bottom material, x = started from air-dry bottom material.

water must be measured. Possibly other ions that may by present in surface water can also catalyse conversion reactions of both compounds.

Higher temperature accelerated conversion of both compounds. The Arrhenius relationship sometimes gave a poor discription of the relationship between the first-order rate coefficients and temperature. More research is needed to clarify this relationship.

Many other factors may influence the conversion rates of pesticides in surface waters, but study of them has only just started. Light appears to be an important factor in conversion. Laboratory tests by Liang & Lichtenstein (1972) showed that only ultraviolet light was effective in the photo-chemical conversion of azinphos-methyl in water ($k_{c,w}$ = 8.7 d^{-1}; $t_{\frac{1}{2}}$ = 0.08 d), whereas yellow or red light yielded conversion rates as low as in the dark . In the laboratory, the influence of light on conversion rates of pesticides in surface water should thus be studied under light conditions representative for the field. Photosensitizers affect the photo-chemical conversion rates of pesticides; therefore extrapolation of rates from the laboratory to the field is extremely difficult (Howard et al., 1978).

After a first period of slow conversion, a strong increase was usually observed in the rate of conversion of dimethoate. This may be related to changes in the systems, but further research will be needed to clarify these changes. Techniques for incubation under aerobic conditions also need further attention. The relatively fast conversion of both compounds in systems with anaerobic bottom material is remarkable. Literature data on conversion rates of organophosphorus pesticides in anaerobic bottom materials are still scarce, but conversion rates of various chlorinated hydrocarbon pesticides in biologically active sludge were more rapid under anaerobic than under aerobic conditions (Hill & McCarty, 1967).

There is an obvious need to predict the conversion rate of pesticides in the field from standardized laboratory tests. However one of the difficulties is to take representative water samples for incubation tests, as the variation in time and space in bacterial species and numbers is a serious problem. Attempts are made to use standardized water systems by inoculating with a filtrate of bottom material and soil. Unfortunately, comparative data on such systems are not yet available. Another possible incubation system is an active-sludge system obtained from a sewage plant.

Because many factors influence the conversion rates of azinphos-methyl and dimethoate in surface water, these laboratory results should not be used directly to predict conversion rates under field conditions. The behaviour of the model compounds in outdoor tank systems is discussed in Chapter 7 and that in ditches in the field is discussed in Chapter 9.

7 Measurements in outdoor tanks: decline in water and penetration into bottom material

7.1 INTRODUCTION

Rate coefficients for the decline of organophosphorus pesticides in outdoor aquatic systems under temperature and light conditions comparable to those in field situations are scarce in literature. Only one outdoor trial with azinphos-methyl in a wading pool filled with pond water and a bottom layer of silt has been studied (Bayer A.G., 1978). They found that at a water temperature of about 29 °C and at pH 7 the rate of decline of azinphos-methyl in pond water was 0.58 d^{-1} ($t_{\frac{1}{2}}$ = 1.2 d). The high water temperature and near-neutral pH are not representative for surface waters in the Netherlands. Rate coefficients for the decline of dimethoate in outdoor waters could not be found in the literature.

To gain more insight into the decline of azinphos-methyl and dimethoate in surface water, outdoor trials were set up in tanks. The importance of a layer of bottom material in the tanks on the physico-chemical behaviour of the model compounds was also investigated.

The extent of penetration of azinphos-methyl and dimethoate into the bottom material in the tanks was studied on a limited scale.

Some attention was paid to differences in rate of decline when the compounds were applied as analytical grade or as formulated products.

7.2 DESIGN OF THE OUTDOOR TANK TRIALS

Setting up the tanks

Six bath tubs were dug into the soil near the laboratory. The rims protruded approximately 5 cm above the soil surface to avoid contamination from surrounding soil. Stainless-steel wire-nettings (mesh size 11 mm) were placed on the tanks to reduce disturbance. The sides were of enamel.

In four tanks, a bottom layer 0.1 m thick was introduced; the other two tanks did not contain bottom material. All six tanks were filled with tap water, originating from deep groundwater. The tanks with bottom material were filled in August 1975; those without bottom material were installed in spring 1976.

After each addition of water with a bucket (10 dm^3), the rise in water level was measured with a stainless-steel rule. From the calibration curve, the volume in each of the tanks could be inferred at any time from the water level.

The bottom material was collected from a comparatively clean watercourse without significant urban influences, called the 'Tutenburgse Wetering', situated near Giesbeek

(Provence of Guelderland). The watercourse was enlarged three years before sampling during land consolidation work. The upper 10 cm of the bottom material from the watercourse was collected with a basket-type cutter having a fine-meshed wire-netting inside the basket. This material was partially dried in air and then sterilized during one day by steaming under a sheet.

To obtain a similar development of biological activity in the four tanks with bottom material, they were inoculated with 2 dm^3 well mixed fresh bottom material, for instance with cyclops, daphnias, snails and tubifex. Furthermore, these tanks were partly planted with a few small plants of Canadian pondweed (*Elodea canadensis*) collected from the sampling ditch.

Application of pesticides

Tanks I and III were kept untreated during all trials. The tanks without a layer of bottom material were designated Tanks V and VI. For quick reference the various treatments are indicated with abbreviations consisting of the characters A for azinphos-methyl, D for dimethoate and F for formulated product. Arabic numerals indicate the various trials (1 to 5) and T plus Roman numeral refers to the tanks (I to VI) (Table 24). After application, the insecticide dose was manually mixed with the water using a skimmer. The initial water volume in the tanks in the first trial was about 0.1 m^3 and was 0.15 m^3 in all other trials.

The first tank trial started in September 1975 with dimethoate applied to Tanks II and IV as analytical grade (98% purity) at a concentration of 10 mg m^{-3}.

In all other tank trials, both azinphos-methyl and dimethoate were applied simultaneously at a concentration of about 100 mg m^{-3}. In June 1976, the second trial started with azinphos-methyl and dimethoate, both analytical grade. The third trial started in July 1976 with a wettable powder of azinphos-methyl (Gusathion, 25% (w/w) w.p.) and a liquid formulation of dimethoate (Rogor, 40% w/v).

Table 24. Data on pesticides in outdoor tank trials. Abbreviations: A for azinphos-methyl, analytical grade (98% purity); AF for azinphos-methyl, formulated product (Gusathion, 25% w.p.); B for blank (untreated) experiment; C refers to an addition of copper sulphate; D for dimethoate, analytical grade (98% purity); DF for dimethoate, formulated product (Rogor, 40% liquid); T plus Roman numeral refers to the tanks.

Trial	Tanks with a layer of bottom material				Tanks with only water	
	TI	TII	TIII	TIV	TV	TVI
1	B	D1 TII	B	D1 TIV	-	-
2	B	A2 TII D2 TII	B	A2 TIV D2 TIV	A2 TV D2 TV	A2 TVI D2 TVI
3	B	AF3 TII DF3 TII	B	AF3 TIV DF3 TIV	AF3 TV DF3 TV	AF3 TVI DF3 TVI
4	B	-	B	-	AFC4 TV DFC4 TV	AFC4 TVI DFC4 TVI
5	B	AC5 TII DC5 TII	B	AC5 TIV DC5 TIV	AC5 TV DC5 TV	AC5 TVI DC5 TVI

During the first three trials, algal bloom caused a daily fluctuation in pH of the water compartment of all tanks. Before the fourth trial started in Tanks V and VI, both tanks were carefully cleaned and refilled with fresh drinking water. To avoid algal bloom in these tanks, the algicide copper sulphate was added to mass concentration of copper 1.5 g m^{-3}. In this fourth trial, the same products as in the third trial were introduced into Tanks V and VI.

In the last trial (No 5) in the autumn of 1976, Tanks II, IV, V and VI were replenished with drinking water and the same concentration (1.5 g m^{-3}) of copper sulphate was added. After 11 days, a double amount of copper sulphate was introduced into those tanks. In the fifth trial, azinphos-methyl and dimethoate were applied as analytical grade to Tanks II, IV, V and VI (Table 24).

Characteristics of the water

Some chemical characteristics of water samples from the outdoor tanks were measured by the Eastern Laboratory for Water Testing, Doetinchem. The results for water samples from the second and the fifth trial are given in Table 25. The water samples may be classified as eutrophic surface water due to the relatively high concentrations of phosphate.

Due to the strong sunshine during 1976, a strong algal bloom occurred in the eutrophic water of all tanks. The algae take up CO_2 during photosynthesis in the daytime and release CO_2 at night. The CO_2 uptake disturbed equilibrium of carbon dioxide and calcium bicarbonate, causing a rise in pH during the day (Figure 18).

Table 25. Chemical characteristics of water samples from outdoor tank trials, measured by the Eastern Laboratory for Water Testing, Doetinchem. Sampling date for Trial 2, 15 June 1976; for Trial 5, 21 September 1976.

Characteristics	Trial 2				Trial 5	
	T II	T IV	T V	T VI	T IV	T V
pH	9.7	9.6	8.7	9.1	7.6	8.1
COD (g m^{-3})	110	125	95	65	180	125
NO_3^- (g m^{-3})	1	1	< 1	< 1	< 1	< 1
NH_4^+ (g m^{-3})	0.29	< 0.03	< 0.03	< 0.03	< 0.52	< 0.13
Total N (g m^{-3})	3.1	3.2	1.9	1.4	0.68	1.4
Orthophosphate (g m^{-3})	0.60	2.4	< 0.03	< 0.03	0.25	0.08
Total phosphate (g m^{-3})	1.1	5.5	0.49	0.36	0.46	0.20
Cl^- (g m^{-3})	18	16	15	20	15	12
Ca^{2+} (g m^{-3})					43	29
HCO_3^- (g m^{-3})					127	87
CO_2 (g m^{-3})					9	2
CO_3^{2-} (g m^{-3})					0	0
Hardness (as CaO) (g m^{-3})					68	49
Conductivity (mS m^{-1})	28.8	23.2	20.9	20.5	25.3	17.6

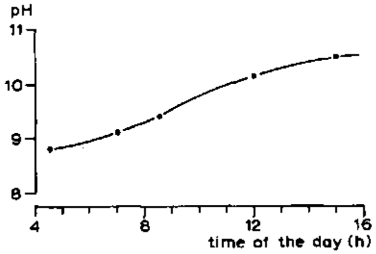


Figure 18. pH in the water compartment (average of six water tanks) against time of day. Measurements on 16 July 1976.

The pH in the water compartments were occasionally measured several times during the day with a digital pH meter. The pH was also mostly checked at intervals of 2 days at 08:30 and 16:00 h. As the relationships between pH and the hydrolysis rates of the model compounds are not linear, the assessment of an average pH in the water compartment is only of limited importance.

Characteristics of bottom material

In April 1977, the year after the trials, water was slowly removed from Tanks II and IV without disturbing the sediment layer. Samples of bottom material were taken with a skimmer. The composition of the upper few centimetres of the mud layer and some physical and chemical characteristics of the mud layer were measured by the Laboratory for Soil and Crop Testing in Oosterbeek (Table 23). The mineral fraction of the bottom material can be classified into the 'clay' textural class. The organic matter content is rather high in comparison with most agricultural clay soils.

For measurement of the volume fraction of liquid and bulk density of the bottom material, mud cores were taken in triplicate from Tanks II and IV, according to procedure described in Section 4.4. The columns of bottom material were frozen at -20 °C and subsequently divided into slices of equal thickness (0.01 m) with a mechanical saw normally used for research on soil slides at the Soil Survey Institute in Wageningen. The slices were weighed (m_b) and dried at 105 °C to constant mass (m_d). The volume of the slices of bottom material (V_b) was calculated from Equation 11, assuming complete saturation of the bottom material and constant density of the solid phase in the upper few centimetres of the mud layer.

$$V_b = (m_b - m_d)/\rho_w + m_d/\rho_s \tag{11}$$

in which

ρ_w = density of water (kg m^{-3})
ρ_s = density of solid phase of bottom material (kg m^{-3})

The density of the solid phase of the bottom material was measured as 2580 kg m^{-3} (at Laboratory for Soil and Crop Testing, Oosterbeek).

The volume fraction of liquid (ε_1) and the dry bulk density (ρ_b) were calculated from Equations 12 and 13, respectively

$$\varepsilon_1 = (m_b - m_d)/(V_b \rho_w) \tag{12}$$
$$\rho_b = m_d/V_b \tag{13}$$

The profile of volume fractions of liquid and of bulk density in the bottom material are shown in Figure 19. Compared with agricultural soils, the volume fractions of liquid are high and dry bulk densities are low, especially in the upper layers. Data are similar to those for ditch bottoms.

Sampling of water and GLC analysis

Rainfall and evaporation resulted in a variation of the water volume in the tanks. Before each sampling, the height of the water surface was measured, after which the volume could be read from the calibration curve.

At the sampling dates, the range of water temperature in the preceding period was read from minimum--maximum thermometers immersed in Tanks I, III and V.

During the first trials, composite water samples totalling 1 dm^3 were collected with a stainless steel ladle. At the beginning of all other trials, composite water samples totalling 0.1 dm^3 were collected with a pipette of 10 cm^3, and at a later stage, when concentrations became low, composite samples totalling 1 dm^3 were again taken with the ladle.

All water samples were extracted with dichloromethane in separatory funnels as described in Section 5.3 and 5.4. Azinphos-methyl in the extracts of the water samples from Trials 3 and 4 was measured by GLC on Column I; the extracts from Trials 2, 3 and 5 were analysed with Column II (Table 14). The concentrations of dimethoate in the extracts of water samples from Trials 1, 3 and 4 were measured on Column I; those from Trials 3 and 5 were analysed on Column II and those from Trial 2 were measured on Column III (Table 15). Some series were thus measured on two different columns at different times, which sometimes gave slight differences in the concentrations but only small differences in the slope of

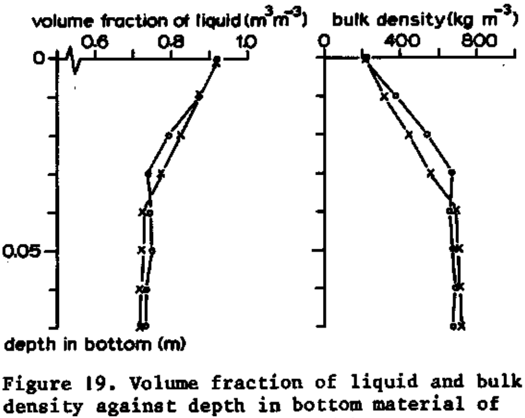


Figure 19. Volume fraction of liquid and bulk density against depth in bottom material of outdoor Tanks II (o) and IV (x).

decline. No interfering substances were found when extracts from the untreated Tanks I and III were measured on all columns. So clean-up of the extracts of water samples from outdoor tanks was not necessary.

Correction for sampling of water

Since the volume of water in outdoor tanks varied with rain and evaporation, total mass of the compounds at the sampling dates were used for plotting the decline of the compounds with time.

Because the water samples withdrawn from the tanks were sometimes rather large (especially during Trial 1 with dimethoate), a correction for volume removed was necessary before continuous decline plots could be made.

The discontinuities due to water sampling in the relationship between the mass of pesticide in the water compartment on a logarithmic scale against time could be eliminated with the following equations:

$$\begin{array}{lll} & & m_n = c_{\mathrm{w},n} \times V_{\mathrm{w},n} \\ t = 0, & n = 1 : & m_1' = m_1 \\ t_1 & n = 2 : & m_2' = m_2/(1 - V_{\mathrm{s},1}/V_{\mathrm{w},1}) \\ t_{n-1} & n \geqslant 3 : & m_n' = m_n/(1 - V_{\mathrm{s},n-1}/V_{\mathrm{w},n-1}) \times (1 - V_{\mathrm{s},1}/V_{\mathrm{w},1}) \end{array} \qquad (14)$$

in which

n = integer, Sampling No (in time series) (1)
m_n = measured mass of pesticide in water compartment before Sampling n (mg)
$c_{\mathrm{w},n}$ = mass concentration of pesticide in water compartment (in time series) (mg m^{-3})
$V_{\mathrm{w},n}$ = volume of water compartment before Sampling n (m^3)
m_n' = mass of pesticide in water compartment corrected for volume of samples withdrawn (mg)
$V_{\mathrm{s},n}$ = volume of water sample (in time series) (m^3)

The correction steps (Equation 14) were introduced into an adapted linear regression program on a Hewlett Packard desk calculator. The first-order rate coefficients (k_r in d^{-1}) for the decline of the substances correspond to the absolute value of the regression coefficients of the regression lines for ln m_n' against time.

The differences between the measured masses and the corrected masses of azinphos-methyl and dimethoate in the water compartment of the tanks, due to withdrawals, could be neglected in Trials 2, 3 and 4 because the volumes withdrawn were relatively small (0.1 dm^3). However, in Trials 1 and 5, a correction was necessary, because the sample volume was 1 dm^3. Moreover in Trial 1, sampling was rather frequent and in Trial 5 also water samples of 2.5 dm^3 were collected for assessment of water quality.

Sampling of bottom material and GLC analysis

The penetration of dimethoate into the bottom layer was measured during Trial 1. Bottom samples were taken with tubes in triplicate on 24 September and 15 October 1975 (Section 4.4). The penetration of azinphos-methyl was investigated during Trial 2 by taking mud cores in duplicate on 10 June and on 15 June 1976. The cross-sectional area of the bottom material columns was about 12.3 cm^2.

The mud cores were stored in a deep-freezer at -20 °C. As the development of a suitable clean-up method for azinphos-methyl took several months, the storage time was nearly half a year. The storage time for bottom cores with dimethoate was less than one month. The frozen mud columns were divided into slices 1-2 cm thick with a carborundum handsaw. The slices were weighed before extraction. After extraction and drying at 105 °C, the dry mass of the bottom material was estimated. The volumes of the wet bottom material were calculated from Equation 11. The depth below the sediment-water interface was calculated from the volume of the slice, and the surface of the bottom column. The saw-cut was 2 mm for the hand-sawn mud columns.

The procedures for extraction and clean-up of the extracts for azinphos-methyl and dimethoate are described in Sections 5.6, 5.7, 5.11 and 5.12, respectively. The cleaned extracts were analysed by GLC on Column II for azinphos-methyl and on Column III for dimethoate (Tables 14 and 15).

In a separate test the effect of storage time on recovery of azinphos-methyl from frozen mud columns was studied . Mud samples were prepared from 10 g of air-dry bottom material and 50 cm^3 of water in a polyethylene cup. These samples were spiked with analytical-grade azinphos-methyl and stored at about -20 °C. They were extracted and analysed after 1, 105 and 242 days in the same way as the slices of bottom material from the tank trials.

Recovery from 16 samples of bottom material spiked with azinphos-methyl was 91%, with a coefficient of variation of 7% (Section 5.11). After 105 and 242 days, about 90% and 102% of the initial amounts were recovered, with coefficients of variation of about 9% and 6%, respectively. These results show that a correction factor for storage time was not necessary. Also no corrections were made for the recovery. The average recovery of dimethoate from bottom material was 95%, so no corrections were made for recovery of dimethoate either.

As a result of the problems encountered in development of suitable clean-up procedures, only a few measurements could be done on penetration of the compounds into the bottom layer of the tanks.

7.3 MEASURED RATES OF DECLINE IN WATER

The plots of the corrected masses of azinphos-methyl in the water compartment against time for Trials 2 to 5 are shown in Figure 20. Plots for dimethoate in Trials 1 to 5 are presented in Figure 21.

Differences in decline rate of the model compounds in the tanks with bottom layer (TII and TIV) in the first three experiments (without addition of copper sulphate) were

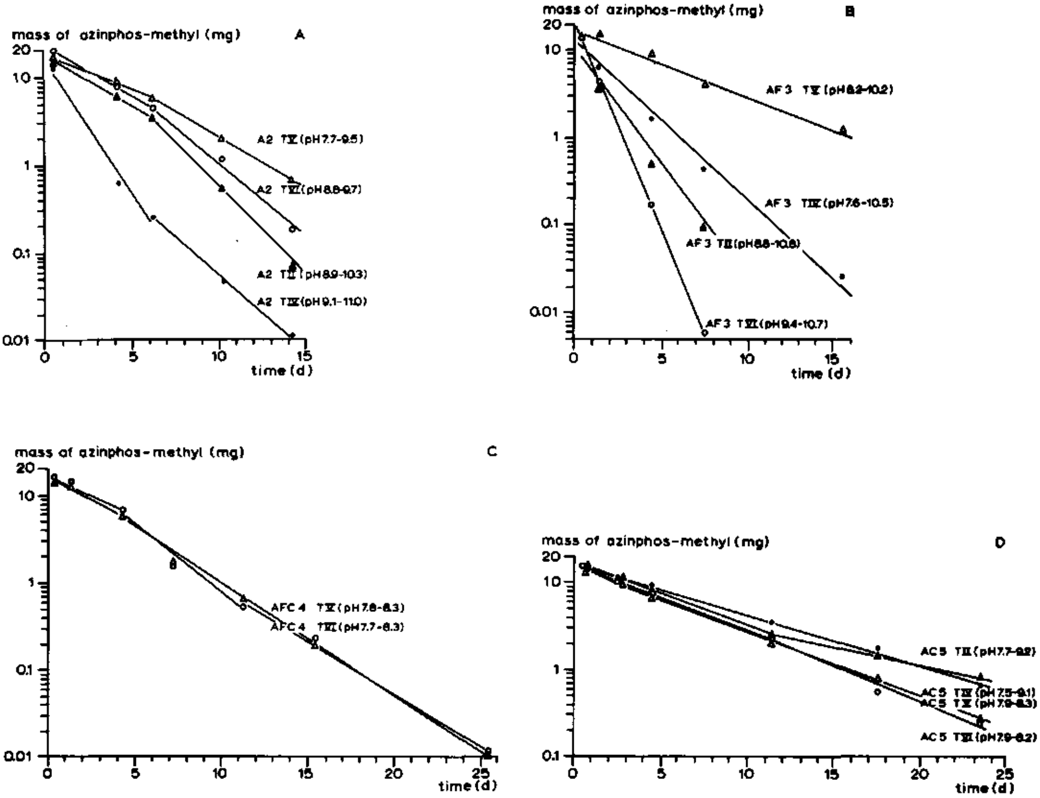


Figure 20. Mass of azinphos-methyl in water compartment of outdoor tanks. A. Trial 2: analytical grade added on 4 June 1976. B. Trial 3: formulated product (Gusathion 25% w.p.) added on 15 July 1976. C. Trial 4: as Trial 3 added on 5 August 1976; copper sulphate added to mass concentration of Cu^{2+} 1.5 g m^{-3} on 4 August. D. Trial 5: analytical grade added on 20 September 1976; copper sulphate added to mass concentration of Cu^{2+} 1.5 g m^{-3} on 19 September and a further 3 g m^{-3} on 1 October. In Trial 5 (Fig. D) the mass is corrected for volume of samples withdrawn. For coding of lines see Table 24.

distinct. The same holds for rates of decline in the tanks without bottom material (TV and TVI) (Figures 20A, B; 21A, B,C). Such differences can probably partly be ascribed to differences in algal bloom, resulting in different pH and light penetration. In Trials 4 and 5, with addition of algicide, pH fluctuations were small (Table 26). Consequently the differences in the decline pattern of the compounds were small (Figures 20C, D; 21D, E).

If the decline can be described with a first-order rate equation, the relationship between the logarithm of the mass of the pesticide and time is linear. As can be seen from most decline plots, the relationship is almost linear for only part of the period of investigation. For those parts of the decline plots, linear regression lines were calculated. These lines are drawn in Figures 20 and 21. The corresponding rate coefficients for the decline of both compounds are given in Table 26.

The rates of decline of the model compounds in the water compartment were much faster than in the laboratory tests (Chapter 6). In tanks without bottom layer, the decline was also rather fast. In trials in which both compounds were applied simultaneously to the same tank, decline of azinphos-methyl was faster than of dimethoate (Table 26).

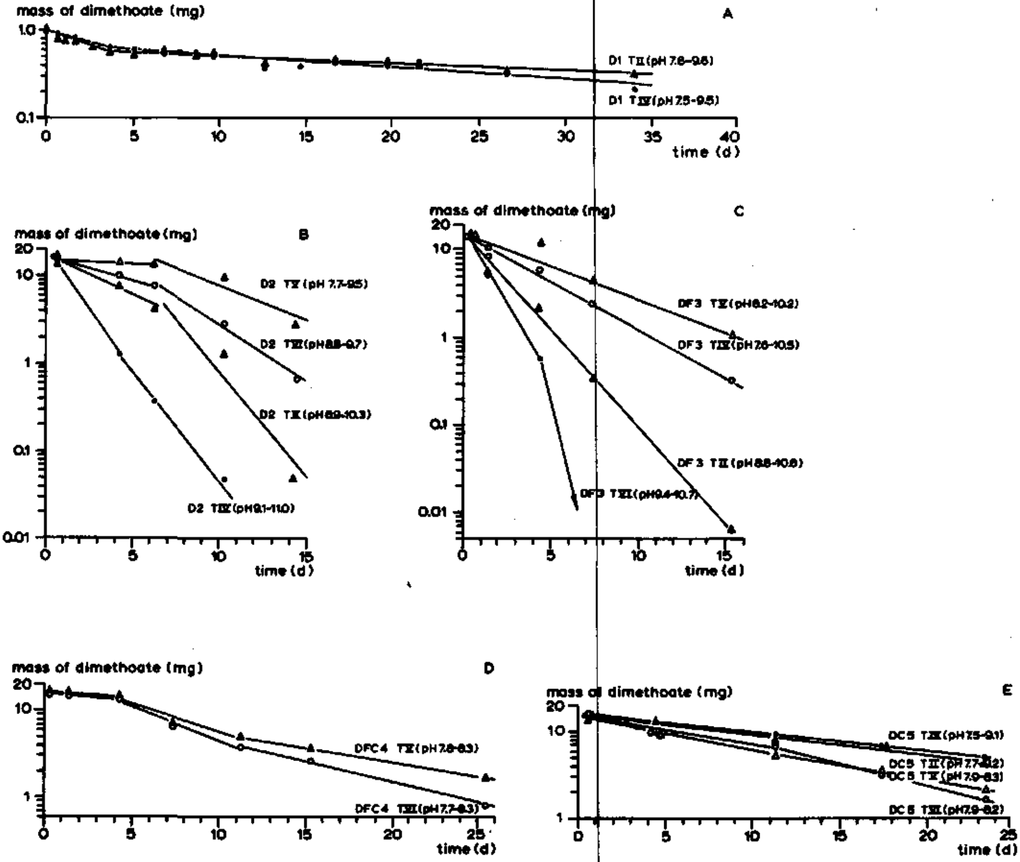


Figure 21. Mass of dimethoate in water compartment of outdoor tanks. A. Trial 1: analytical grade added on 23 September 1975. B. Trial 2: analytical grade added on 4 June 1976. C. Trial 3: formulated product (Rogor 40% liquid) added on 15 July 1976. D. Trial 4: as Trial 3 added on 5 August 1976; copper sulphate added to mass concentration of Cu^{2+} 1.5 g m^{-3} on 4 August. E. Trial 5: analytical grade added on 20 September 1976; copper sulphate added to mass concentration of Cu^{2+} 1.5 g m^{-3} on 19 September and a further 3 g m^{-3} on 1 October. In Trials 1 (Fig. A) and 5 (Fig. E), masses were corrected for volume of samples withdrawn. For coding of lines see Table 24.

Influence of pH and temperature on the decline rates

The ranges of pH in the water compartment of the different tanks, measured in periods with approximately linear decline, are presented in Table 26. The ranges of pH during each trial are shown against the regression lines in Figures 20 and 21. Both figures show an increase in the decline rate at increasing pH range. This indicates that the maximum pH in the water compartment is probably a major factor in the rate of decline of both compounds. For this reason, rate coefficients for decline of azinphos-methyl and dimethoate in the first three tank trials (without copper sulphate) were plotted against the maximum pH in Figure 22. The scatter in Figure 22 results from the influence of other major factors like temperature, algal bloom and light (external and in the water compartment).

Table 26. First-order rate coefficients for decline of azinphos-methyl and dimethoate in water compartment of outdoor tanks. Derived for periods with approximately linear relationships between mass of insecticide (log scale) and time. Abbreviations: A for azinphos-methyl, D for dimethoate, F for formulated compound, C for copper sulphate addition and T for tank.

Time period	Information on water systems					Azinphos-methyl			Dimethoate		
	tank No	pH		water temp. (°C)		code for trial	rate coeff. (d^{-1})	half life (d)	code for trial	rate coeff. (d^{-1})	half life (d)
		8:30 h minimum	16:00 h maximum	av.	range						
1975											
09-23/ 09-27	II	8.2	9.6	16	12-17				D1 TII	0.14	5.0
	IV	8.2	9.5	16	10-18				D1 TIV	0.12	5.6
09-28/ 10-28	II	7.8	9.3	12	3-18				D1 TII	0.021	34
	IV	7.5	9.1	12	5-17				D1 TIV	0.032	22
1976											
06-04/ 06-10	II	8.9	9.7	19	10-24	A2 TII	0.23	3.0	D2 TII	0.22	3.2
	IV	9.3	10.6	21	10-28	A2 TIV	0.72	1.0	D2 TIV	0.67	1.0
	V	7.7	8.4	20	10-25	A2 TV	0.19	3.7	D2 TV	0.013	53
	VI	8.8	9.7	20	10-25	A2 TVI	0.26	2.7	D2 TVI	0.12	5.6
06-10/ 06-30	II	9.0	10.3	20	13-27	A2 TII	0.49	1.4	D2 TII	0.57	1.2
	IV	9.1	11.0	22	14-28	A2 TIV	0.39	1.8	D2 TIV	0.59	1.2
	V	8.1	9.5	20	14-26	A2 TV	0.27	2.6	D2 TV	0.20	3.5
	VI	8.9	9.7	20	14-26	A2 TVI	0.40	1.7	D2 TVI	0.31	2.2
07-15/ 07-30	II	8.8	10.8	21	15-28	AF3 TII	0.59	1.2	DF3 TII	0.50	1.4
	IV	7.6	10.5	21	15-29	AF3 TIV	0.41	1.7	DF3 TIV	0.25	2.8
	V	8.2	10.2	21	15-30	AF3 TV	0.17	4.0	DF3 TV	0.17	4.1
	VI	9.4	10.7	21	15-30	AF3 TVI	1.1	0.63	DF3 TVI	0.80	0.87
08-05/ 08-09	V	7.8	8.3	17	14-21	AFC4 TV	0.25	2.8	DFC4 TV	0.036	19
	VI	7.7	8.1	17	14-21	AFC4 TVI	0.21	3.3	DFC4 TVI	0.010	67
08-09/ 08-16	V	8.2	8.3	20	17-24	AFC4 TV	0.31	2.3	DFC4 TV	0.14	5.0
	VI	8.2	8.3	20	17-24	AFC4 TVI	0.36	1.9	DFC4 TVI	0.18	4.0
08-16/ 08-30	V	8.2	8.3	19	11-24	AFC4 TV	0.29	2.4	DFC4 TV	0.078	8.9
	VI	8.1	8.3	19	11-24	AFC4 TVI	0.28	2.5	DFC4 TVI	0.11	6.5
09-20/ 10-01	II	7.7	8.8	15	11-24	AC5 TII	0.16	4.4	DC5 TII	0.055	13
	IV	7.5	8.0	16	12-23	AC5 TIV	0.13	5.5	DC5 TIV	0.038	18
	V	8.1	8.3	16	12-23	AC5 TV	0.17	4.0	DC5 TV	0.089	7.8
	VI	8.1	8.2	16	12-23	AC5 TVI	0.17	4.0	DC5 TVI	0.067	10
10-01/ 10-13	II	7.7	9.2	15	12-18	AC5 TII	0.095	7.3	DC5 TII	0.059	12
	IV	7.5	9.1	17	12-19	AC5 TIV	0.14	5.0	DC5 TIV	0.052	13
	V	7.9	8.1	15	12-19	AC5 TV	0.17	4.1	DC5 TV	0.083	8.4
	VI	7.9	8.1	15	12-19	AC5 TVI	0.18	3.8	DC5 TVI	0.12	5.8

Extrapolations of the rate coefficients for decline of both compounds in water to pH below 8 are rather uncertain. The coefficient for decline of azinphos-methyl in surface water at pH 7 may be less than 0.1 d^{-1} ($t_{\frac{1}{2}}$ > 7 d). The rate coefficient of dimethoate in surface water with pH 7 could be less than 0.01 d^{-1} ($t_{\frac{1}{2}}$ > 70 d) (Figure 22).

The temperature fluctuations in the water compartments were rather large, ranging from 10 to 30 °C during the summer and from 3 to 24 °C in the autumn (Table 26). Average water temperatures were calculated from the highest and lowest water temperatures read

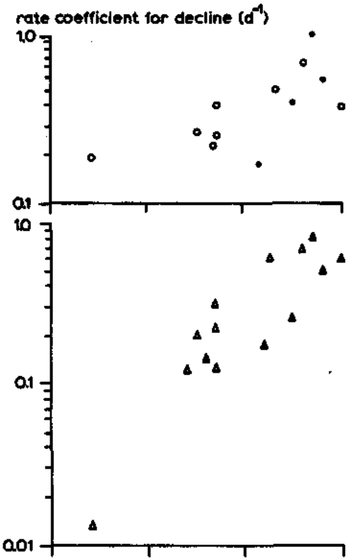


Figure 22. First-order rate coefficients for decline of the model compounds in the water compartment of outdoor tanks against maximum pH during Trial 1 to 3. Average water temperature ranged from 16 to 22 °C. o = azinphos-methyl, analytical grade; ● = azinphos-methyl 25% w.p.; Δ = dimethoate, analytical grade; ▲ = dimethoate, 40% liquid.

from minimum--maximum thermometers. The average water temperature in summer ranged from 17 to 22 °C and those in the autumn from 12 to 17 °C.

The highest rate of decline of azinphos-methyl (k_r = 1.1 d^{-1}, $t_{\frac{1}{2}}$ = 0.63 d) was found at a combination of the highest average water temperature 21 °C) and a high pH ranging from 9.4 to 10.7 (Table 26). The lowest rate of decline of azinphos-methyl (k_r = 0.1 d^{-1}, $t_{\frac{1}{2}}$ = 7.3 d) was measured in the Trial 5 (with copper sulphate), at an average water temperature of 15 °C and a pH range of 7.7 to 9.2 (Table 26). The rate of decline of azinphos-methyl thus varied by about a factor ten.

The rate of decline of dimethoate in the trials varied by about a factor 80. The lowest rate of decline (k_r =0.01 d^{-1}, $t_{\frac{1}{2}}$ = 67 d) was found at an average water temperature of 17 °C and at a pH range from 7.7 to 8.1, in the presence of copper sulphate (Table 26). The decline was fastest (k_r = 0.80 d^{-1}, $t_{\frac{1}{2}}$ = 0.87 d) for the highest average water temperature (21 °C) and the high pH range (9.4-10.7).

Effect of formulation

The rates of decline of the model compounds applied as analytical grade or as formulated products in the water compartment, during Trials 1 to 3 may be compared in Figure 22. No clear difference in rate of decline could be observed between azinphos-methyl as analytical grade and 25% w.p. The same holds for the measurements on dimethoate, whether it was applied as analytical grade or as 40% liquid. For possible effects of the formulations in addition to copper sulphate on the deline rates of both compounds, no clear trends were found.

Effect of copper sulphate

Addition of copper sulphate to the replenished water compartments strongly retarded growth of algae, so that pH fluctuations were strongly suppressed (Table 26, Trials 4 and 5). However during Trial 5 in Tanks II and IV (with bottom layer), this suppression was only temporary, probably due to adsorption of copper sulphate on the bottom material. In Trial 5, rates of decline of both compounds in tanks with bottom material were slower than those in tanks without bottom material, despite the considerably higher pH in the tanks with bottom material (Table 26). One explanation might be a decrease in the catalytic activity of copper sulphate, by adsorption on bottom material. Another explanation might be that the cleaned and replenished tanks without bottom material allowed a greater light penetration than the tanks with a bottom layer, containing also some algae in the water compartment. In view of the faster conversion rate of both compounds in surface water after addition of copper sulphate in laboratory tests (Sections 6.2 and 6.3), the former explanation seems to be more likely.

Effects of adsorption onto bottom material

In situations with a fast adsorption of the insecticides onto the bottom material, a fast decline at the beginning of the trials may be expected. In such cases, the intercept at time zero is lower. The plots for the decline of dimethoate did not show such low intercepts. Some of the decline plots for azinphos-methyl clearly showed a lower intercept than the amount introduced (lines A2 TIV, AF3 TII and AF3 TIV in Figures 20A, B). However the regression lines for A2 TII, AC5 TII and AC5 TIV did not clearly indicate a fast adsorption of azinphos-methyl on the bottom material.

Because of the large fluctuations in pH in the tank trials, it is difficult to draw conclusions on the effect of bottom material on the rate of decline of either compound. The rates of decline of both model compounds during Trials 2 and 3 were faster in tanks with a bottom layer except for AF3 TVI and DF3 TVI (Figures 20B and 21C). However, the extremely fast decline of azinphos-methyl and dimethoate in Tank VI during Trial 3 can be explained by the extremely high pH range of 9.4 to 10.7 (Table 26).

7.4 MEASURED PENETRATION INTO BOTTOM MATERIAL

Masses of azinphos-methyl measured in extracts of slices of bottom material during Trial 2 are presented in Table 27.

The masses of azinphos-methyl in the upper slices were generally much higher than in the lower slices. Over the depth investigated (0-6 cm), a distinct penetration of azinphos-methyl was found. The differences in the masses for duplicate columns were large. The differences between Tanks II and IV were also large (Table 27). The small amounts of azinphos-methyl in the bottom layer of Tank IV can partly be ascribed to the fast decline rate of that tank (Table 26).

The total mass of azinphos-methyl in the bottom compartment of the tanks was calculated and compared with masses of azinphos-methyl in the water compartment (Table 28). After

Table 27. Measured penetration of azinphos-methyl in the bottom layer during outdoor tank Trial 2 started on 4 June 1976. Masses of azinphos-methyl per column slice.

Date	Tank No	Slice[1] No	Layer in bottom (m)	Mass of azinphos-methyl (ng)
10 June	T II	1a	0 - 0.023	860
		1b	0 - 0.020	1650
		2a	0.025 - 0.047	81
		2b	0.022 - 0.038	320
		3a	0.049 - 0.066	65
		3b	0.040 - 0.056	30
	T IV	1a	0 - 0.017	-[2]
		1b	0 - 0.017	130
		2a	0.019 - 0.037	44
		2b	0.019 - 0.041	28
		3a	0.039 - 0.054	26
		3b	0.043 - 0.064	26
15 June	T II	1a	0 - 0.017	820
		1b	0 - 0.019	300
		2a	0.019 - 0.035	160
		2b	0.021 - 0.035	36
		3a	0.037 - 0.051	10
		3b	0.037 - 0.051	33
	T IV	1a	0 - 0.020	190
		1b	0 - 0.026	48
		2a	0.022 - 0.044	33
		2b	0.028 - 0.047	23
		3a	0.046 - 0.079	< 10
		3b	0.049 - 0.062	< 9

1. Slice No 1, 2 and 3 are first, second and third slice; a and b refer to duplicate samples.
2. Failure in analysis.

5.5 days, the mass fractions of azinphos-methyl in the bottom compartment of Tanks II and IV were 17 and 27%, respectively in the total masses recovered in the tank. After 11 days, these values were 55 and 72%, respectively. They indicate that the rate of decline of azinphos-methyl in the water compartment was probably faster than the rate of decline in the bottom material.

Table 28. Mass of azinphos-methyl in the water compartment ($m_{A,w}$) and bottom compartment ($m_{A,b}$) of Tanks II and IV during the second tank experiment started on 4 June 1976.

Date	Tank No	Azinphos-methyl		
		$m_{A,w}$ (µg)	$m_{A,b}$ (µg)	$m_{A,b}/(m_{A,w} + m_{A,b})$ (%)
10 June	T II	3530	740	17
	T IV	250	94	27
15 June	T II	300	360	55
	T IV	30	77	72

Masses of dimethoate in extracts of slices of bottom material during Trial 1 are shown in Table 29.

The masses of dimethoate in the upper slices were higher than in the lower slices, but not as distinct as for azinphos-methyl. The differences between the three columns for each tank were rather small and the differences between Tanks II and IV were also small (Table 29).

After 22 days, the total mass of dimethoate in the bottom layer was 61 µg for Tank II and 38 µg for Tank IV. The masses of dimethoate measured in the water compartments of Tank II and IV were then about 280 µg. The mass fraction of dimethoate in the bottom layer was thus 18% of the total recovery in Tank II and 12% in Tank IV. These values are considerably lower than the percentages obtained for azinphos-methyl. The main reason for the behaviour is the much lower adsorption of dimethoate.

7.5 GENERAL DISCUSSION ON OUTDOOR TANKS TRIALS

Outdoor trials in water tanks may show the rate of decline under field conditions and its variation. However, well defined and more easily controllable tests under laboratory conditions are needed to analyse in more detail the relatively importance of the various processes.

The decline of azinphos-methyl and dimethoate in the water compartment of outdoor tanks was much faster than the conversion, measured in the laboratory in the dark. The effect of light on the rate of decline of both compounds was thus considerable. Therefore laboratory tests in the dark have only limited value for predicting the decline rate of pesticides in outdoor aquatic systems. In the laboratory, more research is needed to assess the effect of light.

Table 29. Measured penetration of dimethoate in the bottom layer during outdoor tank Trial 1 started on 23 September 1975. Masses of dimethoate per column slice.

Date	Tank No	Slice[1] No	Layer in bottom (m)	Mass of dimethoate (ng)
15 October	T II	1a	0 - 0.011	81
		1b	0 - 0.010	79
		1c	0 - 0.010	–[2]
		2a	0.013 - 0.024	41
		2b	0.012 - 0.023	50
		2c	0.012 - 0.023	42
	T IV	1a	0 - 0.011	43
		1b	0 - 0.012	61
		1c	0 - 0.013	52
		2a	0.013 - 0.025	31
		2b	0.014 - 0.025	28
		2c	0.015 - 0.026	18

1. Slice No 1 and 2 are first and second slice; a, b and c refer to triplicate columns.
2. Failure in analysis.

Tank trials are useful in studies on the decline of pesticides in the field. However, even tank trials are rather complex. Algal bloom can easily occur and causes, for instance fluctuation in pH and, variation in light penetration. Tank systems with almost the same initial situation may develop differently.

The pH of the water was a major factor in decline of both model compounds. The pH in many surface waters will not be as high as in these trials, and in general the decline will probably be slower. In shallow, relatively small ditches, however, the same kind of development may occur. More detailed measurements of pH and temperature (preferably continuous) are needed in future tank trials.

A bottom layer in the tank did not determine the decline of compounds in the water compartment.

A clear effect of formulations of both compounds on the rates of decline could not be found.

Copper sulphate suppressed algal bloom and prevented pH fluctuation. However, the influence of Cu^{2+} on the decline rate of both compounds in light could not yet be analysed. With a bottom layer, Cu^{2+} seemed to be inactivated rapidly.

A distinct penetration of the compounds into the bottom layer was detected. The concentration patterns measured would result from diffusion in combination with adsorption, with unknown contributions from mixing by organisms and disturbance of the bottom layer during sampling. Another mechanism for the transfer of pesticides to the bottom may be the deposition with phytoplankton and suspended solids.

The measurements on azinphos-methyl indicated that the decline in the bottom compartment was probably slower than in the water compartment. By using computer simulations on the behaviour of pesticides in aquatic systems with a bottom layer, the contribution of a bottom layer on the rate of decline can be better evaluated (Chapter 8).

The results of these outdoor tank trials will be compared with those from measurements in the field, especially in ditches with standing water (Chapter 9).

8 Computation model on the behaviour of pesticides in a tank of water with a bottom layer

8.1 INTRODUCTION

A computation model was built to describe the behaviour of pesticides in a water tank with a bottom layer. Such a model can be helpful in evaluating the results of the tank trials (Chapter 7) in more detail. Besides, this model can be a good starting point for the computations on ditch sections.

In the computation model, some simplifying assumptions were made. Introduction of the pesticides was assumed to be initially mixed evenly throughout the water compartment of a tank. Pesticides movement by diffusion from the water-sediment interface into the bottom layer was described in a one-dimensional system. Adsorption equilibrium was assumed to be established instantaneously. The rates for decomposition of the insecticides in water and in bottom material were different. The most reliable data available were introduced into the models.

By comparing the results of computations with those of measurements in the outdoor tanks, the most important shortcomings in the computation model and in the data can be traced.

Finally, the computation model is used for a few simulation experiments on the behaviour of pesticides in an aquatic system with a bottom layer. Pesticide characteristics like the diffusion coefficient in the liquid phase of the bottom, the adsorption coefficient, the rate of conversion in bottom material and the rate of conversion in water were varied. These computations may be helpful in evaluating the relative importance of parameters in the behaviour of pesticides in water systems.

8.2 DERIVATION OF THE EQUATIONS

The flux of the substance through bottom material by diffusion in the liquid phase was computed with Fick's law:

$$J_{\mathrm{dif,lb}} = -D_{\mathrm{dif,lb}}\ \partial c_{\mathrm{lb}}/\partial z \qquad (15)$$

in which

$J_{\mathrm{dif,lb}}$ = areic mass flux by diffusion in bottom material (mg m^{-2} d^{-1})

$D_{\mathrm{dif,lb}}$ = diffusion coefficient of substance in liquid phase of bottom material (m^2 d^{-1})

c_{lb} = mass concentration of substance in liquid phase of bottom material (mg m^{-3})

z = depth in bottom (m)

The diffusion coefficient of substance in liquid phase (Graham-Bryce, 1969; Frissel et al., 1970) $D_{\mathrm{dif,lb}}$ was calculated from

$$D_{\mathrm{dif,lb}} = f_1\ \varepsilon_1\ D_{\mathrm{dif,w}} \tag{16}$$

in which

f_1 = labyrinth or tortuosity factor: ratio of surface area of bottom material to liquid phase (1)
ε_1 = volume fraction of liquid: volume of liquid divided by volume of bottom material (1)
$D_{\mathrm{dif,w}}$ = diffusion coefficient of substance in water ($\mathrm{m^2\ d^{-1}}$)

For the conversion of the substance in water and in bottom layer, first-order rate equations were used:

$$R_{\mathrm{c,w}} = k_{\mathrm{c,w}}\ c_{\mathrm{w}} \tag{17}$$

in which

$R_{\mathrm{c,w}}$ = rate of conversion in water ($\mathrm{mg\ m^{-3}\ d^{-1}}$)
$k_{\mathrm{c,w}}$ = rate coefficient for conversion of substance in water ($\mathrm{d^{-1}}$)
c_{w} = mass concentration of substance in water ($\mathrm{mg\ m^{-3}}$)

A similar equation is used for the bottom layer:

$$R_{\mathrm{c,b}} = k_{\mathrm{c,b}}\ c_{\mathrm{b}} \tag{18}$$

in which

$R_{\mathrm{c,b}}$ = rate of conversion in bottom material ($\mathrm{mg\ m^{-3}\ d^{-1}}$)
$k_{\mathrm{c,b}}$ = rate coefficient for conversion of substance in bottom material ($\mathrm{d^{-1}}$)
c_{b} = mass concentration of substance in bottom material ($\mathrm{mg\ m^{-3}}$)

The relevant conservation equation for the pesticide in the water compartment with volume V_{w} was

$$\partial(V_{\mathrm{w}}\ c_{\mathrm{w}})/\partial t = -A_{\mathrm{b}}(J_{\mathrm{dif,lb}})_{z=0} - V_{\mathrm{w}}\ R_{\mathrm{c,w}} \tag{19}$$

in which

A_{b} = surface area of bottom compartment ($\mathrm{m^2}$)

For the bottom material, the conservation equation of the pesticide was

$$\partial c_{\mathrm{b}}/\partial t = -\partial J_{\mathrm{dif,lb}}/\partial z - R_{\mathrm{c,b}} \tag{20}$$

The adsorption--desorption equilibrium was assumed to establish instantaneously, while the adsorption isotherm was taken as linear. The relationship between the concentration of the substance in the liquid phase (c_{1b}) and that in bottom material (c_b) is then:

$$c_{1b} = c_b/(\varepsilon_1 + \rho_b K_{s/1}) \tag{21}$$

in which

ρ_b =	(dry) bulk density of bottom material	(kg m^{-3})
$K_{s/1}$ =	distribution quotient solid/liquid (or adsorption coefficient)	(m^3 kg^{-1})

8.3 DESIGN OF THE COMPUTATIONS

The set of equations (15 to 21) was solved numerically after programming in the computer language CSMP III (IBM, 1975). The program was run on the DECsystem-10 computer of the Agricultural University, Wageningen. The listing of the computer program on the behaviour of azinphos-methyl and dimethoate in tanks with water and bottom material is shown in Appendix A.

In the runs simulating Tank Trial 2 in June 1976, the initial mass was 13.2 mg of azinphos-methyl in Tank II and 13.1 mg in Tank IV. The initial mass of 1 mg of dimethoate corresponded to the dose applied to Tanks II and IV during Trial 1 in the autumn of 1975 (Chapter 7). The dose was assumed to be immediately evenly distributed in the water compartment, while the initial masses in the bottom compartments were zero. The downward areic mass flux from the lowest bottom compartment (wall of the tank) was set at zero. Since volatilization of the model compounds from the water surface was very slow, this process was not introduced into the computation model (Section 3.5).

The volume of water in the tanks was introduced as a function of time according to the measurements during the tank trials. The surface area of the bottom was 0.6 m^2. The bottom layer (0.1 m thick) was divided into 10 computation compartments, with gradually increasing thickness from top to bottom (multiplication factor, m_f, 1.5). The thickness of the topmost bottom compartment was 0.001 m. The effects of different thickness of the topmost bottom compartment and different multiplication factors on the accuracy of the numerical solutions were checked. The bulk density and the volume fraction of liquid of the bottoms of Tanks II and IV were both introduced as a function of depth (Figure 19).

The diffusion coefficient of azinphos-methyl in water at 20 °C was estimated to be 0.41×10^{-4} m^2 d^{-1}, according to calculation methods given by Reid & Sherwood (1966). The same value was calculated for dimethoate at a water temperature of 15 °C.

The tortuosity factor f_1 for diffusion through the liquid phase in the bottom was introduced as a function of ε_1. It was 0.03, 0.10, 0.20, 0.34 and 0.50 m^2 m^{-2} for ε_1 0.10, 0.20, 0.30, 0.40 and 0.50 m^3 m^{-3}, respectively, according to a literature compilation by Leistra (1978). For higher ε_1, no data on the tortuosity factor were found in the literature. The tortuosity factors in the range above ε_1 = 0.50 were obtained by linear interpolation with the maximum value f_1 = 1.0 at ε_1 = 1.0. The diffusion coefficient of the substance in the liquid phase between two bottom compartments was computed by linear interpolation.

The measured adsorption coefficient $K_{s/1}$ of azinphos-methyl onto bottom material in the tanks was 0.073 $m^3 kg^{-1}$. The coefficient $K_{s/1}$ for dimethoate was 0.0032 $m^3 kg^{-1}$ as measured for freshly sampled bottom material (Chapter 6).

The rate coefficients $k_{c,b}$ for conversion of both compounds in the bottom of Tanks II and IV were derived from the values measured in incubation tests with systems of fresh bottom material in water in the laboratory (Chapter 6). The coefficient $k_{c,b}$ of azinphos-methyl at 20 °C was 0.073 d^{-1} (Table 21). The $k_{c,b}$ for dimethoate at 15 °C was 0.01 d^{-1} (Table 22).

The rate coefficients $k_{c,w}$ for conversion of both compounds in the water compartments of Tanks II and IV were in the first instance set equal to the measured rate coefficients for decline of both compounds as tabulated in Table 26. But the latter coefficients include the processes of adsorption onto and diffusion into the bottom layer, so that the actual rate coefficient for conversion in the water compartment would have been lower than the rate coefficients for decline, especially during the first period of the outdoor trials. Therefore, also lower rate coefficients for conversion in the water compartment were introduced which were 0.9 times the measured rate coefficients for decline (Table 26). These lower rate coefficients were introduced to estimate the relative contribution of conversion, penetration and adsorption to the decline.

The computations were carried out with Runge-Kutta's (RKS) integration method over a period of 27 days. The integration procedure used a variable time-step to minimize the integration error. At regular intervals during computations, the simulated material balance of the pesticide in the tank system was checked.

8.4 RESULTS OF THE SIMULATIONS OF TANK TRIALS

Amounts in water compartment and bottom compartments

The computed and measured masses of azinphos-methyl in the water compartment and in the bottom compartments of Tanks II and IV as a function of time are given in Figure 23. The same kind of plots for dimethoate are shown in Figure 24. The figures show that the differences between the measured and computed mass of both compounds in the water compartment were usually small. When the rate coefficients of conversion of the compounds were set at 90% of the measured coefficients of decline, only slightly higher masses in the water and bottom compartment were computed (Figures 23 and 24). The contribution of penetration into the bottom layer to decline of both compounds in the water layer was only limited. For both outdoor trials, the computed mass of substance in the bottom layer was nearly always less than 10% of the dose. The material balances of both pesticides in the tank system after a computation time of 27 d are shown in Table 30. Decreasing the rate coefficient of conversion by 10% resulted in nearly the same material balance for azinphos-methyl. However for dimethoate, it resulted in somewhat higher masses in the water and in the bottom (Table 30).

The limited measurements on azinphos-methyl and dimethoate in the bottom layer do not allow detailed comparison between measured and calculated results for the bottom layer. In all trials, the calculated masses of azinphos-methyl and dimethoate in the bottom

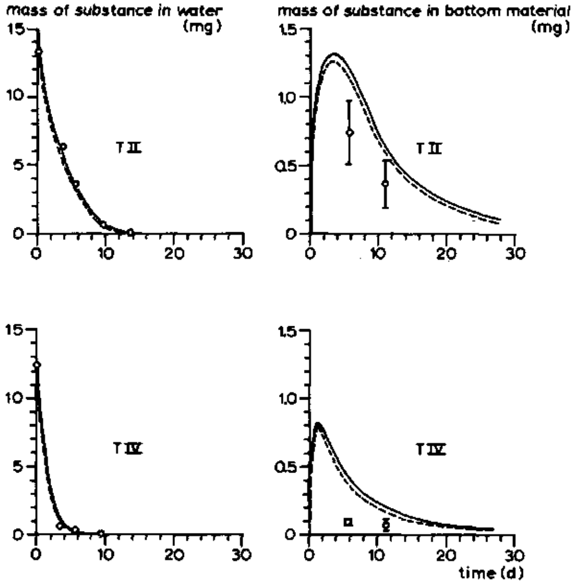


Figure 23. Mass of azinphos-methyl in water and in bottom material of Tanks II and IV. —— = computed mass ($k_{c,w} = 0.9\ k_r$); ---- = computed mass ($k_{c,w} = k_r$); o = measured data of Tank Trial 2 in June 1976 (Chapter 7). Vertical bars are range in mass of substance in the whole bottom material estimated from duplicate bottom columns.

layer were higher than the measured masses (Figures 23 and 24). This might be caused by an incomplete mixing in the water during the outdoor trials. Another reason could be a faster rate of conversion in bottom material under the outdoor situations than under the laboratory conditions. Further too high a value of the tortuosity factor at high ϵ_1 will result in an overestimate of the masses penetrating the bottom layer.

Comparisons between the measured and computed concentrations of azinphos-methyl and dimethoate at various depths in the bottom layer are shown in Figures 25 and 26, respectively. The computed depth of penetration of azinphos-methyl was very small. After 11 d nearly all the remaining azinphos-methyl was computed to be still in the upper 0.02 m of the bottom. However in the tank trials, small amounts of azinphos-methyl were recovered from bottom material below 0.02 m depth (Figure 25). This may be caused by disturbance of the bottom layer by sampling or by organisms.

The calculated penetration depth of dimethoate was larger than of azinphos-methyl (Figures 25 and 26), the main reason being the much lower adsorption of dimethoate.

The calculated depth of penetration for dimethoate was significantly more than sampled during the trial. For the comparison of computed and measured masses in the bottom layer (Figure 24), a correction was necessary for the mass of dimethoate that penetrated below the sampled depth of about 0.025 m. These masses were calculated with the computation model to be about 25% of the computed mass in the bottom layer for both tanks II and IV (Figure 24, crosses). These corrected values show a smaller deviation from the computed masses penetrated than the measured values.

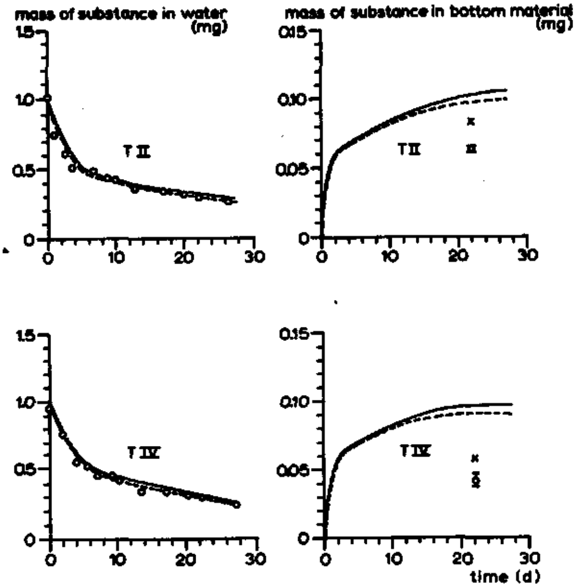


Figure 24. Mass of dimethoate in water and in bottom material of Tanks II and IV. ——— = computed mass ($k_{c,w}$ = 0.9 k_r); ---- = computed mass ($k_{c,w}$ = k_r); o = measured data of the Tank Trial I in September 1975 (Chapter 7); X = value corrected for penetration losses below sampled depth (Section 8.4). Vertical bars are range in mass of substance in the whole bottom material estimated from triplicate bottom columns.

Comparison of the few penetration measurements with the computed results indicate that in future penetration trials for compounds with relatively high adsorption coefficients, thin slices of bottom material should be analysed at appropriate time intervals. With low adsorption, penetration must be studied to greater depths than in this study.

Table 30. Computed items of the material balance of azinphos-methyl and dimethoate in a simulated tank system after 27 d.

Compound	Tank	Rate coeff. $k_{c,w}$[1]	Fraction of initial amount (%)			
			remaining		converted	
			in water	in bottom	in water	in bottom
Azinphos-methyl	II	k_r	0.0	0.8	90.8	8.4
		0.9 k_r	0.1	0.9	90.1	8.9
	IV	k_r	0.0	0.3	96.3	3.4
		0.9 k_r	0.0	0.3	95.9	3.8
Dimethoate	II	k_r	25.0	9.6	63.2	2.2
		0.9 k_r	27.2	10.3	60.2	2.3
	IV	k_r	22.6	8.6	66.7	2.1
		0.9 k_r	25.1	9.3	63.4	2.2

[1] $k_{c,w}$ = k_r (Table 26) or $k_{c,w}$ = 0.9 k_r.

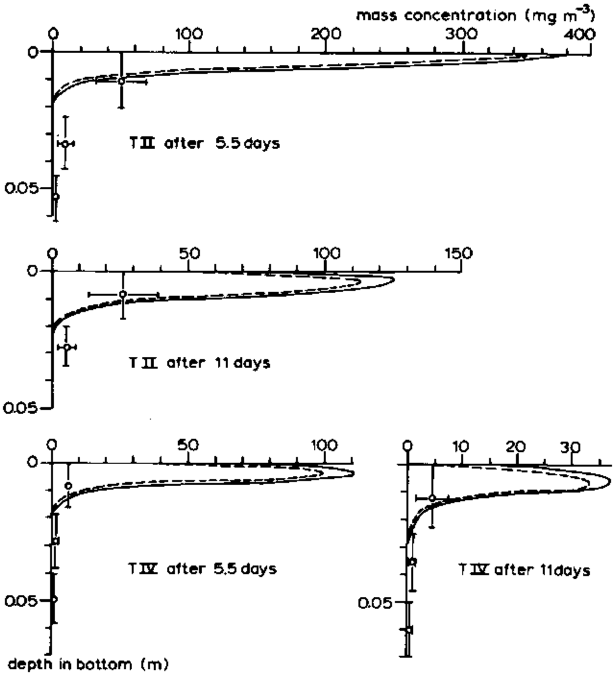


Figure 25. Mass concentrations of azinphos-methyl in the bottom material of Tanks II and IV. —— = computed mass concentration ($k_{c,w} = 0.9\ k_r$); ---- = computed mass concentration ($k_{c,w} = k_r$); o = measured data of Tank Trial 2 in June 1976 (Chapter 7). Horizontal bars are range in concentration of substance in slices of duplicate bottom cores. Vertical bars are average thickness of the bottom slices.

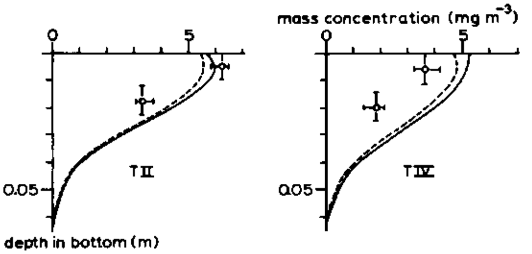


Figure 26. Mass concentrations of dimethoate in the bottom material of Tanks II and IV after 22 days. —— = computed mass concentration ($k_{c,w}$ = 0.9 k_r); --- = computed mass concentration ($k_{c,w}$ = k_r); o = measured data of Tank Trial 2 in June 1976 (Chapter 7). Horizontal bars are range in concentration of substance in slices of duplicate bottom cores. Vertical bars are average thickness of the bottom slices.

The computed results, showed that in situations with high conversion rates in the water compartment only, comparatively small amounts penetrated the bottom layer, even for substances like azinphos-methyl, which are strongly adsorbed. Further trials on penetration will be needed to verify the various assumptions and to improve the approximations of the computation model.

8.5 DESIGN OF THE SIMULATION EXPERIMENTS

Simulation experiments on the conversion of pesticides in the water compartment and the penetration into a bottom layer were carried out with the same computation model as described in Section 8.3. They were intended to test the sensitivity of the model system to changes in various parameters, especially for those which vary strongly in practice and those which were quite uncertain. The parameters that were varied in the different computer runs are given in Table 31.

For all runs the initial mass in the water compartment was set at 100 mg of pesticide and at zero for the bottom compartment. The volume of water in the tank was held constant and the surface area of the bottom layer was taken to be 1 m^2. In Runs 10, 11 and 12, the effect of different water depths on the relative amount of pesticide that penetrated the bottom layer was computed. The bottom layer was divided into 10 compartments with increasing thickness. The thickness of the upper bottom compartment was 0.001 m and the multiplication factor (m_f) was 1.5. In situations with high rate coefficient for conversion of the substance in the bottom layer or with high adsorption coefficients, the thickness of the upper bottom compartment was set at 0.0005 m. The bulk density increased linearly from 200 kg m^{-3} at the sediment--water interface to 680 kg m^{-3} at 0.2 m depth. The volume

Table 31. Parameters introduced into the computer runs of the simulation experiments.

Run No	Water depth (m)	Diffusion coeff. in water (m^2 d^{-1})	Maximum tortuosity factor (1)	Adsorption coeff. (m^3 kg^{-1})	Bottom material		Water	
					rate coeff. of conversion (d^{-1})	half life (d)	rate coeff. of conversion (d^{-1})	half life (d)
1	0.4	0.2×10^{-4}	1.0	0.0	0.0		0.0	
2	0.4	0.3×10^{-4}	1.0	0.0	0.0		0.0	
3	0.4	0.4×10^{-4}	1.0	0.0	0.0		0.0	
4	0.4	0.4×10^{-4}	0.75	0.0	0.0		0.0	
5	0.4	0.4×10^{-4}	0.5	0.0	0.0		0.0	
6	0.4	0.4×10^{-4}	1.0	0.001	0.0		0.0	
7	0.4	0.4×10^{-4}	1.0	0.01	0.0		0.0	
8	0.4	0.4×10^{-4}	1.0	0.1	0.0		0.0	
9	0.4	0.4×10^{-4}	1.0	1.0	0.0		0.0	
10	0.3	0.4×10^{-4}	1.0	0.1	0.0		0.0	
11	0.2	0.4×10^{-4}	1.0	0.1	0.0		0.0	
12	0.1	0.4×10^{-4}	1.0	0.1	0.0		0.0	
13	0.4	0.4×10^{-4}	1.0	0.1	0.00693	100	0.0	
14	0.4	0.4×10^{-4}	1.0	0.1	0.0693	10	0.0	
15	0.4	0.4×10^{-4}	1.0	0.1	0.693	1	0.0	
16	0.4	0.4×10^{-4}	1.0	0.1	0.0693	10	0.00693	100
17	0.4	0.4×10^{-4}	1.0	0.1	0.0693	10	0.0693	10
18	0.4	0.4×10^{-4}	1.0	0.1	0.0693	10	0.693	1

fraction of liquid decreased linearly over the same distance from 0.92 to 0.74.

In Runs 1 to 3, different diffusion coefficients of the pesticide in bulk water were introduced. There was no conversion of the substance in the bottom material and water, and adsorption in the bottom was zero. In Runs 4 and 5, different relationships for the tortuosity factor, f_1, were obtained by interpolating linearly to the values $f_1 = 0.75$ (Run 4) and $f_1 = 0.5$ (Run 5) at volume fraction of liquid $\varepsilon_1 = 1.0$. In four runs (No 6 to 9), adsorption coefficients of pesticides on the bottom material ranged from fairly low (0.001 $m^3\ kg^{-1}$) to very high (1 $m^3\ kg^{-1}$).

The rate coefficients for conversion of the substance in the bottom layer were varied from low to high in Runs 13 to 15. Finally the most realistic situations were simulated in Runs 16 to 18, introducing also various rate coefficients for conversion in the water compartment of the system.

8.6 RESULTS OF THE SIMULATION EXPERIMENTS

Masses in water compartment and bottom compartments

The results with different values of the diffusion coefficient of the substance in bulk water are shown in Figure 27A. Diffusion into the bottom layer was only slow: after 27 days 5.4 to 7.5% of the initial dose was transported into the bottom layer. In the next two runs (No 4 and 5), with different extrapolations of the tortuosity factor, the

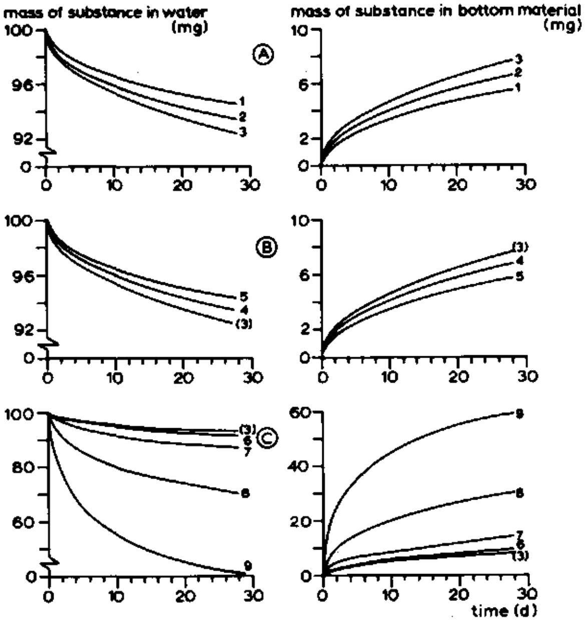


Figure 27. Mass of substance in water compartment and bottom compartments computed with the tank model. Numbers refer to the computer runs listed in Table 31.

penetration was only slightly slower than computed in Run 3 (Figures 27B). Thus the uncertainties in the values for the diffusion coefficient $D_{\mathrm{dif,w}}$ and for the tortuosity factor f_1 at high ε_1 values seem to be of minor importance.

The results of Runs 6 to 9 with different adsorption coefficients ($K_{\mathrm{s/l}}$) on the bottom material are presented in Figure 27C. They show a considerable contribution of adsorption to the decline of the substance in the water compartment. Many pesticides have moderate adsorption values on soils ($K_{\mathrm{s/l}} < 0.01\ \mathrm{m^3\ kg^{-1}}$), but adsorption on ditch bottom materials may be higher by a factor 10 (Sections 6.6 and 6.7). With a adsorption coefficient of 0.1 $\mathrm{m^3\ kg^{-1}}$, 29.6% of the initial dose was computed to diffuse into the bottom in a 27-day period (Run 8).

By decreasing the water depth, the initial mass concentration in the water compartment increased. This induced greater penetration of the substance into the bottom layer (Figure 28A, Runs 10 to 12). At a water depth of 0.1 m and using the same adsorption coefficient as in Run 8, 66% of the dose had diffused into the bottom layer after 27 days (Run 12). Especially in ditches with small water depths, adsorption of pesticides on the bottom layer can thus be of great importance.

The results obtained with various rate coefficients for conversion in the bottom layer are shown in Figure 28B (Runs 13 to 15). Conversion of the substance in the bottom

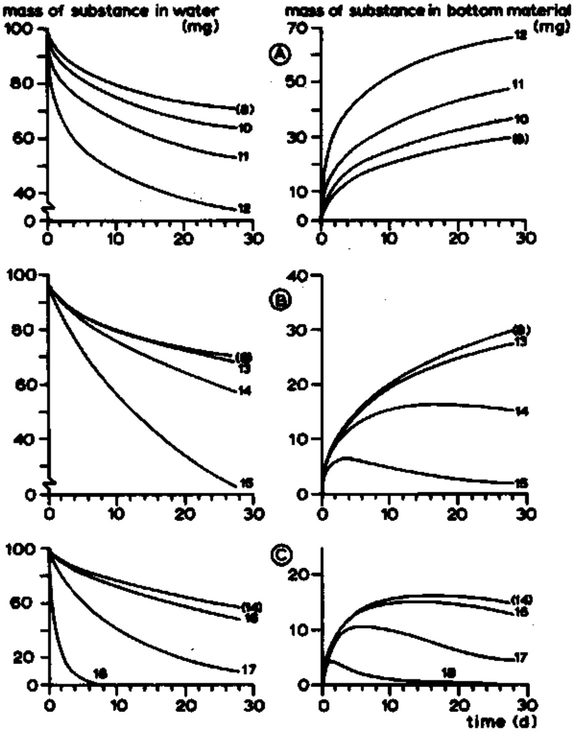


Figure 28. Mass of substance in water compartment and bottom compartments computed with the tank model. For the parameters used in the different computer runs see Table 31.

layer accelerated substantially the decrease in the water compartment, especially after the first few weeks. With a fast conversion rate in the bottom layer (Run 15, $t_{\frac{1}{2},b}$ = 1 d), the total amount in the bottom layer remained low: the maximum value (6.3% of the dose) was computed after three days. Further, the total mass of substance decomposed in the bottom layer after 27 days was 74.3% of the dose.

The results of the runs with various rate coefficients for conversion in the water compartment are presented in Figure 28C. Comparison of Run 14 with Runs 16 to 18 shows the great effect of the rate of conversion in the water compartment. In situations with a relatively high conversion rate in the water compartment (Run 18, $t_{\frac{1}{2},w}$ = 1 d) penetration into the bottom layer will not be important. After 4 days in Run 18, 90% of the dose was converted in the water compartment. In this computer run, the areic mass flux into the first bottom compartment even became negative after 1.5 days.

In all runs, halving the thickness of the upper bottom compartment had only a very small effect on the computed mass of substance in the bottom.

Depth of penetration into the bottom

The concentration patterns in the bottom layer after 9 and 27 days computed in two of the simulation experiments are presented in Figure 29. Without adsorption onto the bottom material (Run 3), concentrations in the upper 0.01 m were much lower than with adsorption (Run 8). The slopes of the concentration curves in Run 8 were markedly steeper than in Run 3. With adsorption, no significant penetration into the bottom was computed below a depth of about 0.02 m in a 27-day period.

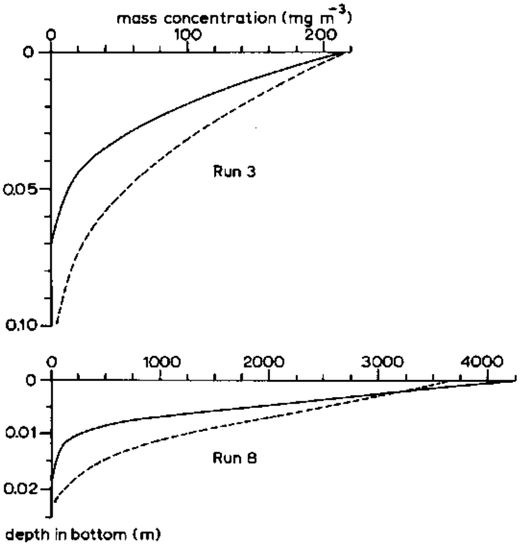


Figure 29. Mass concentration of substance in bottom layer after 9 d (——) and 27 d (---). For the parameters used in the simulation experiments see Table 31.

8.7 GENERAL DISCUSSION

For model computations on the behaviour of pesticides in aquatic systems with bottom material, several parameters are needed. The most important parameters are the rate coefficients for conversion in the water compartment and in the bottom layer ($k_{c,w}$ and $k_{c,b}$, respectively). Diffusion into bottom layers is a fairly slow phenomenon. The adsorption coefficient is also needed to describe the rate of decline of a substance in water. The adsorption coefficient highly affects the penetration depth of substances in the bottom layer.

Unfortunately, in almost any publication of experimental work on the behaviour of pesticides in aquatic systems, one or more of the essential parameters are lacking. Consequently, it was not possible to check the developed computation model in detail against data from the literature. Hamelink & Waybrant (1973) studied the distribution of DDE (a conversion product of DDT) and lindane, which were added to the epilimnion of a thermally stratified flooded limestone quarry (15 m deep), for one year. After three months, 85% of the recovered DDE was present in bottom sediments, while 72% of the measured lindane was still in the water. Their results indicate that the decline of very slowly converted pesticides in aqueous systems may be primarily due to adsorption onto bottom material. Most of the strongly adsorbed DDE was found in the top 0.015 m in all bottom samples. Lindane was found to a depth of 0.055 m.

The contribution of the various mechanisms of decline of herbicides in water bodies of aqueous systems is highly dependent upon the physico-chemical properties of the herbicides. Organic cations like diquat and paraquat are adsorbed on the bottom material within a few days. The weakly adsorbed compound 2,4-D is rapidly converted in water (Frank, 1970). However, such information is only of qualitative nature and thus not suitable for testing computation models.

Comparison of the limited number of measured data on the masses of azinphos-methyl and dimethoate in slices of bottom material during outdoor tank trials with the computed masses of both compounds yielded encouraging results. The calculated depth of penetration was small; therefore the method of sampling the upper centimetre of the bottom layer in aquatic systems is extremely important. Sampling of bottom material with dredge-type bottom samplers will mostly give erroneous results (Chapter 4).

Further experiments with improved procedures are needed to test the validity of the various assumptions and approximations in the computation model. In future experiments on penetration into bottom material, very thin slices of bottom material should be analysed.

More information is needed on the effect of aerobic and anaerobic conditions on the rate of conversion of the substance in the upper few millimetres below the sediment--water interface. Further complications like the existence of different periods in degradation in water or bottom layer might occur (Chapter 6). Also more information is needed on the effect of light on the rate of conversion of pesticides in shallow watercourses.

Only a few first steps have been made in describing pesticide behaviour in aquatic tank-like systems quantitatively with computation models. Much experimental and computational work remains to be done.

9 Measurements of azinphos-methyl and dimethoate in watercourses and farm ditches in the Kromme Rhine area and in the Lopikerwaard Polder

9.1 INTRODUCTION

In the water of the Kromme Rhine, flowing through an area of fruit farming, concentrations of azinphos-methyl were measured by Pons (1972), who found that the concentration of this compound increased downstream and ascribed this trend to the use of azinphos-methyl in fruit farming. The concentrations of azinphos-methyl were measured in this study by thin-layer chromatography (TLC), which may lead to erroneous results if very low concentrations of pesticides are present in waters containing various pollutants and natural substances. More quantitative data on the occurrence of azinphos-methyl in watercourses can be obtained by using clean-up and GLC techniques. In large watercourses, including the Kromme Rhine, a few sampling points were selected for measurement of changes downstream.

To investigate the unintentional contamination of watercourses from fruit farms in more detail, careful selection of other sampling points and more frequent sampling were felt necessary. During this reconnaissance, sampling points were selected in 1975 in ditches on fruit farms with the aim to investigate the occurrence and behaviour of azinphos-methyl and dimethoate in farm ditches. The selected farms had their own pumping station; the water balance of pumped ditches could be estimated more easily than that for watercourses with free discharge.

Since considerable concentrations were found in 1975 in the ditches on two fruit farms, more detailed measurements were set up in 1976 to estimate the water balance and pesticide balance of pumped ditches on those farms. The decline of azinphos-methyl and dimethoate in these pumped ditches was measured. In 1977, spray drift to ditches was measured in detail on the same farms to estimate more accurately the input of pesticides into these ditches.

The ditch system was characterized by various measurements. Many of the data assessed were also used in simulation models for pesticide behaviour in ditches(Chapter 10). The investigated ditch systems could thus be used to derive model systems for the computations and to compare computed and measured results.

9.2 MONITORING OF AZINPHOS-METHYL AND DIMETHOATE IN WATERCOURSES AND IN DITCHES ON FRUIT FARMS DURING 1975

9.2.1 Description of sampling points and procedures

Appropriate sampling points were selected in the Province of Utrecht in consultation with the regional crop protection extension officer, who was familiar with the field situation. The selected sampling points are shown in Figure 30. Three of them were in large watercourses in the Kromme Rhine area. The Kromme Rhine is a distributary of the Nether Rhine. The Kromme Rhine flows through an area with fruit farming situated mainly on the natural levees along the rivers and grassland farming mainly on the heavy backswamp clays. However, fruit farming on some of the latter soils is possible by lowering the groundwater level by pumping the ditches, especially during the winter season. An example of this situation is Sampling Point 5 near Bunnik. Pumped ditches are also found on loamy soils, where some seepage water from the River Lek (the continuation of the Nether Rhine), flowing at a higher level must be removed. These conditions occurred at Sampling Point 6 near Schalkwyk. At Points 5 and 6, windbreaks stood right next to the ditches on one side, while on the other side were inspection paths for ditch cleaning. At these Points 5 and 6, the fruit trees were not immediately next to the watercourse. This is quite a usual pattern of planting.

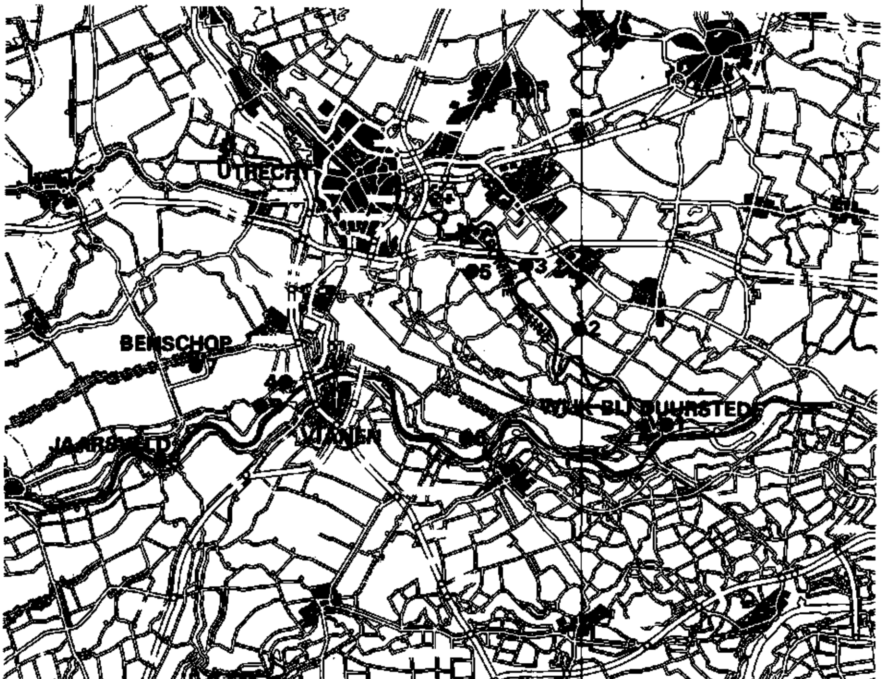


Figure 30. Map of the sampling points in the Kromme Rhine area and in the Lopikerwaard Polder. Sampling points:
1 = Kromme Rhine near the inlet from the Nether Rhine near Wyk by Duurstede.
2 = Langbroeker Canal from the bridge near Sterkenburg Castle.
3 = Kromme Rhine from the bridge near Odyk.
4 = Lopiker Canal near the Biezendyk bend.
5 = Drainage ditch on fruit farm near Bunnik.
6 = Drainage ditch on fruit farm near Schalkwyk.
7 = Drainage ditches on fruit farm near Benschop.
8 = Drainage ditches on fruit farm near Jaarsveld.
9 = Drainage ditches on fruit farm near Lopikerkapel.

Some more exceptional Sampling Points were selected in the Lopikerwaard Polder. At Sampling Points 7 and 8, many fruit trees grew just alongside the ditches, so that during applications of pesticides a part of the spray inevitably descended into the water. The Lopikerwaard is an area with relatively high groundwater levels. The various soil types are mainly used for grassland farming. Ditch water levels in grassland areas tend to be rather high, especially in areas with peaty soil or with loamy and clayey layers on a peaty subsoil. If supplementary pump-drainage is available, fruit farming is possible on some loamy and clayey soils, as around Sampling Point 7 near Benschop, on the natural levees near Jaarsveld (Sampling Point 8) and near Lopikerkapel (Sampling Point 9). Around all sampling points in the Lopikerwaard, some deep seepage may be expected (Studiegroep Lopikerwaard, 1973). Moreover at Points 8 and 9, shallow seepage occurs during high river water levels. The Sampling Point 4 in the Lopiker drainage canal was selected as a representative water-inlet point.

The points in the watercourses and the drainage ditches were sampled before and after spray operations on the fruit farms according to the procedure described in Section 4.2. In 1975, samples were taken 5 times. The samples of water were extracted as soon as possible (Sections 5.3 and 5.4). Some surface water extracts were cleaned up for more accurate measurement of azinphos-methyl and dimethoate (Sections 5.9 and 5.10).

During the monitoring activities in 1975, the concentration of azinphos-methyl in all water samples was measured on one GLC column, since at that time only one appropriate column was available (Table 14, Column 1). Dimethoate concentrations were measured on two columns (Table 15, Columns I and III).

9.2.2 Results and discussion

The average apparent concentrations of azinphos-methyl and dimethoate in extracts of water samples from the large watercourses and the various farm ditches on 5 sampling dates in 1975 are given in Tables 32 and 33, respectively. Most of the concentrations are presented with 'smaller than' marks. These marks are necessary, since the apparent concentrations of azinphos-methyl and dimethoate in the extracts were usually much lower after clean-up; especially for samples from large watercourses. The extracts of water samples were cleaned up about two months later, after storage for several days on a laboratory bench and in a refrigerator at 5 °C. Much of the reduction in concentration after clean-up of the samples from Ditches 6, 7 and 8 (Table 32) may result from decomposition during storage. Evidently, interfering substances had only a minor effect at these relatively high concentrations of azinphos-methyl.

Small amounts of azinphos-methyl and dimethoate were found after one single clean-up of water samples from the Kromme Rhine on 29 July. These data do not show a significant increase in concentration for either compound during flow through the Kromme Rhine area (Tables 32 and 33, Sampling Points 1 and 3). For measurement of the actual amounts of both compounds in the large watercourses, larger water samples, more extensive clean-up and analysis with more GLC columns would have been necessary.

During monitoring in 1975, apparent concentrations of dimethoate in water samples from the large watercourses of the farm ditches were only small (Table 33). Low concen-

Table 32. Average apparent mass concentrations of azinphos-methyl measured in extracts of water samples from large watercourses (Points 1-4) and from farm ditches (Points 5-9) during 1975. For position of sampling points see Figure 30.

Sampling point	Number of samples	Average concentration of azinphos-methyl (mg m^{-3})						
		14 March	6 May	2 June		29 July		19 August
				before clean-up	after clean-up	before clean-up	after clean-up	
1. Wyk by Duurstede	2	<0.5	-	<0.5	<0.02[1]	<0.5	<0.09	<0.9
2. Sterkenburg	2	<0.08	<0.2	<0.2		<0.1		<0.9
3. Odyk	2	<0.4	<0.4	<0.7		<0.6	<0.07	<1.1
4. Biezendyk	2	<0.1	<0.3	<0.3		<0.4	<0.05	<0.1
5. Bunnik	2	<0.02	<1.1	<0.3		<0.4		-[2]
6. Schalkwyk[4]	4	<0.06	<0.2	1.3	1[3]	<0.4	<0.2	0.3
7. Benschop[5]	4	<0.1	<0.2	18	9[3]	<0.1		0.5
8. Jaarsveld[6]	4	<0.2	10.5	6	4[3]	<0.2		0.3
9. Lopikerkapel[7]	3	<0.5	<0.03	<0.4		<0.2		<0.2

1. The detection limit was about 0.01 mg m^{-3}.
2. No water in the drainage ditch.
3. Clean-up two months later on one sample of water.
4. Azinphos-methyl spray at the end of May and June.
5. Azinphos-methyl spray on 30 May and 25 June.
6. Azinphos-methyl spray on 30 April, 16 May, 28 May, 26 June, 7 July.
7. Azinphos-methyl spray only at the end of June.

tration of dimethoate in the farm ditches could be expected since in that year the compound was not applied on the neighbouring fields.

The comparatively high concentrations of azinphos-methyl can be related to the spraying dates on the fruit farms.

Table 33. Average apparent mass concentrations of dimethoate measured in extracts of water samples from large watercourses (Points 1-4) and from farm ditches (Points 5-9) during 1975. For position of sampling points see Figure 30.

Sampling Point	Number of samples	Average concentration of dimethoate in mg m^{-3}							
		14 March	6 May	2 June		29 July		19 August	
				before clean-up	after clean-up	before clean-up	after clean-up	before clean-up	after clean-up
1. Wyk by Duurstede	2	-[1]	-[1]	<0.4	<0.1	<1	<0.11	<0.5	<0.04
2. Sterkenburg	2	<0.6	<0.2	<0.2		<0.03		<0.5	
3. Odyk	2	-[1]	<0.5	<0.3		<1.9	<0.09	<0.5	<0.2
4. Biezendyk	2	<0.1	<0.2	<0.4	<0.1	<1.5	<0.1	<0.5	<0.2
5. Bunnik	2	<0.3	<0.04	<0.05		<0.04		-[2]	
6. Schalkwyk	4	<0.05	<0.06	<0.3		<0.1		<0.03	
7. Benschop	4	<0.06	<0.07	<0.02		<0.02		<0.02	
8. Jaarsveld	4	<0.1	<0.01[3]	<0.3	<0.1	<0.2	<0.1	<0.3	<0.01
9. Lopikerkapel	3	<0.3	<0.02	<0.04		<0.3		<0.2	

1. Highly interfering substances.
2. No water in drainage ditch.
3. The detection limit was about 0.01 mg m^{-3}.

Before the flowering of the fruit trees, the compound was only applied in Jaarsveld. After flowering, fruit trees were sprayed with azinphos-methyl near Sampling Points 6, 7 and 8. The concentrations were highest in drainage ditches near Benschop and Jaarsveld, as would be expected for situations in which fruit trees grow just alongside the ditches. The concentrations of azinphos-methyl in water samples taken at Jaarsveld on 6 May ranged from 9.5 to 11.4 mg m^{-3}; those in the samples from Benschop (2 June) ranged from 10.4 to 22.5 mg m^{-3}. With a windbreak and an inspection path alongside the ditches (Schalkwyk, Point 6, 2 June) the concentration was much lower.

At the end of July, comparatively low concentrations were found in the ditches of all fruit farms, perhaps because of the large rainfall in that month. For example at Points 6, 7 and 8, nearly 100 mm of rainfall was measured within a few days in July. Three days of continuous pumping were necessary to discharge this extreme rainfall.

9.2.3 Preliminary conclusions

From the monitoring during 1975 of azinphos-methyl and dimethoate in watercourses and in ditches on fruit farms, a few preliminary conclusions could be drawn.

- Measurement of small amounts in large watercourses without adequate clean-up procedures will mostly give too high a value.
- At least two GLC column packings with different polarity have to be used.
- Good GLC analysis is rather difficult and very time-consuming. Continuous attention had to be paid to the quality control.
- Further monitoring of the larger watercourses would yield only limited information. There is always a certain 'background' of pollution, probably by intake of polluted water from the main river. Even with rather frequent sampling at several points, it may be difficult to trace the sources of instantaneous contamination and concentration waves may be overlooked.
- On the whole, the concentrations in the larger watercourses seem to be quite low and there are no indications for an increase downstream. This is probably due to factors like the high dilution, the scatter of the orchards between pasture and arable lands, the distribution of applications in time or also the relatively rapid decline rate in surface water.
- Many farm ditches dry up in the summer, especially in the Kromme Rhine area. So during summer there is generally no distinct discharge of surface water from these farm ditches into the larger watercourses.
- When fruit trees are situated just alongside the ditches, greater contamination of ditch water can be expected.
- On most modern fruit farms, windbreaks and inspection paths occur alongside the ditches and the introduction of pesticides into drainage ditches during spraying will be far less.
- The systematic tracing of a pesticide from the source will provide the best chance for reliable quantitative results.
- Attempts are needed to reduce the necessity of time-consuming analyses for an enormous number of water samples for each pesticide of interest. This could be done by simultaneous development of computation models.

- For more detailed investigations, ditches are needed for which water balance can easily be measured and to a certain extent controlled.

9.3 FIELD TRIALS ON THE FATE OF AZINPHOS-METHYL AND DIMETHOATE IN DITCHES AFTER SPRAY DRIFT

9.3.1 Introduction

In view of the relatively high concentrations of azinphos-methyl in samples of water from the drainage ditches in Benschop and Jaarsveld in 1975 (Table 32, Points 7 and 8), these farm ditches were selected for further investigation in 1976.

The concentrations in 1975 raised the following questions.

- Is it possible to measure the input of both compounds into ditches due to spray drift during applications on fruit farms?
- How quickly will the concentration be mixed over the cross-section of the water body in the ditch?
- Is it possible to estimate the rates of decline of the compounds in ditches for periods without discharge or intake of water?
- What will be the effect of adsorption on rate of decline?
- How far and how fast will the compounds penetrate the ditch bottom?

Before the pesticide balance in the field ditches can be solved, the water balance of these ditches must be assessed. The circumstances were far from ideal for solving this water balance, since the soils were heterogeneous and hydrological conditions were rather complex(as is often so in practice).

During the period of pesticide application on both farms in 1976, an attempt was made to approximate the various items of the water and pesticide balances for the pumped ditches. Before and after spraying azinphos-methyl and dimethoate, concentrations were measured in many water samples. Penetration of azinphos-methyl into the ditch bottom material was also measured. The ditch bottom material was characterized, to allow the use of simulation models. Profiles of the volume fraction of liquid and the bulk density were measured at several points in the drainage ditches.

9.3.2 Data on the trial fields in the Lopikerwaard Polder

The ditch sections, which were selected in 1976 for measurements on the water balance and on pesticide behaviour are shown in Figures 31 and 32. In Benschop, two ditch sections were selected, a siphon-linked ditch (designated BSL) and the last supplementarily drained ditch section before the water pump (designated BSD) (Figure 31). The level of the soil surface in Benschop varied from 0.60 m below sea-level (Standard Amsterdam Level, NAP) near Ditch Section 1 to about 1 m below NAP in the immediate surroundings of the pump. The lowest water level of the pumped ditches on the farm in Benschop was about 2.06 m below NAP. At this water level, the electric pump was automatically switched off by a float switch.

Hydrological conditions in Jaarsveld were quite complex. Only three of the many ditches

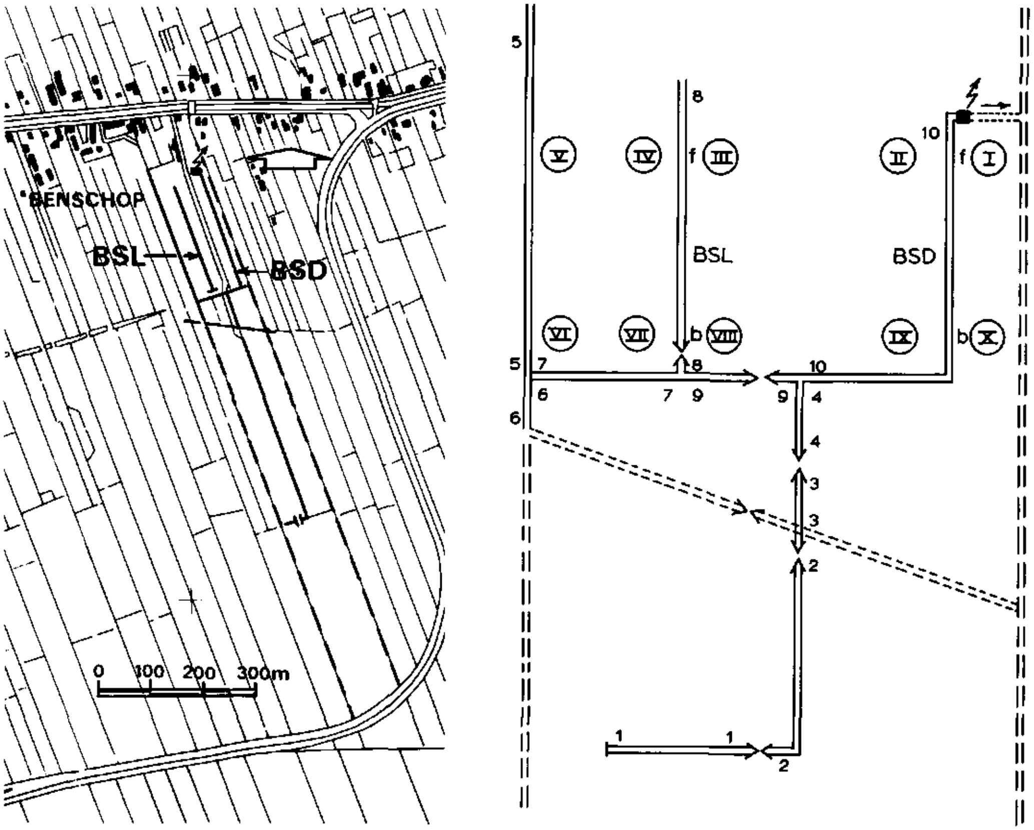


Figure 31. Position and flow pattern of ditches on a fruit farm in Benschop. Sections 1 to 10 had supplementary drainage. The dashed lines represent ditches which were not pumped; these sections were filled to normal polder level. Sections 8 and 10 were studied in more detail. They are indicated as siphon-linked ditch (BSL) and supplementarily drained ditch (BSD), respectively. Abbreviations: b for back and f for front part of a ditch section. Key: →← = siphon, Ⓘ = groundwater tubes, ■ = water pump.

on the farm were studied (Figure 32). These ditch sections are indicated with the abbreviations JB, JM and JF for back, middle and front ditch section, respectively. In Jaarsveld, the electric water-pump was situated on the highest part of the farm about 0.60 m above NAP. Near the windpump, the surface level was about 0.10 m above NAP. The water level, at which the pump was normally stopped, was about 0.79 m below NAP.

Data on the dimensions of the different ditch sections are shown in Table 34, which includes calculated standard deviations of the various parameters. The average coefficient of variation was about 12% for about 20 measurements of the depth and width per ditch section. The variation in the slope of the lower part of the ditch walls was greater, because this slope was reshaped twice a year during ditch cleaning.

In Benschop there was a composite tile-drainage system. To calculate the catchment area of the ditches, it was assumed that the watersheds were halfway between ditches or between ditches and drains. The total drained area in Benschop was about 135 000 m^2 and that for Jaarsveld was about 7 000 m^2.

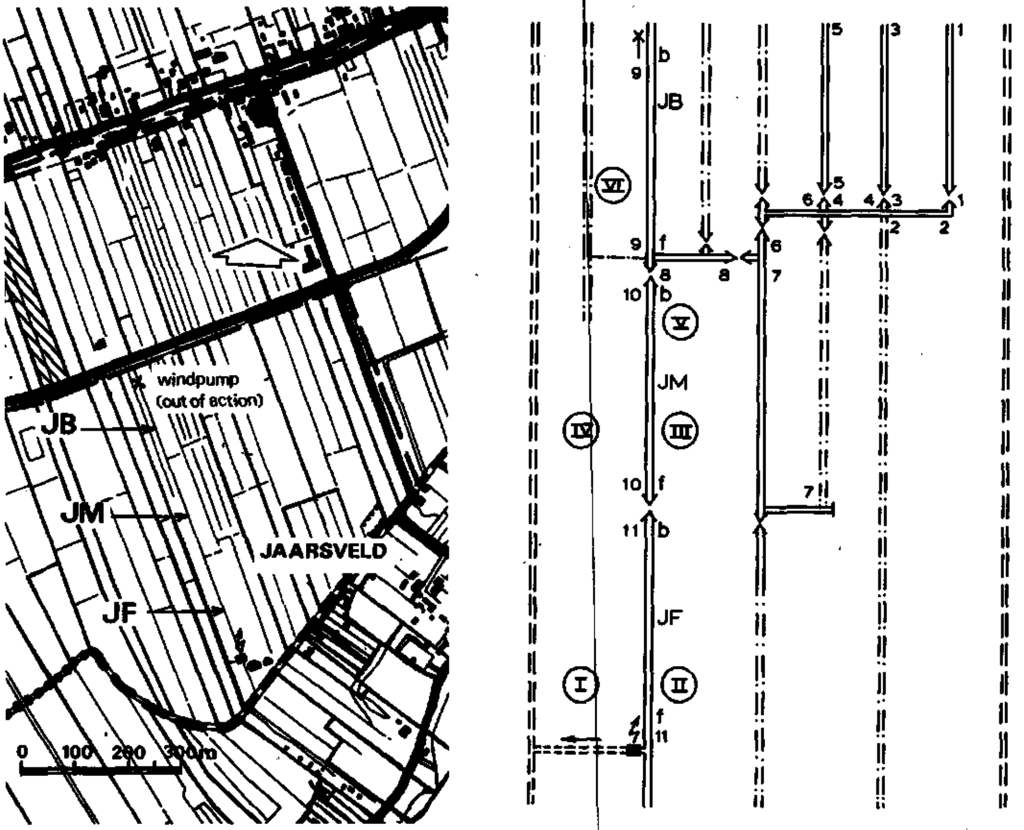


Figure 32. Position and flow pattern of ditches on a fruit farm in Jaarsveld. All sections were pumped. The left dashed line represents a ditch at polder level. The right dashed line is a ditch pumped by a windpump of an adjoining fruit farm. Dashed-dotted lines are former ditches, filled with old trees and top-soil. Sections 9, 10 and 11 were studied in more detail. They are indicated with abbreviations as JB, JM and JF for back, middle and front sections, respectively. Abbreviations: b for back and f for front part of the ditch sections.
Key:⇒⇐= siphon, Ⓘ= groundwater tubes, ■= water pump, ✗= windpump.

9.3.3 Measurement and approximation of the items of the water balance

Measurements on items of the water balance were set up in 1976 for a period of about 2 months, from the beginning of May to the beginning of July. After that, uncontrolled amounts of water were taken in on both farms for sprinkler and furrow irrigation, and it became impossible to measure the water balance.

For the approximation of the various rates of water flow in the ditch sections, a simple computation model was used (Chapter 10). The water balance of a ditch water compartment is in words: rate of change in water volume = rate of precipitation - rate of evaporation - rate of outflow + rate of inflow + rate of flow through the wetted perimeter of the ditch + rate of flow from the drains (Equation 24).

The rate of evaporation from a free water surface was estimated by averaging the data of De Bilt and Naaldwyk meteorological stations (KNMI, 1976) (Figure 33). In the dry and

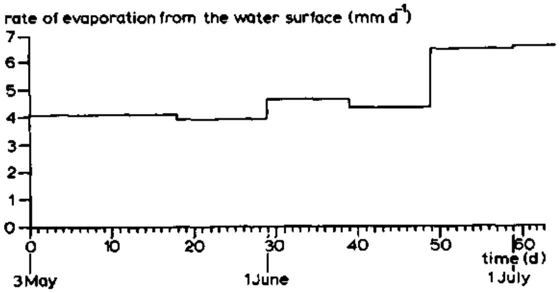


Figure 33. Rate of evaporation from open water. Averaged data of De Bilt and Naaldwyk meteorological stations (KNMI, 1976).

sunny year 1976, the rate of evaporation was high.

During the period of pesticide application, the ditch water-level was measured on sampling dates. The ditch water-levels above the reference levels (at which the pumps normally stopped, Table 34) are shown in Figure 34C and 35C. In view of the relatively dry period, the farmers had raised the switch-off level of the pump a few centimetres above the reference level. The water level before the pumping period on 21 June at Benschop was read from a high-water mark, manifested by a duckweed ring around the pumping tube. The water levels during the pumping periods were estimated by using a computation model (Chapter 10). At Jaarsveld, the fluctuations of the water level could only roughly be approximated. The amounts of rain were read daily by the farmers at 08:00 h. This daily rainfall on both farms is shown in Figures 34A and 35A. The total rainfall in May was 37 mm in Benschop and 42 mm in Jaarsveld. In the Netherlands, the 30-year average rainfall in May is 51 mm (KNMI, 1976). In June, 48 mm of rain was measured on both farms (30-year average is 54 mm).

On both farms the electric water-pump was equipped with a pumping-time meter. The duration of pumping was read by the farmers at 08:00 h each day. Normally the water pumps were equipped with a float switch, which kept the ditch water-level within narrow limits. After the spraying dates in the trial period, the water pumps were not used for some time in order to study the decline in the pesticides in the watercourses. They were switched on by hand when necessary, which resulted in a rather discontinuous pattern of pumping (Figures 34B and 35B).

The approximation of the rate of discharge of the different ditch sections will be discussed in Chapter 10.

At the beginning of the trials in Jaarsveld, unknown amounts of water were taken in from a larger watercourse by a siphon near the back ditch (Figure 32). This intake occurred from 7 to about 12 May and also at the end of June just before the two days with very heavy rainfall (Figures 35A, C). The amount of water taken in during the first intake period in Jaarsveld was not directly measured. It could be only roughly estimated from the rise in water level in the ditch and the rise in groundwater, assuming an average storage factor. During the second intake period in Jaarsveld, just before the heavy rainfall, no accurate data could be obtained on the rise in surface water and groundwater. Consequently it was impossible to approximate the amount of water taken in.

Table 34. Dimensions of ditch sections at the trial sites in Benschop and Jaarsveld in the Lopikerwaard Polder. Height of the land surface near the ditch sections. Levels with respect to Standard Amsterdam Level (NAP). Catchment areas of the ditch sections.

Parameters	Benschop		Jaarsveld		
	siphon-linked ditch (BSL)	supplementarily drained ditch (BSD)	front ditch (JF)	middle ditch (JM)	back ditch (JB)
Length (m)	204 (± 1)	202 (± 1)	184 (± 1)	203 (± 1)	150 (± 1)
Width at the bottom (m)	1.42 (± 0.24)	1.92 (± 0.16)	1.57 (± 0.13)	1.53 (± 0.19)	1.53 (± 0.19)
Depth (m)[1]	0.20 (± 0.03)	0.21 (± 0.02)	0.12 (± 0.02)	0.11 (± 0.01)	0.11 (± 0.01)
Slope 1 (-)[2]	0.46 (± 0.07)	0.32 (± 0.09)	0.36 (± 0.17)	0.17 (± 0.11)	0.17 (± 0.11)
Height of slope 1 (m)	0.40 (± 0.07)	0.42 (± 0.05)	0.56 (± 0.08)	0.46 (± 0.05)	0.46 (± 0.05)
Slope 2 (-)[3]	1	2	1	1	2
Catchment area (m^2)[4]	2750	2700	5900	5900	2240
Catchment area (m^2)[5]	8050	8000	0	0	0
Catchment area (m^2)[6]	0	129000	64100	58200	0
Surface level (m)	-0.8 to -1.0	-0.8 to -1.0	+0.4 to +0.6	+0.2 to +0.4	+0.0 to +0.2
Pump level (m)[7]	-2.06	-2.06	-0.79	-0.79	-0.79

1. Measured at the water level at which the water pump normally stopped.
2. Slope of the lower part of the ditch wall (horizontal distance divided by vertical distance).
3. Slope of the upper part of the ditch wall was estimated.
4. Catchment area with respect to flow through the ditch bottom.
5. Catchment area with respect to flow from drains.
6. Catchment area with respect to flow from tributary ditches or other ditches.
7. Level at which the pump normally stopped.

Groundwater levels were needed to estimate the water flow through the ditch bottom. Some groundwater tubes were placed in the fruit tree rows at various distances from the selected ditch sections (Figure 31 and 32). The levels of the tube heads were taken with a levelling instrument. During pesticide application, the groundwater levels were measured

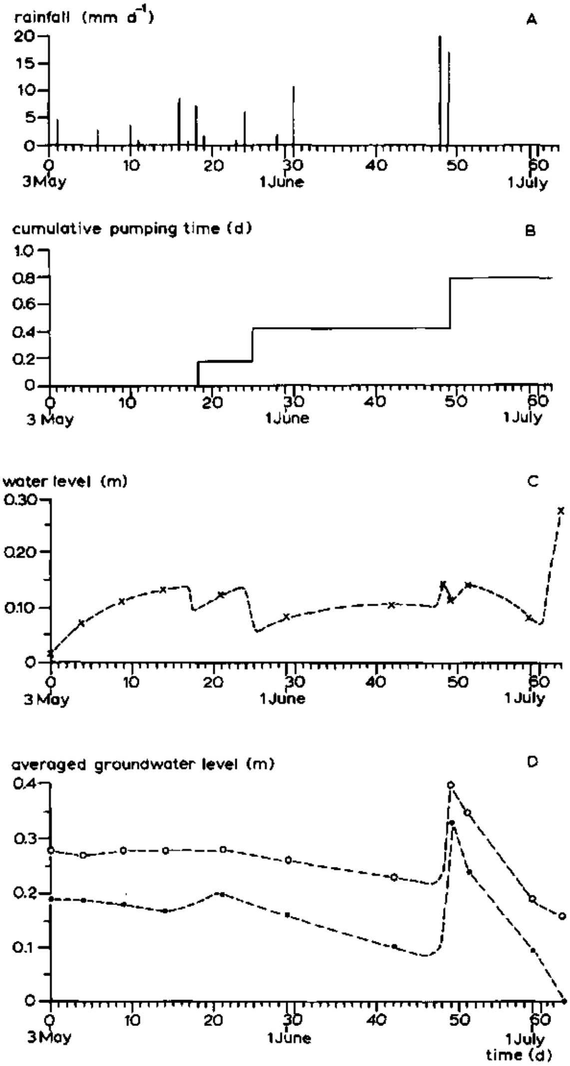


Figure 34. Field observations on the fruit farm in Benschop, during the trial in 1976.
A. Rainfall against time.
B. Cumulative pumping time against time.
C. Ditch water-level above lowest pumping level against time; x = measured levels, --- = approximated levels.
D. Averaged groundwater level above lowest pump level against time; • and o are measured groundwater levels around the siphon-linked ditch (BSL) and the supplementarily drained ditch (BSD), respectively; --- = approximated levels.

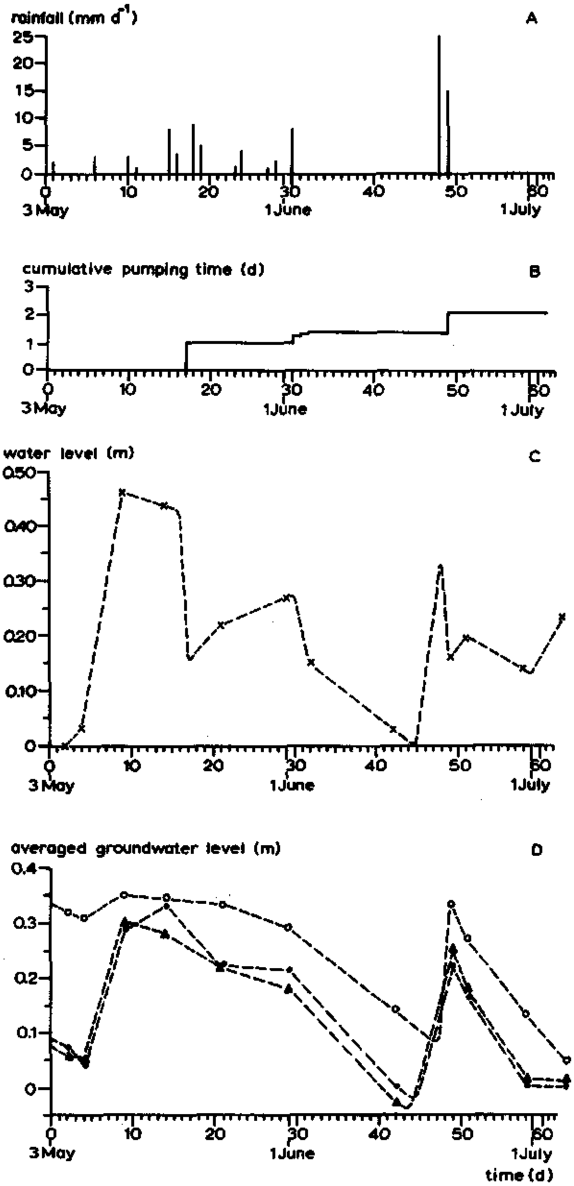


Figure 35. Field observations on the fruit farm in Jaarsveld, during the trial in 1976.
A. Rainfall against time.
B. Cumulative pumping time against time.
C. Ditch water-level above lowest pump level against time; x = measured levels, --- = approximated levels.
D. Averaged groundwater levels above lowest pump level against time; o (around front ditch), • (around middle ditch) and ▲ (around back ditch) are measured levels, --- = approximated levels.

on sampling dates. Those of Tubes III, IV, VII and VIII in Benschop were used to calculate an average groundwater level around the siphon-linked ditch; those of Tubes I, II, IX and X were used for an average groundwater level around the supplementarily drained ditch (Figure 34D). Averaged groundwater levels around the ditch sections at Jaarsveld are shown in Figure 35D. In both field situations, the groundwater rose strongly after the heavy rainfall at the end of June. At Jaarsveld, the groundwater levels around the middle and back ditch rose significantly with the water intake at the beginning of May.

The water flux through the ditch bottom and the rate of flow from drains were calculated from the water balance as a closing entry. A detailed discussion on the design of the computation model and the relevant parameters will be given in Chapter 10.

9.3.4 Surface and groundwater quality

For the characterization of water quality in the various ditch sections and groundwater tubes, some water samples were sucked up with a vacuum sampler (Section 4.2). These samples were analysed by the Eastern Laboratory for Water Testing, Doetinchem. The results are given in Table 35.

The relatively high chloride concentration in the ditches in Jaarsveld can be explained by the intake of water from a larger watercourse with a high chloride concentration.

9.3.5 Characterization of ditch bottoms

For the characterization of the bottom material of the ditches, about 10 cm of the upper layer was sampled with a fauna shovel. Samples were collected in Benschop at four places in the front and back sections of both ditches and in Jaarsveld from two places in the front and back section of the middle ditch (Figure 31 and 32).

With a Perspex bottom sampler, provided with a stainless-steel closing unit (Section 4.4), mud cores were collected at about the same places in the ditches. The lower parts of the columns (from 22 to 30 cm below the sediment--water interface) taken from the front and back sections of the different ditches, were put together. These samples were used for the chemical and granular characterization of the 'sub-bottom' of the ditch bottoms.

The granular and chemical analysis of the bottom material (Table 36) was done by the Laboratory for Soil and Crop Testing at Oosterbeek, according to standard methods described by Hofstee & Fien (1971). The pH(KCl) of the bottom material in the front and back sections of the different ditches was nearly equal. The pH of the sub-bottom was distinctly lower than that of the upper layers of bottom material. With the peaty subsoil at Benschop, the organic matter contents of the upper layers of bottom material there were much higher than at Jaarsveld. This was also found for the sub-bottom of the ditches on both farms. The organic matter content was measured by 'loss on ignition' and by total elementary carbon analysis. Organic matter in top soils in the Netherlands contains on the average 58% carbon. The organic matter content was calculated from the measured elementary carbon content by multiplying by a factor 1.724. The organic matter content in the bottom material measured by the 'loss on ignition' method was corrected for clay and $CaCO_3$, ac-

Table 35. Some chemical characteristics of samples of ditch water and groundwater from the fruit farms in the Lopikerwaard Polder in 1976. For position of sampling sites in ditches and abbreviations see Figures 31 and 32. GWT = groundwater tube; samples of groundwater were previously filtered.

Parameters	Benschop								Jaarsveld							
	BSL f		BSD b		GWT III		GWT IX		JF f		JB f		GWT II		GWT VI	
	05-17	06-14	05-17	06-14	05-17	06-14	05-17	06-14	05-17	06-14	05-17	06-14	05-17	06-14	05-17	06-14
pH[1]	7.4	7.5	7.4	7.0	7.4	7.5	6.0	6.2	7.2	7.5	7.2	7.5	7.4	7.4	7.4	7.4
COD (g m^{-3})	45	45	95	85	470	25	50	20	65	170	45	370	35	15	60	35
Nitrate (g m^{-3})	2	<1	3	1	<1	8	90	20	<1	1	4	<1	12	7	131	<1
Ammonium (g m^{-3})	0.51	0.07	0.51	<0.03	0.66	2.4	10.3	11.1	<0.65	<0.03	0.51	1.0	0.58	<0.03	0.72	1.0
Total N (g m^{-3})	1.3	1.4	2.1	1.7	2.1	3.1	9.1	9.0	1.9	5.9	0.94	4.6	0.84	0.73	1.5	1.8
Orthophosphate (g m^{-3})	<0.03	0.09	2.2	3.4	0.05	0.26	<0.03	<0.03	0.84	1.0	0.45	4.3	<0.03	<0.03	<0.03	<0.03
Total phosphate (g m^{-3})	0.16	0.25	4.0	3.8	0.87	0.34	<0.03	<0.03	1.1	5.3	0.65	12.0	0.29	0.09	0.22	0.17
Chloride (g m^{-3})	18	16	75	87	18	14	54	39	105	181	232	131	40	38	162	116
Conductivity (mS m^{-1})	66.2	54.4	85.1	95	41.9	43.5	239	233	72.7	98.1	107	107.2	63.1	64.8	126.9	96.7

1. Measured in the field.

Table 36. Granular and chemical characterization of the bottom material of the ditches in the Lopikerwaard Polder after drying. Depth of bottom layer sampled in front and back sections 0 to about 10 cm; depth of 'sub-bottom': 22 to 30 cm below the sediment--water interface.

Characteristics	Benschop						Jaarsveld		
	siphon-linked ditch			supplementarily drained ditch			middle ditch		
	front	back	sub-bottom	front	back	sub-bottom	front	back	sub-bottom
pH(KCl)	6.9	6.9	6.0	7.0	7.1	6.5	7.1	7.0	6.5
Organic matter (%)[1]	16.1	26.2	23.4	14.6	20.5	19.7	7.4	11.5	12.3
C Elementary (%)	9.27	15.43	15.20	8.41	11.63	11.46	4.04	5.92	7.22
Organic matter (%)[2]	16.0	26.6	26.2	14.5	20.1	19.8	7.0	10.2	12.4
$CaCO_3$ (%)	3.4	2.8	2.4	5.0	5.7	13.4	2.1	3.3	3.2
Clay (<2 μm) (%)	64.3	59.8	57.4	62.1	55.5	50.4	27.7	33.8	38.4
Silt (2-50 μm) (%)	33.8	36.4	40.4	33.5	36.8	48.3	20.5	20.2	21.4
Sand (>50 μm) (%)	1.9	3.8	2.2	4.4	7.7	1.3	51.8	46.0	40.2
CEC (mmol kg^{-1})[3]	487	623	610	479	570	516	250	313	366
K ,,	6	4	3	6	9	3	3	4	1
Na ,,	2	4	3	3	6	3	4	7	5
Ca ,,	260	303	245	237	297	229	124	167	160
Mg ,,	18	22	27	17	23	14	11	13	13
Solid phase density (kg m^{-3})	2330	2180	2220	2340	2300	2290	2500	2430	2390

1. Loss on ignition.
2. Calculated from: organic matter content = C elementary x 100/58.
3. Based on the entity of cation carrying a single charge.

cording to factors described by Hofstee & Fien (1971). The difference in organic matter content between the two methods was small (Table 36).

The mineral fraction of the bottom material from the ditches in Benschop can be classified as clay, in Jaarsveld as sandy clay-loam to clay-loam (Soil Survey Staff, 1975). The bottom material was classified according to the organic fraction following the classification system given by de Bakker & Schelling (1966). In Benschop, it can be classified as peaty clay and clayey peat to rich in humus, in Jaarsveld as very humous to rich in humus.

The cation-exchange capacity (CEC) of the bottom material was high, as could be expected in view of the high organic matter contents and the high clay contents. In all samples, calcium was the major exchangeable cation.

The solid phase density of the bottom material was determined for calculation of the volume of the solid phase in slices of bottom material in penetration trials (Section 9.3.12). This solid phase density varied from 2180 kg m^{-3} for the 'peaty clay' to 2500 kg m^{-3} for the 'loamy bottom material'.

Profiles of volume fraction of liquid and bulk density

In April 1977, mud cores were collected in triplicate from the various ditch sections for measurement of volume fraction of liquid and bulk density. The cores were taken with the bottom-material sampler, provided with a closing unit on top. The frozen mud columns were divided mechanically into slices about 2 cm thick, as described in Section 7.2.

The volume fractions of liquid in the slices are shown in Figure 36. The plots show the averages obtained from three columns per sampling site. The differences between the three columns were rather small. Near the sediment--water interface, the volume fraction of liquid was nearly the same in all samples. With increasing depth, the volume fraction decreased gradually. At one sampling point, in the front section of the supplementarily drained ditch, there was only a very small decrease. For the lowest slices of bottom material, sometimes relatively high volume fractions of liquid were found, which may be due to disturbance during sampling.

The bulk densities of the bottom material are presented in Figure 36. The differences between the triplicate values per sampling site were rather large. The bulk density of the bottom material near the sediment--water interface was very low. The pattern of increase of the bulk density with depth was rather irregular. The distinct difference between the front and back section of the supplementarily drained ditch in Benschop can be explained by the presence of a peat layer in the sub-bottom of the front section of this ditch. This was confirmed during sampling, since brown pieces of peat were visible through the clear Perspex wall of the sampling tube.

Elementary carbon

The organic matter content is an important characteristic because it is highly correlated with the adsorption of pesticides (Section 6.6). Organic matter contents in the mechanically sawn slices of frozen bottom material shown in Figure 37 were calculated from measured contents of elementary carbon of pooled material from two bottom columns. For the

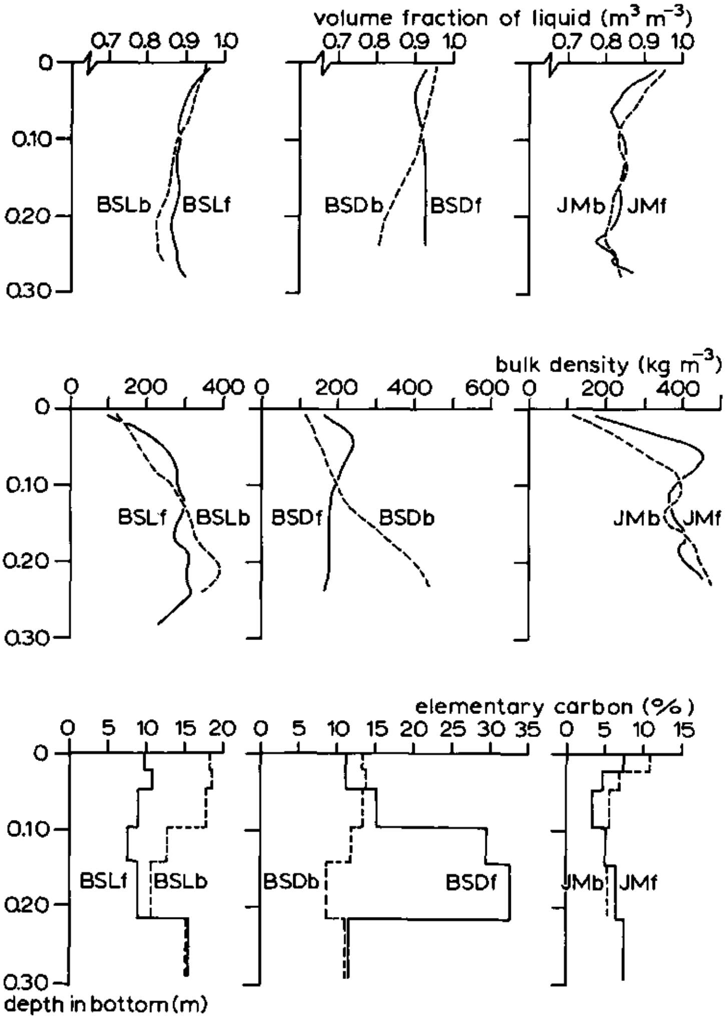


Figure 36. Characterization of ditch bottoms in the Lopikerwaard Polder. Volume fractions of liquid, bulk densities and elementary carbon contents. Abbreviations for sampling site: B = Benschop, J = Jaarsveld, SD = siphon-linked ditch, SD = supplementarily drained ditch, M = middle ditch, b = back and f = front part of the different ditch sections (Figures 31 and 32).

deeper layers, more slices (about 2.2 cm thick) were combined. The pattern of decrease or increase with depth was irregular and rather variable. The presence of peat lumps in the sub-bottom of the front section of the supplementarily drained ditch could explain the wide variability in carbon. The elementary carbon contents for the top layer (sampled to a depth of about 10 cm) of the different ditch bottoms shown in Table 36 agree fairly well with the elementary carbon profiles shown in Figure 36.

Two columns of both the siphon-linked ditch bottom and the supplementarily drained ditch bottom were divided into 2 cm slices. Large variations in carbon contents were found

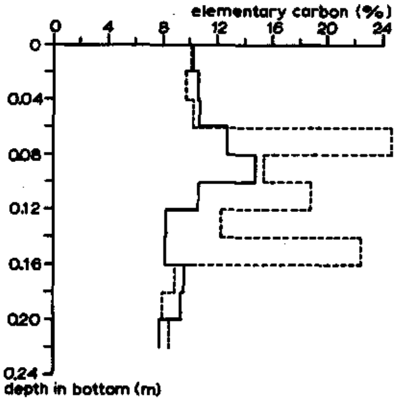


Figure 37. Mass fraction of elementary carbon in 2 cm bottom slices for two ditches in Benschop (—— = siphon-linked ditch and ---- = supplementarily drained ditch).

(Figure 37). This variability shows that it will be difficult to take representative samples of the ditch bottom.

9.3.6 Spraying dates and procedures in 1976

The siphon-linked ditch in Benschop was surrounded by a full-grown apple orchard (standard tree). Along one side of the supplementarily drained ditch was an old pear orchard (standard tree) and on the other side a young apple orchard (spill trees). No paths were present along those ditches. The trees along the ditches were sprayed twice, once in the normal way, and once with only one side of the spray heads (of a Kinkelder low-volume sprayer) operating, spraying only in the direction of the trees just alongside the ditch.

Azinphos-methyl was applied in Benschop in apple and pear orchards on 3 May, 21 June, 2 July and 9 August 1976. The last application was not investigated. On the first two spraying dates, azinphos-methyl, applied as Gusathion 25% w.p., was used in combination with dimathoate, applied as Rogor 40% liquid. The spray concentrations of active ingredient were about 2.7 kg m^{-3} for azinphos-methyl and about 1.6 kg m^{-3} for dimethoate. The amounts of water used for spraying were 15 cm^3 m^{-2} and 25 cm^3 m^{-2} for the young and old orchards, respectively.

A standard apple tree orchard was situated near the front ditch in Jaarsveld. At one side of the middle ditch, a young spill tree plantation was planted and on the other side of this ditch stood standard trees. Alongside the front and middle ditch, there was a farm road. The apple trees along the other side of these ditches were sprayed from the farm road by 'spraying over' the ditch. At both sides of the back ditch, an old apple orchard (standard tree) was planted, very close to the ditch. In 1977 on one side of the ditch, the old plantation was replaced by a new spill plantation.

In Jaarsveld, azinphos-methyl was applied to apple trees on 5 May, 24 May, 21 June, 1 July, 6 August and 19 August (the effects of the last two applications were not investigated). Azinphos-methyl 25% w.p. was sprayed with a concentration of active ingredient about 2.5 kg m^{-3} using a Kinkelder low-volume sprayer. The amounts of water sprayed were about 20 to 30 cm^3 m^{-2} for the young and old trees, respectively.

As mentioned before such situations are unusual in most fruit-growing areas; they represent conditions that greatly favour the pollution of open water with pesticides.

9.3.7 Concentrations of the insecticides in ditch water

Sampling, extraction and GLC analysis

Before application of the pesticides on both farms, dip-water samples were collected from the ditch sections, by the procedure described in Section 4.2. Shortly after and between applications of azinphos-methyl and dimethoate, water samples were collected. On the first four sampling dates, composite dip samples were collected. Later deep and shallow water samples were taken too with the vacuum-type sampler (Section 4.2).

Azinphos-methyl and dimethoate were extracted from the water samples with dichloromethane in a separatory funnel. Some of the extracts of water samples were cleaned up on silica gel columns, as described in Section 5.9 and 5.10. Analysis of azinphos-methyl was mostly on two GLC columns (Table 14). Dimethoate was mostly measured on two columns and sometimes on three columns (Table 15).

Concentrations in 1976

The concentrations of azinphos-methyl and dimethoate measured in water samples taken from the drainage ditches in Benschop are shown in Tables 37 and 38. The concentrations of azinphos-methyl in the ditch sections in Jaarsveld are presented in Table 39. The results show that concentrations were generally very low before spraying. After spraying, concentrations were initially high and decreased gradually.

The concentrations of both compounds in water samples taken before spraying were below 1 mg m^{-3} (no clean-up). An exception was the supplementarily drained ditch in Benschop on 3 May. Since a small part of the farm was sprayed on 1 May and the water pump was not switched off before 3 May, small amounts of the compounds could have been carried into the supplementarily drained ditch.

The concentrations of azinphos-methyl in 1976 were much higher than those measured in 1975 (Table 32). In 1976, the ditches were sampled shortly after spraying, sometimes within 1 h. Besides the pumps were out of operation and different sampling techniques were used.

Effect of different GLC columns and clean-up

The concentrations of the compounds were measured on different GLC columns to reduce the risk of errors caused by interfering substances and to increase the accuracy of measurements. The differences between concentrations of azinphos-methyl measured on different GLC columns were relatively small. The concentrations of azinphos-methyl measured on GLC Column II were in most samples somewhat higher than on Column I. For dimethoate no systematic differences could be found between the concentrations measured with different GLC columns.

The clean-up procedures, as described in Sections 5.9 and 5.10 were used on 10 sam-

Table 37. Mass concentrations of azinphos-methyl and dimethoate in samples of water from different sections of the siphon-linked ditch in Benschop during 1976. Dip, dip sample; B sample taken before spraying; suc, refers to a sample of water sucked up; S, shallow sample 3 cm below the water surface; D, deep sample 5 cm above the sediment-water interface; M, mixed sample throughout the cross-section of the ditch.

Date of sampling	Way of sampling			pH[6]	Concentration (mg m^{-3})														
					azinphos-methyl						dimethoate								
	front section	middle section	back section		front sect. GLC column[4]		middle sect. column		back sect. column		front sect. column[5]			middle section column			back section column		
					I	II	I	II	I	II	I	II	III	I	II	III	I	II	III
3 May[3]	B Dip	B Dip		7.0	<0.3	<0.8	<0.3	<0.5				<0.2	<0.1		<0.2	<0.1			
	Dip[1]	Dip	Dip	7.0	169	191	228	241	170	157		85	103		98	108		66	69
	Dip[1]			7.0	168	179						66	73						
5 May	Dip	Dip	Dip	7.2	71	71	76	78	44	45		32	40		42	47		37	25
7 May	Dip	Dip	Dip	7.1	37	37	51	68	27	39		28	27		48	49		35	31
12 May	Dip		Dip	6.8	10	14			7.6	9.0		31	29					25	24
			S suc	6.8					8.2	8.7								14	11
			D suc[1]	6.8					5.9	7.8								9.4	8.9
			D suc[1]	6.8					6.5	8.5								10	12
17 May	S suc	Dip	S suc	7.1	2.0	2.5	2.7	4.1	1.2	1.8		13	14		22	22		8.2	7.4
	D suc		D suc	7.3	2.5	3.3			1.1	1.4	17	14	19					7.2	6.2
24 May	S suc	Dip	S suc	7.2	0.6	0.7	0.9	1.0	0.6	0.6		12	11		16	13		5.9	4.4
	D suc		D suc	7.4	0.6	0.7			0.5	0.5		12	10					4.5	3.6
1 June	Dip		Dip	7.5	0.7	–[2]			–[2]	–[2]	6.3	13	6.1				7.5	7.5	7.9
14 June	Dip		Dip	7.1	<0.04	<0.08			<0.06	<0.08	1.6	2.1	2.2				0.2	0.5	0.1
21 June	B Dip			7.0	<0.2	<0.5					0.6		0.7						
	S suc	S suc	S suc	7.0	68	65	170	104	65	62	22		21	48		42	23		24
	D suc	D suc	D suc	7.0	0.4	1.0	0.4	1.3	1.0	1.6	1.7		1.9	1.4		1.6	0.7		0.6
23 June	S suc	S suc	S suc	6.9	9.9	11	7.8	14	9.6	12	5.5		4.9	5.3		9.1	–[2]		1.6
	D suc	D suc	D suc	7.2	0.4	0.9	4.1	5.7	14	20	2.2		2.0	2.9		2.7	–[2]		12
1 July	M suc	S suc	M suc	7.0	0.7	1.9	0.6	1.1	1.8	3.7	3.4	4.1	3.5	3.8	4.4	2.6	4.9	5.6	6.1
		D suc		7.0			0.6	1.2						3.2	3.7	3.3			
5 July	M suc	S suc	M suc	7.7	15	14	15	14	2.9	2.2	3.7	3.3	<0.04	1.8	4.5	1.4			0.07
		D suc		7.7			16	16						1.6	3.4	0.6			

1. Duplicate samples.
2. Interfering compounds.
3. Spray dates on 3 May, 21 June and 2 July 1976 (Section 9.3.6).
4. GLC Columns I and II, see Table 14.
5. GLC Columns I, II and III, see Table 15.
6. Average value for different ditch sections.

Table 38. Mass concentrations of azinphos-methyl and dimethoate in samples of water from different sections of the supplementarily drained ditch in Benschop during 1976. For codes for way of sampling see Table 37.

Date of sampling	Way of sampling			pH[7]	Concentration ($mg\ m^{-3}$)															
					azinphos-methyl						dimethoate									
	front section	middle section	back section		front sect. GLC column[4]		middle sect. column		back sect. column		front sect. column[5]			middle sect. column			back sect. column		
					I	II	I	II	I	II	I	II	III	I	II	III	I	II	III
3 May[3]	B Dip[6]		B Dip	7.0	6.2	14			2.2	2.7		3.2	2.9					0.8	0.3
	Dip[1]	Dip	Dip	7.0	21	20	29	31	75	76		8.1	9.4		11	12		35	26
	Dip[1]			7.0	18	18						6.6	4.8						
5 May	Dip	Dip	Dip	7.2	6.5	6.7	17	19	23	33		3.5	2.5		8.9	9.5		19	19
7 May	Dip	Dip	Dip	7.1	7.0	9.5	14	15	22	30		5.5	6.1	13	10	3.5		20	18
12 May	Dip		Dip	7.0	2.6	3.1			4.0	4.0		5.0	4.0					8.3	7.3
			S suc	7.0					3.5	3.9							20	16	12
			D suc[1]	7.0					2.7	3.3								11	9
			S suc[1]	7.0					2.3	3.0							12	10	
17 May	S suc	Dip	S suc	7.2	0.7	0.9	1.8	1.9	2.3	3.1		2.4	2.3	6.9	5.7	3.6		7.3	7.2
	D suc		D suc	7.3	1.0	1.1			2.7	4.3	4.4	2.9	2.0				8.2	6.7	4.0
24 May	S suc	Dip	S suc	7.5	0.9	1.0	0.6	0.7	0.8	0.9		5.2	4.8		3.4	2.9	5.5	5.2	3.7
	D suc		D suc	7.6	0.9	0.9			0.8	1.1		4.6	4.5				6.8	5.3	4.3
1 June	Dip		Dip	7.8	0.4	0.8			0.4	0.4	4.2	4.1	4.2				3.6	4.9	5.0
14 June	Dip		Dip	7.0	0.1	0.1			0.09	0.1	1.3	1.4	1.0				0.7	1.1	1.1
21 June	S suc		S suc	7.0	235	193			93	93	111		131				48		52
	D suc		D suc	7.0	0.3	0.7			0.3	0.7	0.3		0.5				0.6		0.7
23 June	S suc		S suc	7.0	30	30			27	32	17		13				15		13
	D suc		D suc	7.0	26	25			15	20	16		12				10		9.2
1 July	S suc		M suc	7.0	2.6	5.4			1.8	2.8	6.0	6.5	7.1				–[2]	–[2]	0.4
	D suc			7.0	2.4	4.2					4.8	5.1	4.0						
5 July	S suc		S suc	7.4	14	28			2.5	2.7	5.8	5.6	6.0						0.3
	D suc		D suc	7.4	15	26			4.4	4.2	6.0	6.0	6.0						1.0

1. Duplicate samples.
2. Interfering compounds.
3. Spray dates on 3 May, 21 June and 2 July (Section 9.3.6).
4. GLC columns I and II, see Table 14.
5. GLC columns I, II and III, see Table 15.
6. Small part of the farm was already sprayed on 1 May, without stopping the water pump.
7. Average value for different ditch sections.

Table 39. Mass concentrations of azinphos-methyl in samples of water from the different ditches in Jaarsveld during 1976. For codes for way of sampling see Table 37. Abbreviations f and b refer to the front and back sections of the different ditches.

Date of sampling	Way of sampling			pH[3]	Concentration of azinphos-methyl (mg m^{-3})					
	front ditch	middle ditch	back ditch		front ditch		middle ditch		back ditch	
					I[2]	II	I	II	I	II
5 May[1]	B Dip	B Dip	B Dip	7.0	<0.6	<0.8	<1.4	<1.0	<0.1	<0.3
	Dip	Dip	Dip	7.0	153	155	113	118	108	119
7 May	Dip	Dip	Dip	7.2	15	14	61	74	18	18
12 May	Dip	Dip	Dip	7.0	7.9	10	2.8	2.9	1.1	2.4
	f D suc			7.0	21	28				
17 May	Dip	Dip		7.2	7.8	8.6	3.7	4.5		
	f S suc		f S suc	7.2	14	13			1.4	2.1
	f D suc		f D suc	7.2	13	12			1.8	2.4
24 May	Dip	Dip	Dip	7.2	56	77	36	48	1.6	2.2
	f S suc	f S suc		7.1	214	264	19	20		
	f D suc	f D suc		7.2	309	388	40	36		
	b S suc			7.2	55	63				
	b D suc			7.2	53	62				
1 June	f Dip	Dip	Dip	7.8	52	58	7.1	7.8	1.2	1.6
	b Dip			7.8	11	15				
14 June	Dip		Dip	7.5	3.3	2.7			0.4	0.6
	f M suc	f M suc		7.5	17	16	0.3	0.4		
21 June	f S suc	f S suc	f S suc	7.0	315	217	329	406	58	59
	f D suc	f D suc	f D suc	7.0	12	15	72	57	48	50
23 June	f S suc	f S suc	f S suc	7.0	62	66	64	73	5.5	12
	f D suc	f D suc	f D suc	7.0	71	66	98	79	5.0	8.1
	b S suc			7.0	80	68				
	b D suc			7.0	58	60				
1 July	f S suc	f S suc	f S suc	7.1	94	105	114	132	19	27
	f D suc	f D suc	f D suc	7.1	28	29	175	203	20	24
	b S suc			7.4	11	12				
	b D suc			7.4	24	27				
5 July	b S suc	f S suc		7.2	8.8	8.6	2.5	2.6		
	b D suc	f D suc		7.2	8.0	7.1	2.0	1.9		
	f M suc		f M suc	7.4	24	26			2.9	2.8

1. Spray dates on 5 May, 24 May, 21 June and 1 July 1976 (Section 9.3.6).
2. GLC Column I and II, see Table 15.
3. Average value for different ditch sections.

ples of water from the farm ditches. The average relative differences in concentration of azinphos-methyl and dimethoate before and after clean-up were only about 6% for both compounds. These differences were even smaller at concentrations above 1 mg m^{-3}. In view of the relatively high concentrations in the farm ditches, clean-up was omitted in 1976.

Effect of sampling and estimation of mixing time

In 1976, many shallow water samples were sucked up, about 0 to 6 cm below the water surface, and deep samples, about 0 to 6 cm above the sediment-water interface. This gives an indication on the distribution of the compounds over the cross-section of the water body in the ditch. The differences in concentration in shallow and deep samples were greatest after spraying on 21 June in Benschop and Jaarsveld (Tables 37, 38 and 39, respectively).

It is difficult to estimate the time needed for complete mixing of the compounds through the wetted cross-section of the ditch. Transverse mixing mainly occurs by water circulation resulting from temperature differences in the water, by wind action and by dispersion during longitudinal flow. In these field situations, some other factors like local growth of duckweed and sharp variation in water depth made it difficult to estimate the rate of mixing. In the ditches at Jaarsveld, mixing was almost complete after two days, as can be seen from the concentrations in shallow and deep waters on 21 June and 23 June (Table 39). During that period, considerable mixing occurred in the ditches at Benschop although it seemed to be incomplete.

An exception was after spraying of azinphos-methyl on 24 May 1976 in Jaarsveld. In the front section of the front ditch, very high concentrations of azinphos-methyl were found both in deep and shallow samples of water. This exception was due to a defect in the sprayer at the start of spraying.

Variation in concentrations with place

Besides a strong variation in concentration of the compounds with depth and time, variation with place can be seen in Tables 37 to 39. At Benschop, the concentrations in the middle section of the siphon-linked ditch were higher than in its front and back sections. This can be explained by the presence of comparatively small trees alongside part of the middle section of the ditch. During spraying, it was clearly visible that a larger part of the spray passed across the smaller trees.

In Jaarsveld, the concentrations of azinphos-methyl in the front and middle ditch were much higher than in the back ditch. This could be due to the way of spraying across the first two ditch sections (Section 9.3.6).

9.3.8 Direct measurement of spray drift into ditches

In 1977, spray drift to the same ditches as studied in 1976 was measured directly. Before spraying, Tempex (expanded plastic) floats (0.25 m^2) were installed on the water surface at fixed distances in the ditches. On these floats, glass Petri dishes (diameter 0.09 m) were placed. After spraying, the Petri dishes were removed within 1 h from the floats and placed in dark cooled boxes. In the laboratory, the Petri dishes were rinsed three times with acetone (about 15 to 20 cm^3). This rinsing was done as quickly as possible, usually within 3 h of spraying. The recoveries of azinphos-methyl and dimethoate (as tested in a separate test) from the Petri dishes were about 100% and showed a low coefficient of variation (3%).

The effect of sunlight on the rate of decline of azinphos-methyl and dimethoate from the Petri dishes was tested separately on 15 June 1977. Spiked water samples (0.5 cm^3) were added with a pipette to glass Petri dishes and placed in the sun out of doors. In 3 h, azinphos-methyl showed a decline of about 20% and dimethoate decreased by about 12%. In view of the brief exposure of the field samples to sunlight and the cooling of the samples during transport, no correction factor was applied for decline.

Spray drift was measured twice during spraying with azinphos-methyl in 1977, both at Benschop and Jaarsveld. Spray drift of dimethoate was only measured at Benschop. These simple measurements can replace calculation of spray drift into ditches from concentration in the water. There were no interfering compounds, extraction was very fast and contamination could be measured accurately.

Results of measuring spray drift in Benschop

The methods of spraying and the amounts sprayed were the same as in 1976 (Section 9.3.6). Distances between standard apple trees around the siphon-linked ditch were 3 to 4 m. Around the supplementarily drained ditch, the distances between the standard pear trees were 4.5 m and between the spill apple trees were 1.5 m. The distance between floats was 14.3 m for both ditches. The amounts of azinphos-methyl and dimethoate detected in the Petri dishes in Benschop are shown in Table 40. Differences between the duplicate samples were usually small and averaged 5% (0-28%) of the observed amounts. The variation in the longitudinal direction was much larger than in the transverse direction (Table 40, Sampling Sites 3, 4 and 5 in the siphon-linked ditch on 26 August). The coefficient of variation in the average amounts in the longitudinal direction of the different ditches ranged from 29 to 45%.

The amounts of dimethoate in the dishes were lower than those for azinphos-methyl, which corresponded fairly well to the initial concentration in the sprayer (Section 9.3.6).

Table 40. Masses (μg) of azinphos-methyl (A) and dimethoate (D) measured after spray drift in Petri dishes (diam. 0.09 m) placed on floats on the water-surface in ditches at Benschop in 1977. Mean values of duplicate samples. The floats were 14.3 m apart.

Sampling site	Siphon-linked ditch			Supplementarily drained ditch		Ditch Section 5[1]
	31 May		26 August	31 May		26 August
	A	D	A	A	D	A
1 (front)	78	49	17	21	13	1.7
2	58	35	41	27	16	1.6
3	29	17	27(30)(26)[2]	27	16	0.8
4	49	29	25(29)(35)[2]	35	15	0.9
5	34	23	26(26)(28)[2]	25	22	
6	27	16	15	36	20	
7	54	32	43	29	17	
8 (middle)	42	27	47	32	21	
9	57	34	57	27	17	
10	46	28	59	19	13	
11	25	16	59	24	31	
12	36	22	43	46	29	
13	33	19	30	15	10	
14	35	22	68	32	21	
15 (back)	28	17	15	25	15	
Average	42	26	38	28	18	1.3
Coefficient of variation (%)	(36)	(35)	(45)	(29)	(38)	(38)

1. Ditch Section 5 was behind a windbreak on the fruit farm at Benschop (Figure 31).
2. Values of the distribution of the compound over the width of the siphon-linked ditch.

The average amounts of both compounds in the dishes of the supplementarily drained ditch were lower than those of the siphon-linked ditch. At one side of the supplementarily drained ditch, a spill apple tree orchard received a smaller amount of both compounds than the standard trees around the siphon-linked ditch (Section 9.3.6). In a ditch section behind a windbreak, the masses of azinphos-methyl in the Petri dishes were much less than in the other sections (Table 40).

Results of measuring spray drift in Jaarsveld

Azinphos-methyl was applied to the apple trees according to the procedure described in Section 9.3.6. The distance between apple trees ranged from 8.5 m for standard trees to 2 m for spill trees. The distance between the floats with Petri dishes ranged from 16 to 18.7 m. The masses of azinphos-methyl measured in Petri dishes in Jaarsveld are presented in Table 41. The average difference between the duplicate samples was 6% (0-49%).

The amounts in the different ditch sections in Jaarsveld were much higher than those in Benschop. The large amounts in the front and middle ditches can be explained by the procedure of spraying over these ditch sections (Section 9.3.6). The amounts in the back ditch were also high, probably because the trees stood very close to the ditch.

The variation in transverse direction was smaller, just as at Benschop (Sites 8 and 9 in the front ditch on 6 July). The coefficient of variation of the average amounts measured in the longitudinal direction of the ditches in Jaarsveld ranged from 23 to 55%.

Table 41. Masses (μg) of azinphos-methyl (A) measured after spray drift in Petri disches (diam. 0.09 m) placed on floats on the water-surface in ditches at Jaarsveld in 1977. Mean values of duplicate samples.

Sampling site	Front ditch		Middle ditch[1]		Back ditch[1]
	25 May	6 July	25 May	6 July	25 May
1 (front)	218	186	169	178	89
2	138	153	74	246	86
3	102	139	110	170	73
4	76	219	121	157	46
5	61	261	137	135	66
6	199	108	321	137	39
7	119	184	125	113	207
8	117	183(180)[2]	75		81
9	85	220(149)(214)[2]	92		110
10	51	169	95		65
11 (back)	218	209	93		
Average	126	185	128	162	86
Coefficient of variation (%)	(48)	(23)	(55)	(27)	(55)

1. Part of the old apple plantation on one side of the ditch was cleared in June.
2. Values of the distribution of the compound over the width of the front ditch.

Estimate of drift of the insecticides into ditches

The average mass of azinphos-methyl in a Petri dish of area 63.6 cm^2 in the siphon-linked ditch was 42 μg or 6.6 mg m^{-2} of evaporating surface of the ditch. The mass dose of azinphos-methyl divided by ground surface applied on the standard trees around the siphon-linked ditch was 68 mg m^{-2} (Section 9.6.3). To relate contamination to dose, an 'areic ratio of contamination' $m_{r,A}$ could be defined as the ratio between the mass of insecticide falling on an area of water divided by that area and the mass dose divided by ground area of the sprayed orchard. On 31 May and 26 August, after spray drift into the siphon-linked ditch this ratio was about 0.1.

For the pumped ditch, the areic ratio, $m_{r,A}$, for azinphos-methyl was calculated to be 0.08. The corresponding ratios for dimethoate into both ditches were nearly the same as for azinphos-methyl namely 0.1 and 0.09, respectively.

On 25 May in Jaarsveld, the areic ratios for azinphos-methyl, were about 0.26 for the front ditch, 0.32 for the middle ditch and 0.18 for the back ditch. On 6 July these ratios for the front and middle ditches were about 0.39 and 0.41, respectively.

For the ditch section protected by a windbreak, the ratio $m_{r,A}$ was only 0.003.

9.3.9 Estimate of rate coefficients for decline

The mass of the compounds in the water compartment after the first application in Benschop on 3 May 1976 were obtained from the product of averaged concentrations in 'dip' samples taken from the front, middle and back sections (Tables 37 and 38) and water volumes on sampling dates. Since the amounts shortly after spraying were not yet mixed over the cross-section of the water body, these initial masses were considered too uncertain for estimation of rate coefficients.

A decline plot (log concentration at various times) was made for a period without infiltration or discharge by the water pump from 5 to 18 May for both compounds in both ditches at Benschop (Figure 38). Linear regression lines were drawn (Chapter 7). The rate coefficients for decline of azinphos-methyl and dimethoate in ditch water are presented in Table 42 (Period I). The rate coefficients for decline of dimethoate were distinctly lower than those for azinphos-methyl.

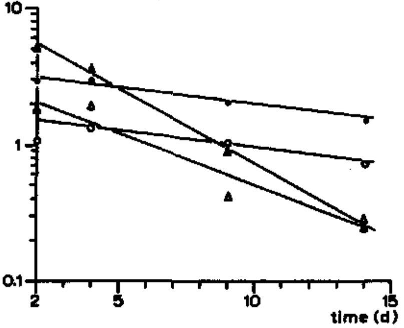


Figure 38. Mass of pesticides in the water compartment of ditches at Benschop at various times after application on 3 May 1976. ▲ = azinphos-methyl in siphon-linked ditch (BSL); ● = dimethoate in siphon-linked ditch (BSL); Δ = azinphos-methyl in supplementarily drained ditch (BSD); o = dimethoate in supplementarily drained ditch (BSD).

Table 42. First-order rate coefficients for decline of azinphos-methyl and dimethoate in drainage ditches at Benschop. Period I from 5 to 17 May, and Period II from 21 June to 1 July 1976.

	Period	pH[1]	Water temp. °C, av., s.d. and range[2]	Azinphos-methyl			Dimethoate		
				rate coeff. (d^{-1})	half life (d)	coeff. of determ.	rate coeff. (d^{-1})	half life (d)	coeff. of determ.
Siphon-linked ditch	I	7.0	14±2(11-19)	0.25	2.8	1.00	0.056	12	0.95
	II	7.0	19±2(15-21)	0.25	2.8	0.99	0.052	13	0.97
Supplementarily drained ditch	I	7.1	14±2(11-19)	0.18	3.9	0.91	0.061	11	0.98[3]
	II	7.0	19±2(15-21)	0.26	2.6	0.98	0.19	3.6	1.00

1. pH was measured in the field.
2. Calculated from daily minimum and maximum temperatures in the water compartment near the water pump.
3. Value on 5 May for dimethoate was rejected.

After the second application of both compounds at the Benschop farm on 21 June 1976, the average masses of both pesticides on 23 June and 1 July were calculated from the average concentration in shallow and deep samples of water and the water volume on both dates. Shortly after the second spraying, shallow samples of water were taken. During the spray-drift experiments in 1977, the relationship between shallow sampling and areic ratio of contamination was measured. By taking into account the water surface area in 1976, the initial masses could be estimated. For a period without infiltration or discharge from 21 June to 1 July, the decline patterns at Benschop are shown in Figure 39. The rate coefficients for decline of both compounds are presented in Table 42 (Period II).

The rate coefficients obtained during both periods of investigation are comparable to the rate coefficients found in the outdoor tanks for periods with similar conditions (compare Tables 26 and 42).

9.3.10 Concentrations of the insecticides in surface water near Benschop and Jaarsveld in 1976

Concentrations of both compounds in surface water outside both farms were measured on a limited scale. The results are shown in Table 43. These data were obtained on different

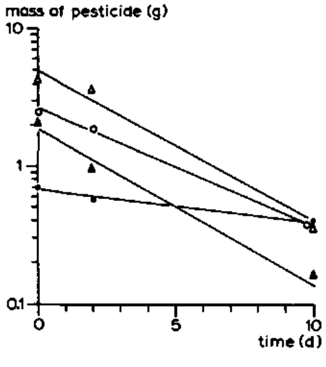


Figure 39. Mass of pesticides in the water compartment of ditches at Benschop at various times after the 2nd application on 21 June 1976. ▲ = azinphos-methyl in siphon-linked ditch (BSL); ● = dimethoate in siphon-linked ditch (BSL); Δ = azinphos-methyl in supplementarily drained ditch (BSD); o = dimethoate in supplementarily drained ditch (BSD).

Table 43. Mass concentrations of azinphos-methyl and dimethoate in samples of surface water in the Lopikerwaard Polder, in 1976.

Date of sampling	Site	pH	Concentration ($mg\ m^{-3}$)				
			azinphos-methyl		dimethoate		
			I[3]	II	I	II	III
7 May	Intake, Jaarsveld	7.2	0.4	0.8			
24 May	Discharge, Benschop[1]	7.6	1.6	1.8		17	16
1 June	Discharge, Benschop	7.8	0.4	0.7	5.8	9.3	9.7
	Benschopper Canal[2]	7.6	0.6	1.1	0.2	8.2	0.1
14 June	Discharge, Benschop	7.0	0.3	0.4	6.2	5.6	7.4

1. Discharge, Benschop: surface water receiving water from the fruit farm at Benschop.
2. Benschopper Canal: near the bridge in Benschop village.
3. GLC Columns (see Tables 14 and 15).

GLC columns without clean-up procedures.

The discharge ditch at Benschop received water from the water pump. The high concentrations of dimethoate in this discharge ditch was possibly due to cleaning of the spray equipment near the sampling point.

The deviant high value for dimethoate in surface water ('Benschopper Canal', 1 June) measured on Column II showed that using only one GLC column packing involved a risk of overestimating the concentration.

9.3.11 Preliminary measurements of concentrations in groundwater

Before spraying in 1976, some groundwater tubes (length 2m; diam. 0.06 m) were placed in bore holes (diam. 0.08 m) (Figures 31 and 32). The lower part of the PVC groundwater tube was perforated, with filter length of 0.5 m. The top of the tube protruded about 0.15 m above the surface. On top of the tubes, screw-caps were placed.

Some groundwater samples were sucked up from these tubes with the vacuum-type water sampler (Chapter 4) for analysis. Concentrations of both compounds in samples of groundwater are presented in Tables 44 and 45. With one exception, the concentrations were very low. Without clean-up, the azinphos-methyl concentrations in groundwater tubes at Benschop were usually below 1 $mg\ m^{-3}$. Although the tubes were emptied a few days before the sampling, contamination caused by leakage along the groundwater tubes might be possible, because the diameter of the bore hole was greater than the diameter of the tube.

During investigation in 1976 at Benschop, hardly any water flow occurred from the ditches into the subsoil. However at Jaarsveld, a considerable infiltration from the middle and back ditch was measured after water intake (rising groundwater in Figure 35D and high chloride concentrations in Groundwater Tube VI on 17 May and 14 June 1976 in Table 35). At Jaarsveld, the azinphos-methyl concentrations in Groundwater Tubes I and II were lower than the concentrations in Tubes V and VI, which showed a much stronger reponse of the groundwater level to raising of the ditch water than Tubes I and II (Figure 35D). So contamination of groundwater from contaminated surface water probably cannot be excluded in areas

Table 44. Mass concentrations of azinphos-methyl and dimethoate in samples of groundwater at Benschop in 1976.

Date of sampling	Ground water tube	pH	Concentration ($mg\ m^{-3}$)				
			azinphos-methyl		dimethoate		
			I[1]	II	I	II	III
17 May	III	6.9	0.2	0.3		0.2	0.05
	IX	4.2	0.07	0.1		0.2	0.03
14 June	III	7.5	0.6	0.8	7.3	7.9	8.2
	IX	6.2	0.1	0.04		0.2	0.03
1 July	II	7.4	0.6	0.6	0.3	0.4	0.08
	III	7.4	0.2	0.3	0.7	0.8	0.4
	VIII	7.4	0.3	0.4	1.0	1.7	1.2

1. GLC Columns (see Tables 14 and 15).

where infiltration is common and where residence times are relatively short.

The concentration of dimethoate in Groundwater Tube III on 14 June 1976 at Benschop was higher than of other measurements (Table 44). For more definite conclusions on possible groundwater contamination, more measurements are necessary. In the future, any leakage along the tubes should be prevented.

9.3.12 Penetration of azinphos-methyl into bottom material

Procedures for measuring penetration

During the measuring periods in 1976 some mud cores were collected in Benschop at four places in the front and back sections of both ditches and in Jaarsveld in the front sections of the front, middle and back ditch (Figures 31 and 32). These mud cores were taken with the Perspex bottom material sampler with a stainless-steel closing unit op top (Chapter 4). The mud columns were stored in a deep-freezer for about half a year. The frozen mud columns were at first divided into slices, with a carborundum handsaw; later the columns were mechanically sawn (Chapter 7).

Table 45. Mass concentrations of azinphos-methyl in samples of groundwater at Jaarsveld in 1976.

Date of sampling	Ground water tube	pH	Concentration ($mg\ m^{-3}$)	
			I[1]	II
17 May	II	6.9	0.3	0.7
	VI	7.0	1.0	1.1
14 June	I	7.0	0.3	0.4
	V	7.0	4.0	2.3
1 July	I	7.4	0.8	0.6
	V	7.4	0.8	1.3
	VI	7.4	0.9	1.1

1. GLC Columns (see Table 14).

The volumes of the wet mud slices were calculated with Equation 11, using the data on the density of the solid phase (Table 36). The depth below the sediment--water interface was obtained by dividing the volume of the wet mud sample by the average surface area of the frozen mud column (49 cm^2). The saw cut was about 2 mm for both hand-sawn and mechanically sawn columns.

The slices were extracted with a mixture of solvents and the extracts were cleaned on silica gel columns in the same way as the extracts from the bottom material in the outdoor tanks (Sections 5.6 and 5.11). The cleaned extracts were analysed by GLC on Column II (Table 14). A significant decrease in concentration during storage of the mud columns was not detected, and no correction factor was introduced (Chapter 7).

Results for penetration

The masses of azinphos-methyl in bottom materials from Benschop and Jaarsveld are presented in Tables 46 and 47, respectively. Unfortunately, several mud columns, including the samples of bottom material taken before the spraying period were lost during storage by failure of one of the deep-freezers. Therefore in the next year (March 1977), new un-

Table 46. Penetration of azinphos-methyl into the bottom of the siphon-linked ditch and the supplementarily drained ditch in Benschop during 1976. f, front of the ditch; b, back of the ditch.

Date of sampling	Siphon-linked ditch			Supplementarily drained ditch		
	site and slice number	depth in bottom (m)	mass of azinphos-methyl in slices (µg)	site and slice number	depth in bottom (m)	mass of azinphos-methyl in slices (µg)
17 May	f1	0 -0.010	0.67	f1	0 -0.008	0.14
	f2	0.012-0.023	0.44	f2	0.010-0.023	<0.01
	f3	0.025-0.036	0.16	f3	0.025-0.036	<0.01
	b1	0 -0.012	0.34	b1	0 -0.011	0.54
	b2	0.014-0.025	0.17	b2	0.013-0.024	0.24
	b3	0.027-0.039	0.07	b3	0.026-0.037	0.15
24 May	f1	0 -0.009	-[1]	f1	0 -0.009	0.07
	f2	0.011-0.021	0.05	f2	0.011-0.026	0.09
	f3	0.023-0.033	0.09	f3	0.028-0.043	0.08
	b1	0 -0.007	0.13	b1	0 -0.021	0.15
	b2	0.009-0.028	0.24	b2	0.023-0.034	0.17
	b3	0.030-0.049	0.01	b3	0.036-0.047	0.08
21 June	b1	0 -0.010	0.29	b1	0 -0.011	0.04
	b2	0.012-0.023	-[1]	b2	0.013-0.023	<0.01
	b3	0.025-0.036	0.18	b3	0.025-0.036	<0.01
	b6	0.063-0.073	0.04	b4	0.038-0.050	0.04
	b10	0.112-0.123	0.01			
23 June	f1	0 -0.011	0.30	f1	0 -0.011	0.86
	f2	0.013-0.022	0.29	f2	0.013-0.024	0.09
	f3	0.024-0.034	0.18	f3	0.026-0.037	0.05
	b1	0 -0.010	1.84	b1	0 -0.010	0.38
	b2	0.012-0.022	0.22	b2	0.012-0.022	0.24
	b3	0.024-0.034	0.14	b3	0.024-0.036	0.11

1. Interfering substances; clean-up failed.

Table 47. Penetration of azinphos-methyl in the bottom of front ditch (JF), middle ditch (JM) and back ditch (JB) in Jaarsveld during 1976. All samples were collected from the front parts of the different ditches.

Date of sampling	Site and slice number	Depth in bottom (m)	Mass of azinphos--methyl in slices (µg)
24 May	JF1	0 -0.019	1.80
	JF2	0.021-0.032	0.49
	JF3	0.034-0.046	0.23
	JM1	0 -0.015	1.55
	JM2	0.017-0.024	0.10
	JM3	0.026-0.033	0.10
	JB1	0 -0.013	0.80
	JB2	0.015-0.024	0.12
	JB3	0.026-0.033	0.09
21 June	JB1	0 -0.010	0.65
	JB2	0.012-0.023	0.22
	JB3	0.025-0.035	0.09
	JB6	0.061-0.071	0.08
	JB10	0.109-0.120	0.11
23 June	JM1	0 -0.010	3.24
	JM2	0.012-0.022	0.78
	JM3	0.024-0.035	0.43
	JB1	0 -0.011	2.53
	JB2	0.013-0.023	2.04
	JB3	0.025-0.035	0.94
1 July	JF1	0 -0.009	0.15
	JF2	0.011-0.022	0.04
	JF3	0.024-0.034	0.02
	JM1	0 -0.010	0.64
	JM2	0.012-0.022	0.21
	JM3	0.024-0.034	0.15
	JM6	0.061-0.071	0.06
	JM10	0.109-0.120	-[1]

[1] Interfering substances; clear-up failed.

treated bottom samples were collected. The masses of azinphos-methyl in the upper layer were below the detection limit for extracts of bottom material, which was 1 ng per slice (50 cm^3). So presumably also in 1976, no measurable amounts were present before spraying.

After spraying, the masses in the upper slices were higher than in the lower slices. The differences between the front and back sections of the ditches in Benschop were large (Table 46). The largest amounts of azinphos-methyl were found in bottom slices from the middle and back ditch in Jaarsveld on 23 June, 2 d after spraying. On that date the water concentrations were likewise high (Tables 47 and 39).

In spite of the small number of bottom cores, some approximations were made on the total masses of azinphos-methyl in the different ditch bottoms in Benschop on 23 June. These total masses were estimated from the average masses in the three upper slices of bottom material and the surface area of the ditch bottom. They were compared to total masses of azinphos-methyl in the water compartments of both ditches in Benschop (Figure 39).
The total mass of azinphos-methyl in the bottom compartment of the siphon-linked ditch on 23 June was estimated at 13% of its mass in the water compartment. The corresponding percentage in the supplementarily drained ditch was only 2%.

The penetration of azinphos-methyl in the bottom layer will be discussed in more detail under computer simulation for these situations (Chapter 10).

9.3.13 General discussion and conclusions

The hydrological circumstances on both farms in the Lopikerwaard Polder were highly complex. Moreover the soil surface was rather uneven, the soil was very heterogeneous and data on the water-conducting substratum were lacking. Consequently, the usual drainage formulae could not be used to estimate water flow through the ditch bottoms. Intake of uncontrolled amounts of water made estimation of the items of water balance difficult. For accurate measurement of water balances, simpler field situations and automatic measuring equipment will be necessary.

The characterization of ditch bottoms showed high organic matter contents, low bulk densities and corresponding high volume fractions of liquid. Data of this kind are rather scarce and need more attention in the future.

Introduction of the insecticides into surface water by spray drift could be measured quickly with Petri dishes. Its extent is highly influenced by local situations (windbreaks, position of trees, paths) and ways of application. Windbreaks (and probably also paths alongside the ditches) reduce the areic ratio of contamination, but more research is needed to assess their effect in different situations. In such measurements of spray drift, the losses by photochemical conversion and volatilization should be measured.

There may be other sources of contamination into watercourses, for example the cleaning of spray equipment after use.

The concentration of the compounds in the farm ditches were fairly high and other substances did not interfere during the GLC analysis. The calculated half-lives of azinphos-methyl in the ditches in Benschop were about 3 to 4 days, and those for dimethoate 4 to 13 days. These half-lives corresponded to the half-lives measured in outdoor tank trials (Chapter 7).

Mixing of the compounds throughout the cross-section of the ditch occurred within a few days. The rate of adsorption and penetration into the bottom material may be lower in situations with slow mixing. More research is needed to investigate the mixing process in more detail.

The data on penetration of azinphos-methyl into the bottom layer were too limited to estimate accurately the fraction of the substance introduced that penetrated. The rate of conversion in bottom material under field conditions was not known, but laboratory data indicate that it may be fairly high (Chapter 6). The contributions of convective transport, diffusion, and biological mixing to penetration of the insecticide into the bottom are not known. These aspects will be discussed in more detail under the computer simulation for these situations.

On the basis of these field trials alone, it is difficult to estimate the contribution of different decline processes. In Chapters 10 and 11, attempts will be made to separate the effects of the various processes by computer simulation of the ditch system. These further studies should enlarge the transferability to other situations and other pesticides with different physico-chemical properties.

10 Computations on the behaviour of pesticides in a ditch compartment

10.1 INTRODUCTION

The contribution of the various processes to the decline of azinphos-methyl and dimethoate in ditches was difficult to assess, especially in periods of water intake or pumping. The extent of penetration of both pesticides into the ditch bottom was also difficult to evaluate from the field experiments (Chapter 9). To overcome these problems attempts are made to describe the behaviour of azinphos-methyl and dimethoate in a ditch system more quantitatively with computation models.

Firstly the relevant water flow in the ditch systems were approximated. Secondly, pesticide movement and conversion were built into a computation model. The model includes flow of the pesticide through the boundary surfaces of the water and bottom compartments. Much attention was paid to the effects of adsorption on and penetration of the pesticides into the ditch bottom. In a simulation experiment, the significance was studied of infiltration through the ditch bottom on extent of penetration of pesticides.

Comparisons of the results of the computations with those of field measurements were only made for the two ditches in Benschop. The large variation in the water levels in ditches at Jaarsveld and the uncontrolled water intake at the beginning of May and at the end of June 1976 presented insurmountable problems for the approximation of the water balance.

10.2 DITCH GEOMETRY AND DERIVATION OF EQUATIONS

The cross-section of the ditch was assumed to consist of stacked trapezia (Figure 40). The slopes of the walls in the lower part of the ditches were steep (Table 34). The wetted perimeter of the ditch (P_1) was calculated from

$$P_1 = b_1 + 2\bar{h}_w \sqrt{s_1^2 + 1} \tag{22}$$

in which

b_1 = width at bottom of ditch (m)

h_w = average water depth (m)

s_1 or $tg\alpha$ = slope of lower part of ditch walls with respect to vertical (1)
(tgα = horiz./vert.) (Figure 40)

The pesticides were assumed to be completely mixed through the ditch water compartment. The ditch bottom was divided into twenty computation compartments.

The surface area of the first bottom compartment at the sediment-water interface $(A_b)_{z=0}$ was computed from the product of the wetted perimeter (P_1) and the length of the

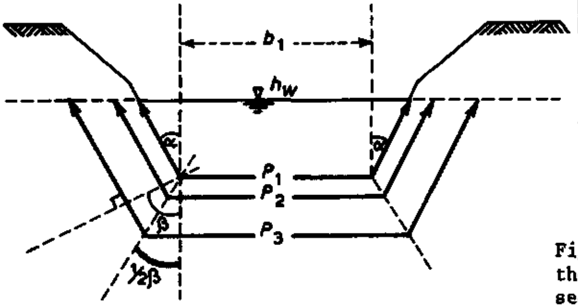


Figure 40. Cross-section of a ditch with the shape of stacked trapezia. For symbols see text.

ditch compartment (l_{com}). The surface area of the second bottom compartment was obtained from the product of 'interface' perimeter P_2 and l_{com}. The perimeter P_2 was computed from Equation 23:

$$P_2 = b_1 + 2d_2 \ \mathrm{tg}(\tfrac{1}{2}\beta) + 2\ (\bar{h}_w + d_2)\ \sqrt{s_1^2 + 1} \tag{23}$$

in which

β = arctg $(1/s_1)$ (Figure 40) (1)

d_2 = depth of upper surface of second bottom compartment (m)

The surface areas of the other bottom compartments were obtained in a similar way.

Water flow

Water flow in the water compartment (Figure 41) was combined into the following conservation equation:

$$\mathrm{d}V_w / \mathrm{d}t = q_p - q_e - q_d + q_{d,u} + q_i - q_{i,d} + q_b + q_{dr} \tag{24}$$

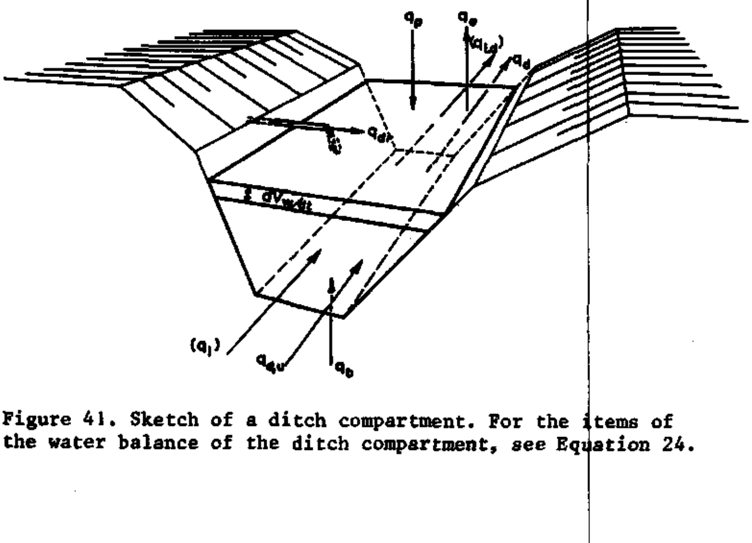


Figure 41. Sketch of a ditch compartment. For the items of the water balance of the ditch compartment, see Equation 24.

in which

dV_w/dt = change in storage of water compartment ($m^3\ d^{-1}$)

q_p = rate of precipitation into water compartment ($m^3\ d^{-1}$)

q_e = rate of evaporation from water compartment ($m^3\ d^{-1}$)

q_d = rate of discharge from water compartment ($m^3\ d^{-1}$)

$q_{d,u}$ = rate of discharge from upstream ditch section ($m^3\ d^{-1}$)

q_i = rate of intake into water compartment ($m^3\ d^{-1}$)

$q_{i,d}$ = rate of intake into down stream ditch section ($m^3\ d^{-1}$)

q_b = rate of flow through wetted perimeter of ditch ($m^3\ d^{-1}$)

q_{dr} = flow rate through drains ($m^3\ d^{-1}$)

The filtration velocity (V_{lb} in $m^3\ m^{-2}\ d^{-1}$) through the different bottom compartments was calculated from

$$V_{lb}(j) = q_b/A_b(j) \tag{25}$$

in which

A_b = surface area of bottom compartment (m^2)

j = index number of bottom compartment (1)

Pesticide movement and conversion

The total areic mass flux of pesticide into bottom material ($J_{s,lb}$ in $mg\ m^{-2}\ d^{-1}$) is composed of contributions by convection, convective dispersion and diffusion:

$$J_{s,lb} = J_{conv,lb} + J_{disp,lb} + J_{dif,lb} \tag{26}$$

in which

$J_{conv,lb}$ = areic mass flux by convection into bottom material ($mg\ m^{-2}\ d^{-1}$)

$J_{disp,lb}$ = areic mass flux by convective dispersion into bottom material ($mg\ m^{-2}\ d^{-1}$)

$J_{dif,lb}$ = areic mass flux by diffusion in bottom material ($mg\ m^{-2}\ d^{-1}$)

The areic mass flux by convection was described by the product of filtration velocity (V_{lb}) and mass concentration of the pesticide in the liquid phase of the bottom (c_{lb} in $mg\ m^{-3}$):

$$J_{conv,lb} = V_{lb}\ c_{lb} \tag{27}$$

The areic mass flux by convective dispersion was calculated with

$$J_{disp,lb} = -l_d \left| V_{lb} \right| \partial c_{lb}/\partial z \tag{28}$$

in which

l_d = dispersion distance (m)
z = depth in bottom (m)

The areic mass flux by diffusion in bottom material ($J_{dif,lb}$) was computed in the same way as described in Chapter 8 (Equations 15 and 16).

The rate of conversion in the ditch water ($R_{c,w}$) and the rate of conversion in the ditch bottom material ($R_{c,b}$) were calculated with first-order rate Equations 17 and 18, respectively.

The flow rate of substance into the water compartment during an intake period ($F_{s,wi}$ in mg d^{-1}) was calculated from

$$F_{s,wi} = q_i \, c_{w,i} \tag{29}$$

in which

$c_{w,i}$ = mass concentration of substance in intake water (mg m^{-3})

The flow rate of substance into downstream ditch section during an intake period ($F_{s,wd}$ in mg d^{-1}) was computed from

$$F_{s,wd} = q_{i,d} \, c_w \tag{30}$$

in which

c_w = mass concentration of substance in water compartment (mg m^{-3})

The flow rate of substance out of the water compartment during a pumping period ($F_{s,wo}$ in mg d^{-1}) was calculated from

$$F_{s,wo} = q_d \, c_w \tag{31}$$

The flow rate of substance into a water compartment from upstream ditch section during a pumping period ($F_{s,wu}$ in mg d^{-1}) was computed from

$$F_{s,wu} = q_{d,u} \, c_{w,u} \tag{32}$$

in which

$c_{w,u}$ = mass concentration of substance in upstream ditch section (mg m^{-3})

The resulting conservation equation for the pesticide in the water compartment with volume V_w (m^3) was

$$\partial(V_w \, c_w)/\partial t = -(A_b \, J_{s,lb})_{z=0} + F_{s,wi} + F_{s,wu} - F_{s,wd} - F_{s,wo} - V_w \, R_{c,w} \tag{33}$$

The conservation equation for the pesticide in the bottom material was

$$\partial c_b/\partial t = -\partial J_{s,lb}/\partial z - R_{c,b} \qquad (34)$$

The relationship between mass concentration in the bottom material (c_b) and the concentration in the liquid phase (c_{lb}) was computed with Equation 21. The adsorption--desorption was assumed to occur instantaneously, while the isotherm was assumed to be linear in the relevant concentration range.

10.3 DESIGN OF THE COMPUTATIONS AND VALUES OF PARAMETERS

The differential equations, boundary conditions and basic relationships were programmed in the computer language CSMP III (IBM, 1975). The program was run on the DECsystem-10 computer of the Agricultural University, Wageningen. The listing of this computation model is given in Appendix B.

The initial masses of the substance in the water compartment and in the bottom compartments were assumed to be zero. The spray-drift was set at a constant rate during the day of spraying. This input was assumed to be completely mixed through the water compartment. The total masses at Benschop on the first spraying date were derived by backward extrapolation of the regression lines in Figure 38 to the ordinate on the date of the spraying. The masses applied during the second spraying were obtained from the values at the intercept with the ordinate in Figure 39.

In Benschop, no water was taken in during the investigation, thus the rate of intake into the water compartment (q_i) and the rate of intake into downstream ditch sections ($q_{i,d}$) could be set to zero. Because the siphon-linked ditch was a branch of the discharge system (Figure 31), no discharge from upstream ditch sections occurred ($q_{d,u} = 0$). During periods with discharge, the concentration of the substance in water flowing from upstream ditch sections into the supplementarily drained ditch in Benschop was assumed to equal the concentration discharged from the siphon-linked ditch.

The dimensions of the ditch sections were introduced from Table 34. The number of computation compartments in the bottom was twenty. The thickness of the first bottom compartment was 0.001 m. The multiplication factor for the thickness of the bottom compartments (m_f) was 1.1. The total thickness of the bottom layer was then computed at 0.06 m. The parameters of the ditch bottom like the bulk density (ρ_b) and the volume fraction of liquid (ε_l) as shown in Figure 35 were introduced as functions of depth.

Description of the water flow

The flow rates of evaporation (q_e) and rainfall (q_p) were calculated from Figures 33 and 34A by multiplying the fluxes (in mm d^{-1}) by the water surface area. In the computation model, the rate of rainfall was distributed evenly over the day preceding the time of observation.

The rate of discharge of the water pump was measured during dispersion experiments (Chapter 11). The rate of discharge from the water compartment (q_d) during a day with pumping was obtained by multiplying the following quantities: a) daily pumping times (Figure 34B); b) rate of discharge of the water pump; c) ratio between the catchement area of the ditch compartment and the total catchment area of the water pump (Table 34). This resulted in discharge rates in Benschop of q_d(BSL) = 135 and $q_{d,u}$(BSL) = 0 $m^3\ d^{-1}$, q_d(BSD) = 1705 and $q_{d,u}$(BSD) = 1570 $m^3\ d^{-1}$. The q_d(BSD) equalled the discharge rate of the water pump.

The heights of the water level (h_w) in the different ditch sections measured on the sampling dates (Figure 34C, Table 34) were used to outline a relationship between h_w and time. In periods without pumping, the water levels of the ditches at Benschop were obtained by linear interpolation between measuring points. The rate of change in volume of the water compartment was computed as a central difference.

The rate of water flow through the wetted perimeter of the ditch was calculated from the water conservation Equation 24 as a closing entry. The flow rates through the bottom (q_b) and drains (q_{dr}) were assumed to be proportional to the drainage surface areas that could be assigned to the ditch itself and to the tile drains.

The approximation of flow rate through the bottom of the ditch was rather difficult. First the water levels were only known on the sampling dates. Secondly the hydrological situation at Benschop was very complex. Consequently the water flow through the ditch bottom could not be directly calculated from measured difference between groundwater level and ditch-water level. The groundwater levels in the various tubes midway between the ditches were distinctly different and they were only measured on sampling dates (Chapter 9). Thirdly, the distribution of the total water discharge by pumping over the different ditch sections could be only roughly estimated.

Because calculations with closing entry values may lead to erroneous results, the filtration velocity through the first bottom compartment (V_{1b} (1)) was also approximated indirectly. This could be done with the following relationship for filtration velocity (Ernst, 1971):

$$V_{1b}(1) = \rho_w\, g\, (h_g - h_w)/\gamma \qquad (35)$$

in which

ρ_w = density of water	($kg\ m^{-3}$)
g = acceleration due to gravity	($m\ d^{-2}$)
h_g = height of groundwater level above ditch bottom	(m)
h_w = height of water level above ditch bottom	(m)
γ = drainage resistance	($kg\ m^{-2}\ d^{-1}$)

Values of drainage resistance (γ) were calculated from value of $V_{1b}(1)$, h_g and h_w on the first four sampling dates. (In this period no water was pumped out or let into the ditches; thus $V_{1b}(1)$ was reasonably known). These drainage resistances were used to estimate the change in water level during a day with water pumping.

First, the change in water level during pumping was roughly estimated, so that filtration velocity $V_{1b}(1)$ could be obtained with q_b in conservation Equation 24. These values of $V_{1b}(1)$ were introduced in the resistance Equation 35, by assuming a constant drainage resistance and with h_w the pattern of the groundwater level during the investigation could be calculated. By comparing the calculated and measured groundwater levels, it was possible to get better approximations for the change in water level during the pumping periods.

Diffusion, dispersion, adsorption and conversion parameters

The average water temperature in the ditches was about 15 °C. The diffusion coefficient ($D_{\mathrm{dif,w}}$) of azinphos-methyl in water at 15 °C was calculated to be 0.35×10^{-4} m^2 d^{-1} and that for dimethoate was calculated to be 0.41×10^{-4} m^2 d^{-1} (Reid & Sherwood, 1966). The same tortuosity relationship was introduced as described in Section 8.3.

The dispersion distance (l_{d}) in the bottom material was unknown. For agricultural soils, rather wide ranges of dispersion distance have been found, for example, a range from 0.01 to 0.06 m (Frissel et al., 1970). The distance introduced in this study was 0.015 m. The adsorption coefficients ($K_{\mathrm{s/l}}$) of azinphos-methyl on the bottom material of the different ditch sections were measured (Table 23).

The rate coefficients for conversion of azinphos-methyl and dimethoate in the water compartments ($k_{\mathrm{c,w}}$) of both ditches at Benschop were approximated to be 0.9 times the rate coefficients measured for the decline (k_{r}) of both compounds for two periods in those ditches (Table 42). This assumption was based on the results of the computations for the tank trials (Chapter 8), which showed that conversion in water may be expected to be the dominant process out of doors. The rate coefficients for conversion of the compounds in the bottom material ($k_{\mathrm{c,b}}$) were derived from rate coefficients obtained in incubation tests (Chapter 6). At 15 °C, $k_{\mathrm{c,b}}$ for azinphos-methyl was estimated to be 0.038 d^{-1} (Table 21) and for dimethoate to be 0.01 d^{-1} (Table 22).

Details on the computation method

The computations for azinphos-methyl in both ditches at Benschop were done by Euler's integration method (RECT) using a time step Δt of 0.005 d, over a period of 59 days. For dimethoate in both ditches the time step had to be reduced to 0.002 d. The computations were checked by halving the time step and by using the Runge-Kutta (RKS) integration method, which automatically selects small time intervals when rates of change are high (IBM, 1975).

For the convective flow in the bottom (Equation 27), the concentration in adjacent compartments were averaged, which minimized numerical dispersion (Goudriaan, 1973).

In situations with upward water flow through the ditch bottom and with a steep concentration gradient (decreasing in downward direction) an artificial downward mass flux, due to dispersion, was simulated. This artefact was mainly suppressed by setting the mass flux into the bottom layer (Equation 26) smaller than or equal to the flux of diffusion in such situations (limited flux equation, Appendix B). This working method still gives a slight overestimate of downward transport in the ditch bottom compared with what would have been computed under these conditions with a correct model. A second method was tested, whereby for upward liquid flow the dispersion term was set all the time at zero. This method gives an underestimation of the penetration into the bottom in relation to a correct model for such conditions.

At regular intervals during computations, the water balance and the material balance of the pesticide in the ditch system were checked.

10.4 COMPUTED RESULTS FOR THE FIELD TRIALS

Results of computation of the water balance

The heights of the water level above the ditch bottom in the siphon-linked ditch and the supplementarily drained ditch at Benschop are shown in Figures 42A and 43A, respectively. The changes in water level during pumping were approximated by comparing the calculated groundwater levels with the groundwater levels measured on sampling dates (Figures 42B and 43B). In view of possible variation in the drainage resistance during the period of investigation, a small difference between the calculated and measured groundwater levels was considered acceptable. During the first two pumping periods (Day 17 and Day 24), a significant rise in the calculated groundwater level was obtained. In these periods, no significant increase in the filtration velocity through the wetted perimeter of the ditch ($V_{1b}(1)$) was computed (Figures 42C and 43C).

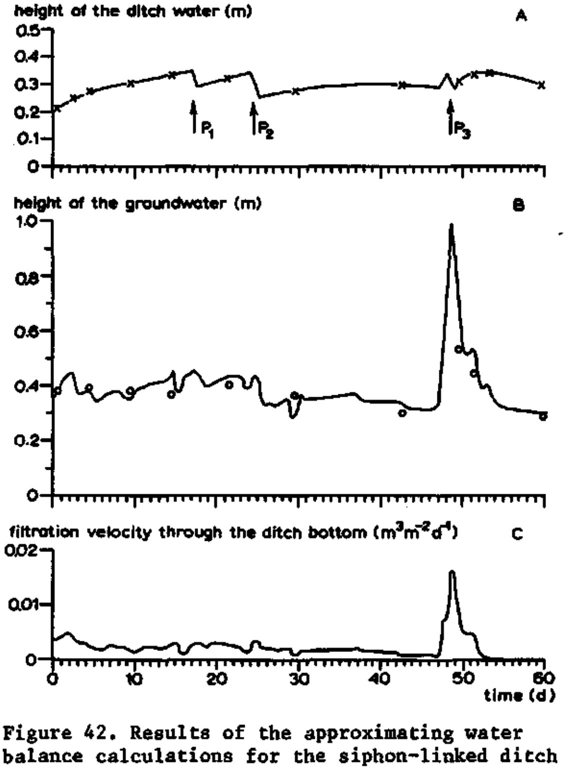


Figure 42. Results of the approximating water balance calculations for the siphon-linked ditch at Benschop in 1976.
A. Height of the water level above the ditch bottom. x, water height at sampling dates; P, pumping period.
B. Calculated height of the groundwater level above the ditch bottom. o, groundwater level on sampling dates .
C. Filtration velocity calculated from Equation 25.

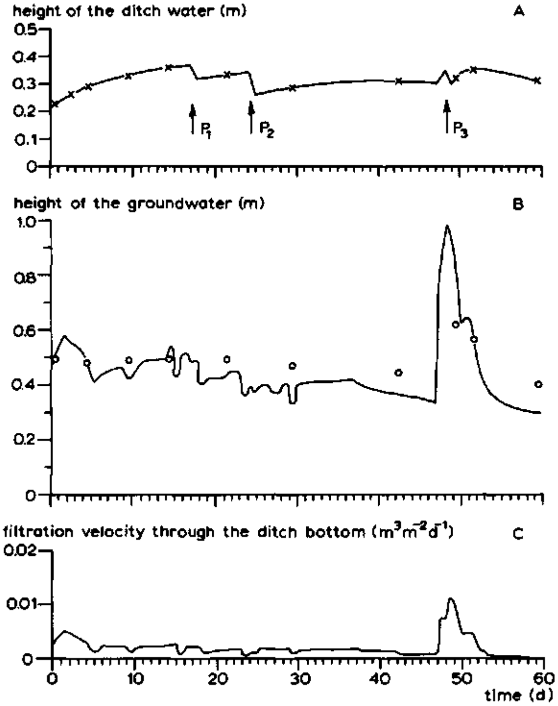


Figure 43. Results of the approximating water balance calculations for the supplementarily drained ditch at Benschop in 1976.
A. Height of the water level above the ditch bottom. x, water height at sampling dates; P, pumping period.
B. Calculated height of the groundwater level above the ditch bottom. o, groundwater level on sampling dates.
C. Filtration velocity calculated from Equation 25.

During the last pumping period (after the heavy rainfall on 20 June and 21 June) (Day 48), the increase in the calculated groundwater level was substantially larger than the increase in the measured groundwater level. This is attributable to a reduction in drainage resistance during the heavy rainfall.

During the investigation, usually small variations in the filtration velocity ($V_{1b}(1)$) were calculated. However, much faster flow through the ditch bottom occurred during the heavy rainfall. The positive values of $V_{1b}(1)$ indicate a continuous discharge of groundwater into the ditch-water compartment. Inflow of groundwater coming from elsewhere may occur to a small extent in this area ('upward seepage'). However the inflow of groundwater in this area could not be accurately assessed from deep and shallow groundwater levels (Hey & Kester, 1977).

Division of the rate of flow through the wetted perimeter of the ditch (q_b) by the surface area of land draining into the ditch gives the flow rate in water layer per day as used in some drainage formulae. This flow rate was rather low and ranged from about 0.000 3 m d^{-1} at the beginning of May down to about 0.000 1 m d^{-1} just before the heavy rainfall. These flow rates are in the same range as the estimates of the upward seepage rate of $0.000\ 2\ \mathrm{m\ d^{-1}}$, mentioned by the Studiegroep Lopikerwaard (1973) for comparable situations.

The items of the water conservation Equation 24 for both ditches, cumulated over the period of investigation from 3 May to 2 July 1976, are shown in Table 48. The discharge from the siphon-linked ditch was relatively small in the dry year 1976. The total discharge from the supplementarily drained ditch was equal to the discharge of the water pump. The substantial discharge from upstream ditch sections into the supplementarily drained ditch was of great importance for pesticide movement during the period with water pumping. The total discharge from this section was more than ten times the average volume of water in the ditch compartment.

The computations with the Runge-Kutta integration method (RKS) produced nearly the same results as those with Euler's integration method (RECT). The differences in the values of the water fluxes when halving the computation time-step were also small.

Pesticide movement and conversion

Pesticide in the water compartment

The computed and measured masses of azinphos-methyl in the water compartment of the siphon-linked ditch and the supplementarily drained ditch as a function of time are given in Figures 44 and 46. The values for dimethoate in both ditches are shown in Figures 45 and 47. The measured mass of substance in the ditch water compartments was derived from the product of average concentration in the ditch sections and the water volume at sampling dates. The ranges in the measured mass shown in Figures 44 to 47 indicate the highest and lowest average concentration in the front, middle or back section of the ditch (Tables 37 and 38).

With $k_{c,w} = 0.9\ k_r$ (Table 42), the decline processes in the water compartment were described fairly well. The same holds for setting $k_{c,w}$ equal to k_r. This confirms the assumption that conversion in the water compartment was the predominant process in the decline under outdoor conditions.

The computed curves for the decline in the water compartment (log scale) were some-

Table 48. Items in the water balance (m^3) of the ditches in Benschop integrated over the period of investigation from 3 May to 2 July 1976. During the period, no water was taken in.

	Siphon-linked ditch	Supplementarily drained ditch
Change in storage	33	42
Total rainfall	29	36
Total evaporation	95	117
Total discharge	111	1407
Total discharge from upstream	0	1295
Total flow through the ditch bottom	53	59
Total flow through the drains	157	176

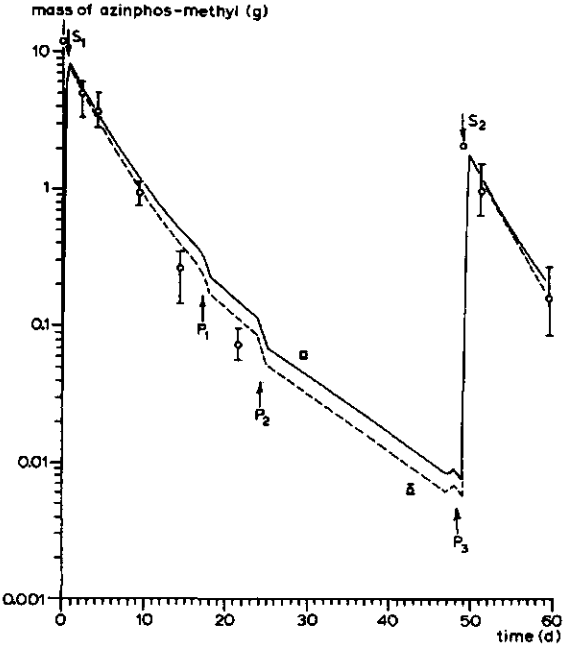


Figure 44. Computed and measured mass of azinphos-methyl in the water compartment of the siphon-linked ditch at Benschop from 3 May 1976. —— = computed mass ($k_{c,w} = 0.9\ k_r$); --- = computed mass ($k_{c,w} = k_r$); o = averaged measured masses; S = spraying dates (Chapter 9); P = pumping period (Chapter 9). Vertical bars are range of measured mass.

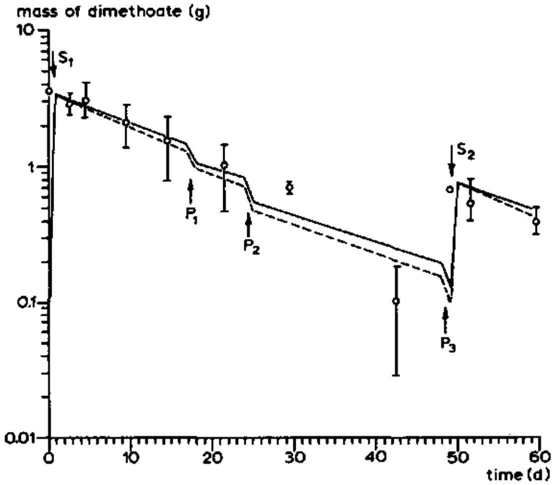


Figure 45. Computed and measured mass of dimethoate in the water compartment of the siphon-linked ditch at Benschop from 3 May 1976. —— = computed mass ($k_{c,w} = 0.9\ k_r$); --- = computed mass ($k_{c,w} = k_r$); o = averaged measured masses; S = spraying dates (Chapter 9); P = pumping period (Chapter 9). Vertical bars are range of the measured mass.

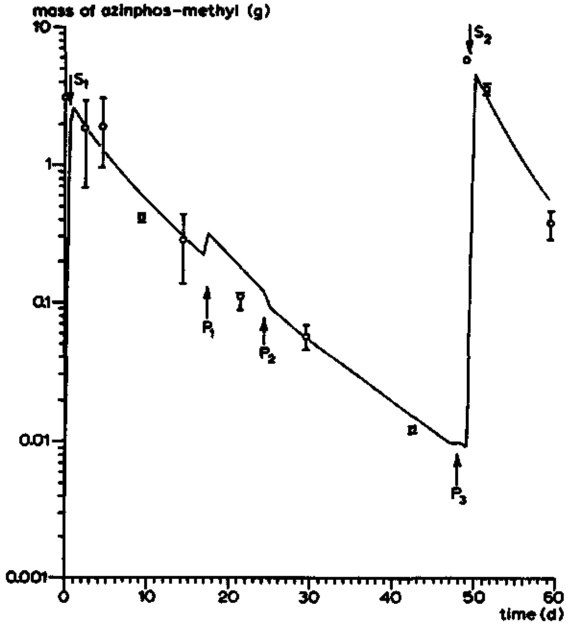


Figure 46. Computed and measured mass of azinphos-methyl in the water compartment of the supplementarily drained ditch at Benschop from 3 May 1976. ——— = computed mass ($k_{c,w}$ = 0.9 k_r); o = averaged measured masses; S = spraying dates (Chapter 9); P = pumping period (Chapter 9). Vertical bars are range of the measured mass.

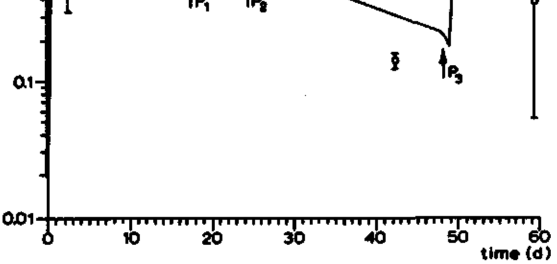


Figure 47. Computed and measured mass of dimethoate in the water compartment of the supplementarily drained ditch at Benschop from 3 May 1976. ——— = computed mass ($k_{c,w}$ = 0.9 k_r); o = averaged measured masses; S = spraying dates (Chapter 9); P = pumping period (Chapter 9). Vertical bars are range of the measured mass.

what concave. This can be partly explained from a slight adsorption and penetration into the bottom layer, which will be simulated to be fastest at the beginning of the experiment. Because of the comparatively small conversion rate of the compound in the bottom layer, the mass flux at the bottom--water interface even became negative (upward flux) after a few days. This contributed to the concave pattern of decline in the water compartment.

During the three pumping periods, a decrease in the mass of the compounds was computed for the siphon-linked ditch. Shortly before the third pumping period a slight increase in the mass of azinphos-methyl in the water compartment was calculated due to upward drainage from the ditch bottom during a day with much rainfall (Figure 44, Day 48). During the first pumping period in the supplementarily drained ditch, relatively strong increase in the mass of both compounds in the water compartment was computed (Figure 46, Day 17). This resulted from the relatively high concentration in the water discharged from upstream ditch sections. The assumption that the concentration in the siphon-linked ditch was representative for the concentration in the inflowing water may not have been correct. The spray-drift into the upstream ditch Section 2 (Figure 31) could have been lower due to the path alongside that ditch section. In ditch sections with a contaminated water flow from upstream sections, it is rather difficult to assess a pesticide balance.

The items of the simulated balance for both compounds in the ditches, cumulated over the period of investigation from 3 May to 2 July 1976 are presented in Table 49, which shows that conversion in the water compartment was the most important item. The different conversion rates in the water had only a small effect. Increasing the conversion rate of azinphos-methyl in water by 11% (to the decline rate itself; Table 42), resulted in only an extra 1.5% of the mass applied being converted in water. For dimethoate the corresponding value was somewhat higher (3%). The masses of both compounds discharged from the supplementarily drained ditch were higher than those discharged from the siphon-linked ditch. During the three pumping periods, a considerable mass of substance was transported from upstream ditch sections into the supplementarily drained ditch (Table 49).

Pesticide in the ditch bottom

The computed and measured masses of azinphos-methyl in the bottom layer of the siphon--linked ditch and of the supplementarily drained ditch at Benschop are given in Figure 48. In both ditches, the calculated amounts are considerably higher than measured. In these computations, it was assumed that the compound is completely mixed throughout the water compartment. However, in practice there are considerable differences between concentrations at various depths in the water body in the first few days after contamination (Tables 36 and 37). The effect of penetration into the ditch bottom is thus likely to be overestimated with the model. The rate of conversion of the pesticide in the ditch bottom ($k_{c,b}$) under field conditions is quite uncertain. The value of $k_{c,b}$ in field situations may deviate from the value of $k_{c,b}$ measured in laboratory incubation studies and introduced into the computations.

The measured and computed concentration patterns of azinphos-methyl in both ditch bottoms are presented in Figures 49 and 50. The computed concentration in the upper centimetre of the ditch bottom was much higher than the measured concentration in the upper

Table 49. Computed items of the material balances of azinphos-methyl and dimethoate in ditch compartments at Benschop after 59 days (3 May to 2 July 1976). These items are expressed in percentages of the mass of substance introduced in both ditches.

Ditch	Compound	Introduced		Conversion rate in water[1]	Fraction of the introduced mass (%)					
		by spray--drift (g)	from up-stream sections (g)		in water compartment	in bottom layer	converted in water	converted in bottom	discharged from water comp.	infiltration into sub-soil
Siphon-linked	azinphos-methyl	12.4	0	0.9 k_r	1.8	2.0	86.3	9.0	0.9	0.0
				0.9 k_r(2)	1.8	1.8	87.1	8.4	0.9	0.0
				k_r	1.5	1.7	87.8	8.3	0.7	0.0
	dimethoate	4.3	0	0.9 k_r	11.5	1.8	69.2	1.8	15.7	0.0
				0.9 k_r(2)	11.4	1.4	70.2	1.2	15.9	0.0
				k_r	10.6	1.7	72.2	1.7	13.8	0.0
Supplementarily drained	azinphos-methyl	9.0	1.3	0.9 k_r	5.7	5.1	71.2	6.2	11.8	0.0
	dimethoate	4.7	7.8	k_r	4.7	0.9	35.7	0.5	58.2	0.0

1. $k_{c,w} = 0.9\ k_r$ for both Periods I and II in field trials at Benschop (Table 42) or $k_{c,w} = k_r$.
2. 'plug flow', in which the dispersion flux (Equation 26) was zero in situations with an upward water flow.

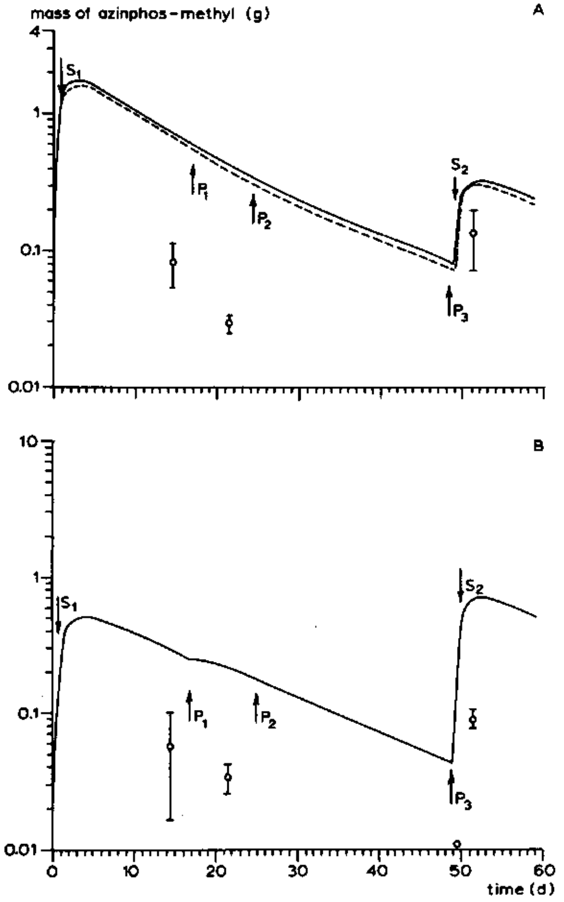


Figure 48. Mass of azinphos-methyl in the ditch bottom of A. the siphon-linked ditch B. the supplementarily drained ditch at Benschop, starting from 3 May 1976. —— = computed mass ($k_{c,w}$ = 0,9 k_r); --- = computed mass ($k_{c,w} = k_r$); o = measured mass; S = spraying dates (Chapter 9); P = pumping period (Chapter 9). Vertical bars are range estimated from duplicate columns.

slice. The computed penetration into the bottom was distinctly less than the measured penetration. Biological mixing and a small disturbance during sampling may have had some influence.

The computed masses of dimethoate in the bottom layer of both ditches at Benschop shortly after the spraying dates were much lower than these for azinphos-methyl. This can be partly ascribed to the higher azinphos-methyl concentrations in the water compartment and further to the much lower adsorption of dimethoate on the bottom material.

The computed concentration profiles of dimethoate in the ditch bottom were less steep than those of azinphos-methyl. The penetration depth for dimethoate was reduced by the slow upward water flow through the ditch bottom.

By omitting the dispersion term (Equation 26) for field situations with an upward

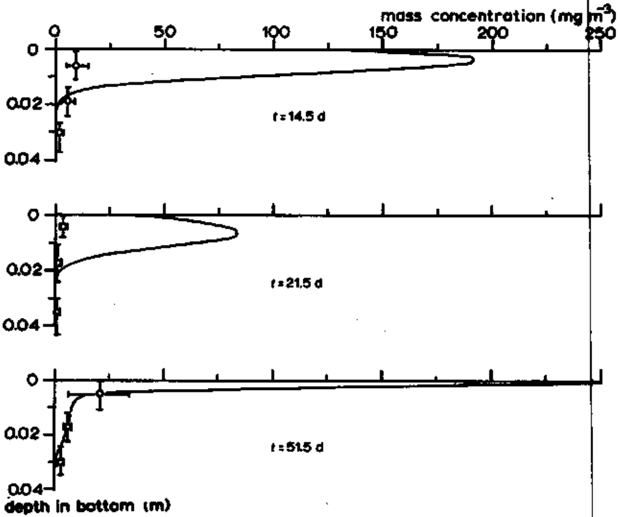


Figure 49. Mass concentrations of azinphos-methyl in the bottom (mg m^{-3}) of the siphon-linked ditch at Benschop. —— = computed mass concentration ($k_{c,w}$ = 0.9 k_r); o = average measured concentrations. Horizontal bars are range of concentrations measured in duplicate. Vertical bars are average thickness of the bottom slices.

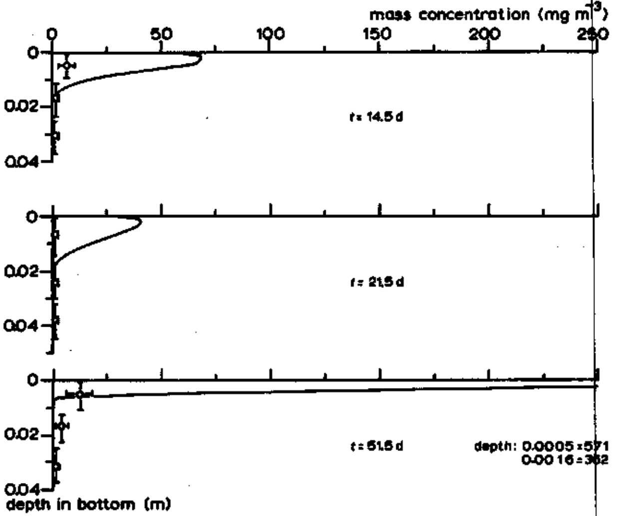


Figure 50. Mass concentrations of azinphos-methyl in the bottom of the supplementarily drained ditch at Benschop. —— = computed mass concentration ($k_{c,w}$ = 0.9 k_r); o = average measured concentrations. Horizontal bars are range of concentrations measured in duplicate. Vertical bars are average thickness of bottom slices.

water flow, a 'plug flow' situation was simulated. This resulted in somewhat smaller fluxes into the bottom than with the limited flux equation (Appendix B), especially during the first few days after the start of computations. However in the field situation, the flux into the bottom compartments became negative (upward flux) after a few days. In such a situation, the 'plug-flow model' will transport the penetrated pesticide too fast out of the bottom compartments. With plug flow, the computed mass of the compounds converted in the bottom was somewhat lower than with the limited-flux equation. Both computed distributions ('limited-flux equation' and 'plug-flow' model) can be considered as extremes: the actual distribution will be intermediate. The difference in the items of the material balance of azinphos-methyl and dimethoate for both model situations were relatively small (Table 49). The model as shown in Appendix B was presumably the most acceptable one because the limitation of the fluxes worked only at the beginning of the computations.

10.5 DESIGN OF THE SIMULATION EXPERIMENTS

In simulation experiments, the effect was studied of drainage and infiltration on the amounts of azinphos-methyl and dimethoate penetrating into the ditch bottom. A simplified ditch system was derived from the back ditch in Jaarsveld. In these simulation experiments, rainfall and evaporation were assumed to be equal, and the water depth was held constant. The rates of discharge and intake, which were varied in the different computer runs, are given in Table 50.

The initial mass of pesticide in the water compartment was 10 g for all runs; that for the bottom compartments was zero. In the drainage ($V_{1b} > 0$) and diffusion ($V_{1b} = 0$) situations, the thickness of the upper bottom compartment was 0.001 m and the multiplication factor for the downward increase in thickness of bottom compartments (m_f) was 1.1. For the infiltration situations ($V_{1b} < 0$), the thickness of the first bottom compartment was 0.002 m, and $m_f = 1.2$. The bulk densities and volume fractions of liquid were taken for the back ditch at Jaarsveld (Table 36).

The rate coefficients for conversion of the pesticides in the water compartment were set at 0.9 times the average rates of decline as measured in field trials (Table 42). The rate coefficient for the conversion in water of azinphos-methyl was 0.21 d^{-1}, that for dimethoate was 0.08 d^{-1}. The rate coefficients for conversion of the compounds in the ditch bottom were 0.038 d^{-1} and 0.01 d^{-1}, respectively. The adsorption coefficient of azinphos-methyl was 0.077 $m^3\ kg^{-1}$ (Table 23), that for dimethoate was assumed to be 0.001 $m^3\ kg^{-1}$.

The computations were with Euler's integration method. The time-step (Δt) for the experiments with azinphos-methyl was 0.005 d; in the computations for dimethoate a smaller time step of 0.002 d had to be used. The model systems were simulated for 27 d. The computations were checked with a Runge-Kutta integration procudure which selects a variable time-step.

10.6 RESULTS OF THE SIMULATION EXPERIMENTS

The computed mass of the substances in the water compartment and in the bottom layer are shown in Figure 51. The decline of the compounds in the water compartment in a situa-

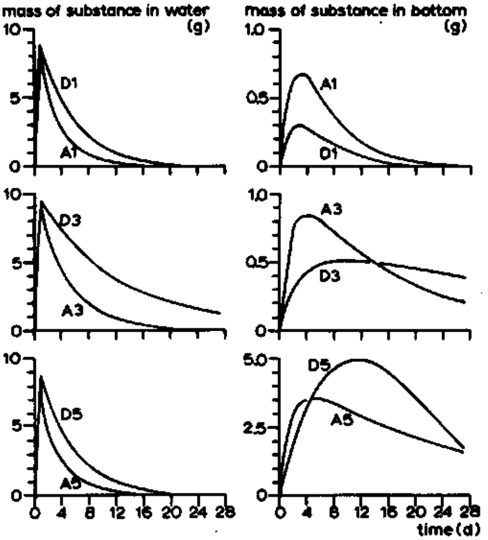


Figure 51. Mass of substance in water and in bottom layer computed in the simulation experiments. Numbers refer to the computer runs listed in Table 50. A, azinphos-methyl; D, dimethoate; Run 1, drainage; Run 3, diffusion (no flow); Run 5, infiltration .

tion without water flow (only diffusion, Runs A3 and D3) was slower than in situations with water flow (drainage or infiltration). During drainage, a certain amount of the compounds is transported out of the water compartment (Runs A1 and D1). During infiltration, a fraction is transported into the bottom layer (Runs A5 and D5). As could be expected, the mass of substance in the bottom layer was much higher with downward water flow (infiltration) than with upward water flow (drainage).

The decline of azinphos-methyl in the water compartment without water flow was much faster than that for dimethoate. This difference was caused primarily by the relatively fast conversion rate of azinphos-methyl in water. The adsorption coefficient of azinphos-methyl was much higher than that for dimethoate and thus the penetrated mass of azinphos-methyl in the bottom layer was higher than that for dimethoate. However, the penetrated mass of both compounds in the bottom had only a limited influence on the decline curves in the situation with no water flow (Figure 51, A3 and D3). In a drainage situation, the mass of azinphos-methyl in the bottom layer was much higher than that for dimethoate (Figure 51, A1 and D1), due to its relatively high adsorption. However, during infiltration (A5 and D5), the maximum mass of dimethoate in the bottom layer was computed to be higher than that for azinphos-methyl. This difference was caused by the relatively low conversion rates of dimethoate in water and bottom material.

The material balances of both pesticides in the ditch system after a computation time of 27 d are shown in Table 50. In drainage situations, the effect of penetration and conversion in the bottom layer of both compounds on the total material balance was very limited. Considerable amounts of the substance were discharged from the water compartment (Table 50).

The infiltration simulation experiments showed that the bottom layer may be an important sink for pesticides in watercourses. Only in the infiltration simulation Run D5 a considerable fraction of the initial mass of dimethoate was computed to be transported out of the lowest bottom compartment (at depth of 0.35 m).

Table 50. Computed items of the material balance of azinphos-methyl and dimethoate in a simulated ditch system after 27 d.

Compound	Run number	Flow conditions in the ditch system			Fraction of the initial mass (%)					
		rate of discharge ($m^3\ d^{-1}$)	rate of intake ($m^3\ d^{-1}$)	filtration velocity[1] ($m^3\ m^{-2}\ d^{-1}$)	in water	in bottom	converted in water	converted in bottom	discharged from water comp.	infiltration into subsoil
Azinphos-methyl	A1	10	0	0.03	0.1	0.2	60.6	2.4	36.7	0
	A2	5	0	0.015	0.3	0.5	73.7	3.2	22.3	0
	A3	0	0	0	0.7	2.1	92.1	5.1	0	0
	A4	0	5	-0.015	0.5	11.0	69.4	19.1	0	0
	A5	0	10	-0.03	0.3	16.1	57.0	26.6	0	0
Dimethoate	D1	10	0	0.03	0.5	0.0	38.3	0.3	60.9	0
	D2	5	0	0.015	2.7	0.2	53.8	0.4	42.9	0
	D3	0	0	0	11.6	3.9	83.3	1.2	0	0
	D4	0	5	-0.015	2.7	32.6	53.7	8.1	0	2.9
	D5	0	10	-0.03	0.6	17.7	38.2	9.8	0	33.7

1. Positive filtration velocity through the ditch bottom means an upward waterflow into the ditch-water compartment.

Penetration depth

The concentration profiles in the bottom layer after 9, 18 and 27 d for Simulation Runs 1, 3 and 5 are presented in Figure 52. When water flow was upward (drainage), the penetration depth was limited to a few centimetres. The penetration depth was slightly overestimated, as the artificial dispersion flux in the computation model could only partly be suppressed (Appendix B) (Section 10.4). For situations without water flow (diffusion), the concentrations in the bottom were considerably higher than in drainage situations. But with downward water flow (infiltration) considerable penetration was computed down to 0.4 m for dimethoate. The penetration for azinphos-methyl in the infiltration computations was about 0.15 m. However the simulation experiments were with a rather low adsorption coefficient ($K_{s/1}$) of azinphos-methyl, as measured for the ditch in Jaarsveld. With a higher adsorption coefficient, as measured for the siphon-linked ditch in Benschop, the difference between the penetration depths of azinphos-methyl and dimethoate would have been more pronounced.

These simulation experiments indicate the possible contamination of groundwater during an infiltration period. In the investigated area, periods of drainage and infiltration occur alternately but over the whole year, drainage is predominant. During infiltration periods, the behaviour of pesticides in the ditch bottom and subsoil should thus be further studied.

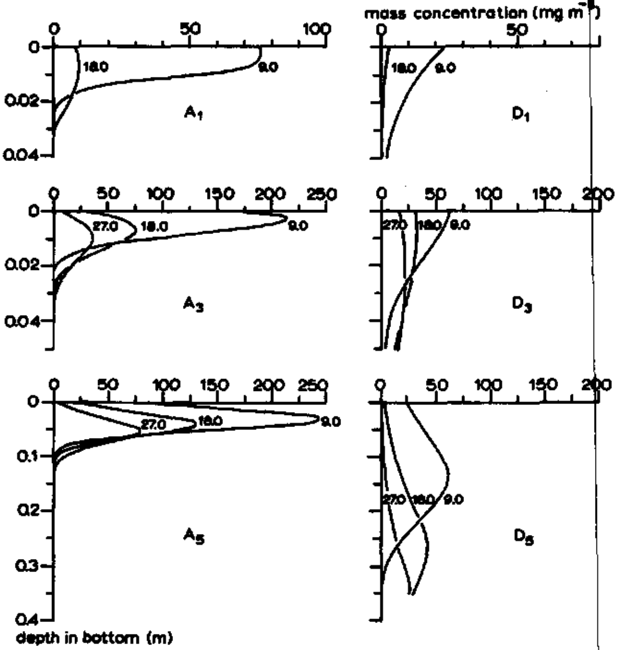


Figure 52. Computed mass concentrations of the substances in the bottom material. Numbers refer to the computer runs listed in Table 50. A, azinphos-methyl; D, dimethoate; Run 1, drainage; Run 3, diffusion (no flow); Run 5, infiltration .

10.7 GENERAL DISCUSSION

The simulation of pesticide behaviour in a ditch system requires an accurate description of water flow in the ditch and through the bottom. In the field situation at Benschop, the rate of water flow through the wetted perimeter of the ditch was difficult to ascertain. Further the distribution of the total discharge rate of the water pump over the various ditch sections could only be roughly estimated. In further experiments in ditch systems, the change in ditch-water levels and groundwater levels should be recorded continuously to improve the characterization of water flow.

The computation model on the behaviour of pesticides in a ditch compartment is suitable for estimation of the contribution of various phenomena to decline in the field. For the ditches at Benschop, conversion in the water compartment was found to be the most important process for decline, especially in periods without pumping.

In a normal situation, in which water levels are kept within narrow limits, considerable amounts of substance can be discharged from the ditch system into larger watercourses, especially when pumping starts within a few days of spraying.

The computation model developed could not be checked against the literature. Unfortunately in almost any article on the fate of pesticides in ditch systems, one or more of the essential parameters are lacking.

In the field situation at Benschop, the contribution of the bottom layer to the decline of the compounds in the water compartment did not seem important. In other fruit-growing areas in the Netherlands, many ditches fall dry or nearly so during summer. In such ditches, the decline process in the ditch bottom may predominate.

The calculated and measured concentration profiles in the bottom, show that in further experiments very thin slices of bottom material should be analysed. For an accurate prediction of concentration profiles in the ditch bottom in infiltration situations, more research is needed on the dispersion coefficients in the bottom material. In drainage situations, penetration depth is slightly overestimated with the computation model, and thus a more accurate model is needed. For compounds with low conversion rates in water and high adsorption coefficients, penetration into the bottom may be a major process. Especially for such situations, more computational and experimental research is needed to improve description of penetration into the ditch bottom.

11 Measurements and computations on the behaviour of substances in ditches with flowing water

11.1 INTRODUCTION

The behaviour of pesticides in ditches with flowing water is determined by many processes such as convection, dispersion, diffusion, adsorption, volatilization, microbial and chemical conversion. In flowing water, dispersion is an important phenomenon, because of the velocity distribution over the cross-section of the watersoure is not uniform.

A short review of some equations normally used for description of convective flow and dispersion in flowing water is given in this Chapter. Up to about 16 empirical equations have been developed for computing the longitudinal dispersion coefficient (Bansal, 1971). However it remains difficult to predict the dispersion coefficient in surface water. The various empirical equations give values that differ widely for a particular flow system. Although many empirical dispersion coefficients are given in the literature, hardly any data on the dispersion of substances in small watercourses can be found. For this reason, a few dispersion experiments were carried out for the supplementarily drained ditch in Benschop and for the front ditch in Jaarsveld.

In view of the toxicity of the studied pesticides, they could not be used in dispersion measurements. Therefore two fluorescent dyes, fluorescein-sodium and Rhodamine WT, were used as tracers. The behaviour of both compounds was investigated during a pumping period after momentary placing as a band across the last ditch section before the two water pumps.

Questions in dispersion experiments in small ditches are as follows. How quickly will a substance spread by dispersion? What dispersion coefficient applies in ditches with flowing water at various times during the year under different conditions of vegetation in the ditch? Will spread be symmetrical or asymmetrical? How great are the deviations from the symmetrical pattern and how can they be explained? What will be the influence of other decline processes? Will there be a considerable difference between the spreading process of compounds, that are either strongly or weakly adsorbed onto the ditch bottom?

All these questions cannot be solved with only a few relatively simple dispersion experiments. Therefore the behaviour of the dyes in flowing water, was also simulated in a computation model, which included convective flow, dispersion, adsorption and conversion of the compounds. The results of the computations were compared with those of the dye dispersion measurements for the ditch sections in front of the water pumps in Benschop and Jaarsveld. The dispersion behaviour of azinphos-methyl after an instantaneous input was simulated with the developed computation model.

11.2 DERIVATION OF EQUATIONS FOR ONE-DIMENSIONAL CONVECTION AND DISPERSION OF SUBSTANCES IN FLOWING WATER

The one-dimensional dispersion coefficient (D_1) is defined by describing the convection and dispersion of a substance in a given ditch by the basic differential equation for one-dimensional convection and dispersion. The dispersion coefficient depends on the velocity distribution over the cross-section and hence on the geometry of the ditch. Under steady flow conditions and without conversion and adsorption of the compound, the differential equation may be written as

$$\partial c_w / \partial t = D_1 \; \partial^2 c_w / \partial x^2 - \bar{u} \; \partial c_w / \partial x \qquad (36)$$

in which

c_w	= mass concentration of substance in water	(mg m^{-3})
D_1	= longitudinal dispersion coefficient	(m^2 d^{-1})
$\bar{u}$	= average flow velocity of water	(m d^{-1})
x	= downstream distance along ditch axis	(m)
t	= time	(d)

The dispersion coefficient can be calculated from experimental data of dispersion in a given ditch using Equation 36. This equation can be solved for the condition of an instantaneous point source; the solution is then

$$c_w = m/(A\sqrt{4\pi D_1 t}) \; \exp\left[-(x - \bar{u}t)^2/(4D_1 t)\right] \qquad (37)$$

in which

m	= initial injected mass of substance	(mg)
A	= average wetted cross-sectional area of ditch	(m^2)

Multiplying both sides of Equation 37 with $\sqrt{t}$ and taking the decadic logarithm of both sides of the equation yields

$$\lg(c_w\sqrt{t}) = \lg\left[m/(A\sqrt{4\pi D_1})\right] - \left[(x - \bar{u}t)^2/(4D_1 t)\right] \lg e \qquad (38)$$

If this model holds, a straight line will be obtained when plotting $\lg(c_w\sqrt{t})$ against $(x - \bar{u}t)^2/t$; the slope of which is equal to $\left[1/(4D_1)\right]$ lg e. For symmetrical concentration patterns ('Gaussian distribution'), the longitudinal dispersion coefficient (D_1) can be obtained from the slope. For asymmetrical concentration curves, different straight lines will be obtained for the front and the tail of the concentration--time relationship. This results in rather different dispersion coefficients for the front and the tail of the concentration curve.

Equation 38 can also be used to estimate D_1 in another way. When the maximum concentration of the compound passes the sampling point $x - \bar{u}t_{max} = 0$ and after rearranging the terms in Equation 38, D_1 can be computed from the following equation:

$$D_1 = m^2/(\bar{A}^2 \, C^2_{\mathrm{w,max}} 4\pi t_{\mathrm{max}}) \tag{39}$$

in which

$c_{\mathrm{w,max}}$ = the maximum mass concentration at a sampling point (mg m^{-3})
t_{max} = time at which the maximum mass concentration is reached at a a sampling point. (d)

The dispersion coefficient (calculated with Equation 39) lies between the values obtained from the slopes of the front and the tail of the concentration curve.

Relationship between dispersion coefficient and water depth

Various investigators have tried to find relationships for predicting the longitudinal dispersion coefficient in natural streams. The comparatively simple equations include terms like average water depth (h_{w}), shear velocity u_*(in m d^{-1}) or the average flow velocity of water $\bar{u}$ (in m d^{-1}). Examples of such equations are

$$D_1 = a \, \bar{h}_{\mathrm{w}} \, u_* \tag{40}$$

and

$$D_1 = k \, \bar{h}_{\mathrm{w}} \, \bar{u} \tag{41}$$

in which

a and k are dimensionless dispersion constants (1)

The shear velocity (u_*) can be related to the average flow velocity ($\bar{u}$) by the following equations:

$$u_* = \sqrt{\tau_0/\rho_{\mathrm{w}}} = \sqrt{g} \, \bar{u} \, R^{-1/6} \, K_{\mathrm{m}}^{-1} \tag{42}$$

in which

τ_0 = shear stress at ditch walls (kg m^{-1} d^{-2})
ρ_{w} = density of water (kg m^{-3})
g = acceleration due to gravity (m d^{-2})
R = hydraulic radius (m)
K_{M} = Mannings coefficient for bottom roughness ($\mathrm{m}^{1/3}$ d^{-1})

The relationship between u_* and $\bar{u}$ in Equation 42 shows that Equations 40 and 41 are analogous.

A wide range of values is reported for the dimensionless dispersion constants. The constant a ranged from 2 to 7500 (Day, 1975). As yet, only a few dispersion experiments in rivers in the Netherlands have been described (Table 51). For these rivers, the dimensionless dispersion constant k ranged from 1.5 to 6.

If the one-dimensional description of the convection and dispersion Equation 36 holds, the maximum concentration of a substance ($c_{\mathrm{w,max}}$) on a downstream distance x after

Table 51. Results of dispersion experiments for rivers in the Netherlands. (After van de Beld & van Straten, 1976).

River	Average flow velocity ($m\ d^{-1}$)	Average water depth (m)	Dispersion coefficient ($m^2\ d^{-1}$)	Dispersion constant k (1)
Groenlose Slinge	4320	1	7200	1.7
Oude Yssel	6000	4	144000	6.0
Hupselse Stream	4800	0.5	3600	1.5

an instantaneous input can be estimated from the following equation (43), which was obtained after rearranging Equations 39 and 41.

$$c_{w,\max} = m/(2\bar{A}\ \sqrt{\pi\ k\ \bar{h}_w\ x}) \qquad (43)$$

For symmetrical dispersion curves, the maximum concentration can easily be predicted with Equation 43, assuming that the relationship between the dispersion coefficient, water depth and average flow velocity (as used in Equation 41) is valid.

11.3 DISPERSION MEASUREMENTS WITH DYES

In the ditch sections in front of the water pumps, four dispersion experiments were carried out with fluorescent tracers. Three experiments were carried out in the supplementarily drained ditch at Benschop and one in the front ditch at Jaarsveld. Three experiments were with fluorescein-sodium. In view of the rapid conversion of this compound in sunlight, Rhodamine WT was used in one experiment; it is slower decomposed in surface water under sunny conditions. Details of the various dispersion experiments are tabulated in Table 52. During the first three experiments, in which fluorescein-sodium was used, the sky was completely cloudy. The last experiment (with Rhodamine WT) was in bright sunny weather.

Most of the water samples were sucked up with the vacuum sampler (Section 4.2). However, during the third dispersion experiment, water was continuously pumped through a spectrophotometer and the results were recorded simultaneously. In view of a rather low maximum pumping speed, small suction tubes were used to reduce the travelling time to the spectrophotometer. A difficulty of small suction tubes was the chance of the suction mouth blocking. One of the tubes situated a few centimetres above the sediment--water interface became blocked during the continuous measurements.

The samples of the first two experiments were measured with a spectrophotometer (Beckman, Acta CV) at 504 nm. In the third experiment, water was continuously pumped through a spectrophotometer (Bausch & Lomb, Spectronic 88) under comparable circumstances. The samples of the dispersion experiment with Rhodamine WT were measured on a fluorometer (Perkin Elmer, Model 204), excitation at 484 nm, analysis at 513 nm. The water samples of the first experiment were also measured with the fluorometer. The average difference between 22 measurements with the fluorometer and with the spectrophotometer was only 3%.

Table 52. *Data on the dispersion experiments with tracers in ditches in the Lopikerwaard Polder.*

Experiment	Date (year-month-day)	Ditch section[1]	Dye[2]	Supplied mass of tracer (g)	Sampling distance[3] (m)	Average water depth (m)	Number of sampling tubes	Position of tubes in ditch	Sampling depth (m)
1	1976-09-27	BSD	Fl	50	100	0.18	1	middle	0.05
2	1976-11-15	JF	Fl	7.5	150	0.21	4	2 x middle	0.05 and 0.15
								2 x near side	both 0.15
3	1978-05-08	BSD	Fl	20	180	0.15	2	middle	0.05
								near side	0.10
4	1978-05-31	BSD	Rh	5	140	0.16	4	2 x middle	0.05 and 0.10
								2 x near side	both 0.10

1. BSD = *supplementarily drained ditch at Benschop; JF = front ditch at Jaarsveld.*
2. Fl = fluorescein-sodium, Rh = Rhodamine WT.
3. Sampling distance measured from the injection point.

Before the start of the dispersion experiments, the discharge rate of the water pumps was measured with the 'Purdue trajectory method' as described by Bos (1976). With this method, the curve of a jet of water from a horizontal discharge pipe is related to the discharge rate through the pipe (analogous to the principle of a projectile). By measuring the drop in the jet of water 0.15 m from the end of the pipe, the corresponding discharge rate can be read from a nomograph (Bos, 1976). The measured discharged rate of the water pump in Benschop was about 1705 $m^3 d^{-1}$ and in Jaarsveld about 1440 $m^3 d^{-1}$.

During the dispersion experiments, water depths were measured frequently near the injection point, near the sampling point and near the water pump to assess the average water depth during the experiments.

Results of dispersion experiments

The concentration--time relationship in the four dispersion experiments are shown in Figure 53. During the second experiment, the differences between the concentrations measured in the middle and near the side of the ditch were very small. For that experiment, the concentrations in samples taken with the different tubes were averaged.

The curves obtained in the Experiments 1, 3 and 4 were asymmetrical. Such a tailing phenomenon can be explained by zones with little or no flow near the sides of the ditch. During the dispersion experiments, it was observed that part of the tracer became entrapped in a zone of low flow rates along the ditch sides. After the main part of the distribution passed, there was a small gradual release of tracer into the main stream. The tailing may also be partly caused by a rise in background level at the end of the experiment.

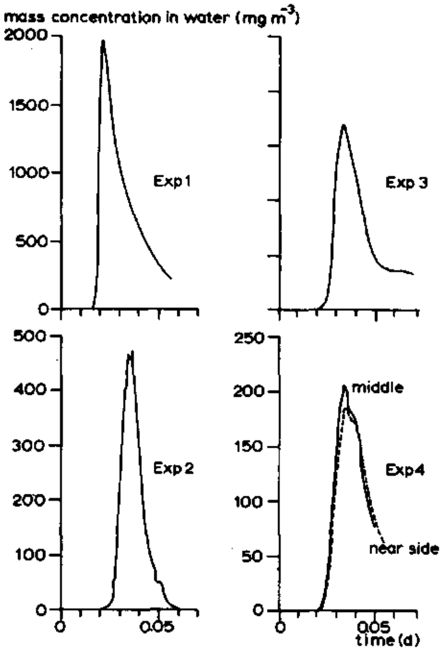


Figure 53. Mass concentration of the dyes measured during dispersion experiments in ditches in the Lopikerwaard Polder. Samples in the fourth experiment were taken in the middle of the ditch and near the side. Experiments 1 to 4 as defined in Table 52.

In the literature, the zone of flow rates is usually referred to as 'dead zone' or 'stagnant zone'. The process of trapping and slowly releasing a tracer in a dead-zone model was described, for instance, by Hayes et al. (1966). Similar models were developed by Coats & Smith (1964) for ion-exchange in soils with a dispersive system with fluid moving through large pores and stagnant fluid in blind pores. However difficulties in the model of Hayes et al. (1966) are estimation of the fraction of the dead zone in the total cross-section and the mass transfer coefficient between the dead zone and the main stream. For these reasons, the relatively simple differential equation for one-dimensional convection and dispersion (Equation 36) was used.

The longitudinal dispersion coefficients were calculated by Equation 39. The coefficients were calculated for Experiments 1 to 4 (Table 53). The dispersion coefficients (D_1) in the supplementarily drained ditch were larger than those for the front ditch (Experiment 2). The variation in D_1 for the supplementarily drained ditch was by a factor about 3. This variation can partly be ascribed to a variation in the flow conditions in the ditch, caused by changes in side vegetation or extent of duckweed (*Lemna minor*) cover. In Experiment 1, more than 50% of the water surface was covered with a duckweed layer. Experiment 2 was in a recently cleaned ditch. During Experiment 3, the supplementarily drained ditch was rather clean. However in Experiment 4, about three weeks later, there was a dense layer of duckweed in front of a grating near the water pump.

The average flow velocities were obtained from the equation: $x - \bar{u}t_{max} = 0$, which is valid when the maximum concentration is reached at the sampling point. The average flow velocities were shown in Table 53. The average discharge rate of the water pump was calculated from the average wetted cross-sectional area of the ditch and the average flow velocity (Table 53). During Experiment 4, the average discharge rate was considerably lower than in the Experiments 1 and 3. This was caused by the presence of a duckweed barrier in front of the pump. During Experiment 4, the water level around the pump was temporarily lowered by 0.27 m after 80 min of water pumping. In Experiment 3, the water level near the pump was lowered only 0.11 m in the same pumping time. The lower water level during Experiment 4 gave rise to a substantially lower pumping capacity than in the earlier experiments (Table 53). The average rate of discharge of the pumps obtained from the dispersion experiments (Table 53) were somewhat lower than the discharge rates measured with the 'Purdue trajectory method'. These differences can be explained mainly by an increase in the elevation height during the dispersion experiments, which resulted in a lowering of the rate of discharge.

Table 53. Longitudinal dispersion coefficients (D_1) measured for ditches in the Lopikerwaard Polder.

Experiment	Average water depth (m)	Average cross-sectional area (m^2)	Average flow velocity ($m\ d^{-1}$)	Average rate of discharge ($m^3\ d^{-1}$)	Dispersion coefficient ($m^2\ d^{-1}$)	Dispersion constant k (1)
1	0.18	0.36	4640	1650	18600	22.3
2	0.21	0.33	4190	1380	5100	5.8
3	0.15	0.30	5640	1660	6280	7.4
4	0.16	0.32	3950	1250	16000	25

The dimensionless dispersion constant k (Equation 41) measured for ditches in the Lopikerwaard Polder ranged from 5.9 to 25.3 (Table 53). These constants were higher than the dispersion constants measured for rivers in the Netherlands (Tables 51 and 53).

11.4 COMPUTATION MODEL FOR THE BEHAVIOUR OF SUBSTANCES IN DITCHES WITH FLOWING WATER

11.4.1 Derivation of the equations

The cross-section of the ditch was assumed to have the shape of a trapezium. The wetted perimeter of the ditch (P) was calculated from Equation 22.

The total areic mass flux of substance in the water ($J_{s,w}$ in mg m^{-2} d^{-1}) was composed of contributions by convection, convective dispersion and diffusion:

$$J_{s,w} = J_{conv,w} + J_{disp,w} + J_{dif,w} \tag{44}$$

The areic mass flux by convection ($J_{conv,w}$ in mg m^{-2} d^{-1}) was described by the average flow velocity in the ditch and the mass concentration of the substance in the water:

$$J_{conv,w} = \tilde{u}\ c_w \tag{45}$$

The areic mass flux by convective dispersion in water was obtained from

$$J_{disp,w} = -D_1\ \partial c_w/\partial x \tag{46}$$

The areic mass flux by diffusion in water was calculated with

$$J_{dif,w} = -D_{dif,w}\ \partial c_w/\partial x \tag{47}$$

The areic mass flux by diffusion in the liquid phase of the bottom ($J_{dif,1b}$) was obtained from Equations 15 and 16.

As in the earlier models, the rate of conversion in the ditchwater ($R_{c,w}$) and that in the ditch bottom ($R_{c,b}$) were computed with first-order relationships (Equations 17 and 18).

The resulting conservation equation for the substance in a water compartment with volume V_w was:

$$\partial(V_w\ c_w)/\partial t = -\partial(V_w\ J_{s,w})/\partial x - A_b(J_{dif,1b})_{z=0} - V_w\ R_{c,w} \tag{48}$$

The conservation equation for the substance in the bottom material was the same as described in Equation 20. The relationship between the concentration in the liquid phase and that in the bottom material was calculated with Equation 21. As in the previous models, the adsorption equilibrium was assumed to establish instantaneously and the isotherm was assumed to be linear in the relevant concentration range.

11.4.2 *Layout of the computations and values of parameters*

The differential equations, boundary conditions and dispersion relationships were programmed in the computer language CSMP III (IBM, 1975). The listing of the third computation model is given in Appendix C.

The mass of dye or pesticide that arrived in the water at time zero was assumed to be mixed throughout the first water compartment. The applied masses were equal to the masses shown in Table 52. The concentration of substance in the water flowing into the first water compartment was taken to be zero.

The dimensions of the supplementarily drained ditch at Benschop and the front ditch at Jaarsveld were introduced from Table 34. The average water heights in both ditch sections were introduced into the model as given in Table 52. The ditches were divided into a hundred computation compartments. Each ditch compartment (2 m long) was composed of a ditchwater and a single bottom compartment. The thickness of the bottom compartment was 0.005 m. The ditch bottom parameters like bulk density and volume fraction of liquid were obtained from Figure 36. Check runs were made by halving the length of the ditch compartments and also by halving the thickness of the bottom compartments.

When the concentration--time relationship was approximately symmetrical (Experiment 2), the average velocity of water flow could be obtained from the time at which the top of the curve passed the measuring position x:

$$\bar{u} = x/t_{\mathrm{max}} \tag{49}$$

For the $\bar{u}$ obtained with Equation 49, see Table 53. For the asymmetrical curve found in the first dispersion experiment, the flow velocity of water was calculated also in another way. For this curve, the average flow velocity of water was approximated form the first moment (M_1) (which corresponds to the average residence time in the ditch water compartment):

$$\bar{u} = x/M_1 \tag{50}$$

in which the first moment M_1 was defined as:

$$M_1 = \int_0^\infty c_{\mathrm{w}}\, t\, \mathrm{d}t / \int_0^\infty c_{\mathrm{w}}\, \mathrm{d}t \tag{51}$$

The average flow velocity $\bar{u}$ for the first dispersion experiment calculated with Equation 50 was about 2970 m d^{-1}. Since the flow velocities in the ditch were high relative to filtration velocities in the ditch bottom (Figure 43), the latter were assumed to be zero during the dispersion experiments.

The diffusion coefficient of fluorescein in bulk water at 15 °C was calculated to be 0.35×10^{-4} m^2 d^{-1}, according to procedures of Reid & Sherwood (1966). The adsorption coefficient ($K_{s/1}$) for fluorescein onto the bottom material of the supplementarily drained ditch was measured in a slurry experiment to be about 0.007 m^3 kg^{-1}. The $K_{s/1}$ for the same tracer in the front ditch at Jaarsveld was extrapolated as 0.003 m^3 kg^{-1}.

The rate coefficient for the conversion of fluorescein in the water compartments for both ditches was estimated to be 0.55 d^{-1} ($t_{\frac{1}{2}}$ = 1.3 d) from data of Feuerstein & Sellick (1963). The rate coefficient for the conversion of fluorescein in the ditch bottom ($k_{c,b}$) was reported to be very low (van de Oever, 1972). Therefore $k_{c,b}$ was set at zero.

All computations were carried out with Euler's integration method. The computations were checked by halving the time step and by using the CSMP Runge-Kutta (RKS) integration procedure (IBM, 1975).

As in the model described before (see Appendix B), the convective flux in the water compartments was calculated by averaging the concentration in adjacent compartments, in order to minimize numerical dispersion. The numerical dispersion due to taking simple finite differences in time with the rectilinear integration method was suppressed by adding a correction term equal to $(\bar{u})^2\ \Delta t/2$ in the dispersion coefficient of Equation 46 (Bella & Dobbins, 1968).

The time step (Δt) used with the rectilinear integration method was selected from the stability condition (Bella & Dobbins, 1968):

$$\Delta t < l_{com}{}^2/(2\ D_1) \tag{52}$$

in which

l_{com} = the length of the ditch compartment (m)

The material balances of the tracers in the ditch system were checked at regular intervals during the computations.

11.4.3 Results of simulations for the tracer experiments

The measured and computed concentration patterns of the dyes were compared only for Dispersion Experiments 1 and 2. A computer simulation of Dispersion Experiment 3 was omitted in view of the severe tailing (Figure 53). During the Dispersion Experiment 4, a grating near the water pump became clogged with duckweed, so the experiment was curtailed and could not be checked in detail with the computation model.

The difference between the computed and measured concentration pattern of fluorescein in Experiment 1 was rather large (Figure 54); for Experiment 2, the correspondence was rather good (Figure 54). The computation model gave best results for a rather clean ditch (Experiment 2). With a dense duckweed cover on top of a ditch (Experiment 1), the measured tailing was much larger than predicted with the computation model. The difference between the computed and measured concentration pattern in the first experiment could be reduced by introducing a somewhat lower flow velocity in the ditch system (Figure 54). This reduced velocity was obtained from the relationship between the first moment of the concentration curve and the average flow velocity of water (Equations 50 and 51). Most probably, the tailing phenomenon in ditches with a duckweed cover can be described better by dead-zone models. But in view of the change in water level during the experiments and the uncertainties in the reduction of rate of discharge after about 1 h of water pumping, the elaborate process of fitting parameters in the dead-zone models was omitted.

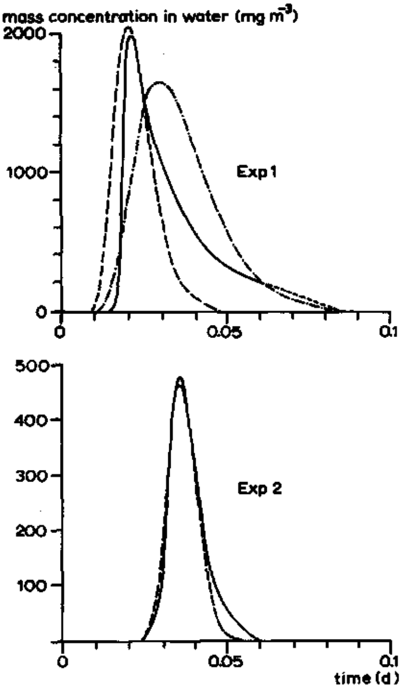


Figure 54. Measured and computed concentration pattern for the 1st and 2nd dispersion experiment in the ditches in the Lopikerwaard Polder. —— = measured mass concentrations (Figure 53); --- = computed mass concentrations (Appendix C); -·- = computed with reduced average flow velocity.

The computed items of the material balance for fluorescein in both dispersion experiments, cumulated over a computation period of 0.1 d, are shown in Table 54. The total mass of dye that was converted in the water compartments was only 2.3-2.6% of the mass supplied. The total mass of the dye in the bottom layer after 2 h of computation was insignificant (0.3%). As expected, the discharged mass of dye from the ditch was the major item of the material balance (Table 54).

Halving the length of the ditch compartment to 1 m while doubling the number of ditch compartments resulted in nearly the same concentration patterns. However as can be expected from Equation 52, run time was considerably increased. The results of computations with Euler's integration method (RECT) were nearly the same as those obtained with the more sophisticated Runge-Kutta integration method (RKS).

Halving the thickness of the bottom compartment resulted temporarily in higher concentrations in the bottom, which can easily be explained by the steeper diffusion gradient. Although the total mass of the dye in the bottom compartments increased, the effect of this

Table 54. Computed items of material balance of fluorescein in Dispersion Experiments 1 and 2, cumulated over 0.083 d (2 h).

Experiment	Mass supplied (g)	Fraction of mass supplied (%)				
		in water	in bottom	converted in water	converted in bottom	discharged from ditch
1	50	0.0	0.3	2.3	0.0	97.4
2	7.5	0.0	0.3	2.6	0.0	97.1

diffusion on the concentrations in the ditch water remained small. For that reason no runs were made with an extended model, including several bottom compartments per ditch compartment.

11.4.4 Design of the simulation experiments with pesticides

Under flow conditions as shown in Table 53 for Dispersion Experiments 1 and 2, a few simulation experiments were carried out with azinphos-methyl and dimethoate. The behaviour of both pesticides after a sudden input (for example due to insufficient care during tank cleaning) into the two ditch sections in the Lopikerwaard Polder was simulated.

The same diffusion and adsorption parameters of azinphos-methyl and dimethoate were introduced as described in Section 10.3. The rate coefficients for the conversion of both pesticides in the ditch water and in the ditch bottom were the same as used in Section 10.5. The relative importance of the longitudinal dispersion coefficient on the maximum concentration of the pesticides in watercourses was tested by doubling the coefficient.

11.4.5 Results of the simulation experiments with pesticides

The calculated concentration--time relationships of azinphos-methyl and dimethoate passing the same sampling points as used in Dispersion Experiments 1 and 2 were nearly the same as the calculated concentration patterns of the tracer (Figure 54). In the two ditch sections at Benschop and Jaarsveld, the difference between pesticide concentration and tracer concentration, at the time that the maximum concentration passed the sampling points, was about 1% for both pesticides. The calculated concentrations of the pesticide were slightly higher than the tracer concentrations, which was caused by the relatively small conversion rate of the pesticides in the ditch water.

The computed items of the material balance of azinphos-methyl and dimethoate for both simulation experiments are shown in Table 55. For short periods of time (2 h) the influence of adsorption and conversion was only slight. In all simulation experiments more than 98% of mass supplied was discharged from the ditch system (200 m length). Comparing the results of the items of the material balance of fluorescein in both dispersion experiments with both pesticides only showed relatively small differences (Tables 54 and 55).

Some simulated concentration--time relationships of azinphos-methyl at downstream

Table 55. Computed items of material balance of azinphos-methyl (A) and dimethoate (D) in simulation experiments on their behaviour in ditches with flowing water, cumulated over 0.083 d (2 h).

Experiment		Mass supplied (g)	Fraction of mass supplied (%)				
			in water	in bottom	converted in water	converted in bottom	discharged from ditch
1	A	50	0.0	0.3	0.9	0.0	98.7
	D	50	0.0	0.3	0.3	0.0	99.3
2	A	7.5	0.0	0.4	1.0	0.0	98.6
	D	7.5	0.0	0.4	0.4	0.0	99.2

distances of 58, 118 and 198 m in both ditch systems are shown in Figure 55. The effect of doubling the longitudinal dispersion coefficient is also presented in Figure 55. By increasing the dispersion coefficient by a factor 2, the maximum concentrations that passed the sampling points, were considerably lower, as would be expected from Equation 43. The maximum concentrations at the sampling points computed with the simulation model were nearly the same as the maximum concentrations calculated with the simple Equation 43. For time periods in which the conversion in water and bottom material can be ignored, the effect of a sudden input of azinphos-methyl and dimethoate into a ditch system can be estimated from Equation 43. For time periods in which the conversion of pesticides may not be ignored in relation to discharge rate in the ditch system, the concentration--time relationship can be better predicted by using the computation model.

11.5 GENERAL DISCUSSION

The dispersion experiment in a clean ditch showed a rather symmetrical concentration--time relationship. Such concentration patterns could be predicted rather well with the computation model. In ditches with a cover of duckweed a different concentration--time relationship was observed. The curves showed a rather steep front and a relatively long tail. The correspondence between the computed and the measured concentration curves was

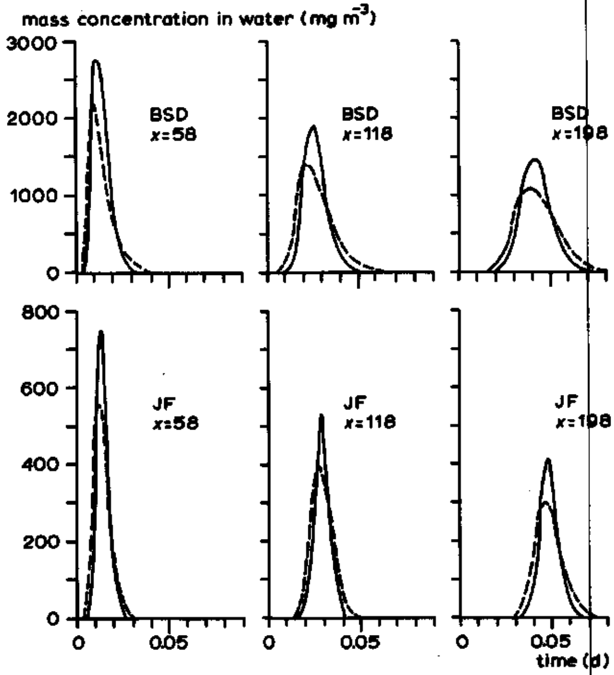


Figure 55. Simulated concentration--time relationships of azinphos-methyl at different downstream distances (x in m) in the supplementarily drained ditch at Benschop (BSD) and the front ditch at Jaarsveld (JF). —— = computed with dispersion coefficients (Table 52); --- = computed with doubled values of the dispersion coefficient.

only reasonable at the top of the concentration curves; at the front and especially at the tail of the curves, there were large deviations between the simulated and measured concentrations. The tailing can probably better be described with dead-zone models.

The water flow was relatively fast. Within 2 h of water pumping, nearly all supplied mass of dye or pesticides was transported out of the ditch system (200 m length). In view of the short residence time in both ditch sections, the other processes like conversion and penetration into the ditch bottom were computed to be of minor importance.

The physico-chemical behaviour of dyes (fluorescein and also of Rhodamine WT) can be compared with the physico-chemical behaviour of dimethoate. Dye experiments, therefore, can be used to simulate the behaviour of certain pesticides. In view of the far easier analytical methods and the lower toxicity of dyes, such a procedure has advantages. However, for pesticides with low solubility in water, the concentration over the cross-section of a watercourse may be different. For them, dispersion experiments with more apolar tracers may be necessary.

The major factor in the maximum downstream concentrations after a sudden input was undoubtly the dispersion coefficient. For many ditch systems, no data on the dispersion coefficients are available. Therefore prediction of the maximum concentration in ditch systems remains difficult. More dispersion experiments are necessary in various ditch systems under various conditions. Based on these experiments, a classification of dispersive behaviour for different types of ditch system may be possible.

In situations with low velocity in the ditch water, the adsorption of pesticides onto the ditch bottom can probably not be ignored. For such situations the description of the ditch system with only one bottom compartment per ditch compartment is too rough and the number of ditch bottom compartments should then be increased. Increasing the number of compartments, however, considerably increase computation time.

The computation model holds only for rather symmetrical concentration--time relationships. In dispersion experiments with severe tailing, the dispersion process cannot easily be described with the one-dimensional computation model. More experimental and computational research remains to be done to predict such concentration--time relationships.

It is hoped that the computation models (Appendixes) can be further elaborated to make them suitable for prediction of the behaviour of pesticides in an aquatic environment, given a set of physico-chemical data on a pesticide and of hydrological data for the field situation.

Summary

The use of pesticides in agriculture and horticulture may result under special circumstances in unintentional pollution of surface water. Some situations in which such pollution can occur are described in Chapter 1. In the Netherlands, the assessment of the extent of these immissions is impeded by the occurrence of pesticides in the River Rhine (Tables 1, 2 and 3). In the present study, one of the sources of agricultural pollution was studied in more detail, i.e. spray drift during application of pesticides in fruit farming. The motivation for the design of the present study is described in Chapter 2.

The study was restricted to the behaviour of two important organophosphorus insecticides azinphos-methyl and dimethoate in surface water. The general characteristics of both insecticides with respect to their behaviour and effects in watercourses are given in Chapter 3. Both compounds have a relatively low saturated vapour pressure (Tables 5 and 6). The rate of volatilization from surface water was calculated to be very low and to be negligible with respect to the conversion in surface water (Section 3.5). The solubility of dimethoate in water is considerable greater than that of azinphos-methyl. An associated property is the considerably lower adsorption coefficient of dimethoate on soil than of azinphos-methyl. Azinphos-methyl is rather toxic for crustaceans and some fishes (Table 10). Dimethoate is hardly toxic for fish (Table 11).

In an orientation stage of the investigation various surface waters were sampled in the Kromme Rhine area and in the Lopikerwaard Polder (Section 9.2). For sampling of water and ditch bottoms, special techniques were developed for the investigation (Chapter 4). Little disturbed samples of bottom material could be taken with a coring device (Figures 3 and 4). After freezing the bottom material, samples were sliced and analysed.

The analytical procedures for azinphos-methyl and dimethoate in surface water and in bottom material are described in Chapter 5. Water samples were extracted with dichloromethane, sometimes followed by clean-up with column chromatography. The insecticides were measured with a gas--liquid chromatograph equipped with a flame-photometer detector. The recovery percentages were high (Tables 12 and 13). Often several columns with stationary phases of different polarity were used for gas chromatography (Tables 14 and 15). Large amounts of interfering substances in all extracts of bottom material could be removed with silica gel columns.

Some basic data for both insecticides were needed to study their quantitative behaviour in surface water. Data on rates of conversion of these compounds in surface water were still too limited. Conversion rates of azinphos-methyl and dimethoate in surface water and in bottom material were measured under controlled conditions in the laboratory (Chapter 6). The rate of hydrolysis of azinphos-methyl strongly increased with pH (Figure 7). This behaviour corresponded with some data in the literature. The conversion of azinphos-methyl in surface water and bottom material could be described with a first-order rate

equation (Figures 8, 12 and 13). The conversion plots for dimethoate in both media followed a first-order conversion pattern only for a limited time (Figures 10, 11 and 14). The rate of conversion of dimethoate increased distinctly with time (Table 22).

Copper ions were catalytic in the conversion of both model compounds in surface water. The increase of the conversion rates at increasing temperature was studied.

The conversion rates of both compounds in anaerobic bottom material, measured in incubation tests in the dark, were considerable greater than in surface water (Tables 18, 20, 21 and 22). Much work remains to be done on the development of laboratory tests, the results of which can be used for prediction of the behaviour of pesticides in surface water.

The conversion rates of the oxygen analogue of azinphos-methyl (Table 7) in surface water and bottom material were greater than those of azinphos-methyl (Tables 18 and 20).

The adsorption of azinphos-methyl and dimethoate on different bottom materials could be described reasonably well with linear adsorption isotherms (Figures 15, 16 and 17). The adsorption coefficients of azinphos-methyl were about 100 times that of dimethoate. The adsorption coefficients of both substances correlated closely with the organic matter content of the different bottom materials (Table 23). The adsorption coefficients of both compounds on bottom materials were much larger than those on agricultural soils.

In an early stage of the investigation, it became clear that trials in ditches can be complicated. Therefore relatively simple trials were also set up in outdoor tanks. The rates of decline of both model compounds in water and the penetration in a layer of bottom material were measured (Chapter 7). The decline of both compounds in the water compartment of the tanks could be described reasonably with a first-order rate equation (Figures 20 and 21).

The decline of azinphos-methyl and dimethoate in the water compartment of the tanks was much faster than the decline measured in incubation tests with surface water in darkness (Tables 18, 20 and 26). Algal bloom caused considerable daily fluctuation in pH of the water (Figure 18). The approximative values for the first-order rate coefficients for the decline of both compounds were closely dependent on the maximum pH (Figure 22). A significant effect of formulation of both model compounds on rates of decline in the water compartment could not be assessed. The presence of a bottom layer in the tanks was not a dominant factor in decline of the model compounds in the water compartment.

Laboratory tests in the dark had only limited value for prediction of the rate of decline of both compounds in surface water. There is an obvious need for laboratory tests to assess the effect of light on the rate of decline of pesticides in surface water in a representative way.

The evaluation of the behaviour of many pesticides in surface water under different conditions requires an enormous research capacity. Since the physico-chemical processes for many pesticides is the same, computation models can be used for quantitative description of behaviour. The first computer simulation model (Appendix A) describes the behaviour of pesticides in a tank system with a bottom layer (Chapter 8). Movement of pesticides by diffusion from the water--sediment interface into the bottom layer was described in a one-dimensional system. Adsorption equilibria were assumed to be established instantaneously. Rates of decomposition in water and bottom material were introduced as first-order rate coefficients.

The relative significance of different decline processes of pesticides in surface water can be described better by the developed computation model. Simulations of the tank trials showed that conversion of both model compounds was the major factor in material balance (Table 30). The computed mass of both insecticides in the bottom layer was always less than 10% of the applied dose. The computed masses were higher than the measured masses (Figures 23 and 24).

The computed depth of penetration of dimethoate was larger than that of azinphos-methyl, mainly because of the relatively low adsorption of dimethoate.

In simulation experiments, the sensitivity was tested of the model of the tank system to changes in parameters (Table 31). Diffusion in the bottom layer was relatively slow. Uncertainties in the diffusion coefficient through the liquid phase in the bottom material appeared to be less important (Figure 27A). The gradual adsorption of pesticides onto bottom material can be of great importance in shallow ditches, especially when the conversion rate in water is low. Penetration into the bottom layer is of minor importance in situations with relatively high conversion rates (half-lives of some days).

Measurements of azinphos-methyl and dimethoate in watercourses and farm ditches in the Kromme Rhine area and in the Lopikerwaard Polder are described in Chapter 9. In an orientation stage, four sampling points in large watercourses and five in farm ditches were sampled in 1975 (Figure 30). Interfering substances in the extracts of water from large watercourses could be reduced by clean-up on silica gel columns. No distinct evidence was found for an increase of the model compounds in the water of the Kromme Rhine, during transport through the area. Relatively high concentrations were found in water of farm ditches on fruit farms in the Lopikerwaard Polder.

These farm ditches were selected for further study in 1976 and 1977. They always contained water during the growing season and on both farms there was a supplementary drainage system, so that a water balance of these ditches could be approximated (Section 9.3.3). All kinds of complications came to light, such as the strongly heterogeneous soils, the complex hydrological situation and the necessity to take in water in the dry year 1976 (Figures 31 to 35). The ditch systems were well characterized by measurements to allow simulation for a model system (Tables 34 and 36). The high organic matter contents, the low bulk densities and the corresponding high volume fractions of liquid in the bottom material were remarkable (Figure 36).

In 1976, after application of both model compounds on the two fruit farms in the Lopikerwaard Polder, the concentrations in the farm ditches were more closely studied (Tables 37, 38 and 39). These were rather high, especially shortly after application. Interfering substances did not interfere during the gas chromatography. The decline of both model compounds in the farm ditches on the fruit farm at Benschop (Lopikerwaard Polder) could be described by a first-order rate equation for a period without intake or discharge of water (Figures 38 and 39). The calculated half-lives of azinphos-methyl in these ditches were about 3 to 4 days, those for dimethoate varied from 4 to 13 days (Table 42). These half-lives agreed with the half-lives measured in tank trials (Table 26). The penetration of azinphos-methyl in the bottom material of the ditches was small (Tables 46 and 47).

Introduction of the insecticides into the farm ditches in 1977 was measured in more detail with Petri dishes placed on floats in the ditches (Section 9.3.8). The extent of introduction depended closely on local situations at the fruit farms (windbreaks, distance from fruit-trees to the watercourses, paths) and the way of application (Tables 40 and 41). The ratio between mass of insecticide introduced per unit surface area of water and mass dose per unit surface area of orchard soil (= areic mass ratio of contamination) was highest by spraying across the ditch (0.4), the lowest ratios were measured for ditches protected by a windbreak (0.003).

Estimation of the various items in the water balance in the ditch was not easy (Figures 41, 42 and 43). The flux of water through the ditch bottom was derived from the water balance as a closing entry. This flux was relatively low and mostly the direction of the flux was into the ditch (positive) (Section 10.4). The distribution of the discharge rate of the water pump over the various ditch sections could be estimated only roughly (Tables 34 and 48). In future experiments in ditch systems, the change in levels of ditch water and ground water should be recorded continuously to improve the description of water flow.

A computation model for the behaviour of pesticides in a ditch compartment with completely mixed water is described in Chapter 10. This computation model (Appendix B) describes fluxes of water and pesticide in the ditch system and also includes fluxes through the boundary surfaces of the water compartment and of the bottom compartments. The introduced rate coefficient for conversion in the ditch compartment was set at 0.9 times the measured rate coefficient for the decline (Table 42). This resulted in a reasonable agreement between the measured and calculated concentration--time relationships in the water (Figures 44 to 47). For the siphon-linked ditch in Benschop, the conversion of the model compounds in the ditch water compartment was the main decline process. In a period of 59 d with low water discharge, 69 to 88% of the introduced model compounds was calculated to be converted in the water (Table 49). For the supplementarily drained ditch in Benschop (last ditch section before the pump), calculations suggested that discharge from the water compartment in the same period might be several tenths of the introduced amount (Table 49). The computed total masses of azinphos-methyl in the ditch bottoms were larger than the measured masses, just as for simulation of the tanks (Figure 48).

In simulation experiments, the effect of penetration into the bottom was very limited in ditches with a flow of water from groundwater (drainage situation) (Figures 51 and 52). With infiltration from the ditch, the ditch bottom can be considered as an important 'sink' (Table 50). More research on the dispersion behaviour in bottom material in infiltration situations is needed to allow accurate description of concentration profiles. The penetration depth with the present computation model in drainage situations is somewhat over-estimated. A technical problem in the model, artificial 'backward' dispersion, cannot yet be removed completely.

Measurement and computation on the behaviour of substances in ditches during water flow (for example by water pumping) are described in Chapter 11. Although many empirical dispersion equations are described in the literature, data on the dispersive behaviour of substances in small watercourses are scarce (Table 51). A few dispersion experiments were carried out with dyes in ditches on both fruit farms in the Lopikerwaard (Table 52). A relatively low dispersion coefficient was measured in a dispersion experiment in a recently cleaned ditch. The dispersion coefficient in a ditch situation with a layer of duckweed was four times as large (Table 53). In such a situation, there was a strong tailing in the concentration--time relationship at the sampling points (Figure 53). The dispersion constants (Equation 41) for these small watercourses were larger than those for streams and rivers in the Netherlands (Tables 51 and 53).

A computation model was built to describe the behaviour of substances in ditches during water flow (Appendix C). The model included many processes like convective flow, dispersion, diffusion, adsorption and conversion of the substances. Good agreement between measurements and computations was only obtained for the conditions in a clean watercourse (Figure 54). The tailing phenomenon in concentration--time relationships can probably better be described with *stagnant-phase* models. *Simulation experiments with both dyes and* model compounds in ditches with a higher flow velocity showed that conversion and penetration into the ditch bottom are negligible in the short period (Tables 54 and 55). Spreading by dispersion was by far the most important process in such field situations (Figure 55).

For situations with low flow velocities in the ditch or for ditches with periods of no water flow, a model may perhaps be compiled by combination of the second model (Appendix B) and the third model (Appendix C). The presence of various processes with far different rates however gives complications in the required computation time.

The computation models were used first of all as research tools to trace and define areas of too limited knowledge. The results of model computations and comparison with results of measurements provide good starting points for future investigations. After further elaboration, the computation models could perhaps be used in predicting the behaviour of pesticides in the aquatic environment, starting from a limited set of physico-chemical data on a pesticide and of the hydrological data from the field situation.

Samenvatting

Het gebruik van bestrijdingsmiddelen in land- en tuinbouw kan onder bepaalde omstandigheden een niet-gewenste verontreiniging van het oppervlaktewater opleveren. Een aantal situaties waarin zulke verontreinigingen kunnen optreden, worden beschreven in hoofdstuk 1. Het vaststellen van de grootte van deze verontreiniging wordt in Nederland nogal bemoeilijkt door de aanwezigheid van bestrijdingsmiddelen in de Rijn (Tabellen 1, 2 en 3). In deze studie is één van de agrarische emissiebronnen meer in detail bestudeerd, n.l. het overwaaien van spuitvloeistof tijdens toepassing van bestrijdingsmiddelen in de fruitteelt. De motivatie van de opzet van dit onderzoek is beschreven in hoofdstuk 2.

Het onderzoek bepaalt zich tot het gedrag van twee belangrijke organo-fosfor insekticiden (azinfos-methyl en dimethoaat) in oppervlaktewater. Een algemene karakterisering van beide insekticiden met het oog op hun gedrag en effekten in waterlopen is gegeven in hoofdstuk 3. Beide stoffen bezitten een tamelijk lage verzadigde dampdruk (Tabellen 5 en 6). Berekeningen over de snelheid van vervluchtiging van deze verbindingen vanuit oppervlaktewater leverden zeer lage waarden op, zodat dit proces verwaarloosbaar lijkt t.o.v. de omzetting in oppervlaktewater (Sectie 3.5). De oplosbaarheid van dimethoaat in water is aanzienlijk groter dan die van azinfos-methyl. Daarmee hangt samen dat de coëfficiënt voor de adsorptie van dimethoaat aan grond aanzienlijk kleiner is dan die van azinfos-methyl. Azinfos-methyl is nogal toxisch voor crustaceeën en sommige vissoorten (Tabel 10). Dimethoaat is relatief weinig toxisch voor vis (Tabel 11).

In een oriënterende fase van het onderzoek werden verschillende oppervlaktewateren in het Kromme Rijn gebied en in de Lopikerwaard bemonsterd (Sectie 9.2). Bemonstering van water en slootbodemmateriaal vereiste speciale technieken die voor dit onderzoek verder werden ontwikkeld (Hoofdstuk 4). Weinig-verstoorde slibmonsters werden gestoken met een kolomsteekapparaat (Figuren 3 en 4). De slibmonsters werden na invriezen laagsgewijs opgedeeld en geanalyseerd.

De werkwijzen bij de chemische analyse van azinfos-methyl en dimethoaat in oppervlaktewater en slootbodemmateriaal zijn beschreven in hoofdstuk 5. De watermonsters werden geextraheerd met dichloromethaan, soms gevolgd door een zuivering d.m.v. kolomchromatografie. De concentraties van de insekticiden werden bepaald met een gaschromatograaf, uitgerust met een vlamfotometerdetektor. De 'recovery'-percentages waren hoog (Tabellen 12 en 13). De beide modelstoffen werden vaak gescheiden op verscheidene gaschromatografische kolommen met stationaire fasen van verschillende polariteit (Tabellen 14 en 15). Grote hoeveelheden storende stoffen in alle bodemmateriaalextracten konden worden verwijderd met behulp van silicagelkolommen.

Voor de kwantitatieve beschrijving van het gedrag van beide insekticiden in oppervlaktewater was een aantal basisgegevens nodig. De gegevens over de omzettingssnelheden van deze verbindingen in oppervlaktewater waren nog te beperkt. Omzettingssnelheden van

azinfos-methyl en dimethoaat in oppervlaktewater en in slootbodemmateriaal werden o.a. bepaald in het laboratorium onder beheerste omstandigheden (Hoofdstuk 6). De hydrolysesnelheid van azinfos-methyl nam sterk toe met toenemende pH (Figuur 7). Dit gedrag was in overeenstemming met enkele literatuurgegevens. De afbraak van azinfos-methyl in oppervlaktewater en bodemmateriaal kon beschreven worden met een eerste-orde snelheidsvergelijking (Figuren 8, 12 en 13). De afbraakcurves voor dimethoaat in beide media volgden voor een beperkte tijd een eerste-orde afbraakpatroon (Figuren 10, 11 en 14). De afbraaksnelheid van dimethoaat nam duidelijk toe met de tijd (Tabel 22).

Koperionen bleken sterk katalytisch te werken op de omzetting van beide modelstoffen in oppervlaktewater. Nagegaan werd hoeveel de omzettingssnelheden van beide stoffen toenemen bij stijging van de temperatuur.

De omzettingssnelheden van beide stoffen in anaëroob slootbodemmateriaal, bepaald in incubatieproeven in het donker, waren aanzienlijk groter dan die in oppervlaktewater (Tabellen 18, 20, 21 en 22). Aan het ontwikkelen van laboratoriumexperimenten waarvan de resultaten kunnen worden gebruikt voor de voorspelling van het gedrag van bestrijdingsmiddelen in oppervlaktewater moet nog veel werk worden gedaan.

De omzettingssnelheden van het zuurstofanaloog van azinfos-methyl (Tabel 7) in oppervlaktewater en slootbodemmateriaal waren groter dan die van azinfos-methyl (Tabellen 18 en 20).

De adsorptie van azinfos-methyl en dimethoaat aan verschillende bodemmaterialen kon redelijk beschreven worden met lineaire adsorptie-isothermen (Figuren 15, 16 en 17). De adsorptiecoëfficiënten van azinfos-methyl waren ongeveer 100 maal de coëfficiënten gemeten voor dimethoaat. De adsorptiecoëfficiënten van beide stoffen correspondeerden goed met het organische stofgehalte van de verschillende bodemmaterialen (Tabel 23). De coëfficiënten voor adsorptie aan slootbodemmaterialen waren veel hoger dan de coëfficiënten voor adsorptie van dezelfde verbindingen aan landbouwgronden.

In een vroeg stadium van het onderzoek werd het duidelijk dat experimenten in sloten zeer gecompliceerd kunnen zijn. Daarom werden ook relatief eenvoudige experimenten uitgevoerd met bassins in de open lucht. De afnamesnelheden van de modelstoffen in water en de penetratie in een laag bodemmateriaal werden gemeten (Hoofdstuk 7). De afname van beide stoffen in het watercompartiment van de bassins kon redelijk goed beschreven worden met een eerste-orde snelheidsvergelijking (Figuren 20 en 21).

De afname van azinfos-methyl en dimethoaat in het watercompartiment van de bassins was veel sneller dan de afname gemeten bij incubatie in oppervlaktewater in het donker (Tabellen 18, 20 en 26). Tengevolge van algenbloei trad er een aanzienlijke dagelijkse schommeling op in de pH van het water (Figuur 18). De benaderende waarden voor de eerste--orde snelheidscoëfficiënten voor de afname van beide stoffen bleek sterk afhankelijk van de maximum pH (Figuur 22). Een duidelijk effect van verschillende formuleringen van beide modelstoffen op de afnamesnelheid in het watercompartiment kon niet worden vastgesteld. De aanwezigheid van een bodemlaag in de bassins was geen dominerende faktor bij de afname van de modelstoffen in het watercompartiment.

Laboratoriumexperimenten uitgevoerd in het donker hebben slechts een beperkte waarde voor het voorspellen van de afnamesnelheid van beide stoffen in oppervlaktewater. Er is duidelijk behoefte aan laboratoriummethodieken waarmee op representatieve wijze het effekt van licht op de afnamesnelheid van bestrijdingsmiddelen in oppervlaktewater kan worden vastgesteld.

De evaluatie van het gedrag van vele bestrijdingsmiddelen onder verschillende omstandigheden in oppervlaktewater vereist een enorme onderzoekscapaciteit. Aangezien de aard van de fysich-chemische processen voor veel verbindingen dezelfde is kunnen rekenmodellen goed benut worden voor de kwantitatieve beschrijving van het gedrag van deze middelen. Het eerste computersimulatiemodel (Appendix A) beschrijft het gedrag van bestrijdingsmiddelen in een waterbassinsysteem met een bodemlaag (Hoofdstuk 8). Beweging van bestrijdingsmiddelen t.g.v. diffusie vanaf het water-sediment grensvlak in de bodemlaag werd beschreven in een één-dimensionaal systeem. Adsorptie-evenwichten werden verondersteld zich onmiddellijk in te stellen. De afbraaksnelheden in water en bodemmateriaal werden ingevoerd als eerste-orde reactiecoëfficiënten.

Het relatieve belang van verschillende afnameprocessen van bestrijdingsmiddelen in oppervlaktewater kan met behulp van het ontwikkelde rekenmodel beter gekwantificeerd worden. Uit de materiaalbalans van beide modelstoffen in simulaties van de bassinexperimenten bleek dat omzetting van de stoffen in water de belangrijkste faktor was (Tabel 30). De berekende massa van de beide insekticiden in de bodemlaag was bijna altijd lager dan 10% van de toegepaste dosering. Deze berekende massa's waren hoger dan de gemeten hoeveelheden (Figuren 23 en 24).

De berekende penetratiediepte van dimethoaat was groter dan die van azinfos-methyl. De hoofdoorzaak voor dit verschil is de relatief lage adsorptie van dimethoaat.

Simulatie-experimenten werden uitgevoerd om de gevoeligheid van het model van het bassinsysteem voor veranderingen in parameters te testen (Tabel 31). Diffusie in de bodemlaag bleek een relatief langzaam proces te zijn. Onzekerheden in de coëfficiënt voor diffusie van de stoffen door de waterfase in het bodemmateriaal bleken minder belangrijk te zijn (Figuur 27A). In sloten met relatief geringe waterdiepte kan de geleidelijke adsorptie van bestrijdingsmiddelen aan bodemmateriaal van groot belang zijn, vooral als de afbraaksnelheid in water gering is. In situaties met een relatief hoge afbraaksnelheid (halveringstijd van enkele dagen) is penetratie in de bodemlaag van ondergeschikt belang.

De metingen van azinfos-methyl en dimethoaat in waterlopen en bedrijfssloten in het Kromme Rijn gebied en in de Lopikerwaard zijn beschreven in hoofdstuk 9. In een oriënterende fase van het onderzoek in 1975 werden vier bemonsteringspunten in grotere waterlopen en vijf bedrijfssloten bemonsterd (Figuur 30). De interferentie door storende verbindingen in extracten van water uit grotere waterlopen kon met behulp van silicagelkolommen aanzienlijk verminderd worden (Tabellen 32 en 33). Er werden geen duidelijk indikaties gevonden voor een toename van de modelstoffen in het water tijdens doorstroming van het Kromme Rijn gebied. Relatief hoge concentraties werden aangetroffen in water van bedrijfssloten op fruitteeltbedrijven in de Lopikerwaard.

Deze bedrijfssloten werden uitgekozen voor verdere onderzoekingen in 1976 en 1977. Deze sloten bevatten steeds water tijdens het groeiseizoen en op beide bedrijven was een onderbemaling aanwezig, zodat een waterbalans van deze sloten kon worden geschat (Sectie 9.3.3). Tijdens de duur van het onderzoek kwamen allerlei complicaties aan het licht, zoals de sterke heterogeniteit van de gronden, de complexe hydrologische situaties en de noodzaak tot het inlaten van water in het relatief droge jaar 1976 (Figuren 31 t/m 35). De slootsystemen werden goed gekarakteriseerd door metingen om simulatieberekeningen voor een modelsysteem mogelijk te maken (Tabellen 34 en 36). Opvallend waren de hoge organische stofgehaltes, de lage volumieke massa's en de hiermee overeenkomende hoge volumefracties bodemvocht in het slootbodemmateriaal (Figuur 36).

In 1976 werden, na de toepassing van beide modelstoffen op de twee fruitteeltbedrijven in de Lopikerwaard, de concentraties in de bedrijfssloten nauwkeurig bepaald (Tabellen 37, 38 en 39). Deze waren tamelijk hoog, vooral kort na de toepassing. Er werd geen last ondervonden van storende stoffen bij de gaschromatografische analyses. De afname van beide modelstoffen in de bedrijfssloten op het fruitteeltbedrijf in Benschop kon (voor een periode zonder waterinlaat en waterafvoer) redelijk beschreven worden met een eerste-orde snelheidsvergelijking (Figuren 38 en 39). De berekende halfwaardetijden van azinfos-methyl in deze sloten waren ongeveer 3 tot 4 dagen, die van dimethoaat varieerden van 4 tot 13 dagen (Tabel 42). Deze halfwaardetijden stemden overeen met de halfwaardetijden gemeten in bassinexperimenten (Tabel 26). De penetratie van azinfos-methyl in de slootbodems bleek relatief gering te zijn (Tabellen 46 en 47).

De immissie van de insekticiden naar de bedrijfssloten werd in 1977 meer in detail gemeten met behulp van petrischalen geplaatst op drijvers in de sloten (Sectie 9.3.8). De mate van immissie bleek sterk afhankelijk van lokale situaties op de fruitteeltbedrijven (windsingels, afstand van de vruchtbomen tot de waterlopen, schouwpaden) en de wijze van toepassing (Tabellen 40 en 41). De verhouding tussen de hoeveelheid insekticide die terecht kwam per oppervlakte-eenheid water en de dosering per oppervlakte-eenheid boomgaardgrond (=immissieverhouding) was het hoogst bij zgn. over de sloot spuiten (0.4), de laagste immissieverhoudingen werden gemeten voor sloten achter windsingels (0.003).

Het schatten van de verschillende posten in de waterbalans van de sloot was niet eenvoudig (Figuren 41, 42 en 43). De waterflux door de slootbodem, als sluitpost afgeleid uit de waterbalans, was relatief laag (Sectie 10.4) en was meestal naar de sloot gericht (positief). De verdeling van de afvoersnelheid van de pomp over de verschillende slootsecties kon slechts globaal geschat worden (Tabellen 34 en 48). In verdere experimenten in slootsystemen zouden de veranderingen in sloot- en grondwaterpeilen continu geregistreerd moeten worden om de karakterisering van de waterstroming te verbeteren.

Een rekenmodel voor het gedrag van bestrijdingsmiddelen in een slootcompartiment met volledig gemengd water wordt beschreven in hoofdstuk 10. Dit rekenmodel (Appendix B) beschrijft naast de relevante water- en pesticidefluxen in het slootsysteem ook de fluxen door de grensvlakken van het watercompartiment en van de bodemcompartimenten. De ingevoerde snelheidscoëfficiënt voor afbraak in het slootwatercompartiment werd gelijk gesteld aan 0.9 keer de snelheidscoëfficiënt voor de gemeten afname (Tabel 42). Dit leverde een redelijke overeenstemming op tussen de gemeten en de berekende concentratie-tijd relaties in het water (Figuren 44 t/m 47). Voor de 'duiker' sloot in Benschop was omzetting van de modelstoffen in het slootwatercompartiment het belangrijkste afnameproces. In een 59-daagse periode met geringe waterafvoer werd berekend dat 69 tot 88% van de geïntroduceerde modelstoffen werd omgezet in het water (Tabel 49). Voor de 'onderbemalen' sloot in Benschop (laatste leidingvak voor de pomp) werd in deze periode berekend dat afvoer vanuit het slootwatercompartiment enkele tientallen procenten van de geïntroduceerde hoeveelheid kan bedragen (Tabel 49). Evenals in de bassinsimulatie-experimenten waren de totale massa's van azinfos-methyl in de slootbodems groter dan de gemeten waarden (Figuur 48).

Uit simulatie-experimenten bleek dat in sloten met een afvoer van water vanuit grondwater (drainagesituatie) het effekt van penetratie in de bodem zeer beperkt was (Figuren 51 en 52). In situaties met infiltratie vanuit de sloot kon de slootbodem als een belangrijke 'sink' worden beschouwd (Tabel 50). Voor een nauwkeurige beschrijving van de concentratiepatronen met de diepte in infiltratiesituaties is meer onderzoek nodig over het dispersiegedrag in slootbodemmateriaal. In drainagesituaties wordt de penetratiediepte met het huidige rekenmodel (Appendix B) iets overschat. Een modeltechnisch probleem betreffende de kunstmatige 'achterwaartse' dispersie kan nog niet geheel worden opgelost.

Metingen en berekeningen over het gedrag van stoffen in sloten tijdens waterstroming (bijv. tengevolge van pompen) staan beschreven in hoofdstuk 11. Hoewel er in de literatuur vele emprirische dispersieformules staan beschreven waren er bijna geen gegevens over het dispersiegedrag van stoffen in kleinere waterlopen (Tabel 51). Enkele dispersie-experimenten werden uitgevoerd met kleurstoffen in sloten op de beide fruitteeltbedrijven in de Lopikerwaard (Tabel 52). In een experiment in een pas 'opgeschoonde' waterloop werd een relatief lage dispersiecoëfficiënt gevonden. In een situatie met een kroosdek was de dispersiecoëfficiënt een faktor vier groter (Tabel 53). In zo'n situatie trad er een flinke staartvorming op in de concentratie-tijd relatie op de meetpunten (Figuur 53). De dispersieconstanten (Vergelijking 41) voor deze kleine waterlopen waren groter dan die voor beken en rivieren in Nederland (Tabellen 51 en 53).

Er werd een rekenmodel ontwikkeld om het gedrag van stoffen in sloten tijdens waterstroming te beschrijven (Appendix C). Het model omvatte vele processen zoals convectieve stroming, dispersie, diffusie, adsorptie en omzetting van de stoffen. Er was alleen een goede overeenstemming met meetresultaten, die verkregen waren in een schone waterloop (Figuur 54). Het verschijnsel van staartvorming in concentratie-tijd relaties kan waarschijnlijk beter beschreven worden met zgn. 'stagnante fase' modellen. Uit simulatie-experimenten met de beide kleur- en modelstoffen in sloten met een relatief grote stroomsnelheid bleek dat de omzetting en penetratie in de slootbodem verwaarloosbaar zijn in de betreffende korte periode (Tabellen 54 en 55). Afvlakking van de concentratieverdeling door dispersie was verreweg het belangrijkste proces in deze situaties (Figuur 55).

In situaties met lage stroomsnelheden in het slootwater of voor sloten met periodes van waterstilstand kan er wellicht een model samengesteld worden door combinatie van het tweede rekenmodel (Appendix B) en het derde rekenmodel (Appendix C). Het vóórkomen van diverse processen met sterk verschillende snelheden levert echter enige complicaties ten aanzien van de benodigde rekentijd.

De rekenmodellen werden allereerst gebruikt als hulpmiddel bij het onderzoek, waardoor gebieden met te weinig kennis duidelijker konden worden opgespoord. De resultaten van modelberekeningen en de vergelijking met meetresultaten verschaffen goede startpunten voor verder onderzoek. Na verdere toetsing kunnen de rekenmodellen wellicht worden ingezet voor het doen van voorspellingen omtrent het gedrag van bestrijdingsmiddelen in oppervlaktewater, uitgaande van een beperkt aantal fysisch-chemische gegevens over een bestrijdingsmiddel en gegevens over de hydrologische situatie in het veld.

Appendices

Appendix A

```
TITLE BEHAVIØUR ØF AZINPHØS-METHYL IN TANK 2 (DIFFUSIØN MØDEL1)
*******************************************************************
* TANK WITH MIXED WATER CØMPARTMENT AND CØMPARTIMENTALIZATIØN ØF BØTTØM
LAYER
STØRAGE DPØRL(10),KSL(10),CAPL(10),CABØTB(10),DEBØSU(11)
STØRAGE TBØT(10),DIFD(10),DEBØCØ(10),BD(10),VFL(10),TØRT(10)
STØRAGE CLB(10),FLRSB(11),RDECB(10),CM(10)
FIXED NBCØM,J,NBCØMP
INITIAL
NØSØRT
*      ABBREVIATIØNS : CØMP.=CØMPARTMENT(S)
*      BASIC UNITS : MILLIGRAM (MG) , METER (M) , DAY (D)
***    DEFINITIØN TANK SYSTEM GEØMETRY
*VWTT=VØLUME ØF WATER CØMP. (M3) AS F(TIME)
FUNCTIØN VWTT=(0.,0.154),(3.64,0.148),(5.64,0.142),(9.64,0.133),....
      (13.64,0.120),(30.,0.120)
* BØSU=SURFACE AREA ØF THE BØTTØM CØMP. (M2)
PARAM BØSU=0.6
* TBØT=THICKNESS ØF BØTTØM CØMP. (M)
* NBCØM=NUMBER ØF BØTTØM CØMP.
* MFAC=MULTIPLICATIØN FACTØR FØR TBØT,WFAC=WEIGHT FACTØR FØR TBØT
PARAM NBCØM=10,MFAC=1.5
      WFAC=1.0/(MFAC+1.0)
PARAM TBØT1=0.001
      TBØT(1)=TBØT1
      DØ 10 J=2,NBCØM
  10  TBØT(J)=MFAC*TBØT(J-1)
      NBCØMP=NBCØM+1
* DEBØCØ=DEPTH ØF CENTRES ØF THE BØTTØM CØMP. (M)
* DIFD=DIFFUSIØN DISTANCE BETWEEN BØTTØM CØMP. (M)
* DEBØSU=DEPTH ØF UPPER SURFACES ØF BØTTØM CØMP. (M)
      DEBØCØ(1)=0.5*TBØT(1)
      DIFD(1)=0.5*TBØT(1)
      DEBØSU(1)=0.0
      DØ 11 J=2,NBCØM
      DIFD(J)=0.5*(TBØT(J-1)+TBØT(J))
      DEBØCØ(J)=DEBØCØ(J-1)+DIFD(J)
  11  DEBØSU(J)=DEBØCØ(J-1)+0.5*TBØT(J-1)
      DEBØSU(NBCØMP)=DEBØCØ(NBCØM)+0.5*TBØT(NBCØM)
      WRITE(6,78)(TBØT(J),J=1,NBCØM)
  78  FØRMAT(1H0,'TBØT=',2X,10E10.3)
      WRITE(6,79)(DEBØCØ(J),J=1,NBCØM)
  79  FØRMAT(1H ,'DEBØCØ=',10E10.3)
***    PHYSICAL CHARACTERISTICS ØF THE BØTTØM
* BDT=BULK DENSITY ØF SØLID PHASE (KG/M3(MEDIUM)) AS F(DEPTH)
FUNCTIØN BDT=(0.,200.),(0.01,370.),(0.02,540.),(0.03,660.),...
      (0.04,650.),(0.05,670.),(0.20,680.)
* VFLT=VØLUME FRACTIØN ØF LIQUID (M3(LIQUID)/M3(MEDIUM)) AS F(DEPTH)
FUNCTIØN VFLT=(0.,0.92),(0.01,0.88),(0.02,0.79),(0.03,0.74),...
      (0.04,0.75),(0.05,0.75),(0.20,0.74)
* TØRTT=TØRTUØSITY FACTØR (M2(MEDIUM)/M2(LIQUID)) AS F(VFL)
FUNCTIØN TØRTT=(0.,0.),(0.1,0.03),(0.2,0.1),(0.3,0.2),(0.4,0.34),...
```

```
      (0.5,0.5),(1.0,1.0)
      DØ 20 J=1,NBCØM
      BD(J)=AFGEN(BDT,DEBØCØ(J))
      VFL(J)=AFGEN(VFLT,DEBØCØ(J))
  20  TØRT(J)=AFGEN(TØRTT,VFL(J))
* DIFW=DIFFUSIØN CØEFFICIENT ØF SUBSTANCE IN BULK WATER (M2(LIQUID)/D)
PARAM DIFW=0.41E-4
* DPØRL=DIFFUSIØN CØEFFICIENT ØF SUBSTANCE IN LIQUID PHASE (M3(LIQUID)/
*                                                              (M(MEDIUM)D))
      DPØRL(1)=VFL(1)*TØRT(1)*DIFW
      DØ 21 J=2,NBCØM
  21  DPØRL(J)=WFAC*(MFAC*VFL(J-1)*TØRT(J-1)+VFL(J)*TØRT(J))*DIFW
***   PARTITIØN ØF SUBSTANCE ØVER BØTTØM PHASES,INSTANTANEØUS EQUILIBRIUM
* KSL=DISTRIBUTIØN RATIØ SØLID/LIQUID PHASE =ADSØRPTIØN CØEFFICIENT
*     (MG/KG(SØLID PHASE))/(MG/M3(LIQUID PHASE))
* KSLT=KSL AS F(DEPTH)
FUNCTIØN KSLT=(0.,0.073),(0.2,0.073)
* CAPL=SUBSTANCE CAPACITY FACTØR RELATING TØ CØNCENTRATIØN IN LIQUID PHASE
*        (M3(LIQUID)/M3(MEDIUM))
      DØ 30 J=1,NBCØM
      KSL(J)=AFGEN(KSLT,DEBØCØ(J))
      CAPL(J)=VFL(J)+BD(J)*KSL(J)
  30  CABØTB(J)=CAPL(J)*BØSU*TBØT(J)
***   DECØMPØSITIØN ØF THE SUBSTANCE
* RCDEWT=RATE CØEFFICIENT(1/D) FØR DECØMPØSITIØN IN WATER AS F(TIME)
FUNCTIØN RCDEWT=(0.,0.23),(5.64,0.23),(5.65,0.49),(30.,0.49)
* RCDEBT=RATE CØEFFICIENT(1/D) FØR DECØMPØSITIØN IN BØTTØM AS F(TIME)
FUNCTIØN RCDEBT=(0.,0.073),(30.,0.073)
***   INITIAL AND BØUNDARY CØNDITIØNS
* MSW=MASS ØF SUBSTANCE IN WATER CØMP. (MG)
* MSB=MASS ØF SUBSTANCE IN BØTTØM CØMP. (MG)
* I REFERS TØ INITIAL CØNDITIØN
INCØN IMSW=13.2
TABLE IMSB(1-10)=10*0.0
* FLRSB=FLØW RATE ØF SUBSTANCE INTØ BØTTØM CØMP. (MG/D)
      FLRSB(NBCØMP)=0.0
DYNAMIC
NØSØRT
***   SUBSTANCE MØVEMENT
* RMSW=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN WATER CØMP. (MG/D)
      MSW=INTGRL(IMSW,RMSW)
* RMSB=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN BØTTØM CØMP. (MG/D)
      MSB=INTGRL(IMSB,RMSB,10)
* CW=CØNCENTRATIØN ØF SUBSTANCE IN WATER CØMP. (MG/M3)
      VWT=AFGEN(VWTT,TIME)
      CW=MSW/VWT
* CLB=CØNCENTRATIØN ØF SUBSTANCE IN LIQUID PHASE ØF BØTTØM CØMP. (MG/M3)
* CM=CØNCENTRATIØN ØF SUBSTANCE IN BØTTØM CØMP. (MG/M3(MEDIUM))
      DØ 50 J=1,NBCØM
      CLB(J)=MSB(J)/CABØTB(J)
  50  CM(J)=CLB(J)*CAPL(J)
      FLRSB(1)=-DPØRL(1)*BØSU*(CLB(1)-CW)/DIFD(1)
      DØ 51 J=2,NBCØM
  51  FLRSB(J)=-DPØRL(J)*BØSU*(CLB(J)-CLB(J-1))/DIFD(J)
***   DECØMPØSITIØN ØF THE SUBSTANCE
* RDECW=RATE ØF DECØMPØSITIØN IN WATER CØMP. (MG/D)
* RDECB=RATE ØF DECØMPØSITIØN IN BØTTØM CØMP. (MG/D)
* TRDECB=TØTAL RATE ØF DECØMPØSITIØN IN THE BØTTØM (MG/D)
      RDECW=AFGEN(RCDEWT,TIME)*MSW
      TRDECB=0.0
      DØ 55 J=1,NBCØM
      RDECB(J)=AFGEN(RCDEBT,TIME)*MSB(J)
  55  TRDECB=TRDECB+RDECB(J)
* TDECW=TØTAL MASS ØF SUBSTANCE DECØMPØSED IN WATER CØMP. (MG)
* TDECB=TØTAL MASS ØF SUBSTANCE DECØMPØSED IN BØTTØM (MG)
      TDECW=INTGRL(0.0,RDECW)
```

```
      TDECB=INTGRL(0.0,TRDECB)
***   ØVERALL RATE EQUATIØNS
* RMSW=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN WATER CØMP (MG/D)
      RMSW=-FLRSB(1)-RDECW
* RMSB=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN BØTTØM CØMP. (MG/D)
      DØ 60 J=1,NBCØM
   60 RMSB(J)=FLRSB(J)-FLRSB(J+1)-RDECB(J)
***   ØUTPUT SECTIØN
      PRTIM=IMPULS(0.0,PRDEL)
      IF(PRTIM*KEEP .LT. 0.5) GØ TØ 100
* TMSB=TØTAL MASS ØF SUBSTANCE IN BØTTØM (MG)
      TMSB=0.0
      DØ 70 J=1,NBCØM
   70 TMSB=TMSB+MSB(J)
  100 CØNTINUE
PRINT VWT,CW,CLB(1-10),CM(1-10),FLRSB(1-11),MSB(1-10),MSW,...
      TMSB,TDECW,TDECB
METHØD RKS
ØUTPUT MSW(0.,15.),TMSB(0.,1.5)
TIMER PRDEL=0.5,ØUTDEL=0.5,FINTIM=27.
END
STØP
ENDJØB
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Appendix B

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TITLE WATER AND PESTICIDE BALANCES FØR DRAINAGE AND INFILTRATIØN DITCH
**********************************************************************
* DITCH WITH MIXED WATER CØMP. AND CØMPARTIMENTALIZATIØN ØF DITCH BØTTØM
STØRAGE TBØT(20),DIFD(20),DEBØCØ(20),BD(20),VFL(20),TØRT(20)
STØRAGE DPØRL(20),KSL(20),CAPL(20),CABØTB(20),DEBØSU(21),CM(20)
STØRAGE BØSU(21),CLB(20),FLRSB(21),RDECB(20),VBØT(20),DTØTB(20)
STØRAGE PUMPT(60),INTAKT(60),EVAPØT(60),RAINT(60),SUPST(60),FDIFLB(20)
FIXED NDAY,J,NBCØM,NBCØMP
INITIAL
NØSØRT
*     ABBREVIATIØNS : CØMP.=CØMPARTMENT(S)
*                         AZIN.=AZINPHØS-METHYL,DIM.=DIMETHØATE
*     BASIC UNITS : MILLIGRAM (MG) , METER (M) , DAY (D)
***   DEFINITIØN ØF DITCH-LAND SYSTEM GEØMETRY
* LCØM=LENGTH ØF THE DITCH CØMPARTMENT (M)
* S=SLØPE ØF DITCH WALLS (HØRZ./VERT.) (-),S1=LØWER,S2=UPPER PART
PARAM LCØM=204.,S1=0.46,S2=1.
* HWS=HEIGHT ØF LØWER DITCH PART WITH SLØPE S1 (M)
* W1=WIDTH AT THE BØTTØM ØF THE DITCH (M)
* W2=WIDTH ØF THE DITCH AT HEIGHT HWS (M)
PARAM HWS=0.40,W1=1.42
      W2=W1+2.0*S1*HWS
* VWDL=VØLUME ØF THE DITCH (M3) UP TØ THE HWS-LEVEL
      VWDL=HWS*(W1+S1*HWS)*LCØM
* DSA=DRAINAGE SURFACE AREA (M2) ASSIGNED TØ THE DITCH(D),TØ THE DITCH BØTTØM
*     (DB),DRAINS(DR)
PARAM DSADB=2750.,DSADR=8050.
      DSAD=DSADB+DSADR
* ISA=INFILTRATIØN SURFACE AREA (M2) ASSIGNED TØ THE DITCH (D),TØ THE
*   DITCH BØTTØM(DB),DRAINS(DR)
PARAM ISADB=2750.,ISADR=0.
      ISAD=ISADB+ISADR
* P=WETTED PERIMETER ØF THE DITCH (M),CALCULATED FRØM AHW
* AHW=AVERAGE HEIGHT ØF THE WATER LEVEL (M)
PARAM AHW=0.30
      P=W1+2.0*AHW*SQRT(S1**2+1.0)
* NBCØM=NUMBER ØF BØTTØM CØMP.
* TBØT=THICKNESS ØF BØTTØM CØMP. (M)
* MFAC=MULTIPLICATIØN FACTØR FØR TBØT,WFAC=WEIGHT FACTØR FØR TBØT
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PARAM NBCØM=20,MFAC=1.1
      WFAC=1.0/(MFAC+1.0)
PARAM TBØT1=0.001
      TBØT(1)=TBØT1
      DØ 10 J=2,NBCØM
  10  TBØT(J)=MFAC*TBØT(J-1)
      NBCØMP=NBCØM+1
* DEBØCØ=DEPTH ØF CENTRES ØF THE BØTTØM CØMP. (M)
* DIFD=DIFFUSIØN DISTANCE BETWEEN BØTTØM CØMP. (M)
* DEBØSU=DEPTH ØF UPPER SURFACES ØF BØTTØM CØMP. (M)
* BØSU=SURFACE AREA ØF THE BØTTØM CØMP. (M2)
      DEBØCØ(1)=0.5*TBØT(1)
      DIFD(1)=0.5*TBØT(1)
      DEBØSU(1)=0.0
      BØSU(1)=LCØM*P
      BETA=ATAN(1.0/S1)
      DØ 11 J=2,NBCØM
      DIFD(J)=0.5*(TBØT(J-1)+TBØT(J))
      DEBØCØ(J)=DEBØCØ(J-1)+DIFD(J)
      DEBØSU(J)=DEBØCØ(J-1)+0.5*TBØT(J-1)
  11  BØSU(J)=LCØM*(W1+2.0*DEBØSU(J)*SIN(0.5*BETA)/CØS(0.5*BETA)+...
      2.0*(AHW+DEBØSU(J))*SQRT(S1**2+1.0))
      DEBØSU(NBCØMP)=DEBØCØ(NBCØM)+0.5*TBØT(NBCØM)
      BØSU(NBCØMP)=LCØM*(W1+2.0*DEBØSU(NBCØMP)*SIN(0.5*BETA)/...
      CØS(0.5*BETA)+2.0*(AHW+DEBØSU(NBCØMP))*SQRT(S1**2+1.0))
      WRITE(6,78)(TBØT(J),J=1,NBCØM)
  78  FØRMAT(1H0,'TBØT=',2X,10E10.3)
      WRITE(6,79)(DEBØCØ(J),J=1,NBCØM)
  79  FØRMAT(1H ,'DEBØCØ=',10E10.3)
      WRITE(6,80)(BØSU(J),J=1,NBCØMP)
  80  FØRMAT(1H ,'BØSU=',2X,11E10.3)
***   PHYSICAL CHARACTERISTICS ØF THE BØTTØM
* BDT=BULK DENSITY ØF SØLID PHASE (KG/M3(MEDIUM)) AS F(DEPTH)
FUNCTIØN BDT=(0.,90.),(0.05,210.),(0.10,270.),(0.15,300.),...
      (0.20,350.),(0.25,330.),(0.5,460.)
* VFLT=VØLUME FRACTIØN ØF LIQUID (M3(LIQUID)/M3(MEDIUM)) AS F(DEPTH)
FUNCTIØN VFLT=(0.,0.96),(0.05,0.91),(0.10,0.88),(0.15,0.87),...
      (0.20,0.84),(0.25,0.85),(0.5,0.80)
* TØRTT=TØRTUØSITY FACTØR (M2(MEDIUM)/M2(LIQUID)) AS F(VFL)
FUNCTIØN TØRTT=(0.,0.),(0.1,0.03),(0.2,0.1),(0.3,0.2),(0.4,0.34),...
      (0.5,0.5),(1.0,1.0)
      DØ 20 J=1,NBCØM
      BD(J)=AFGEN(BDT,DEBØCØ(J))
      VFL(J)=AFGEN(VFLT,DEBØCØ(J))
  20  TØRT(J)=AFGEN(TØRTT,VFL(J))
* DIFW=DIFFUSIØN CØEFFICIENT ØF SUBSTANCE IN BULK WATER (M2(LIQUID)/D)
PARAM DIFW=0.35E-4
* DPØRL=DIFFUSIØN CØEFFICIENT ØF SUBSTANCE IN LIQUID PHASE (M3(LIQUID)/
*                                                             (M(MEDIUM)
      DPØRL(1)=VFL(1)*TØRT(1)*DIFW
      DØ 21 J=2,NBCØM
  21  DPØRL(J)=WFAC*(MFAC*VFL(J-1)*TØRT(J-1)+VFL(J)*TØRT(J))*DIFW
* DISPD=DISPERSIØN DISTANCE (M(MEDIUM))
PARAM DISPD=0.015
***   PARTITIØN ØF SUBSTANCE ØVER BØTTØM PHASES,INSTANTANEØUS EQUILIBRIUM

* KSL=DISTRIBUTIØN RATIØ SØLID/LIQUID PHASE =ADSØRPTIØN CØEFFICIENT
*     (M3/K3(SØLID PHASE))/(MG/M3(LIQUID PHASE))
* KSLT=KSL AS F(DEPTH)
FUNCTIØN KSLT=(0.,0.279),(0.8,0.279)
* CAPL=SUBSTANCE CAPACITY FACTØR RELATING TØ CØNCENTRATIØN IN LIQUID PHASE
*       (M3(LIQUID)/M3(MEDIUM))
      DØ 30 J=1,NBCØM
      KSL(J)=AFGEN(KSLT,DEBØCØ(J))
      CAPL(J)=VFL(J)+BD(J)*KSL(J)
  30  CABØTB(J)=CAPL(J)*0.5*(BØSU(J)+BØSU(J+1))*TBØT(J)
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***   DECØMPØSITIØN ØF THE SUBSTANCE
* RCDEWT=RATE CØEFFICIENT(1/D) FØR DECØMPØSITIØN IN WATER AS F(TIME)
FUNCTIØN RCDEWT=(0.,0.225),(60.,0.225)
* RCDEBT=RATE CØEFFICIENT(1/D) FØR DECØMPØSITIØN IN BØTTØM CØMP. AS F(TIME)
FUNCTIØN RCDEBT=(0.,0.038),(60.,0.038)
***   DEFINITIØN ØF THE ITEMS ØF THE WATER BALANCE
* DISRAT=DISCHARGE RATE ASSIGNED TØ DITCH SECTIØN +PØSSIBLE UPSTREAM
*      DITCH SECTIØN  (M3/D)
PARAM DISRAT=135.
* PUMPT=PUMPING TIME (D),DAILY VALUES
TABLE PUMPT(1-60)=17*0.,0.2,6*0.,0.258,23*0.,0.367,11*0.
* DISUPD=DISCHARGE RATE FRØM UPSTREAM DITCH SECTIØN  (M3/D)
PARAM DISUPD=0.0
* INTRAT=INTAKE RATE ASSIGNED TØ DITCH SECTIØN + PØSSIBLE DØWNSTREAM
*      DITCH SECTIØN  (M3/D)
PARAM INTRAT=0.0
* INTAKT=INTAKE TIME(D),DAILY VALUES
TABLE INTAKT(1-60)=60*0.
* INTDØD=INTAKE RATE INTØ DØWNSTREAM DITCH SECTIØN  (M3/D)
PARAM INTDØD=0.0
* EVAPØT=RATE ØF EVAPØRATIØN FRØM ØPEN WATER (M/D)
TABLE EVAPØT(1-60)=18*0.0041,11*0.004,10*0.0047,10*0.0044,10*0.0065,...
      0.0066
* RAINT=RAINFALL INTENSITY (M/D)
TABLE RAINT(1-60)=0.0045,4*0.0,0.0025,3*0.0,0.0035,0.0005,...
      4*0.0,0.0085,0.0005,0.007,0.0015,3*0.0,0.0005,...
      0.006,3*0.0,0.0015,0.0,0.011,17*0.0,0.020,0.017,11*0.0
* HWT=HEIGHT ØF WATER LEVEL IN DITCH SECTIØN AS F(TIME) (M)
FUNCTIØN HWT=(0.,0.20),(0.5,0.21),(2.5,0.25),(4.5,0.27),(9.5,0.30),...
      (14.5,0.33),(15.5,0.34),(17.,0.35),(18.,0.29),(21.5,0.32),...
      (24.,0.34),(25.,0.25),(29.0,0.27),(30.0,0.28),(37.,0.30),...
      (42.5,0.30),(47.,0.29),(48.,0.34),(49.,0.29),...
      (49.5,0.31),(51.5,0.34),(53.,0.34),(59.,0.30),(60.,0.30)
***   SUPPLY,INITIAL AND BØUNDARY CØNDITIØNS
* SUPST=RATE ØF SUPPLY TØ DITCH WATER DUE TØ SPRAY DRIFT (MG/D)
TABLE SUPST(1-60)=10250.,48*0.0,2100.,10*0.0
* MSW=MASS ØF SUBSTANCE IN WATER CØMP. (M3)
* MSB=MASS ØF SUBSTANCE IN BØTTØM CØMP. (MG)
* I REFERS TØ INITIAL CØNDITIØN
INCØN IMSW=0.0
TABLE IMSB(1-20)=20*0.0
* CWINT=CØNCENTRATIØN ØF SUBSTANCE IN INTAKE WATER (MG/M3) AS F(TIME)
FUNCTIØN CWINT=(0.,0.),(60.,0.)
* CWUPDT=CØNCENTRATIØN ØF SUBSTANCE IN WATER FRØM UPSTREAM DITCH SECTIØN (MG/M3)
*        AS F(TIME)
FUNCTIØN CWUPDT=(0.,0.),(60.,0.)
DYNAMIC
NØSØRT
      NDAY=TIME+1+0.05*DELT
      DAY=NDAY
***   RATE ØF CHANGE IN THE DITCH WATER VØLUME
* P REFERS TØ TIME PLUS DELT , M REFERS TØ TIME MINUS DELT
* CENTRAL DIFFERENCE SCHEME
      HWP=AFGEN(HWT,TIME+DELT)
      HW=AFGEN(HWT,TIME)
      IF(TIME .GT. 0.0) GØ TØ 41
      IF(HW .GT. HWS) GØ TØ 42
      VWD=HW*(W1+S1*HW)*LCØM
      VWDM=VWD
      GØ TØ 43
  42  VWD=VWDL+(HW-HWS)*(W2+S2*(HW-HWS))*LCØM
      VWDM=VWD
      GØ TØ 44
  41  HWM=AFGEN(HWT,TIME-DELT)
      IF(HW .GT. HWS) GØ TØ 45
      VWDM=HWM*(W1+S1*HWM)*LCØM
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      VWD=HW*(W1+S1*HW)*LCØM
  43  VWDP=HWP*(W1+S1*HWP)*LCØM
      GØ TØ 46
  45  VWDM=VWDL+(HWM-HWS)*(W2+S2*(HWM-HWS))*LCØM
      VWD=VWDL+(HW-HWS)*(W2+S2*(HW-HWS))*LCØM
  44  VWDP=VWDL+(HWP-HWS)*(W2+S2*(HWP-HWS))*LCØM
* RVWD=RATE ØF CHANGE IN DITCH WATER VØLUME (M3/D)
  46  RVWD=(VWDP-VWDM)/(2.*DELT)
***   EVAPØRATIØN AND PRECIPITATIØN
      EVAPØ=EVAPØT(NDAY)
      RAIN=RAINT(NDAY)
      IF(HW .GT. HWS) GØ TØ 47
* EVASU=EVAPØRATING SURFACE ØF A DITCH WATER CØMPARTMENT (M2)
      EVASU=LCØM*(W1+2.0*S1*HW)
      GØ TØ 48
  47 EVASU=LCØM*(W2+2.0*S2*(HW-HWS))
  48  CØNTINUE
* QEVAP=RATE ØF EVAPØRATIØN (M3/D)
      QEVAP=EVAPØ*EVASU
* QPREC=RATE ØF RAINFALL INTØ THE DITCH WATER CØMP. (M3/D)
      QPREC=RAIN*EVASU
***   INTAKE AND DISCHARGE
* QDISCH=RATE ØF DISCHARGE ØUT ØF THE DITCH WATER CØMP. (M3/D)
      QDISCH=PUMPT(NDAY)*DISRAT
* QDUPDS=RATE ØF DISCHARGE FRØM THE UPSTREAM DITCH SECTIØN  (M3/D)
      QDUPDS=PUMPT(NDAY)*DISUPD
* QINT=RATE ØF WATER INTAKE INTØ THE DITCH WATER CØMP. (M3/D)
      QINT=INTAKT(NDAY)*INTRAT
* QIDØDS=RATE ØF WATER INTAKE INTØ DØWNSTREAM DITCH SECTIØN  (M/D)
      QIDØDS=INTAKT(NDAY)*INTDØD
***   FLØW THRØUGH DITCH BØTTØM AND DRAINS (CLØSING ENTRY=CLENT)
      CLENT=RVWD+QEVAP-QPREC+QDISCH-QDUPDS-QINT+QIDØDS
* IF CLENT IS PØSITIVE:DRAINAGE AND IF NEGATIVE:INFILTRATIØN
      IF(CLENT .LT. 0.0) GØ TØ 49
* QWBØT=FLØW RATE THRØUGH THE WETTED PERIMETER ØF THE DITCH (M3/D)
      QWBØT=DSADB/DSAD*CLENT
* QWDR=FLØW RATE THRØUGH DRAINS (M3/D)
      QWDR=DSADR/DSAD*CLENT
      GØ TØ 50
  49  QWBØT=ISADB/ISAD*CLENT
      QWDR=ISADR/ISAD*CLENT
  50  CØNTINUE
* FLØDB=FLØW RATE THRØUGH THE DITCH BØTTØM EXPRESSED IN M/D
      FLØDB=QWBØT/DSADB
* VBØT=WATER FLUX THRØUGH THE WETTED DITCH PERIMETER (M3(LIQUID)/(M2(MEDIUM)D))
      DØ 51 J=1,NBCØM
  51  VBØT(J)=QWBØT/BØSU(J)
***   SUBSTANCE MØVEMENT
* RMSW=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN WATER CØMP. (MG/D)
      MSW=INTGRL(IMSW,RMSW)
* RMSB=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN BØTTØM CØMP. (MG/D)
      MSB=INTGRL(IMSB,RMSB,20)
* CW=CØNCENTRATIØN ØF SUBSTANCE IN WATER CØMP. (MG/M3)
      CW=MSW/VWD
* CLB=CØNCENTRARIØN ØF SUBSTANCE IN LIQUID PHASE ØF BØTTØM CØMP. (MG/M3)
* CM=CØNCENTRATIØN ØF SUBSTANCE IN BØTTØM CØMP. (MG/M3(MEDIUM))
      DØ 52 J=1,NBCØM
      CLB(J)=MSB(J)/CABØTB(J)
  52  CM(J)=CLB(J)*CAPL(J)
      CWIN=AFGEN(CWINT,TIME)
      CWUPD=AFGEN(CWUPDT,TIME)
* FLRSWD=FLØW RATE ØF SUBSTANCE INTØ DØWNSTREAM DITCH SECTIØN  (DURING INFIL-
*        TRATIØN PERIØD) (MG/D)
      FLRSWD=CW*QIDØDS
* FLRSWI=FLØW RATE ØF SUBSTANCE FRØM WATER INTAKE (DURING INFILTRATIØN
*        PERIØD) (MG/D)
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      FLRSWI=CWIN*QINT
* FLRSWØ=FLØW RATE ØF SUBSTANCE DISCHARGED ØUT ØF THE WATER CØMP.
*         (DURING PUMPING PERIØD) (MG/D)
      FLRSWØ=CW*QDISCH
* FLRSWU=FLØW RATE ØF SUBSTANCE FRØM UPSTREAM DITCH SECTIØN  (DURING PUMPING
*         PERIØD) (MG/D)
      FLRSWU=CWUPD*QDUPDS
      DTØTB(1)=DISPD*ABS(VBØT(1))+DPØRL(1)
      IF(VBØT(1) .LT. 0.0) GØ TØ 53
* FLRSB=FLØW RATE ØF SUBSTANCE INTØ A BØTTØM CØMP. (MG/D)
      FLRSB(1)=-QWBØT*CLB(1)-DTØTB(1)*BØSU(1)*(CLB(1)-CW)/DIFD(1)
      FDIFLB(1)=-DPØRL(1)*BØSU(1)*(CLB(1)-CW)/DIFD(1)
      FLRSB(1)=AMIN1(FLRSB(1),FDIFLB(1))
      GØ TØ 54
  53  FLRSB(1)=-QWBØT*CW-DTØTB(1)*BØSU(1)*(CLB(1)-CW)/DIFD(1)
  54  CØNTINUE
      DØ 55 J=2,NBCØM
      DTØTB(J)=DISPD*ABS(VBØT(J))+DPØRL(J)
      FLRSB(J)=-QWBØT*WFAC*(MFAC*CLB(J-1)+CLB(J))-DTØTB(J)*...
      BØSU(J)*(CLB(J)-CLB(J-1))/DIFD(J)
      IF(VBØT(1) .LT. 0.0) GØ TØ 56
      FDIFLB(J)=-DPØRL(J)*BØSU(J)*(CLB(J)-CLB(J-1))/DIFD(J)
      FLRSB(J)=AMIN1(FLRSB(J),FDIFLB(J))
      IF(CLB(J) .LT. 0.0001) FLRSB(J)=AMAX1(FLRSB(J),0.0)
      GØ TØ 55
  56  IF(CLB(J-1) .LT. 0.0001) FLRSB(J)=AMIN1(FLRSB(J),0.0)
  55  CØNTINUE
      IF(QWBØT .LT. 0.) GØ TØ 59
      FLRSB(NBCØMP)=0.0
      GØ TØ 60
  59  FLRSB(NBCØMP)=-QWBØT*CLB(NBCØM)
  60  CØNTINUE
***   DECØMPØSITIØN ØF THE SUBSTANCE
* RDECW=RATE ØF DECØMPØSITIØN IN WATER CØMP. (MG/D)
      RDECW=AFGEN(RCDEWT,TIME)*MSW
* RDECB=RATE ØF DECØMPØSITØN IN BØTTØM CØMP. (MG/D)
* TRDECB=TØTAL RATE ØF DECØMPØSITIØN IN THE BØTTØM (MG/D)
      TRDECB=0.0
      DØ 61 J=1,NBCØM
      RDECB(J)=AFGEN(RCDEBT,TIME)*MSB(J)
  61  TRDECB=TRDECB+RDECB(J)
* TDECW=TØTAL MASS ØF SUBSTANCE DECØMPØSED IN WATER CØMP. (MG)
* TDECB=TØTAL MASS ØF SUBSTANCE DECØMPØSED IN BØTTØM (MG)
      TDECW=INTGRL(0.0,RDECW)
      TDECB=INTGRL(0.0,TRDECB)
***   ØVERALL RATE EQUATIØNS
      SUPS=SUPST(NDAY)
* RMSW=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN WATER CØMP (MG/D)
      RMSW=FLRSWI+FLRSWU+SUPS-FLRSB(1)-RDECW-FLRSWD-FLRSWØ
* RMSB=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN BØTTØM CØMP. (MG/D)
      DØ 62 J=1,NBCØM
  62  RMSB(J)=FLRSB(J)-FLRSB(J+1)-RDECB(J)
***   ØUTPUT SECTIØN
* TEVAP=TØTAL VØLUME ØF WATER EVAPØRATED (M3)
      TEVAP=INTGRL(0.0,QEVAP)
* TRAIN=TØTAL VØLUME ØF WATER FRØM RAINFALL (M3)
      TRAIN=INTGRL(0.0,QPREC)
* TINT=TØTAL VØLUME ØF WATER TAKEN IN (M3)
      TINT=INTGRL(0.0,QINT)
* TIDØDS=TØTAL VØLUME ØF WATER INTAKE INTØ DØWNSTREAM DITCH SECTIØN  (M3)
      TIDØDS=INTGRL(0.0,QIDØDS)
* TDISCH=TØTAL VØLUME ØF WATER PUMPED ØUT ØF THE DITCH (M3)
      TDISCH=INTGRL(0.0,QDISCH)
* TDUPDS=TØTAL VØLUME ØF WATER DISCHARGED FRØM THE UPSTREAM DITCH SECTIØN  (M3)
      TDUPDS=INTGRL(0.0,QDUPDS)
* TWBØT=TØTAL VØLUME ØF WATER TRANSPØRTED THRØUGH THE DITCH BØTTØM (M3)
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      TWBOT=INTGRL(0.0,QWBOT)
* TDRAIN=TOTAL VOLUME OF WATER FROM THE DRAINS (M3)
      TDRAIN=INTGRL(0.0,QWDR)
* TSTOR=TOTAL VOLUME OF WATER STORED IN THE DITCH  (M3)
      TSTOR=INTGRL(0.0,RVWD)
* TMSINT=TOTAL MASS OF SUSTANCE TRANSPORTED INTO THE WATER COMP. (VIA INTAKE) (
      TMSINT=INTGRL(0.0,FLRSWI)
* TMSUPD=TOTAL MASS OF SUBSTANCE TRANSPORTED INTO THE WATER COMP. VIA UP STREAM
*           DITCH SECTIONS (MG)
      TMSUPD=INTGRL(0.0,FLRSWU)
* TMSDOD=TOTAL MASS OF SUBSTANCE TRANSPORTED OUT OF THE WATER COMP. INTO
*           DOWNSTREAM DITCH SECTIONS (MG)
      TMSDOD=INTGRL(0.0,FLRSWD)
* TMSOUT=TOTAL MASS OF SUBSTANCE TRANSPORTED OUT OF THE WATER COMP.VIA PUMP (M
      TMSOUT=INTGRL(0.0,FLRSWO)
* TMSINF=TOTAL MASS OF SUBSTANCE INFILTRATED THROUGH THE LOWEST BOTTOM COMP.(M
      TMSINF=INTGRL(0.0,FLRSB(NBCOMP))
* TMSSUP=TOTAL MASS OF SUBSTANCE SUPPLIED TO THE DITCH DUE TO SPRAY DRIFT (MG)
      TMSSUP=INTGRL(0.0,SUPS)
      PRT=IMPULS(0.0,PRDEL)
      IF(PRT*KEEP .LT. 0.5) GO TO 100
* TMSB=TOTAL MASS OF SUBSTANCE IN BOTTOM (MG)
      TMSB=0.0
      DO 70 J=1,NBCOM
  70  TMSB=TMSB+MSB(J)
 100  CONTINUE
PRINT VWD,TEVAP,TRAIN,TINT,TIDODS,TDISCH,TDUPDS,TSTOR,TDRAIN,TWBOT,...
      FLODB,VBOT(1),FDIFLB(1-2),CW,CM(1-20),FLRSB(1-10),TMSB,MSW,...
      TDECW,TDECB,TMSINT,TMSUPD,TMSDOD,TMSOUT,TMSINF,TMSSUP
METHOD RECT
OUTPUT CW,MSW,TMSB
TIMER DELT=0.005,PRDEL=0.5,OUTDEL=0.5,FINTIM=59.0
END
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Appendix C

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TITLE BEHAVIOUR OF SUBSTANCES IN DITCHES WITH FLOWING WATER
************************************************************
* WITH DIFFUSION INTO ONE BOTTOM COMP.;VARIABLE WATER LEVEL AND VARIABLE FLOW
STORAGE FLRSW(101),CW(100),CLB(100),FLRSB(100),RDECW(100),RDECB(100)
FIXED NDCOM,NDCOMP,I
INITIAL
NOSORT
*     BASIC UNITS : MILLIGRAM (MG) , METER (M) , DAY (D)
*     ABBREVIATIONS : COMP.=COMPARTMENT(S)
***   DEFINITION OF DITCH COMPARTMENT GEOMETRY
* LCOM=LENGHT OF THE DITCH COMP. (M)
* S1=SLOPE OF THE LOWER PART OF THE DITCH WALLS (HORZ./VERT.) (-)
* W1=WIDTH AT THE BOTTOM OF THE DITCH (M)
* AHW=AVERAGE HEIGHT OF THE WATER LEVEL IN THE DITCH (M)
PARAM LCOM=2.,S1=0.32,W1=1.92,AHW=0.18
* P=WETTED PERIMETER OF THE DITCH (M)
      P=W1+2.0*AHW*SQRT(S1**2+1.0)
* NDCOM=NUMBER OF DITCH WATER COMP. (-)
PARAM NDCOM=100
      NDCOMP=NDCOM+1
* TBOT=THICKNESS OF BOTTOM COMP. (M)
PARAM TBOT=0.005
* BOSU=SURFACE AREA OF THE BOTTOM COMP. (M2)
      BOSU=P*LCOM
***   PHYSICAL CHARACTERISTICS OF THE BOTTOM
* BD=BULK DENSITY OF SOLID PHASE (KG/M3(MEDIUM))
* VFL=VOLUME FRACTION OF LIQUID (M3(LIQUID)/M3(MEDIUM))
* TORT=TORTUOSITY FACTOR (M2(MEDIUM)/M2(LIQUID))
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* DIFW=DIFFUSIØN CØEFFICIENT ØF SUBSTANCE IN BULK WATER (M2(LIQUID)/D)
PARAM BD=130.,VFL=0.95,TØRT=0.95,DIFW=0.35E-4
* DPØRL=DIFFUSIØN CØEFFICIENT ØF SUBSTANCE IN LIQUID PHASE (M3(LIQUID)/M(MED.)D)
      DPØRL=VFL*TØRT*DIFW
***   PARTITIØN ØF SUBSTANCE ØVER BØTTØM PHASES,INSTANTANEØUS EQUILIBRIUM
* KSL=DISTRIBUTIØN RATIØ SØLID/LIQUID PHASE =ADSØRPTIØN CØEFFICIENT
*     (MG/KG(SØLID PHASE))/(MG/M3(LIQUID PHASE))
PARAM KSL=0.007
* CAPL=SUBSTANCE CAPACITY FACTØR RELATING TØ CØNCENTRATIØN IN LIQUID PHASE
*       (M3(LIQUID)/M3(MEDIUM))
      CAPL=VFL+BD*KSL
      CABØTB=CAPL*BØSU*TBØT
***   DESCRIPTIØN ØF WATER FLØW THRØUGH THE DITCH CØMPARTMENTS
* U=AVERAGE VELØCITY ØF WATER FLØW IN THE DITCH (M/D)
* UT=U AS F(TIME)
FUNCTIØN UT=(0.,4640.),(1.,4640.)
* HW=HEIGHT ØF WATER LEVEL IN DITCH (M)
* HWT=HW AS F(TIME)
FUNCTIØN HWT=(0.,0.18),(3.0,0.18)
* DISCØN=DISPERSIØN CØNSTANT IN AN EMPIRICAL DISPERSIØN EQUATIØN (-)
PARAM DISCØN=22.3
***   DECØMPØSITIØN ØF THE SUBSTANCE
* RCDEWT=RATE CØEFFICIENT(1/D) FØR DECØMPØSITIØN IN WATER AS F(TIME)
FUNCTIØN RCDEWT=(0.,0.55),(1.,0.55)
* RCDEBT=RATE CØEFFICIENT(1/D) FØR DECØMPØSITIØN IN BØTTØM CØMP. AS F(TIME)
FUNCTIØN RCDEBT=(0.,0.),(1.0,0.)
***   INITIAL AND BØUNDARY CØNDITIØNS
* MSW=MASS ØF SUBSTANCE IN WATER CØMP. (MG)
* MSB=MASS ØF SUBSTANCE IN BØTTØM CØMP. (MG)
* I REFERS TØ INITIAL CØNDITIØN
TABLE IMSW(1-100)=50000.,99*0.
TABLE IMSB(1-100)=100*0.0
DYNAMIC
NØSØRT
***   CØMPUTATIØN ØF THE WATER FLØW CHARACTERISTICS
      U=AFGEN(UT,TIME)
      HW=AFGEN(HWT,TIME)
* A=WETTED CRØSS-SECTIØNAL AREA ØF THE DITCH (M2)
      A=HW*(W1+S1*HW)
* VWD=VØLUME ØF WATER IN DITCH WATER CØMP. (M3)
      VWD=A*LCØM
* Q=FLØW RATE ØF WATER INTØ A DITCH CØMP. (M3/D)
      Q=A*U
* DLDISW=LØNGITUDINAL DISPERSIØN CØEFFICIENT IN WATER CØMP. (M2/D)
      DLDISW=DISCØN*ABS(U)*HW
* DTØTW=TØTAL SPREADING CØEFFICIENT IN WATER CØMP. (M2/D)
      DTØTW=DLDISW+DIFW+U**2*DELT/2.0
***   SUBSTANCE MØVEMENT
* RMSW=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN WATER CØMP. (MG/D)
* RMSB=RATE ØF CHANGE IN MASS ØF SUBSTANCE IN BØTTØM CØMP. (MG/D)
      MSW=INTGRL(IMSW,RMSW,100)
      MSB=INTGRL(IMSB,RMSB,100)
* CW=CØNCENTRATIØN ØF SUBSTANCE IN WATER CØMP. (MG/M3)
      DØ 30 I=1,NDCØM
   30 CW(I)=MSW(I)/VWD
* FLRSW=FLØW RATE ØF SUBSTANCE INTØ A WATER CØMP. (MG/D)
      FLRSW(1)=INSW(Q,Q*CW(1),0.0)
      FLRSW(NDCØMP)=INSW(Q,0.0,Q*CW(NDCØM))
      DØ 33 I=2,NDCØM
   33 FLRSW(I)=Q*0.5*(CW(I-1)+CW(I))-DTØTW*A*(CW(I)-CW(I-1))/LCØM
* CLB=CØNCENTRATIØN ØF SUBSTANCE IN LIQUID PHASE ØF BØTTØM CØMP. (MG/M3)
      DØ 35 I=1,NDCØM
     35 CLB(I)=MSB(I)/CABØTB
* FLRSB=FLØW RATE ØF SUBSTANCE INTØ A BØTTØM CØMP. (MG/D)
      DØ 36 I=1,NDCØM
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  36  FLRSB(I)=-DPØRL*BØSU*(CLB(I)-CW(I))/(0.5*TBØT)
***   DECØMPØSITIØN ØF THE SUBSTANCE
* RDECW=RATE ØF DECØMPØSITIØN IN WATER CØMP. (MG/D)
* RDECB=RATE ØF DECØMPØSITIØN IN BØTTØM CØMP.(MG/D)
* TRDECW=TØTAL RATE ØF DECØMPØSITIØN IN THE WATER (MG/D)
* TRDECB=TØTAL RATE ØF DECØMPØSITIØN IN THE BØTTØM (MG/D)
      RCDECW=AFGEN(RCDEWT,TIME)
      RCDECB=AFGEN(RCDEBT,TIME)
      TRDECW=0.0
      TRDECB=0.0
      DØ 40 I=1,NDCØM
      RDECW(I)=RCDECW*MSW(I)
      RDECB(I)=RCDECB*MSB(I)
      TRDECW=TRDECW+RDECW(I)
  40  TRDECB=TRDECB+RDECB(I)
* TDECW=TØTAL MASS ØF SUBSTANCE DECØMPØSED IN WATER CØMP. (MG)
* TDECB=TØTAL MASS ØF SUBSTANCE DECØMPØSED IN BØTTØM (MG)
      TDECW=INTGRL(0.0,TRDECW)
      TDECB=INTGRL(0.0,TRDECB)
***   ØVERALL RATE EQUATIØNS
      DØ 50 I=1,NDCØM
      RMSW(I)=FLRSW(I)-FLRSW(I+1)-FLRSB(I)-RDECW(I)
  50  RMSB(I)=FLRSB(I)-RDECB(I)
***   ØUTPUT SECTIØN
* TMSWØF=TØTAL MASS ØF SUBSTANCE TRANSPØRTED ØUT ØF FIRST WATER CØMP. (MG)
* TMSWØL=TØTAL MASS ØF SUBSTANCE TRANSPØRTED ØUT ØF LAST WATER CØMP. (MG)
      TMSWØF=INTGRL(0.,-FLRSW(1))
      TMSWØL=INTGRL(0.0,FLRSW(NDCØMP))
      PRTIM=IMPULS(0.0,PRDEL)
      IF(PRTIM*KEEP .LT. 0.5) GØ TØ 100
* TMSW=TØTAL MASS ØF SUBSTANCE IN WATER CØMP. (MG)
* TMSB=TØTAL MASS ØF SUBSTANCE IN BØTTØM (MG)
      TMSW=0.0
      TMSB=0.0
      DØ 60 I=1,NDCØM
      TMSW=TMSW+MSW(I)
  60  TMSB=TMSB+MSB(I)
      CW51=CW(51)
      MSW51=MSW(51)
      MSB51=MSB(51)
  100 CØNTINUE
METHØD RECT
PRINT Q,U,DTØTW,RCDECW,RCDECB,TMSW,TMSB,TMSWØF,TMSWØL,TDECW,TDECB,...
      CW51,MSW51,MSB51
ØUTPUT CW51(0.,2000.),MSW51(0.,1000.),MSB51(0.,1000.)
TIMER DELT=0.000025,PRDEL=0.0025,ØUTDEL=0.0025,FINTIM=0.1
END
STØP
ENDJØB
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