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Pesticides in the aquatic environment Appearance and effect

Forekomst og effekt af pesticider i vandmiljøer

Seminar, Tune Landboskole, 12.-14. november 1991

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INTRODUCTION

A seminar covering the appearance and effect of pesticides in aquatic environments was held at Tune Landboskole, Denmark, November 12th to 14th 1991.

The seminar was planned and sponsored by Nordic Council of Ministers (Water Group) and Scandinavian Association of Agricultural Scientists (NJF). The participants (40) came from administration, chemical companies and environmental laboratories.

The seminar coverede both degradation and sorption of pesticides and transport routes and modelling of pesticide transport to the aquatic environment. Furthermore, deposition of pesticides with precipitation, occurance of pesticides in surface and subsurface waters and environmental effects of pesticides in water was presented. Most results were from experiments carried out in the Nordic countries.

INTRODUKTION

Et seminar vedrørende forekomst og effekt af pesticider i vandmiljøer blev afholdt på Tune Landboskole, Danmark, 12-14 november 1991.

Seminaret blev planlagt af Vandgruppen under Nordisk Ministerråd og af Nordiske Jordbrugsforskeres Forening (NJF). De 40 deltagere var dels fra miljøforskningslaboratorier, dels fra kemikalieindustrien og fra administrationen.

Seminaret dækkede nedbrydning og binding af pesticider samt deres transport til vandmiljøet. Også pesticidindhold i nedbør, forekomst af pesticider i overflade- og grundvand og effekter af pesticider i vand blev beskrevet. De fleste resultater stammer fra undersøgelser udført i de Nordiske lande.

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Summary

The use of pesticides in agriculture has led to the appearance of these chemicals and their degradation products in crops, soils, air and water.

The aim of the seminar was to elucidate the present knowledge about pollution of water with pesticides in the Nordic countries and to evaluate the risk of effects in the aquatic environment.

The main topics to be covered were:

a) Transport of pesticides to the aquatic environment.

b) Appearance of pesticides in precipitation.

c) Pesticides in surface and subsurface water.

d) Effects of pesticides in the aquatic environment.

e) Protection of the aquatic environment against pesticide pollution.

After a treatment in an agricultural crop the pesticide may move above the ground in the growth zone and further into the atmosphere, as well as below the ground in both the saturated and unsaturated zone. In all zones, the mobility of water is of great importance for mobility and persistence of pesticides within a certain zone. Disappearance of a pesticide from a zone is, apart from transport, also dependent on decomposition processes, photochemical, chemical and biological, as well as immobilization by incorporation into soil organic matter. The amount of the substance is then reduced or eliminated. However, metabolites may appear, which also must be followed in the environment.

During the mid sixtieth the first reports concerning findings of pesticides in rain appeared. When British scientists discovered lindane, dieldrin and DDT in rain. Most interest has been paid to the chlorinated hydrocarbons which have been found in precipitation almost all over the world. Recently also a number of other pesticides have been found in precipitation. Thus the fungicide iprodion and the insecticide permethrin has been found in the atmosphere in Holland. In Germany rain samples containing atrazine, simazine, mecoprop and dichloroprop have been found.

Generally speaking the concentrations have been highest during the spraying seasons indicating short term transport to be the most important.

Analyses of groundwater and drainage water from Denmark, Finland, Norway and Sweden sampled during the period 1985-1990 show, with few exceptions, relatively low pesticide concentrations. The triazine herbicide atrazine is the most frequently detected pesticide. Also, the triazines simazine and terbuthylazine occur sporadically. The herbicide bentazone occurs in one third of the samples taken in Swedish ground water. High concentrations of

atrazine and hexazinone have been found in shallow ground water in Denmark.

In analyses of surface water from Denmark, Finland, Norway and Sweden, sampled during the period 1985-1990. 35 different pesticides were detected, including 25 herbicides, 7 insecticides and 3 fungicides. Most of these were found at low concentrations and on single occasions. The most frequently found substances, in all investigations, were the commonly used phenoxy acid herbicides dichlorprop and MCPA. In Swedish investigations, the herbicide bentazone has been detected regularly throughout the year. These substances were also found at the highest concentrations, along with the herbicide metamitron. The triazine herbicide atrazine, mainly used on non-agricultural areas, have been found regularly in many of the investigations.

There are presently ongoing investigations of pesticides in surface waters in the four Nordic countries. Monitoring in the future must improve the sampling strategies to increase evaluation possibilities and form a basis for exposure assessment.

Since pesticides to-day have been found in all types of aquatic environments the seminar participants argued that it is of increasing importance that the studies of their effects in those environments are intensified. Hazard identification and assessment should be done as well as risk assessment.

Hazard identification for pesticides in the aquatic environment includes simple key parameters concerning intrinsic hazardous properties of the substances. The properties should also be used for regulatory purposes. Examples of such properties are water solubility, volatility, distribution constants for octanol/water (log P_{ow}), soil/water (K_d) and soil/organic carbon (K_{oc}), degradability and bioaccumulation (BCF).

The purpose of hazard assessment in the aquatic environment is to assess the potential for a substance to cause adverse effects on living species in the aquatic environment. Studies on fish, Daphnia and algae is common for regulatory purposes. However, it is desirable that a hazard assessment include not only single species, but also populations, communities and ecosystems. Performing an hazard assessment requires knowledge of the exposure of the pesticide in the aquatic environment and effect data on organisms with reference to the aquatic compartment of concern. The result of a hazard assessment is often expressed by comparison of predicted or measured concentrations (PECs and MECs, respectively) with the predicted no effect concentration (NOEC) for the concerned species, populations, communities or ecosystems.

The purpose of risk assessment in the aquatic environment is to determine the probability (quantitatively or qualitatively) that a pesticide causes adverse effects on an aquatic ecosystem as a result of the exposure. Both the magnitude, duration and frequency of the exposure as well as the effects on inter- and intra specific relations of the target populations are ideally taken into consideration.

During the seminar was presented studies of fate and effects of thiophosphates in the marine environment. In that environment degradation half-lifes ranged between 15 to 80 days, depending primarily on the thiophosphate and the concentration level tested. The toxicity to marine crustaceans was found to be well below the toxicity of the parental pesticide.

Experiences form a Norwegian project on pesticide effects on common inhabitants in freshwater ecosystems was presented. Information has been collected with acute and sublethal toxicity tests and natural communities have been used, collected from both lotic and lentic environments. A variety of different responses have been seen and for some of the organisms the interspecies variation was great. The general impression was that the most toxic substance was Dimethoate followed by Propiconazole to the fauna elements. The algae was most affected by Propiconazole followed by Atrazine, Simazine and Chlorosulfurone. The tolerance limits for some of the pesticides seem to be at a level seen in the brooks and strems from arable land.

The potential for bioaccumulation is an important element in hazard identification of pesticides in the aquatic environment. For assessment of the bioaccumulation potential of pesticides, test guidelines on P_{ow}-measurements and fish bioconcentration (BCF) tests are available. At the seminar was presented information on possibilities to improve the determination techniques. Information on BCF in fish can only be used to sort out those pesticides, which are not likely to biomagnificate in higher vertebrates and to indicate warning potential for high exposure concentrations in the biota. Test guidelines on indirect bioaccumulation (biomagnification) are needed, because prediction of food chain accumulation of pesticides is concidered important in formalized on hazard assessment schemes. Available evidence suggests that information on indirect bioaccumulation of pesticides in rodents could be used as predictor of bioaccumulation in birds and mammals.

In discussions after the presentations, the seminar participants pointed at certain areas where lack of information is obvious. Transformation studies of pesticides in different types of water and sediments, especially with concern to anaerobic conditions, should be carried out. Many investigations indicate a need for a broad range of effect studies with several compounds to get a good picture of the toxicity of pesticides which have the possibility to affect aquatic communities directly or indirectly. Mesocosm studies might be possible to use, NOEC-levels should be indicated and the possibility of synergistic effects taken into consideration. Methods to determine indirect bioaccumulation (biomagnification) are needed.

Pesticides can be transported to surface waters via surface runoff or via subsurface drainage systems. Pesticides leached below the root zone pose a threat also to groundwaters. Climatic variables, of which the most important is precipitation and its characteristics (quantity, intensity, duration, seasonal distribution), are the driving forces for pesticide transport from soil to waters. The topography of the field (slope, length, width), soil characteristics (hydraulic conductivity, porosity, field capacity) and management practices (cropping system, tillage, use of filter strips) determine the distribution of water between its behaviour in different environments. The most important parameters are the degradation rate and adsorption capacity.

In order to reduce pesticide load to waters both management practices and the characteristics of the pesticides should be improved. Improving the pesticide characteristics means that the pesticides with high degradation rates should be produced and used. However, the main emphasis should be put on changing management practices. Application techniques should be developed in order to reduce the applied amount and to avoid the risk of transport to waters. This includes:

- the use of pesticides only when needed
- the improvement of the quality and maintenance of the application machinery to achieve a reduction of the applied amounts,
- to leave unsprayed protection zones along the watercourses,
- to avoid spills caused by carelessness, e.g. when filling the tank or when cleaning the sprayers, and
- to take weather conditions into account.

When pesticides with high adsorption are used, their loss can be significantly reduced by erosion control measures. The most important measures are the use of reduced tillage techniques instead of conventional plowing, implementation of grass covered filter strips along lakes, rivers and ditches, and strip cropping. The lower the partition coefficient between soluble and solid phases, the higher is the proportion of pesticide loss via surface runoff in the soluble phase and via percolation.

Measures to promote best management practices in farming are legislative and administrative restrictions, information and education of farmers, and monetary incentives. In the Nordic countries administrative measures are mainly connected to the registration process. By intensive education and advisory programs farmers can be motivated to decrease the applied amounts and become aware of the risks of spills. Monetary incentives may in the future play a greater role in reducing the pesticide use and pesticide losses. The possible methods are, e.g., taxation and changes in the subsidy system towards direct payments supporting good agricultural practices.

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Pesticides in the aquatic environment - appearance and effect
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TRANSPORT OF PESTICIDES TO THE AQUATIC ENVIRONMENT

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ABSTRACT

Pesticides have been found in all types of aquatic environments, rain water, surface water, drainage water, ground water and also in sediments. After a spraying operation in an agricultural crop, the pesticide may move above the ground in the growth zone and further into the atmosphere, as well as below the ground in both the saturated and unsaturated zone. The mobility of water is of great importance for the mobility and the persistence of pesticides in all zones. Transport of pesticides in the environment occurs through diffusion, through the influence of wind and water, or through mobility of solid material. During the transport the pesticide may occur as a gas or in solid phase, be solved in water or adsorbed to particles. Important factors governing transport routes for pesticides include wind drift, evaporation, deposition, water mobility on the soil surface and in the ground. Incorrect handling of pesticides, e.g. spillage and unsuitable routines for disposal of spraying residues, may cause heavy contamination of water bodies. Such contamination may also occur when pesticides are used at places where they are extremely mobile or have a long persistence, e.g. farm yards, industrial areas and road sides.

INTRODUCTION

Pesticides have been found in all types of aquatic environment (Torstensson 1990), surface waters as well as ground water. We know that they occur in rain water. Pesticides have also been found in drainage water as well as in sediments.

This unintended but obvious contamination of the aquatic environment may cause problems through direct influence on inhabitants of the water ecosystems. Certain pesticides can bioaccumulate in water-living organisms. Herbicides appearing in irrigation water can cause great damage to sensitive crops. Pesticides are also extremely unwanted contaminants of our drinking water.

What are the reasons for pesticides appearing in the aquatic environment? Only minute amounts of pesticide spraying operations are intentionally directed at waters, e.g. weed removal in ponds and channels. In the following I will discuss the transport mechanisms and routes believed to be the most important for pesticide transport in the environment.

IMPORTANCE OF WATER MOBILITY

After a normal spraying operation in an agricultural crop the pesticide may move above the ground in the growth zone and further into the atmosphere, as well as below the ground in both the saturated and unsaturated zone. In all zones, the mobility of water is of great importance for mobility and persistence of pesticides within a certain zone (Fig. 1). Disappearance of a pesticide from a zone is, apart from transport, also dependent on decomposition processes, photochemical, chemical and biological, as well as immobilization by incorporation into soil organic matter. The amount of the substance is then reduced or eliminated. However, metabolites may appear, which also must be followed in the environment.

ENVIRONMENTAL ZONE	*WATER MOBILITY*		*PESTICIDE*	
			Input	*Losses*
Atmosphere	*Evaporation* ↑	*Precipitation* ↓	*Wind drift*	*Decomposition (photochemical)*
Plant zone	*Evaporation* ↑ *Surface water mobility* →	*Precipitation* ↓ *Irrigation* ↓	*Intended application* *Deposition from the atmosphere* *Wind drift* *Evaporation from soil* *Surface transport*	*Wind drift* *Plant uptake* *Decomposition (photochemical, in plants)* *Surface water transport* *Deposition to soil*
======Soil surface======				
Unsaturated soil to root depth	*Evaporation* ↑ ↑ *Root uptake*	*Down* ↓	*Intended application* *Exudation from roots* *Transport* ↑ ↓ →	*Root uptake* *Decomposition (chemical, biological)* *Bound residues* *Transport* ↑ ↓ →
Unsaturated soil below root depth	*Up* ↑ ← *Horizontal* →	*Down* ↓	*Transport* ↑ ↓ →	*Decomposition (chemical, biological)* *Transport* ↑ ↓ →
Saturated zone (ground water)	*Up* ↑ ← *Horizontal* →	*Down* ↓	*Transport* ↑ ↓ →	*Decomposition (chemical, biological)* *Transport* ↑ ↓ →

Fig. 1. Processes influencing water mobility and transport of pesticides in different environmental zones (partly after Cheng & Koskinen, 1986).

TRANSPORT MECHANISMS

Transport of pesticides in the environment occurs through diffusion, through the influence of wind and water, or through mobility of solid material (Fig. 2). During transport the pesticide may occur as a gas or in solid phase, be solved in water or adsorbed to particles of different kinds. The rate of transport, as well as the rate of different decomposition processes, is influenced by a great number of factors that are illustrated in Fig. 3.

ENVIRONMENTAL ZONE	*TRANSPORT MECHANISM*	*PHASE*
Atmosphere	*Wind*	*GP, SP, SW, B*
Plant zone	*Wind*	*GP, SP, SW, B*
	Surface water	*SW, B*
=======Soil surface=======		
Unsaturated soil to root depth	*Diffusion*	*GP, SW,*
	Water mobility	*SW*
	Ploughing, harrowing, etc.	*B*
	Cracks, channels	*GP, SW, B*
	Root exudation	*SW*
Unsaturated zone below root zone	*Diffusion*	*GP, SW,*
	Water mobility	*SW,*
	Cracks, channels	*GP, SW, B*
	Drainage pipes	*SW,*
Saturated zone (ground water)	*Diffusion*	*SW,*
	Water mobility	*SW,*

Fig. 2. Transport mechanisms of pesticides in different environmental zones. Phase of pesticide: Gas phase (GP), solid phase (SP), solubilized in water (SW), bound to soil particles (B).

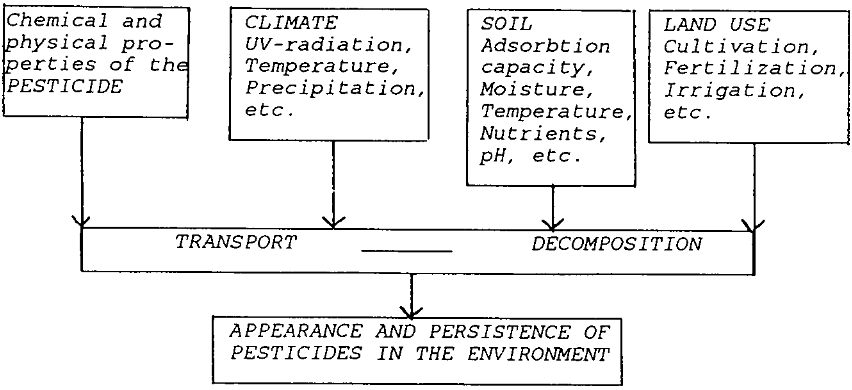

Fig. 3. The appearance and persistence of a pesticide depends on its transport and decomposition, the rates of which are influenced by a great number of factors.

TRANSPORT ROUTES

A survey of possible transport routes that may result in the appearance of pesticides in the aquatic environment is given in Fig. 4. The surface waters include ponds, creeks, streams, rivers, lakes, the sea and also sediments that may occur in them. The numbers within brackets in the Figure refer to further explanations below.

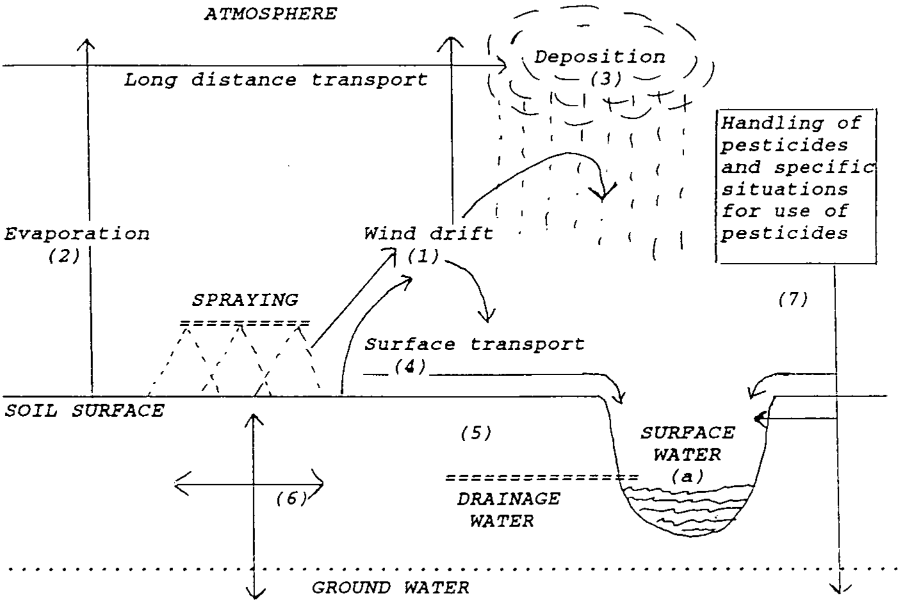

Fig. 4. Important transport routes that may lead to the appearance of pesticides in the aquatic environment.

1). Wind drift of pesticides in connection with spraying operations is a well-known problem (Hagenvall 1990). Wind drift may lead to minor amounts of the pesticide (often 0.1 percent or less), even in slight winds (1-3 m/s), being found hundreds of meters from the sprayed field. In stronger winds, the wind drift may become more obvious.

If there are dry climatic conditions on the spraying occasion, and especially if the sprayer gives small droplets, the water evaporates and the pesticide turns into very fine, solid, particles that are easily transported by the wind over long distances (many km) or even up into the atmosphere for global transport.

Certain pesticides are strongly adsorbed to soil particles and therefore remain in the uppermost soil layer. In dry, windy, conditions these soil particles may be blown away. Particles with a diameter of more than 0.06 mm are normally transported only a few metres by the wind. Even particles with a diameter of more than 0.002 mm fall down relatively soon after the wind has whirled them up. However, still smaller particles, including adsorbed pesticide, may be transported by wind over very long distances.

2). Evaporation of a pesticide from a soil or water surface depends on the vapor pressure, the water solubility, and the adsorption of the pesticide, and is influenced by the temperature. As the vapor pressure is an equilibrium property and an equilibrium with the atmosphere is impossible, the rate of evaporation is determined by the wind and the area where the substance is distributed. At rising temperatures the vapor pressure increases.

After a spraying operation, at least part of the pesticide is dissolved in available water. Because of this, the distribution of the compound between water and air is also of interest. This is particularly important for substances with low vapor pressure and at the same time a low water solubility.

3). Pesticides are deposited by precipitation or dry particles. Measurements made on rain water have revealed a number of pesticides in the USA (Richard et al. 1987), in Germany (ARW 1988; Hurle et al. 1987), in Switzerland (Buser 1990) and in Sweden (Larsson 1989; Larsson & Okla 1989; Kreuger 1990). In an investigation in the Netherlands, permetrin and iprodion were found on airborne particles (Wills et al. 1982).

Atrazine was found even in mountain lakes in Switzerland in the range of 0.15-1 ng/L (Buser 1990). There are no local sources of the herbicide. These lakes recieve water only from snow, ice, and rain, and therefore atmospheric input must have been responsible for the presence of atrazine. The concentration of atrazine (0.3 ng/L) in Lake Mutt (altitude, 2446 m above sea level; volume = 9 x 10^6 m^3) can be visualized from the fact that this concentration corresponds to 3 g in the whole lake. In Lake Zurich the input of atrazine via precipitation directly into the lake during the period March 1988 - March 1989 was estimated to be 1.4 kg (20 g/km^2, surface area 67.5 km^2).

4). Transport of pesticides on the ground surface may occur together with flowing water or by the wind. In the former case, the slope and the ground porosity, as well as the intensity and continuity of the water supply through precipitation or irrigation, is of importance. The adsorption properties of the pesticide are also of great importance. With low adsorption the substance easily penetrates the ground and the risk of loss by surface run-off is little. With strong adsorption of a pesticide a major part of it becomes bound to particles at the soil surface. Those particles may then be transported by wind or water over shorter or longer distances. The losses by surface water run-off vary from less than 0.1 percent to about 10 percent or more, depending on the slope of the area and precipitation (Wauchope 1978).

5). Mechanisms that regulate the mobility of a pesticide in soil are diffusion in the gas and water phase, preferential flow in e.g. cracks and root- or earthworm channels, plowing and harrowing, and exudation from plant roots.

Diffusion is a process by which a chemical substance aims at obtaining an equal distribution in a given space. It implies a transport from areas of high concentration to those with lower. The rate of diffusion depends on the pesticide's concentration and adsorption properties as well as the soil's temperature, porosity and content of water. Diffusion in the gas phase is 10000 times faster than in the water phase.

Pesticides adsorbed to soil particles move with them and may then rapidly penetrate cracks and channels in the soil. Normally immobile pesticides may thus, in minute amounts, penetrate deep into the soil profile.

Pesticides taken up by plant foliage can be transported down to the roots and there be exudated. This transport is rapid and exudation may occur within hours after application. Pesticides are transported through the top soil that normally is a barrier for immobile substances, down to the subsoil. It is known that exudated herbicides can, in some cases, be taken up by untreated plants which have their roots in the vicinity.

6). The most important route of pesticide transport in the soil is with the soil water (Torstensson 1987a). The water solubility and adsorption properties of the pesticide determine, together with the amounts of mobile water, the extent of the transport. The transport is generally downwards, in some cases horizontally, but under dry conditions it may be upwards.

It is of great interest to be able to predict the mobility in soil of a pesticide caused by water flow through the soil. The potential mobility of pesticides can be compared by determining their adsorption to soil (Torstensson 1987a). The main adsorbents of pesticides in soil are clay minerals, organic matter, iron and aluminum hydroxides. For many pesticides there is a strong correlation between adsorbtion and content of organic carbon.

If pesticides are applied on soils with a low content of adsorbing materials, the risk of mobility will nevertheless be high, and also for substances that normally are strongly adsorbed. Another difficulty is problems to foresee macro-pore flow of water that very rapidly may transport pesticides deep down in the soil profile.

The downward transport of pesticides in soil is also influenced by the rate of decomposition of the compounds (Torstensson 1987b). In the top soil, with high biological activity, we normally have the highest rate of decomposing activities. In the subsoil, biological activities are low and, consequently, rates of decomposition are also low.

Gustafson (1989) prepared a simple method for assessing pesticide leachability in soil. An index is derived based entirely on the physical properties of those pesticides that have been found either leachable or essentially immobile. The index is based on graphical examination of a plot formed by two widely available pesticide properties: the half-life in soil ($t_{½}$) and the partition coefficient between soil organic carbon and water (K_{oc}). Scores assigned with this index agree with the results of several recent well-water monitoring programs.

7). Incorrect handling of pesticides, e.g. spillage and unsuitable routines for disposal of spraying residues and washing water, may cause heavy contamination of water bodies.

Such contaminations may also occur when pesticides are used at places where they are extremely mobile or have a long persistence, e.g. soils with low adsorbtion and decomposition capacity, like farm yards, industrial areas or road sides. Spraying directly into open ditches should also be avoided.

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DEGRADATION AND SORPTION/DESORPTION OF PESTICIDES IN THE SOIL ENVIRONMENT

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Introduction

Soil and water are two of the most important natural resources which are essential for agriculture. Normally, a pesticide will be applied to a soil surface or a standing crop. The fate of such a product in the soil and also the dispersion in the environment, depends mainly on the characteristics and the overall functioning of the soil ecosystem. To reduce the environmental risks, potentially associated with pesticide use, a clear understanding of environmental processes is needed. Factors important for determining the environmental behaviour of a compound are its chemical structure, its physical properties, the type of formulation, the method of application, and the local climatic and agricultural conditions. Important questions like biological activity and biodegradability are fundamentally linked to the chemical structure. Much ingenuity has been invested to synthesize molecules which optimize the biological activity and the rate of degradation in the environment. The risk of health hazards will depend on the toxicity of the pesticides involved; its application frequency and dosage; and its persistence and mobility in soil.

Rates of loss. An important aspect of the subsequent behaviour of a compound applied to soils is the time for which their residues will persist. In this paper, the degradation of pesticides is discussed primarily in terms of persistence processes. Persistence in the field will vary according to soil properties and weather conditions. Thus site to site variation and variation during the growing season should be expected. Important variables such as soil texture, nutrient status, pH, organic matter, sand and clay content are all involved in the building up of the soil structure being highly complex biological and chemical medium. All of these variables may interact and determine the degradation rate of a particular compound. In addition, soil microorganisms are highly involved in degradation and factors affecting microbial activity in soil will also influence the rate of loss.

Findings vs time

During the year 1987, 15 localities were monitored for 15 different compounds. The results from 4 of these localities with

Table 1. Amounts (µg/l) of the herbicides MCPA, dichlorprop and propachlor found at different times of sampling at different localities.

Compound	MCPA						Dichlorprop				
--Time for sampling	30/1	12/6	30/6	27/8	7/9		30/1	12/6	30/6	27/8	7/9
Community: <u>Ullensaker</u>											
Brook: Haugerbekken											
Soil type: Clay											
Catchment area: 1.5 km^2											
90 % cultivated											
µg/l.	.	2.0	1.0	.	0.2		.	0.7	0.3	3.0	2.0
Time of sampling	20/1	14/4	10/6	14/7	31/7	24/8	20/1	14/4	10/6	14/7	24/8
Community: <u>Lier</u>											
Brook: Renskaugbekken											
Soil type: Silty clay											
Catchment area: 3 km^2											
70 % cultivated											
µg/l	.	.	.	0.2	0.2	.	.	.	0.3	0.2	0.3
--Time of sampling							20/1	14/4	10/6	24/8	
Community: <u>Ramnes & Sem</u>											
River: Aulielva											
Soil type: Silt & clay											
Catchment area: 250 km^2											
20 % cultivated											
µg/l							.	.	0.4	0.5	
--Compound	Propachlor										
--Time of sampling	28/1	24/4	18/6	24/7	24/8						
Community: <u>Østre Toten</u>											
Brook: Totenvika											
Soil type: Morainic deposits											
Catchment area: 1 km^2											
95 % cultivated											
µg/l	.	.	14.3	0.9	0.6						

regard to the herbicides MCPA, dichlorprop and propachlor are presented in Table 1.

According to Smith and Hayden (1981) the half-life for MCPA in soil is 6-8 days, while the duration of residual activity in soil is 3-4 months (The Agrochemicals Handbook, 1986). The water solubility of MCPA is high (1500 mg/l) as is the leachability. Experiments performed at the Plant Protection Institute confirmed this. A light silt-sandy soil from Solör (community of Våler, Hedmark) gave a K_d-value of about 1.0 and lysimeter experiment showed that MCPA followed the water-front in columns. In sandy soils, there is a considerable risk that compounds like MCPA will reach drainage water at places having surplus rainfall. A heavier soil containing clays, however, has stronger sorption capacity and gives more time for decomposition.

Dichlorprop belongs to the same chemical group as MCPA. The water solubility, however, is somewhat higher (2200 mg/l) and the half-life is about twice as high as for MCPA. In practical use the ratio dichlorprop/MCPA is 3:1. This can explain the higher concentrations of dichlorprop than MCPA found in surface waters, during the autumn (Table 1). This is in accordance with what is reported from Sweden (Kreüger, 1986).

Propachlor is chemically defined as an aniline. Water solubility is 700 mg/l and half-life is estimated to be 5-15 days. Considering the short half-life time, it seems unlikely that this compound could be detected 2 months after the first detection. One explanation may be: Repeated use of this compound, as it is allowed for onion and leeks. An intensive rainfall right after application gave surface runoff with detectable amounts of propachlor. In this permeable soil a vertical transport of propachlor occurred which again gave less favourable condition for degradation.

An experiment with chlorsulfuron, applied on a silty clay soil at a dosage of 4 g/ha, resulted in 2 % leaching into surface and drainage water during a period of 4 1/2 months (Bechmann et al. 1990) The elapse of run off is shown in Figure 1.

The increase in the amount registered at the end of the year in surface water, may be explained by the plowing of the soil a few days before sampling transferring chlorsulfuron from a deeper root zone to the surface layers.

In addition to chlorsulfuron, propiconazole (Tilt) was also applied twice (24/6 and 4/7), totally 250 g active ingredient pr. hectare. Only 0.33 % was found in the surface and drainage water. Propiconazole in runoff as a function of time is shown in Fig. 2.

Propiconazole was also applied in 1989 and 1990 (Aspmo et al. 1991). Conventional tillage was practiced and oats were grown. Time of applications were 7/7 and 1/7 for the two years, respectively. The results are shown in Figure 3.

Even though a lot of samples were analyzed in 1989, propiconazol was not detected in the surface water. In the drainage water, however, propiconazole could be detected 5 weeks after the application. Heavy rainfalls one week after the application in 1990 resulted in the highest peaks for both of the two water groups.

Autumn harrowed clay soil and snow melting in February resulted in erosion, and both MCPA and dichlorprop were detected in surface water. The results are shown in Figure 4.

1988/89: MCPA and dichlorprop were applied 7/6-88. The compounds

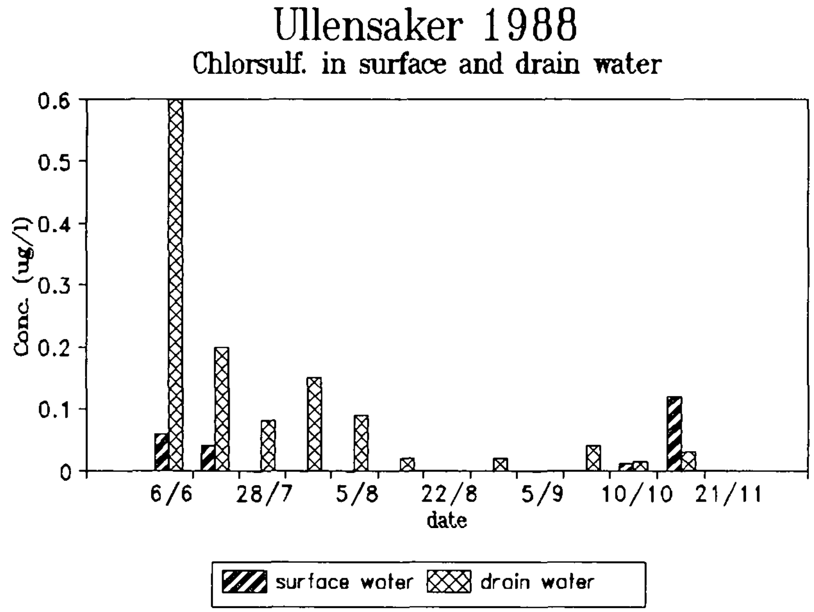

Fig. 1. Chlorsulfuron in drainage- and surface water vs time.

were not detected neither during the growth season nor during next year.

1989/90: MCPA and dichlorprop were applied 9/6-89. MCPA and dichlorprop were found in October and MCPA also in November/December. Melted snow water was analyzed in January 1991 without any detection of the compounds involved. As mentioned before surface runoff sampled in February contained the two herbicides.

On a silty clay soil from the same area (Ullensaker), dimethoate (Rogor) was applicated 21/6 1988. No detectable level appeared up to the next growth season when a new application took place, 15/7. Dimethoate was first observed after soil tillage and the autumn wheat had been sown. From the end of October to the end of February next year, dimethoate was detected in 7 of the 8 samples

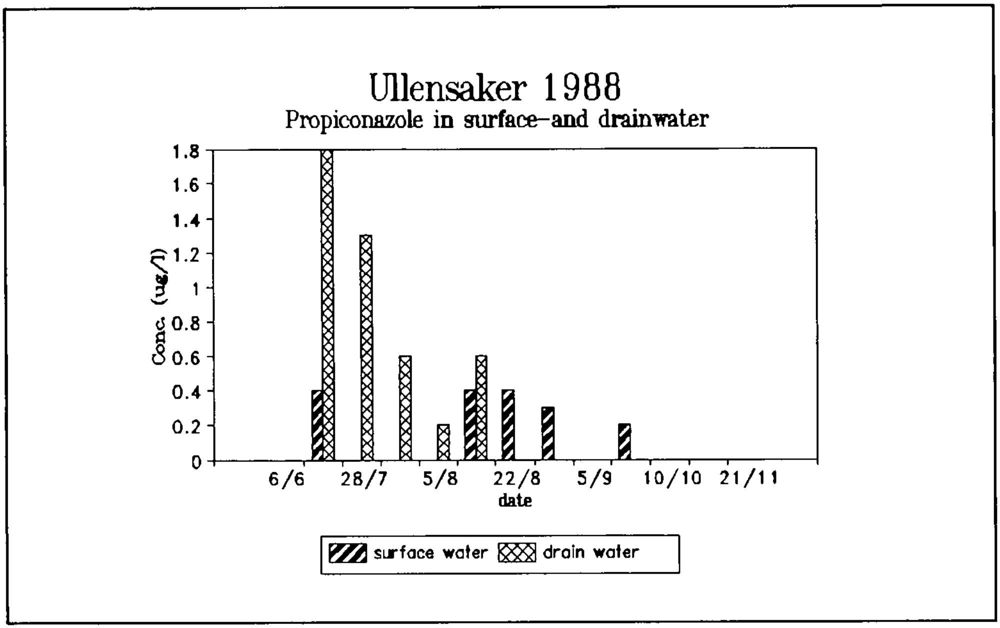

Fig. 2. Propiconazole in drainage- and surface water vs time (1988).

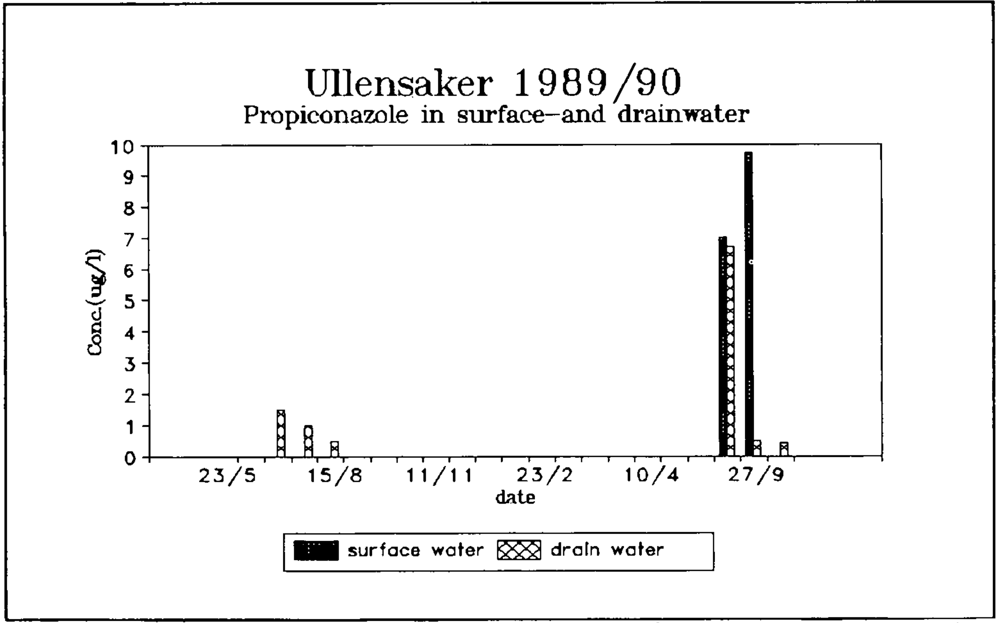

Fig. 3. Propiconazole in drainage- and surface water vs time (1989 and 1990).

taken. The results are presented in Fig. 5.
The persistence of simazine and atrazine have been studied in a case study where the compounds have been used for 20 years to

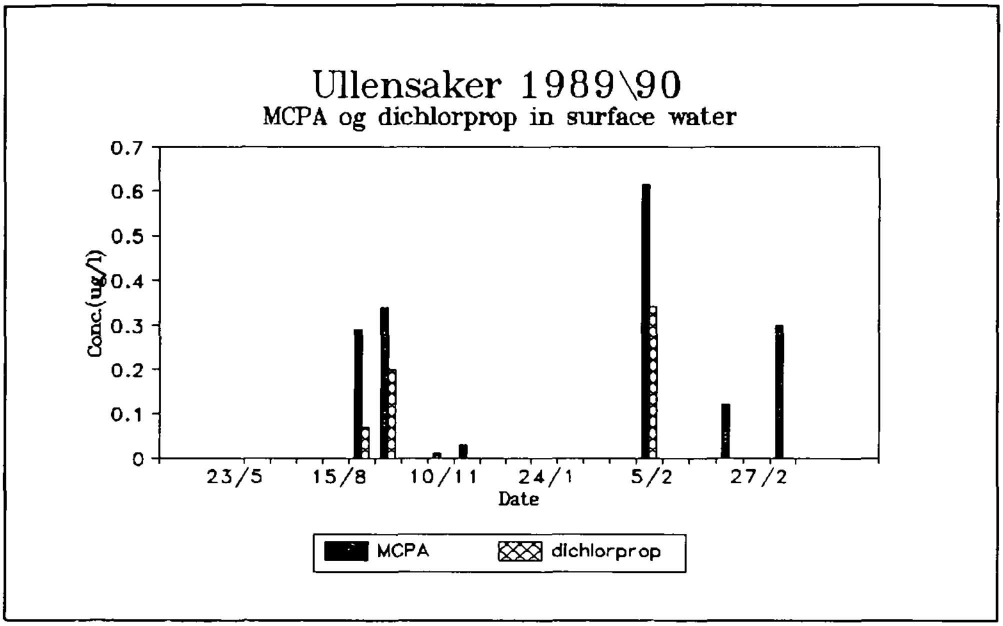

Fig. 4. MCPA and dichlorprop in surface water vs time.

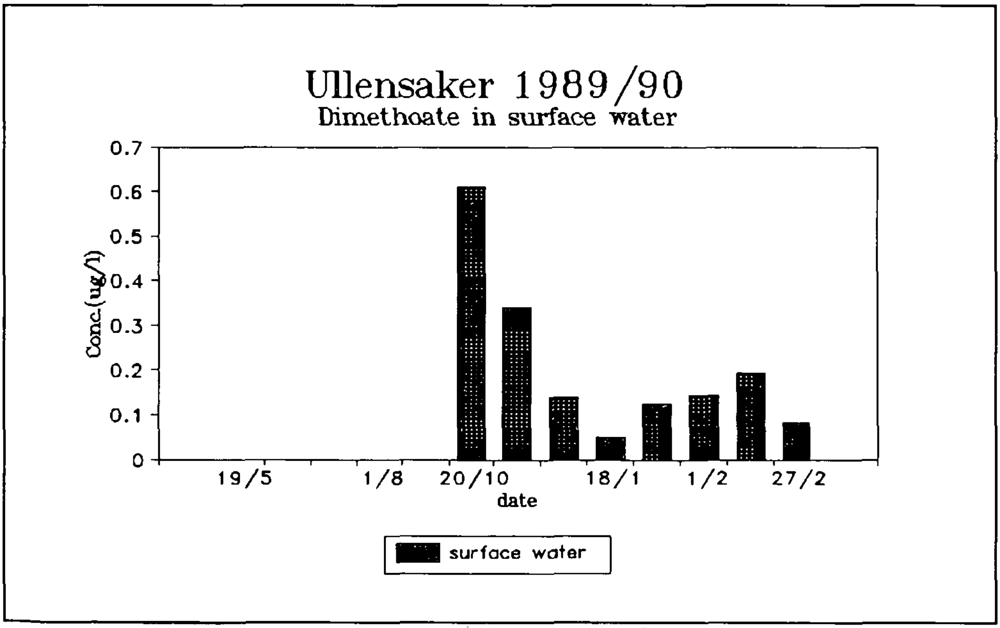

Fig. 5. Dimethoate in surface water vs time.

control vegetation. The soil was very light (sand pit) lying upon the ground rock with a fall gradient to a spring water outlet. This pond supplied several house holds and for flower crops in a glasshouse with water. The use of this water resulted in great damage to thousands of plants. All use of the herbicides was stopped in 1986. According to chemical analyses at a detection level of 0.1 microgram pr. litre, both simazine and atrazine are present in the water source. The results are presented in Fig. 6.

This case study tells us that pesticides leached to deeper zones can stay there for a long time. The degradation processes are very slow and it seems very important to be aware of small residue amounts of pesticides in the water being used to supply growing plants, specially if a drip watering system is involved.

The persistence of pesticides in the field can vary between years and can be attributed to extended periods of unusually dry or cool weather, and are more pronounced when sequences of unusual weather follow one another, such as cool spring and dry summer or dry autumn and cold winter (Walker 1983).

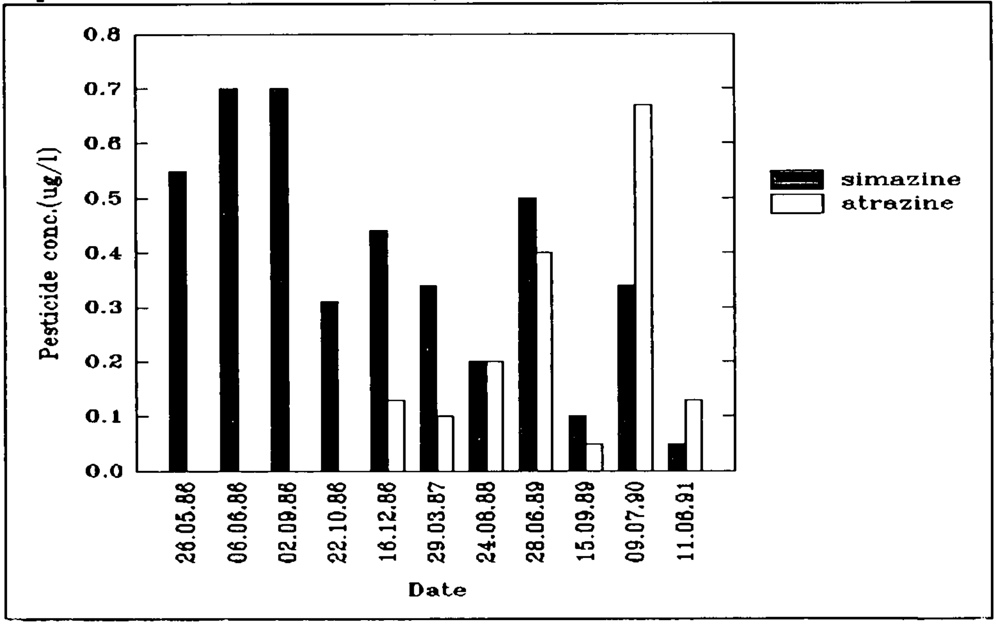

Fig. 6. Amounts of simazine and atrazine found in a pond from a spring outlet vs time. No application after 1986.

Metabolites - degradation products

Pesticide regulation in several countries requires data on soil metabolism (aerobe, anaerobe and microbial studies) on two or more standard soils and field dissipation experiments. Information on the character of the major metabolites and an estimation of their persistence in soil are also needed (Guth, 1980). Especially from Holland, where groundwater level is about 2 meters below soil surface, pesticides and their degradation products are threatening drinking water (Haasteren, 1990).

Monitoring studies in The Netherlands show that several degradation products from almost water insoluble pesticides are frequently found in groundwater. The concentration levels of these degradation products are much higher than usually reported from areas where pesticides are found in ground- and surface water. Substances specially brought into focus are degradation products from soil sterilization compounds and the dithiocarbamates like mancozeb, forming ETU.

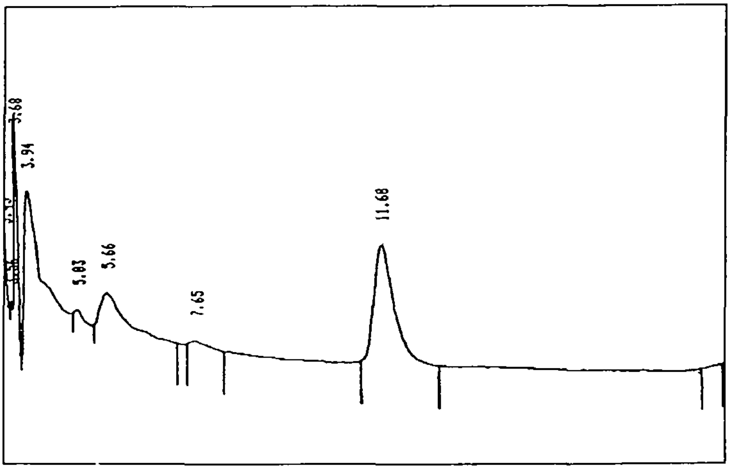

Fig. 7. HPLC - chromatogram for dichlorprop (11.68) in soil from Haslemoen.

Use of radiolabelled pesticides, combined with separation by means of HPLC (high pressure liquid chromatography) or other separating technics, should be an important tool as a first step in isolating metabolites. The degradation products could then be futher identified by the use of MS (mass spectrometry). Results from an experiment using ^{14}C labelled dichlorprop are illustrated in Fig. 7. The figure shows the chromatogram of dichlorprop at the beginning of the degradation experiment. Dichlorprop is represented by the peak at 11.68. During the experiment degradation products are formed, represented by the three other peaks on the chromatogram (Fig. 8). The eluation fractions were measured using liquid scintillation counting to localize the degradation products of dichlorprop.

In the future, effects and behaviour of degradation products from pesticides in the environment, will be an important subject.

Sorption

Binding types

The pesticides are usually grouped into three classes depending on their predominant charge characteristics:

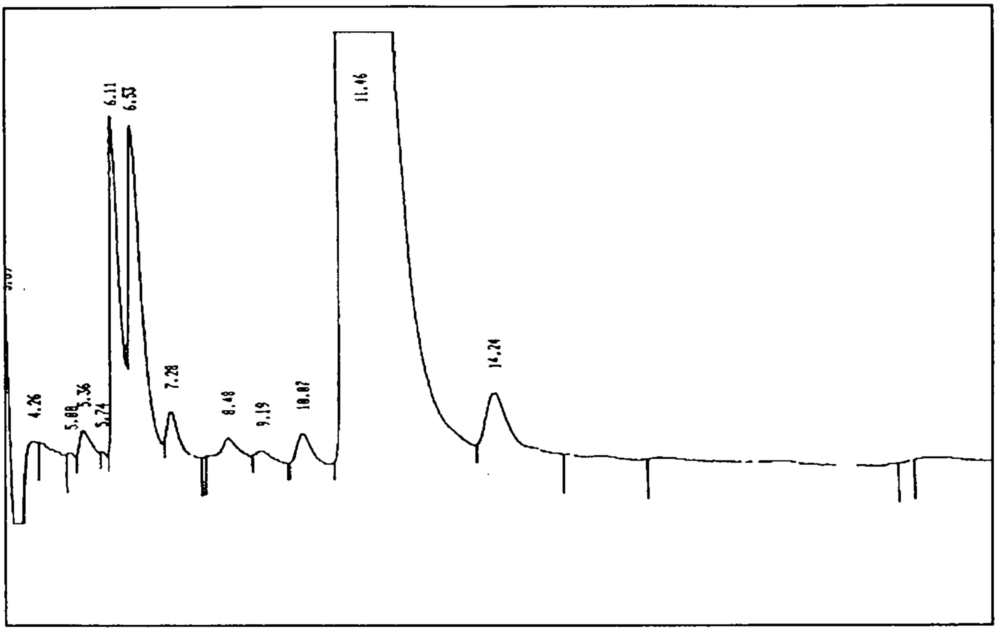

Fig. 8. HPLC - chromatogram for dichlorprop (11.46) in soil from Haslemoen. Within 14 days, 20% of the dichlorprop was degraded (6.11, 6.53 and 14.24).

cationic; anionic; and non-ionic (Theng, 1974). Other mechanisms of sorption may also occur depending on the nature of the pesticide and the surface of soil components. Cationic compounds belonging to the first class, such as bipyridylium halides and difenzoquat methyle sulphate, are generally applied as their aqueous salt. Being compleatly ionized, they are sorbed to clay and soils by an ion exchange process, replacing the inorganic cations initially present at the surface. The cation exchange capacity (CEC) of the soil may determine the extent of sorption. Investigations on sorption of difenzoquat$^+$ to clay minerals showed that smectite accounted for about 70 % of the CEC (Fig. 9). From a log-log plot of the isotherm, the K_f-value (Freundlich coefficient) is obtained by reading the intercept of the y-axis at the unit concentration (Fig. 10).

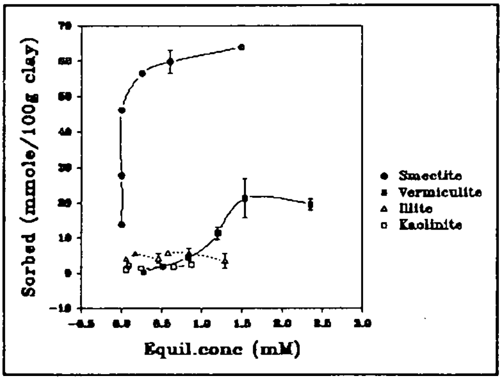

Fig. 9. Sorption of difenzoquat$^+$ by Ca^{++}-smectite, -vermiculite, -illite and kaolinite. Vertical bars represent standard deviation.

Observations indicate that difenzoquat$^+$ is strongly sorbed, especially to smectite, where the cations are evidently intercalated. X-ray diffraction of the complexes shows that smectite expands when small amounts of difenzoquat$^+$ is sorbed (Fig. 11). Intercalation of the bipyridylium halides by smectite and vermiculite has been shown earlier by Hayes et al. (1978a, 1978b).

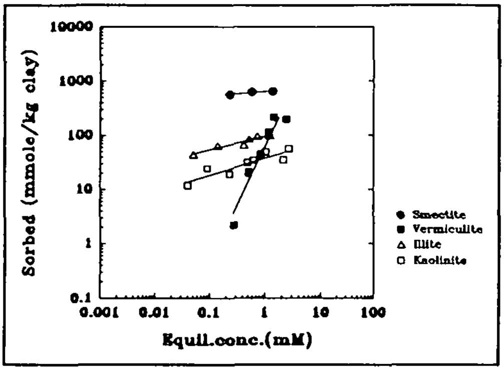

Fig. 10. Freundlich sorption isotherms of difenzoquat$^+$ on Ca^{2+}-smectite, -vermiculite, -illite and kaolinite.

This sorption mechanism is important in soils with expanding clay minerals. In soils without these special minerals together with relatively small amounts of organic matter, the extent and strength of sorption is not large. This is illustrated in an investigation on sorption of difenzoquat$^+$ to different soils from Haslemoen in southern Norway.

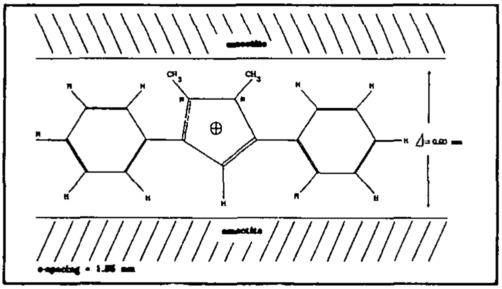

Fig. 11. Orientation of difenzoquat$^+$ in the inter-lamellar spaces of Ca^{2+} -smectite.

Table 2. Grain size distribution of different soil layers from Haslemoen (Atterberg system).

	grain size distribution (%)						
	sand			silt			clay
depth	coarse	medium	fine	coarse	medium	fine	
0-25cm	0	1	14	38	31	8	7
35-70cm	0	0	55	34	7	1	2
70-105cm	0	5	92	3	0	0	0

Grain size distribution and chemical properities of different soil layers from Haslemoen are given in Table 2 and 3. Soils from the following depths were used. A: the plough layer 0-25 cm, consisting of coarse silt mixed up with organic matter and residues from the previous years harvesting, classified as silt loam. B: 35-70 cm, a distinct zone beneath the plough layer, consisting of a mixture of coarse silt and fine sand, classified as sandy laom.

Table 3. Chemical properties of soil from Haslemoen.

depth (cm)	Tot. C (g/100g)	Base sat. %	CEC (meq/100 g)	pH
0-25	2.1	48.6	12	6.0
35-70	1.0	85.2	4	5.7
70-105	0.1	91.5	2	5.4

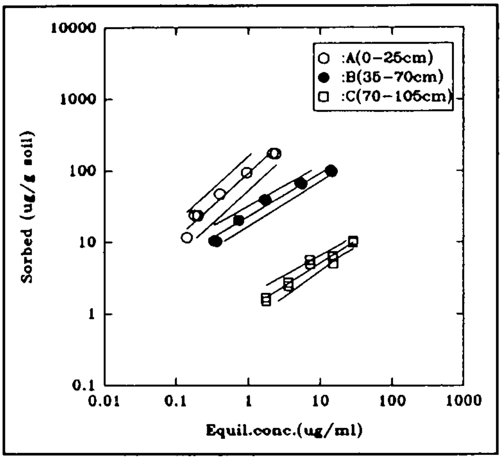

Fig. 12. Freundlich sorption isotherms of difenzoquat$^+$ on soils A, B and C from Haslemoen at 3°C (the 95% confidence level is shown).

C: 70-105 cm, soil consisting of about 92 % fine sand, classified as fine sand (Soil Sci. Soc. Am., 1979). The small amount of clay minerals found was illite and some vermiculite (Sperstad, 1991). From Freundlich sorption isotherms of difenzoquat methyl sulphate (Fig. 12) and MCPA, K_f-values were calculated. The K_f-values of difenzoquat methyl sulphate were approx. 90, 22 and 1.5 for siltloam (0-25 cm), sandy loam (30-75 cm) and fine sand (70-105 cm), respectively. This should indicate that the sorption mechanism, and the strength of the binding, is greatly dependent on the properties of the soil (Table 4).

Table 4. Freundlich k-values (K_f) of difenzoquat$^+$ and MCPA in different soil layers from Haslemoen. The k-values are estimated at 3°C and 11°C.

depth	Difenzoquat methyl sulphate		MCPA	
(cm)	3°C	11°C	3°C	11°C
0-25	91.2 (0.98)	85.2 (0.99)	0.9 (0.95)	1.5 (0.95)
35-70	22.9 (0.98)	22.8 (0.99)	1.5 (0.94)	1.4 (0.91)
70-105	1.2 (0.97)	1.5 (0.97)	1.0 (0.91)	1.0 (0.96)

For the other two classes of pesticides, the attraction forces are weaker, especially in the class of anionic pesticides. This can be illustrated with experiments carried out with the diclorprop and MCPA.

Sorption of dichlorprop, MCPA, atrazine and tribenuron-methyl to different soil types.

^{14}C-labelled pesticides are used in the sorption experiments described below. Futher information on the experiments is given in Riise (1991), Riise and Salbu (sub. for publ.) and Riise et al. (sub. for publ.).

Table 5. Partitioning coefficients calculated from linear isotherms (17°C).

Soil Type	Soil A	Soil B	Soil C	Soil D	Soil E
Classif.	Org. rich	Org. rich	Loam	Silty clay loam	Sand
Org.C (%)	30.4	14.6	3.3	1.3	1.4
pH	4.4	4.1	5.0	5.1	5.3
Dichlorprop					
K_d	34.7	17.4	1.62	0.84	0.72
K_{oc}	113	118	50	62	54
MCPA					
K_d	27.4			1.16	
K_{oc}	90			89	
Atrazine					
K_d	89.1	38.6	5.8	1.37	2.16
K_{oc}	293	265	175	106	154
Tribenuron-methyl					
K_d	17.9	12.5	55.2	28.3	1.21
K_{oc}	59	86	1673	2173	86

Organic rich soils show high sorption capacity for dichlorprop, MCPA and atrazine compared to soils low in organic carbon (Table 5). By normalizing K_d to K_{oc}, soil to soil variations is reduced, which indicates that the content of organic C is very important for the retention of dichlorprop, MCPA and atrazine in soils.

Linear sorption isotherms based on batch equilibrium data of dichlorprop and soils from different depth layers at Haslemoen, show higher K_d values for the top layer (0-18 cm) compared to the underlying layers (35-60 cm and 70-95 cm). This is in agreement with the results given in Table 4. Thus, the top layer has higher sorption capacity for difenzoquat$^+$, MCPA and dichlorprop, compared to the underlying layers, and the mobility of the pesticides increases with depth.

Tribenuron-methyl behaves differently to dichlorprop, MCPA and atrazine, as loam and silty clay loam show higher sorption capacity than the organic C rich soils (Table 5).

Normalizing K_d to K_{oc} increases instead of decreases the soil-to-soil variations, indicating that organic C is of minor importance for the sorption of tribenuron-methyl.

Sorption as a function of pH.

Dichlorprop: The sorption of dichlorprop to soil is very dependent on pH, and as seen from Fig. 13, the sorption decreases as the pH increases. This indicates an increasing mobility of dichlorprop with pH. Due to the weak acid properties of dichlorprop, its ionization decreases with decreasing pH. The neutral form of dichlorprop shows higher sorption to soils than its corresponding anion. Normalizing K_d to K_{oc} reduces much of the soil-to-soil variation (Fig 13), indicating that hydrophobic binding is of major importance for the sorption of dichlorprop to soil.

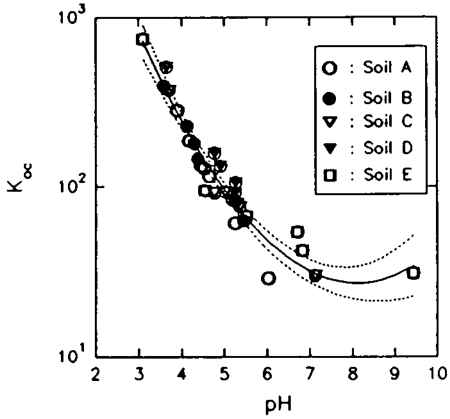

Fig. 13. K_{oc} of dichlorprop vs pH for different soil types.

Tribenuron-methyl: The sorption of tribenuron-methyl to soils with high content of organic C (soil A and B) and to the sand soil (E) are only to a certain degree dependent on pH (Fig. 14).

The soils with high content of clays (soil C and D) show high sorption capacity for tribenuron-methyl, especially at low pH-values. This may indicate a more specific binding of tribenuron-methyl to clays which is very pH-dependent.

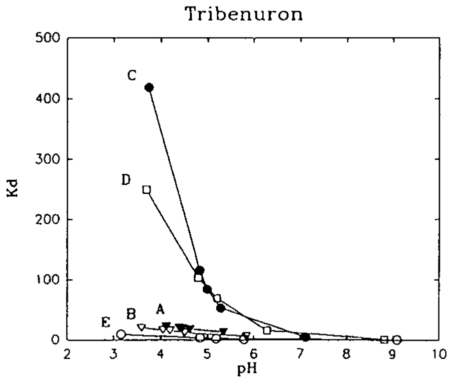

Fig. 14. K_d of tribenuron-methyl vs pH for different soil types.

K_{ow} as a function of pH

Octanol-water partitioning coefficients (K_{ow}) are determined by batch extractions of octanol and water solutions spiked with ^{14}C-labelled pesticides. The pH of the water solutions is adjusted by adding dilute HCl or NaOH.

MCPA and dichlorprop: Except for somewhat lower K_{ow} values of MCPA, the relationships between K_{ow} and pH are quite similar for MCPA and dichlorprop (Fig. 15). The lipophilicity of the phenoxyacids is inversely related to pH as the neutral form becomes dominating at low pH-values.

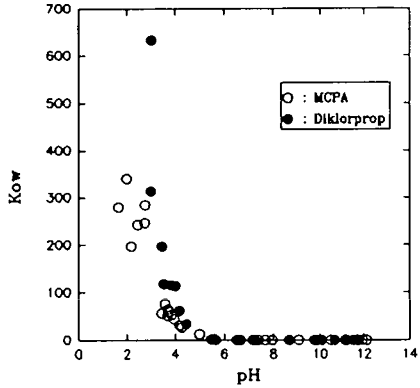

Fig. 15. K_{ow} of MCPA and dichlorprop as a function of pH.

Atrazine: The K_{ow} values of atrazine show relatively small variations as a function of pH (Fig. 16). Atrazine has higher K_{ow} values than MCPA and dichlorprop at pH values above 4. This explains the higher K_{oc} values of atrazine compared to MCPA and dichlorprop (Table 5).

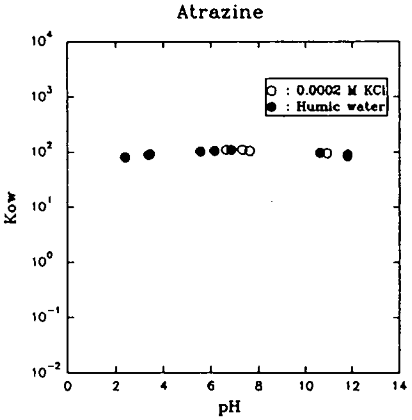

Fig. 16. K_{ow} of atrazine as a function of pH. 0.2 mM KCl and humic water are used as water phases.

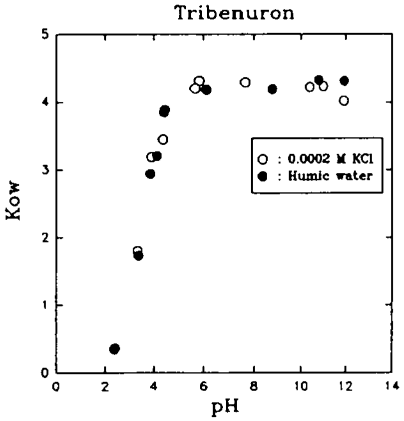

Fig. 17. K_{ow} of tribenuron-methyl as a function of pH. 0.2 mM KCl and humic water are used as water phases.

Tribenuron-methyl: According to the results given in Fig. 17, the K_{ow} values are increasing from less than 1 to 4 in the pH-range 2-4. Above pH 4 the K_{ow} value shows a relatively stable value of approximately 4. Thus tribenuron-methyl is most polar at low pH values.

Assosiation of pesticides with colloids.

Pesticides associated with colloids may behave differently from pesticides in "free" solutions with respect to mobility and bioavailability. Pesticides associated with colloids are often thought to be less bioavailable than "free" pesticides.

Illite-suspension (10-100 mg illite/l) spiked with ^{14}C-labelled tribenuron-methyl are ultrafiltered by the use of hollow-fibres (nominal molecular weight cut off 3 kDa). The results indicate that the association of tribenuron-methyl with high molecular weight compounds (< 3 kDa) is significant. The degree of association is inversely related to pH.

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NORDIC SEMINAR
Pesticides in the aquatic environment - appearance and effect
November 12-14, 1991. Tune Landboskole, Denmark.

PESTICIDES IN PRECIPITATION - A REVIEW

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The use of pesticides in the US in 1988 has been estimated to 1.5 mill. tons of active ingredients (42). The use of herbicides increased 280% from 1966 to 1981 (1). Insecticides increased also, but only a few percent. The fate of this huge amount is deposition on plants, soil, drift to open waters, transportation to subsoil-water, directly and indirectly evaporation to the atmosphere. It has been estimated that 90 percent of chlorinated hydrocarbon pesticides (OCP), evaporate in tropic areas (46).

Compared to their predecessors, currently used herbicides are less persistent and show less tendency to bio-acumulate, but are more soluble in water, and therefore more mobile in the environment (1).

Numerous reports are available on almost all types of molecules present in the atmosphere, from metabolites of natural origin to modern synthesis products from industry (60).

Once in the atmosphere, the molecules have a very good possibility of being transported from one locality to the other. The public normally do not consider this as a fact, unless the event can be seen as for example smoke. But the nuclear accident in Chernobyl, which resulted in heavy atmospheric transport of radioactive material, was traced far away (47, 48) and made people aware of pollution of biologically active substances as a problem of global interest.

This is also the case with pesticides.

Introduction of modern pesticides after the second world war did not initializede a pronounced interest in pollution of the environment. This is an example of the difficulties introducing new inventions. It took nearly twenty years before the side effects of pesticides was apparent to the public, not to forget Rachel Carsons book "The silent spring" in beginning of the sixtieths.

It was in the same period that first papers concerning pesticides in rain appeared. British scientists discovered in 1965 lindane, dieldrin and DDT in rain (4, 5, 6).

Almost at the same time, papers from the US reported longrange transport of CHP, including p,p'-DDT (15, 16).

Reports of pesticides and PCB in rain on the open Atlantic and the West Indies (10, 11, 12, 13, 14) and on remote tropic islands, indicated global pollution with these compounds.

Even at the poles could deposition in snow and animals be detected.

Analysis of antarctic snow in 1969 showed DDT (7) and was followed up with CHP in air 1982 and 1983 (35, 36). Recent investigations at the antarctic show CHP and PCB in snow and animal tissue (43, 44).

In 1974, PCB was found in arctic mammals (8), and in 1975 in marine arctic and subarctic food chains. In 1982 CHP was measured in arctic air samples (33, 34).

In 1976 was published the first reports on PCB in the Great Lakes (17). 10 to 100 ng/L was found. This started an intensive flow of reports from The Lakes.

PCB in rain and snow was reported in 1977 and 1978 (18, 19) and in 1979 CHP was detected in rain in the Great Lake area (20).

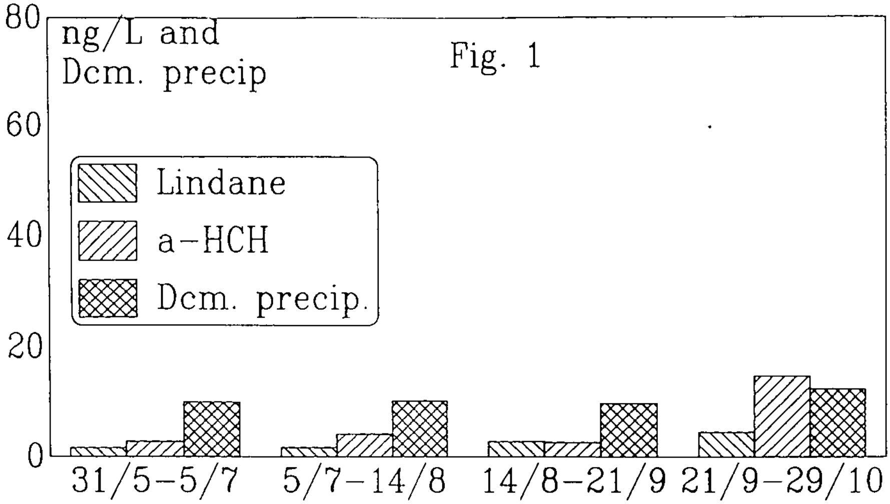
Samples from two small islands of Lake Superior, one in the west and one in the east part of the lake, were investigated. alfa-HCH was measured at the highest concentration followed by lindane, the gamma isomer of HCH, PCB, methoxychlor and lower levels of other CHP's was detected. A west-to-east decrease in concentration levels was observed and attributed to washing-out without replacement over the open water between them. The prevailing wind in this area was from west to east (22).

The same author continued his investigations and reported in 1988 (23) detection of alfa-HCH, 0.89-66 ng/L, lindane, 1-34 ng/L, dieldrin, n.d.-0.92 ng/L, endrin, n.d.-4.8 ng/L, p,p'-DDT, n.d.-1.2 ng/L.

Lindane and alfa-HCH was detected to be on the same level for two of the localities, one situated in the Great Lake area and the other close to Nova Scotia, until middle of September. But after September is seen an increase in the northern locality, indicating either a local release or a long-range transport (Fig. 1 and 2).

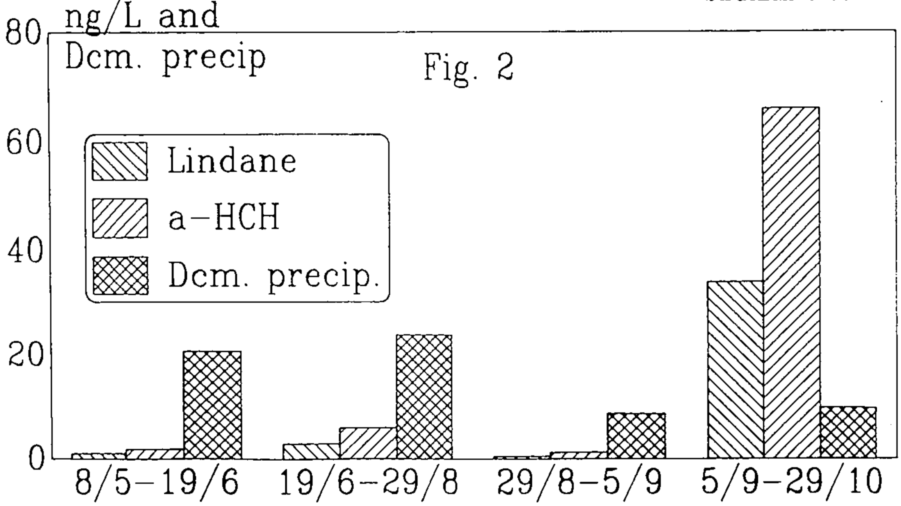
Lindane and a-HCH in rain at Agawa Bay, Canada, 1984.

Strachan 1988



Lindane and a-HCH in rain at Kouchibouguac, Canada, 1984.

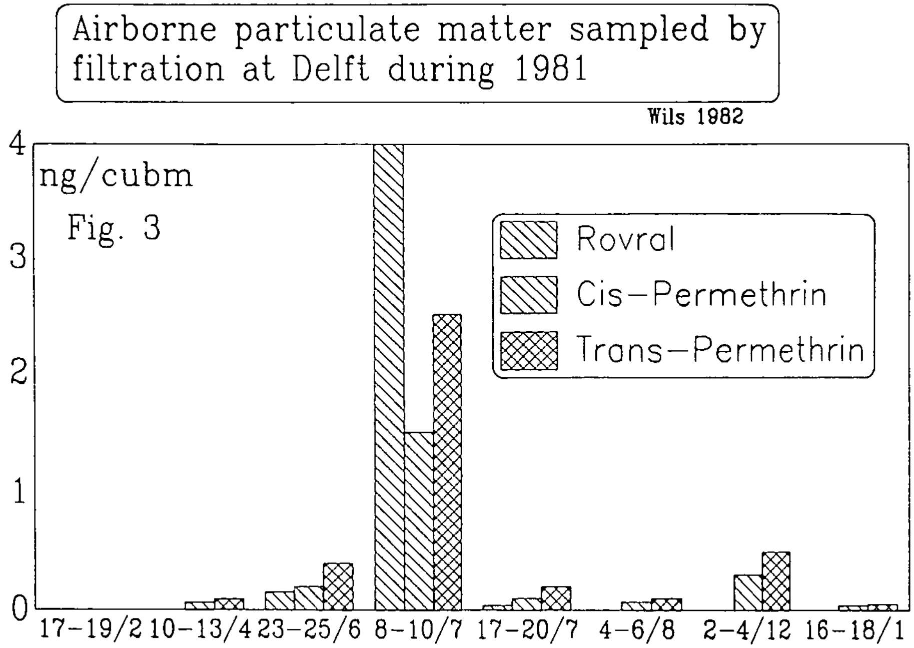
Strachan 1988



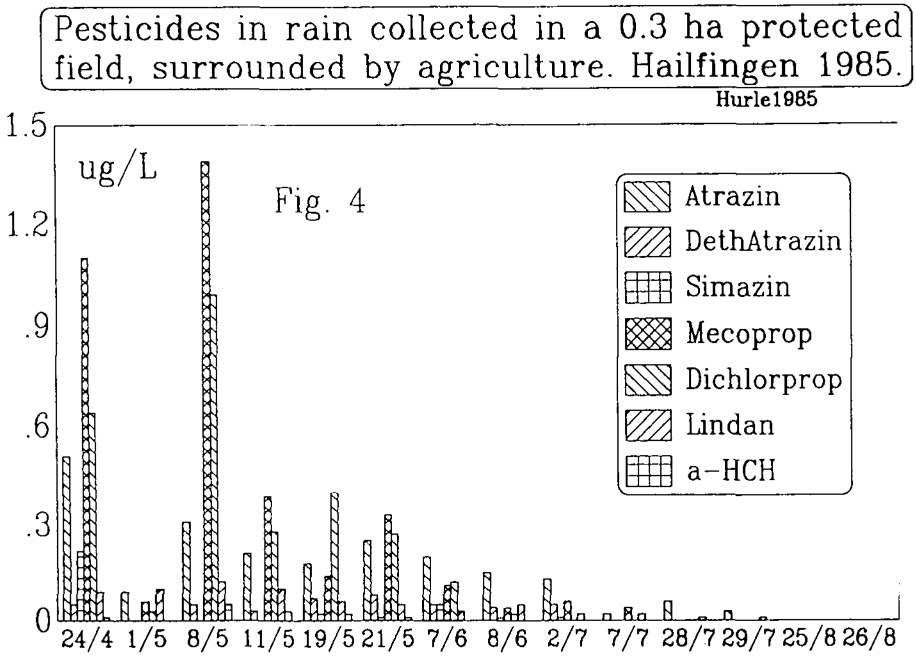
A review on pesticide deposition in the Great Lake area was made in 1981 (21). In this publication the author conclude for DDT's, a 1.5 to 5 times higher dry than wet deposition.

Up until 1981 only CHP was reported in rainwater. But atrazine was reported in Maryland 1981 as high as 2.19 µg/L (2).

In Delft, Holland, 1982 a fungicide, rovral, and synthetic pyrethroid insecticide, permethrin, was detected in air as particulate (24). The conc. of rovral was 4 ng/m^3 air, cis- and trans-permethrin approx. 2 ng. In these results are seen a seasonal correlation with concentration, highest for all compounds in the beginning of July. Permethrin could be detected as late as December in concentrations as high as 0.5 ng/L (Fig. 3).



In Germany near Köln in 0.3 ha protected area, but surrounded of traditional agriculture, rain samples contained atrazine, desethylatrazine, simazine, mecoprop, dichloprop, lindane and gamma-HCH, but not desethylsimazine and terbutylazine (26), (Fig. 4). The concentration of especially mecoprop was high, 1.2 to 1.5 ug/L, and also was a seasonal correlation observed in this report, with maximum at end of April to first of May and then declining. A decrease in conc. is seen the first of May. No precipitation data follow the report to explain this as a wash-out.



Seasonal variations of pesticides in rain, especially in agricultural areas, is reported in many papers and is illustrated from samples taken in Ohio and Indiana in 1985 (1) (Fig. 5). Wash-out of pesticides from the atmosphere reflects lower concentrations in the later samples (1) (Fig. 6).

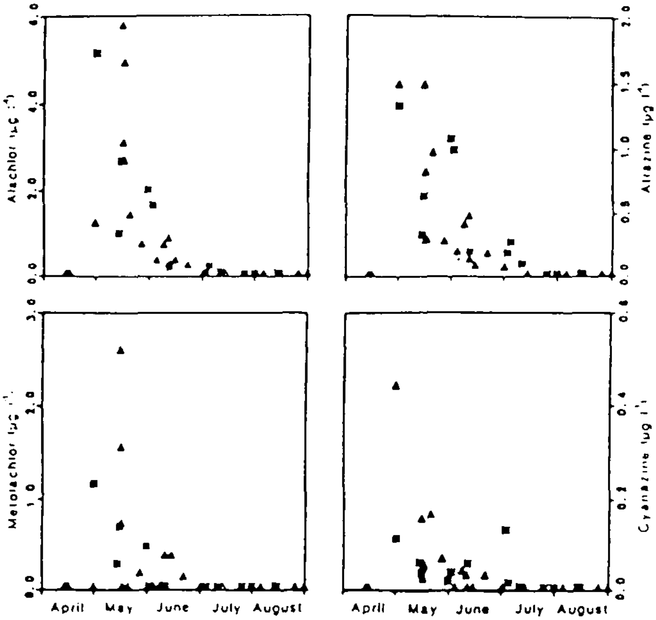


Fig. 5. Concentration of alachlor, atrazine, metolachlor and cyanazine in rain water, April through August 1985. Asterisks, samples from Indiana; triangles, samples from Ohio.

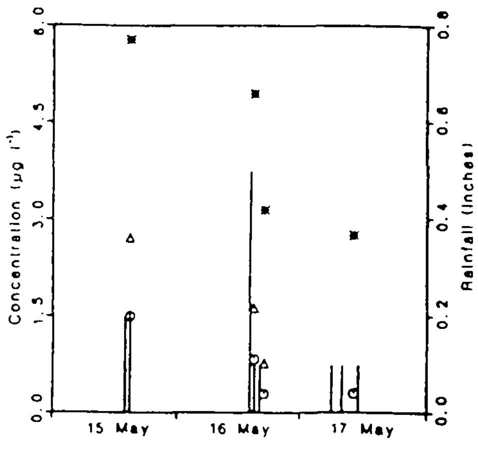
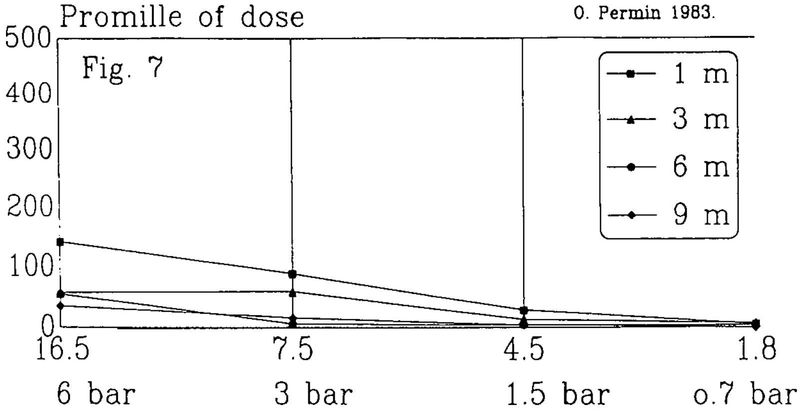


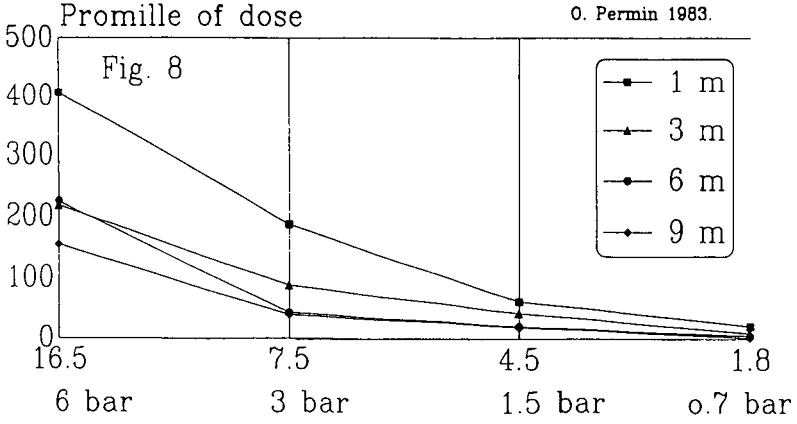
Fig. 6. Declining concentrations of alachlor (asterisks), metolachlor (triangles) and atrazine (circles) during a three-day rainy period at Tiffin, Ohio, 15-17 May 1985. Hourly rainfall is shown by the vertical lines.

The importance of sampling for background levels in non agriculture areas is best illustrated looking at reports dealing with wind drift. As seen on fig. 7 to 12, the drift is depending on the spray equipment (38, 39, 40). Furthermore it has been shown in numerous danish experiments (61), that normal recovery in wind drift experiments is around 80 to 90 percent using a fluorescent tracer. 10 percent immediate loss from agricultural sprayings, will definitely disturb background measurements.

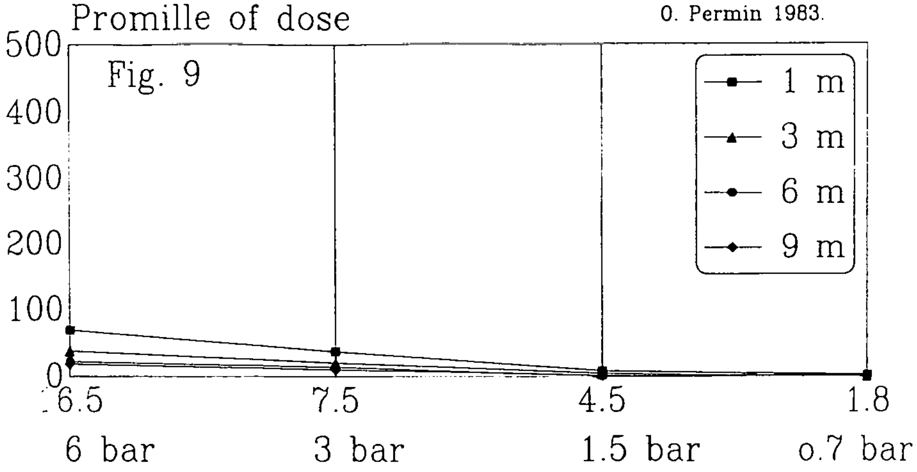
Spray drift of 200 l/ha, fan nozzle wind velocity 2-3 m/s, at 1, 3, 6 and 9 m distance versus % liquid applied in drops < 150 um.



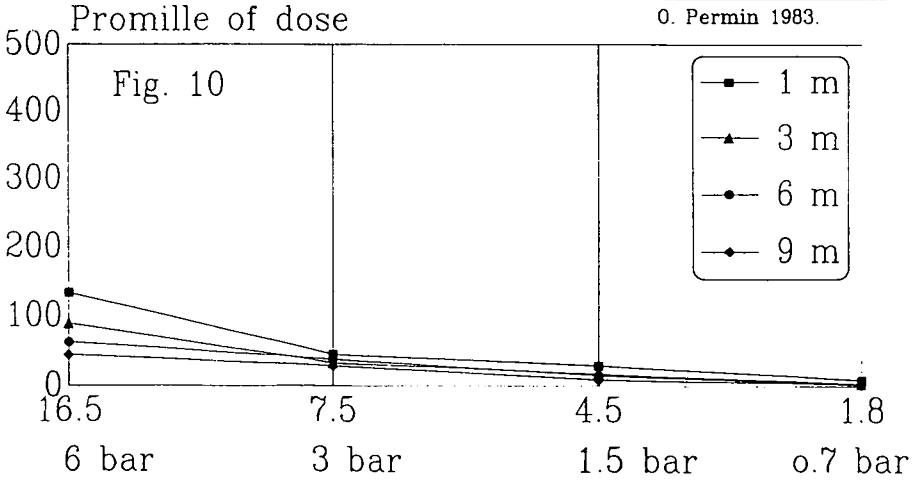
Spray drift of 200 l/ha, fan nozzle, wind velocity 5-7 m/s at 1, 3, 6 and 9 m distance versus % liquid applied in drops <150 um.



Spray drift of 400 l/ha, fan nozzle, wind velocity 1.5–3 m/s. at 1, 3, 6 and 9 m distance versus % liquid applied in drops <150 um.



Spray drift of 400 l/ha, fan nozzle, wind velocity 4–7 m/s at 1, 3, 6 and 9 m distance versus % liquid applied in drops <150 um.



Spray drift at 3 bar, fan nozzle, wind velocity 1-2 m/s, at 1, 3, 6 and 9 m distance versus liquid applied in drops < 150 um.

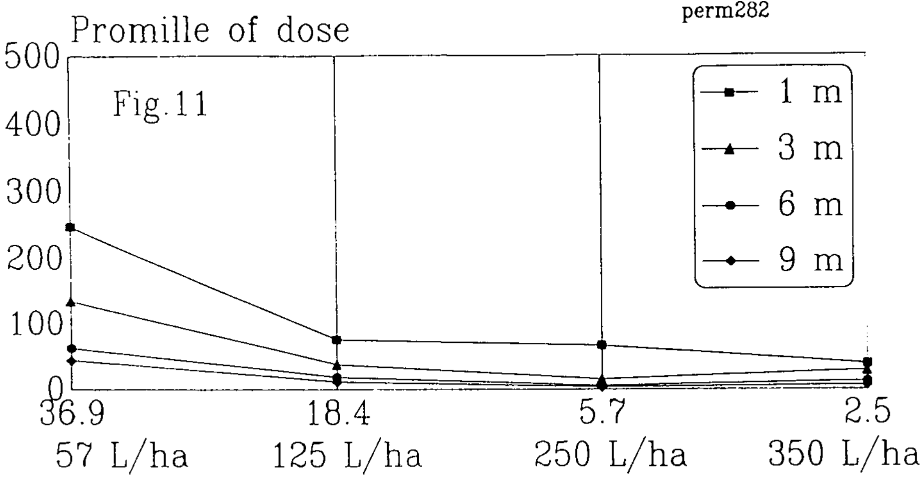


Fig.11

Spray drift at 3 bar, fan nozzle, wind velocity 4-6 m/s, at 1, 3, 6 and 9 m distance, versus liquid applied in drops < 150 um.

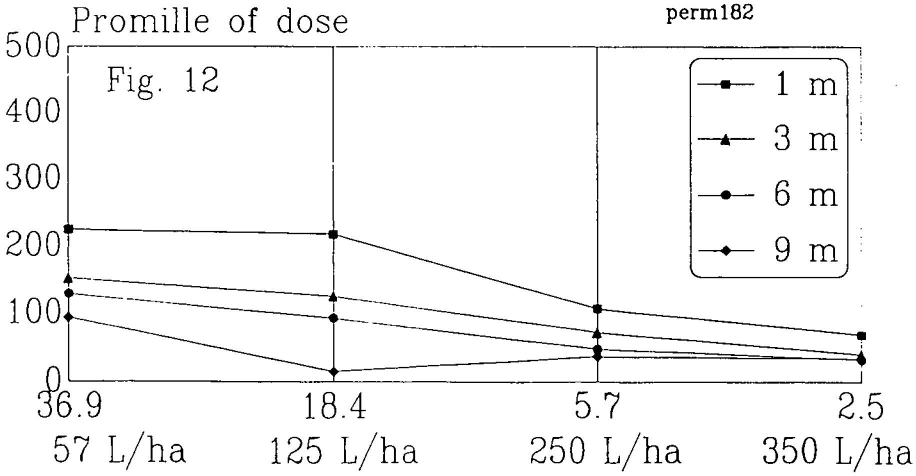
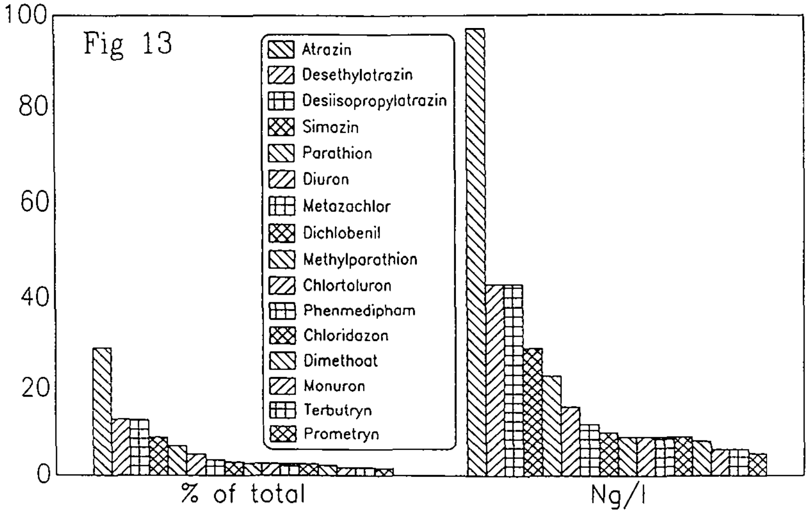


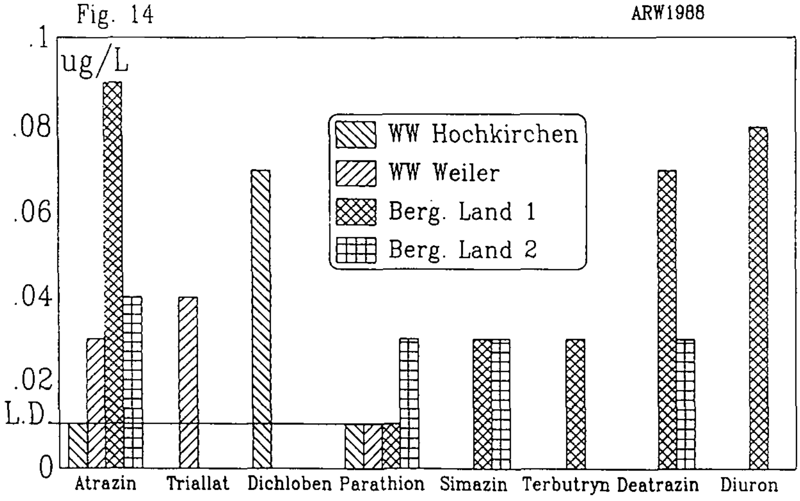
Fig. 12

Another German report (25), have found a wide variety of pesticides in water protection areas (non pesticide areas), collected first half of July (Fig. 13). The sum of the pesticides on one locality was 0.368 µg/L (Fig. 14). The local influence is limited in these investigations and may give an indication on a background of pesticide concentration in the area. No precipitation data before sampling follows the report.

Rain in Weiler (Koln), may to aug. 1988. ARW.



Selected pesticides from rain collected in water protection areas (non pesticide areas) in Germany. Samples collected 1-15/july 1988.



The first report of CHP in Scandinavia came in 1972 (28), later in 1973/74 (30), 1981 (31) and 1987 (32). Sampling of wet and dry deposition (29) resulted in detection of PCB's, DDT and DDE from the 11 stations placed from north to south at a distance of 1600 km. Highest deposition was recorded in the south and west part lowest in the northern part.

11 years later a similar sampling was done (27). It was concluded that the sum of DDT was significantly reduced. The level of PCB was nearly the same. The pattern of decreasing deposition from south to north found in the previous report, was repeated here indicating long range transport from southern sources outside Sweden responsible for deposition. This pattern was found also for DDT in the lower atmosphere. DDT, DDE and PCB was almost exclusively present in the gas phase, only in very few samples detectable in the particle filter.

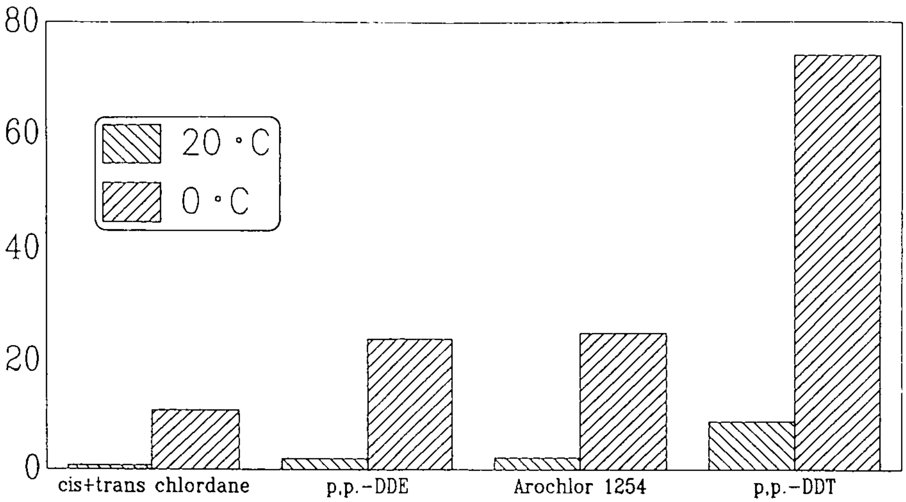
The average concentrations were positively correlated to mean temperatures of the sampling stations. Consequently, the levels of pollutants was higher during the warmer summer periods and lower during winter.

Distribution of DDT and other CHP in vapour/particles is shown by (32) and fig. 15.

Average percent filter retained organichlorines in urban air, Stockholm, Denver and Columbia.

Fig. 15

Bidleman87



The discussion in the literature of vapour/particle distribution is very intense (56, 57, 58, 59), but there is good agreement on the view that this type of measurements are difficult and often have a high degree of uncertainty associated with them.

High volume air samples taken in Stockholm and 100 km south of the city (32) showed among other measured pollutants, sum of p,p'-DDT and p,p'-DDE to be 7.2 pg/m^3, HCH 489 pg/m^3 and chlordane 8.4 pg/m^3. Ten years earlier the same type of investigations was done (30) on 20 locations from the south (Skurup) to the north (Kiruna) of Sweden. Data for each sample were not given, but average concentrations (arithmetic mean) of p,p'-DDT on each location were reported and ranked from 50 to 350 pg/m^3. The highest levels being observed during the summer. The arithmetic mean of all samples was 142 pg/m^3.

The use of DDT has been restricted in many countries the last 20 years, but it is used and needed especially in the tropics. DDT is still regularly in use in Africa, The Middle East, South East Asia, Southern hemisphere for malaria control and in agriculture (52, 53).

The swedish results show that banning of DDT 10 years earlier, resulted in lower levels, but levels was still high enough to influence zooplankton in Sweden (37).

It is thoughtful to read the report on the discovery of positive correlation between production and use of lindane, DDT, toxaphene and peat cores in northeastern part of the US. Even many years after stop using these chemicals, we can still find them in our environment (51).

Why do we mainly find CHP's in the samples? They are used very frequently and they are stable with half lives up to years. Sunlight metabolize the pollutants (54, 55) especially the OP (organophosphorous) compounds. The conversion of OP's to their respective oxones is done by UV-light and means an increase in toxicity. Evaluating the atmospheric pollution should include close metablites indicating the origin.

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NORDIC SEMINAR
Pesticides in the aquatic environment - appearance and effect
November 12-14, 1991. Tune Landboskole, Denmark.

BULK DEPOSITION OF HEXACHLOROCYCLOHEXANE (HCH).

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ABSTRACT

Bulk deposition of gamma-HCH (Lindane) and alpha-HCH has been measured monthly at two locations in Western Jutland, Denmark. Bulk deposition samplers collects wet deposition and some dry deposition. Each sampler consisted of a glass funnel mounted on a glass bottle. At the laboratory the samples were extracted with dichloromethane, cleaned up on a Florisil column and alpha- and gamma-HCH were quantified using capillary GC with EC detection.

Results from 1990 is presented. The total deposition for the two stations is quite similar. A one year deposition estimate to the area is approximately 2-3 $\mu g/(m^2$ year) of alpha-HCH and 15-17 $\mu g/(m^2$ year) of gamma-HCH. The deposition to the North Sea is estimated to about 10 tons HCH (alpha+gamma) per year.

The two stations roughly follows the same pattern of HCH deposition, indicating the absence of a pronounced local source. The concentrations and deposition of alpha-HCH varies less than gamma-HCH, the latter being between a factor 1 and 20 higher than alpha-HCH. High values of gamma-HCH are seen during spring and early summer probably caused by Lindane usage and long range transport.

INTRODUCTION

Hexachlorocyclohexane (HCH) is a persistent chlorinated organic compound, which may undergo atmospheric long range transport before wet and dry deposition. In ecosystems it may accumulate and cause biological effects.

HCH exists as several isomers with different orientation of the chlorine atoms. The two most important isomers, the alpha- and gamma-forms (Lindane) are shown i Fig. 1

a) alpha-HCH b) gamma-HCH (Lindane)

Fig. 1. Structure and orientation of atoms, alpha- and gamma-HCH.

Lindane is still used in Denmark as an insecticide, but in quite small amounts. From 1976 to 1990 there were traded between 5 and 15 tons per year. It is mainly used for seed coating, but also in forests, gardening, preservation of timber, and in minor amounts e.g. against ants and fleas. In Table 1 the yearly sales from 1976 to 1990 is shown (Bendixen, pers. com.).

In Western Europe Lindane (~99 % gamma-HCH) is used, but in some other countries is used the technical mixture of HCH, consisting of about 82% alpha, 13% gamma and 5% other isomers (Agarwal et al., 1987), gamma-HCH being the active insecticide.

Table 1. Sale of Lindane in Denmark in tons per year (Bendixen, pers. com.).

year	1976	1977	1978	1979	1980	1981	1982	1983
tons	11.6	9.1	11.4	11.3	12.4	9.0	8.7	7.3
year	1984	1985	1986	1987	1988	1989	1990	
tons	5.8	8.4	5.2	10.4	8.1	14.6	8.4	

The vapor pressures of alpha- and gamma-HCH are quite similar. The water solubility of gamma-HCH is about 5 times higher than that of alpha-HCH (Tatsukawa et al., 1972) (See Table 2).

Table 2. (After Tatsukawa et al., 1972).
Physical chemical data for alpha- and gamma-HCH.

	Solubility, water (ppm, 25°C)	vapor pressure (mm Hg, 20°C)
alpha-HCH	1.6	0.02
gamma-HCH	7.9	0.03

Several authors have found a higher gamma/alpha ratio in precipitation compared to air (Atlas & Giam, 1981; Bidleman & Leonard, 1982; Brorström-Lundén, 1991). This may indicate that gamma-HCH is more effectively washed out of the atmosphere compared to alpha-HCH.

In studies with glass fiber filters followed by an adsorbent generally a minor part of the HCH is found on the filter indicating a large part in the gas phase (e.g. Brorström-Lundén, 1991; Oehme & Stray, 1982), but this effect may however be caused by blow off from the filter to the adsorbent.

Johnson et al. (1986) used a diffusion denuder method (having the ability to distinguish between gas and particle phase) in sampling HCH from ambient air at a suburban location near Lake Ontario, Canada. They found a varying part of the air concentration in the particle and vapor phase. The mean values were 22 % alpha-HCH and 36 % gamma-HCH in the particle-associated fraction; Lindane predominantly found in the vapor phase near a suspected source.

In measurements of air concentrations alpha-HCH generally is found at a higher level than gamma-HCH (Oehme & Stray, 1982; Bidleman et al., 1987; Selenka & Eckrich, 1983; Johnson et al., 1986). Typical HCH concentrations measured in ambient air are roughly found at a level between 0.1 and 10 ng/m^3 for both alpha- and gamma-HCH in Europe and North America, lower in background areas and much higher levels are found in India (Kaushik et al., 1987).

In precipitation alpha- and gamma-HCH is found in a varying ratio with a tendency to highest levels of gamma-HCH in Western Europe (Brorström-Lundén, 1991; Villeneuve & Cattani, 1986) and highest levels of alpha-HCH in American studies (Strachan et al., 1980; Pankow et al., 1984; Strachan & Huneault, 1984; Ligocki et al., 1985) and in background areas (Bidleman & Leonard, 1982; Atlas & Giam, 1981; Pacyna et al., 1986). Typical levels in precipitation are between 1 and 50 ng/L for alpha- and gamma-HCH, much higher levels are found in India (Agarwal et al., 1987).

According to Pacyna et al. (1986) the gamma:alpha ratio seems to be useful to distinguish between sources of air pollutants measured in the Arctic. Gamma:alpha ratios ranging from 1:4 to 1:1 were found for the "European" air, 1:10 to 1:7 for North America and 1:10 to less than 1:100 for the former Soviet Union.

In sampling of wet deposition two principally different kind of samplers are used: wet-only samplers, which are only open when it is raining, and bulk samplers which are open all the time. The magnitude of the dry deposition depends on the surface characteristics and a funnel is less effective in sampling dry deposition compared to many natural surfaces. Dry deposition to a bulk sampler outside an emission influenced area is normally small compared to wet deposition.

HCH in precipitation can be sampled in bottles and determined after extraction of the rain water in the laboratory (Brorström-Lundén, 1991; Villeneuve & Cattani, 1986) or after in situ concentration on an adsorbent (Wells & Johnstone, 1978; Pankow et al., 1984; Strachan & Huneault, 1984). A review of sampling methods is made by Egebäck (1991)

Looking at alpha- and gamma-HCH together is very complex because:

- the sources can be pure gamma-HCH (Lindane) or the technical mixture of HCH (mainly alpha-HCH).
- photochemical isomerization may occur mainly resulting in conversion of the gamma form to the alpha form (Malaiyandi & Shah, 1984).
- gamma-HCH might be deposited faster than alpha-HCH.
- after deposition HCH might undergo microbial isomerization before reemission.

EXPERIMENTAL.

Sampling Stations.

The sampling stations are placed in forest clearings far from local sources of contamination such as industry and agricultural activity.

The samplers are placed in the terrain partly protected against high winds. This is done to minimize turbulent wind fields around the funnels leading to a under catch of small rain drops.

The location of the sampling stations is shown in Fig. 2.

Husby is placed in a fly sand area now covered with heath and low pine plantation 1 km from the coast.

Ulborg is placed in a forest clearing 3 km to nearest farmland and 19 km from the coast.

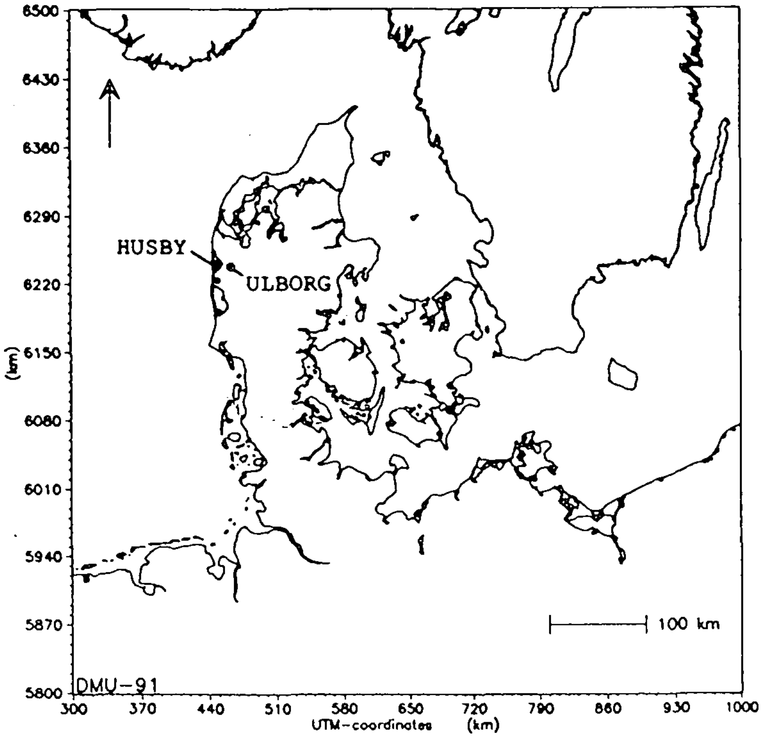


Fig. 2. Location of measuring stations: Ulborg and Husby Klit.

Sampling and analysis.

Bulk deposition is collected at the two stations.

At each station four samplers consisting of a glass funnel (diameter 20 cm) mounted to a glass bottle (2 liters) were used in parallel. The edges of the funnels were placed 1.5 m above the ground. The bottles were changed twice a month and the funnels were changed once a month.

In the winter time the bottles were protected from freezing by adding sodium chloride.

Two bottles from the first half of the month and two bottles from the second half were combined, resulting in two replicates per month. The sample volume was typical between 2 and 6 liters (four bottles).

At the laboratory the samples were extracted in the bottles, three times with dichloromethane on a magnetic stirrer for 30 minutes. The extracts from the four bottles were combined and concentrated (vacuum) to about 1 mL. Then the samples were added to a Florisil column for clean up. The first fraction were eluted with n-hexane, alpha- and gamma-HCH were eluted in the second fraction by using 1:1 dichloromethane:n-hexane. Dodecane was added as a keeper before the eluates were concentrated (nitrogen) to dryness and soluted in 1 mL of iso-octane. Pentachlorobenzene was used as internal standard.

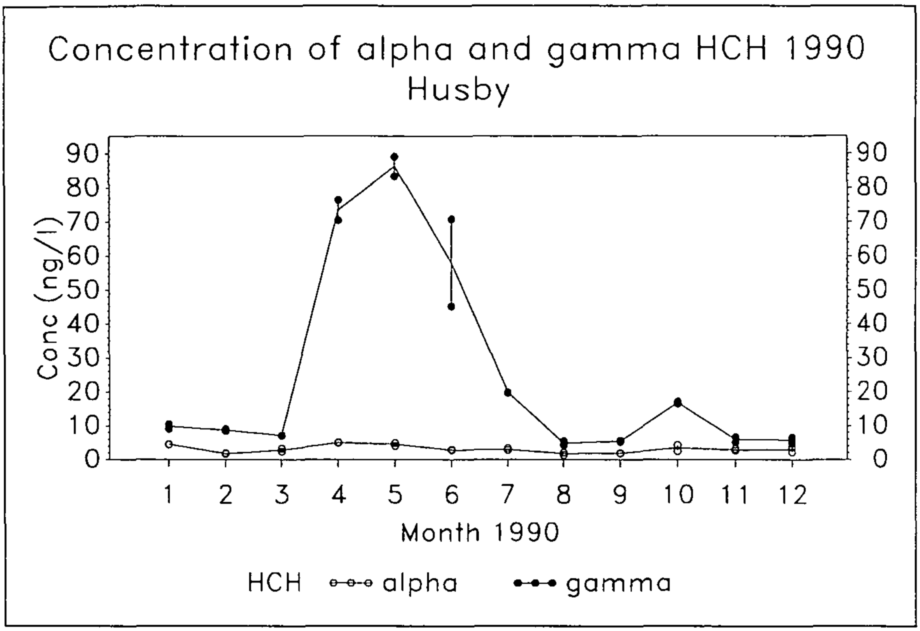
The quantification of alpha- and gamma-HCH was made on a HP 5890 series II gaschromatograph (GC) with an electron capture detector. The column was a 60 m x 0.25 mm i.d. fused silica with 0.1 µm 5% cross-linked phenylmethylsilicone (DB-5) and the GC was equipped with a HP 7673 autosampler and a HP Vectra PC QS/20 for data analysis. The identification was checked on a 60 m x 0.25 mm i.d. fused silica column with 0.15 µm 14% cross-linked cyanopropylphenyl (DB-1701).

The detection limit was below 0.5 ng/L rain water for a 2 liter sample. Blank values (purified water in bottles following the normal procedure) was not detectable. The recovery for the clean up procedure and the GC analysis was 0.80 ± 0.08 (s.d.) for alpha-HCH and 0.80 ± 0.06 (s.d.) for gamma-HCH; the results were corrected with this figures. Furthermore there was a loss in the extraction step at about 20 % for alpha-HCH while there was no detectable loss of gamma-HCH.

RESULTS AND DISCUSSION.

Results from bulk deposition measurements of alpha- and gamma-HCH at the two stations Ulborg and Husby Klit, Western Jutland, Denmark, as monthly figures (1990) are shown in Figs. 3 - 7.

Fig. 3 shows the concentration of alpha- and gamma-HCH at the Husby and Ulborg station during the year 1990. The two stations follows the same picture: gamma-HCH gives higher values than alpha-HCH. Especially in spring and early summer a large peak was found for gamma-HCH.



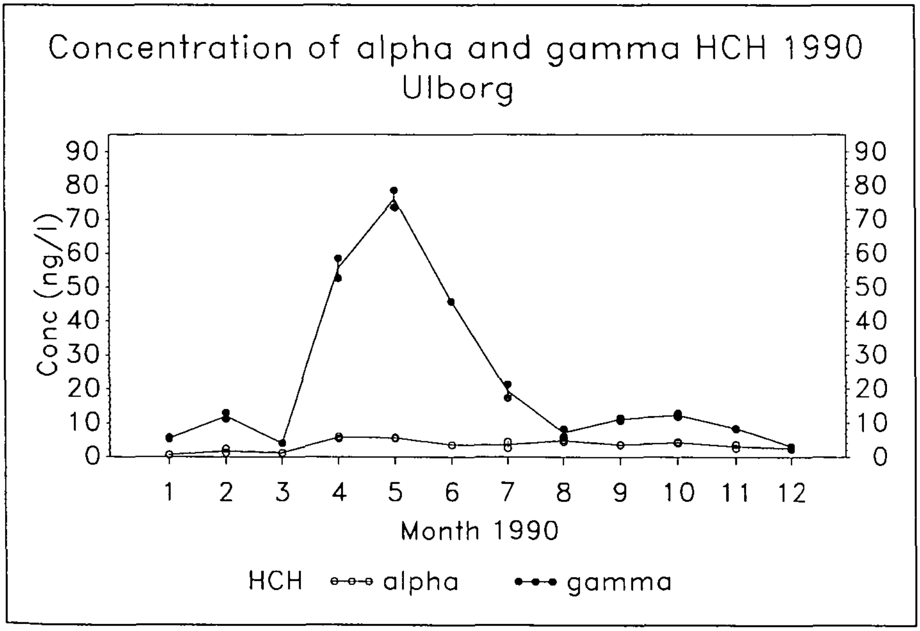
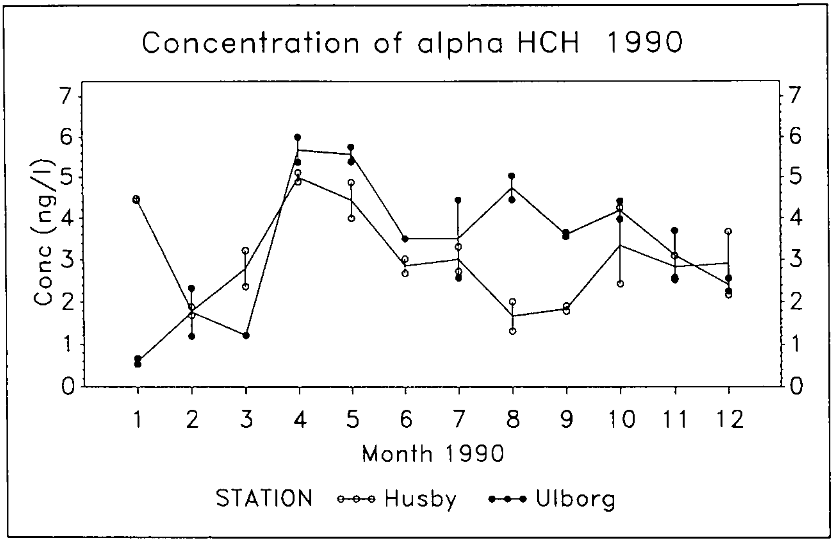


Fig. 3 HCH concentrations (ng/L) measured in bulk deposition sampled at Husby (above) and Ulfborg (below) 1990.

In Fig. 4 (below) gamma-HCH is plotted for the two stations together. It is seen that the peak is a little bit higher for the Husby station.



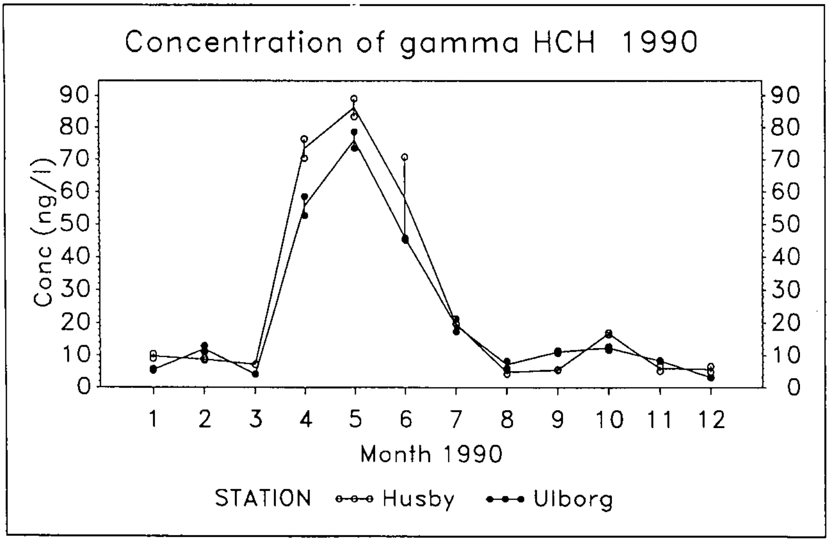


Fig. 4. Concentrations of alpha-HCH (above) and gamma-HCH (below) (ng/L) in bulk deposition at Husby and Ulfborg 1990.

Fig. 4 (above) shows the concentration of alpha-HCH in a smaller scale. Even though the concentrations are highest in April and May the concentration during the year is much more constant compared to gamma-HCH.

The ratio between gamma- and alpha-HCH is plotted in Fig. 5. Gamma:alpha ratios between 1:1 and 20:1 are found with highest ratio in spring and early summer.

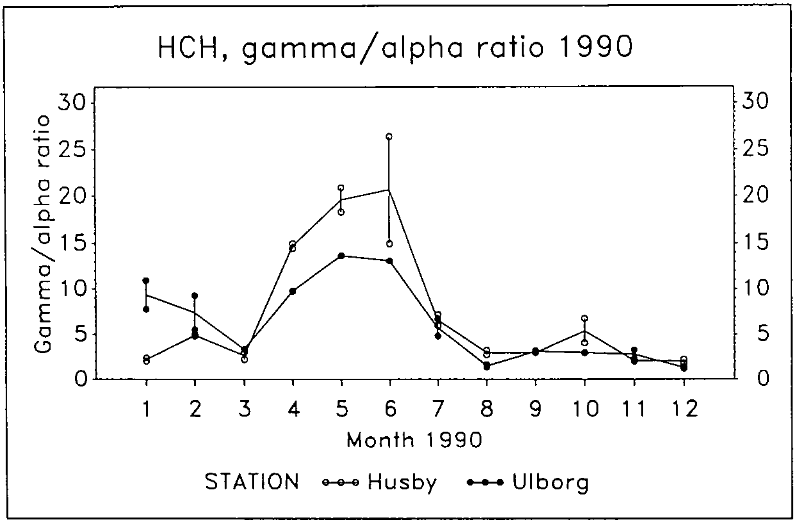


Fig. 5. Ratio between gamma- and alpha-HCH found in bulk deposition at Husby and Ulfborg 1990.

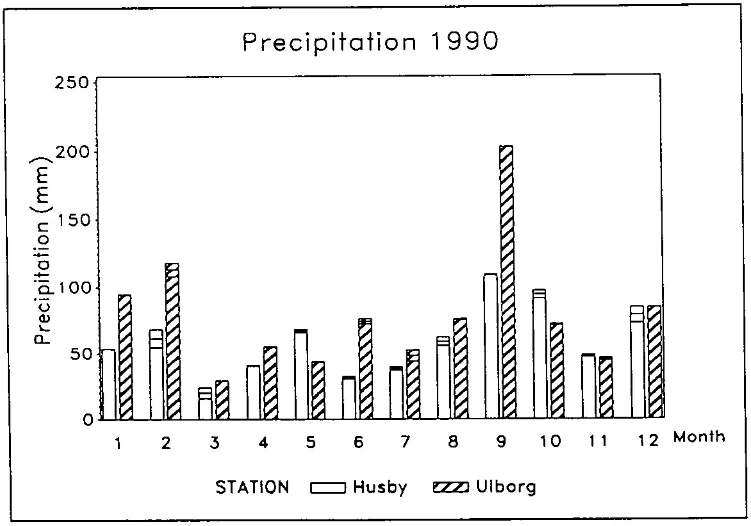


Fig. 6. Amounts of precipitation (mm) sampled at Husby and Ulfborg 1990. (Minimum, mean and maximum value indicated for each month).

The amount of precipitation sampled at the two stations is shown in Fig. 6. Annual precipitation rate is highest at Ulborg, as Husby is closer to the coast.

The deposition of gamma-HCH is shown in Fig. 7 (below). A top in the spring and early summer is caused by high concentrations and a smaller top in September-October is caused by high amounts of precipitation.

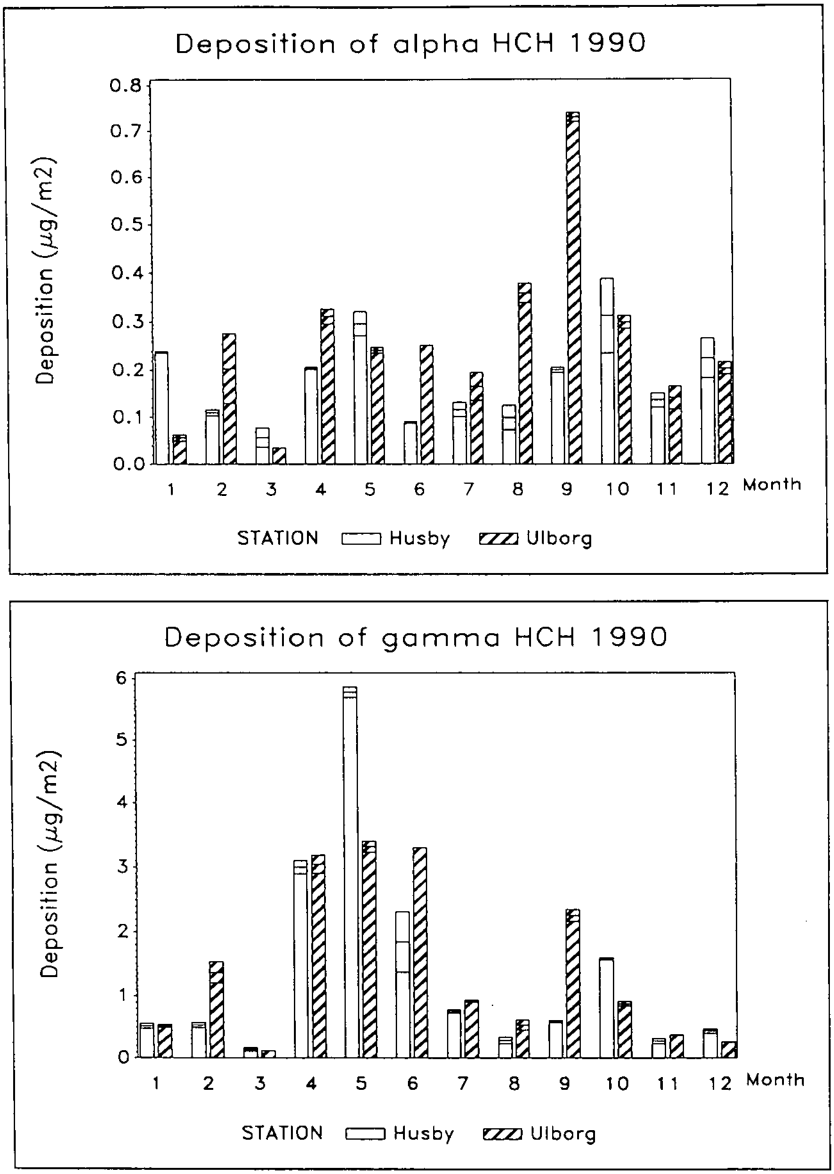


Fig. 7. Bulk depositions of alpha-HCH (above) and gamma-HCH (below), µg/(m^2 month), at Husby and Ulfborg 1990.

Fig. 7 (above) shows the deposition of alpha-HCH. As for the concentrations the deposition is more constant during the year compared to gamma-HCH.

There are several possible explanations for the gamma-HCH peak in spring and summer:

- a local source of Lindane: The equal patterns of the two stations indicates the absence of a pronounced local source.
- reemission of earlier deposited HCH when the weather gets warm in the spring: If this was the case we would probably find the same pattern for alpha-HCH too.
- wind directions varying during the year: This is very difficult to look at with only monthly values. There is a tendency to more eastern wind directions in April and May, but not in June).
- use of Lindane during spring and summer followed by long range transport: This might be a proper explanation.

The concentration peak is slightly higher at Husby compared to Ulborg. Husby has less precipitation than Ulborg. If we assume the same air concentrations in Husby and Ulborg, the precipitation in Husby might get higher gamma-HCH concentrations by wash out of gamma-HCH from the air.

Table 3 shows the precipitation weighted mean concentrations for the year and the total deposition with standard deviations. The alpha-HCH concentrations are alike for the two stations but the gamma-HCH concentration are slightly higher for Husby. Ulborg has more precipitation than Husby, which means a relatively higher deposition.

Table 3. Precipitation weighted mean concentration and total deposition (with standard deviations) for the year 1990.

Total 1990		Husby	Ulborg
Precipitation (mm)		702 ± 11	938 ± 7
Concentration	alpha	3.0 ± 0.2	3.2 ± 0.1
(ng/L)	gamma	22.5 ± 1.1	18.0 ± 0.6
Deposition	alpha	2.1 ± 0.1	3.0 ± 0.1
($\mu g/m^2$)	gamma	15.8 ± 0.5	16.9 ± 0.4

The deposition of HCH (alpha + gamma) was found to about 19 $\mu g/(m^2$ year); which corresponds to 1.5 tons per year to the area of Denmark (~80.000 km^2, including sea area). This figure is about 18 % of the amount traded in Denmark in 1990 (8.4 tons). A deposition of about 18 % of the amount used (mainly seed coating) indicates long range transport.

Bulk deposition of HCH to the North Sea (525.000 km^2) is from the measurements in this study estimated to 10 tons/year. An earlier estimate by Wells & Johnstone (1978) is 2.1 tons/year. Aalst et al. (1983) has estimated the dry deposition to between 10 and 100 tons/year, derived from measurements in Delft, Netherlands. These atmospheric inputs should be compared to an estimated river input of 2.5 tons/year (Aalst et al., 1983).

CONCLUSIONS

- gamma-HCH is found in precipitation at higher levels than alpha-HCH.
- there is observed a peak for gamma-HCH in spring and early summer probably caused by use of Lindane followed by long range transport.
- The two stations Husby and Ulborg follows the same pattern and have almost the same levels. This indicates the absence of a pronounced local source.
- the deposition for the area is measured to 2-3 $\mu g/(m^2$ year) for alpha-HCH and 15-17 $\mu g/(m^2$ year) for gamma-HCH.
- The estimated deposition of HCH (alpha + gamma) to the area of Denmark is about 18 % of the amount traded in 1990 (mainly seed coating) indicating long range transport.
- deposition to the North Sea is from the measured deposition estimated to about 10 tons per year.

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NORDIC SEMINAR
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OCCURRENCE OF PESTICIDES IN NORDIC SURFACE WATERS

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SUMMARY

During the past couple of years, there has been an increased number of monitoring programs concerning pesticides in surface waters throughout the Nordic countries, all with somewhat varying objectives. There are large differences between the programs in the number of sampling sites selected, the number of samples collected and the number of pesticides being analysed.

Pesticides have been found in surface waters in all four Nordic countries. During the last six years, 35 different pesticides have been detected, including 25 herbicides, 7 insecticides and 3 fungicides. Most of these were found at low concentrations and on single occasions. The most frequently found substances, in all investigations, have been the highly used phenoxy acid herbicides dichlorprop and MCPA. In Swedish investigations the herbicide bentazone has been detected regularly throughout the year. These substances have also been found at the highest concentrations, along with the herbicide metamitron which is used in large amounts in sugar beet cultivations. The triazine herbicide atrazine, mainly used on non-agricultural areas, have been found regularly in many of the investigations.

There are presently ongoing investigations of pesticides in surface waters in the four Nordic countries. To constitute a basis for exposure assessment, monitoring in the future should improve the sampling strategies to increase evaluation possibilities. Minimum background data for adequate evaluation should include the following: watershed size, land use pattern, soil type, precipitaiton, water flow rate, amount and type of pesticides used and spraying season. For better recommendations to the users on how to minimize losses of pesticides to the waterbodies, there is also a strong need to increase our knowledge of the different transport pathways within a watershed, including all possible processes (spills, runoff, leaching, wind drift etc.).

INTRODUCTION

There has been, until recently, little information within the Nordic countries on exposure data for current generation pesticides in surface waters. This can partly be ascribed to restrictions in analytical methods for scanning a wide variety of currently used pesticides in a single analytical run. In addition, no specific water quality standards for either surface water, irrigation water or drinking water were established for commonly used pesticides. During the late 1980-s various programs have been set up to improve knowledge of pesticide residues in surface waters within the Nordic countries. A summary of the results of different monitoring studies and a discussion on how to improve monitoring in the future will be given below.

PESTICIDES IN SURFACE WATERS IN THE NORDIC COUNTRIES

During the past couple of years, there has been an increase in monitoring programs concerning pesticides throughout the Nordic countries, all with somewhat varying objectives. There are large differences between the programs in the number of sampling sites selected, the number of samples collected and the number of pesticides included in the analyses of the water samples (Table 1).

Denmark

The first investigation of pesticides in Danish stream waters started in 1990 (Bügel Mogensen & Spliid, 1991). Samples from two survey areas, each with two stream water stations, have been analysed for eleven herbicides. Also, soil water and drainage discharge within the areas were analysed. One area consists of clayey soil and the other of sandy soil.

Pesticides were detected throughout the year, with the phenoxy acid herbicides (i.e. 2,4-D, dichlorprop, MCPA and mecoprop) being found most frequently in May-June and in October-November. Of the two watersheds, more substances, and at higher concentrations, were found in the one with clayey soil. The maximum concentration found was 5.3 µg/l of mecoprop.

In the area with the clayey soil , the occurrence of pesticides in stream water was more frequent and the concentrations higher than in soil water and in drainage water. This result indicates that there are additional important sources of pesticide contamination of stream water apart from leaching. In the sandy soil area, the concentrations of pesticides in stream water were instead a little below those found in soil water.

Table 1. Summary of pesticide monitoring studies in surface waters in the Nordic countries, 1966-1990.

Country	Years	No of sites	No of samples	No of pesticides	References
Denmark	1990-	4	69	11	Bügel Mogensen & Spliid, 1991
Finland	1975	19	19	3	Kiviranta & Miettinen, 1976
Finland	1985-1987	2	33	21	Rekolainen, 1989
Finland	1991-	10	ca 80	80	Hirvi, 1991
Norway	1986	5	15	2	Berglind, 1987
Norway	1987	8	52	15	SPV & GEFO, 1987
Norway	1989-	6	ca 60	15	Nilsen, 1991
Sweden	1966-1969	153	153	3	Erne, 1970
Sweden	1983	5	5	4	Öresundskommisionen, 1984
Sweden	1985-1987	29	259	80	Kreuger & Brink, 1988
Sweden	1988	56	112	17(80)	Sandberg & Erlandsson, 1990
Sweden	1988-1990	170	840	7-80	Åkerblom, 1991a
Sweden	1989-1990	6	55	80	Dich et al.
Sweden	1990-	1	54	31(80)	Kreuger, 1991
Sweden	1991-	ca 30	ca 70	7-80	Åkerblom, 1991b

Finland

In October 1975, nineteen larger rivers were sampled on one occasion and the water analysed for phenoxy acids and chlorinated phenols (Kiviranta & Miettinen, 1976). MCPA (0.2-1.6 μg/l), 2,4-D (0.2-8.0 μg/l) and 2,4,5-T (0.1-6.8 μg/l) were found in 26%, 42% and 58% of the investigated rivers respectively. Chlorinated phenols, originating from wood industry preservatives, were found in almost 80% of the investigated rivers, but at lower levels than the phenoxy acids.

During 1985-1987 two agriculturally loaded rivers were investigated and the occurrence of about twenty currently used pesticides were analysed (Rekolainen, 1989). In total, 14 substances were detected. The phenoxy acid herbicides MCPA, dichlorprop and mecoprop were present in 60-70% of the samples and peak concentrations reached 5 μg/l. In the rainy summer of 1987, relatively high concentrations of metamitron, dinoseb, propachlor and dimethoate (3.1-4.6 μg/l max. conc.) were also detected. The peak concentrations, and also in many cases the overall occurrence were found to be highly dependent on rainfall events after the application period.

Norway

In 1986, five small streams were investigated and analysed for the phenoxy acids MCPA and dichlorprop (Berglind, 1987). They were detected at all sampling locations and the maximum concentrations of MCPA and dichlorprop were 0.5 μg/l and 6.2 μg/l respectively.

The following year (1987) a more extensive investigation was carried out in eight rivers, with 15 commonly used substances being analysed (SPV & GEFO, 1987). Pesticides were found in six of the rivers and five different substances were detected at concentrations between 0.2 and 14 μg/l. Dichlorprop was the most frequently found substance.

Four county administrations have been participating in a monitoring program since 1989 as a part of a governmental plan for environmental pollution control (Nilsen, 1991). There are differencies between the counties in sampling intensity and the number of substances being analysed. A maximum of 15 different pesticides are included in the analyses. The first results showed that some herbicides were frequently present in stream water at low concentrations, but with occasional elevated concentrations (2-4 μg/l).

Sweden

During 1966-1969 samples were collected from 153 sampling sites along major rivers throughout the country (Erne, 1970). The samples were analysed for phenoxy acids and chlorinated phenols. The detection limit was 2 μg/l and positive samples of phenoxy acids were found in 29% of the river water samples. Several very high residue values were encountered (>1000 μg/l), but these, along with a major proportion of the smaller values, were known to be the result of different kinds of discharges and accidental spills.

In June 1983, five rivers in the south of Sweden were sampled on one occasion and phenoxy acids were detected at an average concentration of 14.7 μg/l (Öresundskommissionen, 1984).

During 1985-1987 a more intensive program for pesticide monitoring in stream waters was undertaken (Kreuger & Brink, 1988). Methods for analysing about 80 currently used pesticides were developed (Åkerblom & Jansson, 1986). Streams in agricultural areas were selected and sampled at monthly intervals during May-September. The number of sampling sites increased from 7 to 29 during the three year period.

Eighteen compounds were identified, including eleven herbicides, two fungicides and five insecticides. The most frequently found pesticides were the phenoxy acids (63% of the positive samples) with peak concentrations at the time of spraying (May-June). During the non-spraying season the concentrations were lower, between 0.1 and 1.0 μg/l. Throughout the three years, positive samples of one or several compounds of phenoxy acids occurred in 37% of the water samples taken in May, 78% in June, 57% in July, 24% in August and 18% in September. The maximum measured concentration of total content of phenoxy acids in one single stream was 25 μg/l. Along with the phenoxy acids, the herbicide atrazine was found in some streams during the whole sampling season. In large watersheds or watersheds with only smaller parts of the area being used for agricultural production, no pesticides were found or only small amounts were detected on single occasions. Thirteen of the eighteen identified compounds were only detected in water from streams in the intensely cultivated areas (average 65% agricultural land in the investigated watersheds) in the very south of Sweden.

In 1988, the National Food Administration investigated the pesticide content of municipal drinking water originating from 56 surface water supplies all over Sweden (Sandberg & Erlandsson, 1990). Water from each supply was sampled on two different occasions, once in the beginning of the summer and once in the autumn. Seventeen pesticides were included in the analyses at the normal detection limits (0.1-0.5 μg/l), with another 60 pesticides being included in the analyses at levels 2-10 times above normal (Åkerblom et al., 1990). Detectable amounts of pesticides were determined in three cases at low levels (0.1-0.9 μg/l) in early summer in the untreated drinking water. However, no pesticides were detected in the finished drinking water for human consumption. The pesticides found were MCPA, dichlorprop and bentazone.

During 1988-1990, many county administrations included pesticides in their environmental monitoring programs for water pollution control (kerblom, 1991a). Samples were collected from a total of 170 sampling sites in 14 counties. There were differences between the counties in sampling intensity, from once a year to twice a week during the spraying season. 840 surface water samples were collected throughout the three years. Also the number of substances included in the analyses varied, from only the phenoxy acids and related compounds, up to a maximum of around 80 substances (compare Table 1 in Åkerblom, 1991a).

Twenty compounds were identified, including 15 herbicides, 1 fungicide and 4 insecticides. The most frequently detected pesticides were MCPA and bentazone, which were found in more than 20% of the samples. Eleven of the twelve most frequently found pesticides, found in 0.6% or more of the analysed samples, were also encountered in the previous investigation in 1985-1987. Eight of the detected pesticides were found only once or twice throughout the three years. Pesticides occurred most frequently and at highest concentrations during the spraying season, but low concentrations were found during the whole year, especially of phenoxy acids and bentazone. The frequency of several of the pesticides (i.e. phenoxy acids, bentazone and metazachlor) has decreased during the three years, seemingly due to a sales reduction of some of these substances and also to an increased knowledge of the correct handling of pesticides among farmers. It is, however, difficult to make definite statements concerning the reasons for this apparent decline in pesticide residues in water due to the varying sampling strategies, both between years and between counties. In several counties pesticides are continuously included in the monitoring programs of surface water quality (Åkerblom, 1991b).

During 1989-1990 the industry carried out an investigation of chemicals in Swedish waters, including pesticides (Dich et al.). Altogether 55 surface water samples were taken from five rivers and one lake, with connection to drinking water supplies. The samples were analysed for around 80 different pesticides, including the low dose sulfonylurea herbicides chlorosulfuron and metsulfuron. Phenoxy acids along with bentazone were detected in eight of the samples at low concentrations (0.1-0.3 μg/l). No sulfonylureas were detected.

In 1990, a watershed in the southernmost part of Sweden was selected for intensive investigation of pesticide exposure patterns, including sampling technique, transport processes and estimation of average losses (Kreuger, 1991). The watershed has an area of 9 km^2 consisting of 95% arable land (clay soil). Information on pesticide usage (type of pesticides, amounts and spraying occasions) and handling within this area is collected annually from the farmers. Around 40 different substances were used during 1990 and nearly 80% (by weight) of these were included in the analyses. At the outlet of the watershed an automatic sampler (ISCO model 2700) collected, on a daily or weekly basis, time integrated water samples from May to September. Pesticides were detected throughout the sampling season with peak concentrations at the time of spraying and elevated concentrations also during storm flow events. During this period, 0.1-0.2% of the phenoxy acids used and 0.7% of bentazone used were lost from the watershed, with maximum concentrations of 40, 20 and 10 μg/l for MCPA, dichlorprop and bentazone respectively. Two pesticides used on farmyards, atrazine and terbuthylazine, were also frequently found in the water samples. Altogether, 15 different substances were detected at the outlet of the watershed, including 13 herbicides, 1 fungicide and 1 insecticide. In sediment samples taken in July, 2 fungicides and 1 insecticide were found. Two of these were only detected in the sediment samples and never in the water samples.

General conclusions of Nordic monitoring studies

During the last six years, 35 different pesticides have been detected in Nordic surface waters, including 25 herbicides, 7 insecticides and 3 fungicides (Table 2). Most of these were found at low concentrations and on single occasions. The table does not comprise substances included in the analyses of an investigation and that were not detected on any

Table 2. Pesticides detected, and their respective maximum concentrations, in different monitoring studies accomplished since 1985 within the Nordic countries

Substance	Type	Denmark Max. conc. µg/l	Finland Max. conc. µg/l	Norway Max. conc. µg/l	Sweden Max. conc. µg/l
atrazine	h	0.3	n.a.	1.8	9
bentazone	h	n.a.	n.a.	n.a.	80
bromacil	h	n.a.	n.a.	n.a.	1
bromoxynil	h	0.5	n.a.	n.a.	n.d.
chlorsulfuron	h	n.a.	n.a.	0.12	n.d.
cyanazine	h	n.a.	n.a.	n.a.	3
2,4-D	h	0.6	0.14	n.a.	1
dichlorprop	h	0.7	4.5	6.2	20
dimethachlor	h	n.a.	n.a.	n.a.	0.3
dimethoate	i	n.a.	4.6	n.d.	n.d.
dinoseb	h	0.01	3.1	n.a.	n.a.
DNOC	h	0.2	n.a.	n.a.	n.a.
a-endosulfan	i	n.a.	0.02	n.a.	0.07
fenitrothion	i	n.a.	0.06	n.d.	0.1
ioxynil	h	0.1	n.d.	n.d.	n.d.
lenacil	h	n.a.	n.a.	n.a.	0.7
lindane	i	n.a.	n.a.	n.d.	0.6
linuron	h	n.a.	2	n.d.	2
malathion	i	n.a.	n.a.	n.a.	0.1
MCPA	h	0.6	3.2	2.8	40
mecoprop	h	5.3	3.9	n.a.	6
metabenzthiazuron	h	n.a.	n.a.	n.a.	0.6
metalaxyl	f	n.a.	n.a.	n.d.	1.3
metamitron	h	n.a.	4.2	n.a.	45
metazachlor	h	n.a.	n.a.	n.a.	7
metoxuron	h	n.a.	n.a.	n.a.	0.3
metribuzine	h	n.a.	n.a.	0.4	3
permethrin	i	n.a.	n.a.	n.d.	0.6
pirimicarb	i	n.a.	4.6	n.a.	4
propachlor	f	n.a.	n.a.	14.3	5
propiconazole	f	n.a.	n.a.	0.4	3
simazine	h	0.04	0.7	4.5	1.1
terbuthylazine	h	n.a.	0.17	n.d.	1.1
trifluralin	h	n.a.	0.23	n.a.	n.d.
vinclozolin	f	n.a.	n.a.	n.a.	0.5

n.a. = not analysed; **n.d.** = not detected.
h = herbicide; f = fungicide; i = insecticide.

occasion. The most frequently found substances, in all investigations, have been the commonly used phenoxy acid herbicides dichlorprop and MCPA. In Swedish investigations, the herbicide bentazone has been detected regularly throughout the year. These substances have also been found at the highest concentrations, along with the herbicide metamitron which is used in large amounts in sugar beet cultivations. The triazine herbicide atrazine, mainly used on non-agricultural areas, have been found regularly in many of the investigations.

MONITORING IN THE NINETIES

In the Swedish Government-s environmental proposition (En god livsmilj, 1991) it is stated that "the aim is that no pesticide residues should occur in surface- and ground water". This high ambition is to be attained by several different actions, including among others increased supervision, intensified information, education and research. Also mentioned is improved monitoring, forming a basis for the authorities to evaluate changes as a consequence of the proposed actions (LBS, 1991).

Environmental risk assessment includes estimations of both exposure and toxicity of pesticides in the aquatic environment. Toxicity assessment, including acute and chronic testing, and considering synergism and environmental factors, is not the topic of this paper, but should be remembered in the overall discussion.

For adequate exposure assessment, as a part of risk evaluation, we need good quality data on pesticide exposure patterns and characteristics. The ecological effects of pesticides on flora and fauna in surface waters is dependent on both peak concentrations and the time of exposure. The objectives of the majority of the above mentioned investigations have been to find whether concentrations of pesticides could be detected in surface waters on single occassions. This is not enough to assess the ecological risks posed by pesticides in surface waters. To constitute a basis for exposure assessment, monitoring in the future should improve the sampling strategies to increase evaluation possibilities. Also when regulatory pollution control measurements are determined, transport calculations are useful in evaluating possible changes. Minimum background data for adequate evaluation should include the following: watershed size, land use pattern, soil type, precipitaiton, water flow rate, amount and type of pesticides used and spraying season.

For better recommendations to the users on how to minimize losses of pesticides to the waterbodies, there is also a strong need to increase our knowledge of the different transport pathways within a watershed, including all possible processes (spills, runoff, leaching, wind drift etc.).

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NORDIC SEMINAR
Pesticides in the aquatic environment - appearance and effect
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PESTICIDES IN WATER - PAST AND FUTURE NATIONAL MONITORING PROGRAMS IN SWEDEN

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The Swedish environmental protection agency has sponsored a monitoring program concerning the impact of agriculture on the aquatic environment, the so-called "Jordbrukets recipientkontroll, JRK". The studies have been undertaken by the authori-ties in the different counties. They have included monitoring of nutrients as well as pesticides, mainly in streams but also in wells and ground water tubes. The studies are presently under evaluation, and a future monitoring program will be suggested, based on hitherto gathered experiences from the monitoring program as well as from other investigations. Here some glimpses from the pesticide part of this work will be given.

RESULTS OF MONITORING 1988-1990

From 1988 to 1990 water was sampled in fifteen of the twenty-four Swedish counties for the determination of pesticide resi-dues. In one county streams were monitored for pesticides already in 1987. Surface water was monitored in all but one county. Ground water was monitored in the I-county (the island of Gotland), which has a special geolocigal situation. In all, a little more than a thousand samples were analysed for phe-noxy acid herbicides, bentazone and clopyralide. Half of these samples were also analysed for about 80 different insectici-des, fungicides and herbicides, cf Table 1. Thus, in total around 50 000 determinations of individual pesticides were performed. Analyses were performed according to Åkerblom et al (1990), and they were carried out at the National Laboratory for Agricultural Chemistry, Uppsala and at Agrolab Scandinavi-ca, Kristianstad, Sweden.

All samples were from agricultural areas. In all, sampling was performed at about 200 sites, mainly in the southern parts of Sweden, i.e., Götaland and Svealand. Most samples were taken during the spraying season. They were taken as grab samples. Some streams were sampled up to twice a month from May to October, whereas others were sampled on a single occasion. Catchment areas of the streams varied considerably. Thus the material is quite heterogenous.

Table 1. Pesticides searched for their main use and typical detection limits. A=acaricide, F=fungicide, H=herbicide, I=insecticide

"Phenoxy acid herbicide" method

Substance	*Main use*	*Detection limit, ug/l*
bentazone	H	0.1
clopyralid	H	0.3
2,4-D	H	0.1
dicamba	H	0.1
dichlorprop	H	0.1
MCPA	H	0.1
mecoprop	H	0.1

"Multiresidue" method

Substance	*Main use*	*Det. limit, ug/l*	*Substance*	*Main use*	*Det. limit, ug/l*
aldrin	I	0.1	hexazinone	H	0.5
atrazine	H	0.1	iprodione	F	0.5
azinphos-methyl	I	0.1	isofenphos	I	0.2
bromacil	H	0.5	isoproturon	H	1
bromophos	I	0.1	lenacil	H	0.5
carbaryl	I	1	lindane (= HCH-gamma)	I	0.1
carbofuran	I	0.5	linuron	H	0.3
carbosulfan	I	0.5	malathion	I	0.1
carboxin	F	1	metalaxyl	F	0.5
chlorfenvinphos	I	0.2	metamitron	H	1
chlorpropham	H	0.5	metazachlor	H	0.1
chlorpyrifos	I	0.1	methabenzthiazuron	H	0.3
chlorothalonil	F	0.1	methoxychlor	I	0.1
cyanazine	H	0.1	metoxuron	H	0.2
cyfluthrin	I	0.5	metribuzin	H	0.1
cypermethrin	I	0.2	mevinphos	I	0.1
DDD-p,p'	I	0.1	parathion	I	0.1
DDE-p,p'	I	0.1	parathion-methyl	I	0.1
DDT-o,p'	I	0.1	pendimethaline	H	0.2
DDT-p,p'	I	0.1	pentachloroaniline	(m)	0.1
deltamethrin	I	0.1	permethrin	I	0.5
desmetryn	H	0.5	phenmedipham	H	1
diazinon	I	0.1	phosalone	I	0.2
dichlobenil	H	0.1	phosphamidon	I,A	0.1
dichlofluanid	F	0.1	pirimicarb	I	0.1
dichlorvos	I	0.1	prometryn	H	0.1
dieldrin	I	0.1	propachlor	H	0.3
dimethachlor	H	0.3	propanil	H	0.5
dimethoate	I	0.1	propiconazole	F	0.2
dinobuton	A	1	propoxur	I	0.2
diuron	H	0.5	propyzamide	H	0.5
endosulfan-alfa	I	0.1	pyrazophos	F	0.1
endosulfan-beta	I	0.1	quinomethionate	F	0.3
endosulfan-sulphate	(m)	0.1	quintozene	F	0.1
EPTC	H	0.2	simazine	H	0.1
ethiofencarb	I	0.2	sulfotep	I	0.1
fenfuram	F	0.4	terbacil	H	0.2
fenitrothion	I	0.1	terbutryn	H	0.1
fenpropimorph	F	0.5	terbuthylazine	H	0.1
fenvalerate	I	0.2	tetradifon	A	0.1
flucythrinate	I	0.2	triadimefon	F	0.5
HCH-alfa	I	0.1	triadimenol	F	0.5
HCH-beta	I	0.1	tri-allate	H	0.1
HCH-delta	I	0.1	trifluralin	I	0.2
HCH-gamma	I	0.1	trichloronat	I	0.1
			vinclozolin	F	0.1

In spite of this heterogenicity, the material is so extensive that some general estimates can be made on the prevailing situation in agricultural streams. Pesticides were detected at 100 of the 180 surface water sampling sites. Out of the 80-90 different pesticides looked for in the analyses, 20 were found. In Table 2 the frequency of findings of different substances is given. The M-county, the most southern county in Sweden, has the most intense agriculture and is presented separately. The highest frequency of findings was in May-June for most substances. Atrazine was found most frequently in July-August, and bentazone was found evenly from May to Octo-ber. There is a tendency of decreasing frequency of findings during the years 1988-1990. This apparent decrease may to some extent be due to the fact that samples were collected partly from different sites in different years.

Table 2. Frequency of findings of pesticides in surface water. Number of samples with pesticides detected/total number of samples analysed are given, both in figures and in %.

Pesticide	*All counties except I- and M-counties*			*M-county*		
	Number of findings	*total analysed*	*%*	*Number of findings*	*total analysed*	*%*
bentazone	156	754	21	39	84	46
MCPA	160	"	21	25	"	30
dichlorprop	69	"	9	23	"	27
mecoprop	39	"	5	32	"	38
2,4-D	12	"	2	5	"	6
atrazine	32	450	7	21	83	25
simazine	3	"	0.7	1	"	1
terbuthylazine	4	"	1	5	"	6
cyanazine	3	"	0.7	4	"	5
metazachlor	1	"	0.2	12	"	15
metribuzine	6	"	1	0	"	-
pirimicarb	1	"	0.2	2	"	2
lenacil	2	"	0.4	0	"	-
bromacil	1	"	0.2	0	"	-
endosulfan	0	"	-	1	"	1
malathion	0	"	-	1	"	1
methoxuron	1	"	0.2	0	"	-
permethrin	1	"	0.2	0	"	-
propachlor	0	"	-	1	"	1
vinclozolin	0	"	-	1	"	1

The concentrations found were in most cases quite low, cf Table 2. E.g., the sum of the concentrations of the triazines never exceeded 1.5 ug/l. Only 5 out of 800 stream samples had concentrations of individual pesticides or pesticide groups above 10 ug/l, maximum being 80 ug/l. More frequent sampling would probably have given more samples with elevated concent-rations - with infrequent sampling it is difficult to "hit" the peak concentrations. It is not sure that the frequency of samples with elevated concentrations would increase with increased sampling frequency.

This material can only give a general idea of the situation in Sweden. It can not answer questions such as

have restrictions on certain pesticides and information to farmers led to decreased concentrations in the streams?

what is the total load of pesticides on the aquatic environment?

is the pesticide load of concern to the aquatic environment?

FUTURE MONITORING PROGRAM

The purposes of a future monitoring program would be

- to ensure that anticipated effects of requirements and restrictions at registration of a pesticide are met in real life
- to quantify effects of the programs of reduction by 50% of pesticide use in terms of discharge to the aquatic environ ment
- to give early indications of potential risks for contamination of drinking water - this will be especially important when Sweden joins the European Community and shall comply with the directive on MAC (maximum allowable concentration in drinking water) of 0.1 µg/l
- to control that concentrations of pesticides are kept at an environmentally acceptable level

In a future program the following aspects must be taken into account:

* quantitative data on transport of pesticides in streams are achievable only if samples are taken continuously (with ISCO sampler or similar) and water flow is measured

* effects of regulations of pesticides can be estimated only if sampling sites are fix during a number of years

* up to now mainly lipophilic compounds (out of compounds in the "phenoxy acid" method) have been looked for. Analytical methods should be set up for watersoluble compounds, both parent compounds and bioactive metabolites

* lipophilic compounds are more prone to be adsorbed by particles. Thus sediment should be sampled and analysed for such compounds

- reliable pesticide residue analyses are extremely costly. The lower the detection limit the higher the cost. Therefore substances and analytical levels should be selected according to ecological significance and other relevant criteria

- for this, more must be known on biological effects and bioavailability of pesticides in natural waters and sediment

- ground water should preferably be sampled in dedicated ground water tubes. Water from wells is fairly easily contaminated and may not reflect the ground water situation

- ground water tubes should be installed at different depth so that downward movewent of pesticides can be followed

- analytical laboratories involved should participate in intercalibrations and other quality assurance work

A future monitoring program in Sweden may have the following structure:

About six sites in Sweden are chosen as "A-sites". A model for these sites is the area at Vemmenhög in south of Sweden presented in this report (Kreuger, 1991). The catchment area should be 500-1500 ha of agricultural land, with general far-ming activities. The six different areas should represent different soil characteristics, climate, main crops, etc. Their hydrology, geology, cropping and pesticide use should be investigated.

Surface water and sediment should be sampled at the spot where the stream leaves the chosen area. Water is sampled continuously forming weekly or biweekly composite samples during the most intense spraying period, and monthly composite samples during the rest of the year. Sediments are collected three times a year, in July, October and March. Groundwater is sampled two to three times a year, at three levels.

For comparison between the different sites, some commonly used pesticides/metabolites are analysed in all samples. In addi-tion, pesticides are chosen according to use in the specific area.

From findings in the "A-sites" it should be possible to esti-mate behaviour of pesticides "in real life", on locations with different characteristica. It would be possible to follow effects of different regulations and other actions. And mass balances could be calculated.

It is desirable that aquatic organisms are included for monitoring effects, when reliable such systems are available (cf. Aanes, 1991; Crossland et al., 1991).

In order to get a more general view of the situation in big streams, samples should be taken in streams with a catchment area of 100-500 km2 ("B-sites"). The agricultural area should be at least 30%. These samples would also in part reflect long distance transport of pesticides. It might be beneficial if the B-site streams were recipients for the A-site streams. Preferably, the sampling sites should be chosen close to the effluent of the stream into the sea - the last recipient. At the B-sites surface water is sampled continuously as for A-si-tes, but maybe during a shorter period of the year. Sediments, but not ground water, would be sampled.

A monitoring program as sketched above would give more precise results than achieved today. It will be quite costly, 5-10 million SEK a year, including continuous method development/ testing and intercalibrations at the analytical laboratory. It is therefore important to allow time for choosing sampling sites, testing sampling devices and conditions, and setting up analytical methods for relevant pesticides/metabolites. Thus, an introductory period of two years is suggested. Any comments before the program is settled are most welcome!

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CONCENTRATIONS OF PESTICIDES FOUND IN GROUND WATER

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ABSTRACT

Analyses of ground and drainage water from Sweden, Norway, Finland, Germany and Denmark sampled during the period 1985-1990 show with few exceptions relatively low pesticide concentrations.

Atrazine is the pesticide, which occurs in most water samples. Besides Atrazine, the triazines Simazine and Terbutylazine occur sporadically.

The pesticide bentazone occurs in one third of the samples taken in Sweden. Bentazone also occurs in the ground water samples from Germany. In Denmark the pesticides Atrazine and Hexazinone have been found in high concentrations in shallow ground water samples.

Pesticidkoncentrationer i grundvand

I midten af firserne startede Sverige, Norge, Finland og Danmark større undersøgelser over grund- og drænvandets indhold af pesticider, som følge af almindelig landbrugsmæssig praksis (fladeforurening). De analyser, der er udført på grund- og drænvandsprøver før midten af firserne, stammer primært fra lokaliteter, hvor der har været punktkilde forureninger.

I Norge blev der i 1987 udført en undersøgelse over indholdet af pesticider i overfladevand og grundvand. Undersøgelsen omfattede de 15 pesticider, der blev anvendt i nærheden af de 7 lokaliteter, hvorfra vandprøverne blev udtaget. Lokaliteterne er udvalgt således, at de repræsenterer variationer i klima, terræn og jordtyper, kombineret med forskellige produktionsmønstrer herunder de mest anvendte pesticider. Hvilke pesticider der er analyseret for fremgår af tabel 1, detektionsgrænserne for de forskellige pesticider varierer fra 0,05 $\mu g\ l^{-1}$ til 0,5 $\mu g\ l^{-1}$. Der blev ikke påvist nogen af pesticiderne i grundvandsprøverne. Der er fundet pesticidforureninger i en enkelt brønd beliggende ved Mysen[1)], som modtager en del af sit vand via den nedbør, som falder på et industriområde, hvor der er blevet anvendt atrazin og simazin gennem en 20-årig periode. Området er uden bevoksning og dæklagene består overvejende af sand. Brugen af atrazin og simazin stoppede i 1986, men analyser frem til sommeren 1991 (Ole Martin Eklo, personlig meddelelse) viser, at vandet stadig indeholder både atrazin og simazin dog i faldende koncentrationer. Atrazin og simazin koncentrationerne er fulgt fra sommeren 1986 og 5 år frem, der er maksimalt målt ca. 0,9 μg l^{-1} af atrazin og ca. 0,7 μg l^{-1} af simazin. I andre enkeltmålinger fra nogle brønde er der fundet: MCPA, dichlorprop og atrazin. I Norge anvendes grundvand kun få steder som drikkevand, alligevel vil analyser af norsk grundvand indgå i en ny undersøgelse, som omfatter terrestrisk overvågning af landbruget.

Table 1. Pesticider i norsk grundvand fra 7 lokaliteter (1987).

Pesticides in Norwegian ground water from 7 locations (1987).

pesticider pesticides	n/N*	detektionsgrænse detection limit μg l^{-1}
Atrazine	0/18	0.1
Chlorfenvinphos	0/18	0.2
Diazinon	0/18	0.1
Dichlorprop	0/18	0.1
Dimethoate	0/18	0.1
Fenitrothion	0/18	0.1
Lindane	0/18	0.05
Linuron	0/18	0.5
MCPA	0/18	0.1
Metribuzin	0/18	0.1
Propachlore	0/18	0.5
Propiconazole	0/18	0.2
Simazine	0/18	0.1
Terbutylazine	0/18	0.1
Tolylfluanide	0/18	0.2

* n = antal af positive prøver (number of positive samples)
N = det samlede antal prøver (total number of samples)

I Finland er der fra 1985 til 1987 påvist dimethoat og 2 phenoxysyrer i drænvand i koncentrationer op til maksimalt 1,0 μg l^{-1} jvf. tabel 2. I sommeren 1991 er der udtaget vandprøver fra 50 brønde til analyse for pesticidrester, der foreligger endnu ingen (10.11.1991) resultater.

Table 2. Pesticider i finsk drænvand (fra 1985 til 1987)

Pesticides in Finnish drainage water (from 1985 to 1987)

Pesticider Pesticides	n/N*	højeste koncentration max. conc. µg l⁻¹
Dichlorprop	9/17	0,45
Dimethoate	4/17	0,12
MCPA	9/17	1,0

* n = antal af positive prøver (number of positive samples)
N = det samlede antal prøver (total number of samples)

I Sverige er der påvist 18 pesticider i grundvandet - jvf. tabel 3 - fra 1987-1990. Bentazon findes i 1/3 af de prøver, hvor der er analyseret for det. Phenoxysyrerne: dichlorprop, MCPA og mechlorprop ses i mindre end 10% af prøverne, triazinerne: atrazin, simazin og terbutylazin ses i nogle enkelte prøver.

Table 3. Pesticider i svensk grundvand (inkl. prøver af brøndvand analyseret 1987-90).

Pesticides in Swedish ground waters (includes samples of well water analysed 1987-90)

Pesticdider Pesticides	n/N*	detektionsgrænse detection limit µg l⁻¹
Atrazine	11/230	0.1
Bentazone	112/338	0.1
Bromacil	2/230	0.4
Clopyralid	17/338	0.1
Cyanazine	1/230	0.1
Dichlorprop	20/338	0.1
Dimethoate	1/230	0.1
Diuron	1/230	0.1
Lindane	1/230	0.1
Lenacil	1/230	0.5
MCPA	23/338	0.1
Mechlorprop	7/338	0.1
Metazachlore	2/230	0.1
Propicanazole	1/230	0.4
Prometryn	1/230	0.1
Simazine	3/230	0.1
Terbuthylazine	6/230	0.1
Tri-allate	1/230	0.1

* n = antal af positiver prøver (number of positive samples)
N = det samlede antal prøver (total number of samples)

De pesticider, som er fundet i det danske drænvand og højtliggende grundvand i perioden fra 1985-1990, stammer fra fladeforureninger i forbindelse med landbrug og skovbrug på sandede og lerede lokaliteter. Hovedparten af de danske undersøgelser er udført på lokaliteter, hvor de hydrogeologiske og sprøjtemæssige forhold er velkendte. De højeste pesticidkoncentrationer - jvf. tabel 4 - ses i forbindelse med dyrkning af juletræer på lerjord, forureningen stammer fra ukrudtsmidlerne atrazin og hexazinon. De øvrige pesticider ses kun i meget lave koncentrationer. En mere systematisk og landsdækkende undersøgelse over grundvandets kvalitet og hermed drikkevandets er sat igang, men der foreligger endnu ingen resultater.

Table 4. Pesticider i dansk grund- og drænvand (1985 til 1990).

Pesticides in Danish ground and drainage water (from 1985 to 1990).

pesticider pesticides	n/N[*]	koncentrationsniveau concentration range $\mu g\ l^{-1}$	detektionsgrænse detection limit $\mu g\ l^{-1}$
Atrazine	53/58	0.01 - 7.79	0.01
2,4-D	1/31	0.03	0.01 0.4[»]
Dicamba	0/18		0.3 - 0.4
Dichlorprop	3/41	0.04 - 0.12	0.01 0.4[»]
Ioxynil	0/3		0.01
Isoproturon	0/3		0.01
MCPA	4/41	0.03 - 0.08	0.01 0.6[»]
Mechlorprop	2/23	0.06	0.01
Hexazinone	39/42	0.07 - 42.66	0.01
Simazine	0/13		0.01

[*] n = antal af positive prøver (number of positive samples)
N = det samlede antal prøver (total number of samples)

[»] 18 af det samlede antal prøver er analyseret under forhold som medførte den høje detektionsgrænse (18 of the total number of samples have been analysed using the higest detection limit).

De undersøgelser, som indtil nu er udført og publiceret i Sverige, Norge, Finland og Danmark i forbindelse med pesticidforurening af grundvand og drænvand, er ikke landsdækkende, men er baseret på nogle udvalgte forhåbentlig typiske lokaliteter.

I Tyskland har de pesticid producerende firmaer (IPS) gennemført en meget omfattende undersøgelse over drikkevandets kvalitet ved at udtage vandprøver fra forskellige brøndtyper beliggende i tilknytning til bl.a., skov, vindyrkning, landbrug og bymæssig bebyggelse. Prøverne er udtaget i områder, hvor dæklagene repræsenterer forskellige geologiske perioder eksempelvis formationer fra kvartær og tertiær. Ved at kombinere disse parametre har de tilstræbt en slags "worst-case".

De kriterier, som er lagt til grund for udvælgelsen af de ialt 35 pesticider, som undersøgelsen omfatter, er: høj mobilitet i jord, lang halveringstid, høj dosis og anvendelsesmønstret. De 35 pesticider, som er blevet udvalgt på baggrund af ovenstående, fremgår af tabel 5.

Table 5. Pesticider udvalgt af IPS

Pesticides selected of IPS

Aminotriazole
Atrazine
Azinphos-ethyl
Azinphos-methyl
Bentazone
Bitertanol
Carbofuran
Chloridazon
Cyanazine
2,4-D
2,4-DP (2,4-Dichlorprop)
Desmedipham
Demeton-S-methyl sulfon
1,2-Dichloropropan
1,3-Dichloropropen
Dinoseb acetate
Fluazifop butyl
Isoproturon
Lindane
MCPA
Mechlorprop
Metamitron
Metazachlor
Methabenzthiazuron
Methamidophos
Methyl isothiocyanat
Oxydemeton methyl
Parathion
Pendimethalin
Phenmedipham
Pyridate
Simazine
Triadimefon
Triadimenol
Vinclozolin

Der er i perioden 1985-87 udtaget vandprøver fra 206 brønde og gennemført 12.674 analyser. I 20 ud af de 206 brønde var pesticidindholdet over 0,1 $\mu g\ l^{-1}$ (den i EF højst tilladte koncentration af et enkelt pesticid), hvilket svarer til at ca. 1% af brøndene var forurenede.

I 88 af de ialt 12.674 udførte analyser var pesticidindholdet mellem detektionsgrænsen (0,05 $\mu g\ l^{-1}$) og 0,10 $\mu g\ l^{-1}$, i 54 af de 12.674 udførte analyser var pesticidindholdet over 0,10 $\mu g\ l^{-1}$.

Af de 35 mulige vandforurenende pesticider blev 7 fundet i koncentrationer, som overskrider grænseværdien på 0,1 $\mu g\ l^{-1}$, jvf. tabel 6, nemlig atrazin, bentazon, chloridazon, 1,2-dichlorpropan, mechlorprop, pyridat og simazin. Herudover blev 5 pesticider fundet i koncentrationsniveauet mellem detektionsgrænsen og grænseværdien på 0,1 $\mu g\ l^{-1}$, det er pesticiderne: dichlorprop, dinoseb-acetat, isoproturon, pendimethalin og vinclozolin. Af de 35 udvalgte pesticider er ca. 33% påvist. Som det fremgår af tabel 6 er 1,2-dichlorpropan det eneste pesticid, som optræder i en koncentration, der overskrider 1,0 $\mu g\ l^{-1}$.

Table 6. Pesticider i tysk grundvand (1985-1987)

Pesticides in German ground water (1985-1987)

pesticider pesticides	n/N^*	koncentrations-niveau concentration range $\mu g\ l^{-1}$	detektions-grænse detektion limit $\mu g\ l^{-1}$
Atrazine	46/154	0.05 - 0.26	0.05
Bentazone	17/398	0.05 - 0.85	0.05
Chloridazon	1/322	0.19	0.05
Dichlorprop	1/141	0.07	0.05
Dinoseb acetat	3/685	0.06 - 0.10	0.05
1.2-Dichlorpropan	31/124	0.05 - 5.10	0.05
Isoproturon	32/678	0.05 - 0.08	0.05
Mechlorprop	24/142	0.05 - 0.37	0.05
Pendimethalin	1/144	0.10	0.05
Pyridate	1/155	0.30	0.05
Simazine	8/66	0.05 - 0.14	0.05
Vinclozolin	1/77	0.07	0.05

* n = antal af positive prøver (number of positive samples)
N = det samlede antal prøver (total number of samples)

I de her beskrevne undersøgelser er atrazin et gennemgående vandforurenende pesticid, det ses i forholdsvis mange vandprøver. Gruppen af phenoxysyrer her specielt: mechlorprop, MCPA og dichlorprop optræder i prøver af grund- og drænvand fra de fleste lande. Bentazon findes især i det svenske og tyske grundvand.

Debatten omkring grundvandsforurening er stadig meget aktuel, der iværksættes i de fleste lande meget omfattende projekter for at kontrollere kvaliteten af drikkevandet bl.a. ved at udtage prøver af grundvandet.

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NORDIC SEMINAR
Pesticides in the aquatic environment - appearance and effect
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THE DANISH GROUNDWATER MONITORING PROGRAMME.

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During a 3 year-period from 1989 to 1991 1000 samples are taken at different locations all over the country and at different depths below surface.

The following pesticides are withtaken in the programme:

MCPA, (2,4-D), Mecoprop, Dichlorprop.
DNOC, Dinoseb.
(Atrazine, Simazine).

The substances in paranthesis are not obligatory.

The counties in Denmark are resposible for the implementation of the programme and the National Environmental Research Institute, (NERI) was in 1990 and 1991 asked to anlyse 101 samples.

In 1990 48 samples were analysed by NERI.

MCPA was found in 2 samples (0.03 µg/l, 0.01 µg/l).
Mecoprop was found in 3 samples (0.04 µg/l, 0.11 µg/l, 0.43 µg/l).

In 1991 51 samples were analysed by NERI.

2,4-D was found in 1 sample (0,23 µg/l).
Mecoprop was found in 3 samples (0.01 µg/l, 0.02 µg/l, 0.05 µg/l).
Dichlorprop was found in 5 samples (0.03 µg/l, 0.06 µg/l, 0.08 µg/l, 0.10 µg/l, 0.11 µg/l).

The detection Limit was 0.01 µg/l.

In addition to the pesticides-analysis, the programme consists of analysis of phenols, aromatics,volatile organic halogens, elements, detergents and simple parameters.

The Geological Survey of Denmark is resposible for collection of all the data from the groundwater monitoring programme, and a total report will be issued in the begining of 1992. Then the programme is going to be evaluated before further acivities will be implemented.

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TRANSPORT OF PESTICIDES FROM ARABLE LAND TO SURFACE WATER AND GROUND WATER

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Presentation of the research programme at the National Environmental Research Institute.
Four projects are either in progress or being started in the autumn 1991. On the map (fig 1) the numbers 1-4 indicate the experimentel sites of the corresponding projects.

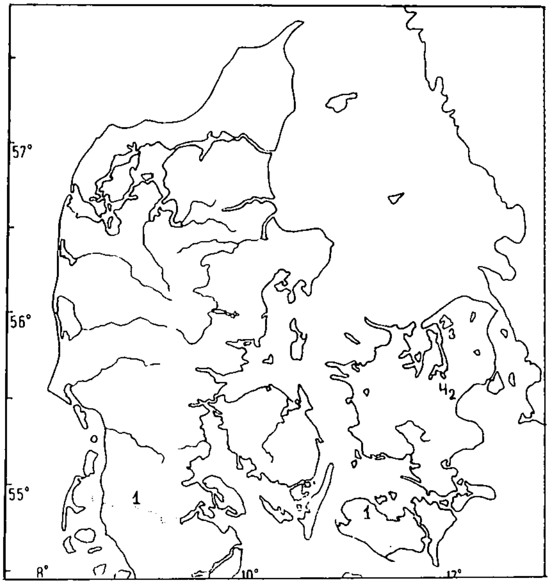

Fig. 1. Position of experimental sites.

		Localities
1.	Leaching of pesticides to drainage water and surface water	1
2.	Transport and degradation of pesticides in moraine clay	2
3.	Mapping of selected pesticides in soil and soil water at unsaturated condition	3
4.	Pesticide runoff from arable land	4

1. Leaching of pesticides to drainage water and surface water.

Leaching of some selected herbicides (atrazine, simazine, MCPA, 2,4D, mechlorprop, dichlorprop, DNOC, dinseb, bromoxynil, ioxynil, and isoproturon) from arable land has been investigated during two years at two survey areas. One area (on Lolland) consists of clayey soil the other one (Southern Jutland) of sandy soil.

Correspondent samples of soil water, drainage water, and stream water have been anlysed.
Soil water has been collected by suction cups, drainage water and stream water samples are collected each second week as instant samples. In 1991 a continuous water sampler has been established at one stream water station to get integrated samples from every day in about two months.
Preliminary results have been published (Mogensen og Spliid 1991). These results are also included in the proceedings by G. Felding and J. Kreuger.

The integrated samples reveal that the occurrence of pesticides often lasts for several days (table 1). This fact is not visible from the analysis of instant samples.

Table 1. Concentration of herbicides in stream water. µg/l

Week	Day	Atrazine	Simazine	MCPA	2,4 D
26	1	0,10	0,02	-	-
	2	0,20	0,03	0,74	-
	3	-	0,07	0,13	-
	4	-	-	-	-
	5	0,23	-	0,35	-
	6	0,20	-	0,78	-
	7	0,17	0,04	0,27	0,15
29	1	0,12	0,04	-	0,08
	2	0,09	-	-	-
	3	0,31	0,03	-	-
	4	0,40	-	-	-
	5	0,42	-	-	-
	6	0,16	-	0,54	-
	7	-	-	-	-
30	1	-	-	-	-
	2	0,10	-	-	-
	3	-	-	-	0,05
	4	-	-	-	0,05
	5	-	-	-	0,05
	6	-	-	-	0,04
	7	-	-	-	0,05

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Modelling Pesticide Transport to Surface Waters:

RISK ASSESSMENT AND EFFECTS OF MANAGEMENT PRACTICES

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Abstract

In this paper a mathematical simulation model is used for assessing the risk of pesticide runoff and for the estimation of the effectiveness of different management practices on pesticide runoff. The model employed is a modified version of the CREAMS model. The results show that different erosion control measures, such as reduced tillage and filter strips, can significantly reduce the sediment-bound pesticide loss, but only to small extent the dissolved-phase pesticide loss. Also the requirements for quantitative assessments on a regional scale are briefly discussed.

Introduction

Pollution of ground water and surface waters is an important environmental aspect of pesticides use in agriculture. In the Nordic countries both ground and surface water is used as a source for drinking water. In surface waters the occurrence of pesticides can have harmful effects also on aquatic life. Pesticides can be transported to surface waters via surface runoff or via subsurface drainage systems. Pesticides leached below the root zone pose a threat also to groundwaters.

Due to the short lifetime of many modern pesticides and the random character of runoff events, it is difficult to detect the occurence of pesticides in ditch and river systems or to estimate the pesticide loads to lakes and estuaries using routine monitoring procedures. Mathematical simulation models can be used as an effective and quick tool to estimate peak concentrations and mass loads of pesticides, to evaluate the effectiveness of pollution control practices, and to make risk assessments.

Several models have been developed to describe pesticide leaching from the root zone. Some of them are research-oriented, like LEACHMP (Wagenet and Hutson 1986) and the model developed by Leistra and Dekkers (1976), while GLEAMS (Leonard et al. 1987) and PRZM (Carsel et al. 1985) are management-oriented. Only a few erosion models contain a component for pesticide transport via surface runoff (dissolved-phase and sediment-phase): GLEAMS, CREAMS (Knisel 1980), and a model developed by Haith (1980).

Several studies have shown that deep percolation, surface runoff, soil erosion, chemical persistence, and the strength ofadsorption of pesticides to the soil particles are the major factors affecting pesticide leaching and runoff (e.g. Bailey and White 1970, Wauchope 1978, Haith 1986). Percolation, runoff, and soil erosion are in turn determined by soil, vegetation and weather patterns. It can be concluded that the goodness of the models describing pesticide leaching and runoff depends primarily on a good prediction of hydrology and erosion and on a good description of the pesticide decomposition and sorption processes under varying soil and weather conditions.

The objective of this paper is to present a short overview of existing models and model estimations for pesticide loss via surface runoff and to give an example of risk assessment and to illustrate how models can be used to estimate the effectiveness of different management practices on pesticide loss.

The model

All model simulations for this study were carried out with the CREAMS model (Knisel 1980) modified for Finnish conditions (Kallio et al. 1989, Rekolainen and Posch 1991). In CREAMS the surface runoff is estimated using the Soil Conservation Service's Curve Number method (U.S. Department of Agriculture 1972), and the erosion estimation is based on the USLE (Universal Soil Loss Equation, Wischmeier and Smith 1978).
The most important modifications made to the original CREAMS model were the implementation of a new snow accumulation and snowmelt model, a new plant growth model based on the WEPP formulations (Water Erosion Prediction Project, Lane and Nearing 1989), and the calculation of rainfall erosivity (EI-factor) in the USLE according to Finnish breakpoint rainfall data.

The pesticide model is based on a mass balance for the top 1-cm soil layer. It is assumed that pesticides below this depth are not available for surface runoff loss. Since only surface application is can be modeled, all of the pesticide is potentially available for runoff loss. The model also takes into account the foliar fraction of the application and the foliar washoff during rainfall events. Pesticide in the soil is considered to decay exponentially with time. The model traces pesticide losses due to surface runoff and sediment loss. The partitioning is based on a linear equilibrium adsorption isotherm.

The model has been tested for surface runoff and soil loss (Rekolainen and Posch 1991), but not for pesticide concentrations or losses. To make load predictions the model should be tested against observed data. Nevertheless, the model can be used for risk assessment and comparative studies on the effectiveness of different management practices on pesticide losses.

Risk assessment of peak concentrations and loads

Surface water pollution by pesticide runoff is affected by random hydrologic events. A high runoff event shortly after application may contribute most of the annual load and may even lead to toxic concentrations for some aquatic organisms. The assessment of the risk of such episodic pollution events is based on estimates of the probability of extreme pesticide runoff concentrations and loads.

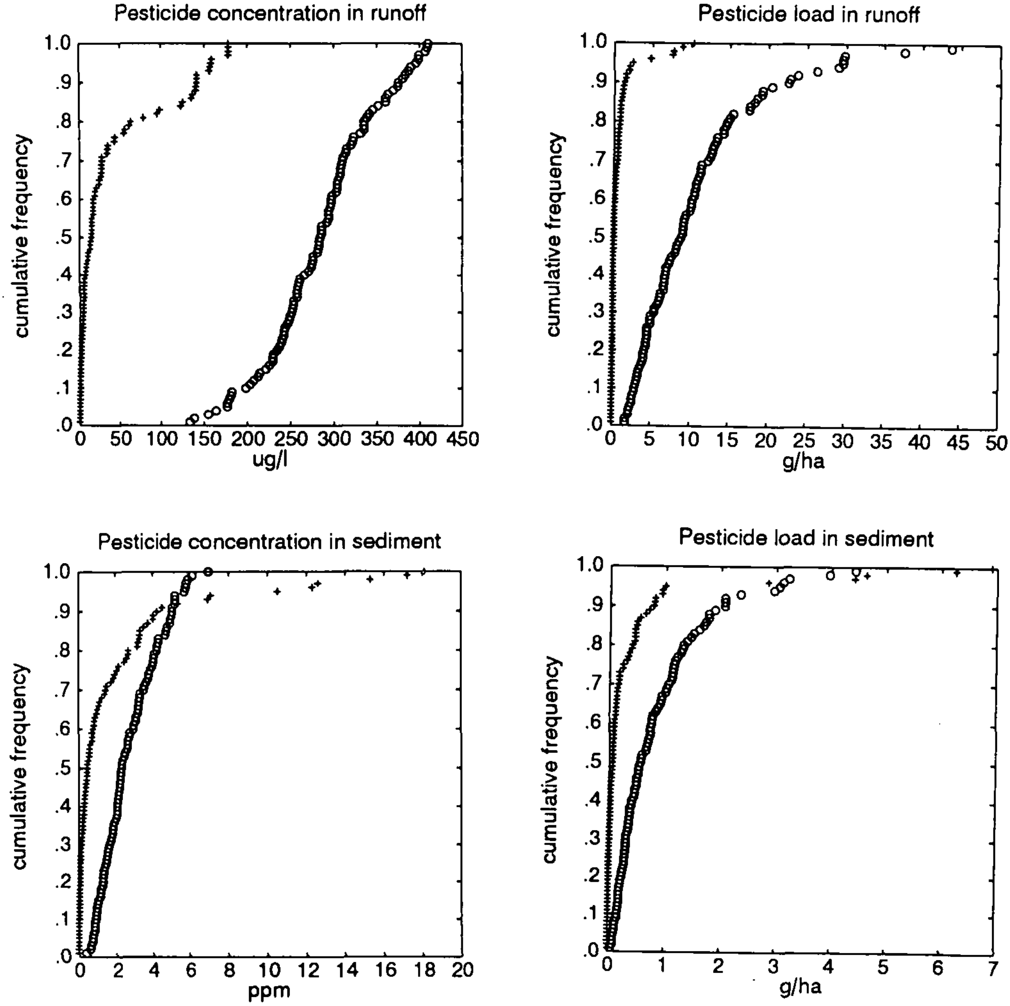


Fig. 1. Cumulative frequencies of annual maximum daily atrazine (o) and MCPA (+) concentration and load in sediment and runoff water.

A study of extreme event analysis of annual daily maximum loads has been reported by Haith (1987). A similar study with the model described above is presented here for the annual daily maximum concentration and load in runoff and sediment. Two pesticides (MCPA and atrazine) were simulated for a hypothetical field with silty soil and 100 m uniform 5% slope. The field was under continuous barley cultivation and it was tilled by moldboard plow in autumn (conventional tillage). The simulation was carried out for 100 years and the maximum daily concentration and load of every year was recorded. These values are shown as cumulative frequencies in Figure 1. separately for runoff and sediment.

For all four variables the distributions are highly skewed for MCPA, which means that only in very few cases (few years out of hundred) there is a risk for high concentrations or high loads. For example, although the annual daily maximum of MCPA concentration in sediment ranged from 0 to 18 ppm, 90% of these maxima were below 5 ppm. Atrazine behaves differently because of its lower adsorption to soil particles, higher solubility in water, and higher resistance against degradation. For example, our assessment shows that there is a risk that every second year the daily maximum concentration in water phase exceeds 280 $\mu g\ L^{-1}$ (compared to 15 $\mu g\ L^{-1}$ for MCPA).

Evaluation of pollution control practices

Due to the short-lived nature of many modern pestices and the random character of runoff events, it is difficult to estimate overall loads by routine (infrequent) monitoring. At present, pesticide runoff data from field studies in Finland are too sparse to provide the general information needed for regulatory purposes and water quality management. Mathematical models can be used both to estimate the loads of chemicals to surface waters and to evaluate the effectiveness of pollution control practices.

Policy conclusions concerning the effectiveness of management practices cannot be made on the basis of individual model studies, since pesticide losses is highly dependent on climate, soil type, and cultivation even if the chemical characteristics are identical. In order to make such an assessment for a large region, data on climate, soil types, topography and the spatial and temporal distribution of cropping systems as well as tools for handling such large amounts of data (Geographical Information Systems) are required. Many of the management practices in agriculture are designed for reducing soil loss (e.g. conservation tillage practices, filter strips, strip cropping). Although reduced tillage and also the use of filter strips may change the hydrologic characteristics of the soil, they mostly reduce the sediment-bound fraction of pesticide loss.

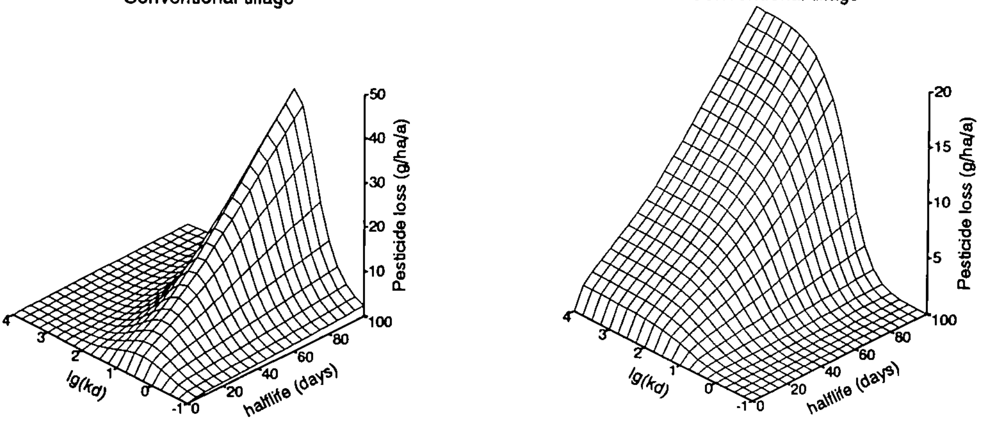
In this paper we present an exercise, where the modified CREAMS model was used to estimate the effect of reduced tillage techniques and filter strips on pesticide loss in sediment and dissolved phase. The simulated field area was the same as above: silty soil, 5% uniform slope, continuous barley cultivation. As a reduced tillage technique chisel-plow instead of moldboard plow in autumn was simulated. The filter strip simulated was a 5 m wide strip with dense grass at the lower end of the slope. Simulations were performed for a wide range of partition coefficients (K_d from 0.1 to 10000), and half-life times in the soil (1-100 days). It can be seen from Figure 2 that with a low half-life time both sediment-phase and dissolved-phase pesticide loss is low. As expected, for high partition coefficients the sediment-phase fraction is higher than the dissolved fraction. For decreasing partition coefficient the sediment fraction decreases and the dissolved fraction increases until K_d reaches a value of about 10. In the K_d-range from 0.1 to 10 both fractions decrease. The explanation for this is that CREAMS also takes into account the percolation of the dissolved fraction of pesticides into deeper soil layers, and the percolation fraction strongly increases for low K_d values. From Figure 2 it can be seen that reduced tillage as well as filter strips can reduce the sediment-phase loss of pesticides considerably, but the runoff loss is less pronounced. The result is to be expected: reduced tillage and filter strips are erosion control measures, which decrease soil loss, but only to a minor extent surface runoff.

Dissolved-phase

Conventional tillage

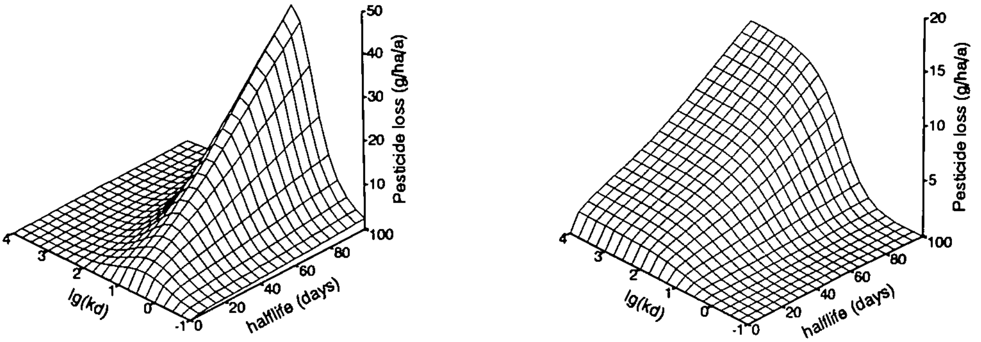
Sediment-phase

Conventional tillage



Reduced tillage

Reduced tillage



Filter strip

Filter strip

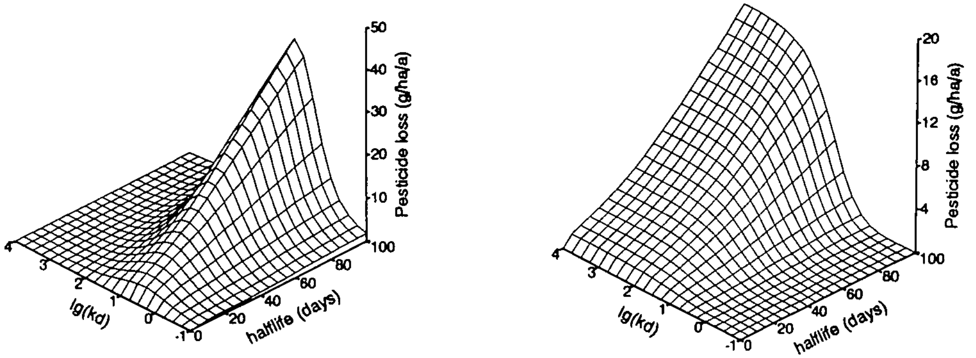


Fig. 2. Mean annual pesticide loss as a function of the partitioning coefficient (K_d) and half-life time in the soil. The pesticide loss is shown for the dissolved phase and the sediment phase for conventional moldboard tillage, reduced tillage (autumn tillage with chisel-plow), and for a conventionally tilled field with a 5 m filter strip.

Conclusions

Existing pesticide runoff models are not tested and validated enough to make accurate loss predictions. However, they can be used to compare the effectiveness of different management practices on reducing pesticide losses and also to make risk assessments of pesticide runoff for different pesticides under different environmental conditions. However, in order to make quantitative assessments on a regional scale, databases for climatic, topographic, geologic and agricultural variables are needed as well as software for linking these databases with models.

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FATE AND EFFECTS OF THIOPHOSPHATES IN THE MARINE ENVIRONMENT

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INTRODUCTION

Organo-phosphorous compounds, widely applied for the control of insect pests in agriculture, comprise such substances as Parathion, Malathion, Bromophos, Dichlorvos, Dimethoate a.o. The toxicity of these to the target organisms and man (including the metabolic partways in mammals and crops) is well-known. In the past decade important information has also been reported concerning the fate of these compounds and their toxicity to terrestrial and aquatic organisms.

Present strategies for regulating the use of pesticides are primarily concerned with the hazards of the active compound and known degradation products. New concepts for the environmental management of xenobiotic substances have recently been introduced, focussing not only on the hazards of industrial products, but on all "life-stages" of the product: raw materials applied, production processes, the products, their application and disposal ("birth to death" concept). Applying this concept, the potential impact from the industrial processes leading to the pesticide including the raw materials applied should also be focussed on.

Thiophosphates (Trialkyl (methyl or ethyl) phosphorothioates/dithioates) are examples of substances formed as side reactions in the industrial production process of organophosphorous insecticides and as degradation products in wastewater treatment involving chemical oxygenation. Neither the pathways for microbiological degradation nor the metabolic transformation of the organophosphorous insecticides indicate these substances as major transition steps. Thiophosphates are present in some of the technical pesticide products in low concentrations (e.g. 1.5-2.5 pct. in Ethion, 0.6 pct in Chemathoate and 1 pct in Fyfanon).

Examples of structural formulae for organo-phosphorous insecticides and for Thiophosphates are shown in Tables 1 and 2, respectively.

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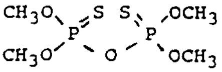
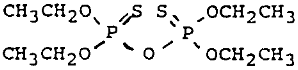
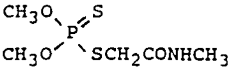
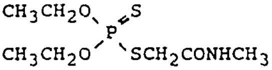
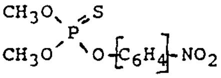
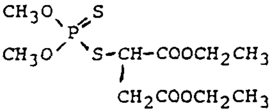
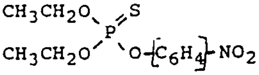
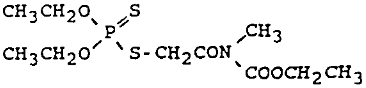
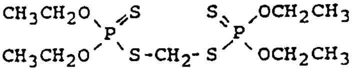
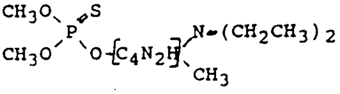
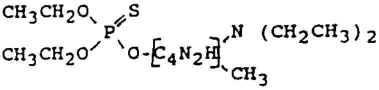
M-Sulfotep:	
E-Sulfotep:	
Dimethoat:	
Diethoat:	
MP3: Methyl- parathion	
Fyfanon:	
EP3: Parathion	
Mecarbam:	
Ethion:	
Pirimiphos- methyl:	
Pirimiphos- ethyl:	

Table 1. Examples of organophosphorous insecticides and their structural formula.

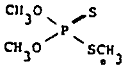
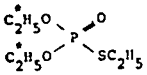
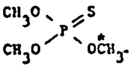
Compound	Formular	Chemical purity %	Specific activity µCi/mg	Total activity µCi
O,O,S-trimethyl-Phosphoro-Dithioate		99	14,3	2000
O,O,S-Triethyl-Phosphoro-Thioate	 198,24	75	0,8	226
O,O,O-Trimethyl-Phosphoro-Thioate		80-85	0,8	440
Sodium-acetate	$^{*}CH_3COONa$	-	679	250

Table 2. Radiochemical specification of Thiophosphates applied in this study. Sodium acetate has been applied for the study of microbiological activity in the seawater inoculum.

In the environment, the parental compound relatively quickly loses its primary structure. Half-life in soil (laboratory studies) has been reported as 1-1.5 weeks for Parathion, less than 7 days for Dimethoate and 7-8 weeks for Ethion (reported to be the most persistent of these insecticides). In the aquatic environment, degradation is relatively slow. The primary degradation for Ethion has been reported from around 24 days to more than 16 weeks. Half-lives for Parathion and Dimethoate have been reported to be 1 week and 8 weeks, respectively, the degradation rates being highly influenced by the magnitude and diversity of the microbial biomass, by factors influencing the activity of the microorganisms (temperature, redox conditions, pH, nutrients etc) and by factors influencing the bioavailability of the compound (content of organic matter a.o.). Other processes may also lead to disappearance of the compound, e.g. hydrolysis and photodegradation.

Most of the data available on biodegradation of pesticides are restricted to the primary degradation of the compound, i.e. experimental data showing the disappearance of the chemical identity. This information should not be taken to be synonymous with mineralisation, i.e. that the compound is degraded to CO_2 and H_2O etc., as a number of more or less stable degradation products are often formed. Data on toxicity to terrestrial and aquatic organisms of degradation products are often very limited.

The present contribution deals with the biodegradation of Thiophosphates under conditions resembling the pelagic marine environment and acute and chronic toxicity to a sediment-dwelling harpacticid, Nitocra spinipes.

The following substances were studied:

- o,o,s - trimethylphosphorodithioate (TMPD)
- o,o,s - triethylphosphorothioate (TEPT)
- o,o,o - trimethylphosphorothioate (TMPT)

BIODEGRADATION STUDIES

The compounds applied were radio-labelled with C-14, as indicated (Table 2). 10 and 100 µg/l of each of the compounds were incubated separately in marine water. The solutions were shaken and incubated in the dark under aerobic conditions at 15°C. The experiments were run in triplicate for each concentration (1 litre batches). To check the microbiological activity of the seawater, an experiment with (14-C)-Sodiumacetat was also included in two different concentrations. Acetate is normally easily degraded in seawater, and should degrade within approx. one week if sufficient microbiological activity is present. For each concentration of the 3 compounds, a physical/chemical control experiment was included, in order to evaluate the degree of abiotic degradation or other routes of disappearance. To these tests 50 mg/l of mercury chloride was added to stop microbiological activity. With all experimental setups traditional blanks were run in parallel.

The marine water applied for the experiments was collected from the North Sea at an environmental monitoring location not directly affected by wastewater from CHEMINOVA AGRO A/S. The water sample was applied for testing less than 24 hours after collection. Before use, the water sample was filtered through a coarse filter. After filtering, the colony-forming microorganisms were determined on Marin Agar (Difco) amounting to 1.04×10^4 cfu/ml. This figure is believed to be within normal range for not directly polluted North Sea water.

The degradation of the Thiophosphorous compounds and acetate was followed regularly for up to 76 days by liquid scintillation measurements of the 14-C content in non-filtrated subsamples (5-7 ml) of each test solution. Before measurement, the content of 14-C-CO_2 in the vials was removed by acidification (1 M HCL) followed by bubbling with N_2-gas. Specific chemical measurements were performed on subsamples from experiments initially containing 100 µl/l of the test compounds. The analysis was carried out by CHEMINOVA AGRO A/S.

TOXICITY STUDIES

The acute and chronic toxicity to the sediment-dwelling marine harpacticide Nitocra spinipes was studied.

For the acute toxicity study, 20 premature individuals were exposed to each of a series of concentrations separated approx. by a factor of 2. The concentration range tested was 50 - 200 mg/l for TMPT and TEPT and 0.1 - 33 mg/l for TMPD. The concentration levels were selected on the basis of preliminary screening tests. At each tested concentration 5 individuals were exposed to 10 ml solution (4 replicates) for 96 hrs. without change of test solution (static test). Static test mode was selected due to information that the substances tested were easily water-soluble, not readily biodegraded and having a low tendency to evaporate. The study was performed at 20°C and 20°/oo salinity. After each 24 hour period, any mortality was registered and pH, oxygen saturation and temperature were measured. Based on the results obtained, the concentrations lethal to 10, 50 and 90 percent of the tested population after 24, 48, 72 and 96 hrs were calculated.

The chronic toxicity study was initiated on females with egg-sac. For each tested concentration, 20 females were exposed separately to a 25 ml solution of the substance. The concentration range tested was defined on the basis of the acute toxicity test: 0.1 - 30 mg/l for TMPT and TEPT and 0.1 - 12 mg/l for TMPD. The applied test conditions were concordant with the acute toxicity study. After approx. 14 days, the test was terminated and number of living offspring from each female was examined. The average number of offspring per female was calculated and compared with the offspring of non-exposed females. Based on these data, the highest concentration of the tested chemicals having no significant effect on number of offspring (NOEC), and the lowest concentration having a significant effect was calculated.

To evaluate the relative sensitivity of the applied population of Nitocra spinipes, an acute test was performed with the chemical Potassium dichromate ($K_2Cr_2O_7$).

The method applied for investigating the acute and chronic toxicity to Nitocra spinipes has been derived from Bengtson, B.E. (1981) and Renberg, L. et al. (1980).

RESULTS & DISCUSSION

Biodegradation:

Sodium acetate was easily degraded with a biological half-life of approx. 2 days (Figure 1). As indicated by the shape of the degradation curve, the first phase of the degradation approximates a 1st order reaction showing the "mineralisation" of the acetate. The latter part of the curve, however, has a very low declination and is believed to indicate the assimilation of the 14-C in microorganisms and hence the "turnover" of the microorganism population involved. The half-life seen for acetate is in accordance with former studies with biomass deriving from the pelagic marine environment, and thus indicates that a non-inhibited microorganism population has been applied for the study.

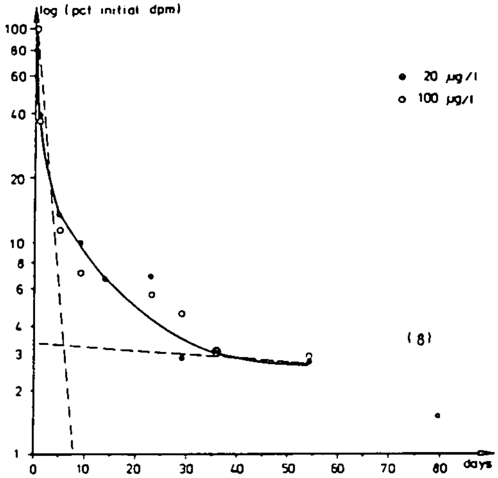


Fig. 1. Degradation of Sodium acetate. Mean of three replicates is indicated.

The results obtained for TMPD, TEPT and TMPT are shown in figures 2, 3 and 4, respectively. Means of the 3 replicates are given for each experiment. The standard deviation on the mean was 10 - 20 percent. The results of the specific chemical analysis (only test concentrations of 100 μl/l) are shown in Table 3.

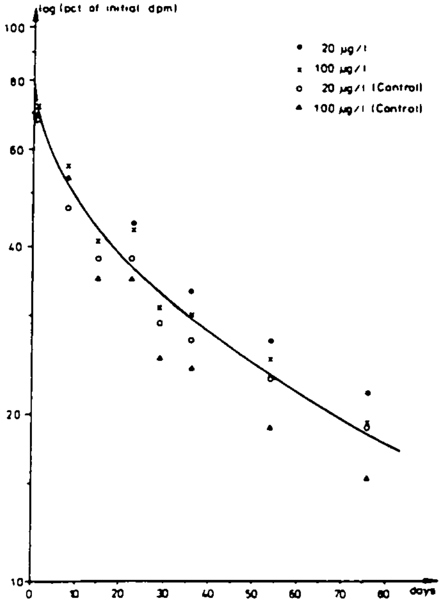


Fig. 2. Degradation of o,o,s-trimethylphosphorodithioate (TMPD). Mean of three replicates is indicated.

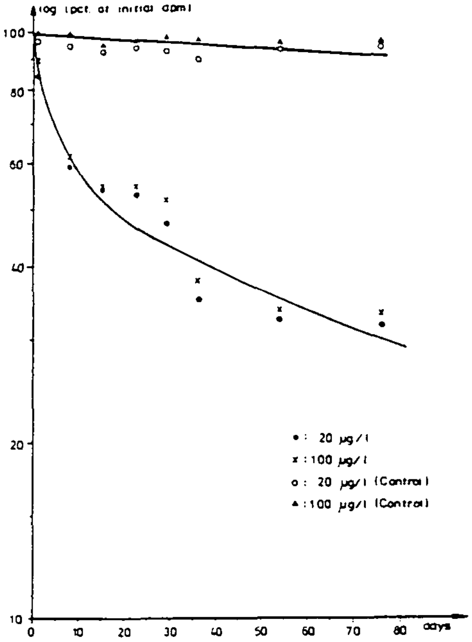


Fig. 3. Degradation of o,o,s-triethylphosphorothioate (TEPT). Mean of three replicates is indicated.

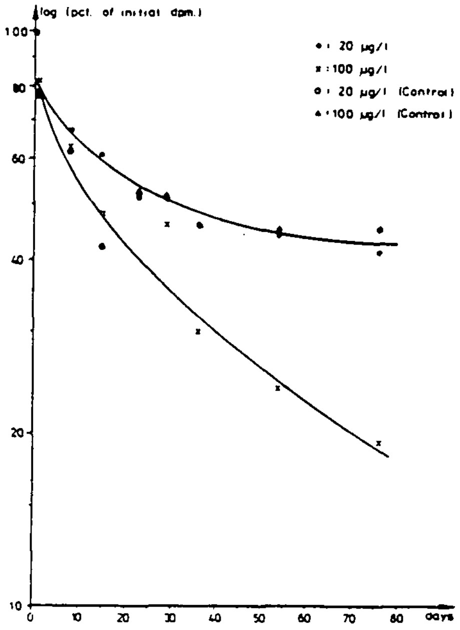


Fig. 4. Degradation of o,o,o-trimethylphosphorothioate (TMPT). Mean of three replicates is indicated.

Tabel 3. Concentrations of TMPD, TEPT and TMPT as measured by specific chemical analysis. Only experiments with initially 100 µg/l were analysed. Detection limit: approx. 10 µg/l.

days from start	TMPD		TEPT		TMPT	
	Test	Control	Test	Control	Test	Control
20	40	-	-	-	<10	-
42	30	20	<10	100	<10	<10
76	<10	<10	<10	50	<10	<10

TMPD is degraded with a half-life of approx. 10 days. The degradation is primarily non-biological (hydrolysis), as no significant difference is observed between the physical/chemical controls and "biological" tests. Also no major difference is seen for the degradation of the two concentration levels applied. The results of the specific analysis (Table 3) is in agreement with the 14-C measurements. Considering the position of 14-C in the molecule (Table 2), both 14-C measurements and specific analysis most likely reflect only the primary degradation of the substance: the hydrolysis of the $S-CH_3$ bond. Thus, the substance is presumably hydrolysed to form Dimethyl-phosphoro-dithioate, on which very little information is presently available.

TEPT is degraded biologically with a half-life of approx. 25 days irrespective of the applied concentration. The biodegradation follows a 2nd order degradation pattern (Figure 3), the slow degradation phase having a half-life of approx. 70 days.

Hydrolysis apparently plays a minor role, as less than 10 percent of the degradation seen after 76 days can be explained from the physical/chemical control test. The performed specific analysis does indicate, however, that 50 percent of the compound is hydrolysed during the 76 days of incubation. As the molecule has been marked by 14-C in the ethyl groups at the oxygen position and not, as was the case for TMPD, at the sulphur position, the degree of degradation as measured by chemical analysis is presumably the best estimate. TEPT is presumably hydrolysed to form Diethyl-phosphoro-thioate.

The slow degradation phase ($T_{1/2}$=70 days) may partly be due to an insufficient test environment for biological activity (depletion of nutrients a.o.) but is believed primarily to indicate the rate of degradation of the diester.

For TMPT, hydrolysis is shown to be a substantial route of degradation (Figure 4), and only for the test concentration 100 µg/l is biodegradation indicated to be a major route, the initial concentration being reduced to less than 20 percent after 76 days of experiment. The biological half-life is approx. 10 days for the first phase and approx. 50 days for the second phase.

While the specific analysis indicates that 90 pct. of the substance has lost its chemical identity after 20 days of experiment, the 14-C measurements show that only 60 pct. is degraded. As only one of the 3 methyl-groups has been marked with 14-C, all being substituted at oxygen positions, the actual primary degradation would be expected to be 3 times higher than measured by 14-C measurements. Thus, the 60 pct. degradation observed is actually higher than expected compared to the specific analysis.

The differences in degradation observed between the test concentrations 20 and 100 µg/l may theoretically be due to differences in adaptation of the microorganisms to the "high" and "low" concentration level (Alexander,M. 1985).

Toxicity

The acute toxicity to Nitocra spinipes is shown in Figures 5, 6 and 7, respectively, for the 3 compounds. In addition to the calculated effect concentrations, the relation between effect concentration and exposure time is also shown.

	LC 10	LC 50	LC 90
24 timer	16 (8,3-20)	26 (22-31)	37 (32-46)
48 timer	11 (6,4-15)	20 (17-25)	30 (25-38)
72 timer	8,2 (4,6-12)	16 (12-25)	23 (18-40)
96 timer	3,7 (0,8-5,8)	12 (9,1-17)	20 (15-31)

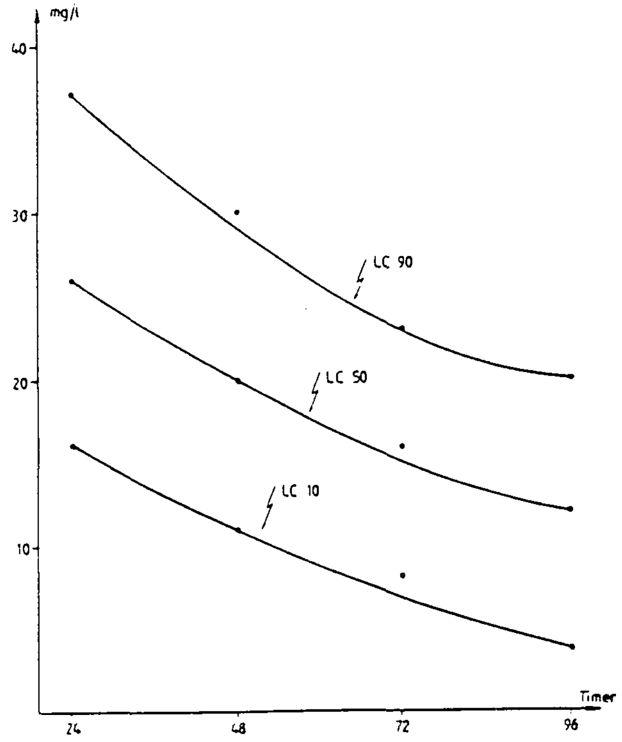


Fig. 5. o,o,s-trimethylphosphorodithioate (TMPD). Concentrations lethal to 10, 50 and 90 percent of a population of Nitocra spinipes after 24, 48, 72 and 96 hours of exposure (LC10, LC50 and LC90). 95% confidence limits are indicated in brackets. The relationship between effect-concentrations and exposure time is shown.

	LC 10	LC 50	LC 90
24 timer	> 200	> 200	> 200
48 timer	124 (37-195)	310 (222-998)	495 (329-1879)
72 timer	71 (31-94)	162 (142-194)	254 (216-330)
96 timer	52 (19-73)	130 (113-150)	207 (180-254)

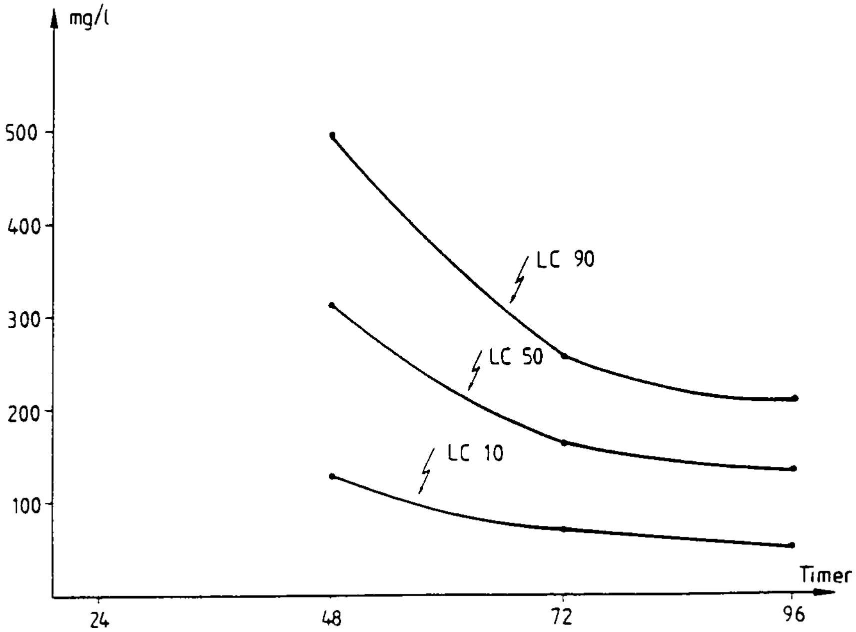


Fig. 6. o,o,s-triethylphosphorioate (TEPT). Concentrations lethal to 10, 50 and 90 percent of a population of Nitocra spinipes after 24, 48, 72 and 96 hours of exposure (LC10, LC50 and LC90). 95% confidence limits are indicated in brackets. The relationship between effect-concentrations and exposure time is shown.

	LC 10	LC 50	LC 90
24 timer	> 194	> 194	> 194
48 timer	168 (101-.)	361 (234-.)	552 (332-.)
72 timer	46 (.-96)	274 (191-930)	502 (324-2050)
96 timer	40 (.-76)	188 (151-276)	334 (256-567)

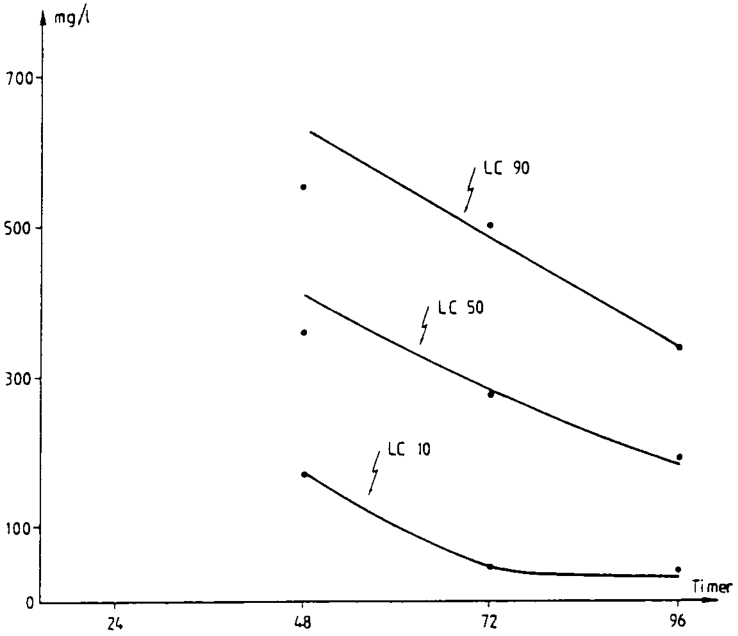


Fig. 7. o,o,s-trimethylphosphorothioate (TMPT). Concentrations lethal to 10, 50 and 90 percent of a population of Nitocra spinipes after 24, 48, 72 and 96 hours of exposure (LC10, LC50 and LC90). 95% confidence limits are indicated in brackets. The relationship between effect-concentrations and exposure time is shown.

While no major differences in toxicity level are observed for the two thioesters TMPT and TEPT (96 hrs.LC50 = 188 and 130 mg/l, respectively), the dithioester is shown to be approx. 10 times more toxic (96 hrs.LC50 = 12 mg/l), the most obvious reason being the differences in numbers of free sulphur groups in the molecules. For the chronic toxicity study, the same relative difference in toxicity is observed (NOEC = 3.2, 3.2, and 0.37 mg/l, respectively for the 3 compounds)(Table 4). Approx. a factor of 10 is observed between acute and chronic toxicity for TMPT and TEPT, while the difference for TMPD is less than a factor of 3.

Substance	NOEC mg/l	14d EC20 mg/l	14d EC50 mg/l
TMPT	3.2	3.2-10.8	>32.4
TEPT	3.3	3.3-11.1	>33.3
TMPD	0.37	1.2-3.7	>12.3

Table 4. Effect-concentrations for chronic toxicity to Nitocra spinipes. No observed effect-concentrations (NOEC) and effect-concentration for 20% and 50% reduction of offspring after 14 days of exposure.

The exposure time versus effect concentration curves indicate that the effect concentrations for TMPT and TMPD do not level off during the 96 hrs exposure period. An indication of a threshold level might have been expected for these water-soluble, very low lipophilic substances within the 96 hrs. study period, as in fact observed for TEPT. An explanation might be found in different degradation (hydrolysis) rates for the substances, which might increase the concentrations of the corresponding Diesters having a free sulphur group and thus presumably a higher toxicity than the non-hydrolyzed substances.

CONCLUSION

The study performed indicates a relatively low toxicity to marine crustaceans of the phosphoro-thioates, while the phosphoro-dithioate studies have a significantly higher acute toxicity, presumably related to the two sulphur groups.

The primary degradation of the compounds is a combination of hydrolysis and biological activity. Degradation half-life irrespective of the process involved is approximately 10 - 25 days based on 14-C measurements and specific chemical analysis. The results obtained indicate that corresponding diethyl-/dimethyl phosphorothioates are formed, and that the degradation rates of these are significantly lower than the parental compounds. The application of both 14-C measurements and chemical analysis for the description of the fate of the chemicals should be recommended for future ""simulation" studies of organic chemicals to prevent misinterpretation of data.

The experiments performed indicate the primary degradation and toxicity of phosphoro-thioates/dithioates under conditions intended to resemble natural environmental conditions. Remarkable differences in both toxicity and degradation of these very similar substances have been shown.

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Alexander, M., 1985. Biodegradation of Organic Chemicals. Env. Sci. Technol., 18(2) p. 106-11.

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Renberg, L. et al. 1980: Chlorinated quaiacols and catechols bioaccumulation potential in bleaks (Alburnus alburnus, Pisces) and reproductive and toxic effects on the harpacticoid Nitocra spinipes (Crustacea). Chemosphere 9: 143-150.

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NORDIC SEMINAR
Pesticides in the aquatic environment - appearance and effect
November 12-14, 1991. Tune Landboskole, Denmark

SOME PESTICIDES USED IN VORWEGIAN AGRICULTURE AND THEIR ENVIRONMENTAL EFFECTS ON COMMON INHABITANTS IN FRESHWATER ECOSYSTEMS. TOLERANCE LIMITS - ACUTE AND CRONIC EFFECTS

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Keywords: Pesticides, toxicity, freshwater organisms.

ABSTRACT

The project "Pesticides in Norwegian agriculture" (FPJV) started in 1988 to collect information about the environmental effects of some commonly used pesticides in Norwegian agriculture. Since then a lot of knowledge has been collected from a variety of bioassays with fresh water organisms about possible effects in water courses draining arable land.

The information is collected with acute and sublethal toxicity tests using algae, zooplankton, macroinvertebrates and fish. Both single species tests and natural communities have been used, collected both from lotic (running-water) and from lentic (standing-water-lakes) environments.

A screening was done with seven commonly used pesticides in Norwegian agriculture to get information about their possible effects in freshwater ecosystems. Five of the pesticides were herbicides (Simazine, MCPA, Dichlorprop, Chlorsulfuron and Atrazine), one was a fungicide (Propiconazole) and one was an insecticide (Dimethoate). A variety of different responses was seen and for some of the organisms the interspecies variation was great. There was a general impression that the most toxic substance was the insecticide Dimethoate followed by the fungicide Propiconazole to the fauna elements. The algae was most affected by the herbicides Atrazine, Simazine and Chlorsulfuron. But also Propiconazole showed increased toxicity to some species of algae. The tolerance limits for some of the pesticides seem to be at a level seen in the brooks and streams from arable land. Our work indicates therefore a need for a broad range of tests to get a good picture of the toxicity of a substance which has the possibility to affect aquatic communities directly and indirectly.

Introduction

The project "Pesticides in Norwegian agriculture" (FPJV) was started in 1988 to get more information about the environmental effects of some commonly used pesticides in Norwegian agriculture. Lentic and lotic ecosystems may be affected by pesticides from treated fields which eventually enter water courses. This have already been demonstrated on several occasions (Morrison and Wells 1981, Dewey 1986, Muirhead-Thomson 1987). During the summer period 1987, eight Norwegian waterbodies where monitored for a selection of commonly used pesticides in agriculture (GEFO and SPV 1987). In 6 of these waterbodies a variety of pesticides was found in concentrations ranging from the detection limit (0,1 μg/l) up to about 20 μg/l.

In 1988 the Norwegian State Pollution Control Authority (SFT) and the Agricultural Research Council of Norway founded a five years research programme to reveal what ecological disturbances pesticide residues may cause in the aquatic environment in Norway.

Experimental studies have been performed in NIVAs test-laboratories and in the field to access the effects of several extensively used pesticides on aquatic life (Table 1). The results have indicated that toxic effects may occur at environmentally realistic concentrations of some of the pesticides investigated. The paper gives a status of the knowledge collected so far during three and a half year of the project.

Table 1. Pesticides studied in the FPJV project

Pesticide	Trade name	Type	Category
Atrazine	Pramitol A	triazine	herbicide
Simazine	Gesatop	triazine	herbicide
MCPA	San-75	phenoxy	herbicide
Dichlorprop	Hedonal DP	phenoxy	herbicide
Chlorsulfuron	Glean	urea - triazine	herbicide
Propiconazole	Tilt 250 EC	triazole	fungicide
Dimethoate	Rogor L 20	organophosphorus	insecticide

Algae

Algae and cyanobacteria are known to be comparatively sensitive to many chemicals, and the inclusion of these organisms in test batteries has been shown to improve the capacity of the battery to predict the most sensitive ecosystem response (Sloff et al. 1983).

To get knowledge about the effect of 7 different pesticides (Table 1) on the growth rate of freshwater phytoplankton, 6 species of algae were investigated (Table 2). With such a variation of test algae one would probably be able to get a picture of the interspecies variation in sensitivity. For hazard assessment purpose, a range of EC50 values obtained from simple screening tests with a battery of test algae will usually provide more useful information than one EC_{50} value determined with a high degree of precision for one test algae (Källqvist and Romstad 1991).

Table 2. Phytoplankton species used in the microplate toxicity tests.

Species	NIVA-strain	abbreviation
Selenastrum capricornutum	CHL 1	Sel.
Chlamydomonas noctigama	CHL 25	Chlam.
Cyclotella sp.	BAC 8	Cycl.
Cryptomonas pyrinoidifera	2/81	Crypt.
Microcystis aeruginosa	CYA 43	Micr.
Synechococcus leopoliensis	CYA 20	Synec.

Among the pesticides tested, the phenoxy-herbicides MCPA and dichlorprop and the organophosphorus insecticide dimethoate showed low toxicity to algae (Table 3), and effects of these pesticides on natural algal communities are unlikely to occur in streams draining arable land in Norway.

Table 3. EC_{50}-values (mg/l active ingredient) for the effect of pesticides on the growth rate of the tested phytoplankton species. (Abbreviations, see Table 2). (From Källqvist and Romstad, 1991).

Pesticide	Selen.	Chlam.	Cycl.	Crypt.	Micr.	Synec.
Atrazine	0.20	0.33	0.43	0.50	0.63	0.13
Simazine	0.20	0.45	0.80	0.50	0.50	0.12
MCPA	120	50	7	15	10	5
Dichlorprop	200	>320	7	90	100	55
Chlorsulfuron	0.8	0.6	10	60	10	0.15
Propiconazole	5.0	0.0008	3.3	0.13	10	4.5
Dimethoate	35	5.5	14	16	8.5	10

The triazine herbicides, atrazine and simazine affected the growth of algae at concentrations that have been recorded in natural waters, and the use of these pesticides may therefore cause environmental effects. Chlorsulfuron had a toxicity comparative to atrazine for the most sensitive species and should also be considered as a potential environmental risk, although concentrations in the toxic range have not been recorded in Scandinavian waters.

The fungicide propiconazole has the potential to affect the species composition of algal communities at environmentally realistic concentrations because of extremely high inter-species variation in sensitivity that was found for this pesticide (Fig. 1). Particularly was that true for different strains of Chlamydomonas (Fig. 2).

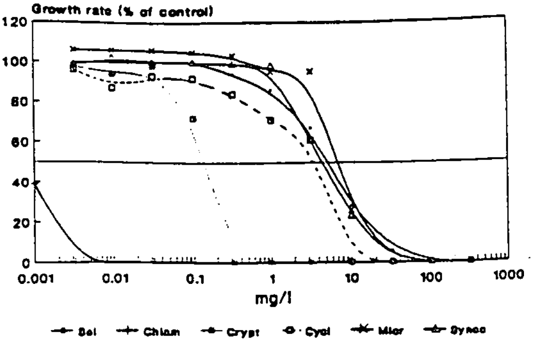

Fig. 1. Effect of propiconazole on 6 species of phytoplankton. (Abbreviations, see Table 2). (From Källqvist and Romstad, 1991).

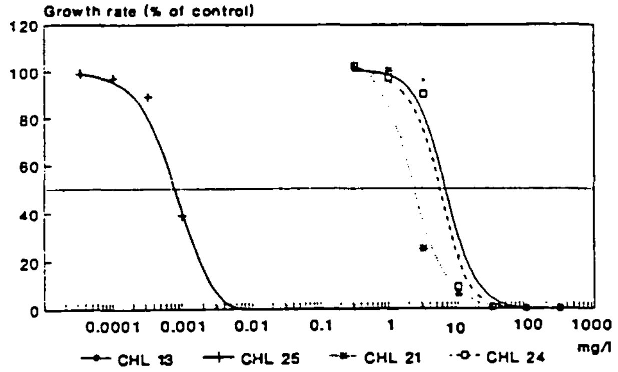

Fig. 2. Effect of propiconazole on 4 strains of Chlamydomonas spp.
CHL 13 and CHL 21= C.reinhardtii, CHL 24 = C.cf.obesa
CHL 25 = Chlamydomonas noctigana. (From Källqvist and Romstad, 1991).

Zooplankton

To study the effect of pesticides on zooplankton, tests were done with Daphnia magna and D. pulex and three of the pesticides: Chlorsulfuron, Propiconazole and Dimethoate, were chosen for further investigations (Fig. 3). In acute laboratory tests the LC50 value was greater than 100 mg/l of Chlorsulfuron and the LC50 value for Propiconacole was less that 10 mg/l. Dimethoate had far higher toxicity for both species with a LC50 value ≈ 0.02 mg/l (Hessen, 1991).

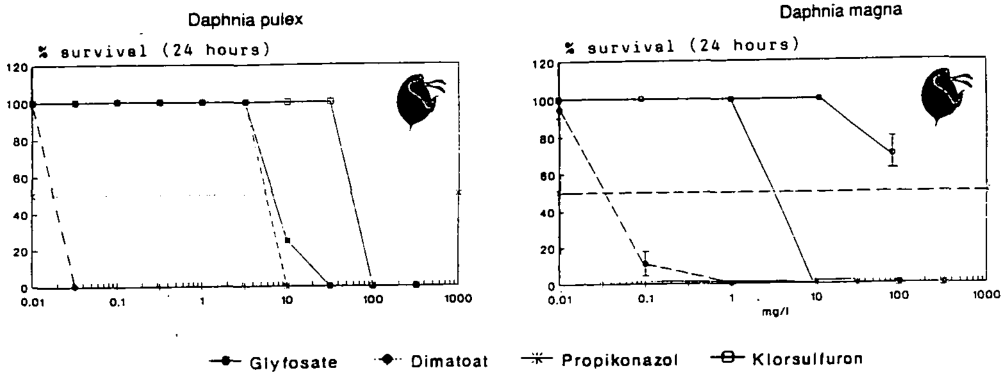

Fig. 3. Laboratory screening of acute toxicity on the cladocerans Daphnia pulex and D. magna.

Enclosure tests with natural communities; Limnocorrals

In toxicity studies most often the aim is to gain knowledge on expected effects in natural environments, meaning that indirect effects through food chains could be more important than the direct effects (cf. Lampert et al 1989). From the laboratory tests with single species we moved out into the field to NIVAs enclosure test station in lake Omdalsvann. Here we have developed a lake test laboratory, with 18 enclosures (21 m^3) made of plastic bags with a diameter of 2.5 m and a depth of 4 meters. The bags are closed in the bottom and open at the top, and are filled with water from the lake with the natural communities of algae and zooplankton.

These small enclosures of lake water were given initially some small amounts of phosphorus and nitrogen to avoid shortage of nutrients. Two of the enclosures were used as controls without any addition of pesticides. Three of them were used to study the effect of Chlorsulfuron, another three for the study of Propiconazole. Further, three were added Dimethoate and the concentrations in the enclosures of the reactive pesticide was 1 µg/l, 10 µg/l and 100 µg/l.

In a test period of 15 days a lot of samples were taken to describe the species composition, the volume of phytoplankton and zooplankton, the photosyntetic activity and the content of chlorophyll, chemical analyses were done to measure the amount of phosphorus and nitrogen and the residual concentration of the different pesticides used. The results was compared with the situation in the enclosures used as controls.

The data from the enclosure test shows that there had been no degradation of Dimethoate, but for Propiconazole the degradation has been nearly 40% - photodegradation can be the reason for this. The results emphasize that even "easy degradable" pesticides can have a relative long life time when they enter the aquatic environment, which then increase the bioavailability of these substances.

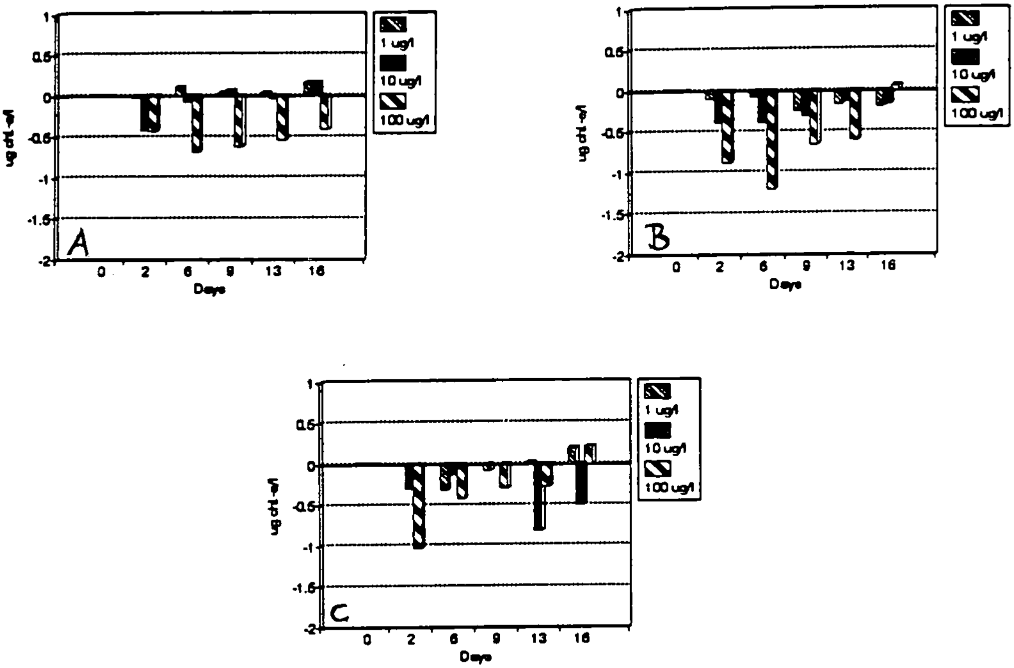

Fig. 4. Deviations in chlorophyll-a concentrations relative to control enclosures - A = Chlorsulfuron, B = Propiconazole, C = Dimethoate (From Källqvist et al 1991).

From the analysis of the phytoplankton in the different enclosures we have seen a reduced response to the initial nutrients (which was given in the beginning of the test) to all the different pesticides and concentrations used. In the enclosures with 100 µg of pesticide/l there was a significant reduction both in the volume of algae and in the amount of chlorophyll. This tendency was also seen in the 10 µg enclosures, but was not so clear in the 1 µg enclosures (Fig. 4). On the other hand, studies of the species composition show very clearly that a concentration of 1 µg/l of pesticides was high enough to give drastic changes compared to the phytoplankton communities seen in the control (Abdel-Hamid et. al, 1991). The diversity index (Shannon Wiener) in the controls was about 2,76 to 2,69, but there was a drastic reduction in the enclosures where pesticides were added. The lowest value was 1.8 and was measured 2 days after exposure (Fig. 5).

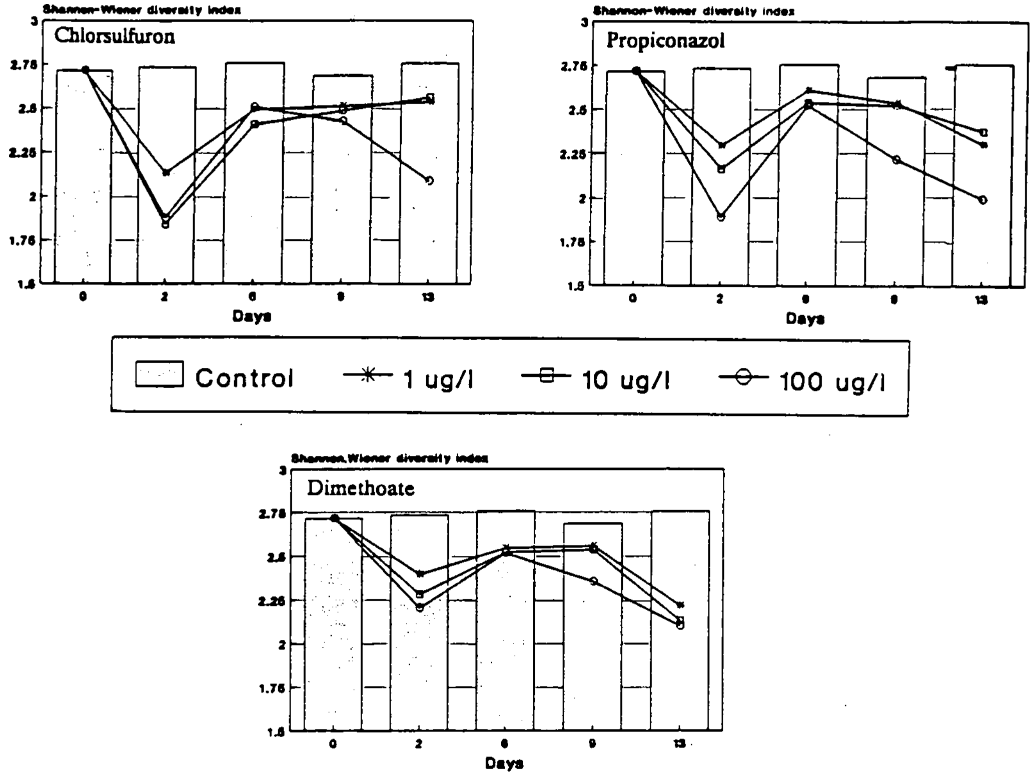

Fig. 5. Effects of pesticides on phytoplankton species diversity. Data from enclosure tests with natural communities of algae. (From Abdel-Hamid et al. 1991).

As was shown through the toxicity test in the laboratory, there was a great variation in the tolerance between the different species of phytoplankton (Table 3). The measuring of the photosynthetic activity after further addition of pesticides when the test period was over, shows no reason to support any values for adaption (an increased tolerance) among the phytoplankton (Källqvist et al 1991).

The outdoor experiments with our 21 m^3 enclosures give several ecological responses which were not seen in the laboratory tests. The strong negative effect, seen in the enclosure with 100 µg/l of Dimethoate on the biomass of phytoplankton was unexpected. In earlier laboratory tests we were not able to detect any effect of Dimethoate under 1000 µg/l on the species of algae used.

Our results from the study of zooplankton in the different enclosures supported what was seen in the laboratory tests: Dimethoate was the far most toxic pesticide. It was not possible to find any indirect effects on the zooplankton community from the herbicides, in the 15 days of testing.

As the crustacean zooplankton was susceptible to the insecticide this was reversed for the planktonic rotifers which gave no negative response to Dimethoate (Hessen et al., 1991).

Studies which have been done in Norway in the laboratory and in the field with enclosure experiments (Hessen et al. 1991) give us the impression that the tested herbicides should not represent a major problem for zooplankton in lakes if we compare it with the detected concentrations in Norwegian surface waters.

Studies in Germany done by Lampert et al. (1989) still suggest that various toxins may be active in very low concentrations. Also the strikingly low degradability of dimethoate in water should call for a special attention on this pesticide with regard to effects on crustacean zooplankton and other aquatic artropodes. Various species and taxa of zooplankton respond however highly different on the various toxins, clearly stating that general conclusions based on single-species tests are premature (Hessen et al., 1991).

MACROINVERTEBRATES

Introduction

In bioassays benthic macroinvertebrate populations from lotic environments were exposed to seven pesticides commonly used in agriculture in Norway: MCPA (herbicide), Dichlorprop (herbicide), Atrazine (herbicide), Propiconazole (fungicide), Dimethoate (insecticide, acaricide) and Simazine (herbicide) and Chlorsulfuron (herbicide) (Table 1).

In throughflow aquaria with continually dosing of the pesticides 96h LC_{50} tests were conducted. Information on sublethal effects for Dimethoate (1 ppb) and Propiconazole (5 ppb) was collected through 4-5 week experiments using simplified macroinvertebrate communities, composed in indoor experimental streams (Aanes, 1989) (Fig. 6). Drift activities of different populations were registered, together with changes in community structure.

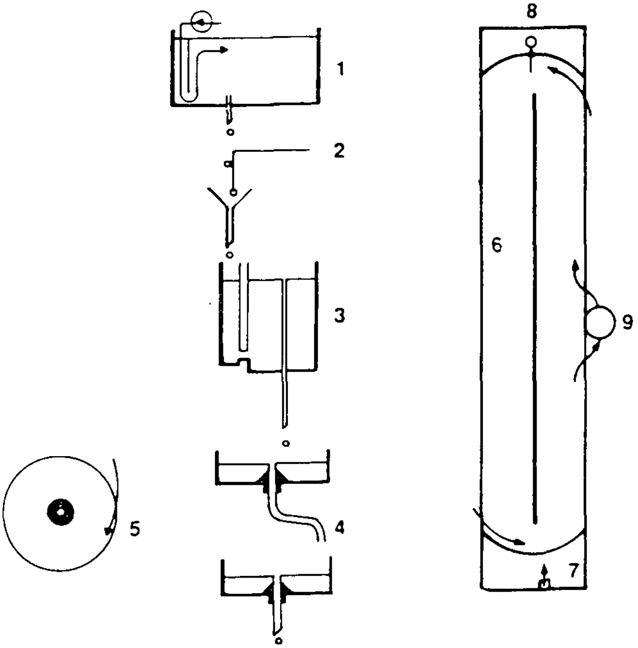

Fig. 6. The laboratory test apparatus. 1) water reservoir with filtered water, 2) pesticide from peristaltic pump, 3) mixing vessel, 4) and 5) circular aquaria 6) experimental stream, 7) inflow, 8) outflow, 9) apparatus for collecting drift.

ACUTE EFFECTS

Materials and methods

Five common species of the macrofauna were used in the tests: The snail Physa fontinalis, the crustacean: Amphipod, Gammarus lacustris, three insects, the mayflies Baetis rhodani and Heptagenia sulphurea, and the netspinning caddisfly Hydrophsyche siltalai. The first two are primarily lake species, but are also found in lotic environments (Økland 1969). The last three species are confined to running waters. The animals were in the last instar and were sampled a few days before the tests.

Seven pesticides were tested, including five herbicides, one fungicide and one insecticide (Table 1). All concentrations referred to in the tests are calculated values of the active pesticide chemicals in the commercial products.

A through-flow system was used with the pesticides continually dosed from a peristaltic pump (Fig. 6). There was an input of 30 l of test water/hour to each of the circular aquaria. The water quality was representative for Norwegian unpolluted lowland waters (Table 4). To prevent particles from entering the test system, all input water was natural lake water filtered through a series of 10, 5, and 1 µm column filters. Artificial substrate was made up of different sized glass spheres. The two ephemeropteran species were put into separate boxes in the lower row of aquaria to minimize interspecific disturbance. All experiments were run for 96 hours using five test solutions and one control. The water temperature was 15 ± 1°C. Dead animals were removed, and heavily affected animals as well as exuvia were registered two or three times a day. LC_{50} values were calculated according to a Logit model.

Table 4. Chemical data of the test water used in the experiments. Mean values.

Parameter		Parameter	
pH	6.3	Ca, mg/l	3.7
Conductivity, mS/m at 25 C	0.2	Mg, mg/l	0.41
Colour, mg Pt/l	21	Na, mg/l	1.1
COD, mg O/l	4.0	K, mg/l	0.35
Total nitrogen, µg N/l ...	300	Cd, µg/l	0.30
NO_3, µg N/l	180	Cu, µg/l	2.0
Total phosphorous, µg P/l	4.5	Zn, µg/l	<10
Cl, mg/l	1.3	Pb, µg/l	1.0
Hardness, mg $CaCO_3$/l	11	Al, µg/l	110

Results

MCPA, Simazine and Dichlorprop were tested only at the 10 ppm concentration. Mostly small effects were seen; 90% or more of the animals survived. The highest lethality was observed among Hydropsyche siltalai and Physa fontinalis in MCPA (40% and 20% respectively in 96 h) (Fig. 7).

Chlorsulfuron seems to be more toxic than MCPA, Simazine and Dichloroprop. Nearly 90% of the Gammarus lacustris died in the 10 mg/l concentration, and also the snail and the mayfly B. rhodani showed an increased mortality. But at the same time some of the results were confusing and rather contradictory (Fig. 7).

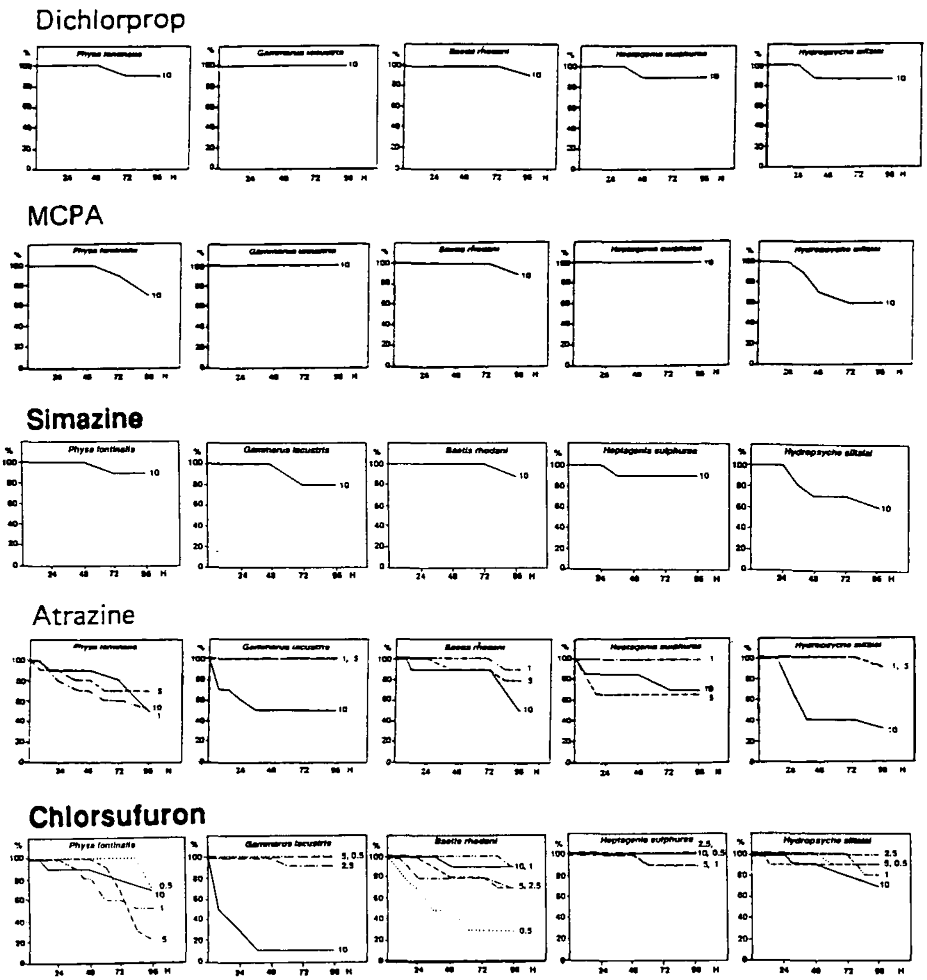

Fig. 7. Survival curves for five macroinvertebrate species exposed to five pesticides. (From Bækken and Aanes, 1989, 1990)

Atrazine was tested at the concentration levels 10, 5 and 1 ppm. All animals were severely affected at 10 ppm. Except for Heptagenia sulphurea, less than 50% survived the 96 h period. In the 1 and 5 ppm solutions the number of survivors varied, but mostly the effects were small (Fig. 7).

Propiconazole was tested at the 10, 5, 1, 0.5 and 0.25 ppm concentrations. The fungicide showed that all individuals died within few hours in the 10 ppm solution (Fig. 8). In the 5 ppm solution the animals survived for a longer time, but all were dead within 96 h. Between 50% and 100% survived at lower concentrations. The toxicity measured as 96 h LC_{50} was quite similar for all species, with values ranging from 0.87 ppm for Baetis rhodani to 1.3 ppm for Gammarus lacustris (Table 5).

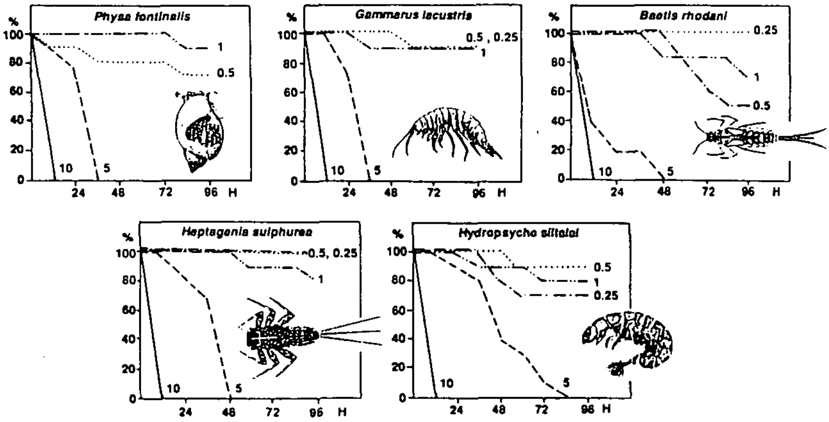

Fig. 8. Survival curves for five macroinvertebrate species exposed to Propiconazole.

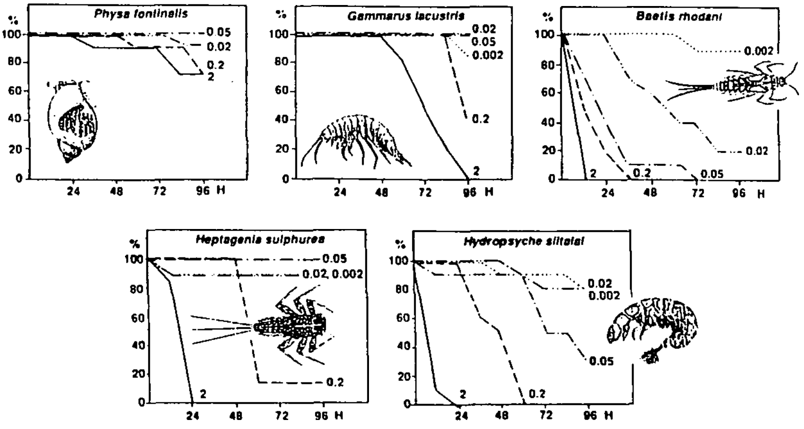

Fig. 9. Survival curves for five macroinvertebrate species exposed to Dimethoate.

For Dimethoate the test concentrations were 2, 0.2, 0.05, 0.02 and 0.002 ppm. Physa fontinalis showed to be the most tolerant species to this pesticide; 25% died in 96 h in the 2 ppm solution (Fig. 9). For the other species LC_{50} values ranged from 0.007 ppm for Baetis rhodani to 0.18 ppm for Gammarus lacustris (Table 5). Among the species with intermediate sensitivity, Heptagenia sulphurea was more tolerant than Hydropsyche siltalai. Survival curves showed that both Baetis rhodani and Hydropsyche siltalai died within few hours in the 2 ppm solution. 50% of Gammarus lacustris survived that solution for 72 h, but they were in a state of coma from the first day. No one survived for 96 h.

Table 5. 96 hours LC_{20}, LC_{50} and LC_{80} values for five invertebrates in relation to one fungicide: Propiconazole and one insecticide: Dimethoate. The units are ppm. (From Aanes & Bækken, 1989).

Species	Propiconazol			Dimethoate		
	LC20	50	80	LC20	50	80
Gastropoda						
Physa fontinalis	0.7	1.3	2.6	-	-	-
Crustacea						
Gammarus lacustris	0.7	1.3	2.5	0.06	0.18	0.54
Ephemeroptera						
Baetis rhodani	0.4	0.9	2.0	0.003	0.007	0.015
Heptagenia sulfurea	-	1.0	-	0.024	0.081	0.27
Trichoptera						
Hydropsyche siltalai	0.5	1.2	2.8	0.006	0.023	0.092

SUBLETHAL EFFECTS

Materials and methods

Sublethal effects on the benthic fauna in running water ecosystems were studied in indoor experimental streams. 30 trays were filled with a defined combination of sand, gravel and pebbles and colonised by a natural stream biota for 5 weeks in a nearby stream. 10 trays, randomly picked out, were put into each of two indoor experimental streams. The remaining 10 trays represented the animal communities at the start. Each stream was 5 m long (Fig. 6). Most water was recirculated, but there was a continuous renewal of 105 l/h. The acute tests showed that two of the tested pesticides was more toxic than the others. It was decided to go further with sublethal concentrations to search for effects over a 5 week period. Such effects have been shown both for herbicides and insecticides (Streith and Peter 1978, Arthur et al. 1983, Seuge and Bluzat 1983, Dewey 1986).

One stream was treated with a low dose of Dimethoate (0.001 ppm) in the first test, and with Propiconazole (0.005 ppm) in the second. The other stream was untreated. One part of the stream water was channelled out into a net and pumped back again, and the number of drifting animals counted. During the first day the mesh size of the net was 500 µm, but was then shifted to 250 µm.

In the sublethal experiment with the Propiconazole we also studied how benthic algae previously colonized unglazed ceramic tiles in a natural stream was affected. Together with these tiles we also put in sterilized tiles in the experimental streams to see how the colonization of algae on new tiles was affected. The tiles were illuminated and the day length was 16 hours.

After 5 weeks the tiles were analysed. The chlorophyll a was measured and a semiquantative study of the algae community on the tiles was done.

RESULTS

Dimethoate

In the Dimethoate treated stream there were always more or equal number of individuals drifting compared to the reference stream (Fig. 10A). Our hypothesis has been that the benthic animal community if it is affected responds to low concentrations of insecticide with an increased drift rate. This has been shown for a wide range of chemicals and has been reported from several pesticide contaminated streams (Wallace and Hynes 1975, Muirhead-Thomson 1987, Sebastien and Brust 1989).

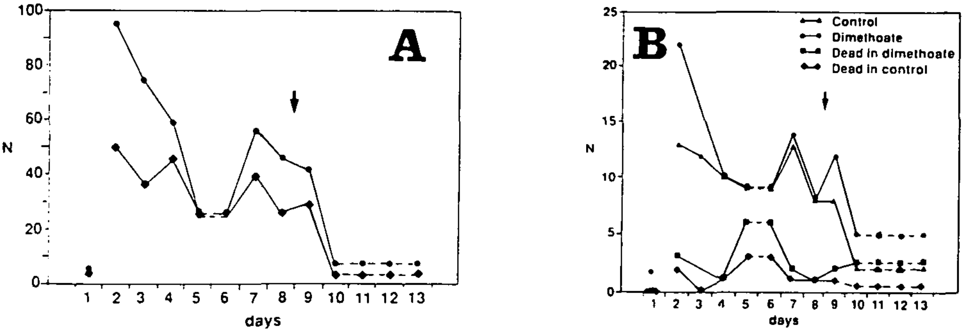

Fig. 10. A) Total number of animals found in drift/day in the Dimethoate treated (0.001 ppm) (•------•) and untreated stream (♦---♦).
B) Total number of chironomids found in drift/day, and the number of these that were dead. Arrow indicates the 12 hour period of 0.005 ppm dimethoate.

The total number of animals found in the drift during the registration period was 487 in the treated stream and 306 in the untreated one. Most of these were chydorids. Another group frequently encountered was the chironomids (Fig. 10B). The plecopteran species Leuctra digitata was only sparsely found; a total of 20 in the treated and 11 in the untreated stream (Fig. 11).

During the first day the number of drifting animals was low (Fig. 10A). On day 2, after the drift net was shifted, the number of animals caught increased considerably; 95 and 50 were found in the treated and untreated stream respectively. At the end of the period the numbers were 7 and 2. A peak was seen on day 7. On day 9 we increased the pesticide concentrations to 0.005 for 12 hours. The number of chironomids drifting the following day increased slightly, followed by another decrease. By now about 70% of the drifting animals in both streams were chironomids, whereas in the beginning the proportion was about 20%. The number of dead chironomids found in drift was relatively high on day 5 and 6 (Fig. 10B), and during the last 4 days period, when 50% or more were dead in the stream treated with 0.001 ppm Dimethoate.

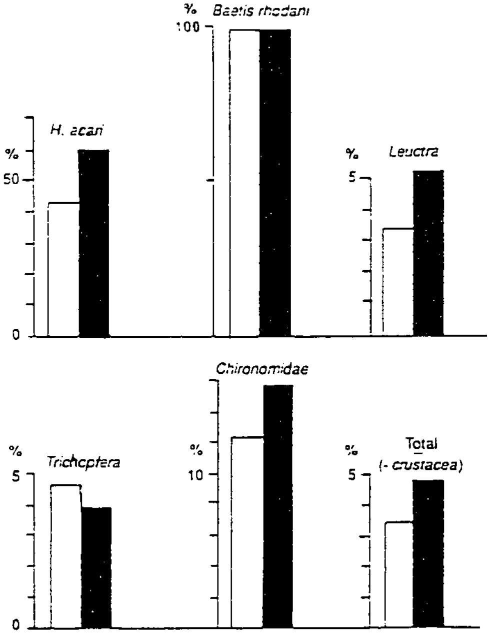

Fig. 11. The number of drifting animals in relation to their frequency in the bottom fauna.

Dimethoate stream ■

Control stream □

When the experiment with Dimethoate was ended all the animals in the streams were counted. For most of the groups (Fig. 12) there was a reduced abundance in the Dimethoate stream compared to the control stream. For the coleoptera larvae the reduction was more than 70% and for trichoptera more than 50%. A significant increase in the abundance was found only for the oligochaeta. Gastropodes were slightly more abundant in the Dimethoate treated stream.

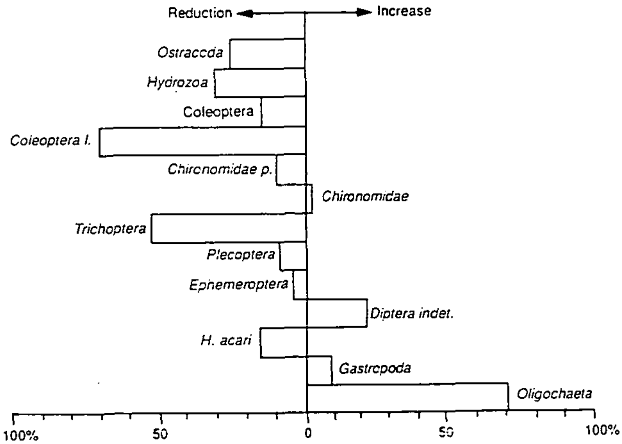

Fig. 12. Dimethoate. Changes in the community structure at the end of the experiment.

PROPICONAZOLE

Macroinvertebrates

The total number of drifting animals/day in the propiconazole treated stream revealed no pattern indicating effects like those we found in the bioassay with Dimethoate. There seems to be a tendency that were more animals drifting in the untreated stream (Fig. 13).

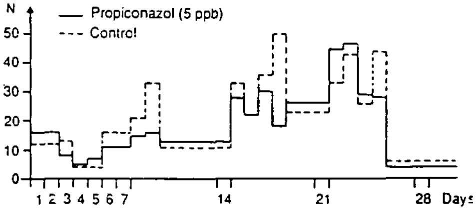

Fig. 13. Total numbers of animals found in the drift/day.

The only two groups with a higher drift rate in the Propiconazole stream were the larvae of the caddisflies. Hydropsyche and the blackflies Simuliidae (Fig. 14). Both are filter feeders living on the top of the substrate. The simuliidae population was reduced by 75% in the Propiconazole treated stream compared to the control stream. At the same time there has been and increase of young individuals hatching during the experiment in the Propiconazole stream compared to the control. That is particularly true for the small and unidentified dipterans, larva of plecoptera and the ostracods (a group of water fleas) (Fig. 15).

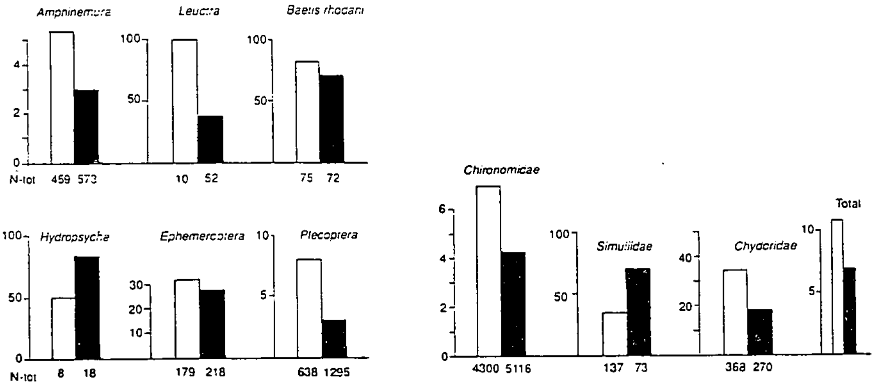

Fig. 14. Propiconazole. The number of drifting animals in relation to their frequency in the bottom fauna.

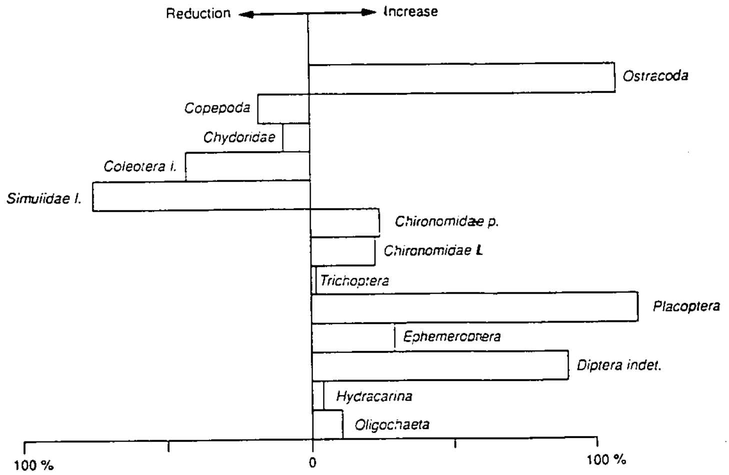

Fig. 15. Propiconazole. Changes in the community structure at the end of the experiment.

Algae

The algae community in the Propiconazole stream was gradually reduced. At the end of the experiment it was not possible by a visible examination to detect any remaining algae on this tile in the Propiconazole treated stream. A microscopical examination showed small numbers of only 4 algae species while at least 9 was present at start. Surprisingly we also found a lot of fungus on that tile.

In the control stream only small changes were seen (Table 6), mainly connected to new algae which have started to grow on the colonized tile.

For the new tiles which were put in the streams at the beginning of the experiment there had been an active colonization in the control stream, whereas only some single cells could be found in the treated stream. An examination of the chlorophyll content on these tiles gave 5,3 mg chlorophyll a per tile (10.9 cm^2) in the control stream. In the Propiconazol stream chlorophyll a was not detected.

Table 6. Semi quantitative analysis of the natural algal community on ceramic tiles, "old" (colonized in a natural stream and placed in the experimental stream). When the test was started "new" sterilized tiles were placed in the streams to study the colonization of algae. Results after 5 weeks in an experiment with 5 ppb Propiconazole. (From Aanes & Bækken 1989).

		Control		Propiconazol	
At start		old	new	old	new
*	Anabaena flos-aqua				
	Binuclearia tectorum	*			
**	Bulbochaete sp.	**		*	
	Cosmarium spp.	*	*		
	Euastrum elegans	*			
***	Muogeotia sp. (5 μm)	***	*		+
***	Muogeotia sp. (11-14 μm)	***	**		+
**	Muogeotia sp. (20-23 μm)	**	**		
**	Oedogonium sp. (5-8 μm)	**	*		+
	Oedogonium sp. (20 μm)			*	
	Staurastrum sp.	*			
	Teilingia granulata	*	*		
***	Zygnema sp.	**	*	*	
***	Achnantes sp.	***	**		
	Eucocconeis lapponica	*			
***	Tabellaria flocculosa	***	*	*	+
*	Vorticella sp.				
	Fungus			**	

*** dominating species
** common
* rare
+ single cells

DISCUSSION

When testing stream organisms a continuous through-flow system is highly recommended (Muirhead-Thomson 1987). This ensures a constant level of pesticides and minimizes additional stress caused by stagnant water and variable water quality. The kind of animals used in this study are not common in standard toxicity tests. But as inhabitants of affected ecosystems they should be used more frequently. Information as to their reactions to the present pesticides is scarce in the literature. However, data on other invertebrates such as Daphnia magna as well as fish confirms that atrazine is the most toxic of the tested herbicides (Ciba-Geigy Ltd. 1975, Macek et al. 1976, Gustafsson 1987). Whereas Dimethoate was highly toxic to both the crustacean and the insect larvae, gastropods seem to be more tolerant, as shown for Physa fontinalis. A similar result has previously been found for P. fontinalis in relation to the insecticide Lindan (Green et al. 1986). The tolerance of the insect species to Dimethoate was in the same range as previously shown for the plecopteran Pteronarcys californica with a 96 h LC_{50} value of 0.043 ppm (Sanders and Cope 1986). Also for Gammarus lacustris the present results are in accordance with a previously recorded 96 h LC_{50} value; 0.20 ppm (Mayer and Ellersieck 1986).

Pesticide concentrations found in surface waters are generally low. In a recent study maximum MCPA, Dichlorprop and Atrazine concentrations in some Norwegian surface waters were 2.6, 3.0 and 0.5 ppb respectively (Gefo/Statens plantevern 1987). These concentrations are not expected to produce any acute effects on the macroinvertebrate fauna, may be with the exception of drift responses. But there may be long term effects. This has been shown for both herbicides and insecticides (Streit and Peter 1978, Arthur et al. 1983, Seugè and Bluzat 1983, Dewey 1986).

Parts of the invertebrate fauna of streams may respond to an impairment of the environmental conditions with escape behaviour resulting in increased drift. We found higher drift rate in the stream treated with 0.001 ppm Dimethoate. Assuming the streams are identical, identical drift rates are expected. Consequently Dimethoate may be responsible for the observed differences. This suggestion is supported by the high proportion of dead chrionomids in the treated stream during the last days. However, drift patterns in the two streams are very similar indicating that other factors identical for the streams, are responsible for some of the drift.

In the bioassay with Propiconazole the concentration of 0.005 ppm did not give a clear drift reaction. One explanation for this might be that Propiconazole slows down the mobility of the animals. Only for two group the Hydrophsyche and Simuliidae, we found an increased drift rate in the treated stream. We had an unexpected increase in the abundance for most groups in the Propiconazole stream indicating that Propiconazole at least does not negatively affect the hatching of insect eggs. Although the results were not so distinct as they were in the bioassay with Dimethoate the negative effects on the benthic algae were significant. The whole algal community was wiped out and replaced by fungus, amazingly as Propiconazole is a fungicide.

CONCLUSION

Macroinvertenrates

As conclusion on our experiments so far: The 96 h LC_{50} values ranked the seven pesticides with respect to negative effects on benthic fauna in lotic environments in four groups.

1. For the three herbicides: Dichlorprop, Simazine and MCPA we did not get any acute effects with 10 ppm concentrations.
2. For Atrazine and Chlorsulfuron much of the same picture was shown, but effects were a little more visible than in group 1.
3. In this group we placed Propiconazole which are much more toxic than the pesticides in group 1 and 2. The fungicide Propiconazole may also affect the benthic fauna in running waters because of the negative effect on the benthic algae, important food organisms for the benthic fauna.
4. The most serious problems for the benthic fauna were clearly connected to the insecticide Dimethoate. Here we found great negative changes in benthic communities at sublethal concentration of only 0.001 ppm.

Table 7. Sublethal effects of 1 ppb Dimethoate and 5 ppb Propiconazole on the benthic fauna and algae studied in a 5 weeks period in artificial streams.

	DIME-THOATE: 1 ppb	PROPICO-NAZOLE: 5 ppb
Increased DRIFT	+	÷
Increased in no. of dead animals	+	0
Increased movement out of the cages	+	÷
Reduced abundance	+	÷
Negative effect on early life stages	+	÷
Reduced break down of allochtonus material	?	÷/0
Reduced development of benthic algae	?	+

Fish

In the FPJV project the effect of pesticides on freshwater fish started this autumn. The result so far are preliminary and we are in an early phase in our fish study. In Table 8 96 hour LC_{50} values are given for small trout (0+) (<u>Salmo trutta L.</u>) which were born this spring. The values for the different pesticides which are tested are given as the amount of active pesticide chemical in the commercial products. The results showed that the 96 hour LC_{50} values for trout gave much the same respond as for macroinvertebrates with a LC_{50} value for small trout on 0.14 ppm of Dimethoate and for Propiconazole the value is 1.2 ppm.

Table 8. Results of 96 hour semi static tests with trout (0+) (Salmo trutta L.) given as LC_{50} values for 9 different pesticides.

Pesticides	**Values**
Endosulfan	1.8 mg/l
Dimethoate	0.14 mg/l
Propiconazole	1.2 mg/l
Atrazine	25 mg/l
Glyphosat	5.4 mg/l
Clorsulfuron	38 mg/l
Simazine	83 mg/l
Dichlorprop	91 mg/l
MCPA	300 mg/l

Compared to the toxicity of Endosulfan only Dimethoat and may be Propiconazole have a toxicity which would be of some interest for further studies, but the concentrations are still much higher than values found in recipients draining arable land.

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PESTICIDES IN DRINKING WATER. RESIDUE LIMITS AND TOXICOLOGICAL PROBLEMS.

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INTRODUCTION

Since the early 1980s it has become apparent in many countries that not only surface waters but also ground water can be contaminated by pesticides used in agriculture and from other activities. Quite often point source contamination due to improper use and handling of the pesticides is the cause, but in intense farming areas especially, diffuse contamination due to normal and approved use of the pesticides may also be the case. The fear of such contamination impairing drinking water quality has given rise to worldwide surveys on the presence of pesticide residues in different kinds of water supplies. The first results on the wide-spread contamination of ground water came from the U.S.A. around 1980. In Europe the earliest estimations of pesticides in ground water due to normal agricultural use were made in Germany, the Netherlands, Italy and United Kingdom in 1985 and 1986. Substances detected in these investigations were atrazine and simazine, bentazon, phenoxy herbicides and dichlorpropane.

The use of pesticides in agriculture has decreased in Sweden, especially since 1987, when the government introduced the 50% reduction programme. That means the amount of pesticides used in agriculture had to be reduced by 50% in 1990 compared to 1985. This programme was succesfully carried out and a new goal of another 50% reduction until the middle of the 1990s is set. In comparison with other countries the amount of pesticides used per hectare in Sweden is low, a couple of kilos at most, compared with as much as 25 kg of active substance per hectare in the most intensely farmed areas in the Netherlands.

In Sweden, like in many other countries, both surface and ground water is used as drinking water supplies, in our country most of the public supplies, however, are of surface water origin, but e.g. in the Netherlands about 70% of the drinking water originates from ground water and in Denmark most of the water supplies are ground water. In the Netherlands there are very intense farming activities and in combination with their sandy soils which allows contaminants to penetrate quite readily there is a much greater problem with contamination of drinking water supplies than in Sweden for example. Also in the UK and France high levels of different pesticides in drinking water supplies has been detected.

Pesticide analysis in water

As pointed out before an increasing numbers of pesticide residues have been detected during the 1980s in both surface water and ground water in various parts of the world. In view of such reports the National Food administration (NFA) in collaboration with the National Laboratory for Agricultural Chemistry carried out, in 1988, an investigation of pesticide residues in 56 surface waters used for the production of drinking water and in addition in two ground water wells.

Samples were taken at various locations all over Sweden from waters considered to be in danger of becoming contaminated, not only from farming activities but also from golf courses, forest and garden nurseries, roads and railroads. Samples were taken twice from the raw water and the corresponding drinking water at each water supply. The first samples were taken close to the treatment with pesticides, in May or June and the second in September or October. Most of the pesticides used in Sweden could be determined by the analytical methods used.

Although surface waters considered to be in danger of becoming contaminated were chosen for the investigation, only a few cases of detectable amounts of pesticides were found in surface waters used for the production of drinking water in the spring samples. The pesticides found were MCPA, dichlorprop and bentazon, mainly at levels around the limit of determination. In no case, pesticides were found in the corresponding drinking water. In the fall sampling, residues were found only in the two ground water wells.

In investigations carried out more or less continously on the initiative of county or municipal authorities in different parts of Sweden, mainly on ground water (wells), residues of additional pesticides have been detected, including several belonging to the triazine group. In some areas of Sweden there seems to be a greater risk of contamination than in others. Such an area is e.g. the island of Gotland, where the cracks in the limestone, the main ground material on the island, allows the pesticides to penetrate readily to the ground water. In most cases improper handling and use of pesticides is thought to be the source of contamination, but in a few cases this is not the case and still some years after the last use of bentazon in the surroundings, this substance can be detected in a couple of ground water wells. These investigations carried out in Sweden indicate that pesticide residues can be found in ground water. Although it is not yet considered a great problem, attention has to be payed to minimize the risk for future contamination.

Results from the Netherlands points to two related problem areas which should be more investigated in our country as well. These are the risk of metabolites of the used pesticide being present in the ground water and that a long time may elapse before a substance is detected in the ground water.

Dutch surveys have shown that in some cases higher concentrations of metabolites than of the parent compound can be present. The metabolites, which may be of greater toxicity than the pesticide itself, are not found in regular pesticide analyses and special attention should be given to this problem. Dutch experimental data and model calculations have, moreover shown that there is a risk for a long latency period before the peak concentrations of some pesticides are reached and it might not be detected in the ground water until many years later, even if the use has ceased. From this follows that although we, at present, do not consider pesticide contamination of water supplies a great problem in Sweden, we cannot be sure that metabolites are not present or that the problem will not increase as long time may elapse before pesticides reach the ground water and may be detected. This points to the need of a continous survey of pesticide residues as well as their metabolites.

According to Swedish authorities, the National Food Administration and the Chemicals Inspectorate among others, the normal use and handling of pesticides must not contaminate ground water or surface water supplies. The former minister of agriculture puts it even more strongly by stating that society cannot accept the occurence of pesticide residues in ground water, surface waters and foodstuffs. It is thus of importance that very mobile and persistent substances should not be used if there is a risk that a drinking water supply may become contaminated. The approval for such pesticides may be withdrawn if deemed necessary. In some cases the soilprofile may be of such character that even an use considered to be normal can give rise to detectable levels of a pesticide in the water. In the light of the results of the Swedish investigations and those from other studies, the mobility and persistence of the substances, the National Chemicals Inspectorate has withdrawn the approval of pesticide products containing atrazine as well as restricted the use of bentazon products.

Evaluation of pesticide residues

The findings so far in the Swedish investigations are not considered to be of any significance from a health point of view, but the NFA claims that residues of pesticides must not be found in drinking water. This is stated in the drinking water ordinance of 1990. This opinion is shared by many other countries as well as the EEC, which has, already in 1980, set a MAC value (maximum admissible concentration) of 0,1 ug/l for individual pesticides and 0,5 ug/l for the total amount of pesticides. This "surrogate" zero level has been criticized by some member countries, esp. the UK. One of the reasons for this criticism is that not all pesticides can be determined at this level and besides for some substances covered by this parameter the level is too high from a toxicological point of view. At a recent conference in Milan concerning atrazine and other pesticides, a reprensentative of the EEC strongly pointed out that the commission has no intention for the time being to change its approach to the MAC-value for pesticides.

If pesticides are detected in public drinking water it is obligatory for the responsible water work to take action - both in Sweden and in the EEC-countries. No derogations is available within the EEC for toxic substances. The "Drinking Water Directive" provides that in situations where the MAC for pesticides is exceeded, an extension of time to comply with the MAC and a programme of action would need to be agreed by the European Commision. With conventional treatment techniques pesticides cannot be removed effectively. With present knowledge, some polar pesticides can partially be removed by activated carbon and/or ozone, combined treatment with hydrogen peroxide is also tested, none of which are considered as conventional treatment techniques (so far). This partial removal of some pesticides does not in any way mean that other pesticides and their degradation products also will be removed. Moreover, it is discussed if unwanted products may be formed during the treatment with ozone for example. If a granular activated carbon (GAC) filter is used it must be handled with care and regenerated at regular intervals both from a microbiological point of view and because of the saturation with organic contaminants of different origin. In some EEC-countries, e.g. the UK, France and Italy, there are many water supplies where the MAC for pesticides is exceeded today and great efforts are made to find suitable methods for eliminating these contaminants. In view of the difficulties to find reliable and easily applicable methods for removing pesticide contaminants, it seems necessary to decrease the contamination of the ground water as much as possible to be able to meet the requirements for drinking water. This might be reached by only permitting the use of easily degradable and less mobile substances, by reducing the amount of pesticides used and to educate farmers and other users so that contamination can be avoided as far as possible. Restrictions for use of specific pesticides in water catchment areas may also be a tool to reduce the risk for contamination, such restrictions have been introduced e.g. in the Netherlands, Germany and Italy. Common European environmental criteria, including guidelines for the protection of ground water, for the acceptance of pesticides, are now being discussed in the Council of Europe Expert Committee on Pesticides.

If residues of pesticides are found in a Swedish water supply, the responsible water work has to contact the NFA to make an evaluation of the contamination possible and to take action, i.e. to try to find out the source and to try to remove the contaminant. Depending on the toxicity and the amount of the substance present it is decided if the water is fit for consumption or not during the "action time". It is important to have results from more than one analysis of the same water in order to verify the results and determine if there is a risk for continuous or short term exposure. Mostly the long term toxicity of the substance is of greatest importance but if a high concentration of a contaminant is present in the water the acute toxicity may also play a role. When an international evaluation of the toxicity of a substance is available this is used as a basis for the NFA evaluation, otherwise toxicity data from literature and data available to the Chemicals Inspectorate is evaluated.

In some other countries, such as the USA, another appproach than "no detectable levels" is used. This is also valid for the guideline values recommended by the WHO.

Although WHO does not recommend "no detectable levels" as guidelines for the evaluation of drinking water quality, the organisation states that: "Although the guideline values describe a quality of water that is acceptable for lifelong consumption, the establishment of these guidelines should not be regarded as implying that the quality of drinking water may be degraded to the recommended level. Indeed, a continous effort should be made to maintain drinking water quality at the highest possible level".

When setting health related guideline levels WHO uses toxicity studies in animals or reports on human toxicity as a basis for its evaluation. Generally, concentrations of pesticides in ground water have been found at low levels, as is the case for many other types of drinking water contaminants, but they might be present during a longer period of time. Therefore the concern is being focused on the potential for chronic effects, such as cancer, mutations, birth defects and immunological changes. If possible a NOAEL (no observed adverse effect level) is calculated, if not a LOAEL (lowest observed adverse effect level) is calculated. A TDI (tolerable daily intake) is derived from the NOAEL applying an uncertainty factor. The guideline value for adults is then calculated by allocating, in most cases, 10% of the TDI to drinking water and assuming that an adult of 60 kg (formerly 70 kg) drinks two liters of water each day. For some substances, e.g. organochlorine compounds, only 1% of the TDI, is allocated to drinking water.

In the USA the EPA is required to set RMCLs (recommended maximum contaminant level goal) and MCLs (maximum contaminant level) for any potential drinking water pollutant at a level that has no known or anticipated adverse effects. MCLs are the enforceable standards and must be set as close to RMCLs as is feasible. Feasible means "with the use of the best technology, treatment techniques and other means which the Administrator finds are generally available, taking costs into consideration" (SDWA). These levels have to be reviewed every third year. The EPA also issues "Health Advisories", HAs, for guidance, which are not enforceable limits and available for more substances than existing MCLs. The HAs are given for a child of 10 kg and an adult of 70 kg assuming 1 day, 10 days, longer term and lifelong exposure to a contaminant.

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