POINT AND NON-POINT SOURCE LEACHING OF PESTICIDES IN A TILL GROUNDWATER CATCHMENT

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Content

Preface

Participating institution

This report was funded by the Danish Pesticide Research Programme as a collaborative project between Danish Geotechnical Institute (DGI), Geological Survey of Denmark and Greenland (GEUS), National Environmental Research Institute (NERI), the County of West Sealand (CWS) and CNS-Miljø ApS.

Evaluation committee

The work has been followed and discussed by an evaluation committee established by the Danish Environmental Protection Agency (DEPA).

The members of the committee were:

Charirmann: Steen Marcher (DEPA)

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Distribution of work tasks

The distribution of work tasks among the project institutions was: DGI: Responsible of planning and coordination of the project, responsible of field work, excavations, augering, and installation of angled monitoring boreholes, large undisturbed column sampling and column laboratory experiments, tritium investigations and 2D-FRACTRAN modelling of tritium transport, pesticide monitoring in time series from angled boreholes, compilation and editing of the final report. DMU: Pesticide analyses, contribution to final report. GEUS: Water balance modelling for the project area, modelling of laboratory experiment, adsorption laboratory studies and sensitivity analyses of controlling parameters in pesticide leaching. CWS: Removal of contaminated soil excavated from point source spill and supply of replacement soil, collaboration in historic mapping of pesticide use. CNS: Historic investigation and mapping of pesticide use in the project area.

Acknowledgments

The project group would like to acknowledge the help and collaboration from Per Døvling (Viminoco A/S), Ole Vang (former manager of Skælskør orchard) and Harboe Bryggerierne A/S (owner of Skælskør orchard). Furthermore, we would like to thank ph.d. Larry D. McKay (University of Tennessee, U.S.A.) for participation in the planning and initial field work of the project. Finally we would like to thank ph.d. Ayou Hoff (Risø, Denmark) for reviewing the manuscript and the Danish Pesticide Research Programme administrated by the Danish Environmental Protection Agency for funding of the project.

Summary

Objective and scope

The objective of the project is to assess the risk of pesticide leaching from controlled application of pesticides in an orchard, and from an associated spill where pesticides and equipment for spraying have been handled for an extensive period. Additionally, the objective is to evaluate the influence of fractures as transport parts for pesticide leaching in a clayey till groundwater catchment.

Hydrogeology

Investigations were carried out in the area of Skælskør and the Skælskør orchard, where the sub-soil till is approximately 20-25 m thick and overrides a local sand layer and the main limestone aquifer of the region. From the limestone aquifer groundwater is extracted for drinking water supply to Skælskør town and suburban areas.

Pesticide application

Mapping of pesticides, which had been applied in Skælskør orchard since 1960, revealed that among a wide range of active ingredients phenoxyherbicides have been applied in amounts corresponding to average application on farm land. Also simazine, atrazine, terburtylazine, and amitrol have been applied in significant amounts.

Monitoring sites and installations

Pesticide leaching in Skælskør orchard was investigated and compared with the leaching from repeated spills of pesticides in the machinery yard associated with the orchard. At both sites groundwater and soil samples from the till sequence have been collected for pesticide and tritium analyses. Groundwater samples were collected six times from five 15-25 m deep monitoring wells (14 screens), over a period of approximately one year. The samples were analyzed for dichlorprop, mecoprop, MCPA, 2,4-D (phenoxyherbicides) simazine, atrazine, and terbuthylazine (triazines).

Pesticide leaching from point source spill

In the point source site area (machinery yard) repeated spills of pesticides may have occurred for more than 40 years. In the upper 5-7 m of the geological profile, very high phenoxyhercicide concentrations (mainly dichlorprop and mecoprop) occurred in all samples analyzed (sum concentrations up to 1 mg/l in water samples). Corresponding simazine contrations were significantly lower (approximately 5 ?/l). The occurrence of high pesticide concentrations in the upper part of the profile ("hot spot" zone of contamination) is correlated positively with peak concentration values of bomb tritium (maximum concentrations in precipitation in 1963) found at 5-7 m depth.

Below the upper "hot spot" zone of the point source area, pesticide findings were erratic in time and space. In 29% of water samples (out of a total of 48 samples) pesticides were below detection. Concentrations of phenoxyherbicides and simazine were 3-5 orders and 1-2 orders of magnitude lower, respectively, than in the "hot spot" zone. In the sand aquifer underlying the till sequence, sum contrations of phenoxyherbicides and trazines were from below the detection limit and up to approximately 1 ?g/l. The findings of the individual pesticides in the aquifer were erratic in time.

Leaching experiments, applying large undisturbed columns collected from the point source site (2-6 m depth), were consistent with the field observations by revealing very high concentrations of mobile residual dichlorprop and mecoprop (sum concentrations up to 2 mg/l).

The pesticides identified in the point source pesticide spill reflect to some extent the types and relative amounts applied in the orchard as shown by the mapping based on spray records and statistical sources. In general 2,4-D and MCPA are identified in relatively less amounts than expected from the mapping, while the opposite relation appears fro mecoprop.

Pesticide leaching from orchard

In the orchard the only phenoxyherbicide identified repeatedly was MCPA (0.01-4.8 ?g/l) which was found in 24% of the water samples (out of a total of 42 samples). Mecoprop and dichlorprop were identified once each. Simazine occurred in 17% of water samples collected (0.04-1.0 ?g/l) and atrazine was identified once. In general, the pesticide findings of the monitoring wells occurred erratically in time and space (no detection in 60% of water samples). The distribution shows no correlation with peak concentration values of bomb tritium found at 5-7 m depth. The lack of correlation indicates significant influence of immobilizing processes on pesticide leaching in the orchard till profile.

MCPA, simazine and terbuthylazine have been used systematically in the orchard for 20-30 years. Dichlorprop and 2,4-D have similarly been applied for at least 10 years prior to the monitoring. The lack of systematic findings of key primary products (i.e. dichlorprop and 2,4-D) in the ground water suggest, that phenoxyherbicide products to a high extent have been degraded close to the ground surface. It should be noticed that MCPA may occur both as a primary herbicide product and as a metabolite of mecoprop degradation. No other metabolites have been analyzed for.

Leaching experiments, conducted with three large till columns collected from 2-6 m depth in the orchard, revealed concentrations of mobile simazine and terbuthylazine, and in one column also mecoprop. Simazine sorption experiments carried out with the till material indicate that simazine, and possibly also other trazines, to some extent are taken up by the clay minerals of the till. Hence, triazine exchange between pore water and clay minerals of the till appears to be more complex than predicted from a simple equilibrium distribution coefficient.

Pesticide application in the orchard has occurred exclusively in spring and summer, while on farm land MCPP application also in autumn has been common practice since the beginning of the 1980'ies. Autumn application may imply an increased risk (period of precipitation surplus) of rapid leaching to the groundwater.

Water supply wells of Skælskør

The Skælskør town main aquifer extraction wells were analyzed to represent the end of groundwater streamlines of the project area i.e. monitoring the integrated groundwater recharge from the orchard, point sources and farm land. No pesticides were detected in the water from the wells.

Transport in fractures at lab scale

Fractures in the till were mapped in the 4-6 m deep excavations carried out in the orchard and the point source site. Preferential transport in the fractures is shown to occur by column experiments at the lab scale. The large undisturbed column applied for the experiments were collected from 2-6 m depth. Soil pressure experiments also conducted with the columns revealed that only minor changes in bulk hydraulic conductivity occurred even at a maximum confining cell pressure of 240 kPa (equivalent of 15-20 m deposional overburden). This result suggests that the fractures observed may have the potential to stay open at greater depths than in the upper 5-6 m.

Transport in fractures at field scale

However, numerical analyses of three bomb tritium profiles obtained from the till sequence indicate that the influence of fractures on chemically conservative solute transport is small or absent at depths below the upper few metres at the field sites. The distribution of tritium is consistent with transport modelled by piston flow in the till matrix. Realistic results of tritium transport were obtained with an Equivalent Porous Media model (EMP model) simulating piston flow having a bulk hydraulic conductivity of $6 \cdot 10^{-9}$ m/s (equivalent with the estimated vertical recharge of 30-60 mm/year in the project area). Evaluating the observed tritium distribution from the concept of piston flow, the pore water in the lower part of the till sequences should be dominated by water older than 1953. This is consistent with the observed tritium values lower than 1 TU below approximately 10-15 m depth.

Predictive modelling

Further sensitivity analyses by numerical modelling of fracture flow indicate that in case the shallow zone fractures (fracture hydraulic conductivities determined by the large column experiments) are extended through the aquitard and degradation of the pesticides is ignored, a breakthrough at a concentration level at 1 ‰ of the input concentration should be expected within a few years, given the vertical recharge of 30-60 mm/year to the main aquifer (estimated by water balance modelling). As drinking water limit values for pesticides are several orders of magnitude lower than the input concentration as measured e.g. in the point source pesticide spill of the orchard, leaching of pesticides at concentrations above the drinking water limit values should be expected within a few years even through large thickness of till.

Transport in sandlayers

In all of the calculations it is assumed that no other hydraulic conductive heterogenities than fractures occur in the till. In the monitoring wells thin sandstreaks were observed and in the excavation at the point source site an inclining sandlayer occurred. Inclining sandlayers and sand streaks may constitute alternative paths of transport into underlying aquifers. Pesticide transport along these paths may account for some of the deep pesticide findings in the till and in the sand aquifer below the point source spill.

Dansk sammendrag

Undersøgelsens formål

Undersøgelsen formål er at vurdere risikoen for grundvandet ved kontrolleret anvendelse af sprøjtemidler i Skælskør frugtplantage, sammenlignet med udvaskning fra spild af sprøjtemidler på en tilhørende maskinplads. På maskinpladsen er sprøjtemidler og sprøjteudstyr blevet håndteret de sidste cirka 40 år. Det er endvidere undersøgelsens formål at vurdere indflydelsen af sprækker som transportveje for udvaskningen af pesticider gennem morænelserssekvensen i projektområdet.

Hydrogeologi

Moræneleren i projektområdet er 20-25 m tyk og overlejrer et lokalt sandlag og det regionale grundvandsmagasin. Fra det regionale grundvandsmagasin indvindes grundvand til Skælskør.

Anvendelse af pesticider

Siden 1960 er der i plantagen, blandt en lang række andre virkstoffer anvendt phenoxyherbicider i mængder, der svarer til gennemsnitsforbruget inden for agerbrug. Herudover er der anvendt tilsvarende mængder af simazin, atrazin, terbuthylazin og amitrol. Anvendelsen i plantagen har ligget i forårs- og sommer-månederne (periode med netto-nedbørsunderskud). Inden for agerbrug er der i takt med vinterafgrøders større andel af det samlede kornareal sket en stigende anvendelse af mechlorprop om efteråret (periode med netto-nedbørsoverskud).

Grundvandsmonitering

Pesticidudvaskningen i Skælskør frugtplantage er moniteret og sammenlignet med udvaskningen fra plantagens maskinplads, hvor der antages at være sket gentagne pesticidspild. Begge steder er der analyseret jord og grundvandsprøver for pesticider og tritium.

Der er udtaget grundvandsprøver fra 14 filtre i tidsserier (6 gentagelser i løbet af et år) fra 5 skrå moniteringsboringer (15-25 m dybe). Prøverne er blevet analyseret for dichlorprop, mechlorprop, MCPA, 2,4-D (phenoxyherbicider), simazin, atrazin og terbuthylazin (traziner).

Pesticidudvaskning fra punktkilder

På punktkildearealet (maskinpladsen) kan der være sket spild af pesticider i forbindelse med håndtering af sprøjteudstyr og sprøjtemidler gennem de sidste 40 år. Grundvandsmoniteringen viser, at der i alle prøver udtaget i de øverste 5-7 m af det geologiske profil er meget høje indhold af pesticider (primært dichlorprop og mechlorprop) med sum-koncentrationer større end 1 mg/l i vandprøver. I samme prøver var simazin koncentrationerne væsentligt lavere (cirka 5 ?g/l). Forekomsten af meget høje koncentrationer i den øverst del af det geologiske profil ("hot spot" zonen) er sammenfaldende med tritium fordelingen, der viser maximum værdier i 5-7 m's dybde.

Under "hot spot" zonen i punktkilden fordeler pesticidfundene sig spredt i tid og rum (i 29% af 48 prøver blev pesticid ikke påvist). Koncentrationer med phenoxyherbicider og simazin er henholdsvis 3-5 og 1-2 størrelsesordner mindre end i "hot spot" zonen. I sandgrundvandsmagasinet under morænen var indholdet under detektionsgrænsen og op til ca. 1 ?g/l i sum-koncentrationer af phenoxyherbicider og triaziner.

Udvaskningsforsøg med store intakte søjler udtaget i "hot spot" zonen i punktkilden bekræfter resultaterne fra moniteringsboringerne. Fra søjlerne blev udvasket høje indhold af primært dichlorprop og mechlorprop med sum-koncentrationer op til 2 mg/l.

Pesticiderne påvist i punktkilden afspejler i nogen udstrækning pesticidforbruget i plantagen, som det er opgjort ud fra sprøjtejournaler og statiske oplysninger. Generelt er phenoxyherbicider 2,4-D og MCPA påvist i mindre mængder end forventet, mens det omvendte forhold gør sig gældende for mechlorprop.

Pesticidudvaskning fra Plantage

Ved grundvandsmoniteringen i frugtplantagen er MCPA det eneste phenoxyherbicid, der er fundet gentagne gange (0.01-4.8 µg/l). Dette aktivstof blev påvist i 24% af vandprøverne (ud af i alt 42 vandprvøer fra plantagen). Mechlorprop og dichlorprop er hver påvist i 1 vandprøve. Af trazinerne blev simazin påvist 17% af vandprøverne (0.04-1.0 µg/l), og atrazin i 1 vandprøve. Fundene er spredte i rum og tid (ingen detektion i 60% af prøverne) med kun få gentagelser i samme filter. Der er ikke påvist nogen korrelation med forekomsten af maksimum værdier af bombetritium (maksimun koncentration i nedbør i 1963) fundet i 5-7 m's dybde og tritium koncentrationer under detektionsgrænsen (1 TU), som forekommer ved dybder større end 12-17 m.

MCPA, simazin, terbuthylazin og amitrol (ikke analyseret for amitrol) er blevet anvendt systematisk i frugtplantagen gennem 20-30 år. Diklorprop og 2,4-D har tilsvarende været anvendt i mindst 10 år inden moniteringen. Manglen på systematiske fund af primæraktivstoffer (f.eks. diklorprop og 2,4-D) indikerer, at phenoxyherbicidprodukterne i betydelig udstrækning er blevet nedbrudt tæt ved terræn. Det bør bemærkes, at MCPA kan forekomme både som nedbrydningsprodukt af mechlorprop og som primært virkstof. Der er ikke analyseret for andre mulige nedbrydningsprodukter.

Udvaskningsforsøg udført med store intakte morænelersprøver udtaget fra 2-6 m dybde i morænelersprofilen i plantagen viser, at der er mobilt simazin og terbuthylazin i moræneleren. I en af søjlerne blev der påvist mobilt mechlorprop. Simazin sorptionsforsøg udført med morænematerialet viste, at simazin i nogen grad kan "optages" i morænens lermineraler. Dette viser, at bindingen af simazin (og formelig også andre triaziner) ikke kan beskrives ud fra en almindelig ligevægtsdistributions koefficient.

Opmåling og forsøg med sprækker

I de hydrogeologiske undersøgelser af morænen blev der påvist og opmålt gennemgående sub-vertikale sprækker i 4-6 m dybe udgravninger i plantagen og i punktkilden. Præference transport i sprækkerne blev påvist i laboratorieforsøg med de store intakte morænelerssøjler udtaget fra 2-6 m's dybde i udgravningerne. Tryk eksperimenter med jordsøjlerne viste, at den hydrauliske ledningsevne kun blev svagt reduceret under overlejringstryk på 240 kPa (svarende til 15-20 m's dybde i det geologiske profil). Forsøgene indikerer, at sprækkernes hydrauliske egenskaber kan bevares i større dybde end i de øverste 5-6 m, hvorfra søjlerne er udtaget.

Sprækker som transportveje i feltskala

De tre tritium profiler fra moniteringsboringerne i plantagen og punktkilden indikerer, at der er ringe eller ingen indflydelse af sprækker på stroftransporten under de øverste meter af profilet. Modelanalysen af profilerne viser, at tritiumfordelingen svarer til transport ved stempelstrømning og med en vertikal nedsivningsrate på 30 mm/år og en bulk hydraulisk ledningsevne på $6{\cdot}10^{-6}$ m/s. Ved vurdering af tritiumprofilerne udfra stempelstrømningsprincippet, forventes porevandet i den nedre del af morænelerssekvensen at være domineret af vand, som er infiltreret før 1953. Dette indikeres af tritiumværdier under 1 TU.

Numerisk følsomhedsanalyse

Numerisk modellering og følsomhedsanalyse af sprækkestrømningen indikerer, at i en situation, hvor de vertikale sprækker fra udgravningerne fortsætter gennem hele morænelerssekvensen, vil mobile pesticider optræde i en koncentration på 1 ‰ af udvaskningskoncentrationen fra rodzonen i løbet af få år. I modelleringen er set bort fra nedbrydning af pesticider, og der er regnet med en vertikal strømningshastighed på 30-60 mm/år, som er estimeret ud fra vandbalancemodelleringen.

Preferencetransport i sandlag

I alle beregninger er forudsat, at ingen andre hydraulisk ledende heterogeniteter end sprækker forekommer. På plantagens maskinplads (punktkilden) blev der i udgravningen observeret et hældende sandlag. Denne type helt eller delvis gennemsættende sandlag vurderes at kunne transportere pesticider hurtigere end beregnet i den præsenterede modelanalyse af sprækketransport.

1 Introduction

Scope of investigation

The objective of the project is to assess the risk of pesticide leaching from controlled application of pesticides in an orchard and from an associated spill, where pesticides and equipment for spraying have been handled in an extensive period. Furthermore, the objective is to evaluate the leaching in a clayey till groundwater catchment to the underlying aquifer and the influence of fractures in the till as transport paths for pesticide leaching.

Pesticide contamination of drinking water supply wells, streams and shallow groundwater has been identified as an increasing problem in Europe and elsewhere (Fielding et al., 1991, U.S. Environmental Protection Agency, 1992 and GEUS 1995).

Sources of pesticide leaching

In Denmark more than 99% of the drinking water comes from ground water. Several sources of contamination may contribute to the pesticide findings in the groundwater. Leaching from controlled application on farm land (diffuse source) has been considered to be the main source of contamination. Another important source may be point source spills, which have resulted from the handling of pesticides in association with spraying. However, examples of the relative important of different sources have not previously been reported in denmark.

Contaminant leaching in clayey tills

An other main issue of the investigation is the influence of fractures on the pesticide transport in clayey till deposits. 40-50% of the Danish groundwater is covered by Quaternary deposits of glacial clay till, typically 10-40 m in thickness. Recent investigations in Denmark (Jørgensen 1990, Fredericia 1990, Jørgensen and Fredericia 1992, Jørgensen 1995, Hindsby et.al., 1996, Jørgensen and Spliid 1997, Jørgensen and McKay in review, Jørgensen et.al., in review, Thorsen et.al., in review and Broholm et.al., (a,b) in review), and in Canada (D'Astous et.al., 1989, Rusland et.al., 1991, McKay et.al., 1993), have shown that contaminants can migrate at significantly faster rates due to fractures in shallow tills than in the massive unfractured till matrix which is typically characterized by very low hydraulic conductivities. In the reported project, hydrogeological emphasis is on the influence of deep fractures on transport, as evaluated by laboratory experiment, field observations and the distribution of tritium in the geological profile.

2. Site description

2.1 **Site of investigation and land use**

Types of landuse

The project area represents the groundwater catchment of Vester Vandværk in Skælskør, Figure 1. The total area is 226 hectares of which 75 hectares are Skælskør orchard and 140 hectares are agricultural land. Approximately 60% of the agricultural area is cropped with wheat while the remaining part is grassland, meadows and beach. Approximately 11 hectares of the project area is houses, gardens and roads.

Delineation of project area

The project area is delineated from the topography and the hydraulic potentials of the main aquifer (Figure 1). The area is confined so that the catchment area of the Skælskør water plant is included in the area.

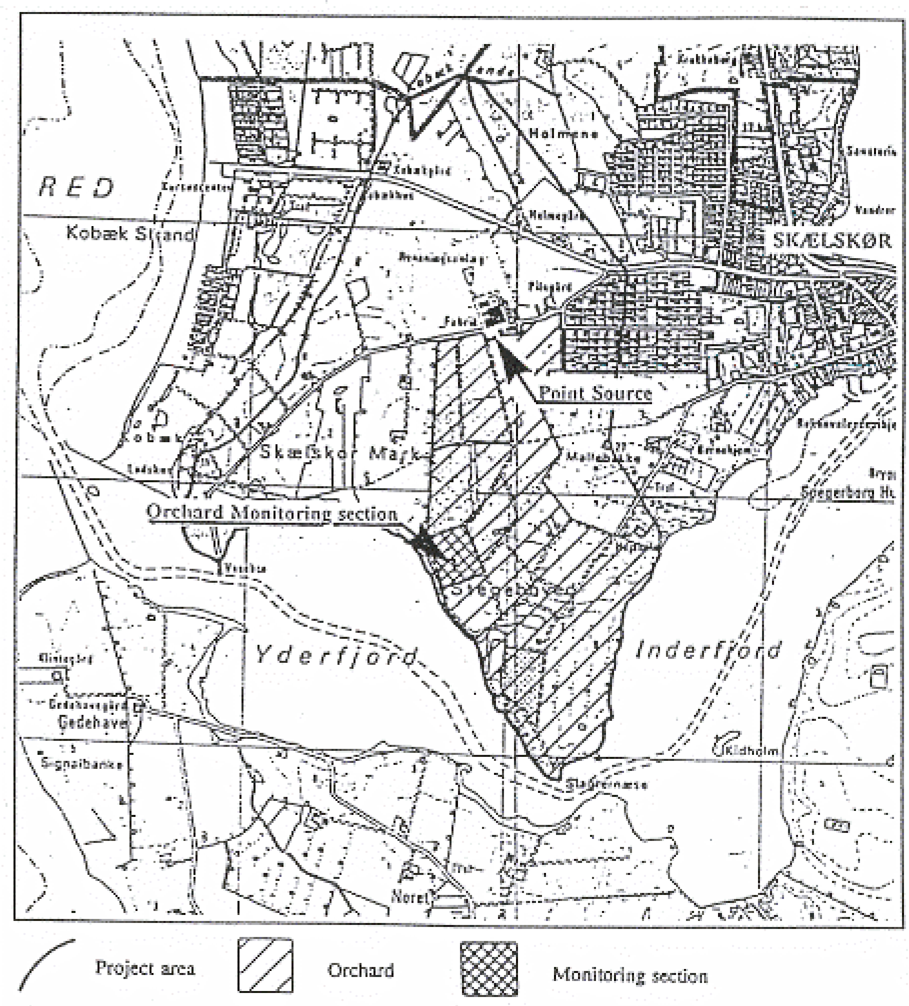


Figure 1
Project area and location of point source site spill, orchard and monitoring section in orchard

Projektområde og lokalisering af punktkildeforurening, Skælskør frugtplantage og moniteringsparcel i plantagen

The southwestern limit of the area is the coastline. The western limit is along the topographical drainage area. The Northern limit is along the creek, Kobæk Rende. North of the water plant the boundary chosen is a line perpendicular to the equipotential lines of the main aquifer of the area. South of the water plant the topographic drainage area constitutes the boundary of the project area.

2.2 Geology and hydrogeology of the site

Prequarternary deposits

The geology is described from 9 wells in the ares (GEUS map 1412 I Skælskør). In the project area the prequarternary deposits consist of Bryozoan limestone of the Danian age in the northern part and of White chalk of Maastrichtian age in the southern part. The prequarternary surface has distinct topography, from to to 30 m below sea level. On a greater scale there is a depression in the prequarternary surface, now partly reflected by "Skælskør yderfjord" and cove.

Hydrogeology

The main aquifer of the Skælskør area consists of the Bryozoan limestone. The transmissivity of the aquifer has been calculated from pumping tests and is in the range of $(0.2 - 1.4)\cdot 10^{-3}$ m^2/sec. The water table in the main aquifer has been monitored, Figure 2. Flow directions in the aquifer are towards the well field of skælskør Vester Vandværk.

The Quaternary deposits in the project area are 30 to 40 m in thickness. The deposits consist mainly of clay till. There are two approximately 1 m thick meltwater sand layers in the till at a depth of 8 - 9 m and 18 - 19 m below sea level. Locally a thin sand layer occurs on top of the Bryozoan limestone. Some minor postglacial freshwater peat and gytja plus marine gytja and sand deposits are situated in depressions of the slightly undulating landscape.

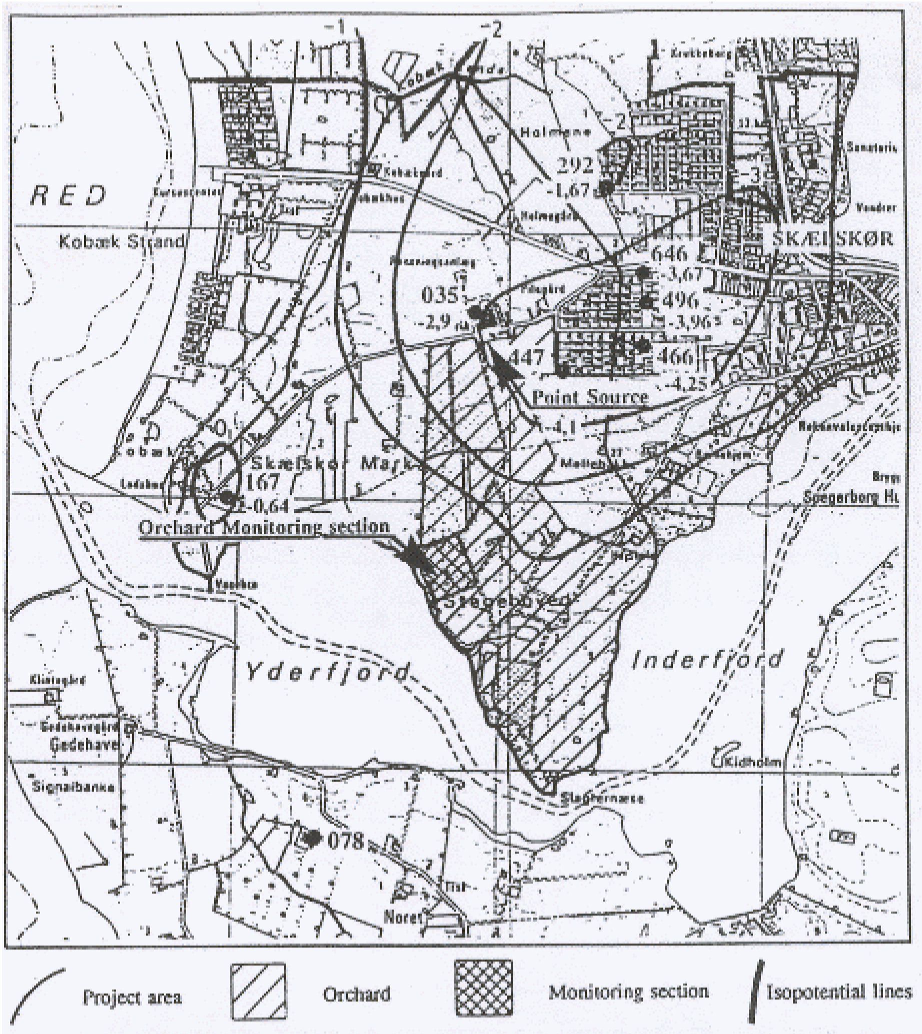


Figure 2
Groundwater equipotential map of main aquifer

Akvipotentialekort over det primære grundvandsreservoir

3. Materials and methods

3.1 **Boreholes and screens**

Angled monitoring boreholes

Five 45^o angled boreholes (15 - 25 m deep) were installed with multi-level water sampling systems. Three boreholes are situated at the point source site and two boreholes are situated in the orchard. During augering, casing and telescoping were applied to minimize vertical transport of pollutants down in the boreholes. This risk of artifact contamination was further minimized by using the angled augering technique, which allows installations of filters underneath a "hot-spot" area in ground surface without penetrating the "hot-spot" itself.

Installations in boreholes

Installation of water samplers, standpipes for monitoring hydraulic head and bentonite sealing between the individual screened intervals are displayed in Figure 3 and 4. Depth of screens and stratigraphic formation of water sampling in the monitoring programme are shown in Table 1. Applied water sampling equipment in contact with the groundwater during sampling was made of glass, stainless steel or teflon to minimize chemical interaction between possible contaminants and sampling equipment.

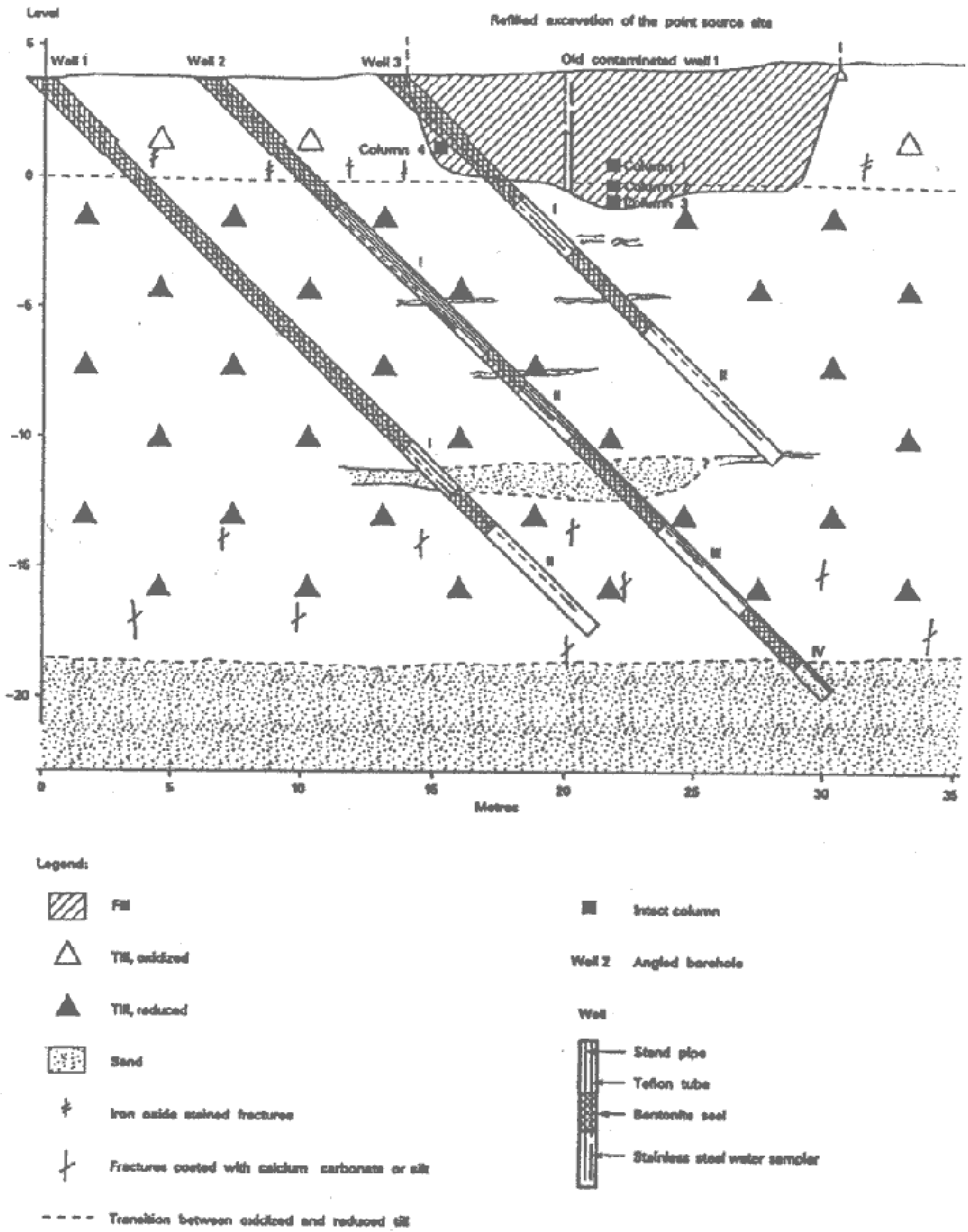
Table 1
Depth of screens in monitoring wells and stratigraphic formation of water sampling

Dybde af filtre i monitoringsboringer og strategrafisk oprindelse af vandprøver

	Boring/filter	**Depth m**	**Geology**
Point source	SI/I SI/II	14.1-15.9 17.3-21.2	Till Sand
	S2/I S2/II S2/III S2/IV	5.0-10.6 11.9-13.9 17.3-20.5 22.6-23.8	Sand Till Till Till
	S3/I S3/II	5.0-7.0 10.0-15.0	Till Till
Orchard	S4/I S4/II S4/III	4.7-7.0 10.6-14.0 19.8-22.0	Till Till Till
	S5/I S5/II S5/III S5/VI	1.8-3.5 4.7-7.0 10.6-15.5 19.8-22.6	Till Till Till Till

Figure 3
Angled monitoring wells and locations of collected intact till columns and soil samples at the point source site shown in, a) geological cross section and b) certical view

Skrå monitoringsboringer og lokalisering af udtagede intakte søjler og jordprøver på punktkilden i, a) geologisk snit og b) situationsplan a)



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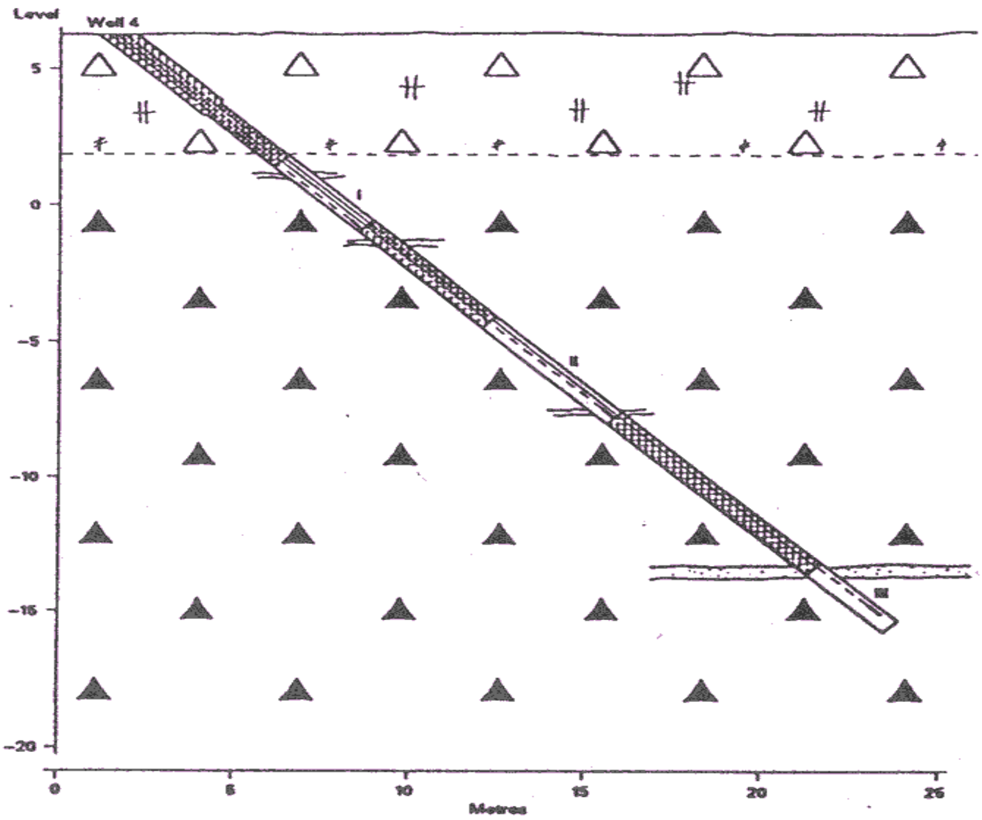
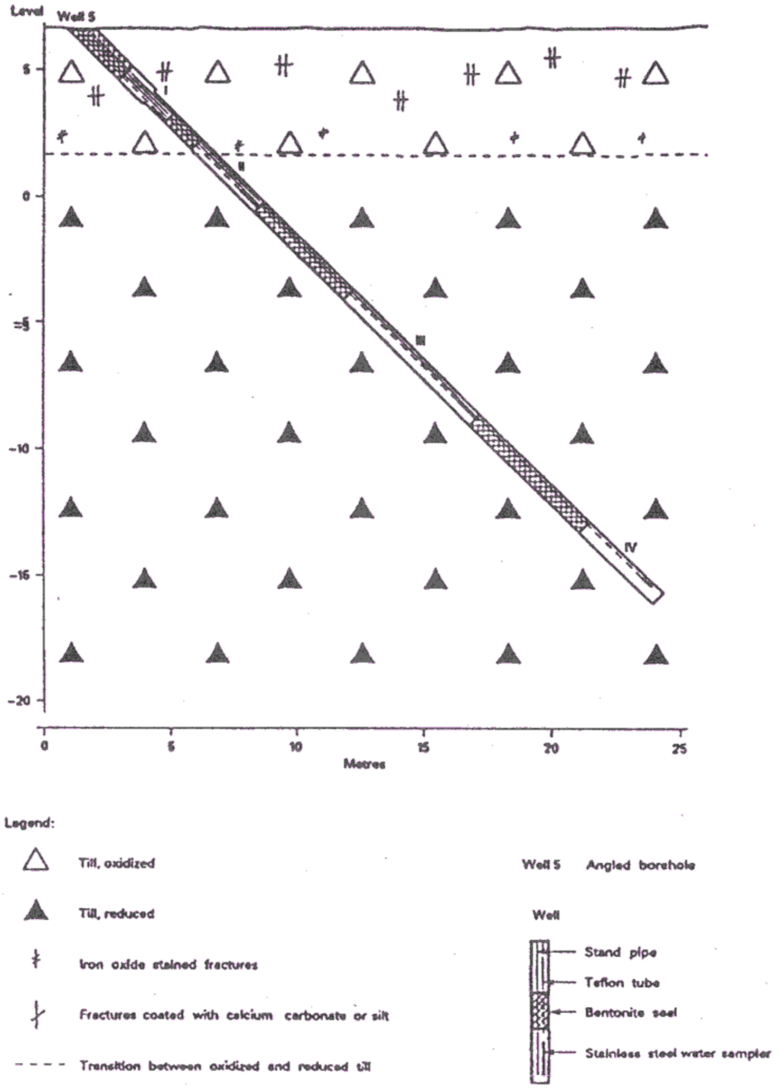
a)

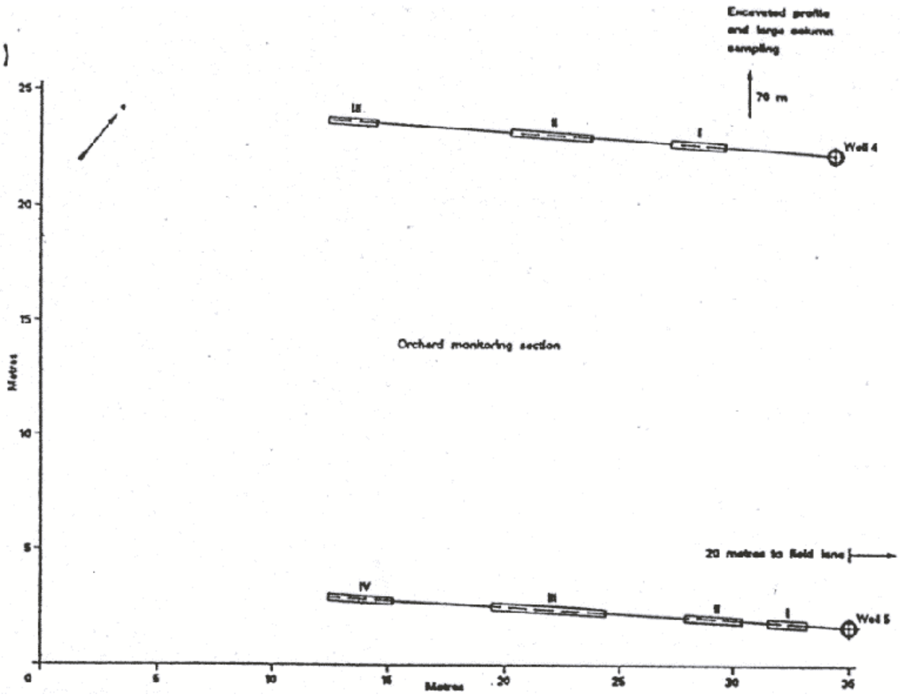


a)



Level
Well 5
I
II
III
IV
5
0
-5
-10
-15
-20
0
5
10
15
20
25
Metres
Legend:
Till, oxidized
Till, reduced
Iron oxide stained fractures
Fractures coated with calcium carbonate or silt
Transition between oxidized and reduced till
Well 5
Angled borehole
Well
Stand pipe
Teflon tube
Bentonite seal
Stainless steel water sampler

b)



Excavated profile and large column sampling
70 m
III
II
I
Well 4
Orchard monitoring section
20 metres to field lane
IV
III
II
I
Well 5
25
20
15
10
5
0
5
10
15
20
25
30
35
Metres
Metres

Figure 4
Angled borings of the orchard monitoring section shown in, a) vertical view and b) horizontal view

Skrå monitoringsboringer i frugtplantagen (moniteringsparcel) i, a) geologiske snit og b) situationsplan

3.2 **Soil and groundwater sampling**

3.2.1 **Excavation and sampling of large undisturbed till columns**

Point source site and orchard

Undisturbed columns were sampled from profiles excavated at the point source site (4 columns) and in the orchard (3 columns). The columns were circular with a diameter of 0.5 m and a height of 0.5 m, being large enough to represent fractures and macropores in the till. Sampling was preferably made in fracture zones. Sampling depth at the point source site was 2.6 - 4.6 m below ground surface and in the orchard 2.0 - 6.0 m. During sampling the columns were embedded in a fluid rubber casing which fixed the columns after hardening in a combined mould and transport steel cylinder. Before hardening, the fluid rubber enters a few millimetres into the till matrix. Thereby the outer surface of the columns is sealed, and problems with flow along this boundary during the experiments is eliminated. After fixation, the columns were detached from the till formation. The steel cylinder was removed after transport of the columns. During installation of the columns in the laboratory, they were operated using vacuum corresponding to an external pressure of 30 to 60 kPa to avoid disturbance.

Sampling depths and method

3.2.2 **Soil sampling for chemical analyses**

Shelby tube cores (length 0.5 m) from the boreholes 2, 3 and 4 were sampled every second vertical metre and between these tubes, ordinary soil samples were collected. At the point source site, soil sampling (1 - S8) for pesticide analyses was made in the profile along with the columns sampling, Figure 3b.

3.2.3 **Groundwater sampling**

Time series of water samples

A time series of 6 groundwater sampling events over a period of approximately 1 year was performed from the 15 screens of the 5 angled monitoring wells. Before each sampling event, the screens were emptied 1-5 times. Sampling was carried out applying a closed glass/teflon vacuum system (Prehnard-system, Prehnard aps.) to prevent possible atmospheric contamination during sampling. Samples were injected directly from the wells into the extraction liquid (dichloromethane) in the sampling bottles. The samples were stored at 2^{o} until analyses.

3.2.4 **Chemical analyses**

Non-reactive tracer concentrations in the influent and effluent were continuously monitored with an electric conductivity meter (Radiometer A/S) and data logger. In another experiment (Hindsby et.al., 1996) it was shown that the conductivity meter measurements could be correlated to the breakthrough of chloride (as measured by specific analyses). Recorded effluent conductivities (e_e) were normalized (e^*) to influent conductivities (e_i) with the expression: $e^* = (e_e - e_{background})/(e_i - e_{background})$. Influent and effluent pH were monitored at the beginning and end of each experiment using a

Radiometer pH-meter. Extraction of pesticides in water and till samples was made with dichloromethane. The extracts were refrigerated until analysis described in the following:

Solvents Dichloromethane and acetonitrile (HPLC-grade) were from Rathburn (Walkenburn, Scotland). HPLC-grade water was purified in a Milli-Q (Millipore, Bedford, MA, USA) filtration system. PIC-A low UV-ionpairing reagent was from Waters Associates (Milford, Ma, USA). Propylene glycol was from Fluka Chemie (Buchs, Switzerland). Disoduimhydrogenphosphate was from May and Baker LTD (Dagenham, England).

Pesticide substances MCPA, 2-4-D, mecoprop, dichlorprop and dinoseb were obtained from KVK (Køge, Denmark), simazine and atrazine were from Fisons (Cambridge, England). DNOC were from Fluka Chemie (Buchs, Switzerland). For quality control custom made pesticide ampoules from Supelco (USA) were diluted and used to verify the standards.

Apparatus LC system consisted of two Waters model 510 pumps, a Water WISP 712 Autosampler and a Waters model 440 ultraviolet absorbance detector with extended wavelength module (229 and 405 nm). A Waters Novapak C-18 4 ?m column (150 x 3.9 mm) with a Supelguard - column (Supelco, USA) was used. System handling, gradient control and data treatment was carried out with Maxima 820 software from Waters.

Water samples - liquid extraction 2 L water samples were placed on a magnetic stirrer and extracted with three times (15 min each) 100 ml dichloromethane. The organic phases were combined and dried (anhydrous sodium sulphate). The organic phase were concentrated after adding 50 ?g/l propylene glycol as keeper on a rotary evaporator at 35 ^{o}C. Remaining dichloromethane was removed by evaporation at 40 ^{o}C under nitrogen flow. The residue was redissolved in 1 ml of A-eluent (See HPLC procedure).

Soil samples - Soxhlet extraction 50 g soil sample was mixed with 50 g anhydrous Na_2SO_4 (which had been cleaned up by Soxhlet extraction following the same procedure as described below). The total amount was mixed and homogenised in a mortar and transferred to a 33 x 18 mm Soxhlet tube. The sample was covered with precleaned cotton. Soxhelt extraction was carried out on a water bath with dichloromethane/acetone (4:1) for 24 hours at 72 ^{o}C.

The organic phase was reduced on a rotary evaporator at 31 ^{o}C and 290 mBar to 2 ml. 50 ?g/l propanediol was added as a keeper and the reduced phase was transferred with dichloromethane to a vial.

The residual dichloromethane/acetone was removed under nitrogen flow at 40 ^{o}C and the sample was redissolved in 1 ml A-eluent (See HPLC procedure).

HPLC procedure The chromatography was performed with gradient elution at a flow rate at 1 ml/min at 25 ^{o}C in a column oven. A-eluent was prepared by dilution of the content of one PIC-A low UV reagent bottle in 1 L of Millepore filtrated water and by adding 300 ml acetonitrile. B-eluent was pure acetonitrile. The eluents were filtered through 0.22 ?m Millepore filter and degassed during elution with helium sparging. The gradient profile was as follows: Initial conditions, 93 % A-eluent, after 7 minutes at initial conditions linear gradient for 4 minutes to 60 % A-eluent which was hold for 2 minutes returning in 1 minute to initial conditions which was hold in 5 minutes to restablize the system.

Detection limits were for all compounds in the order of 0.01 ?g/l for water samples and 0.4 ?g/kg for soil samples defined as three times the standard deviation for the total method.

3.3 **Experimental set-up of undisturbed columns**

In-situ pressure/temperature

The undisturbed till columns were installed in large flexible-wall pressure cells and connected to a percolation system by influent and effluent teflonlines, Figure 5. The experimental system enables realistic conditions for solute transport experiments and hydraulic measurements in the laboratory. In the cells the in-situ pressure and temperature of the till formation were restored during the hydraulic and solute transport experiments. Once installed in the pressure cell, the columns were water saturated by slowly pumping solution into the bottom of the column. Flow in the system was driven by hydrostatic pressure defined by the hydraulic head difference of the influent system and the effluent system. The flow was continuously monitored with weight transducers and a data logging system. Effluent from the pesticide experiments was injected directly into bottles prepared with extraction liquid (dicloromethane). The effluent samples were stored at 2 ^{o}C until analysis.

Applied permeameter pressure for the individual columns is shown in table 2.

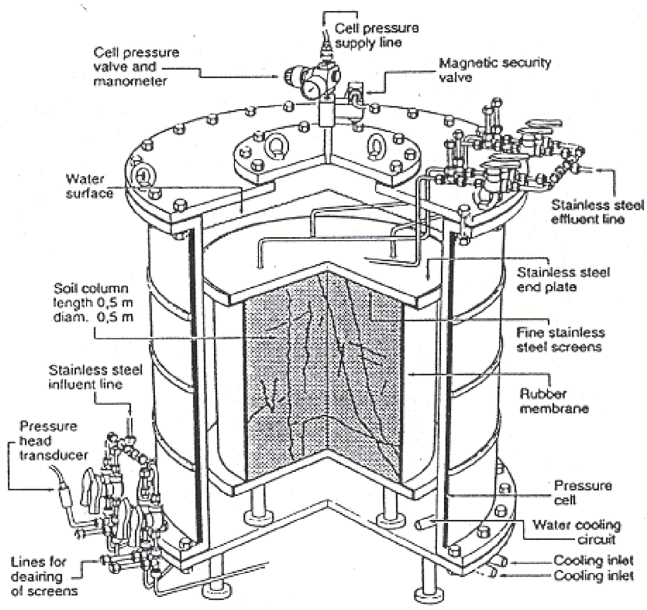


Figure 5
Flexible wall permeameter set-up for flow and pesticide leaching experiments using large undisturbed clayey till columns.

Trykcelle til forsøg med strømning og transport af pesticider i intakte morænelersblokke

Table 2
Applied triaxial cell permeameter pressure

Triaxial tryk anvendt i permeabilitet- og udvaskningsforsøg med intakte søjler

	Column	Depth m	Applied triaxial cell permeameter pressure
Point source site	1	3.3-3.8	55 kPa
	2	4.1-4.6	62 kPa
	3	4.7-5.2	68 kPa
	4	2.6-3.1	45 kPa
Orchard	1 a	2.0-2.5	45 kPa
	2	2.0-2.5	45 kPa
	3	4.0-4.5	61 kPa
	4	5.5-6.0	75 kPa

3.4 **Laboratory investigations of hydraulic conductivity and pesticide leaching**

Pesticide leaching and hydraulic experiments were carried out with the large diameter (0.5 m) undisturbed till column specimens, sampled from various depths in the excavated profiles of the point source site and the monitoring section of the orchard.

Bulk permeability tests of the undisturbed till columns were performed by recording effluent yield from the columns at different hydraulic gradients. The type of flow system represented by the columns were analyzed by leaching the columns with $CaCl_2$ followed by flushing with groundwater.

Leaching with groundwater

The water used for leaching was obtained from a confined aquifer at a site that is geologically similar to the site where the columns were taken. The chemical composition (major ions in mg/l) of the water in the aquifer was: TDS 730; Ca^{2+} 120; Mg^{2+} 31; Na^{+} 31; HCO_3^{-} 408; SO_4^{-2} 73; Cl^{-} 72; and the pH was 7,4.

3.5 **Pesticide adsorption experiments**

Samples of experiments

Analysis of the till clay mineralogy was carried out using the Shelby tube core material collected from well 1 at the point source site at depths of 2.0, 2.3, 2.5, 2.8, 3.0 and 3.5 m and from well 4 in the orchard at depths of 2.1, 11.0, 22.2 and 30.3 m. Investigations of simazine adsorption were carried out using core till material from well 4 at depths of 2.1 m and 22.2 m.

The grain size fraction <30 ?m was separated by sedimentation, and the fraction <2 ?m was separated in a particle-size centrifuge. For X-ray diffraction, clay mineralogy was investigated by preparation of oriented slides of specimens saturated by K^{+} and analyzed air-dry or heated to 300 ^{o}C, or saturated by Mg^{2+} and analyzed air-dry or after treatment with glycerol.

X-ray Diffractometry

The mineralogy of the samples was investigated by X-ray diffraction using Cok? -radiation (pulse height selection) on a Philips 1050 goniometer with fixed slits.

Adsorption experiments

In order to investigate the adsorption of simazine, two samples from well 4, one shallow and one deep (from 2.1 m depth and 22 m depth, respectively) were selected; pH (in water with a 1:2.5 sediment: water ratio) was 7.3 for the 2.1 m sample and 7.8 for the 22 m sample. 5 g of sample was dispersed in 10 ml of a 1 ppm solution of simazine in water. After centrifugation, the supernatant was decanted into a flask. For each sample, this procedure was repeated twice with the simazine solution and the three times with distilled water, the supernatant being added to the volume in the flask. The concentrations of simazine in the flask and in the prepared simazine solution were determined by HPLC (see section 3.2.4).

3.6 **Mapping of pesticide used in the project area**

Pesticides of mapping

Pesticides used in the project area were mapped including identification of what pesticides have been applied and calculation of applied amounts together with the area distribution of application. The following eight herbicides were selected for the mapping: Dichlorprop, mecoprop (MCPP), MCPA, 2,4-D, simazine, atrazine, terbuthylazine and amitrol.

In the mapping, distinction was made between pesticides used in the orchard and pesticides used in the agricultural areas adjacent to the orchard.

Subdivision of project area

Given the quality of information available, three different approaches of mapping were used with distinction between:

- The agricultural area, 1956-1994
- The orchard, 1956-1983
- The orchard, 1984-1992.

Quality of information

No information is available about the amounts and distribution of pesticides used in the agricultural sections of the project area. The amounts used were therefore estimated from the total agricultural consume in grain growing areas of Denmark. The sources used for estimation are the agriculture statistical review and the annual consume of pesticides reported by Kemikaliekontrollen and the Danish EPA.

Detailed spraying records

For the period before 1984 there are no relevant spraying records available from the orchard. The calculation of the use in the period up to 1984 was based on information of which products having been used, as informed by the former managers of Skælskør orchard, combined with standard spray treatment plans of the period.

For the period 1984-1992 detailed spraying records from the orchard were available. They contain in general all important information about the products used, the dose and the total calculated use in each treatment. Due to the high quality of this material it has been possible to calculate the load on plot level for all pesticides used in the period 1984-1992.

CNS report of mapping

For further details of methods used for mapping pesticide use, see Attachment I, CNS report.

4 Results of investigations

4.1 **Geological and hydrogeological investigations**

4.1.1 **The glacial sequence**

Point source site

In the point source area the excavated profile was approximately 4-5 m deep and 16 m wide, Figure 6a. Described from the top of the profile unsorted fill including cobbles, gravel, black soil and grey sand occurred. The fill layer had a thickness of 0.5 m and was underlain by freshwater lake deposits of gytja formed in a natural depression, now levelled by the fill. Below the gytja a clay rich sandy till greyish-brown (oxidized) with vertical fractures of reddish staining and a lengths of 0.3-1.5 m was exposed. Inclining from 2.5 to about 4 m depth in the excavation an 0.5-1 meter thick sand layer occurred with pronounced planar bedding and cross bedding (dislocated meltwater sand). From approximately 4 m's depth the till was olive grey and chemically reduced.

Revealed by the angled borings, chemically reduced conditions (olive grey) continued below the excavation. The till was calcareous and silty with gravel and intercalated by minor sand lenses/layers, Figure 3. A sandy body occurred at 15-17 m depth and at approximately 23 m depth a sand layer was reached. The sand layer is believed to represent the more widespread sand aquifer know from other borings to override the main limestone aquifer.

Orcard

The geological profile excavated in the orchard is displayed in Figure 6b. In the upper 1-1.3 m the profile was intensively burrowed by roots and earthworms. In the lower part of this zone, biopores and fractures (macropores) were bleached, indicating the maximum seasonal elevation of the water table (water saturation), typical of autumn and winter (Jørgensen & Fredericia, 1992 and Jørgensen & Spliid, 1997). The soil (upper approximately 1 m) was classified as a Typic Hapludalf, according to the American Soil Taxonomy system.

Below the top-soil, the excavation (approximately 6 m deep) exposed a yellowish brown oxidized till which appeared uniform to the redox transition at 4.5-5.5 m depth. Below this depth the till was greyish and chemically reduced. In the bottom part of the profile minor sand lenses/layers appeared, i.e. a 1-10 cm thick horizontal layer of silty sand and gravel, which may be representative of the intercalations also found deeper in the angled borings. Below the excavation the reduced till continued, as revealed by the angled borings. The till was mainly silty with gravel, and intercalated by minor sand lenses/layers, Figure 4.

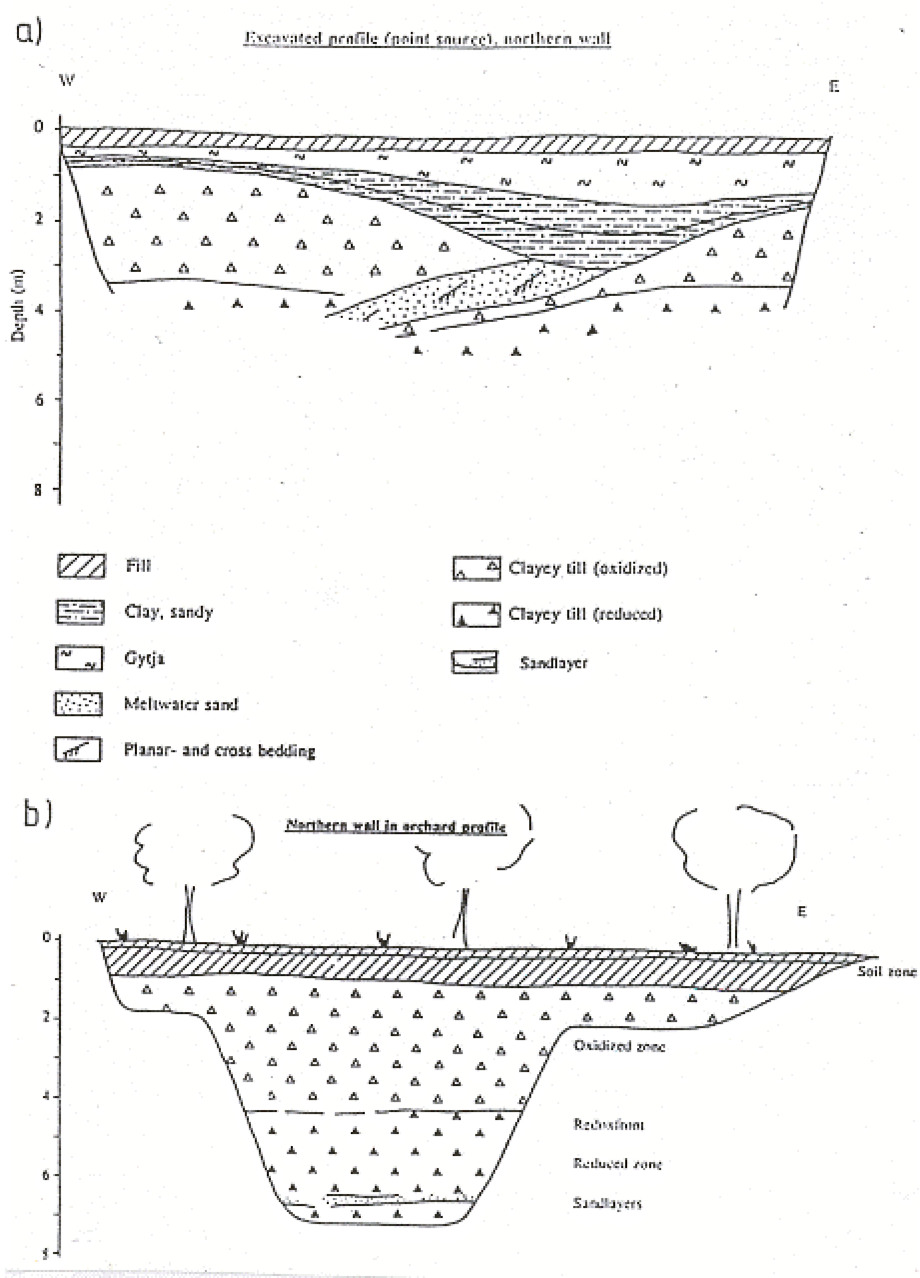


Figure 6
Geological profile of excavations, in a) the point source site and b) orchard (monitoring section)

Geologisk profile i udgravninger i, a) punktkilden og b) plantagen (moniteringsparcel)

4.1.2 **Description of fractures**

Point source site

The fractures in the point source area were mapped in the depths of 2-3 m and 4.5 m below surface. A total of 24 fractures was measured. At both levels there was a weak preferred orientation of fracture strikes at 45^o and 150^o. Most of the fractures were near vertical (+/- 15^o) except from two fractures with the orientation 51/22SE and 90/30S, Figure 7a. Some fractures surfaces occur in the meltwater sand layer (shown in Figure 7a) and can be followed from the sand layer into the underlying till. This suggests an origin of the fractures as tectonic rather than as a result of desiccation. The only good exposure with larger fractures was in the NW corner of the profile. The average fracture spacing was about 0.3 m, but rather poorly defined due to weak chemical staining of the fracture walls.

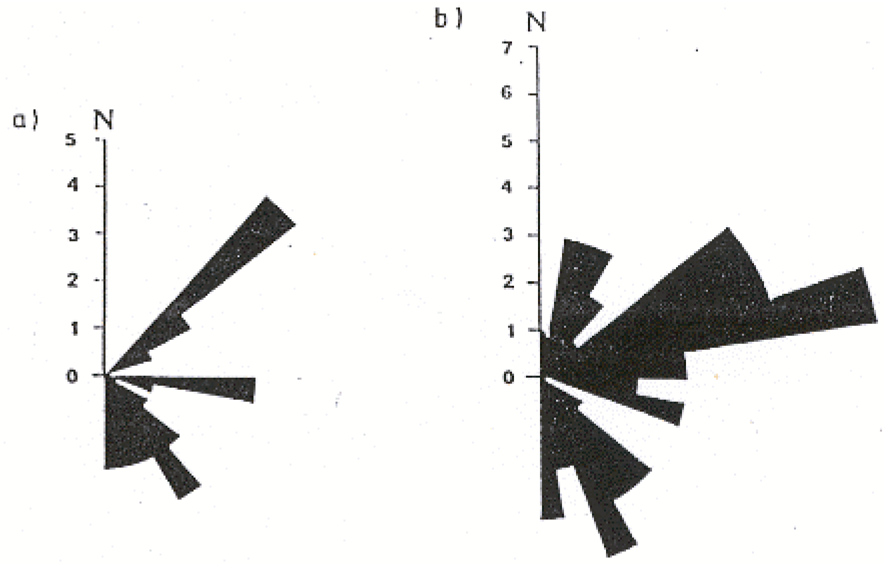


Figure 7
Fracture strikes measured in, a) the point source site and b) the orchard (monitoringsection). N is number of measurements

Sprækkeorienteringer (strygning) målt i, a) punktkilden og b) plantagen (moniteringsparcel). N er antallet af målinger

Orchard

The fractures in the orchard have been similarly measured. From the top of the profile the upper 1.5 m was heavily fractured. The fractures often seemed to be connected by boulders. Only in the upper metres of the reduced till zone the fractures were visible due to ironoxide stained fracture walls. However, at greater depths the till tends to bread along fracture planes. The orientation of the fractures shows a vague maximum at 70^o and 150^o, Figure 7b. The majority of the fractures were sub-vertical, but some sub-horizontal fractures were also observed. At larger depth the fracture spacing increased, and below 4 to 5 m only a few fractures were identified. However, the lack of staining of the fracture walls may obscure the identification of fractures.

Comparing the fracturing of the orchard and the point source site, the former appears to be more intensive. This is corroborating with a prevailing water saturation which is indicated (by the lake deposits on top of the profile) to occur at the point source site. As a consequence of permanent water saturation jointing by desiccation is expected to be rare and staining of fracture walls is expected to be weak. Thus, fractures of glacial origin should be expected to be the dominant fracture type at point source site.

4.1.3 **Groundwater levels and hydraulic gradients**

The pressure heads in the monitoring wells were measured through 1993 and 1994. The measurements showed a pronounced seasonality, Figure 8. In the upper screens in the till the pressure heads fluctuated from level +2.9 m to +1.7 m. Vertical hydraulic gradients of 0.1 - 0.7 were measured with a direction from the till towards to the sand aquifer. The pressure head in the sand aquifer (measured in well 2, screen IV), decreased through the period from level +0.3 m to 1.7 m with a gradient of approximately 0.6 directed from the till to the sand aquifer. The average hydraulic gradient across the aquitard was 0.2.

4.1.4 **Tritium profiles**

Types of samples

Tritium was measured in water samples distilled from Shelby tube cores (three profiles) and in water samples collected from the screens (five profiles) of the wells. Tritium profiles corresponding to each of the sample types are shown in Figure 9.

Depths of peak and minimum values

It appears that the core data are uniform in the three wells showing tritium concentration peak values at 5-7 m depth in all wells. At depths of more than 12-17 m, the core tritium is below the limit of detection (1 TU). The data representing the screens essentially follow the same pattern. However, two deep screens (point source wells 1 and 2) had tritium values above the limit of detection, while no tritium was measured in the core samples from the same depths.

When evaluating the tritium profiles it should be noticed that the core data are point measurements, while the screens represent water which may have been transported several metres by fractures due to pumping (prior to and during the sampling). In particular, partially penetrating vertical fractures may cause artificial redistribution of tritium (and other contaminants) due to pumping, because these fractures prior to pumping had minor contribution to adjective transport (due to their dead-end termination in the till). Such transport may account for the occurrence of tritium in the two deep screens mentioned above. Alternatively, tritium may have been transported inside the wells. However, this appears to be less likely, since, the screens above the screens with enhanced tritium, had no tritium.

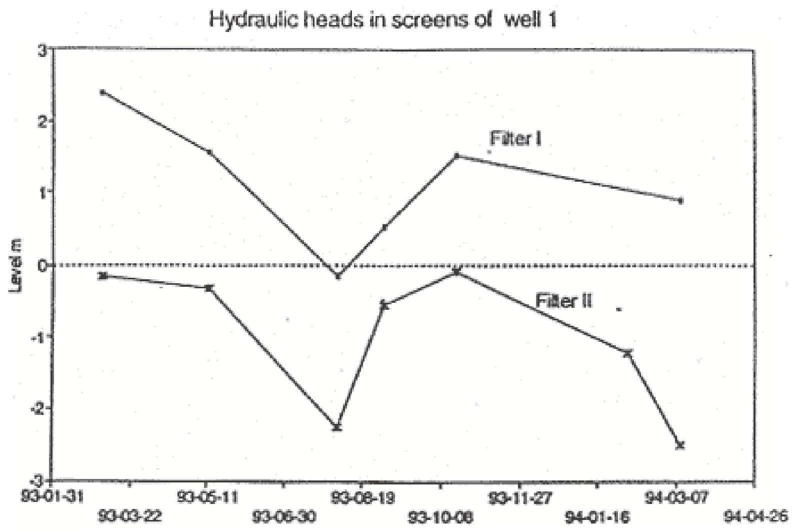
Hydraulic active zone

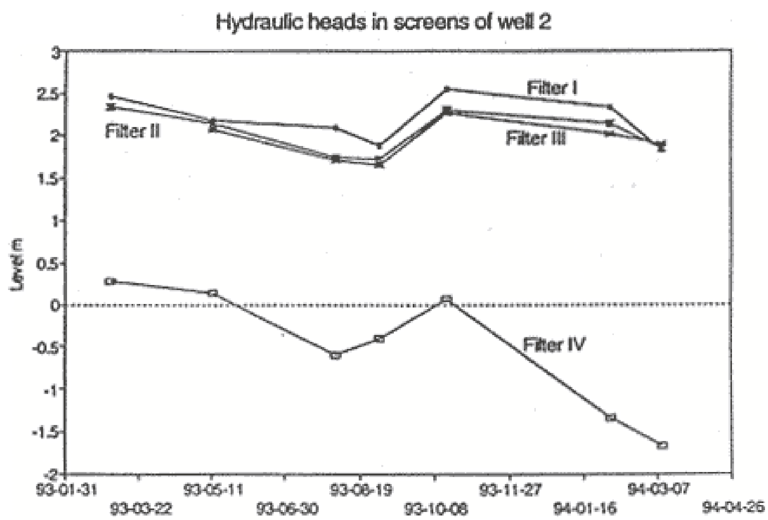
The repeated occurrence of high tritium values in the top of the profiles suggests the occurrence of a "hydraulically active layer" of approximately 5-10 m thickness. Fractures may extent from this layer into the lower till. However, evaluated from the core samples, highly conductive fractures are not expected to penetrate the entire till sequence. Further interpretation of flow mechanisms in the till aquitard is carried out by numerical analyses presented in the modelling section (section 5.3).

4.1.5 **Hydraulic laboratory experiments**

Hydraulic conductivity and soil pressure

Applying the large undisturbed columns, collected from 2-6 m's depth in the orchard and the point source site, two series of hydraulic experiments were carried out. In one serie, bulk hydraulic conductivities were determined at the in-situ soil pressures representing of the individual column sampling depths. In a following serie of experiments bulk hydraulic conductivities of the columns were measured at experimentally increased confining pressures representing depositional overload at different depths in the till.





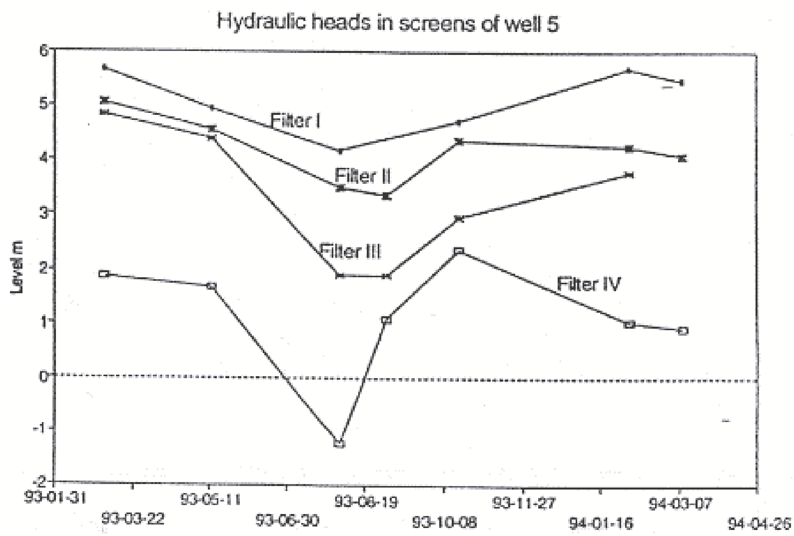
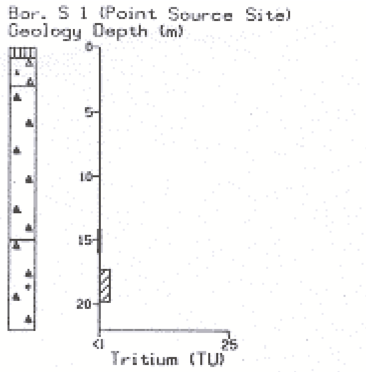
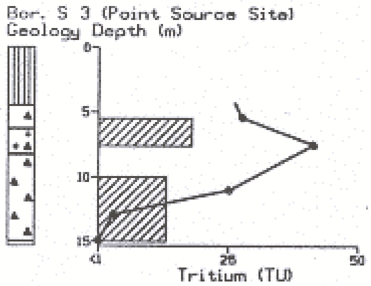


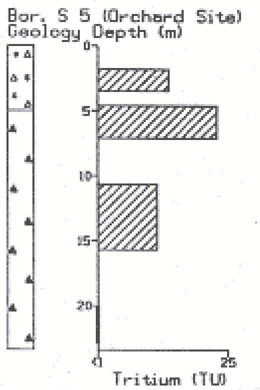
Figure 8
Hydraulic heads measured in monitoring wells 1 and 2 (point source)

and 5 (orchard monitoring section)

Hydraulisk trykhøjder i moniteringsboringerne 1 og 2 (punktkilde) og 5 (plantagen)







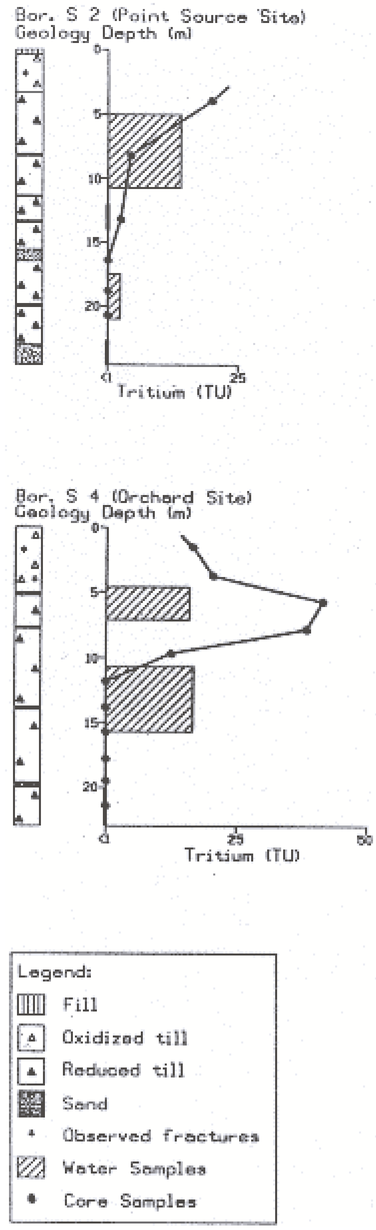


Figure 9
Tritium profiles of the angled monitoring wells in the point source site and orchard

Tritiumprofiler for skrå monitoringsboringer i punktkilden og plantagen

The results of the in-situ pressure experiments are summarized in Table 3. Additionally, in the table are shown hydraulic conductivities of the unfractured till matrix determined with small samples collected from selected large undisturbed columns.

Hydraulic apertures and conductivity of fractures

Base case hydraulic conductivities (K_f) of fractures and the fracture apertures (2b) were calculated using the approach of Snow (1969), where:

$$K_f = \frac{2(k_b - K_m)\ 2\ B}{2(2b)} 1 \qquad (4.1)$$

and

$$2\,b = \sqrt[3]{\frac{(K_b - K_m)2B\ ?\ \ 6?}{?\ \ ?\ \ g}}\ 2 \qquad (4.2)$$

K_m = hydraulic conductivity of matrix,
? = fluid density,
g = acceleration of gravity,

?	=	dynamic viscosity of water and

2B	=	fracture spacing

Fracture porosity

Fracture porosity (n_f) is given by

$$n_f = \frac{2 \ (2b)}{2B} 3 \quad (4.3)$$

The calculated values are shown in Table 3. Fracture porosities of the columns are 0.0001-0.0008 which is equivalent to 10-80 ml. Column volumes of total porosity are 25-32 l. Based on the fracture values calculated mean flow velocities in the fractures are 2-34 m/day at a hydraulic gradient of 1.

Table 3
Observed fracture spacings and calculated physical data in undisturbed columns

Observerede sprækkeafstande og beregnede fysiske data for uforstyrrede søjler

	Spacing (2B) m	**Fracture aperture (2b) ? m**	**Fracture porosity (n_f)**	**Fracture hydraulic conductivity m/s**	**Bulk hydraulic conduction m/s**
Column 1, orchard	0.05-0.07	20-22	0.0008	$2.5 \cdot 10^{-4}$	$2.0 \cdot 10^{-7}$
Column 2, orchard	0.05-0.10	7-8	0.0003	$3.1 \cdot 10^{-5}$	$7.2 \cdot 10^{-9}$
Column 3, orchard	0.05-0.10	6-8	0.0002	$2.2 \cdot 10^{-5}$	$6.0 \cdot 10^{-9}$
Column 1, point source	0.20-0.25	12-13	0.0001	$9.0 \cdot 10^{-5}$	$1.2 \cdot 10^{-8}$
Matrix from Column 1, point source	-	-	0	0	$2.0 \cdot 10^{-9}$
Column 2, point source	0.25-0.30	16-17	0.0001	$1.6 \cdot 10^{-4}$	$2.0 \cdot 10^{-8}$
Matrix from Column 2, point source	-	-	0	0	$1.0 \cdot 10^{-9}$
Column 3, point source	0.25-0.30	13-14	0.0001	$1.0 \cdot 10^{-4}$	$1.2 \cdot 10^{-8}$
Column 4, point source	0.15-0.20	25.27	0.0003	$3.9 \cdot 10^{-4}$	$1.2 \cdot 10^{-7}$

The experiments reveal significant difference in hydraulic conductivity and control of fractures on flow in the columns. The hydraulic conductivity of the columns was decreasing with column sampling depth. This is consistent with the field observation of the fracture density decreasing with depth.

Flow in fractures

In the shallow Column 1, orchard flow was controlled by fractures, and the hydraulic conductivities observed were comparable with values of fractured oxidized clayey till observed at other sites in Denmark (Jørgensen 1995). In this column bulk hydraulic conductivities were 2-3 orders of magnitude higher than the conductivity of the matrix.

In the deeper columns the hydraulic conductivities were approximately 1 order of magnitude higher (Columns 2 and 4, point source) or close to the hydraulic conductivity of the matrix (Columns 2 and 3, orchard). This is indicating a significant contribution to transport by matrix flow with depth.

4.1.6 **Stability of fractures at depositional overburden**

The effect of soil depth on fracture hydraulic conductivity (stability of fracture apertures) was investigated by determining hydraulic conductivities at various permeameter cell pressure simulating increasing depositional overburden.

Confining pressures

The experiments were initiated at in-situ soil pressures of the columns. From these pressures a confining maximum cell pressure of 240 kPa (corresponding to 20-25 m depth) was established through the steps 90, 120, 160, 240 kPa. The hydraulic conductivities were measured at steady state flow at each pressure level after consolidation of the columns had ceased. The results is shown in Figure 10 and Table 4.

Table 4

Hydraulic conductivities measured at in-situ soil pressures and at increased pressures

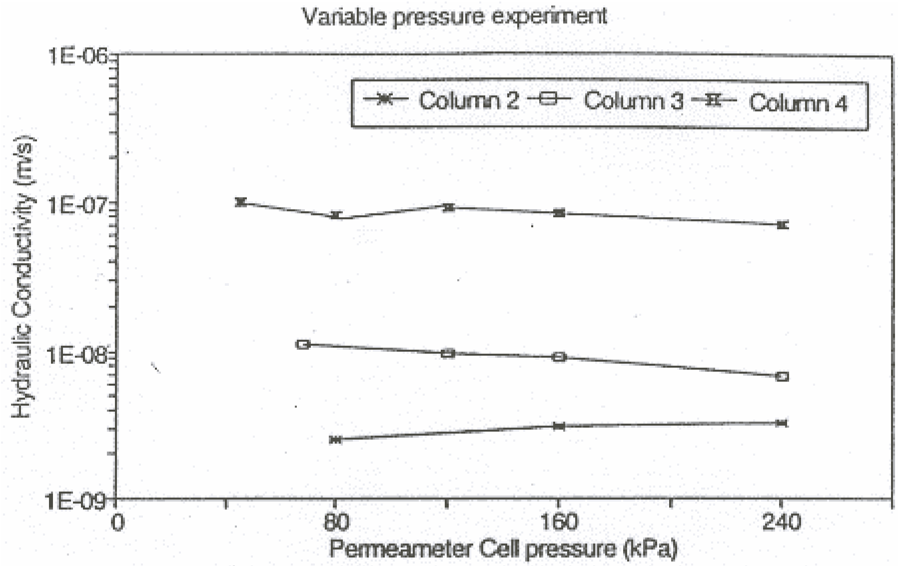
Hydrauliske ledningsevner målt ved trykstigningsforsøg

	K_b m/sec			
	in-situ	120 kPa	160 kPa	240 kPa
Column 1, orchard	$1.2 \cdot 10^{-6}$	$1.2 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$
Column 3, orchard	$1.6 \cdot 10^{-8}$	-	$1.6 \cdot 10^{-8}$	$1.7 \cdot 10^{-8}$
Column 2, point source	$2.5 \cdot 10^{-9}$	-	$3.1 \cdot 10^{-9}$	$3.2 \cdot 10^{-9}$
Column 3, point source	$1.1 \cdot 10^{-8}$	$9.6 \cdot 10^{-9}$	$8.9 \cdot 10^{-9}$	$6.8 \cdot 10^{-9}$
Column 4, point source	$1.0 \cdot 10^{-7}$	$9.2 \cdot 10^{-8}$	$8.4 \cdot 10^{-8}$	$7.1 \cdot 10^{-8}$

Influence of soil pressure

The data displayed reveals, that only minor changes in bulk hydraulic conductivities occurred even at the maximum cell pressure of 240 kPa. It may be predicted from the cubic law (eq. 4.2) that flow (L^3/T) of a fracture is a cubic function of the fracture aperture (L). Consequently, even small changes in fracture aperture should result in significant reduction of fracture hydraulic conductivity, and in cases where fractures control flow, also the bulk hydraulic conductivity should be reduced significantly.

The minor variations in bulk hydraulic conductivity suggests that fracture apertures may only be weakly influenced by depositional overload, and consequently, may be conductive at greater depths than at the upper 2-6 m represented by the columns. However, the difference in duration for consolidation at the lab scale versus the field scale is orders of magnitude when measured in years. It should therefore be noticed that possible long term effects of consolidation have not been analyzed by the experiments.



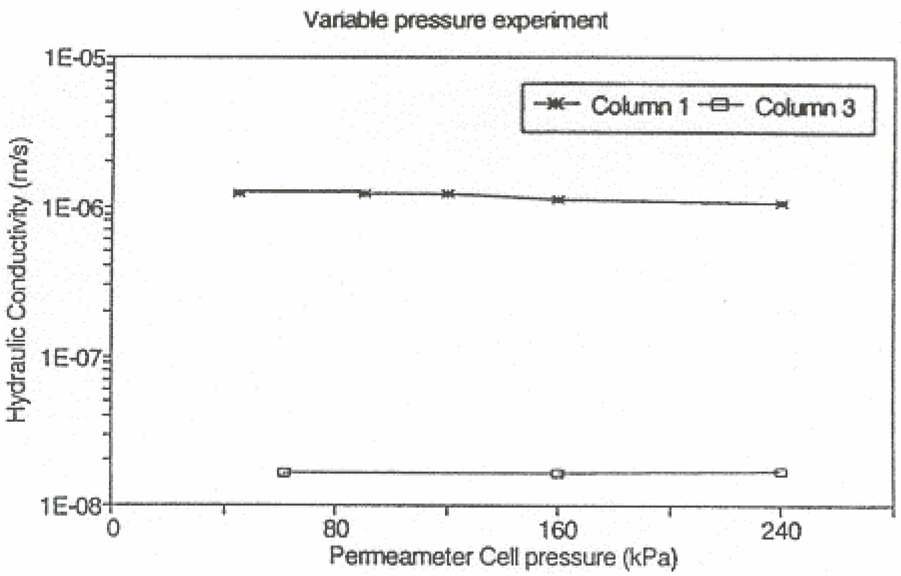


Figure 10
Hydraulic conductivities versus applied confining cell pressure of large undisturbed columns measured during soil pressure experiments

Hydrauliske ledningsevner målt under trykstigningsforsøg med intakte søjler

4.2 **Pesticides in soil and groundwater**

4.2.1 **Degradation of pesticides**

Oxic degradation

Pesticide degradation has major influence on breakthrough concentrations of leaching in fractured clay till and on the recovery after contaminant source has ceased. The effects are analyzed by Jørgensen and Spliid (1979). For assessment of risks, however, there is minimal information available about pesticide degradation rates in the deeper (>1 m depth) geological environments. One of the few published studies (Agertved and Rügge, 1992) showed degradation of mecoprop in an oxic sand aquifer while no degradation was measured for atrazine (similar to simazine with respect to persistence).

Anoxic degradation

Another investigation of a contaminant plume rich in organics from Vejen

Landfill (Heron and Futtrup, 1991) showed little or no degradation in the central anoxic part of the contaminant plume, while apparently rapid degradation of mecoprop occurred in the oxic margin of the advancing plume. This suggests a higher persistence of phenoxyherbicides at anoxic conditions than under oxic conditions. Mecoprop may transform via biodegradation into the potentially mobile degradation products MCPA and 4-chloro-2-methylphenol (Agertved & Rügge, 1992). Another portion of the pesticide is built into stable organic soil compounds, and eventually some of the pesticide can be strongly adsorbed (Helweg, 1993 and next section, this report).

4.2.2 **Pesticide adsorption on clay minerals**

Mechanisms

In the soil layers of the root zone the mineral surfaces are to a certain extent covered by adsorbed organic matter and not fully available for adsorption of pesticides. In deeper layers of clay soils the negatively charged clay surfaces are exposed and adsorption may be very significant for cationic pesticides (Weber, 1966; Bailey et al., 1968; Weed and Weber, 1968) Neutral pesticides may be adsorbed through van der Waal's forces (Mengelgrin and Tsvetkov, 1985; Rodriguez et al., 1988). Anionic pesticides are normally repelled by the clay mineral surface (Bailey et al., 1978, Mortland, 1970), but may be adsorbed through bonding to adsorbed inorganic cations.

Samples analyzed and mineralogy

Powder diffractometry carried out with total till matrix samples which were ground to pass a 0.25 mm sieve, showed the presence of quartz, feldspars, calcite and clay minerals. The amounts of quartz and feldspares increase with decreasing amounts of clay <2 ?m in the samples. The presence of large amounts of calcite in all samples demonstrates the low degree of weathering of the till.

The clay mineralogy was analyzed in the all core samples collected from the point source excavation and from well 4 m in the orchard.

The clay fraction at 1.3 m depth in the point source was dominated by vermiculite and further contained some smectite, illite, kaolinite, and chlorite, whereas the other samples contained vermiculite, illite, and smectite in fair amounts together with small amounts of chlorite and kaolinite.

The sample form the orchard at 2.1 m depth was different by not containing chlorite in detectable amounts. The similar clay mineralogy of coarse- and fine-grained samples fits well with the low degree of weathering as deducted from the presence of calcite.

Sorption experiments

Pesticide adsorption was investigated with core sample material sampled in well 4 at the depths of 2.1 and 22 m. The amounts of simazine adsorbed at natural pH by the samples were 1.8 and 5.6 ?g/10 g sample, at 2.1 m and 22 m depth, respectively. This corresponds roughly to 0.2 and 0.5 g/m^3 of sediment, respectively.

Sorption capacities

For these two samples, with approximately the same clay mineralogy, the difference in simazine adsorption capacity correlates well with the amounts of clay <2 ?m. It may tentatively be concluded, that for the simazine the clay fraction is the active adsorber. Assuming this, one can calculate the simazine adsorption capacity of the clay fraction to 5 ?m simazine per gram clay fraction at pH 7.8. Further experiments are needed to elucidate the role of the different clay minerals in the adsorption process. It is surprising that simazine is adsorbed in these rather large amounts at a pH of 7.5 where simazine is predominantly a neutral molecule, since the largest adsorption capacity from experiments with standard smectite (Weber, 1996) was found at low pH values where trazines are protonated. The calcium present on the exchange sites of the clay minerals in the present samples may, however, play a role in the adsorption process.

4.2.3 **History of pesticide application**

Objectives of pesticide mapping

The pesticides applied in the project area were mapped to evaluate cause-effect relationship of pesticide application and groundwater quality. For a comparison of the potential sources of pesticides contamination in the project area the mapping was carried out in the following units of land use:

- orchard section with monitoring wells
- orchard
- agricultural area.

Pesticides in orchard and sources of information

Distribution of the three units is shown in Figure 1.

The earliest records of pesticide use in the orchards is from 1919. However, the pesticide mapping was limited to cover 2nd and 3rd generation pesticides from approximately 1956, as these were considered to be the most important hazards to groundwater quality. The following list of compounds to be mapped was selected from the quality control guidance for water supply wells: DNOC, atrazine, simazine, 2,4-D, MCPA, mecoprop and dichlorprop. The list was extended with amitrol and terbuthylazin, as these were relevant in parts of the orchard.

For the period 1956-1984 the pesticide use was estimated. Mapping was based on the general information of agricultural statistics, consultants' recommendations and interviews of the former managers of Skælskør orchards etc.

Table 5 gives information of pesticide use in the orchard.

Table 5
Use of pesticides in the orchard in the period 1962 - 1992

Pesticider anvendt i Skælskør frugtplantage i perioden 1962 - 1992

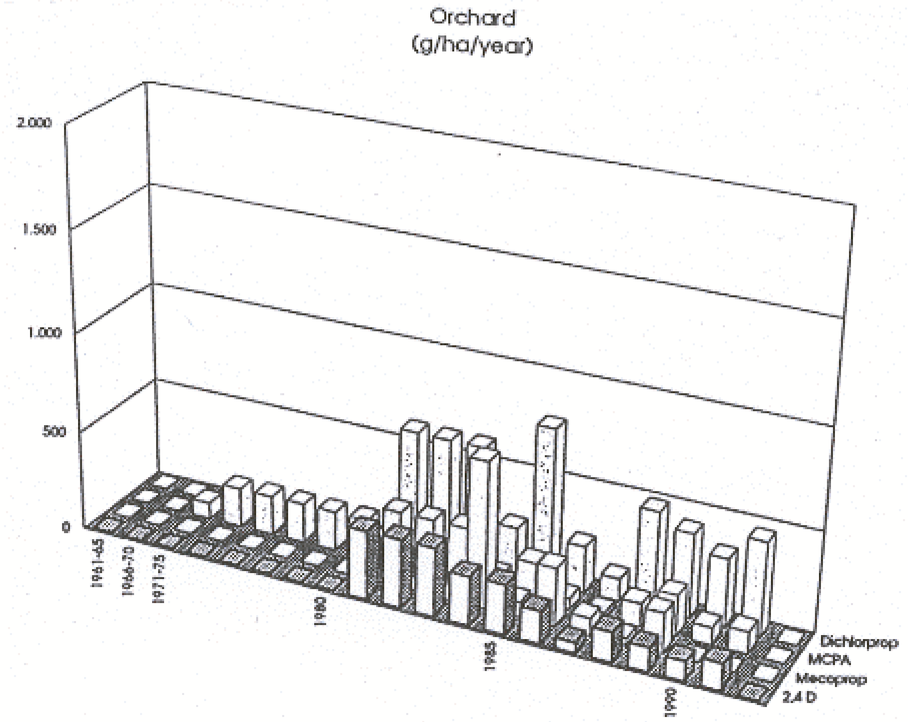
Product/period	Dose kg/ha/ year	Active ingredient	Dose (active ingredient) kg/ha	Load on the area	Average loak kg/ha/year
Simazine, 1962-71	2-3	simazine 50%	1,25	40%	0,50
Simazine, 1972-83	2-3	simazine 50%	1,25	24%	0,30
Weedazol, 1965-73	5	amitrol 21,3%	1,07	40%	0,43
Amitrol, 1974-1983	1	amitrol 95%	0,95	20%	0,19
Pramitol-M 80, 1972-83	2-3	terbuthylazon 80%	2,00	16%	0,32
Herbatox-M 750, 1974-83	1,3	MCPA 75%	0,98	20%	0,20
Herbatox-DPD 450, 1981-83	3-5	2,4D 300 g/l	1,20	20%	0,24
		dichlorprop 300 g/l	1,20		0,24
Herbatox-Combi 3, 1981-83	3-5	2,4 D 120 g/l	0,48	20%	0,10
		dichlorprop 420 g/l	1,68		0,34
		MCPA 100 g/l	0,40		0,08

The mapping of pesticides used in the orchard in 1984-92 was based on high quality records subdividing the orchard into 20 sections of individual treatment given by the conditions and cultures. Details of criteria for mapping and evaluation of quality of available information are given in CNS-report, Enclosure 1.

History of pesticide application

MCPA was the first phenoxyherbicide to be used regularly in Skælskør orchard, Figure 11. It was introduced in the early 1970'ies while dichlorprop, 2,4-D and mecoprop were introduced ten years later in the early 1980'ies. Focusing specifically on the monitoring section of the orchard (Figure 12) the phenoxyherbicide dichlorprop was used in 2 time higher amounts that in the rest of the orchard, Figure 11.

The amounts used of 2,4-D and MCPA were approximately 1.5 times higher than the average value for the orchard. Metoprop is the only phenoxyherbicide which has been used in less amounts in the monitoring section than the average for the total orchard.



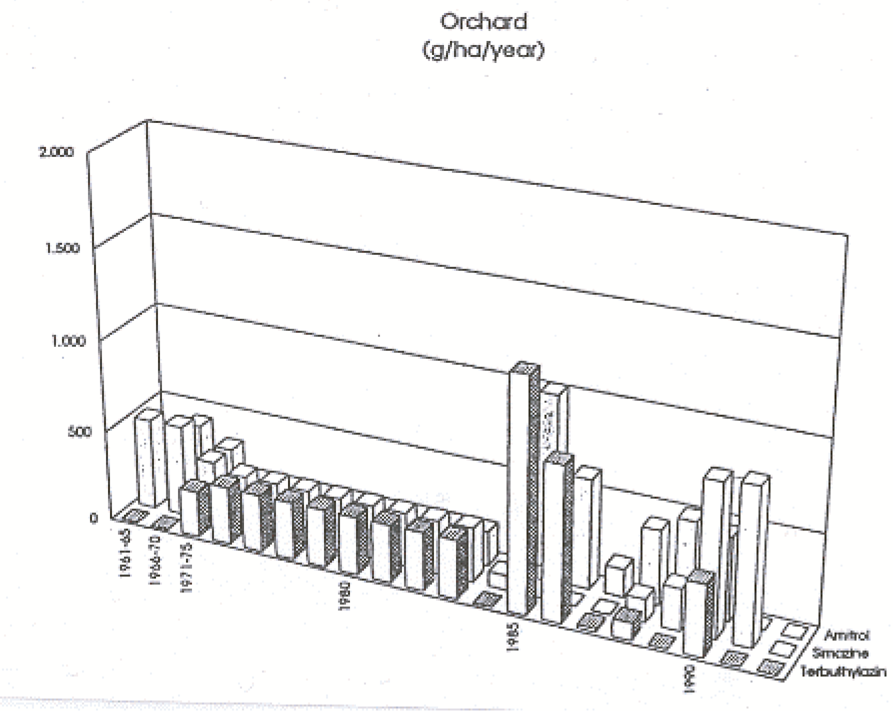
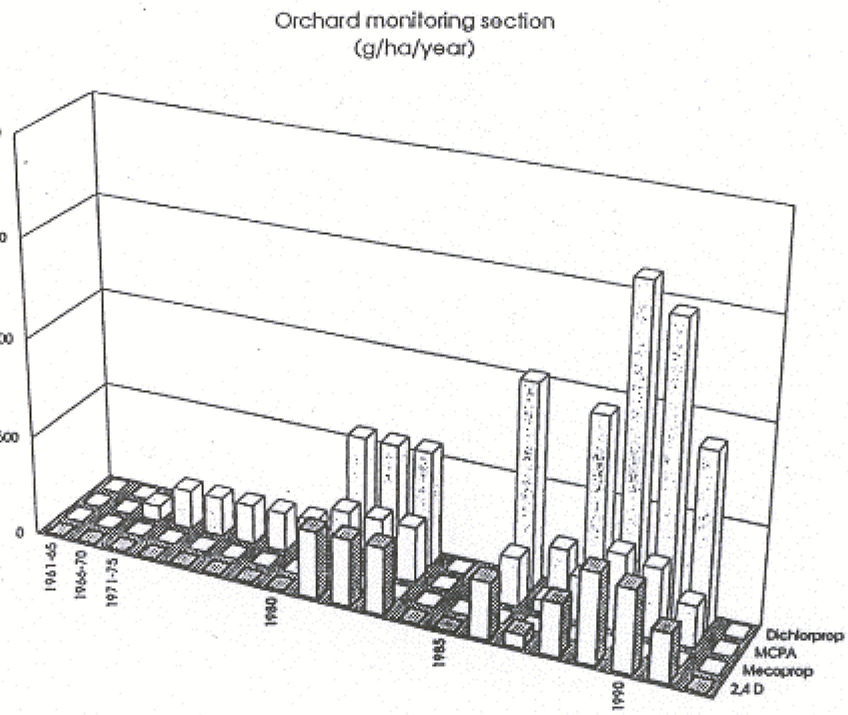


Figure 11
Use of selected pesticides in Skælskør orchard (1965-1992)

Udvalgte pesticiders anvendelse i Skælskør frugtplantage (1965-1992)



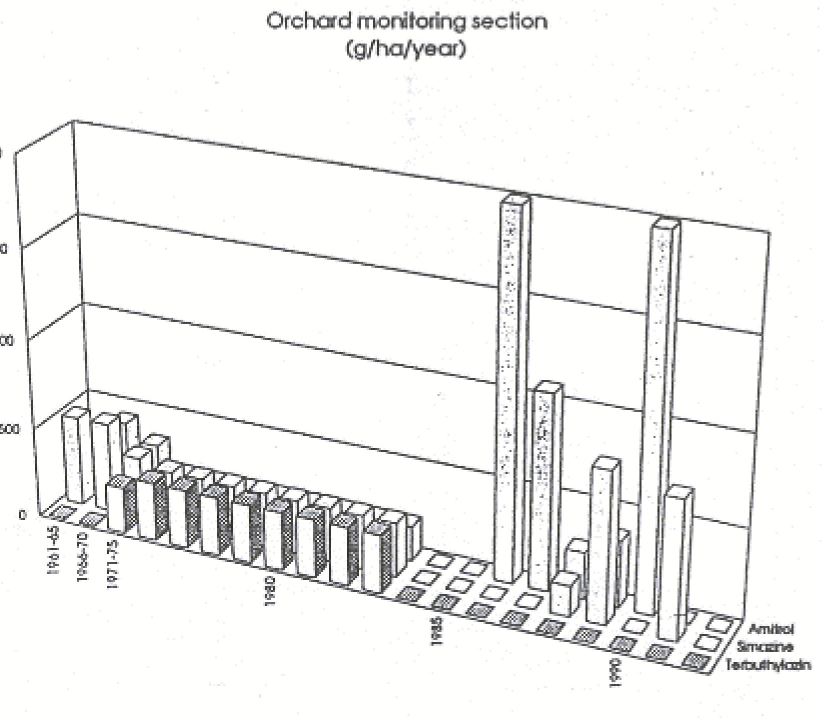


Figure 12
Use of selected pesticides in monitoring section (Skælskør orchard) in period 1965-1992

Udvalgte pesticiders anvendelse i monitoringsparcel (Skælskør frugtplantage) i perioden 1965-1992

The herbicides amitrol and simazine have been used in the orchard since the early 1960's and terbuthylazine since early 1970'ies, Figure 11. In the monitoring section amitrol has been used in high amounts, while simazine and terbuthylazine have been used less than in the remaining part of the orchard. According to the mapping none of these latter herbicides have been used in crops on arable land, Figure 13.

Summary information of pesticide use in the three mapping units is shown in Table 6. Comparing the phenoxyherbicide use in the orchard with the agricultural area in the table, the following differences in the pattern of use are to be noticed:

History of use on farm land

In the agricultural area the phenoxyherbicides were introduced in 1960-1970 while in the orchard they were introduced in 1970-1980. In the orchard the phenoxyherbicides have only been used in the summer (May/June). Since 1980 in agricultural areas application of MCPP in the autumn has become common. Application in autumn implicates increased risk of leaching from the root-zone of newly applied pesticides due to maintained surplus of precipitation and water saturation of the soils (Jørgensen and Spliid, 1997).

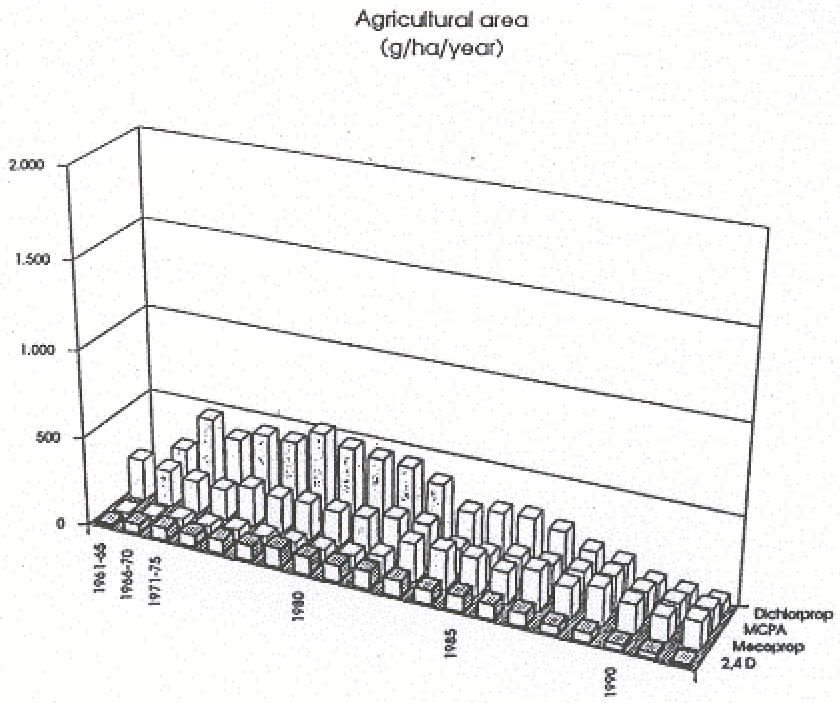
Table 6
Summary information of pesticide used in the three mapping units

Sammenfattende oplysninger om pesticidanvendelser i de tre kortlægningsenheder

Active ingredient	**Period of use (total amount in kg/ha)**		
	Monitoring section	**Average in orchard**	**Agricultural areas**
Dichlorprop	1981-1991 (7.90)	1981-1991 (4.85)	1996-1994 (6.23)
Mecoprop (MCPP)	1961-1991 (0)	1984-1989 (1.41)	1961-1994 (2.65)
2,4 D	1981-1991 (2.77)	1981-1991 (2.20)	1961-1994 (1.41)
MCPA	1971-1991 (3.33)	1971-1991 (2.73)	1956-1994 (4.11)
Total of phenoxy herbicides	14.0	11.2	14.4
Amitrol	1961-1990 (9.62)	1961-1990 (5.50)	- (0)
Simazine	1961-1991 (5.50)	1961-1991 (5.98)	- (0)
Terbuthylazine	1971-1983 (2.83)	1971-1990 (5.44)	- (0)
Total of amitrol, Simazin and terbuthylazin	17.95	16.9	0
Total	31.95	28.11	14.4

While the amounts of pesticides shown for the orchard in Table 6 are based on specific records, the amounts shown for the agricultural areas are average figures, representing the total sale of phenoxyherbicides in Denmark distributed evenly on the total area of Danish wheat lands. The resulting figures are considerably lower than the actual amounts used in areas where phenoxyherbicides have been the actual active compound. This is because other pesticides than phenoxyherbicides have been used in many areas.

In areas where phenoxyhericides were used specifically before 1980, the applied amount in spring and winter was 2000 g/ha and 2400 g/ha, respectively. After 1985 the use on arable land has been reduced to approximately half the amount. However, since 1980 application in autumn and winter has become common.



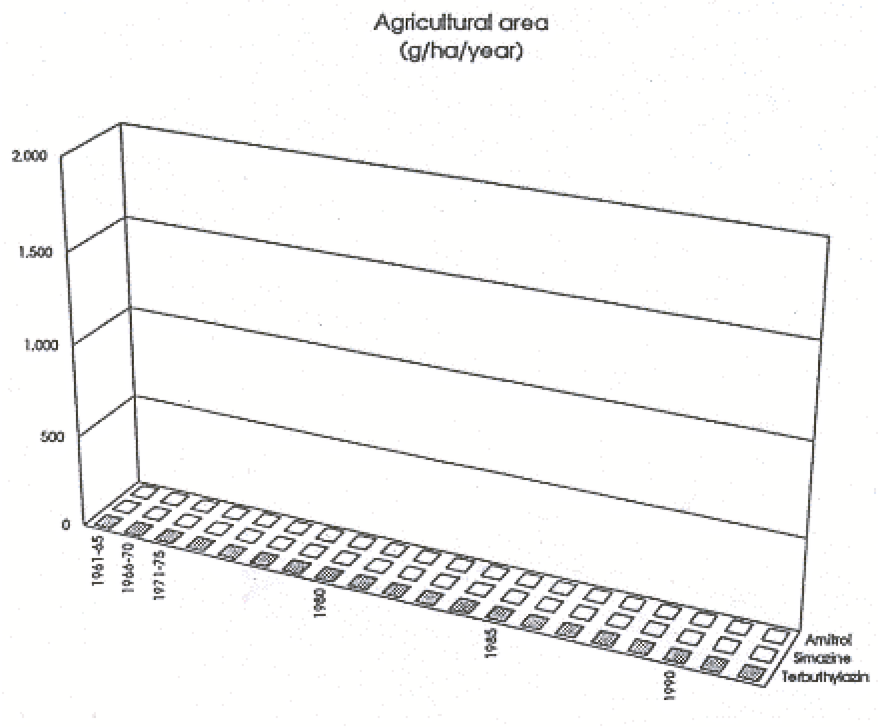


Figure 13
Use of selected pesticides in the agricultural area (1965-1992)

Udvalgte pesticiders anvendelse i landbrugsområdet (1965-1992)

4.2.4 **Pesticide monitoring at the point source site**

Pesticides adjacent to fractures

In the point source excavation, soil samples were collected to cover the distribution of pesticides adjacent to pronounced fractures. The samples were analyzed for the pesticides simazine, MCPA, 2,4-D, mecoprop, dichlorprop and atrazine. The results are shown in Table 7 and the locations of sampling in Figure 3.

At S1 and S2 four soil samples (S), representing increasing distance to the fractures, were analyzed separately. Simazine, mecoprop and dichlorprop were detected in the samples, but no concentration gradients were shown to exist between fractures and matrix. Based on this result the samples from the remaining profiles were mixed to represent average concentrations within a distances of 0.3 m from fractures. In S1, S2 and S4 the total content of pesticides exceeded 200 ?g/kg.

Table 7
Pesticides in soil samples from the excavation at the point source site (?g/kg). For location see figure 3

Pesticider i jordprøver fra udgravning i punktkilden (?g/kg). Prøvetagningspunkter er vist i Figur 3

Sample no	**Lateral distance from fracture m**	**Depth m**	**Simazine**	**MCPA**	**Mecoprop**	**Dichlorprop**
S6	0-0.3	2.5	48	6.3	9	n.d.
S8	0-0.3	2.7	1.8	6.8	3	n.d.
S7	0-0.3	2.9	0.5	3.9	7	n.d.
S4	0-0.3	3.0	140	6.9	61	n.d.
S1.0	0.0	4.0	25	n.d.	76	85
S1.1	0.1	4.0	13	n.d.	60	98
S1.2	0.2	4.0	13	n.d.	51	59
S1.3	0.3	4.0	13	n.d.	63	75
S2.0	0.0	4.0	66	n.d.	91	106
S2.1	0.1	4.0	66	n.d.	120	153
S2.2	0.2	4.0	16	n.d.	78	112
S2.3	0.3	4.0	70	n.d.	73	100
S5	0.0.3	4.0	65	11.7	-60	n.d.

n.d.: below detection limit.

Pesticide analyses of undisturbed Shelby tube core samples from below the excavation (well 2 and well 3) are shown in Table 8. The highest content of pesticides were found in the uppermost samples of well 3 at 5.4 m depth (with a total of 273 ?g/kg) and in the soil samples just below in well 2 (with a total 12.9 ?g/kg).

Table 8
Pesticides in core samples from the wells 2 and 3 at the point source site (concentration in ?g/kg)

Pesticider i kerneprøver fra moniteringsboringerne 2 og 3 i punktkilden (koncentrationer i ?g/kg)

Well no	Depth m	Simazine	MCPA	Mecoprop	Dichlorprop
2	8.0	1.3	9.0	n.d.	n.d.
2	11.0	0.4	n.d.	n.d.	n.d.
2	11.0a	n.d.	8.2	n.d.	n.d.
2	12.9	n.d.	12.9	n.d.	n.d.
2	16.4	6.4	n.f.	n.d.	n.d.
2	18.8	n.d.	2.4	n.d.	n.d.
2	20.6	n.d.	n.d.	n.d.	n.d.
3	2.1	36	7.2	n.d.	n.d.
3	5.4	4.0	n.d.	16	253
3	7.4	n.d.	n.d.	n.d.	n.d.
3	7.4	n.d.	n.d.	n.d.	n.d.
3	19.7	n.d.	n.d.	n.d.	n.d.
3	12.9	n.d.	n.d.	n.d.	n.d.
3	14-7	n.d.	n.d.	n.d.	n.d.

n.d.: not detected

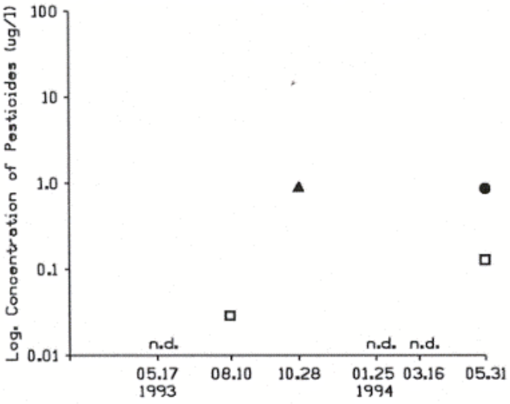
Pesticides in monitoring wells

Figure 14a show pesticide concentrations in water samples collected from 8 screens, six times over a period on approximately one year in monitoring wells 1, 3 and 4 below the point source excavation. Very high concentration of dichlorprop and mecoprop (sum concentrations up to 1 mg/l) and high concentrations of simazine in the upper screen (5-6.7 m depth) of well 3 which is consistent with the high concentrations of the same pesticides in the core sample from the same depth. In the upper filters especially the phenoxyherbicides have been identified in high concentrations in the time series, while the identification in the lower filters appears to be erratic.

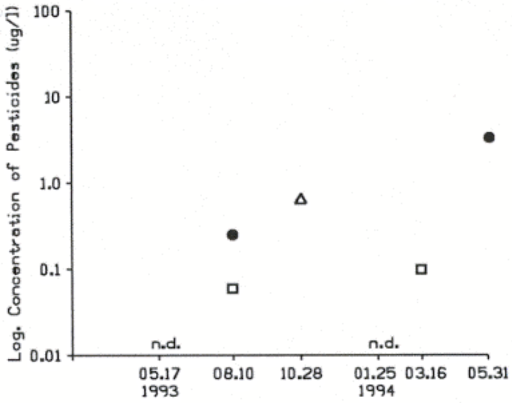
Point Source

Well 1

S 1.1 (Point Source) (Depth 14.1 - 15.9 m)

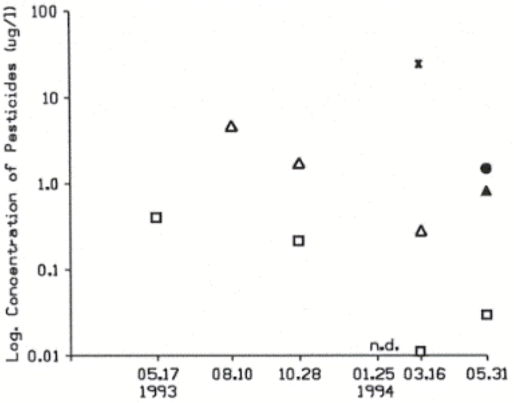


S 1.2 (Point Source) (Depth 17.3 - 21.2 m)

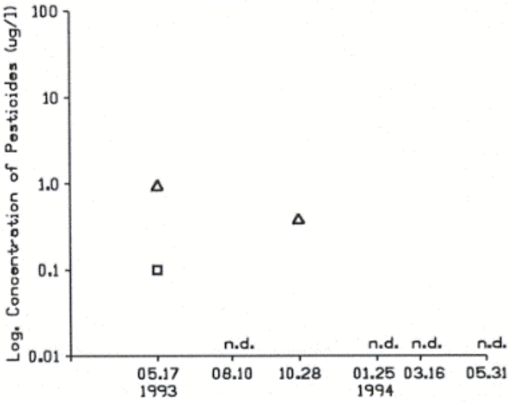


Well 2

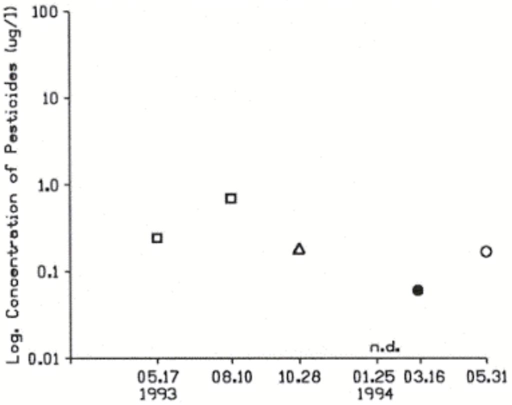
S 2.1 (Point Source) (Depth 5.0 - 10.6 m)



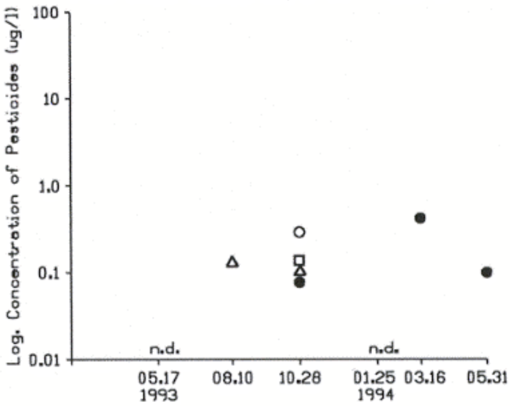
S 2.2 (Point Source) (Depth 11.9 - 13.9 m)



S 2.3 (Point Source) (Depth 17.3 - 20.5 m)

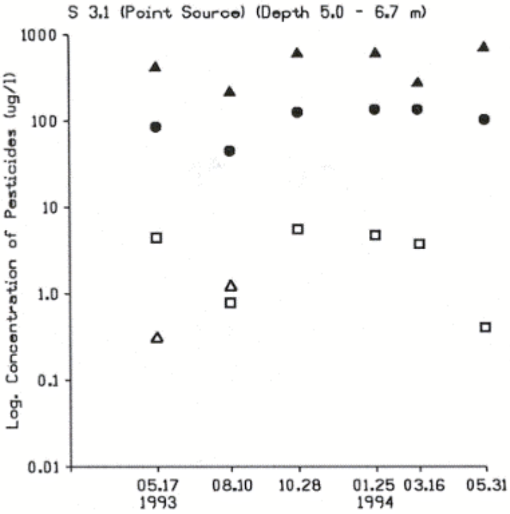


S 2.4 (Point Source) (Depth 22.6 - 23.8 m)

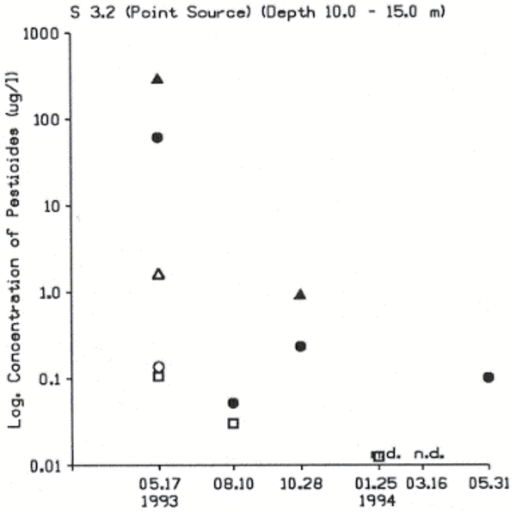


Well 3

S 3.1 (Point Source) (Depth 5.0 - 6.7 m)



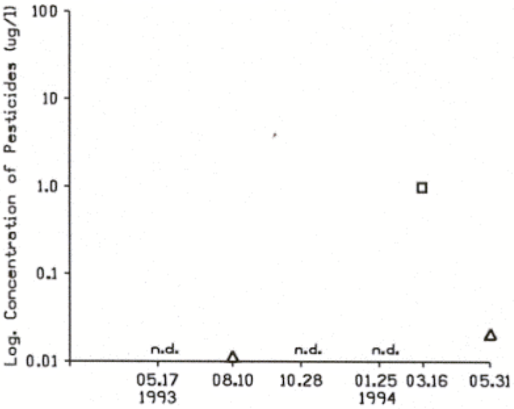
S 3.2 (Point Source) (Depth 10.0 - 15.0 m)



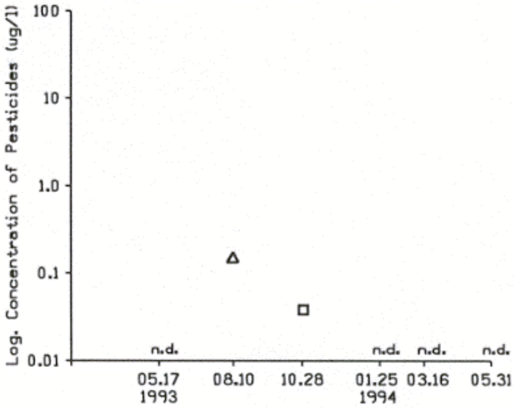
Orchard

Well 4

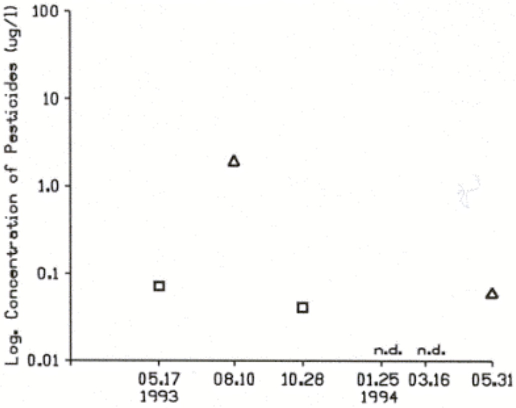
S 4.1 (Orchard) (Depth 4.7 - 7.0 m)



S 4.2 (Orchard) (Depth 10.6 - 14.0 m)



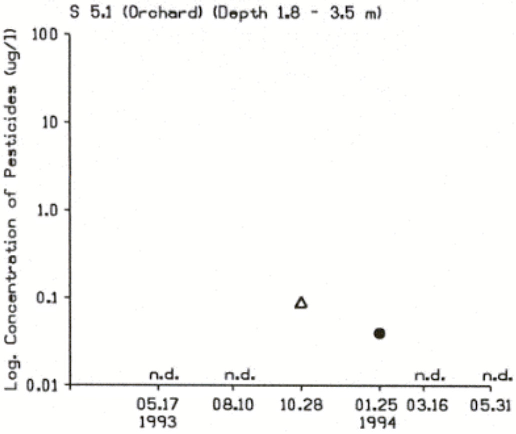
S 4.3 (Orchard) (Depth 19.8 - 22.0 m)



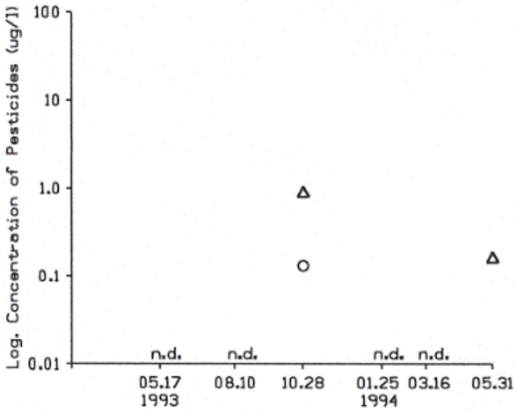
Legend:
□ Simazine ● Mecoprop
△ MCPA ▲ Dichlorprop
○ Atrazine ✖ 2.4-D

Well 5

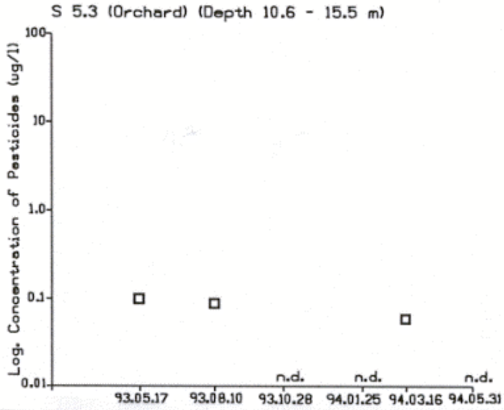
S 5.1 (Orchard) (Depth 1.8 - 3.5 m)



S 5.2 (Orchard) (Depth 4.6 - 7.0 m)



S 5.3 (Orchard) (Depth 10.6 - 15.5 m)



S 5.4 (Orchard) (Depth 19.8 - 22.6 m)

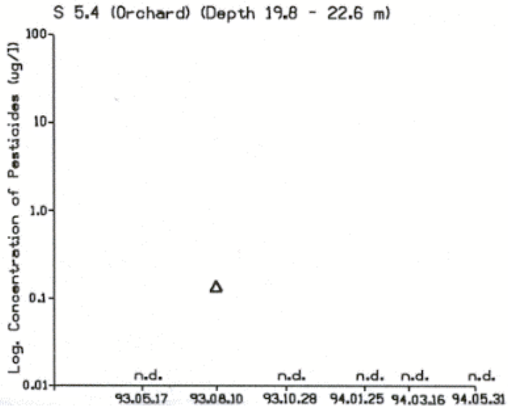


Figure 14
Pesticide concentrations in water samples collected from the monitoring wells, a) Machinery yard (point source) and b) Skælskør orchard

Pesticidkoncentrationer i vandprøver udtaget fra moniteringsboringer a) plantagens maskinplads (punktkilde) og b) Skælskør plantage

"Hot spot" zone spill

It may be noticed that the pesticides identified in the "hot spot" area at the point source site to some extent reflect the types and relative amounts of pesticides used in the orchard as shown by the mapping based on spray records and statistical sources (section 4.2.3). In general 2.4 D and MCPA are identified in relatively less amounts than expected from the mapping, while the opposite relations appear to exist for MCPP.

Evaluating the vertical pesticide leaching, the monitoring reveals that only shallow penetration of the very high pesticide concentrations observed at the point source site has occurred. Evaluated together with the depth of the tritium leaching, the vertical transport below the upper 10 m's appears to be limited, and there are no indications of rapid vertical transport in fractures.

Regional groundwater

The Skælskør town main aquifer water extraction wells were analyzed to represent the end of groundwater streamlines in the project area i.e. monitoring the integrated groundwater recharge from the orchard, point sources and farm land. No pesticides were detected in the water from the wells.

4.2.5 **Pesticide monitoring in the orchard**

Sample materials

In the orchard (monitoring section) undisturbed Shelby tybe core samples and time series of water samples were analyzed for the pesticides simazine, atrazin, terbuthylazone, MCPA, 2,4-D, mecoprop, dichlorprop.

Pesticides in the core samples collected from well 4 are shown in Table 9.

Table 9
Pesticides in core samples from well 4 in the orchard (concentrations in ?g/kg)

Pesticider i kerneprøver fra moniteringsboring 4 i Skælskør frugtplantage (koncentrationer i ?g/kg)

Well no	Depth m	Simazine	MCPA	Mecoprop	Dichlorprop
4	1.5	0.04	n.d.	n.d.	n.d.
4	3.6	n.d.	n.d.	n.d.	n.d.
4	7.8	n.d.	n.d.	n.d.	n.d.
4	9.6	n.d.	n.d.	n.d.	n.d.
4	11.5	n.d.	n.d.	n.d.	n.d.
4	13.4	n.d.	n.d.	n.d.	n.d.
4	13.4 a	n.d.	7.9	n.d.	9.4
4	15.7	n.d.	n.d.	n.d.	n.d.
4	19.5	n.d.	n.d.	n.d.	n.d.

n.d.: not detected

Monitoring wells Low concentration of simazine have been identified in the uppermost core sample at 1.5 m depth. Additionally, MCPA and dichlorprop have been identified in a thin sandlayer at 13.4 m depth while no pesticides were identified in a sample collected a few centimetres from the sand layer.

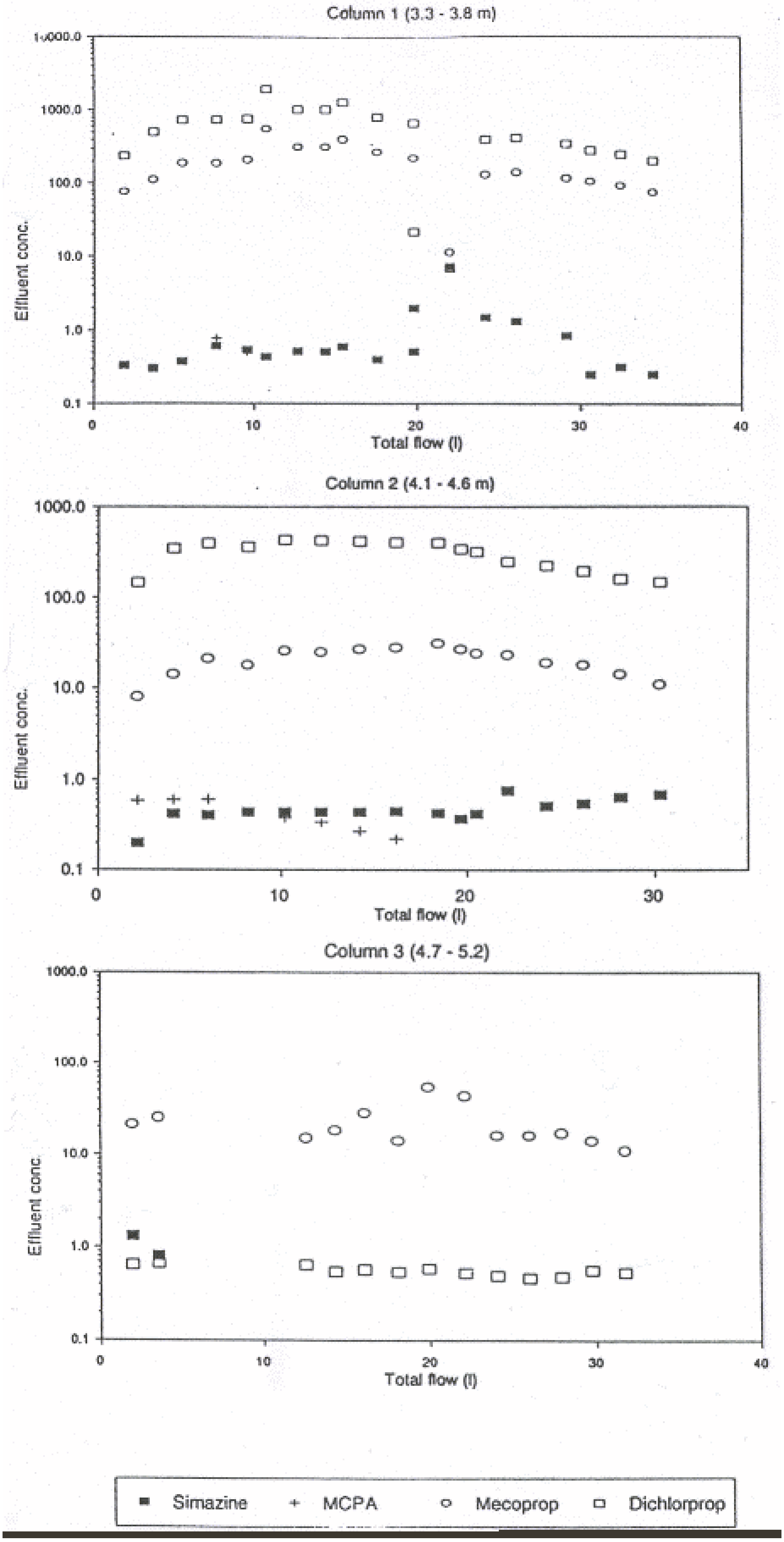
Monitoring wells Water samples were collected from the 7 screens six times over a period of approximately one year from monitoring wells 4 and 5. The results of the time series is shown in Figure 14b.

Low concentrations of simazine and MCPA were identified repeatedly in water samples from the till. The two pesticides have been applied intensively in the orchard and monitoring section for 20-30 years (Figure 11 and 12). However, concentrations in the water samples were erraticly distributed in time and space i.e. with no vertical trend. Dichlorprop was not identified in any of the samples. This pesticide has been applied intensively in the orchard for at least 10 years (Figure 11 and 12).

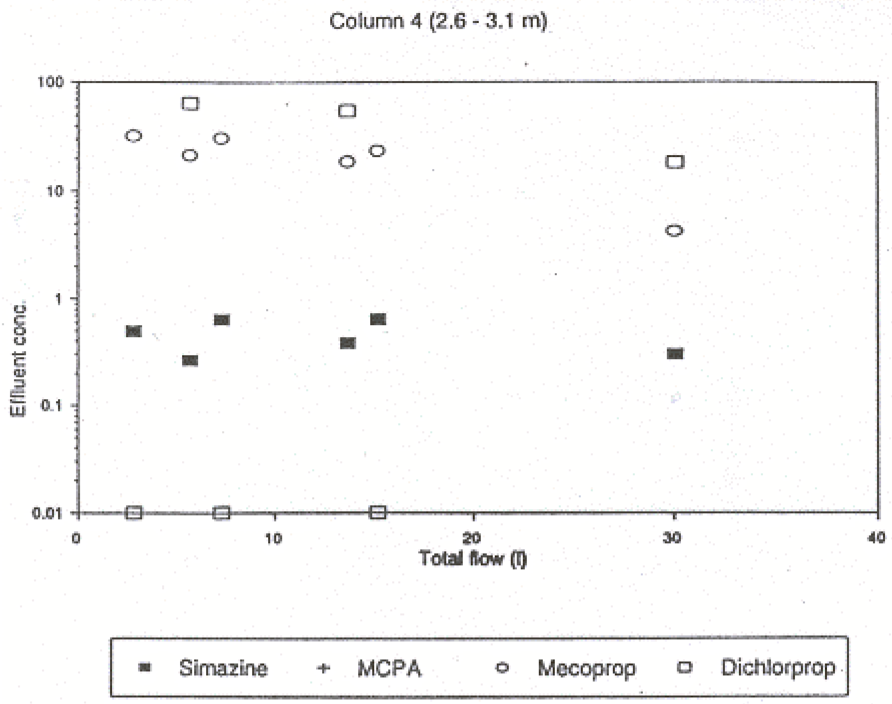
Pesticide in monitoring wells The pattern of the pesticide finding has a low correlation with the tritium data (shown in Figure 9). While tritium shows pronounced trends of concentration versus depth and no detectable values below approximately 15 m's depth (depth of hydraulic active "zone" of the till), pesticide distribution is erratic in time and space. Single identifications of MCPA and simazine occurred at depths of less than 1 TU. The erratic pattern of pesticide findings observed may be a result of redistribution of pore water in dead end fractures during pumping (water sampling).

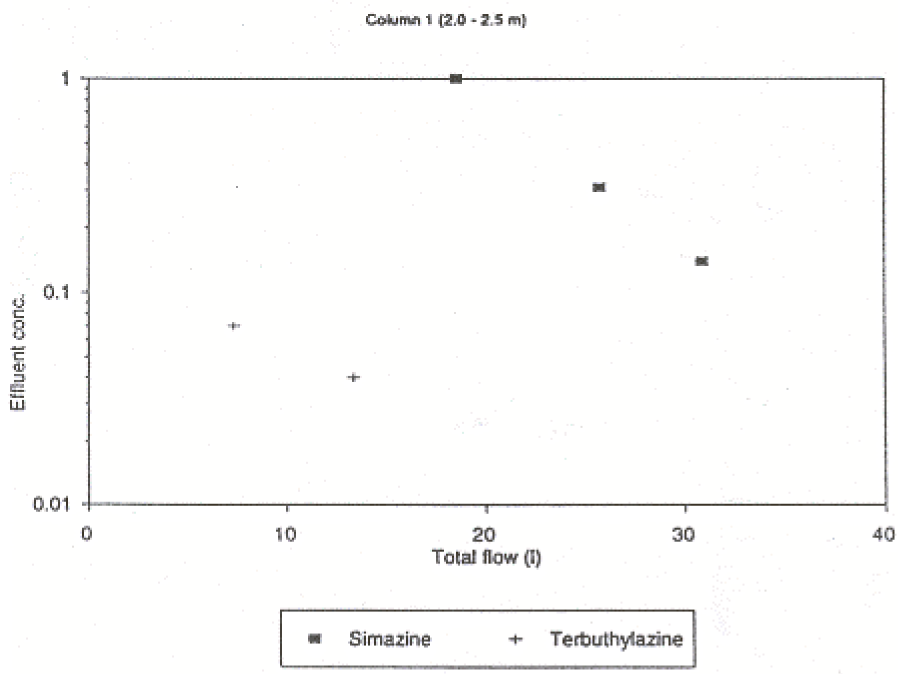
4.2.6 **Residual pesticides in large undisturbed columns**

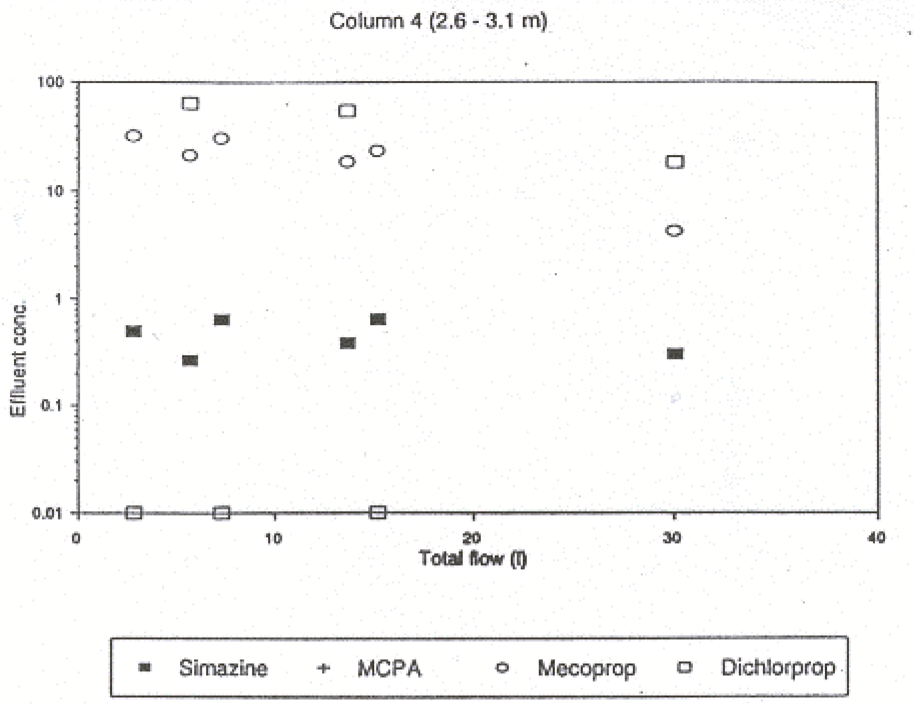
Leaching experiments Leaching experiments were carried out to investigate the amounts and the mobility of residual pesticides in the upper 5 - 6 m of the till in the orchard (monitoring section) and the point source site. The experiments were carried out by flushing the large undisturbed columns collected from the two sites with uncontaminated groundwater. Experimental conditions of leaching are given in section 3.3, and the results are shown in Figures 15.



Column 1 (3.3 - 3.8 m)
Effluent conc.
Total flow (l)
Column 2 (4.1 - 4.6 m)
Effluent conc.
Total flow (l)
Column 3 (4.7 - 5.2)
Effluent conc.
Total flow (l)
Simazine
MCPA
Mecoprop
Dichlorprop


Column 4 (2.6 - 3.1 m)
100
10
1
0.1
0.01
Effluent conc.
0
10
20
30
40
Total flow (l)
Simazine
MCPA
Mecoprop
Dichlorprop


Column 1 (2.0 - 2.5 m)
1
0.1
0.01
Effluent conc.
0
10
20
30
40
Total flow (l)
Simazine
Terbuthylazine



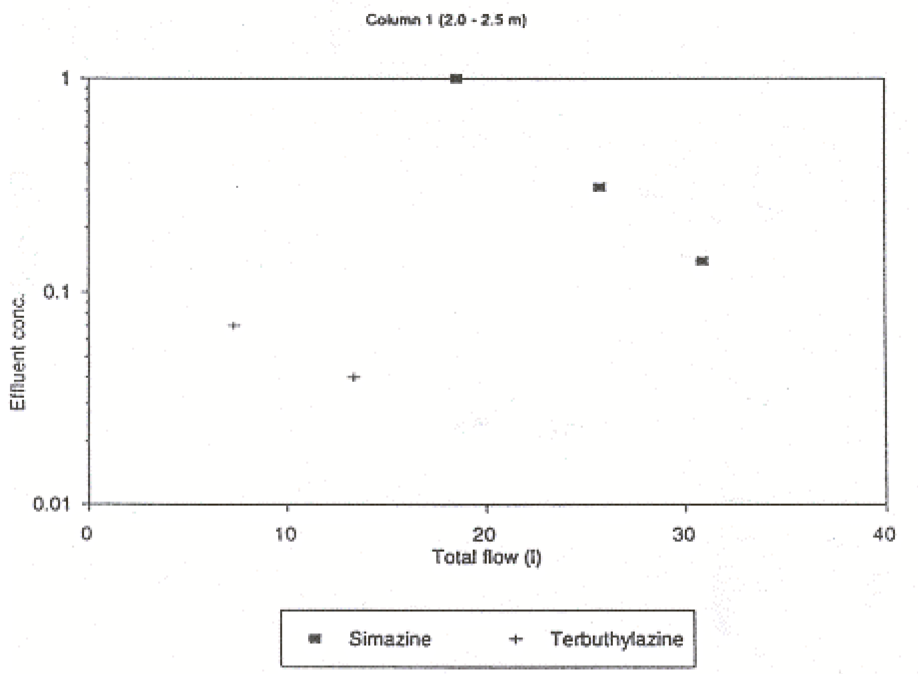


Figure 15
Leaching of residual pesticides from undisturbed till columns (diam.=0.5 m) collected in machinery yard (point source spill) and Skælskør orchard (monitoring section)

Udvaskning af residuale pesticider fra uforstyrrede morænesøjler (diam.=0,5 m) udtaget fra maskinplads (punktkilde forurening) og Skælskør plantage

Point source site

The point source columns had very high residual concentrations of mobile dichlorprop and MCPP (sum concentrations up to 2 mg/l). Relatively lower concentrations of simazine and erratic concentrations of MCPA (sum < 10 ?g/l) were identified while no 2.4-D was identified. The concentrations of dichlorprop and MCPP leached from the point source columns decreased 2-3 orders of magnitude from the shallow column (3.3 - 3.8 m's depth) to the deep column (5.2 m depth) and MCPA disappeared with depth.

Orchard site

In the columns from the orchard the observed levels of mobile pesticides were in general much lower than at the point source site. MCPA and 2.4 D were not identified in spite that these phenoxyherbicides have been applied in the monitoring section for 10 - 20 years (Figure 12 and Table 5). Dichlorprop was not identified (consistent with the field monitoring results) in spite of the extensive use in the orchard. This suggests that degradation of this pesticide occurres in the root zone. However, from the deepest column sampled in the reduced till mecoprop was identified at concentrations between 1- 10 ?g/l. This is in spite that mecoprop, according to the spray records, has only been used to a minor extent in the monitoring section. The occurrence may be a result of mecoprop application in the period after 1992 or before 1984 where no spraying records are available. Simazine and terbuthylazine were identified in low concentrations in some of the effluent samples from all three orchard columns. Concentrations were less than 1 ?g/l and occurred erraticly in time as also observed in the field monitoring.

5 Numerical modelling

Objectives and issues

The objective of the modelling was to give an estimate of pesticide leaching from the till sequence into a main reservoir. This includes modelling of laboratory tracer experiments on undisturbed columns, and considerations on upscaling of experimental laboratory data to the geological scale. The chapter also includes transport analysis of the distribution of tritium (profiles presented in Figure 9), sensitivity analyses to identify important factors in case of fracture flow, considerations about the predictability of the transport, and modelling methodology (fractured media flow versus porous media flow).

5.1 **Groundwater modelling**

A steady-state, three-dimensional numerical groundwater flow model of the sand and chalk aquifers underlying the Skælskør site was calibrated with the objective of estimating the flux of groundwater through the overlying till.

5.1.1 **Computer Code**

MODFLOW

The computer code used to simulate groundwater flow is the USGS's Modular Three-Dimensional Finite-Difference Ground-Water Flow model (McDonald and Harbaugh, 1988), commonly referred to as MODFLOW. This code solves the mathematical equations that describe groundwater flow in three dimensions using a finite-difference approach that estimates hydraulic head and flow as functions of time and space. This code was chosen because of its flexibility in evaluating various aquifer conditions, relative ease of use, and accuracy.

5.1.2 **Conceptual Model**

ZEUS database and hydrogeology

The conceptual model of hydrogeology of the Skælskør area was developed from borehole logs, and groundwater level data obtained from the ZEUS database (Gravesen & Fredericia, 1984), Vestsjælland County and Skælskør water supply. The groundwater system is conceptualized as consisting of a shallow till underlain by sand and limestone aquifers. The till is recharged by precipitation. Groundwater flow within the till consists of a horizontal component which discharges to surface water bodies and agricultural drains, and a vertical component which discharges to the underlying sand an chalk aquifers. The sand and chalk aquifers are confined and are recharged solely from vertical flow through the till. A clay unit present in the northeastern corner of the model area separates the sand and chalk aquifers. The groundwater discharges from the aquifer system to the sea and from the extraction wells within the sand and chalk aquifers.

Objective of MODFLOW mode

The objective of the MODFLOW modelling is to estimate the vertical groundwater flux or recharge from the till to the underlying aquifers. Therefore, the system was further simplified to consist of a sand aquifer underlain by a limestone aquifer. The interaction with the overlaying till is conceptualized as a recharge boundary where land is present and a discharge boundary where the sea is present. The model area is presented in Figure 16. Maps of the potentiometric surface of the sand and chalk aquifers are presented in Figure 17 and 18. Horizontal groundwater flow directions within these aquifers generally radiate from inland topographic highs and are perpendicular to the coastline.

Transmissivity estimates for the sand and chalk aquifers were obtained from the ZEUS database and from pumping tests made by Skælskør water supply. Transmissivity values for the sand aquifer range from $5 \cdot 10^{-6}$ to $2 \cdot 10^{-2}$ m^2/day. For the limestone aquifer the range is $1 \cdot 10^{-5}$ to $1 \cdot 10^{-3}$ m^2/day.

5.1.3 **Model Area and Grid**

The model domain is presented in Figure 16. It encompasses a rectangular area of 22.350 metres (east-west) by 16.885 metres (north-south). A non-uniform model grid was used. Grid cell dimensions are 100 metres by 100 metres in the vicinity of Skælskør and increase to 1000 metres by 1000 metres along the model boundaries.

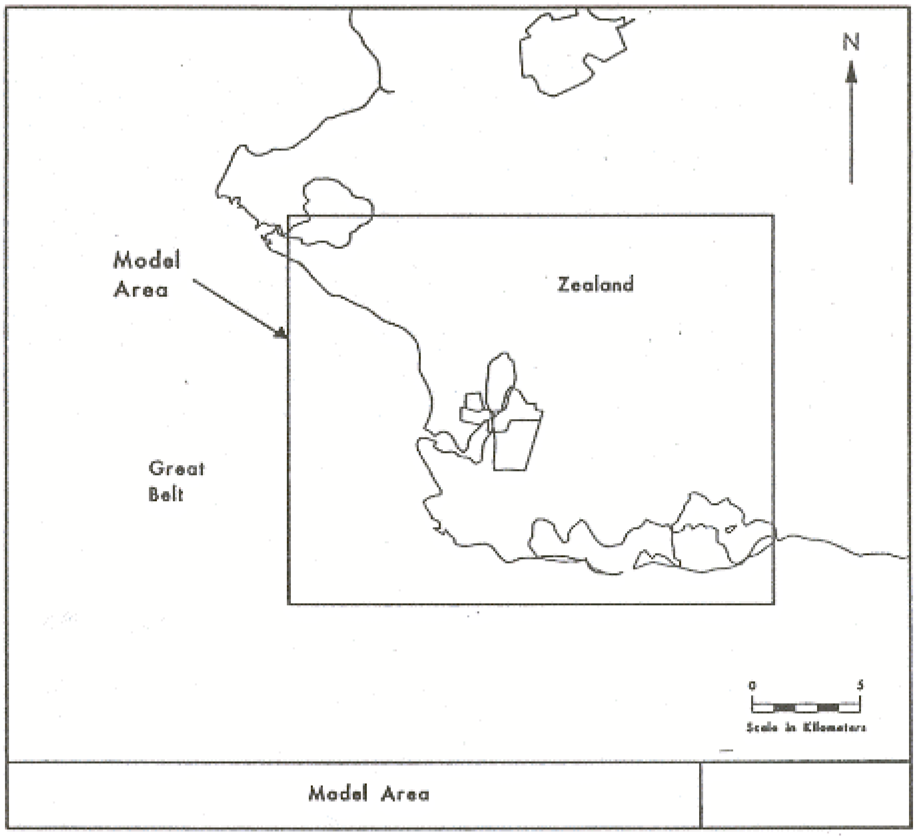


Figure 16
Area of numerical groundwater modelling

Grundvandsmodelleringsområde

5.1.4 **Layers**

The groundwater flow model consists of two layers which represent the sand and chalk aquifers. The thickness of the sand aquifer is represented in the model as zones of 0, 10, 20, and 30 m. The thickness of the chalk aquifer is held constant throughout the model area and is specified as 50 m. The clay which is locally present between the sand and chalk aquifers was represented implicitly in the model by the specification of a vertical conductance term. A constant thickness of 20 m and a vertical hydraulic conductivity of $1 \cdot 10^{-9}$ m/s was assumed in the calculation of the vertical conductance of this clay layer.

5.1.5 **Calibration Data**

Available groundwater level data for the model area are limited. The ZEUS database was queried for groundwater level data for the sand and chalk

Groundwater levels

aquifers for the time periods of 1940 to 1960, 1960 to 1980, and 1980 to 1994. The groundwater level data represents a mixture of water levels at the time of drilling and measurements in completed wells. Additionally these data are a composite of water levels representing different times of the year and wet and dry years. However, it is assumed that the data sets represent average water levels for each time period. Comparisons of contour

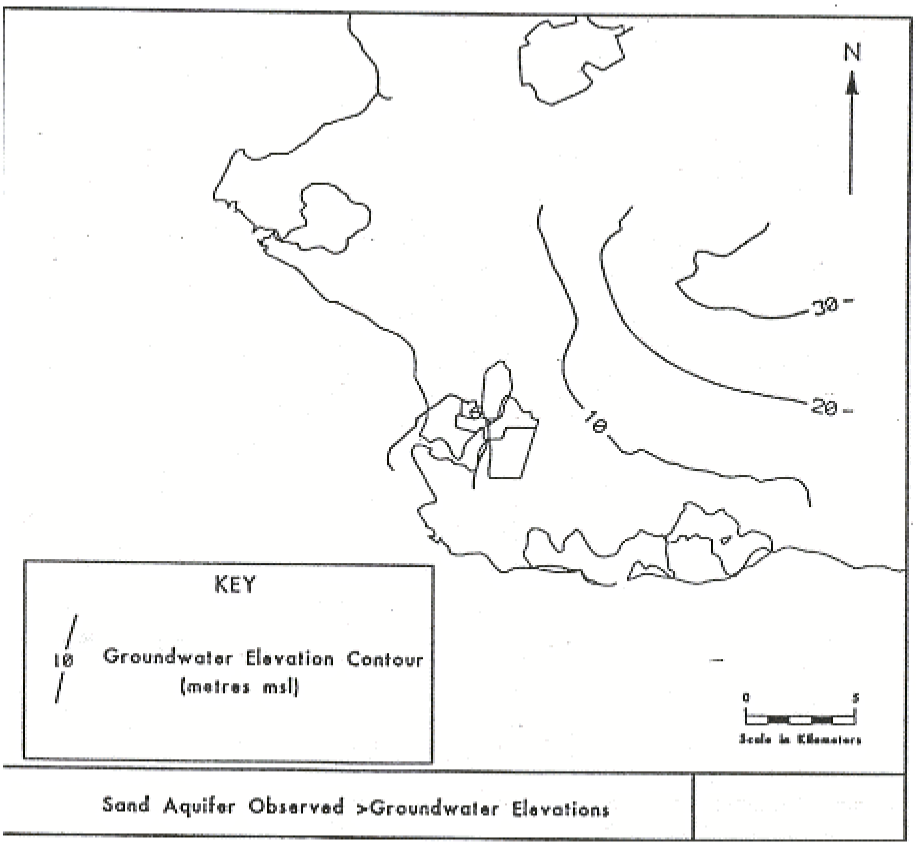


Figure 17
Equipotential map of the sand aquifer

Ækvipotentiale kort over det primære sand grundvandsreservoir

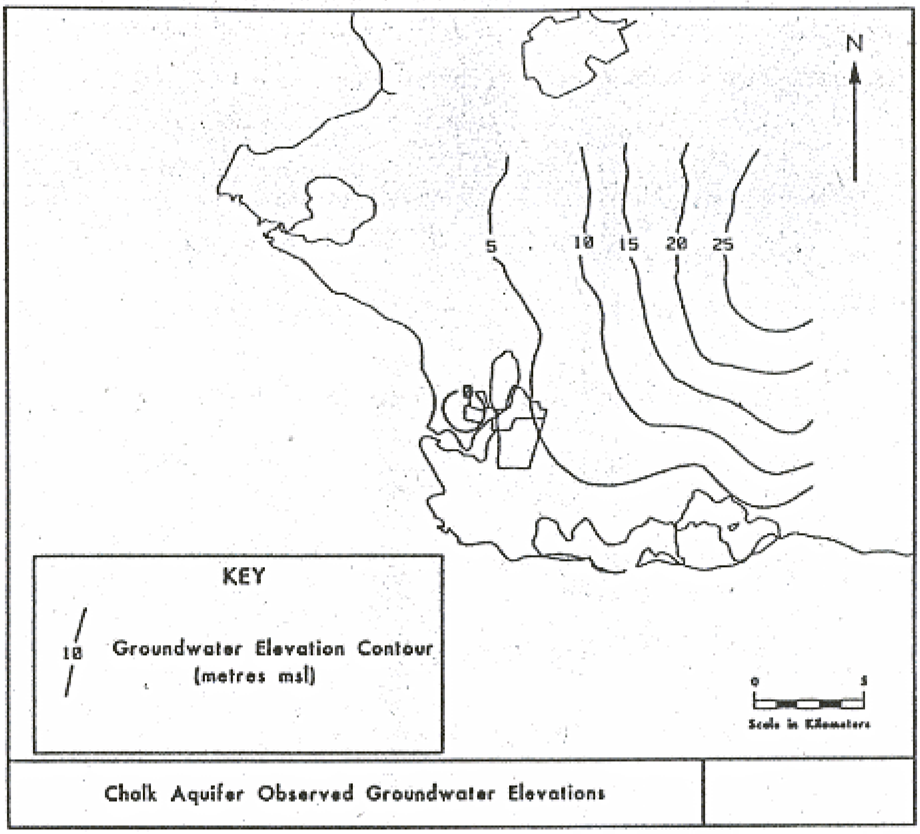


Figure 18
Equipotential map of the limestone main aquifer

Ækvipotentiale kort over det primære kalkstensgrundvandsreservoir

maps of the groundwater levels for these time periods did not reveal any trends in water levels. The water level data for the time period of 1980 to 1994 (Figure 17 and 18) was chosen for the calibration data set.

5.1.6 **Boundary Conditions**

Discharge of system

The boundary conditions for the model are shown on Figure 19. the upper surface of the model (top of sand aquifer) is simulated as a constant flux boundary, representing recharge to the sand and chalk aquifers from the till. The lower surface of the model (bottom of the chalk aquifer) is simulated as a no-flow boundary. Discharge from the two aquifers to the sea is dependent upon the head difference between the sand aquifer and sea level, the vertical conductance term which represents the vertical hydraulic conductivity and the thickness of the till unit. A head-dependent boundary was used to simulate the interaction between the aquifers and the sea. A conductance term for the till was calculated from an assumed constant thickness of 20 m and a vertical hydraulic conductivity of $1 \cdot 10^{-9}$m/s.

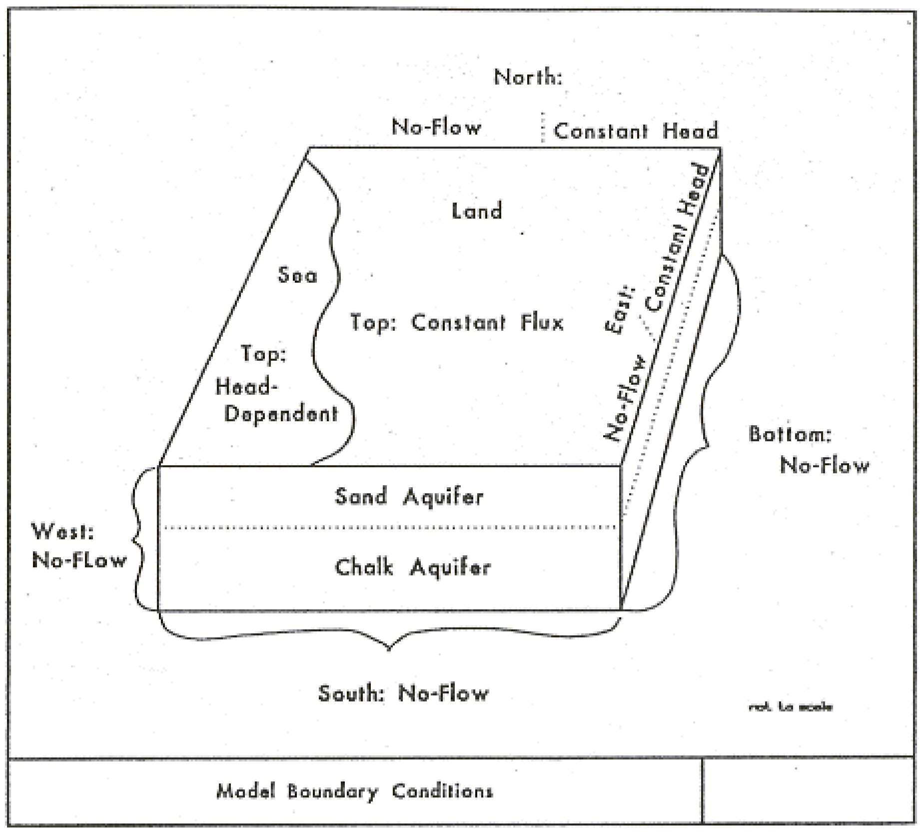


Figure 19
Column diagram depicting the model boundary conditions

Randbetingelser for grundvandsmodelleringen

The northern and eastern boundaries of the model were originally specified as no-flow boundaries. These boundaries are approximately perpendicular to contours of the hydraulic head in each aquifer and therefore approximate streamlines. Furthermore, by setting no-flow condition at the northern and eastern boundaries, the recharge to be modelled is reduced to the upper surface recharge. However, the northern and eastern boundary conditions had to be modified to include the specification of some model cells as constant head, in order to simulate the head difference of approximately 5 m between the sand and chalk aquifers in the northeast corner of the model area.

Values of constant head area

Values of constant head were based upon the contour map of the observed groundwater levels. Groundwater extraction in the sand and chalk aquifer was simulated using sink terms which represent pumping wells. The locations and pumping rates of these extraction wells are shown on Figure 20.

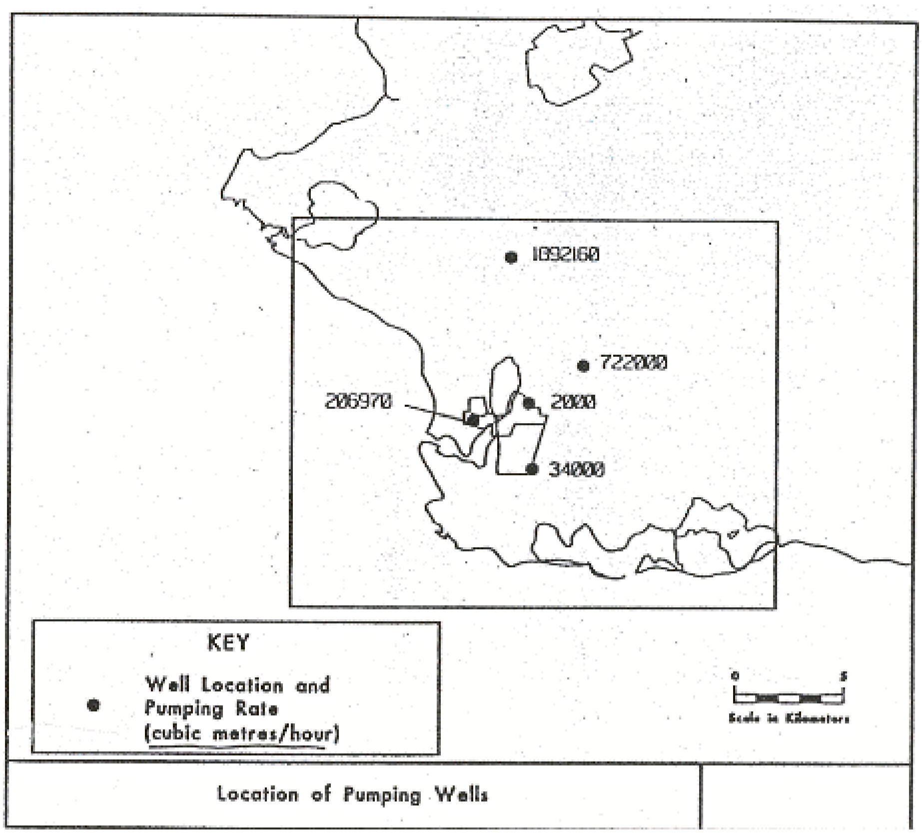


Figure 20
Location of extraction wells and rates of pumping within the model area

Lokalisering af indvindingsboringer i modelområdet med angivelse af pumperater

5.1.7 **Calibration**

Fitting procedure

The model was calibrated by specifying the recharge rate and varying the transmissivity of the sand and chalk aquifers within reported ranges, and adjusting the recharge until an acceptable fit was obtained between observed and simulated steady-state hydraulic heads. It was by using several different combinations of recharge rates and transmissivity values determined that the model could adequately simulate the observed hydraulic heads in the sand and chalk aquifers. The model results indicate that the vertical groundwater recharge through the till sequence is 30 to 60 mm/year. These values compare favourably with recharge estimates of 37

Adjacent studies

to 46 mm/year from the till to underlying aquifers reported by Christensen (1994) for an adjacent area north of the present study area.

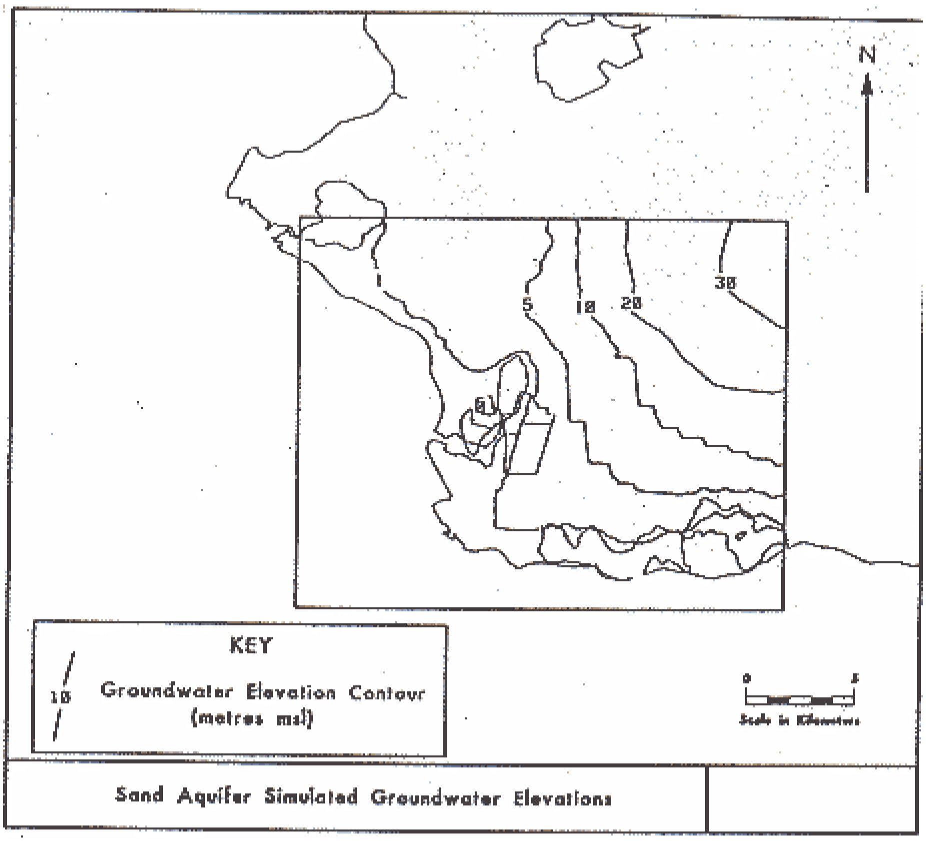


Figure 21
Simulated steady state equipotential lines of the sand aquifer

Simulerede ækvipotentiale linier i sandreservoir

Simulated groundwater levels in the sand and limestone aquifers are presented in Figure 21 and 22. The levels are simulated by using a recharge of 40 mm/year and transmissivity values of $1 \cdot 10^{-4}$ - $1 \cdot 10^{-3}$ m^2/s and $2.5 \cdot 10^{-3}$ m^2/s for the sand and chalk aquifers, respectively.

5.2 **Modelling of undisturbed columns**

Computer codes

Figure 23 a,b show the $CaCl_2$ breakthrough curves for five undisturbed columns from the undisturbed columns at the point source site and the orchard. The curves are represented as normalized concentrations versus cumulative volume of effluent (in litres). Using the codes 2D-FRACTRAN Computer codes (Sudicky and McLaren, 1992) and CRAK (Sudicky, 1988) the breakthrough curves been modelled. 2D-FRACTRAN simulates steady-state groundwater flow and transient contaminant transport in porous or discretely fractured porous media. CRAK works under the assumption that advection only occurs in the fractures (disregards flow in the matrix) but includes matrix diffusion. In 2D-FRACTRAN, fractures can have variable length and spacing. CRAK only handles one set of equal aperture fractures with constant spacing. Since CRAK only allows advection in the fractures, the flow velocity is overestimated; however, compared with other model

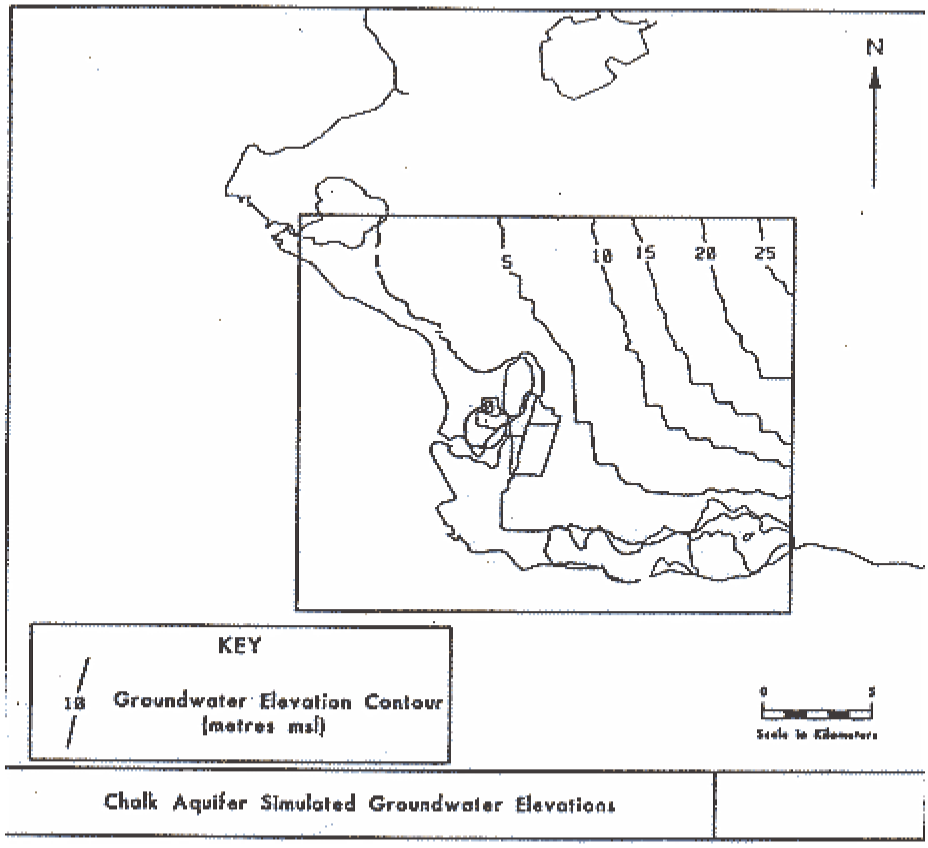


Figure 22
Simulated steady state equipotential lines of the limestone main aquifer

Simulerede ækvipotentiale linier i det primære reservoir

uncertainties, this assumption is considered to be of minor importance. In both models fracture walls are simplified as parallel planar surfaces.
The aim of the modelling is to achieve estimates of the aperture and spacing for the conductive fractures of the undisturbed columns. Fracture and porous media properties of the seven columns are listed in Table 10. Parameter values used for the modelling of column experiments and the following field scale modelling are show in Table 11.

Table 10
Column data used for modelling

Data anvendt i modellering af forsøg med intakte jordsøjler

Column	Fracture spacing in cm				Poro-sity	Gra-dient	Tracer		K_m ** m/s	K_b m/s
	Vertical		Horizontal				T_{on} (hours)	T_{off} (hours)		
	1.+2. order	3. order	1.+2. order	3. order						
Columns from the orchard										
1*	5-7		10-12		30	0.3	0	168	5?10^{-10}	2?10^{-7}
2	5-10		5-10	1-2	30		-	-	5?10^{-10}	7.2?10^{-9}
3*	10-20		18-20		25	4	0	172.3	5?10^{-10}	6?10^{-9}
Columns from the point source site										
1	20-25	2-3	25	1.0-1.5	30		-	-	5?10^{-10}	1.2?10^{-8}
2*	25-30	2-3		0.5-1.0	30	3.5	0	?	5?10^{-10}	2?10^{-8}
3*	25-30	2-3		1.0-1.5	25	5.0	0	?	5?10^{-10}	1.1?10^{-8}
4*	15-20		15-20	0.5-1.0	30	1.0	0	1608	5?10^{-10}	7?10^{-8}

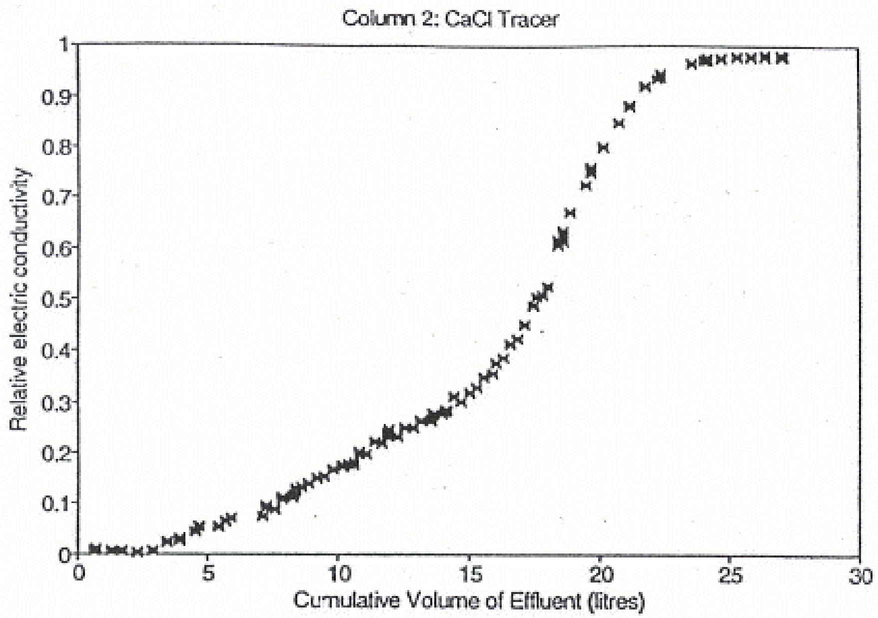
* *columns with a $CaCl_2$ breakthrough curve*
** *based on Foged & Wille, (1992)*

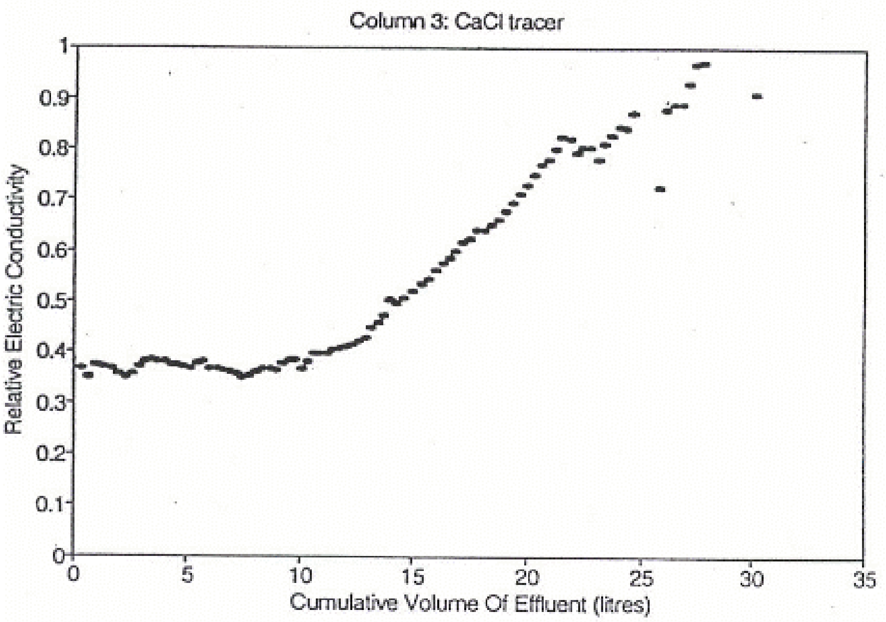
Table 11
Base case values of material properties used for modelling of column experiments and field scale examples

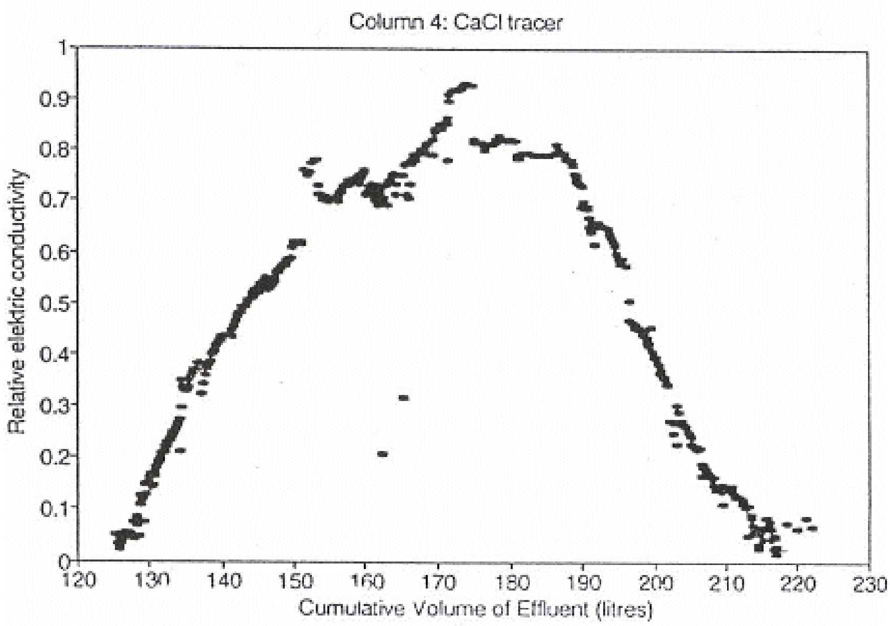
Materiale værdier anvendt til modelling af søjleforsøg og feltskala eksempler

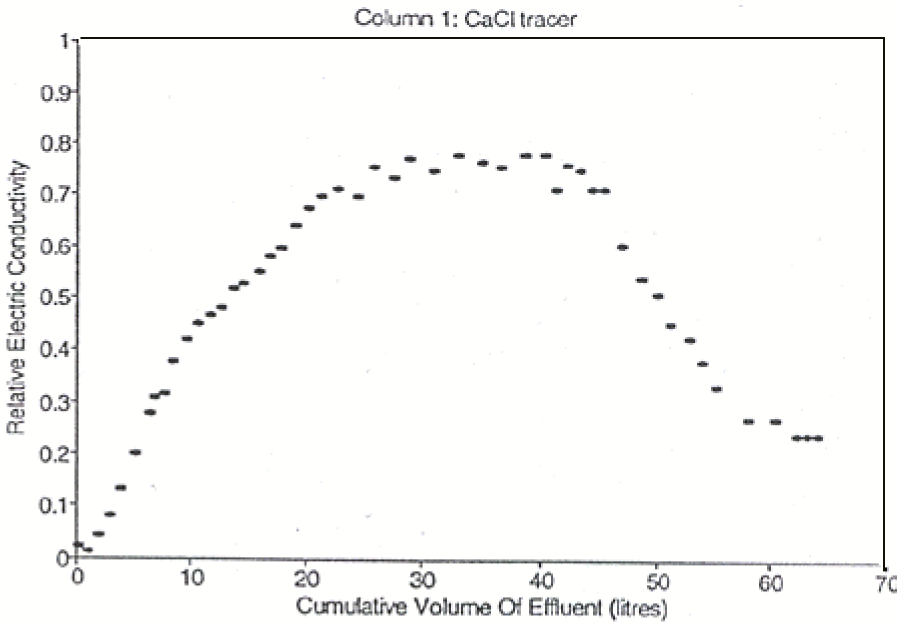
Parameter	**Value**	**Unit**
Matrix permeability	5?10^{-10}	m/s
Porosity	0.25	
Viscosity (at 10?C)	1.31?10^{-3}	kg/ms
Gravitational acceleration	9.81	m^2/s
Effective diffusion coefficient:		
Chloride	6.0?10^{-10}	m^2/s
Tritium	7?8?10^{-10}	m^2/s
Retardation factor:		
Chloride	1	
Tritium	1	
Input concentrations	1	

Conductive fractures were identified in the columns after infiltration of a fluorescent dye tracer. The total porosities are from a similar till at Enø (Fredericia, 1991). The gradients are average values for the tracer experiments and the bulk hydraulic conductivities (K_b) are calculated from


Column 2: CaCl Tracer
Relative electric conductivity
Cumulative Volume of Effluent (litres)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
5
10
15
20
25
30


Column 3: CaCl tracer
Relative Electric Conductivity
Cumulative Volume Of Effluent (litres)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
5
10
15
20
25
30
35


Column 4: CaCl tracer
Relative elektric conductivity
Cumulative Volume of Effluent (litres)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
120
130
140
150
160
170
180
190
200
210
220
230



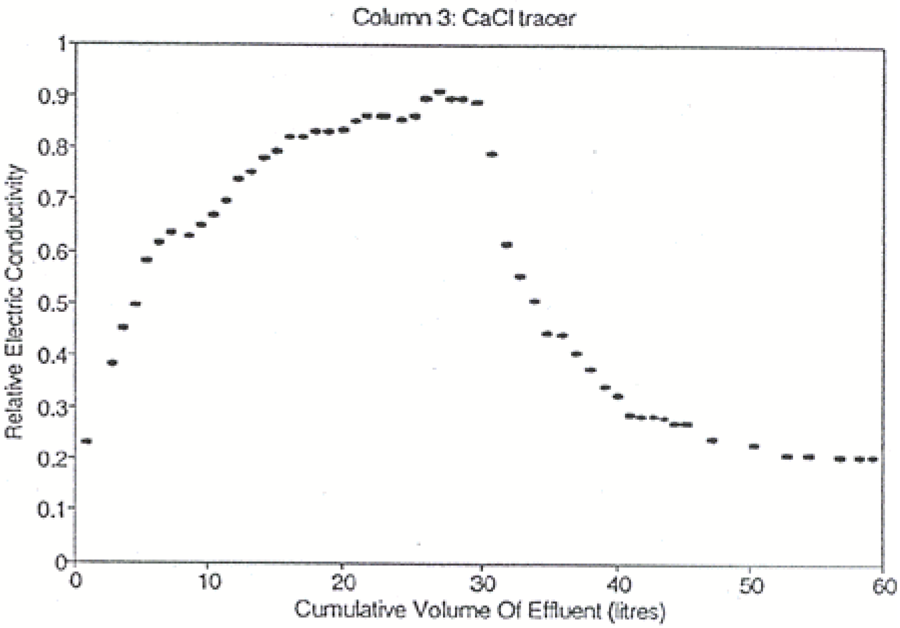


Figure 23
Transport of applied $CaC1_2$ tracer in Columns 2, 3 and 4 from the machinery yard (point source) and Columns 1 and 3 from Skælskør orchard

Transport af tilsat $CaC1_2$ tracer til undersøgelse af stoftransport i søjlerne 2, 3 og 4 fra maskinplads (punktkilde) og 1 og 3 (Skælskør frugtplantage)

the gradients and volumetric flow rates. T_{on} and T_{off} represent the beginning and end of the chloride tracer application. During the infiltration experiment, the hydraulic conductivity of columns was not constant (due to generation of gas in the columns). This has resulted in some unreproducible changes in $CaCl_2$ breakthrough for column 3 (point course site) at about 550 hours.

Fracture apertures and spacing

Modelling the breakthrough curves for the undisturbed columns from the orchard, results in larger active fracture spacings than observed from the distribution of dyed fractures after the experiment, Table 12. The reason for this discrepancy may be that the major part of the flow is in some, but not all of the fractures. Oppositely, modelling of the columns from the point site results in fracture spacings smaller than measured from dyed fractures in the columns. This may reflect local differences in the till; at the point site the till contained only a few not very pronounced larger fractures. This is also indicated by the breakthrough curves which are characterized by flow in the total porosity.

Table 12
Modelled and measured active fracture spacing

Modellerede og observerede sprækkeafstande

	Modelled active fracture spacing	**Modelled fracture aperture**	**Measured active fracture spacing**
Column 1, orchard	0.35 m	48 ?m	0.05 m-0.07 m
Column 3, orchard	1.0 m	21 ?m	0.1 m-0.2 m
Column 2, point source	0.12 m	11 ?m	0.30 m-0.25 m
Column 3, point source	-	-	0.25 m-0.30 m
Column 4, point source	0.05 m	21 ?m	0.15 m-0.20 m

As the flow rate of column 2 from the point source site changed after 550 hours, only data prior to 550 hours were used for modelling this column. For column 3 from the point source site, it was not possible to match the late but steep increases in the $CaCl_2$ breakthrough curve.

5.3 **Field scale numerical modelling of transport**

Objectives and strategy

The undisturbed columns and the field measurements of fractures represent the upper 0-6 m of the till. Fracture occurrent, density and distribution below this depth is uncertain because no direct measurements exists. To evaluate the influence of deep fractures on transport, the tritium profiles (shown in Figure 9) are modelled in the following section using a fracture modelling approach versus an EPM-modelling approach.

5.3.1 **Upscaling of fracture flow from columns**

Procedure of upscaling

The fracture density and the hydraulic parameters of the low part of the till may be assumed to resemble the distribution observed in the large undisturbed columns. The following procedure was used for vertical extrapolation of the fracture data: Fracture apertures in the large undisturbed columns have been estimated from the $CaCl_2$ experiments. Given the fracture and the hydraulic gradient measured in the field, the fracture density can be calculated either by using the difference in bulk and matrix hydraulic conductivity or by using the estimated amount of groundwater recharge in the area.

Hydrogeology of base case fracture model

In the upscaling, transport through a layer of 20 m till has been simulated by varying the fracture spacing and aperture, for a fixed bulk hydraulic conductivity (calculated from the recharge (q = 40 mm/year) and the gradient (i=0.2) using the formula q=K · where q=recharge). A matrix hydraulic conductivity of $5 \cdot 10^{-10}$ m/s was assumed (reported by Foged and Wille (1992) for a similar till). In this case fractures contribute with more than 90% of the bulk hydraulic conductivity ($6 \cdot 10^{-9}$ m/s as estimated by the water balance modelling, section 5.1.6). The fracture aperture of 21 ?m estimated in column

3, orchard (Table 11) is selected to represent the fracture throughout the till sequence. Fracture spacing was fitted (0.45 m) to produce the bulk hydraulic conductivity $6.0 \cdot 10^{-9}$ m/s. The vertical flow in the set-up is 38 mm/year at a hydraulic gradient of 0.2 m (field measured mean value). The flow resembles the calibrated recharge of 40 mm/year (+20/-10). This value is significantly less than the net precipitation-evaporation) 150 mm/year, and consequently a large part of the discharge in this area must be by tile drains and by horizontal flow in the uppermost part of the till where fractures are most frequent. Possibly also small sand layers may, if interconnected, contribute to the horizontal flow.

Influence of drains and interflow

5.3.2 **Modelling of tritium profiles**

Hydrogeological models

The overall hydrogeological setting used for both the fracture modelling and EPM modelling approaches is the 20 m deep aquitart with a vertical recharge of 38 mm/year. This setting is also used (unless otherwise is specified) for the sensitivity analysis of fracture transport presented in the following section.

Fracture approach versus EPM approach

In the fracture modelling approach the till is represented by the fractured aquitard derived in the previous section. In the EPM modelling approach the till is represented by a homogenous aquitard having the same bulk hydraulic conductivity as in the fracture case. Hydraulically the EPM set-up is motivated by the test carried out with the unfractured till matrix from the point source site (Table 3). The tests showed matrix hydraulic conductivities of $1 \cdot 10^{-9}$ and $2 \cdot 10^{-9}$ m/s. These values are in the same range (within range of uncertainty) as the estimated field scale bulk hydraulic conductivity ($6 \cdot 10^{-9}$ m/s) and as the deep large undisturbed columns (Table 3). The results suggest that at the field scale, fracture contribution to vertical bulk flow, may be very small or absent with depth in the till.

Tritium input in modelling

By modelling, the vertical transport of the peak tritium "pulse" infiltrated in 1963 is simulated. Sensitivity of applying this simplified tritium input versus a complete tritium input function is tested and discussed by Jørgensen and Spliid (1997). Values of fracture and porous media properties used in the modelling are given in Table 11.

Results of modelling

The observed and modelled tritium profiles are shown in Figure 24. It appears that the EMP (no fractures) simulated tritium distribution resembles both the depth of the tritium peak values and the maximum depth of tritium occurrence in the till. In contrast the fracture simulation predict deeper penetration of the tritium peak and tritium occurrence throughout the till, which is not consistent with observations.

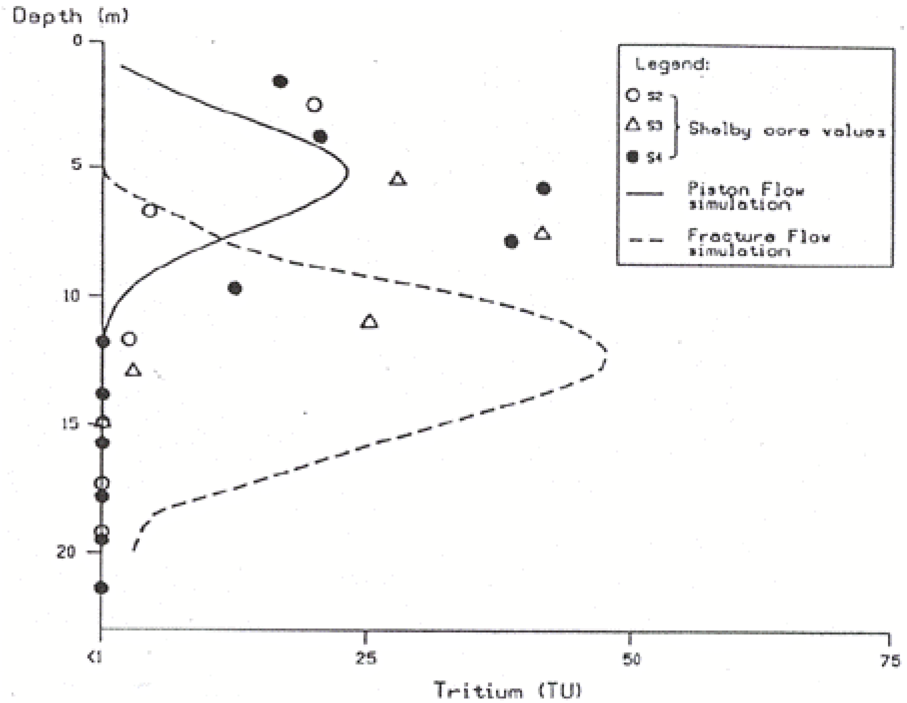


Figure 24
Measured and simulated depth in the till sequence of tritium peak values and lower termination. Measured profiles are from point source site (monitoring wells 2 and 3) and orchard (monitoring well 4). Tritium transport was simulated from a single year tritium in-put (corresponding to peak tritium concentration in precipitation in 1963). Vertical recharge in the simulations is 30 mm/y which is estimated from the water balance modelling

Målte og simulerede dybder i till-sekvensen af tritium maximum af undergrænsen for tritium. Målte profiler er fra punktkilden (motineringsboring 2 og 3) og frugtplantagen (moniteringsboring 4). Tritium fordelingen er simuleret ud fra et enkelt års tritium-input i infiltrationen svarende til 1963 maxima. Vertikale strømningshastighed er 30 mm/år svarende til den vertikale grundvandsdannelse estimeret ud fra vandbalance modellering

Conclusion

In conclusion, the modelling indicate that the influence of fractures on chemically conservative transport at the field scale is small or absent at depths below the upper few metres at the field sites. Hence, realistic modelling results of chemically non-reactive contaminant transport may be obtained with an EPM model using the bulk hydraulic conductivity of $6{\cdot}10^{-9}$ m/s (estimated by the water balance modelling).

5.4 **Sensitivity analyses**

The sensitivity analysis is conducted with the same base case geological framework (unless otherwise is specified) as used in the previous section, i.e. 20 m fractured clayey till overriding an aquifer, and a vertical recharge of 38 mm/year.

Flow and contaminant transport is highly sensitive to fracture aperture (flow is a cubic function of fracture aperture). A series of simulations with increasing fracture apertures have been conducted. In all simulations, the vertical recharge is constant (achieved by increasing fracture spacing to out-balance increasing aperture), Figure 25.

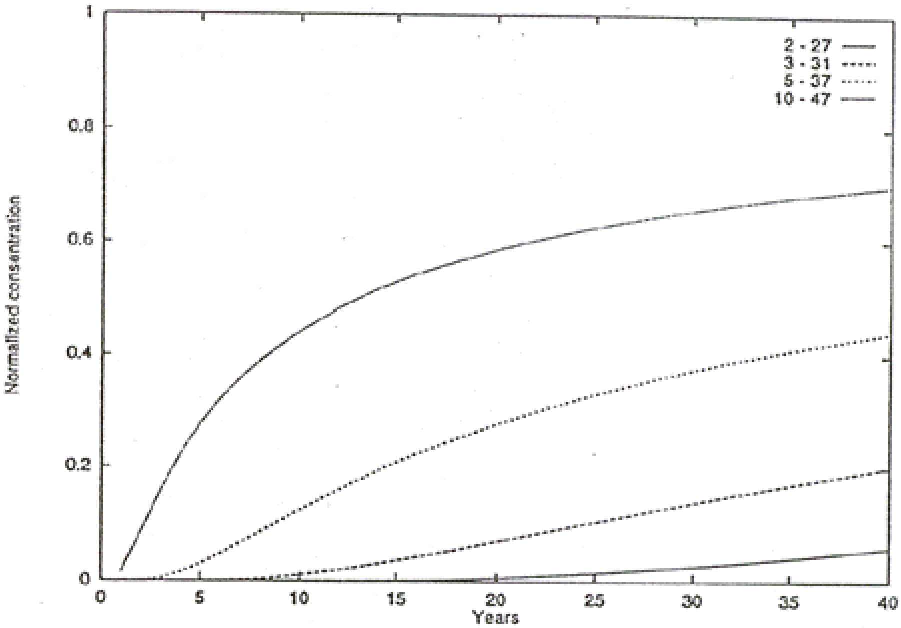


Figure 25
Simulated breakthrough of non-reactive tracer (chloride) through 20 m of fractured till. Breakthrough curves to the main aquifer are shown for different fracture spacings and fracture apertures at constant hydraulic conductivity of the till. For 1% of infiltrated concentrations to arrive in the main aquifer within 10 years, fracture apertures of 31 ?m or more are required (the legend in the topright corner shows couples of fracture spacing and aperture values used in the simulations)

Simuleret gennembrud af en non-reaktiv tracer (klorid) gennem 20 meter sprækket moræneler. Gennembrudsgiver til det primære grundvandsmagasin er vist for forskellige kombinationer af sprækkeafstande og sprækkeaperturer ved konstant bulk hydraulisk ledningsevne. For sprækkeåbninger større end 31 ?m når gennembruddet en relativ koncentration på 1% af udgangskon-centrationen inden for 10 år

In table 13 is shown (summarizing Figure 25) the number of years for a chemically conservative tracer to arrive in the underlying aquifer at three concentration levels. The level of 1 ‰ of the input concentration is reached after 10 years at a fracture aperture of approximately 30 ?m.

Table 13
Years for a chemically conservative tracer to break through 20 m of fractured till (i = 0.2) at three concentration levels

Antal år for konservativt stof gennembrud på tre koncentrationsniveauer gennem 20 meter sprækket moræneler (i = 0,2)

Fracture spacing and aperture	**Contraction relative to input concentration**		
	1 ‰	**1 %**	**10 %**
1 m/21 ?m	36	> 40	> 40
2 m/24 ?m	14	22	> 40
3 m/31 ?m	6	10	24
5 m/37 ?m	2.5	3.5	9
10 m/47 ?m	-	< 1	2.5

The results shows that if widely spaced (> 10 m), highly conductive fractures occurred in the aquitard (not exposed in the field excavations or represented by the columns), the transport can be significantly faster than predicted from the upscaling based on field measurements and data from the undisturbed columns. Evaluated from the angled tritium profiles, however, there is no indication that such a flow system occurred, i.e. there is no lateral variations in tritium concentrations (Figure 9) which should be the result of matrix diffusion from conductive fractures. The observed tritium profiles have lateral homogenous tritium fronts, and at depth, the values below the limit of detection limit are stable over vertical and horizontal distances of more than 10 m in the profiles.

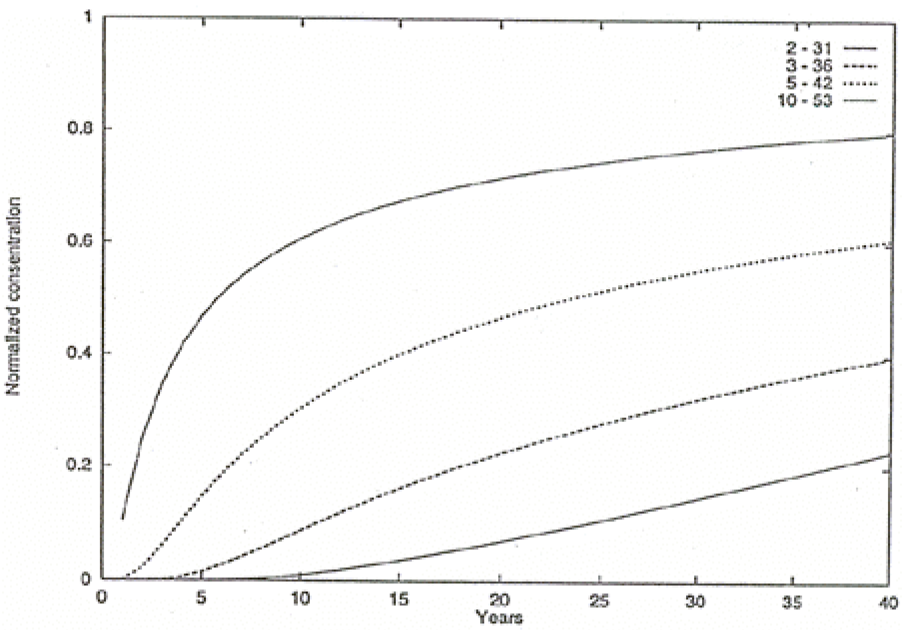
Numerical analysis of the lateral tritium distribution as function of widely spaced highly conductive fractures is presented in Jørgensen and Spliid (1997).

The amount of recharge was used to calculate the bulk hydraulic conductivity of the till in section 5.1.7. The following simulations show the effect of recharge in the range of 30 mm/year to 60 mm/year (range of uncertainty), if the change in hydraulic conductivity is adjusted by changing the fracture aperture, Table 14 and 15.

Table 14
Input parameters for sensitivity analysis of recharge

Parametre anvendt til følsomhedsudstyr af grundvandsdannelse for konservativt stof gennembrud gennem 20 m sprækket moræneler

	Recharge m/year	**Gradient**	**K_b m/s**
Run 1	0.03	0.2	$4.8 \cdot 10^{-9}$
Run 2	0.06	0.2	$9.5 \cdot 10^{-9}$



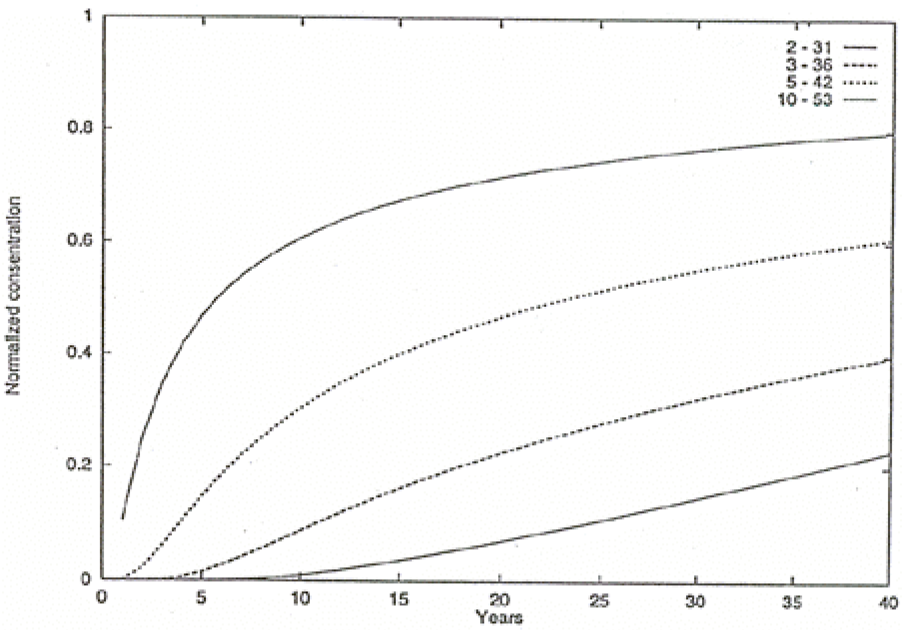


Figure 26
Breakthorugh to main aguifer to a non-reactive solute (chloride) at recharges of, a) 30 mm/year and b) 60 mm/year. Flow system as in previous figure

Gennembrud til det primære reservoir af non-reaktivt stof ved grundvandsdannelser på a) 30 mm/år og b) 60 mm/år. Samme strømningssystem som i foregående figur

Table 15
Years for a chemically conservative tracer (chloride) to break through 20 m of fractured till (i = 0.2 and spacing 3 m)

Antal år for konservativt stof gennembrud på tre koncentrationsniveauer gennem 20 meter sprækket moræneler med sprækkeafstand på 3 m ved tre sprækkeaperturer (i = 0,2)

Recharge, aperture	**Concentration relative to input concentration**		
	1 ‰	**1 %**	**10 %**
5	0.3	2	5
10	4.5	7.5	18
15	11	17	> 40
20	18	30	> 40

Figure 26 shows the simulated breakthrough of a non-reactive contaminant to the main aquifer for recharges at 30 mm/year and 60 mm/year. From the simulations it appears that the contaminant arrival time charges significantly within the uncertainty of recharge.

Aquitard thickness

The influence of aquitard thickness on the breakthrough of a non-reactive contaminant to the main aquifer is shown for aquitart thickness of 5 to 20 m in Figure 27. Corresponding arrival times are summarized in Table 16.

Table 16
Years for a reactive tracer (retardationfactor = 3) to break through 20 m of fractured till as a function of till thickness (i = 0.2 fracture, spacing 3 m and fracture aperture = 31 ?m)

Effekt af morænetykkelse på antallet af år for en adsorberende tracer (retardationsfaktor = 3) stof gennembrud til tre koncentrationsniveauer gennem 20 meter sprækket moræneler (sprækkeafstand = 3 m, sprækkeapertur = 31 ?m og i = 0,2)

Thickness of till cover m	**Concentration relative to input concentration**		
	1 ‰	**1 %**	**10 %**
5	0.3	2	5
10	4.5	7.5	18
15	11	17	> 40
20	18	30	> 40

The simulations show that the aquitart thickness is a most important factor in controlling transport of solutes, and that thin covers of till may have very rapid breakthrough of contaminants into underlying aquifers.

Alternative flow paths

It should be noticed that fractures are assumed to be the only hydraulically conductive element of heterogenity in the till. In cases where inclining sand layers and sand streaks occur (as observed in monitoring wells and the point source excavation, Figure 6a) such layers may transect the aquitart and, compared with similar layers in horizontal positions, transport contaminants from the till into underlying aquifers much faster than predicted by simulations presented. Dislocated sandlayers and sand streaks are common in tills in the Danish areas.

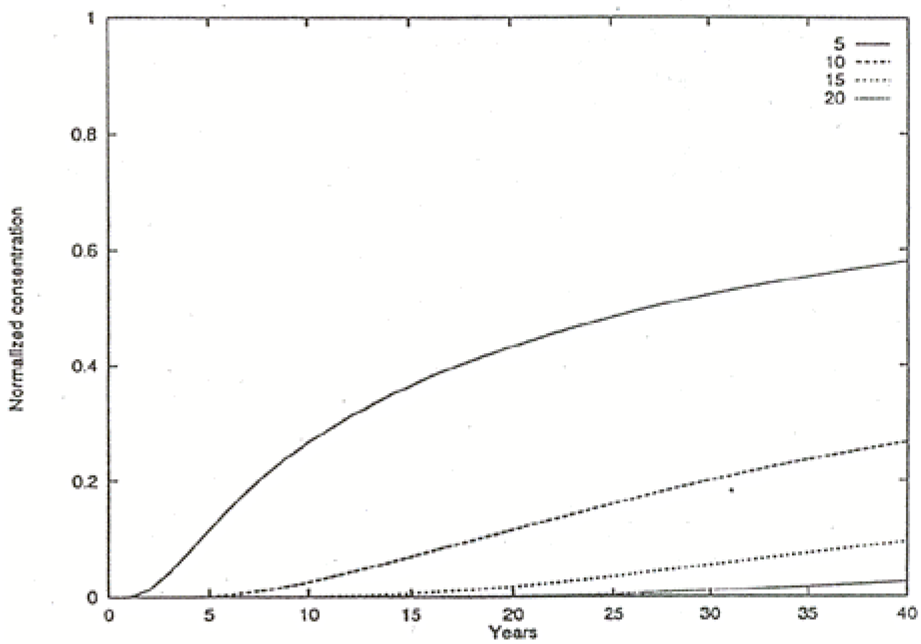


Figure 27
Effect of thickness of on breakthrough of non-reactive solute (chloride) to main aquifer

Effekt af morænemægtighed på gennembrud af not-reaktiv tracer (klorid) til grundvandsreservoir

5.5 **Determining criteria for modelling pesticide distribution by applying EPM flow versus fracture flow models**

Choice and requirements

Application of EPM-models is common practice in prediction of contaminant behaviour in groundwater. These models require less computer processing capacity (CPU) than fracture models, because they are based on assumptions of homogeneous geology and measured or assumed bulk hydraulic parameters. Fracture models require more geological data, more computer capacity and may therefore only be preferred when necessary. Hence, an important issue is to decide when it is appropriate to use the less CPU-intensive EPM model instead of the CPU-intensive discrete fractured media (DAM) modelling approach.

Approaches of analysis

The choice of model type, in general, depends on both flow controlling factors (gradient, bulk hydraulic conductivity and thickness of the till layer) and the distribution of fractures (spacing and aperture). This problems has been analyzed using both a theoretical and numerical approach. For the theoretical approach the formulas developed by Van der Kamp (1992) have been used and for the practical approach the computer code CRAK (McKay, 1993) has been used. CRAK is a modified version of CRAFLUSH (Sudicky, 1988) that simulates on set of parallel vertical fractures (equal spacing and aperture), where the flow controlled by the gradient and a bulk hydraulic conductivity, and where an increase in fracture spacing leads to an increase in fracture apertures to keep the flow constant.

Hydraulic factors

Since the following equations do not take the hydraulic conductivity of the matrix (K_m) into account, they can only be used in cases where the major part of flow is in the fractures; $K_f >> K_m$ (K_f = hydraulic conductivity of the fractures).

Based on the cubic law it is possible to calculate the relation between fracture spacing, hydraulic conductivity and fracture aperture:

$$K_b = \frac{? \;\; ? \;\; g \; ? \;\; (2\,b)^3}{12 \;\; ? \;\; ? \;\; ? \;\; 2\,B} 4 \qquad (5.1)$$

where,

K_b = bulk hydraulic conductivity,
? = density of water,
g = gravitation constant,
2b = fracture aperture,
? = viscosity,
2B = distance between fractures.

Figure 28 is based on this formula and shows the relation between K_b, 2b and 2B. The inclining lines on the figure are isolines of fracture apertures.

Figure 28
Relation between bulk hydraulic conductivity, fracture spacing and fracture aperture. The sloping lines are isolines of apertures i.e. a hydraulic conductivity of 10^{-7} m/s will result from fractures with an aperture at 50 ?m and a spacing at 0.79 m as well as from fractures with an aperture at 100 ?m and a spacing at 6.2 m

Relation mellem bulk hydraulisk ledningsevne, sprækkeafstand og sprækkeapertur. Hældende linier er isoaperturlinier, der knytter sammenhørende værdier af hydraulisk ledningsevne og sprækkeafstand, f.eks. svarer en hydraulisk ledningsevne på 10^{-7} m/s til en apertur på 50 ?m ved en sprækkeafstand på 0,79 m, men til en apertur på 100 ?m ved en sprækkeafstand på 6.2 m

Van der Kamp (1992) defines the transition between where an EPM approach is valid and where it is not as "For EPM conditions to exist throughout most of the solute-invaded zone the time of arrival to the solute has to be much larger than the equilibration time of the column":

$$2\,B^2 \;\; ? \;\; K_b \;\; \Box \;\; D_K \;\; ? \;\; h \; ? \;\; n \;\; ? \;\; \frac{D}{i} 5 \qquad (5.2)$$

where,

2B = fracture spacing,
K_b = bulk hydraulic conductivity,
h = thickness of fractured layer,
n = porosity
D = diffusion coefficient,
i = hydraulic gradient,
D_K = is a constant with an ideal value at 0.1 (0.1 is adequate usually and

will extent the region in which EPM modelling is acceptable).

Equation (5.2) describes the criterion for EPM conditions and the equation (5.3) that delineated the fracture spacing - hydraulic conductivity space into EPM and DAM types of transport can be written as follows:

$$2B = \sqrt{\frac{D_K \; ? \; h \; ? \; n \; ? \; D}{i \; ? \; K_b}} \, 6 \qquad (5.3)$$

This formula can be visualized by plotting fracture spacing against hydraulic conductivity for varying values of gradient, diffusion and thickness of the fractured media. The base data used for the following (Figures 29-33) are:

- Thickness of fractures till = 10 m
- Porosity = 30%
- Effective diffusion coefficient = $6 \cdot 10^{10}$ m^2/s
- D_K = 1.0

Interaction between determining factors

Figure 29 shows the effect of gradients in the range 0.01 to 1.0 the behaviour of the transport type, Figure 30 shows the effects of different thickness (2 m to 20 m) of fractured till layers on the transport system, Figure 31 the effect of change in diffusion coefficient ($6 \cdot 10^{-11}$ m^2/s to $6 \cdot 10^{-9}$ m^2/s) and Figure 32 the effects of change in both thickness of the fractured till layer and the gradient ranging from a 2 m till (with a gradient = 1) to a thick 20 m till (with a gradient = 0.01). From Figure 28-31 (and equations 5.1 to 5.3) it can be seen that the thicker till, the higher diffusion and lower gradient increase the fracture spacing - hydraulic conductivity zones that can be modelled using faster EPM approach.

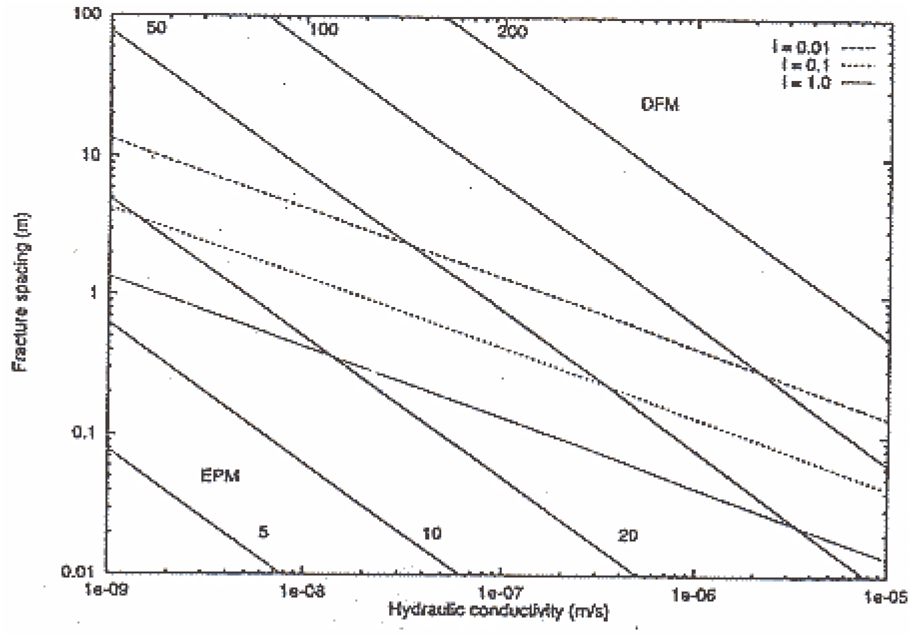


Figure 29
Combinations of fracture spacings, bulk hydraulic conductivities and hydraulic gradients resulting in requirements of equivalent porous modelling (EPM) approaches versus discrete fracture modelling DAM) approaches. Dashed lines separates the EPM area (bottom section of diagram) from the DAM area (top section of diagram)

Sammenhørende sprækkeafstande af bulk hydrauliske ledningsevner, hvor stoftransport kan modelleres med en ækvivalent porøs medium (EPM) model eller forudsætter sprækkemodellering (DAM). I området under de stiplede linier modelleres med EPM model og i området over de stiplede linier modellers med DAM model

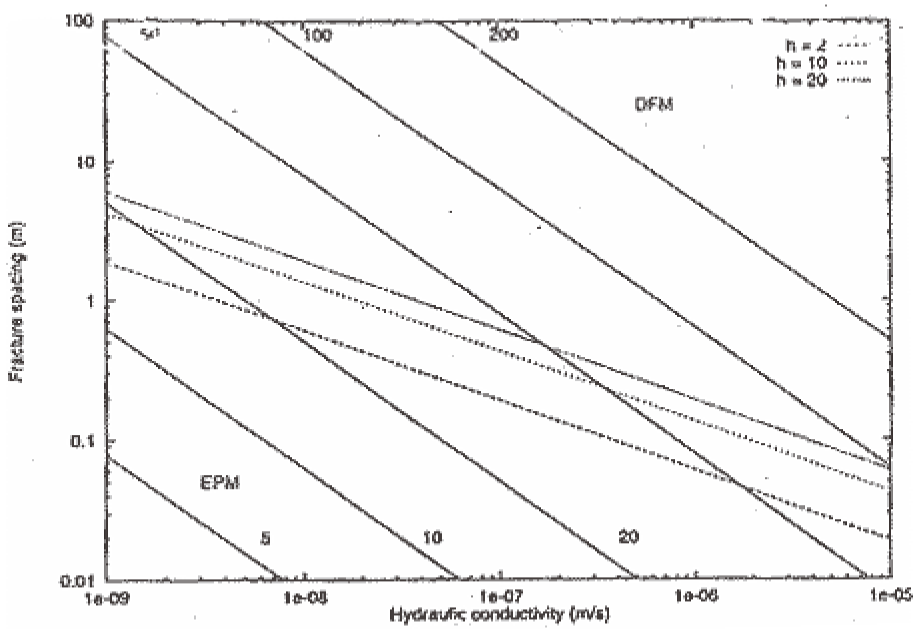


Figure 30
Combinations of fracture spacing and bulk hydraulic conductivities requiring equivalent porous modelling (EPM) versig discrete fracture modelling (DAM) given different aquitard thickness. The dashed lines separated the EPM area (bottom section of diagram) from the DAM area (top section of diagram)

Sammenhørende sprækkeafstande af bulk hydrauliske ledningsevner ved forskellige aquitard tykkelser, hvor stoftransport kan modelleres med en akvivalent porøs medium (EPM) model eller forudsætter sprækkemodellering (DAM). I området under de stiplede linier modelleres med EPM model of i området over de stiplede liner modelleres med DAM model

Breakthrough curves and application

A series of breakthrough curves as a function of time with varying fracture spacing was simulated using CRAK.

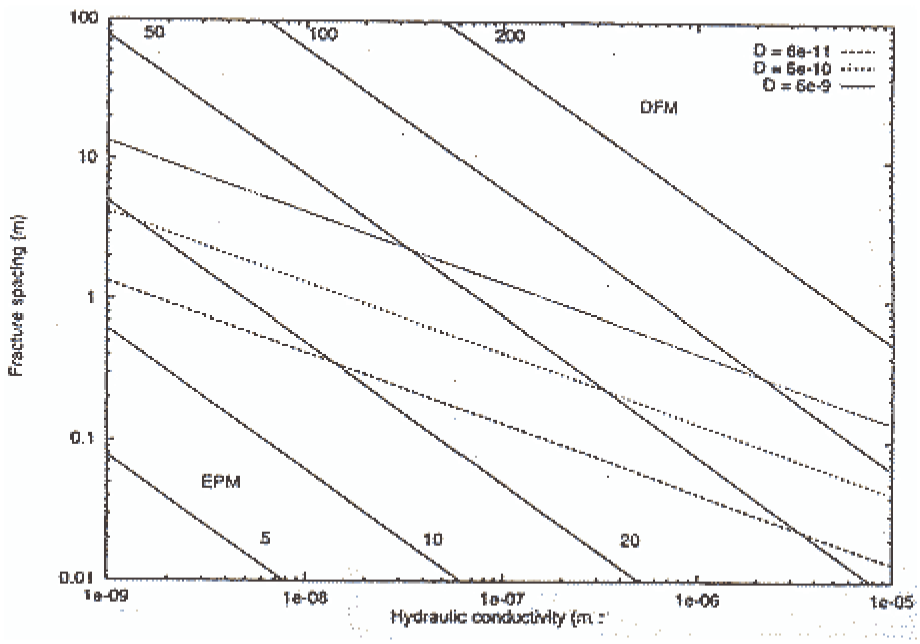


Figure 31
Combinations of fracture spacings and bulk hydraulic conductivities requiring equivalent porous modelling (EPM) versus discete fracture modelling (DAM) given different diffusion coefficients. The dashed lines separates the EPM area (bottom section of diagram) from the DAM area (top section of diagram)

Sammenhørende sprækkeafstande af bulk hydrauliske ledningsevner ved forskellige diffusionskoefficienter, hvor stoftransport kan modelleres med en ækvivalent porøs medium (EPM) model eller forudsætter sprækkemodellering (DAM). I området under de stiplede linier modelleres med EPM model og i området over de stiplede linier modelleres med DAM model

The set up for the simulations is the same as for Figure 28-31.

Figure 33a shows the location of the simulations in the fracture spacing - hydraulic conductivity "space" and the line that separates EPM from DAM transport behaviour (based on D_K = 1.0). The breakthrough curves shown in Figure 33b represent the fracture spacings and apertures in Figure 33a. The curves from simulations with a fracture spacing of 1 m and greater are clearly influenced by transport in fractures. For fracture spacings less than 0.2 m there is no clear sign of DAM behaviour. The form of the breakthrough curves when crossing the EPM - DAM boundary changes from increasing.

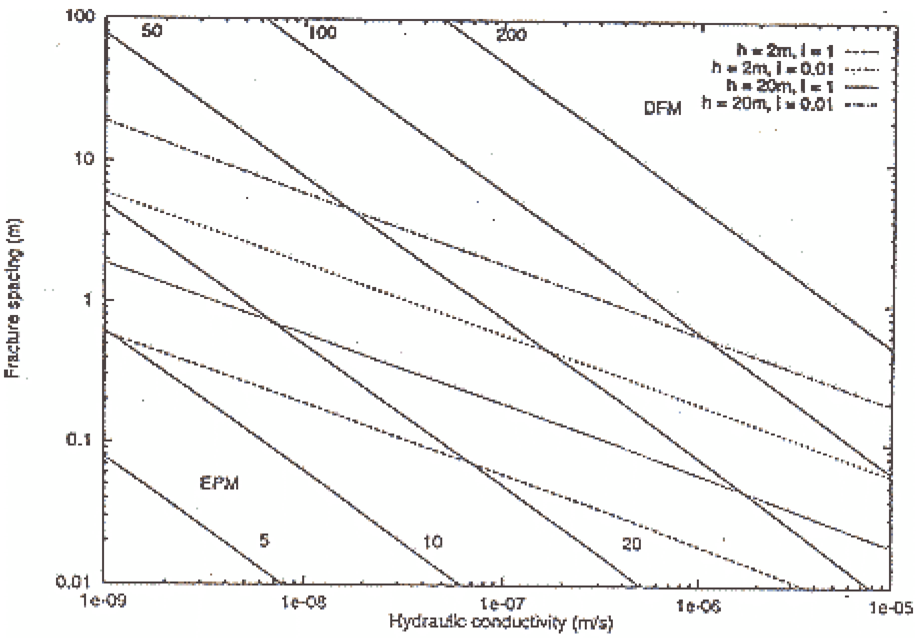


Figure 32
Combinations of fracture spacings and bulk hydraulic conductivities and aquitard thickness and hydraulic gradient. The dashed lines separated the EPM modelling area (bottom section of diagram) from the DAM modelling area (top section of diagram)

Sammenhørende sprækkeafstande af bulk hydrauliske ledningsevner ved forskellige størrelser af aquitard tykkelse og hydraulisk gradient. I området under de stiplede linier modelleres med EPM model og i området over de stiplede linier modelleres med DAM model

slope curves to decreasing slope curves. Thus, the two fracture spacing values (0.1 and 0.2) lying below the EPM - DAM boundary (Figure 33a) generate breakthrough curves with increasing slope (Figure 33b) while the higher fracture spacing values (2-10 m) lying above the boundary yield breakthrough curves with decreasing slopes (Figure 33b). The fracture spacing near the boundary (0.5 m and 1 m) yield breakthrough curves that display a mixture of EPM and DAM transport. This change is easy to see, so it is possible to use CRAK to get a quick overview at individual sites where to use the EPM and where to use the DAM approach.

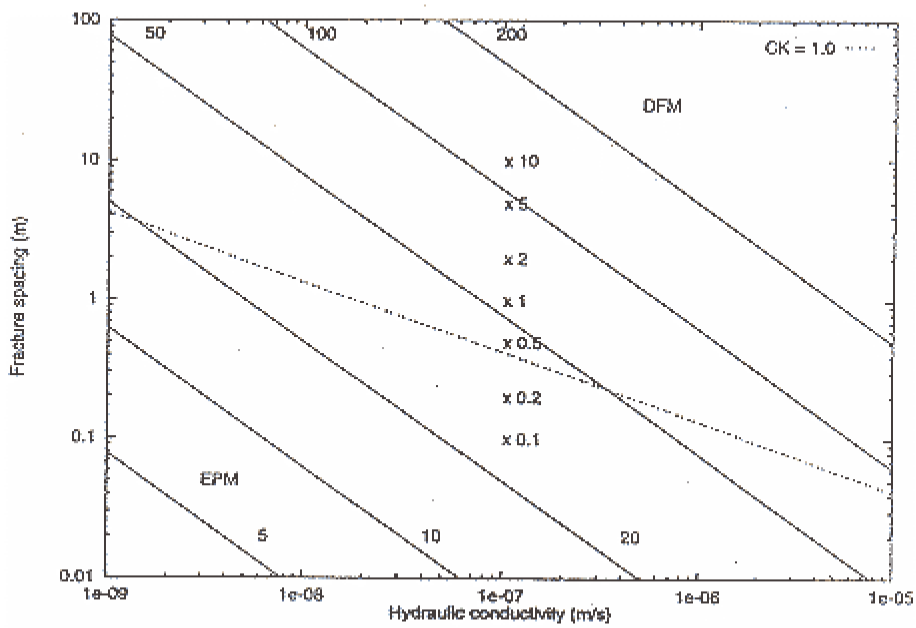


Figure 33a
Plotting positions of the Fig. 17b simulations shown in relation to EPM and DAM type of transport

Plotte-positioner af simuleringerne vist i Fig. 19b i relation til EPM og DCM type transport

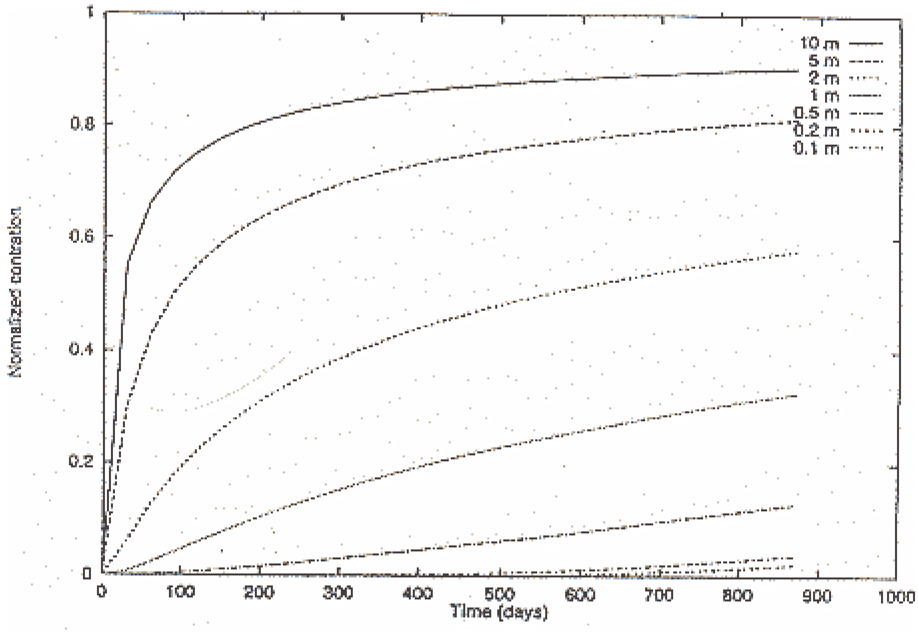


Figure 33b
CRAK code simulation at seven fracture spacings all giving the same bulk hydraulic conductivity of $1 \cdot 10^{-7}$ m/s. It appears from the diagram that given a hydraulic gradient at 0.1 a 10 m thick till and a diffusion at $6 \cdot ^{-10}$ m^2/s, fracture spacing smaller that 0.5 m may be simulated using the EPM approach while simulations with fracture spacings larger than 0.5 m requires an DAM approach

CRAK simuleringer ved syv sprækkefordelinger med samme bulk hydrauliske ledningsevne (10^{-7} m/s). Det fremgår af diagrammet, at ved en hydraulisk gradient på 0,1, en morænetykkelse på 10 meter og en effektiv diffusionskoefficient på 6^{-10} m^2/s, kan situationer med sprækkeafstande mindre end 0,5 meter simuleres med EPM model, mens større sprækkeafstande kræver DAM modellering

6 Conclusion

In a clayey till groundwater catchment at Skælskør, pesticide leaching from the Skælskør orchard has been compared with leaching from a pesticide source spill in the machinery yard belonging to the orchard.

From approximately 1960 to 1992 phenoxyherbicides were applied in Skælskør orchard in amounts corresponding with average application on farm land. Also simazine, atrazine, terbuthylazine and amitrol have been used in significant amounts.

Groundwater samples from the till sequence were collected six times over a period of one year from five 15-25 m deep monitoring wells (14 screens). The samples were analyzed for dichlorprop, mecoprop, MCPA, 2,4-D, (phenoxyherbicides) simazine, atrazine and terbuthylazine (trazines).

In the point source site, very high pehnoxyherbicide contrations (mainly dichlorprop and mecoprop) and lower simazine concentrations, were found in a "hot spot" zone down to 5-7 m depth in the geological profile (sum contrations up to 1-2 mg/l). Below the "hot spot" zone, pesticide contrations decreased several orders of magnitude.

In the sand aquifer at the point source site (underlying the till sequence), sum contrations of phenoxyherbicides and triazines were below detection and up to 1 ?g/l. All pesticide findings, except for the "hot spot" contamination in the point source site, were erratic in time and space.

Pesticide application in the orchard exclusively occur in spring and summer, while on farm land additional application in autumn (primary period of precipitation surplus) of mecoprop has been common since the beginning of the 1980'ies.

In the orchard, the only phenoxyherbicide identified repeatedly was MCPA (in 24% of water samples at 0.01-4.8 ?g/l). Simazine occurred in 17% of water samples collected (0.04-1.0 ?g/l). In laboratory leaching experiments also terbuthylazin and mecoprop were identified. Findings of MCPA may occur both as a primary product and as a metabolity of mecoprop degradation. No other metabolites has been analyzed for.

Applied primary phenoxyherbicide products (MCPA, dichlorprop and 2,4-D) appear to undergo extensive immobilisation i.e. degradation, near the ground surface in the orchard. A significant capacity for uptake of simazine in the clay minerals of the till was measured.

Field scala tritium profiles and laboratory experiments indicate that the influence of fractures on solute contamination transport is small or absent at depths below the upper few metres at the field sites. The distribution of tritium in the till profiles is consistent with numerical modelling of transport in the till by piston flow.

Sensitivity analyses carried out by numerical modelling of fracture flow indicate that in case the shallow hydraulically conductive fractures are extended through the till and degradation of the pesticides is ignored, a breakthrough in the main aquifer at a concentration level at 1 ‰ of the input concentration should be expected within a few years.

Inclining sand layers and sand streaks observed in the till may constitute alternative transport paths for pesticide leaching. Transport along these paths may account for some of the deep pesticide findings in the till and the sand aquifer below the point source spill.6.

In the point source site, very high phenoxyherbicide concentrations (mainly dichlorprop and mecoprop) and lower simazine concentrations, were found in a "hot spot" zone down to 5-7 m depth in the geological profile (sum concentrations of approximately 1 mg/l). Below the "hot spot" zone, pesticide contrations decreased several orders of magnitude.

In the sand aquifer at the point source site (underlying the till sequence), sum concentrations of phenoxyherbicide and trazine were below detection to approximately 1 ?g/l.

All pesticide findings, expect for the "hot spot" contamination in the point source site, were erratic in time and space (total of 87 water samples).

Sensitively analyses by numerical modelling of fracture flow indicate the following: in case the shallow zone fractures (fracture hydraulic conductivities determined by the large column experiments) are extended through the aquitard and degradation of the pesticides ignored, a breakthrough at a concentration level at 1 ‰ of the input concentration should be expected within a few years.

Fracture transport simulations can not, at the present level of knowledge, be used as a quantitative prediction tool. It is, however, possible to use the models to analyze effect of the different uncertain parameters and perform "worst case" simulations.

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