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Norwegian Scenarios II

Final report from the period 2007-2008

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Sammendrag:

Dette er en avslutningsrapport for prosjektet Norske Scenarier II, del to, som har vært et samarbeid mellom Bioforsk Plantehelse, Universitetet for miljø og biovitenskap (UMB) og Mattilsynet. Prosjektet har hatt som mål å utvikle norske scenarier for modellene PRZM og MACRO som kan brukes ved godkjenning av nye plantevernmidler.

Summary:

This is a final report for the project Norwegian Scenarios II, part two, that has been performed in collaboration between Bioforsk Plant Health and Plant Protection, The Norwegian University of Life Sciences and the Norwegian Food Safety Authority. The aim of the project was to establish Norwegian scenarios for the models PRZM and MACRO and to use them for approval of new pesticides.

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Preface

The final report in the project Norwegian Scenarios II, part two, has been a cooperation between Bioforsk Plant Health and Plant Protection Division, Norwegian University of Life Sciences (UMB) and the Norwegian Food Safety Authority. The project has been carried out as an assignment from the Norwegian Food Safety Authority, financed by the "Handlingsplanen for redusert risiko ved bruk av plantevernmidler (2004-2008)". The aim of this project has been to establish scenarios from experimental fields which could be representative for Norwegian conditions and to use them for approval of new pesticides in Norway.

For the investigated period, 2007-2008, runoff studies of the pesticides propiconazole and metalaxyl have been performed at two different fields, Bjørnebekk and Syverud. Based on the runoff data, calibration/validation of the models PRZM and MACRO has been achieved.

Bioforsk Plant Health and Plant Protection Division have been responsible for the coordination and the implementation of the project, the application of pesticides at the experimental fields, analysis of the water samples from the fields and the simulations with the model PRZM. The Norwegian University of Life Sciences has been responsible for the field experiments, runoff data, collection of water samples and the simulations with the model MACRO.

Project associates for this part of the project (part two) has been Marit Almvik, Randi Bolli, Ole Martin Eklo and Kjell Wærnhus from Bioforsk Plant Health and Plant Protection Division, Trond Børresen, Lars Egil Haugen (the last period connected to Norwegian Water Resources and Energy Directorate) and Gunnhild Riise from UMB and Roger Holten and Terje Haraldsen from the Norwegian Food Safety Authority.

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1. Sammendrag

Den Europeiske Union (EU) har utviklet ulike modell-scenarier for både grunnvann og overflatevann, som skal brukes ved godkjenning av nye plantevernmidler. Et sentralt spørsmål er om disse scenariene dekker typiske norske forhold når det gjelder nedbør, helling, snødekke, frysing og tining. Målet med prosjektet har derfor vært å utvikle norske scenarier som kan være representative for norske forhold for senere å kunne bruke modellene ved godkjenning av nye plantevernmidler. Modelleringsarbeidet har vært basert på primærdata fra to forsøksområder i Oslo, Akershus; Syverud og Bjørnebekk, hvor avrenningen av to pesticider med ulik mobilitet har vært beregnet på grunnlag av vannproporsjonal prøvetaking.

Avrenning av metalaksyl og propikonazol

Avrenning av plantevernmidlene metalaksyl og propikonazol ble undersøkt på to felter med ulike jordegenskaper; Syverud og Bjørnebekk. Jorda på Syverud har god aggregatstruktur, stor infiltrasjonskapasitet og liten erosjonsrisiko, mens jorda på Bjørnebekk er planert mellomleire og svært erosjonsutsatt. På Syverud ble avrenningen separert i overflate og drensavrenning, mens på Bjørnebekk ble kun overflateavrenning undersøkt. En type jordarbeiding er inkludert i forsøksoppsettet på Syverud, høstpløying (HPL). På Bjørnebekk er det to typer jordarbeiding, høstpløying og vårpløying (VPL). Alle rutene er vårpløyd.

Tapet av plantevernmidler varierte for de ulike feltene, avhengig av plantevernmiddel, jordtype, jordbearbeiding og hydrologisk strømningsmønster innen det enkelte felt. Avrenning av det mobile pesticidet metalaksyl var noe større enn for propikonazol som bindes sterkere til jord. Avrenningen av begge plantevernmidlene var generelt større på jord som er erosjonsutsatt (Bjørnebekk) sammenlignet med jord med god aggregatstruktur (Syverud).

Klimaforholdene kort tid etter sprøyting er veldig viktig i forhold til avrenningsmønsteret til plantevernmidlene. Både på Bjørnebekk (høstpløying) og Syverud (høstpløying) viste overflateavrenningen en markert topp av begge plantevernmidlene i tilknytning til avrenningsepisoder kort tid etter sprøyting. I grøfteavrenningen på Syverud viste metalaksyl tilsvarende topp under avrenningsepisoden kort tid etter sprøyting. Avrenning av propikonazol i grøfteavrenning på Syverud viste imidlertid et jevnere forløp med gjennomgående lave konsentrasjoner.

Tapet av metalaksyl var generelt høyere enn for propikonazol, utenom overflateavrenning fra Syverud, der tapet av propikonazol var høyest. Det største tapet av metalaksyl ble observert fra feltet som var høstpløyd på Bjørnebekk. Dette har sammenheng med at det var mindre avrenning fra det vårpløyde feltet, spesielt i perioden rett etter sprøyting. Det største tapet av propikonazol ble også observert på det høstpløyde feltet på Bjørnebekk. Det skyldes nok at partikkeltapet var større fra det høstpløyde feltet sammenlignet med det som ble pløyd om våren. I tillegg adsorberes propikonazol til jordoverflaten, noe som øker muligheten for partikkelbundet overflateavrenning for dette stoffet.

Hydrologien er sterkt styrende for avrenning av plantevernmidler og spesielle klimaforhold fremmet stort tap av pesticider i perioden 2007/2008. Større tap av metalaksyl og propikonazol i 2007/2008 sammenlignet med 2005/2006 skyldes i hovedsak mer nedbør om sommeren, mer nedbør og høyere temperaturer om vinteren.

Sammenligning av simuleringer gjort med modellen PRZM og målinger av propikonazol og metalaksyl fra Syverud og Bjørnebekk

I denne delen av prosjektet var målet å bruke feltdataene fra 2007/2008 for å validere modellen PRZM. Dette er en modell som blir brukt i EU for godkjenning av plantevernmidler.

Simuleringene ble utført i tre steg; en ukalibrert simulering etterfulgt av kalibrering ved å justere sensitive parametre og til slutt en validering av modellen. Dataene fra sesongen 2005/2006 ble brukt for kalibrering.

Modellen simulerer både overflatevann og grøftevann fra begge feltene tilfredsstillende. Det var noen problemer i perioder som ofte er karakterisert av frossen jord, frysing/tining og høy overflateavrenning under snøsmeltingen. Den kumulative mengden av vann fra begge feltene lå innenfor en faktor på 10 i forhold til observasjonene. Et problem med modellen, som også Reichenberger (2005) har påpekt, er at modellen ofte predikerer for mye både vannavrenning og pesticidavrenning ved lite nedbør og små avrenningsepisoder, og den predikerer for lite ved mye nedbør og store avrenningsepisoder. Både på Syverud og Bjørnebekk simulerer modellen for mye avrenning av metalaksyl og propikonazol i overflatevann i forhold til observerte verdier. I grøftevann blir begge pesticidene underestimert. Når man beregner årlig gjennomsnittskonsentrasjon viser det at simuleringene av metalaksyl i overflatevann er bra fra begge feltene, med et forhold fra 1 – 12 mellom simulerte og observerte verdier. Simuleringene for propikonazol er litt dårligere med et forhold fra 3 – 21 mellom simulerte og observerte verdier. En ny versjon av PRZM vil bli introdusert og tatt i bruk fra 2010. Foreløpige kjøringer med denne modellen har vist langt bedre simuleringer med propikonazol og utlekking til drensvann/grunnvann.

Simuleringer med modellen MACRO

Nasjonale scenarier i de nordiske landene er hovedsakelig utviklet ved hjelp av modellen MACRO. Scenariene er en kombinasjon ved å bruke MACRO som et grunnvannscenario eller et grøftevann-scenario. Resultatene beskrevet er fra Syverud som er en drenert leir jord.

MACRO simulerer vannbevegelsen i perioden 2005/2006 som daglig fluks og akkumulerte verdier, og resultatene viser god tilpasning mellom simulerte og målte verdier. Målte og simulerte verdier for akkumulert mengde grøftevann for perioden 2007/2008 viste også god tilpasning med noen forskjeller tidlig i juni, som antagelig skyldes lokale regnskyll. Forskjellen mellom observerte og simulerte konsentrasjoner av bromid i grøftevann var større. Målingene viste at bromid beveget seg ned til grøftesystemet raskere enn det modellen simulerte begge årene. Den simulerte konsentrasjonen og den akkumulerte mengden av propikonazol i grøftevann var nesten null. Den målte konsentrasjonen var <0.1 µg/l. Forskjellen mellom modell simuleringene og feltdataene indikerer at det er andre prosesser enn ionetransport som er viktig for sterkt adsorberende pesticider. Simulerte og observerte konsentrasjoner av metalaksyl lå i samme størrelsesorden i 2005/2006. For perioden 2007/2008 var de målte verdiene nesten null på det tidspunktet metalaksyl beveget seg til grøftesystemet i følge simuleringsresultatene. De akkumulerte verdiene viser at den simulerte utlekkingen av metalaksyl fortsetter etter at feltforsøket er avsluttet med en konsentrasjon som er 4-5 ganger høyere.

2. Abstract

The European Union (EU) has developed different scenarios for both ground water and surface water for approval of new pesticides. The questions raised; will these scenarios cover special Norwegian conditions such as high precipitation, strongly sloping fields and the occurrence of snowmelt on frozen ground? The aims of this project were therefore to establish scenarios based on runoff data from Norwegian experimental fields, and test if the models are representative for Norwegian conditions and can be used for approval of new pesticides in Norway. Two pesticides with different mobility characteristics have been included in the work.

Runoff of metalaxyl and propiconazole

Runoff of the pesticides metalaxyl and propiconazole were measured at two experimental fields with different soil properties; Syverud and Bjørnebekk. The soil at Syverud has a better aggregate stability, higher infiltration rate and is less susceptible to erosion compared to the soil at Bjørnebekk. The soil at Bjørnebekk is artificially levelled and very exposed for erosion. At Syverud both surface- and drainage water was collected, while at Bjørnebekk only surface water was available. The experimental plot at Syverud was subject to autumn ploughing (APL). At Bjørnebekk both plots with autumn ploughing and spring ploughing (SPL) were included. All plots were subject to spring ploughing.

Loss of pesticides with different sorption capacity is to a large extent dependent on soil properties, agricultural practices and hydrological flow pattern. Runoff of the mobile pesticide metalaxyl was in general larger than for propiconazole which has a higher affinity to soil. The runoff was larger from the soil which is more susceptible to erosion (Bjørnebekk) compared to the soil with good aggregate stability (Syverud).

Climatic conditions shortly after application of pesticides are of great importance for the runoff pattern. At Bjørnebekk (autumn ploughing) and Syverud (autumn ploughing), the surface runoff showed a pronounced peak of both pesticides in connection to runoff episodes shortly after application. In the drainage water at Syverud, metalaxyl showed a similar peak during the runoff episode shortly after application. The runoff of propiconazol in the drainage water at Syverud showed however a more even progress with generally low concentrations.

The losses of metalaxyl were generally higher than for propiconazole, except for surface runoff at Syverud, where the losses of propiconazole were highest. The largest losses of metalaxyl occurred at Bjørnebekk at plots subject to autumn ploughing. Less transport of metalaxyl from the plot without autumn ploughing can be explained by less surface runoff, especially at the period shortly after the pesticide application. The largest loss of propiconazole was observed at Bjørnebekk, at plots subject to autumn ploughing. There was a much higher loss of particles from the autumn ploughed plot compared to the spring ploughed plot at Bjørnebekk. Propiconazole has high affinity to soil surfaces, which increase the possibility for particle-bound surface runoff.

The runoff of pesticides is very dependent of the hydrology and special climatic conditions promoted high losses of pesticides in the period 2007/2008. Greater losses of metalaxyl and propiconazole in 2007/2008 compared to 2005/2006 can mainly be explained by high precipitation in the summer and high precipitation and temperatures during the winter.

Comparison of simulations done with the model PRZM3 and measurements of propiconazole and metalaxyl from Syverud and Bjørnebekk

In this part of the project the main goal was to use the collected field data to validate the model PRZM. This is a model which is used in EU for approval of new pesticides.

The simulations was performed at three stages; an uncalibrated simulation followed by a simulation with calibration using the sensitive parameters and at the end, a validation of the model. Field data from 2005/2006 was used for calibration while measurements from 2007/2008 were used for validation.

The model predicts the flow of surface water and drainage water from both fields adequately. There were some problems in periods characterized by frozen soil, freezing and thawing cycles, and high surface runoff during snowmelt events. The cumulative amount of water from both Syverud and Bjørnebekk, were within a factor of 10 from the measurements. A problem with the model, which also is in accordance with Reichenberger (2005), is that the model tends to overpredict both the water flow and pesticide runoff for low-intensity rainfalls and small runoff events, and to underpredict for high-intensity rainfalls and large runoff events. At both catchments the model estimates too much runoff for metalaxyl and propiconazole in surface runoff compared to observed values. In the drainage water both pesticides are being underpredicted. Calculations of the mean annual concentrations show that the simulations of metalaxyl are quite good from both catchments in surface runoff, with a ratio from 1 to 12 between predicted and measured values. The simulations of propiconazole are somewhat poorer with a ratio from 3 to 21 between simulated and observed values. A new version of PRZM will be launched in 2010. This version simulate propikonazole and leaching to groundwater much better than the previous version and will be used for future simulations.

Simulations with MACRO

National scenarios in the Nordic countries are mainly developed with the simulation model MACRO. The scenarios are a combination of using MACRO as a groundwater scenario or a drainage scenario. The results described in this report are from Syverud, which is a drained clay soil.

MACRO simulates the water flow in the period 2005/2006 as daily fluxes and accumulated values, and the comparison between simulated and measured values shows a good fit. Measured and simulated values of accumulated drainage for 2007/2008 show a good fit, but there was some deviation in early June probably due to local showers. Measured and simulated concentration of bromide in the drainage water showed larger disagreement. The measurements showed that bromide reached the drainage system faster than simulated both years. The simulated concentration and accumulated amount of propiconazole in the drainage water was almost zero. The measured concentration of propiconazole was <0.1 µg/l. The disagreement between model simulations and field measurement indicate that other processes than ionic transport is important for strongly adsorbed pesticides. Simulated and measured concentrations of metalaxyl are of the same order of magnitude in 2005/2006. For 2007/2008 the measured concentrations are close to zero when metalaxyl reaches the drainage water according to the simulations. The accumulated values show that the simulated leaching of metalaxyl continues after the end of the measurement period and reaching 4-5 times higher amounts.

3. Introduction

There has been an increasing use of pesticide leaching models in risk assessment work done in EU. Through work in the Forum for the Co-ordination of Pesticide Fate Models and their Use (FOCUS), EU has developed scenarios for both ground water and surface water, but the scenarios do not cover special Norwegian conditions such as high precipitation, strongly sloping fields and the occurrence of snowmelt on frozen ground. The aim of this project was therefore to establish scenarios from experimental fields which could be representative for Norwegian conditions and to use them for approval of new pesticides in Norway.

The project has been divided in two parts and this last report describes the field studies carried out in 2007/2008 and model simulations/validations using this data.

Runoff of pesticides depends on properties of the pesticide, soil, soil treatment and the climate conditions. In these field experiments, two pesticides with different mobility characteristics (metalaxyl and propiconazol), were applied at two fields (Syverud and Bjørnebekk) with different soil erodibility and water flow pattern. A similar study was conducted in the period June 2005 – May 2006 (Eklo et. al., 2008), a period with less precipitation and different seasonality with respect to precipitation events compared to the period June 2007 – April 2008.

Runoff data from the fields has been used to calibrate and validate the models PRZM and MACRO in order to establish scenarios which can be used by the Norwegian Food Safety Authorities in their risk assessment work.

4. Runoff of metalaxyl and propiconazole

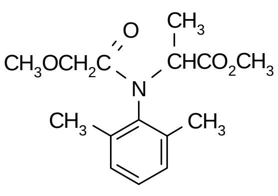
Gunnhild Riise, Marit Almvik and Trond Børresen

4.1 Introduction

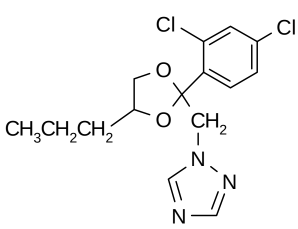
There are several advantages with small scale field experiments. The plots are subject to ordinary agricultural practices and natural variations in weather conditions. At the same time the experimental conditions can be more easily controlled compared to large scale catchment studies. Seasonal, annual and areal variations in runoff of pesticides are to a large extent related to differences in properties of the pesticide, the soil, soil treatment and the climate conditions. In this study, two pesticides with different mobility characteristics, metalaxyl and propiconazole, were applied at two Norwegian fields with different soil erodibility and water flow pattern.

Metalaxyl is a fungicide with high water solubility (7100 mg/L), which is stable to both aquatic photolysis and hydrolysis at environmental pH. In soil, metalaxyl is mobile pesticide (Koc = 500 ml/g). Previous sorption studies showed that Kd < 1 (appendix 8.4). It is usually moderately persistent in soil; common values are half-lives of approx. 42 days (Footprint database). Previous investigations of laboratory degradation rates (DT_{50}) in soil at 20°C have shown that metalaxyl is degraded with a DT_{50} of 38 days in topsoil (0-20 cm) from Syverud, whereas the half-life in Bjørnebekk topsoil is much longer: 107 days. In subsoil (20-40 cm), a DT_{50} of 32 days was found at Syverud and a DT_{50} of 546 days at Bjørnebekk. Metalaxyl is moderately persistent in the Syverud soil and persistent in the Bjørnebekk soil. The Norwegian predicted no chronic effect concentration (PNEC) for metalaxyl is set to 120 µg/L.

Propiconazole is a fungicide with moderate water solubility (150 mg/L), which is stable to aqueous photolysis but may be hydrolyzed with a half-life of 54 days at pH 7. In soil, propiconazole is slightly mobile/immobile (Koc = 1086 ml/g). Previous sorption studies showed Kd values between 5.7-25.7 (appendix 8.4). Typical DT_{50} for propiconazole in soil at 20 °C is 90 days (Footprint database). Previous investigations of laboratory degradation rates in Syverud and Bjørnebekk soils at 20 °C have shown that propiconazole has a DT_{50} of 281/389 days (topsoil/subsoil) in Syverud soil and 144/172 days in Bjørnebekk soil. Hence, propiconazole is a persistent pesticide in the Syverud and Bjørnebekk soils. The Norwegian PNEC value for propiconazole is set to 0.13 µg/L.



Metalaxyl



Propiconazole

At one of the fields, Syverud, water leaving the field is separated into surface runoff and drainage water. Differences in agricultural practices were also one of the studied variables, as plots with and without autumn ploughing were included in the investigation.

Water proportional sampling of water transported from the plots, allows the calculation of water fluxes and losses of pesticides. A similar study was conducted in the period: June 2005 – May 2006, a period with less precipitation and another seasonality with respect to precipitation events compared to the period June 2007 - April 2008. In addition, higher temperatures, especially during the winter period, extended the runoff period for the current compared to the previous study. In this sense valuable information on different climate conditions on the runoff of pesticides are obtained.

4.2 Materials and methods

4.2.1 Treatment of the sites

Plots at Bjørnebekk were subjected to two different treatments, spring and autumn ploughing, while the plot at Syverud was ploughed in autumn. All plots were ploughed in spring before sowing. Plots with autumn ploughing are referred to as APL and spring ploughed plots as SPL. It was grown barley in 2007 and oats in 2008. Similar agricultural practices have been performed since 1990 for both sites.
The ploughing depth is about 20 cm on all plots, and time for ploughing is given in table 1.

Table 1. Ploughing times for Syverud and Bjørnebekk in 2007 and 2008. APL = autumn ploughing and SPL = spring ploughing:

Treat.	2007		2008	
	Syverud	Bjørnebekk	Syverud	Bjørnebekk
SPL	16. April	17. April	27. April	27. April
APL	31. October	27. September	13. October	25. September

Before the experiment at Syverud was established, the area was used for meadow and pasture for many years which resulted in a good soil structure with high infiltration capacity and saturated hydraulic conductivity as well as very high aggregate stability. The drainage system was installed about 1960, and the runoff measurements started about 1980. The surface layer (0-20 cm) consists of 23 % clay, 49 % silt and 28 % sand (loam /silt loam). The C-tot is 3.2 % in the ploughed layer. The texture is relatively uniform down to 65 cm. The plots are about 28 meter long and 7 meter wide and the slope is about 13 %.
The area at Bjørnebekk was artificially levelled before 1980, when the field experiment was established. The soil consists of 27 % clay, 62 % silt and 11 % sand (silty clay loam) in the ploughed layer (0-20 cm). The C-tot is rather low, with a value of 1.4 %, due to levelling of the soil. The clay content increases in the deeper layers. The soil structure is weak and the aggregate stability very low. The plot length is 21 m and plot width is 8 m and the slope is 13 %.

4.2.2 The pesticides

Metalaxyl, formulated as Ridomil MZ (75 g metalaxyl/kg) and propiconazole, formulated as Tilt Top (125 g propiconazole/l) were applied at a rate of 300 g Ridomil MZ/daa and 100 ml Tilt Top/daa to the Syverud and Bjørnebekk fields.

For the quantitative analysis, pure standards of metalaxyl and propiconazole (purity > 98 %) were purchased from Dr. Ehrenstorfer GmbH, Germany.

4.2.3 Application of pesticides and the bromide tracer

Soil down to a depth of 60 cm was sampled from the fields at various positions before spraying in order to measure residual levels of pesticides from previous applications.

Two plots at Syverud (plot no. 3 and 4) and two plots at Bjørnebekk (plot no. 3 and 6) were sprayed the 7th of June 2007 with metalaxyl, propiconazole and potassium bromide (10 kg KBr/daa). The two plots at each site were sprayed with one tank of pesticide solution, whereas the bromide was applied with one full tank for each plot.

A small volume (approx. 50 ml) from the spraying solution was stored for analysis for comparison to the expected concentrations.

The uniformity of application of pesticides and bromide on the fields was measured by making 4 subplots (A-D) of each plot and distributing 12 Petri dishes filled with topsoil across the surface before spraying. These soil samples were stored at -20 °C until analysis. The concentration in the soils was compared to the calculated, expected concentration.

The plots were presown with spring grains (barley). The height of the plants was measured by taking the average of 10 plants at the plots. The distribution of the plants was measured visually before spraying. Pictures were also taken from the fields.

The field spraying plan is found in appendix 8.2.

Figure 1. The Syverud field (left) and the Bjørnebekk field (right) on 7 June 2007.

4.2.4 Collection of samples

The individual plots are separated by soil mounds at each side, and a ditch in the upper end. At the lower end of the field is a perforated pipe that collects surface runoff from the field. Water that drains through the pipes enters a tilting bucket that records the amount of water leaving the plots. The number of tilts is recorded continuously by data loggers with 5 min. resolution. Water proportional samples were collected from surface runoff at Bjørnebekk and from surface and drainage water at Syverud. The depth of the drains is approximately 1 m. The sampling frequency varied from a couple of days to several weeks depending on amount of runoff. Water samples were collected on plastic bottles of PE quality and transferred to Bioforsk for analysis.

4.2.5 Extraction and analysis

4.2.5.1 Metalaxyl and propiconazole

Metalaxyl and propiconazole were extracted from the soil samples by shaking 10 g fresh soil with methanol for 30 minutes and centrifuging (10.000 rpm, 15 minutes) to separate the soil from the extract. Approx. 1 ml of the extract was transferred into a HPLC vial. The extract was separated by reversed phase chromatography and the analytes detected with a diode array detector with λ = 210 nm and a bandwidth of 8 nm. The limit of quantification was 0.04 µg/g for metalaxyl and 0.1 µg/g for propiconazole. The recovery of metalaxyl was 99-106 % and the recovery of propiconazole was 95-104 %. Final metalaxyl and propiconazole results were expressed on oven dry soil weight basis (105 °C, 24 h.).

The spraying solution of metalaxyl and propiconazole was diluted 1:1000 in methanol and analysed directly.

4.2.5.2 Bromide

Bromide was extracted from the soil samples by mixing 20 g fresh soil with 40 ml distilled water, shaken for 30 minutes and then centrifuged (10000 rpm, 10 minutes) to separate the soil from the extract. Bromide concentrations were determined in room-tempered solutions using a bromide ion selective electrode (Orion Research, Boston MA). Recovery of bromide with this method was 89 %, with a quantification limit at 0.24 mg Br/kg. Final bromide results were expressed on oven dry soil weight basis (105 °C, 24 h.).

Blanks and spiked control samples were included for each batch of both pesticide and bromide analysis. These samples were treated and analysed in the same way as the ordinary samples. The recovery was calculated from the concentrations found in the spiked samples. No pesticides were detected in the blank samples.

4.3 Results

4.3.1 *Application of pesticides*

4.3.1.1 Plant height and distribution

The average plant height 7th of June was:
Syverud: 21 ± 3 cm
Bjørnebekk: 14 ± 3 cm
The plants covered 40 and 44 % at Syverud (plot 3 and 4 respectively) and 26 and 31 % of the soil surface at Bjørnebekk (plot 3 and 6 respectively).

4.3.1.2 The pesticides

Quality assurance control of the application of the pesticides at the plots was examined by analysing 12 soil samples from each plot and analysing the spraying solution, see table 2.

Table 2. Accuracy of pesticide application and uniformity of spraying of across the plots at the Syverud and Bjørnebekk fields.

	Syverud			
	Metalaxyl		Propiconazol	
	Plot 3	Plot 4	Plot 3	Plot 4
Concentration of pesticides in 12 soil samples:				
Prepared conc.	21.8 g/daa	21.8 g/daa	12.1 ml/daa	12.1 ml/daa
Found conc.	24.9 g/daa	17.3 g/daa	13.6 ml/daa	9.5 ml/daa
Accuracy:	**114 %**	**79 %**	**112 %**	**78 %**
Uniformity of application measured from analysis of 12 soil samples:				
	23 %	13 %	22 %	17 %
Pesticide concentrations in the spraying solutions:				
Planned conc.	0.90 g/L		0.50 g/L	
Found conc.	1.01 g/L		0.36 g/L	
Accuracy:	**112 %**		**72 %**	

	Bjørnebekk			
	Metalaxyl		Propiconazol	
	Plot 3	Plot 6	Plot 3	Plot 6
Concentration of pesticides in 12 soil samples:				
Prepared conc.	19.8 g/daa	19.8 g/daa	11.0 ml/daa	11.0 ml/daa
Found conc.	21.6 g/daa	21.8 g/daa	11.4 ml/daa	11.4 ml/daa
Accuracy:	**109 %**	**110 %**	**104 %**	**104 %**
Uniformity of application measured from analysis of 12 soil samples:				
	16 %	25 %	19 %	33 %
Pesticide concentrations in the spraying solutions:				
Planned conc.	0.90 g/L		0.50 g/L	
Found conc.	1.01 g/L		0.39 g/L	
Accuracy:	**112 %**		**77 %**	

The accuracy (A) of pesticide application was good at Bjørnebekk (the detected amounts in the soil samples amounts to 104-110 % of the planned or prepared concentration). At

Syverud, more pesticides seem to have been applied to plot 3 (A = 112-114 %) than to plot 4 (A = 78-79 %).

The uniformity of pesticide application across the plots varies from 13-23 % at Syverud and from 16-33 % at Bjørnebekk. These results are fairly good, but the % deviation across plot 6 at Bjørnebekk is a bit too high (25-33 %).

The analysis of the pesticide solutions show that the metalaxyl amounts are over-estimated (112 % recovery) whereas the propiconazole amounts are lower than expected (72-77 % recovery). The low propiconazole amounts are however not reflected in the amounts recovered from the soil samples. Hence, the results from the analysis of the solutions could be caused by precipitation of propiconazole in the tank or losses through adsorption. This phenomenon was also seen from the analysis of the pesticide solution used in the 2005/2006 field study.

4.3.1.3 Bromide

Quality assurance control of the application of bromide at the plots was examined by analysing 12 soil samples from each plot and analysing the spraying solution, see table 3.

Table 3. Accuracy of bromide application and uniformity of bromide spraying across the plots at the Syverud and Bjørnebekk fields.

	Bromide			
	Syverud		Bjørnebekk	
	Plot 3	Plot 4	Plot 3	Plot 4
Concentration of bromide in 12 soil samples:				
Prepared conc.	6.7 kg/daa	6.7 kg/daa	6.7 kg/daa	6.7 kg/daa
Found conc.	7.1 kg/daa	6.6 kg/daa	5.6 kg/daa	6.6 kg/daa
Accuracy:	**106 %**	**99 %**	**83 %**	**99 %**
Uniformity of application measured from analysis of 12 soil samples:				
	28 %	29 %	24 %	35 %
Bromide concentrations in the spraying solutions:				
Planned conc.	67 g/L	67 g/L	67 g/L	67 g/L
Found conc.	56 g/L	56 g/L	51 g/L	59 g/L
Accuracy:	**83 %**	**84 %**	**76 %**	**88 %**

An amount of 6.7 kg bromide/daa was planned to be applied to the plots (corresponding to 10 kg KBr/daa). The analysis of soil samples showed good correspondence between the planned and the detected amounts in the soil (accuracy of 83-106 %).

The uniformity of application of bromide across the plots was acceptable (24-35 % deviation across the plots).

The bromide solution contained somewhat lower bromide amounts than planned for, with 76-88 % accuracy, but the amounts found in the soil samples were still good.

4.3.2 Climate conditions and runoff pattern

The investigated period was very wet. A nearby field station FAGKLIM at Ås received 1066 mm precipitation compared to a normal annual value of 785 mm precipitation, giving nearly 300 mm above normal values (table 4). Especially, the summer months June and July in 2007 and January of 2008 received high amounts of precipitation. A value of 176 mm precipitation in January 2008 is in fact a record for this meteorological station, which has been run since 1874!

The average temperatures were, except for June 2007, generally above normal values, resulting in a higher mean temperature than normal. For the investigated period the mean temperature was 7.1 ºC, which is 1.8 ºC above the normal value of 5.3 ºC. During the winter period, only December 2007 had monthly average values below zero. Warmer weather during the winter months, gives enhanced possibilities for runoff during the cold period of the year.

Table 4: Average monthly precipitation (mm) and temperature (ºC) at Ås (Sørås) during the period: 1. June 2007-31. May 2008. Monthly average values during the normal period (1960-1990) are given in cursive (Dept. of Mathematical Sciences and Technology (IMT), UMB).

Year	2007							2008				
Month	J	J	A	S	O	N	D	J	F	M	A	M
Prec.	129	142	75	72	31	97	88	176	66	99	64	28
(mm)	*68*	*81*	*83*	*90*	*100*	*79*	*53*	*49*	*35*	*48*	*39*	*60*
Temp.	16.1	15.4	15.7	10.7	6.7	1.0	-1.3	1.1	1.9	0.7	6.1	11.2
(ºC)	*14.8*	*16.1*	*14.9*	*10.6*	*6.2*	*0.4*	*-3.4*	*-4.8*	*-4.8*	*-0.7*	*4.1*	*10.3*

Syverud:

The Syverud field has a rather high infiltration capacity, and even though the summer months of June and July 2007 received high amounts of precipitation, there was little excess of water available for surface runoff. Not until late autumn and winter, there was a significant contribution from surface runoff (fig. 2a). Transport of water through the drainage system, however, took place more or less continuously all the investigated period, with especially high values in the late autumn and the winter period (fig. 2b). Special climatic condition during the winter season, with high temperature and precipitation values, explains the high runoff during the cold season. In total 615 mm of water was transported as drainage and surface water during the period: 1. June 2007 – 4. April 2008, divided into 499 mm as drainage and 115 mm as surface runoff. In a previous investigated period (2005-06), 513 mm left the field in total as surface and drainage water. The major difference between the two investigated periods is amount of surface runoff. Surface runoff made up 115 mm in 2007-08, and only 25 mm in 2005-06. Enhanced winter temperatures and precipitation in 2008 were the major reasons for the differences in surface runoff. Another striking difference between the two investigated periods is the delay in runoff after application of pesticides. In the previous period (2005-06), samples were not collected until late August 2005, while in this period (2007-08), the first samples, collected after application of pesticides, were taken in June.

Syverud

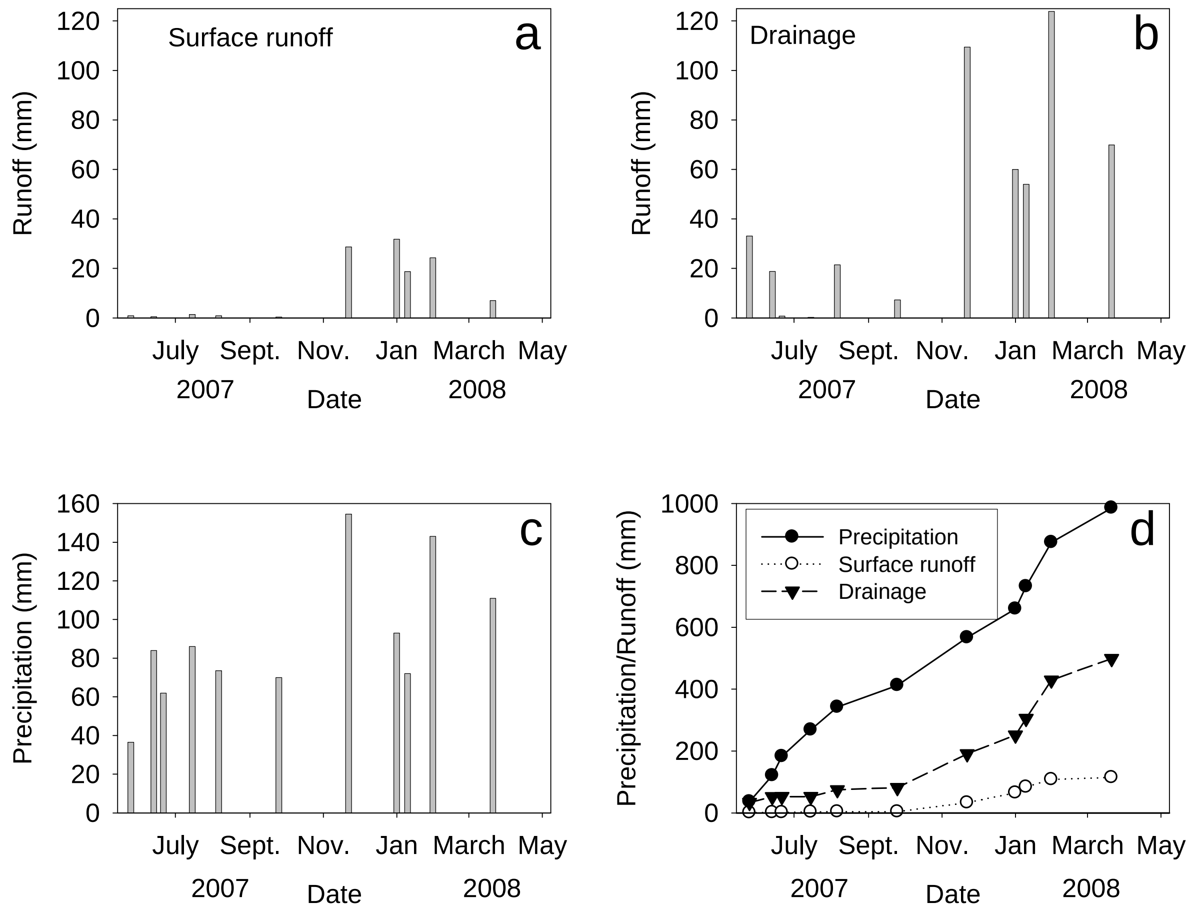


Figure 2: Runoff of surface (a) and drainage water (b) from the experimental plot at Syverud during the period: 1 June 2007 – 4 April 2008. Periodic values of precipitation (c) and accumulated values of precipitation and runoff (d) are all given in mm for the same investigation period.

Bjørnebekk:

The soil at Bjørnebekk is more susceptible to erosion and surface runoff compared to Syverud. High amounts of water are transported as surface runoff at Bjørnebekk due to low infiltration capacity. Higher amount of surface runoff was observed at APL compared to SPL, especially during the summer and autumn periods. Differences in runoff between the two plots have been observed earlier, indicating higher infiltration capacity and deeper percolation of water in plots without autumn ploughing (SPL). Straw and weeds that cover SPL plots, at time of the year when APL plots are barren, may promote increased infiltration of water. Differences in soil compaction among APL and SPL plots can be another reason. The highest amount of runoff was observed during late autumn and winter, such as for Syverud. At Bjørnebekk accumulated values for surface runoff were 444 mm and 340 mm for APL and SPL plots (fig. 3). In comparison, accumulated runoff at Syverud for the same time period, were 499 mm and 115 mm for drainage and surface runoff, respectively. Also for Bjørnebekk higher amounts of runoff were observed during this investigation period (2007-08) compared to the previous period (2005-06), as the runoff values for the APL and SPL plots were 290 mm and 115 mm in the period 2005-06 compared to 440 mm (APL) and 340 mm (SPL) in 2007-08.

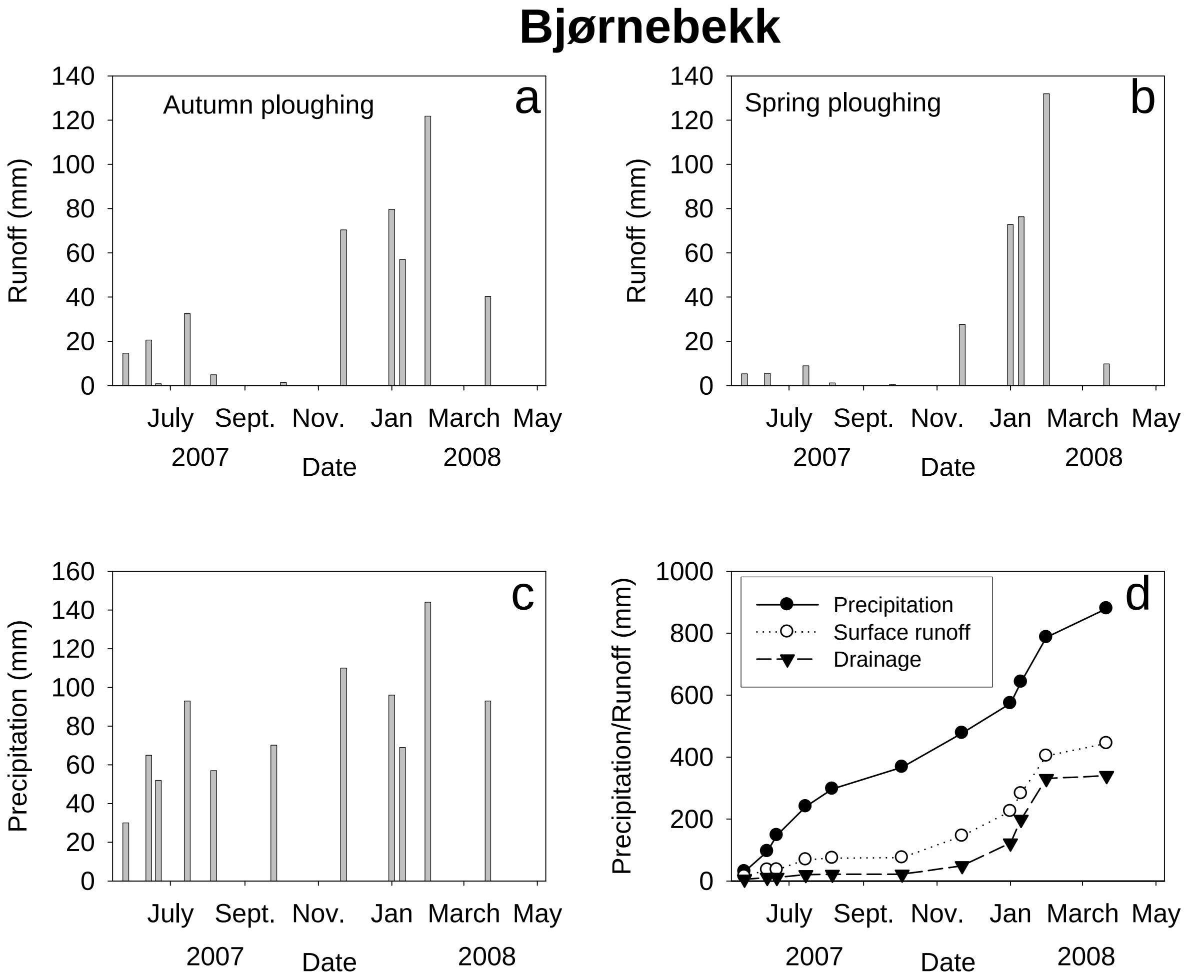


Figure 3: Surface runoff from plots with autumn ploughing (a) and without autumn ploughing (b) from the experimental field Bjørnebekk during the period: 1 June 2007 – 4 April 2008. Periodic values of precipitation (c) and accumulated values of precipitation and runoff (d) are all given in mm for the same investigation period.

4.3.2.1 Runoff of particles

Syverud:

Except for an episode immediately after pesticide application, the loss of particles from the Syverud plot through surface runoff was moderate (fig. 4a). Due to high aggregate stability, the soil is relatively resistant against erosion. For water that infiltrates the soil, sieving and physical attraction mechanisms retain particles in the soil and reduce the particle content in the drainage water. Enhanced values of particles in the drainage water, is generally related to high flow episodes and indicates macropore flow, such as in late January 2008 (fig. 4 b).

Bjørnebekk:

Major differences in particle transport appear between the plots with different agricultural practices (fig. 4c and d). Both during the summer period, and especially during the late autumn and winter period, high particle concentration in runoff from the APL plot occurs. For the plot without autumn ploughing (SPL), the particle concentration is more moderate, with similar or somewhat above the values observed in surface runoff from Syverud.

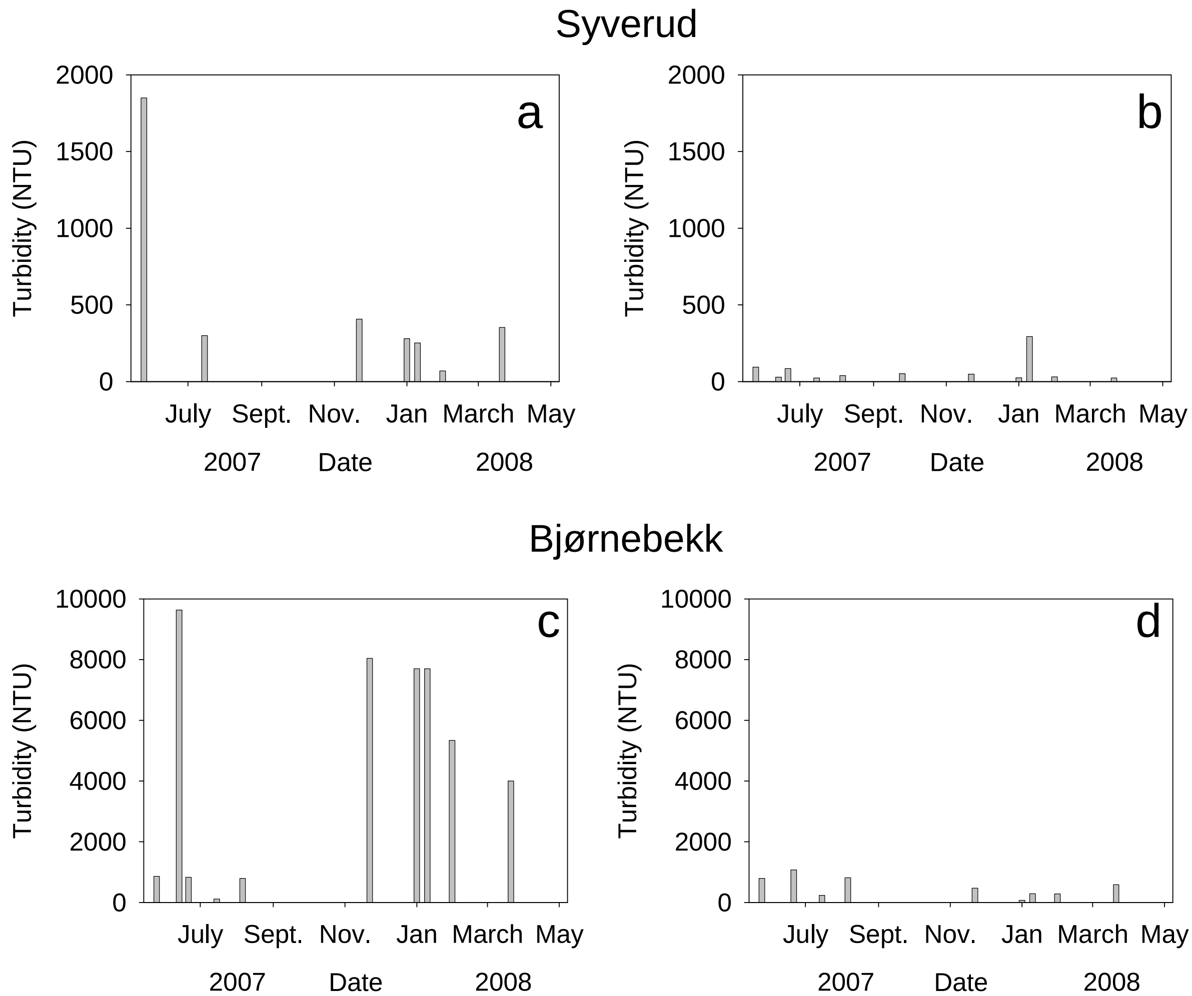


Figure 4: Concentration of particles, measured as turbidity (NTU) at Syverud in surface runoff (a) and drainage water (b) and at Bjørnebekk from plots with autumn ploughing (c) and spring ploughing (d) during the investigated period: 1. June 2007 – 4. April 2008.

4.3.2.2 Runoff of pesticides

Syverud

Metalaxyl:

Climatic conditions shortly after application of pesticides are of great importance for the runoff pattern. A rather high peak concentration of metalaxyl (3.0 µg/l) was registered in surface runoff at the first sampling event (29.07.07) after application of pesticides. In the following period, only low values of metalaxyl were measured in the surface runoff. The peak concentration in drainage water (2.4 µg/l) appeared at an earlier date (05.07.07) than in the surface runoff, indicating a very high mobility of metalaxyl. Metalaxyl is indeed classified as a mobile pesticide, but the early appearance is most probably caused by a higher sampling frequency of the drainage water. Low concentration of metalaxyl was measured 9. October 2007, and thereafter it was only detected in one more drainage water sample (24. January 2008).

Propiconazole:

Similarly to metalaxyl, the highest concentration of propiconazole, in surface runoff (0.3 µg/l), was measured at the first representative sampling event after application of pesticides. The peak was, however, less sharp than for metalaxyl, as low concentrations of propiconazole were measured during the whole investigated period. In drainage water, the highest propiconazole concentration (0.07 µg/l) appeared at the same date as for metalaxyl (05.07.07). Also for the drainage water, the propiconazole peak was more diffuse and a new peak emerged during a melting period in January 2008.

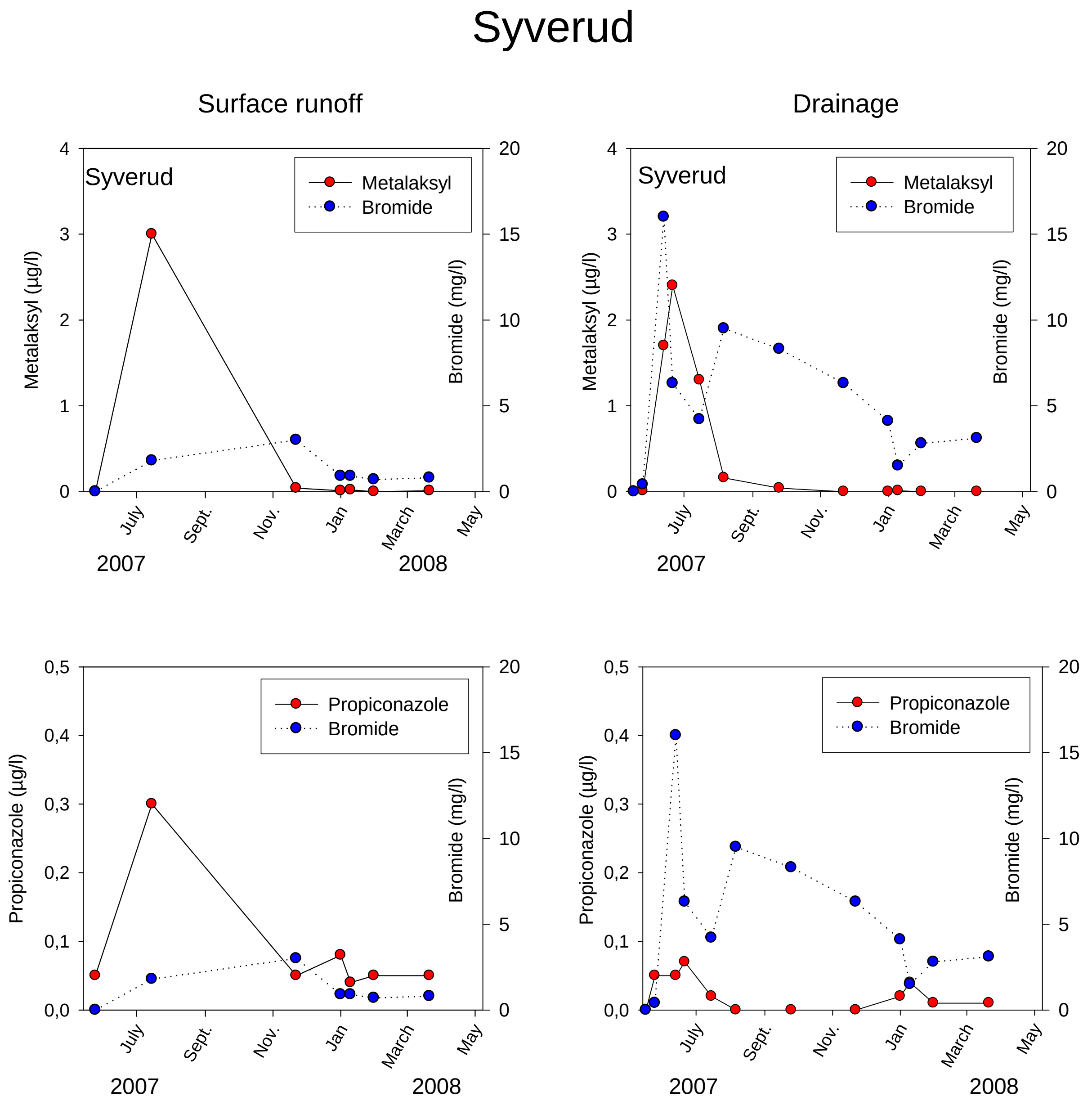


Figure 5: Concentration of metalaxyl (µg/l), propiconazole (µg/l) and bromide (mg/l) in surface runoff and drainage water from Syverud (autumn ploughing) during the period: 1 June 2007 – 4 April 2008.

Bromide:
Higher values of bromide in the drainage water compared to surface runoff reflects the high infiltration rate of the Syverud soil. The bromide values in the drainage water show a sharp reduction after a peak value in June 2007, before the values increase again at the end of August 2007. The reduced bromide values seem to be linked to a period with low drainage, where bromide preferably is retained in the soil.
Compared to the previous investigated period (2005-06), the peak concentrations of metalaxyl was higher for both the surface and drainage water in 2007-08. For propiconazole, however, the concentrations were more similar. Higher application rate of propiconazole for the period 2005-06 may explain the lack of difference between the two

periods, as there were more favorable conditions for pesticide runoff in the 2007-08 periods. For the period 2005-06, there was a long period of time between application of pesticides and runoff events, which delayed the pesticide runoff and reduced the maximum concentrations in runoff, both due to pesticide degradation and sorption to soil.

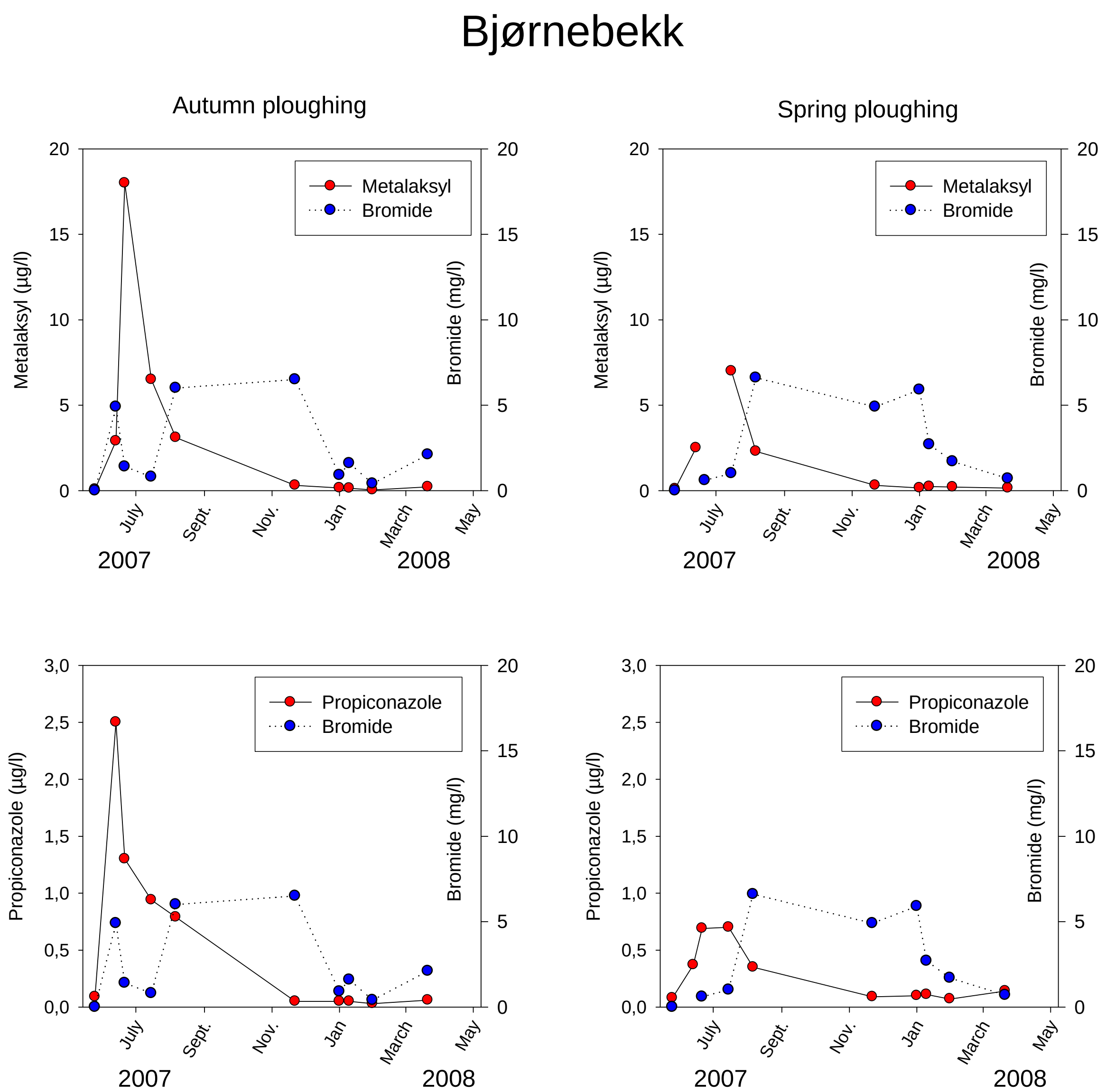


Figure 6: Concentration of metalaxyl (µg/l), propiconazole (µg/l) and bromide (mg/l) in surface runoff at Bjørnebekk, at plots with autumn ploughing (APL) and spring ploughing (SPL), during the period: 1 June 2007 – 4 April 2008.

Bjørnebekk

Metalaxyl:

Bjørnebekk is an erosive soil, with low infiltration capacity where a major part of the water transport is directed as surface water. The runoff pattern influence the transport of pesticides, as the runoff of pesticides, generally, was higher for Bjørnebekk compared to Syverud. Peak concentration at Bjørnebekk was registered at the same time as for Syverud (05.07.07), but with a much higher concentration (18 µg/l). During the previous investigated period (2005-06) a peak concentration of 6 µg/l of metalaxyl was registered late in August 2005. Unfortunately, due to analytical problems, metalaxyl values for SPL plots are missing at 5 July 2007, at the expected time of maximum concentration.

Comparing concentrations of metalaxyl from APL and SPL plots for the other sampling dates, the values are relatively similar. The differences in concentration of the mobile pesticide between the two plots are therefore minor, even though the amount of runoff (mm) varies.

Propiconazole:
The peak for propiconazole appeared at an earlier date (27. 06.07) and at a much higher concentration for the plots with APL compared to SPL. As seen from fig. 6, the peak concentration of propiconazole corresponds to a runoff episode with high transport of particles from the APL plot, which might enhance the runoff of particle bound pesticides. There was no sharp peak for propiconazole in the plot with SPL, but the reduction in concentration proceeded more slowly compared to APL, indicating high persistence in soil. Relatively high values were measured during the winter and spring season. The last samples collected 4. April 2008 contained 0.14 and 0.06 µg/l of propiconazole in runoff from SPL and APL, which are well above the detection limit and close to the Norwegian PNEC value (0.13 µg/l). Thus, as shown earlier, propiconazole can be quite persistent and able to leach for a long period of time in the soil.

Bromide:
Similar to surface runoff at Syverud, there is no single sharp bromide peak in the surface runoff at Bjørnebekk. For the APL plot there is an early bromide peak in the beginning of July, followed by reduced values, before the concentration rises in the autumn period and levels off again. For the SPL plot, both the increase and decrease in bromide is delayed compared to APL. This may reflect a more rapid response in the APL compared to SPL due to reduced water retention capacity in the soil with APL.

4.3.2.3 Loss of pesticides

Metalaxyl

Except for surface runoff at Syverud, the losses of metalaxyl were generally higher than for propiconazole. This is related to the high water solubility and mobile character of metalaxyl. The amount and transport pathway of water, prior to excessive degradation losses of the pesticide, are therefore to a large extent determining the losses of metalaxyl. The largest losses of metalaxyl occurred at Bjørnebekk, at plots subject to autumn ploughing. Less transport of metalaxyl from the plot without autumn ploughing, can to a large extent be explained by less surface runoff, especially at the period shortly after the pesticide application (fig. 7). A missing value for metalaxyl (5 July 2007), at the plot subject to spring ploughing, also explains some of the difference between the two treatments. Due to low runoff in the period between 27 June and 5 July (fig. 3b), however, the influence on the calculated loss is limited. Assuming similar concentration in runoff from APL and SPL, at maximum 0.06 % of metalaxyl was lost at 5. July, which is not included in the overall budget on loss of metalaxyl from SPL. Low runoff values at the SPL plot, especially during the summer months, when the pesticide concentrations are at their highest, also explains the differences in average metalaxyl concentrations for the APL and SPL plots (table 5).
Generally, there was a lower loss of metalaxyl at Syverud compared to Bjørnebekk. Comparing the two different flow paths at Syverud, there was a larger loss of metalaxyl through the drainage than the surface runoff, as the water transport is a much more extensive through the drainage system compared to the surface runoff. The average concentration is also somewhat higher in the drainage compared to the surface runoff, which might reflect a slower degradation rate in the deeper soil layers.

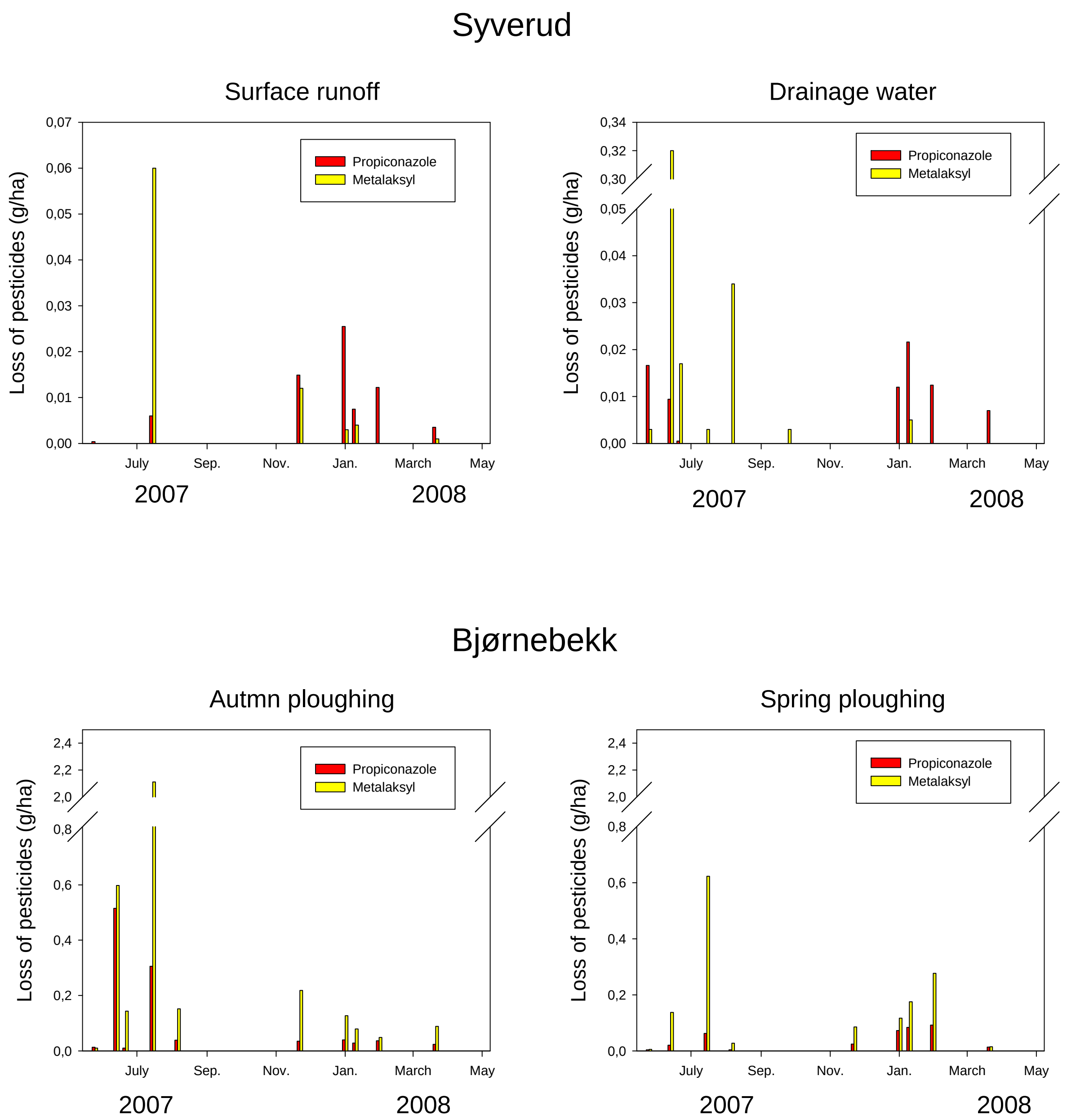


Figure 7: Loss of the pesticides propiconazole (g/ha) and metalaxyl (g/ha), from Syverud in surface runoff (a) and drainage water (b) and from surface runoff at Bjørnebekk at plots with autumn ploughing (c) and spring ploughing (d).

Propiconazole

Generally, there was a larger loss of propiconazole from Bjørnebekk compared to Syverud, especially at plots with autumn ploughing. In addition to differences in water transport, differences in particle transport among the plots might influence the loss of propiconazole. As seen from fig. 4, there was a much higher loss of particles from the APL plot compared to the SPL plot at Bjørnebekk. For pesticides with high affinity to soil surfaces, particles can facilitate the transport, such as for propiconazole.

At Syverud, the loss of propiconazole is rather low, as propiconazole to a large extent is retained in the soil. In contrast to the mobile pesticide metalaxyl, the difference in losses through surface and drainage water is not large, even though much more water is transported through the drainage system (table 4). This makes the average concentration of propiconazole higher in the surface runoff compared to the drainage water. The fact that propiconazole is present in drainage water at all, indicates flow through macropores.

Table 5: Runoff of water (mm), loss (g/ha) and average concentrations (µg/l) of the pesticides metalaxyl and propiconazole, during the period 01.06.2007- 04.04.2008. The ranges (max-min) are given in parentheses. Results are given for surface runoff at Bjørnebekk (BJ) and surface runoff (S) and drainage water (D) at Syverud (SY). The plots at Syverud are subject to autumn ploughing (APL), while the plots at Bjørnebekk have two different treatments, autumn ploughing (APL) and spring ploughing (SPL).

Plot	Type	Treat.	Runoff	Loss		Concentration	
			(mm)	Metalaxyl	Propicon.	Metalaxyl	Propicon.
				(g/ha)	(g/ha)	(µg/l)	(µg/l)
BJ	S	APL	444	3.579	1.047	0.81	0.24
				(0.01-2.11)	(0.01-0.52)	(0.04-18)	(0.03-2.5)
BJ	S	SPL*	340	1.463	0.380	0.43	0.11
				(0.01-0.62)	(0.00-0.09)	(0.10-7.0)	(0.07-0.70)
SY	S	APL	115	0.061	0.068	0.053	0.059
				(0-0.042)	(0-0.026)	(0-3.0)	(0-0.3)
SY	D	APL	499	0.385	0.079	0.077	0.016
				(0-0.320)	(0-0.022)	(0-2.4)	(0-0.07)

*Values of metalaxyl from 5. July 2007 are missing

4.3.2.4 Loss of pesticides in the present study (2007-08) compared to a previous study (2005-06)

Special climate conditions promoted high loss of pesticides in the investigated period (2007-08). Higher loss in 2007-08 compared to the period 2005-06, was due to high precipitation in summer and high precipitation and temperatures in the winter of 2007-08. For the mobile pesticide metalaxyl, the highest loss occurred at Bjørnebekk APL plots, next to Bjørnebekk SPL plots for both the investigated periods. At Syverud, more metaxyl were passing through the drains than the surface runoff, due to high infiltration capacity for both the investigated periods. With respect to propiconazole, a relatively larger amount (%) was lost through the surface runoff from both the Syverud and the Bjørnebekk field in 2007-08 compared to the previous period. More extensive periods with water saturated conditions leading to higher surface runoff and transport of particles are the most probable reason for the enhanced transport of propiconazole through surface runoff. Similar amount of propiconazole was lost through the drains at Syverud and through the surface runoff from the SPL plots at Bjørnebekk in 2005-06 (0.07 %). For this investigation period, the surface runoff of propiconazole from the SPL plots at Bjørnebekk was much higher than the transport trough the drains at Syverud (table 5).

Table 6: Loss of metalaxyl and propiconazole in percent of the amount applied at Bjørnebekk and Syverud, during the period 1 June 2007 – 4 April 2008. The plots received 225 g/ha of metalaxyl (a.i) and 125 g/ha of propiconazole (a.i) in June 2007 and 225 g/ha of metalaxyl (a.i) and 250 g/ha of propiconazole (a.i) in June 2005.

Plot	Runoff	Treatment	Metalaxyl (%)		Propiconazole (%)	
			2005-06	2007-08	2005-06	2007-08
BJ	S	APL	0.69	1.59	0.15	0.84
BJ	S	SPL*	0.26	0.65	0.07	0.30
SY	S	APL	0.01	0.03	0.01	0.05
SY	D	APL	0.12	0.17	0.07	0.05

*Values of metalaxyl from 5. July 2007 are missing

5. Model simulations

5.1 Comparison of simulations done with the model PRZM3 and measurements of propiconazole and metalaxyl from Syverud and Bjørnebekk – SE Norway

Randi Iren Bolli and Ole Martin Eklo, Bioforsk

5.1.1 Introduction

In this last part of the project the main focus was to collect field data for a second year (2007-2008) to validate the model using this data. The model used was PRZM3 (**P**esticide **R**oot **Z**one **M**odel). Simulations of the results from 2001-2002 and 2005-2006 (Eklo et. al., 2008) were achieved by PRZM version 3.12.2, which was provided from the EPA Center for Exposure Assessment Modeling (CEAM) Web site. There were some problems attached to this version of the model. The function which simulated the soil temperature with the use of temperature and moisture corrected degradation was not working. It was neither not possible to use the normalized Freundlich coefficient K_F together with the Freundlich exponent 1/n. Because of these problems it was decided to re-run the data obtained in 2005-2006 and to do the validation with the data from 2007-2008, using the FOCUS – PRZM (3.21 beta version) (FOCUS, 2001). Pesticides in these simulations were metalaxyl and propiconazole.

5.1.2 Materials and methods

5.1.2.1 The PRZM model

PRZM (**P**esticide **R**oot **Z**one **M**odel) is a one-dimensional, dynamic compartment model that can be used to simulate chemical movement in unsaturated soil systems within and below the root zone (Carsel et al., 2006). The original version of the PRZM model was released in 1984 (Carsel et al., 1984) but it has been continuously improved since then. The version PRZM 3.21ß is used in the FOCUS surface water scenarios (FOCUS, 2001) for runoff and erosion modeling. The PRZM model is able to simulate surface runoff, erosion, leaching, decay, plant uptake, foliar wash off and volatilization of pesticides. Water and chemical transport is the two major components.

A more detailed description of the model can be found in Carsel et al. (2006).

5.1.2.2 Parameter estimation

The parameter estimation was performed at two stages: an uncalibrated simulation followed by a simulation with calibration using the sensitive parameters. The hydrology module is always calibrated first and the pesticide module last. This is important, as water is the carrier of pesticides through the soil and knowledge of the water flow is a prerequisite of a valid description of the movement of pesticides in soil. This is a suggested procedure of Good Modelling Practice (GMP) obtained in the Cost Action 66 project (Vanclooster et. al., 2000). There were three main sources of information that the

parameter estimation was based on: measurements or calculation based on measurements, the PRZM3 manual or other literature sources and expert judgements.
After calibration with data from one year field study, the next step was validation with field data from another year. In the validated simulations it is not allowed, according to Good Modelling Practice, to change parameters except data which is dependent of the climate and pesticide properties if new pesticides are introduced in the experimental field.

Tables 7 – 11 show the main parameters which were chosen to calibrate the model. Table 7 shows the meteorological input parameters for the model.

Table 7. Meteorological input parameters for the PRZM3 - model

Site PRZM3 parameters	Syverud	Bjørnebekk
Pan factor	1	1
Snowmelt factor (cm/°C above freezing)	0.20	0.20
Pan factor flag (zero, daily pan evaporation data read; one, temperature data read)	0	0
Minimum depth of which evaporation is extracted (cm)	10	10

Table 8 shows the input parameters chosen for the crop parameters.

Table 8. Crop input parameters for the PRZM3 – model. Case study with a barley crop

Site PRZM3 parameters	Syverud		Bjørnebekk	
Number of different crop	1		1	
Barley	2005	2007	2005	2007
Emergence date	3/5	3/5	3/5	3/5
Maturation date	19/9	19/9	19/9	19/9
Harvest date	28/9	28/9	28/9	28/9
Maximum interception storage (cm)	0.16		0.16	
Maximum rooting depth (cm)	30		30	
Maximum area coverage of the canopy (%)	90		90	
Maximum canopy height at maturation (cm)	80		80	

Pesticide application parameters and chemical values are shown in table 9.

Table 9. Management input parameters for the PRZM3 model

Site PRZM3 parameters	Syverud		Bjørnebekk	
Year	2005	2007	2005	2007
Application date	16/6	7/6	16/6	7/6
Total application of propiconazole (kg/ha)	0.250	0.125	0.250	0.125
Total application of metalaxyl (kg/ha)	0.225	0.225	0.225	0.225
Depth of application (cm)	4		4	
Total depth of soil core (cm)	100		50	
Plant uptake factor	0.5		0.5	
Diffusion coefficient for the pesticide in air (cm^2/day)	4300		4300	
Henry's law constant propiconazole	9.2×10^{-5}		9.2×10^{-5}	
Henry's law constant metalaxyl	1.6×10^{-5}		1.6×10^{-5}	
Enthalpy of vaporization propiconazole (kcal/mol)	22.7		22.7	
Enthalpy of vaporization metalaxyl (kcal/mol)	22.7		22.7	

Table 10 gives an overview of the horizon and compartment thicknesses of the soil profile.

Table 10. Horizon and compartment thickness of the soil profile used in calibrated and validated simulations

Site	Horizon	1	2	3	4	5	Total core (cm)
Syverud	Horizon thickness (cm)	10	15	25	20	30	100
	Compartment thickness (cm)	0.1	5	5	5	5	
Bjørnebekk	Horizon thickness (cm)	10	10	30			50
	Compartment thickness (cm)	0.1	5	5			

Table 11 shows the decay rates and sorption coefficients of the pesticides propiconazole and metalaxyl.

Table 11. Decay rate (per day) and dissolved (DWRATE) and adsorbed (DSRATE) phase and Freundlich coefficients (K_F and $1/n^{ads}$) of propiconazole (P) and metalaxyl (M) for each horizon used in calibrated and validated simulations

Horizon	Parameter	Syverud	Bjørnebekk
1	DWRATE P	0.00247	0.00481
	DWRATE M	0.01824	0.00648
	DSRATE P	0.00247	0.00481
	DSRATE M	0.01824	0.00648
	K_F P	32.0	15.8
	K_F M	0.65	0.75
2	DWRATE P	0.00247	0.00481
	DWRATE M	0.01824	0.00648
	DSRATE P	0.00247	0.00481
	DSRATE M	0.01824	0.00648
	K_F P	32.0	15.8
	K_F M	0.65	0.75
3	DWRATE P	0.00178	0.00403
	DWRATE M	0.02166	0.00127
	DSRATE P	0.00178	0.00403
	DSRATE M	0.02166	0.00127
	K_F P	14.9	4.6
	K_F M	0.41	0.75
4	DWRATE P	0.00178	
	DWRATE M	0.02166	
	DSRATE P	0.00178	
	DSRATE M	0.02166	
	K_F P	14.9	
	K_F M	0.41	
5	DWRATE P	0.00178	
	DWRATE M	0.02166	
	DSRATE P	0.00178	
	DSRATE M	0.02166	
	K_F P	14.9	
	K_F M	0.41	
	$1/n^{ads}$ P	1.13	0.82
	$1/n^{ads}$ M	0.9	0.82

5.1.3 Results and discussion

The results from the field experiments in 2005 – 2006 have been used to calibrate the model from the two different sites at Syverud and Bjørnebekk. Data achieved from experiments done in 2007 – 2008 was used to validate the model by using the same soil type and pesticide properties, but different meteorological data.

5.1.3.1 Simulation of water flow

Various strategies were attempted in order to get a good adaption of the runoff. The parameter which had the biggest influence on the water flow was the curve number. The curve number method in the model, partitions the total amount of rainfall into water that runs off the surface and water that is infiltrated and/or stored on the surface. Curve numbers are a function of soil type, soil drainage properties, crop type and management practice (Carsel et al., 2006). The higher the curve number, the more frequently runoff will occur, and the higher the runoff volume per event will be.

To validate the hydrology module the parameters from the calibrated simulation of the field were used with meteorological data from 2007 – 2008. None of the parameters were changed.

Syverud

Figure 8 and 9 shows the calibrated simulations of surface water and drainage water from the experimental field at Syverud.

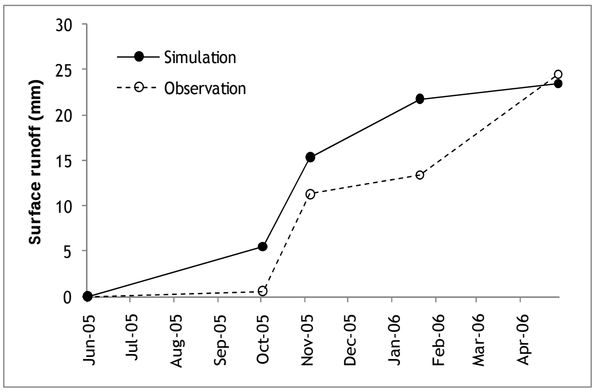


Figure 8. Cumulative calibrated simulation of surface water at Syverud, 2005 – 2006

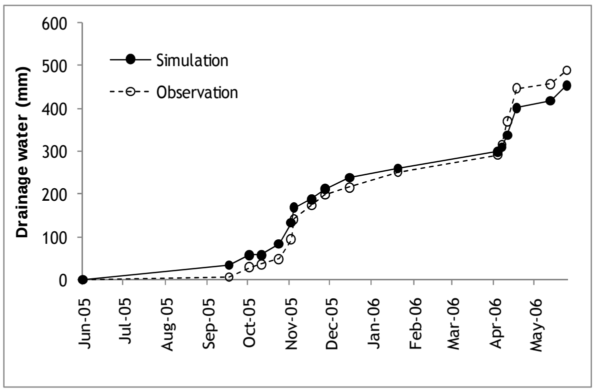


Figure 9. Cumulative calibrated simulation of drainage water at Syverud, 2005 - 2006

Figure 8 and 9 shows the results after calibration. The total amount of simulated water runoff was about 4 % lower than the observed values. According to Resseler et al. (1996) a satisfactory simulation occurs when the difference between the simulated and the observed amount of water do not exceed 25 % during a year. For drainage water there is quite good adaption between the simulated and the observed values. The difference is 7 % between the total amount of predicted and observed drainage water.

Figure 10 and 11 shows the validated simulation of surface water and drainage water.

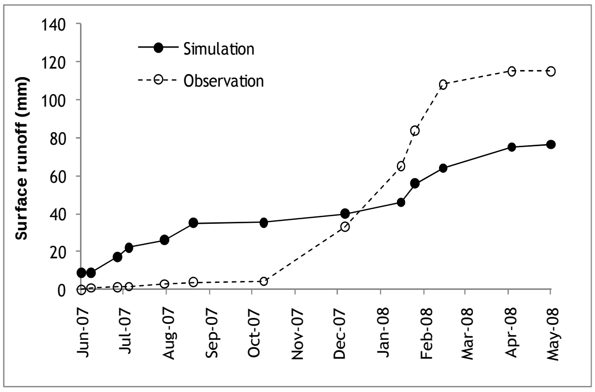


Figure 10. Cumulative validated simulation of surface water at Syverud, 2007 - 2008

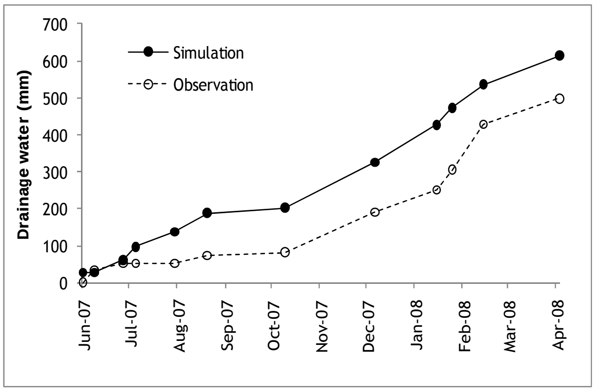


Figure 11. Cumulative validated simulation of drainage water at Syverud, 2007 - 2008

Figure 10 and 11 shows the results after validation. For surface water the difference between the total amount of simulated and observed values was 34 %, while the difference for drainage water was 19 %.

Bjørnebekk

Figure 12 and 13 shows the calibrated and validated simulations of surface water from the experimental field at Bjørnebekk.

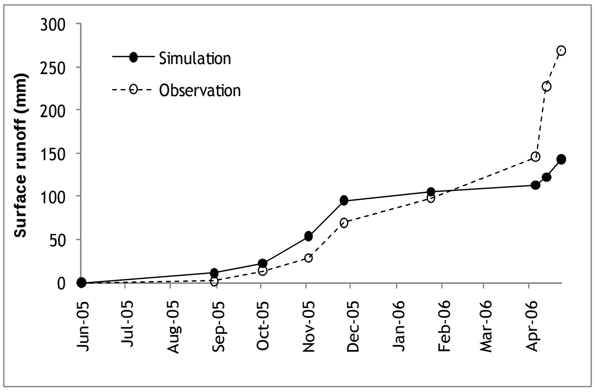


Figure 12. Cumulative calibrated simulation of surface water at Bjørnebekk, 2005 - 2006

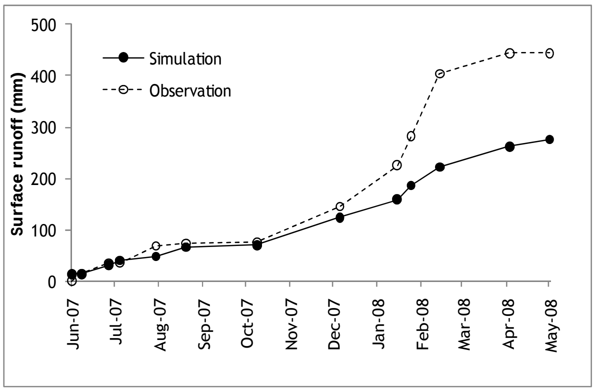


Figure 13. Cumulative validated simulation of surface water at Bjørnebekk, 2007 - 2008

Figure 12 shows the result after calibration. The difference between the total amount of simulated water and observed values were about 47 %. For validated data, the difference was 38 % (figure 13).

The cumulative amount of water simulated from both Syverud and Bjørnebekk was within a factor of 10 from the measurements. Reichenberger (2005) have done some considerations about the acceptability limit for the deviation between simulated and measured values. According to these considerations the acceptability limit for surface runoff was set to a factor of 10. Model and comparison studies have also shown that model predictions for individual runoff events typically matched field data within a factor of 2-3X. Cumulative values (e.g. runoff summed over the study period) typically agreed within a factor of 3X (FOCUS, 2001).

PRZM predicts the water flow (both surface runoff and drainage water) from Syverud and Bjørnebekk adequately. The timing of runoff events was simulated satisfactory in most cases, but there were some problems in periods characterized by frozen soil, freezing and thawing cycles, and high surface runoff during snowmelt events. PRZM considers the effect of snowmelt in the runoff equation, but the curve numbers are not adjusted to account for the effects of snowpack or frozen ground on runoff generation (Reichenberger, 2005).
The model also tends to overpredict the water flow for low-intensity rainfalls and small runoff events and to underpredict for high-intensity rainfalls and large runoff events, which is in accordance with Reichenberger (2005). This is probably due to the daily calculation step of PRZM and the non-consideration of actual rainfall intensities. Meteorological data used for environmental fate modeling generally consists of daily values for precipitation, temperature and evapotranspiration. The daily resolution of weather data is used primarily because daily data is easier to obtain than data with finer temporal resolution. For environmental processes such as leaching, which occur over time scales of weeks to years, daily weather data provides adequate resolution to describe the driving force of infiltration with a reasonable degree of accuracy. For more transient processes such as runoff and erosion, which have time scales of minutes to days, the use of daily weather creates significant uncertainties (FOCUS, 2001).

5.1.3.2 Simulation of the pesticides propiconazole and metalaxyl

To simulate the pesticides, pesticide parameters is implemented in the calibrated hydrology module.

Both K_D/ K_F – values and soil half life are sensitive parameters in the model. Pesticide runoff potential is sensitive to K_D/ K_F because pesticide transport to soil reduces concentrations in the water phase. This means that total surface transport is strongly influenced by erosion and transport with dissolved particles. The pesticide half life for a given compound is different in different soil environments. Soil temperature, water content and other variables affect the dissipation rate (Truman et al., 1998). K_D/K_F – values and pesticide half lives used in the simulations was decided in laboratory experiments (appendix 8.4).

Syverud
Figure 14 and 15 shows the calibrated values for the total amount of propiconazole in surface runoff and drainage water from Syverud.

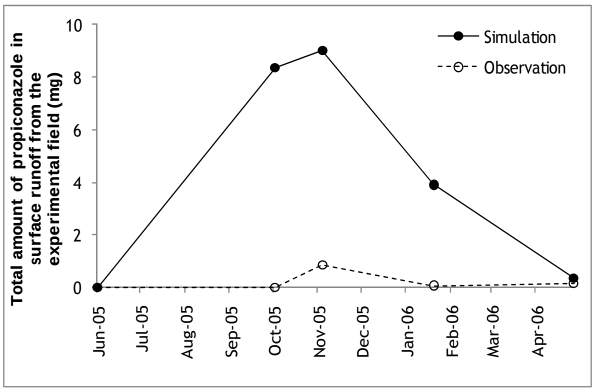


Figure 14. Calibrated values for the total amount of propiconazole in surface runoff from Syverud, 2005 – 2006.

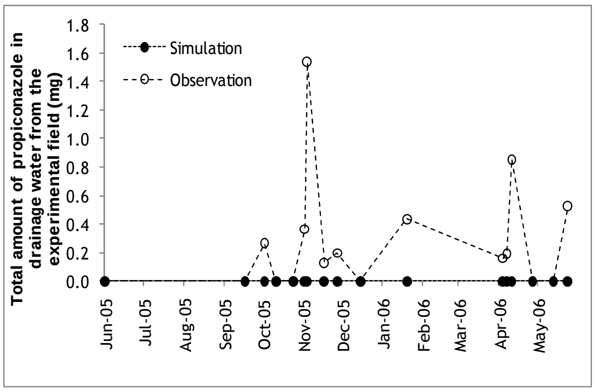


Figure 15. Calibrated values for the total amount of propiconazole in drainage water from Syverud, 2005 - 2006

Figure 16 and 17 shows the validated values for the total amount of propiconazole in surface runoff and drainage water from Syverud.

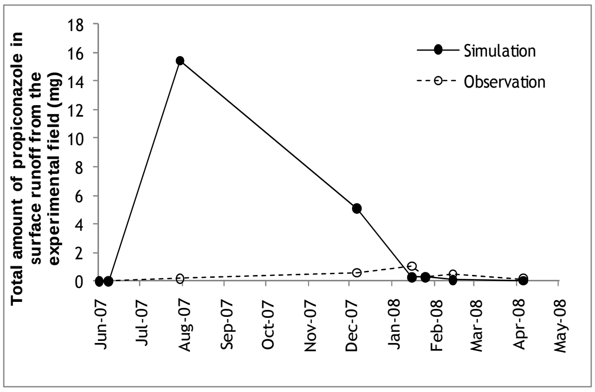


Figure 16. Validated values for the total amount of propiconazole in surface runoff from Syverud, 2007 – 2008

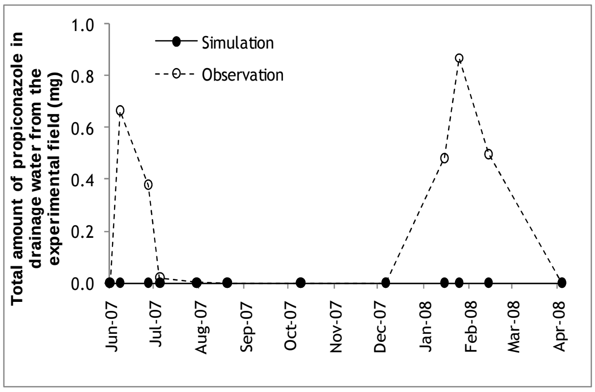


Figure 17. Validated values for the total amount of propiconazole in surface runoff from Syverud, 2007 – 2008

In general, the model estimates too much propiconazole in the surface water compared to observed values. In drainage water the model underpredict the concentrations of propiconazole. Propiconazole is a pesticide which adsorbs relatively strong to soil and dissolved soil particles in water. Observed values from drainage water shows that adsorbed propiconazole might be released by thawing in the spring.

Figure 18 and 19 shows the calibrated values for the total amount of metalaxyl in surface runoff and drainage water from Syverud.

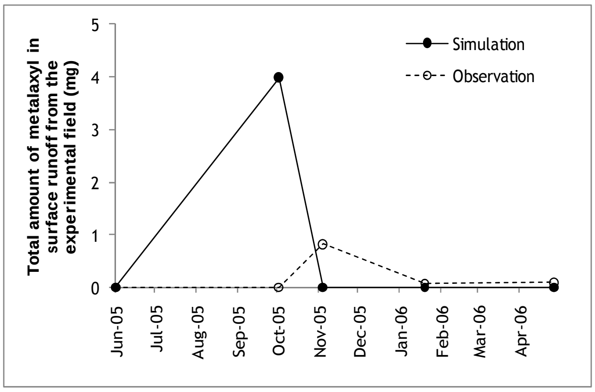


Figure 18. Calibrated values for the total amount of metalaxyl in surface runoff from Syverud, 2005 – 2006.

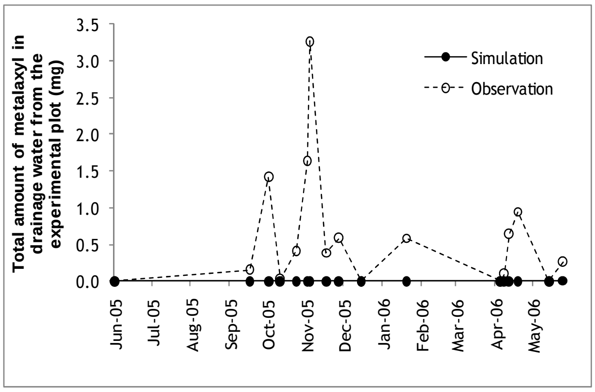


Figure 19. Calibrated values for the total amount of metalaxyl in surface runoff from Syverud, 2005 – 2006.

Figure 20 and 21 shows the validated values for the total amount of metalaxyl in surface runoff and drainage water from Syverud.

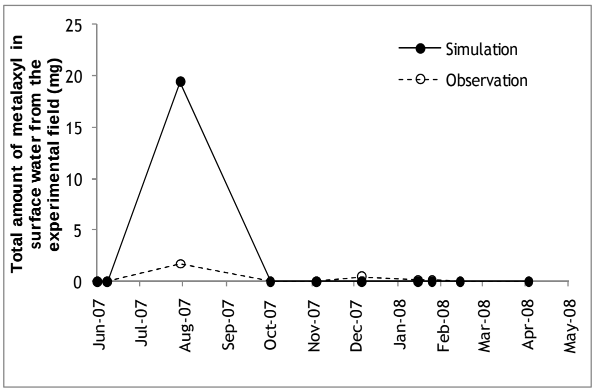


Figure 20. Validated values for the total amount of metalaxyl in surface runoff from Syverud, 2007 – 2008.

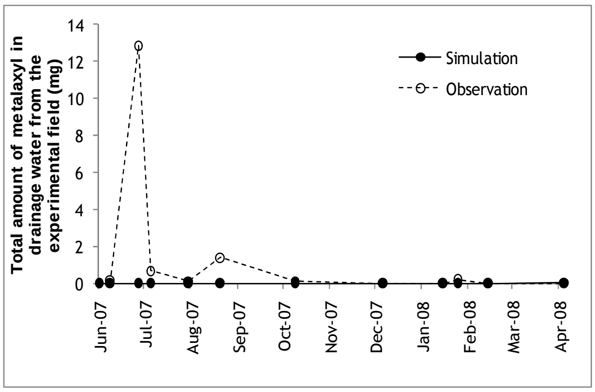


Figure 21. Validated values for the total amount of metalaxyl in surface runoff from Syverud, 2007 – 2008.

The model estimates too much metalaxyl in surface water compared to the observed values. Simulated and observed concentrations of the pesticide follows the same pattern, but with a tendency to give a high concentration at the beginning of the period. Metalaxyl is underpredicted in drainage water.

Bjørnebekk

Figure 22 and 23 shows the calibrated and validated values for the total amount of propiconazole in surface runoff from Bjørnebekk.

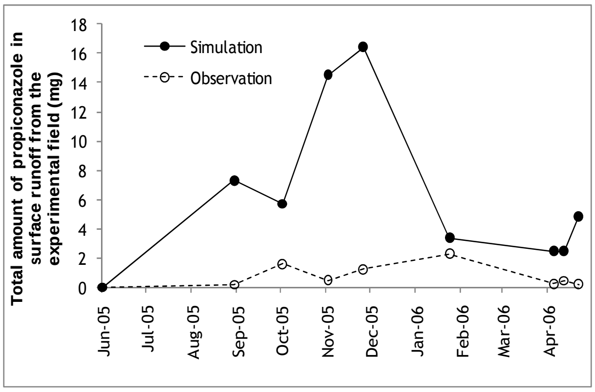


Figure 22. Calibrated values for the total amount of propiconazole in surface runoff from Bjørnebekk, 2005 - 2006

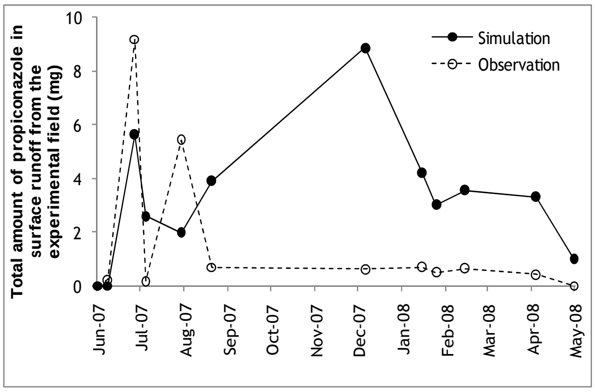


Figure 23. Validated values for the total amount of propiconazole in surface runoff from Bjørnebekk, 2007 – 2008

Figure 24 and 25 shows the calibrated and validated values for the total amount of metalaxyl in surface runoff from Bjørnebekk.

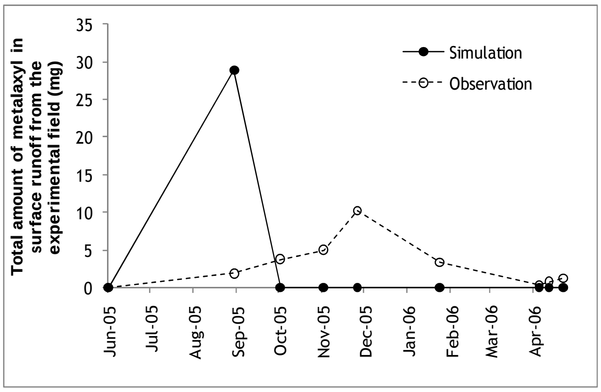


Figure 24. Calibrated values for the total amount of metalaxyl in surface runoff from Bjørnebekk, 2005 - 2006

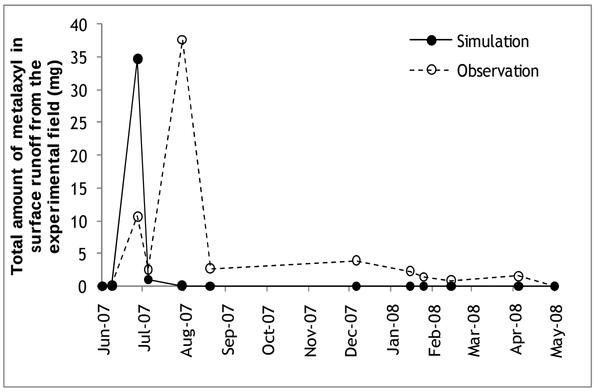


Figure 25. Validated values for the total amount of metalaxyl in surface runoff from Bjørnebekk, 2007 – 2008.

As for Syverud, the model estimates too much propiconazole in the surface water compared to the observed values. It seems, especially for this catchment, that propiconazole is distributed in two runoff events for both the periods 2005-2006 and 2007-2008.

The model estimates too much runoff for metalaxyl in surface water compared to the observed values. Simulated and observed concentrations of the pesticide follow the same pattern, but with a tendency for metalaxyl to give a high concentration at the beginning of the period.

As for the water flow, the model tends to overpredict pesticide runoff for low-intensity rainfalls and small runoff events and to underpredict for high-intensity rainfalls and large runoff events (Reichenberger, 2005).

5.1.3.3 Calculations of the annual mean concentrations

Table 12 and 13 shows the annual mean concentration of propiconazole and metalaxyl from Syverud and Bjørnebekk in the periods 2005-2006 and 2007-2008, respectively.

Table 12. Annual mean concentrations for metalaxyl and propiconazole in surface runoff and drainage water from the Syverud catchment in the periods 2005-2006 and 2007-2008

		Total amount of water (mm)		**Total amount of pesticides (mg)**		**Annual mean concentration (µg/l)**	
		Simulated	Observed	Simulated	Observed	Simulated	Observed
2005-2006	**Surface runoff**	23.4	24.5				
	Metalaxyl			3.99	0.98	*0.424*	*0.100*
	Propiconazole			21.6	1.07	*2.296*	*0.109*
	Drainage water	454	489				
	Metalaxyl			0.0025	10.4	*1.4E-05*	*0.053*
	Propiconazole			2.5E-18	4.65	*1.37E-20*	*0.024*
2007-2008	**Surface runoff**	76.5	115				
	Metalaxyl			19.4	2.46	*0.631*	*0.053*
	Propiconazole			21.1	2.72	*0.686*	*0.059*
	Drainage water	614	499				
	Metalaxyl			0.042	15.5	*0.0002*	*0.077*
	Propiconazole			2.18E-15	2.91	*8.8E-18*	*0.015*

Table 13. Annual mean concentrations for metalaxyl and propiconazole in surface runoff from the Bjørnebekk catchment in the periods 2005-2006 and 2007-2008

		Total amount of water (mm)		**Total amount of pesticides (mg)**		**Annual mean concentration (µg/l)**	
		Simulated	Observed	Simulated	Observed	Simulated	Observed
2005-2006	**Surface runoff**	143	269				
	Metalaxyl			28.9	26.5	*1.135*	*0.553*
	Propiconazole			57.1	6.7	*2.243*	*0.140*
2007-2008	**Surface runoff**	276	444				
	Metalaxyl			35.8	63.7	*0.729*	*0.806*
	Propiconazole			38.1	18.6	*0.776*	*0.235*

The tables show that PRZM is not a good model tool to simulate the amount of pesticides in drainage water. The results are somewhat better for the surface runoff. In the Syverud catchment, the model predicts the annual mean concentration for metalaxyl 4 and 12 times higher than the observed values. For propiconazole the model predicts the annual mean concentration 12 and 21 times higher than the measured values.

For the Bjørnebekk catchment the model simulates the annual mean concentration for both pesticides quite well. The ratio between predicted and measured values for metalaxyl has a factor of 1 and 2. For propiconazole the model simulates the annual mean concentrations 3 and 16 times higher than the observed values.

The simulated pesticide runoff losses are affected by uncertainty from both water transport and chemical transport simulation. According to Reichenberger (2005), the deviation between simulated and measured values can be expected to be higher for pesticide runoff than for the corresponding runoff volumes. But, if the purpose is to do an aquatic risk assessment, an under- or overpredicition of pesticide input into a surface water body by more than a factor of 10 cannot be considered as acceptable. The acceptability limit was therefore also set to a factor of 10 between simulated and measured values. According to these considerations, some of the results achieved of pesticide runoff from the catchments are acceptable. The simulations of metalaxyl are quite good from both catchments in the surface water. The simulations of propiconazole are somewhat poorer, especially from Syverud.

5.1.4 Conclusions

- PRZM predicts the water flow (both surface and drainage water) from the experimental fields adequately. The timing of runoff events was simulated satisfactory in most cases, but there were some problems in periods characterized by frozen soil, freezing and thawing cycles, and high surface runoff during snowmelt events.

- The cumulative amount of water simulated for both experimental fields were within a factor of 10 from the measurements.

- PRZM tends to overpredict both the water flow and pesticide runoff for low-intensity rainfalls and small runoff events, and to underpredict for high-intensity rainfalls and large runoff events.

- At both catchments the model estimates too much runoff for metalaxyl and propiconazole in surface water compared to observed values. Simulated and observed concentrations of pesticides in the runoff follow the same pattern, but with the tendency for metalaxyl to give high concentrations at the beginning of the period. At the Bjørnebekk catchment, propiconazole is distributed in two runoff events.

- Both pesticides are underpredicted in the drainage water. Observed values show that adsorbed propiconazole might be released by thawing in the spring.

- Calculations of the mean annual concentrations show that the simulations of metalaxyl are quite good from both catchments in surface runoff, with a ratio from 1 to 12 between predicted and measured values. The simulations of propiconazole are somewhat poorer with a ratio from 3 to 21 between simulated and observed values.

5.2 Simulations with MACRO

Lars Egil Haugen

5.2.1 Introduction

Forum for the Co-ordination of pesticide fate models and their Use (FOCUS), started in 1993, have developed "realistic worst case scenarios" FOCUS-scenarios of a Tier 1 EU-level assessment of leaching potential. The scenarios are lists of properties and characteristics (soil, plant and climate) independent of simulation models. The groundwater scenarios (9) have been implemented in four models PEARL, PELMO, PRZM and MACRO (only at Chateaudûn). The surface water scenarios (10) are developed for use with the simulations models MACRO, PRZM and TOXSWA. "The models interact with each other in the sense that either MACRO or PRZM is always combined with the fate model TOXSWA. If a drainage scenario (6 scenarios) is used, MACRO provides the input file for TOXSWA and if a run-off scenario (4 scenarios) is considered PRZM provides the input file for TOXSWA." (FOCUS 2000).

After a Tier 1 evaluation a further assessment of the leaching potential with respect to national conditions is important in the process of national authorisations. National scenarios in the Nordic countries are mainly developed with the simulation model MACRO. The scenarios are a combination of using MACRO as a groundwater scenario or a drainage scenario. The results described in this report, are for a drained clay soil located in south-eastern Norway (drainage scenario). The parameterisation of the MACRO model is from field experiments with small grains representing the main agricultural production in the region. The same model version of MACRO as used in the original FOCUS-scenarios (MACRO 4.2) is used.

5.2.2 Materials and methods

5.2.2.1 Parameterisation

The first parameterisation of MACRO was performed with measurements from a field experiment at Ås (1999-2001). The content of bromide, metalaxyl and isoproturon were measured in 20 cm soil layers down to about 1 m at 11 different times from autumn 1999 to spring 2001. Winter wheat was sown in September 1999 and 2000. The soil was an Aeric Endoaqualf (NIJOS 1999) with a clay content of 30-40 weight % in the subsoil and 1.9 % organic carbon in the topsoil. A preliminary conclusion from the field experiment was that the lack of comparison with measured water and solute fluxes made parameterisation uncertain. The simulation indicated relative high concentration of the pesticides in the drainage water which had to be evaluated further. This was the reason for extending the investigations to include field lysimeters, where flow and concentration in drainage water were measured.

The site with field lysimeter, Syverud, is 4-5 km from the first experimental site. The clay content is above 20 % (loam soil (USDA)) and the slope 13 %. The total carbon content is 3.2 %. Soil water retention was measured on samples from 3 depth at the following matrix potentials: 0, -0.8, -2, -5, -10, -50, - 100 and -1500 kPa. The plots, from which surface runoff and drainage water are collected, are about 6 m wide with a slope length of 25 m (totally about 200 m^2) (see Lundekvam (2007) for further description). Spring barley was sown in spring on the plots. Spraying with bromide, metalaxyl and propiconazole was performed at 16th June 2005 and 7th June 2007. Drainage and surface runoff were measured and volume-weighted water samples from drainage and surface runoff were collected.

Some soil characteristics for the site are shown in table 14. The reduction in degradation rate of the pesticide with depth is the same as recommended by FOCUS.

Table 14. Some soil physical characteristics for the loam soil at Syverud.

	Layer thickness, cm		Weigth percent			Dry			
Horizon	Measured	Used in simualtion	Clay	Silt	Sand	Bulk density, g/cm^3	Porosity, vol%	ASCALE [1)]	Ksat[2)] cm/time
Ap1	0-10	3/6	25	49	26	1,34	50,0	4	-
Ap2	10-23	6	25	49	26	1,37	48,8	4	181
Eg	23-50	6/5/10	23	53	24	1,65	40,1	20	78,3
Btg	50-100+	10/20				1,66	37,1	50	55,7
Bg	>100	80				1,63			

1) Estimated aggregate half-width (mm) – parameter in MACRO
2) Saturated hydraulic conductivity

The parameter file which gave the best results for bromide-transport from the first field experiment was used as the starting point. The following changes were performed according to site specific data and recommendation for FOCUS-MACRO parameterisation:

- Soil profile
    - Number of layers reduced to 15 from 22 (according to guidelines for FOCUS-MACRO)
- Start conditions
    - Soil water content set according to drainage depth and measured soil field capacity
- Soil physical characteristics
    - According to measured soil water retention for three depth at the site
- Site specific data
    - The snow melting function changed from 2 to 4,5 mm per degree.
    - Drainage distance changed from 10 to 8 m. Drainage depth 1, 0 m is the same.
- Solute transport
    - Used recommended values for dispersitivity (5 cm) and mixing depth (0.1 mm)
    - Anion exclusion set to 0.
- Plant growth
    - Spring barley
    - Deep root system
    - Critical water potential set to -100 kPa

The first experimental period 2005/06 was used for parameterisation and the second period 2007/08 for “validation”.

5.2.2.2 Climate

Air temperature and precipitation measured at Ås are shown in figure 26. The data shows higher precipitation early in the growing season in 2007 than in 2005. The winter 2007/08 is milder and have higher precipitation than the winter 2005/06.

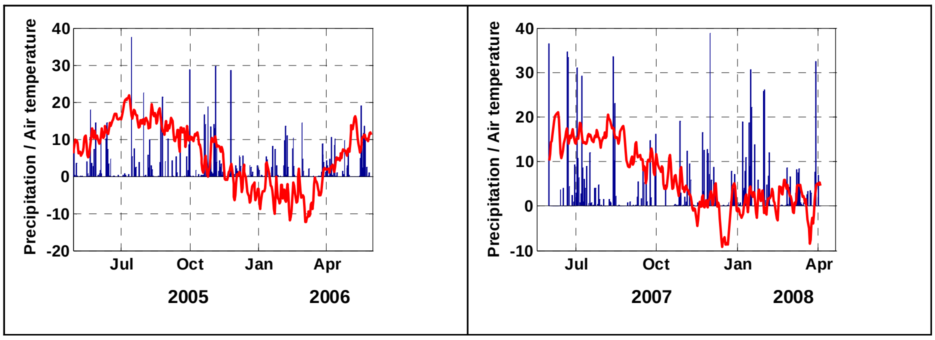


Figure 26. Daily values of air temperature (°C) (red line) and precipitation (mm) (blue bar) at Ås for the two experimental seasons

5.2.3 Results

5.2.3.1 Water flow

Water flow from both the drainage system and surface runoff were measured at the experimental site. The calibration of the water flow were performed on data from the first period, 2005 to end of 2006, were daily runoff values existed. For the second period only accumulated values of runoff between sampling dates were available.

During the first simulation period, 2005/06, there were 3 episodes with measured surface runoff. As expected the MACRO-simulation did not simulate these episodes. In figure 27a measured and simulated drainage flow is shown. The comparison, both as daily fluxes and accumulated values, shows a good fit. There is only a minor tendency to an underestimation of the peaks in the model simulations.

Measured and simulated values of accumulated drainage for 2007/08 also shows a good fit, but there is some deviation in early June probably due to local showers. Measured surface runoff during snow melt was about 100 mm in 2008 and is the main reason for the increased deviation during late winter 2008.

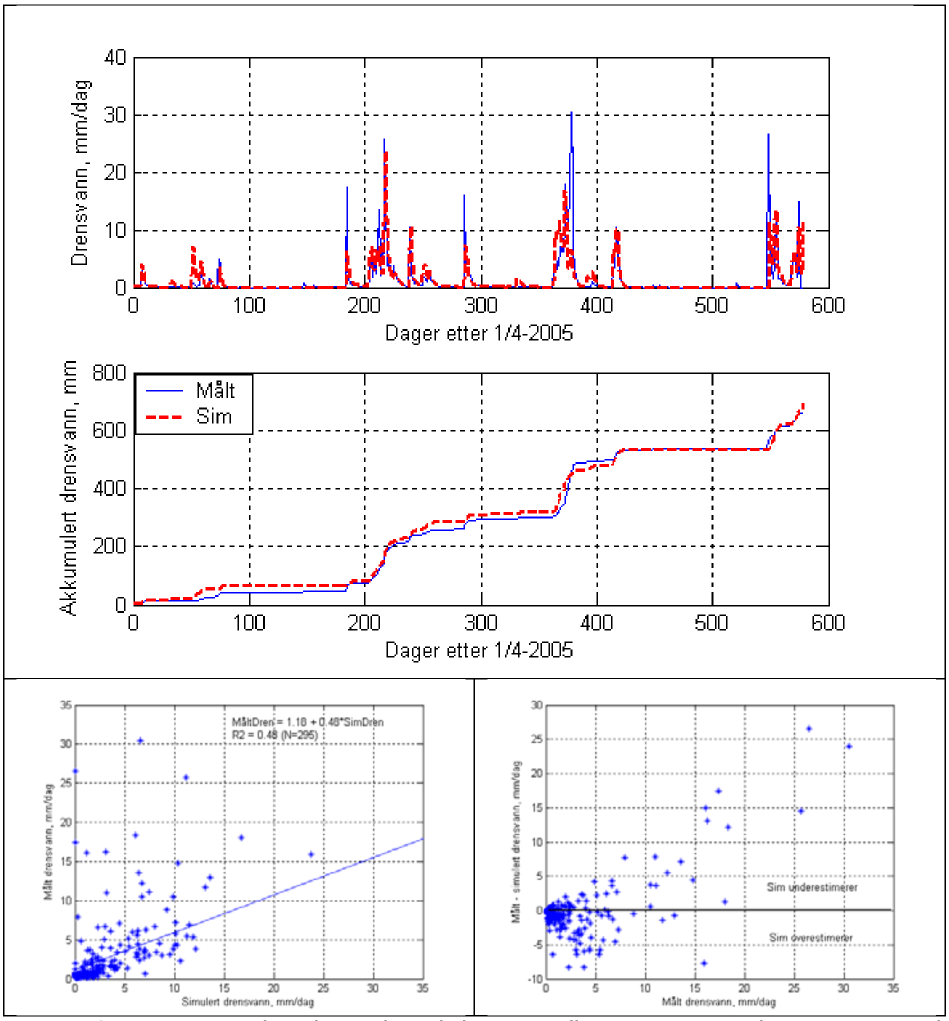


Figure 27a. Measured and simulated drainage flow rate (mm/day)(upper) and accumulated drain flow (mm) (middle) and measured versus simulated (lower left) and measured(x) versus difference between measured and simulated (lower right). The results are given as daily values from 1st April 2005.

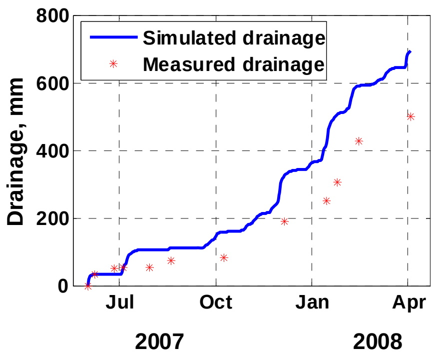


Figure 27b. Measured and simulated accumulated drainage flow (mm) 2007/08.

Measured and simulated concentration of bromide ("tracer for the water flow") in the drainage water showed larger disagreement, figure 28. The measurements showed that bromide reached the drainage system faster than simulated both years. It is interesting to note that one of the results from the first field experiment was that the bromide concentration measured in soil samples from different depth indicated a fast, early transport of bromide which also is found here. The highest concentration was measured in the early autumn drainage episode in 2005 and in the end of June 2007. Different parameterisations were tried for 2005/06, including anion-exclusion, but none of them were able to simulate the fast transport. The accumulated losses of bromide to drainage water until the spring next year was about the same for the measurements and simulation in 2005/06.

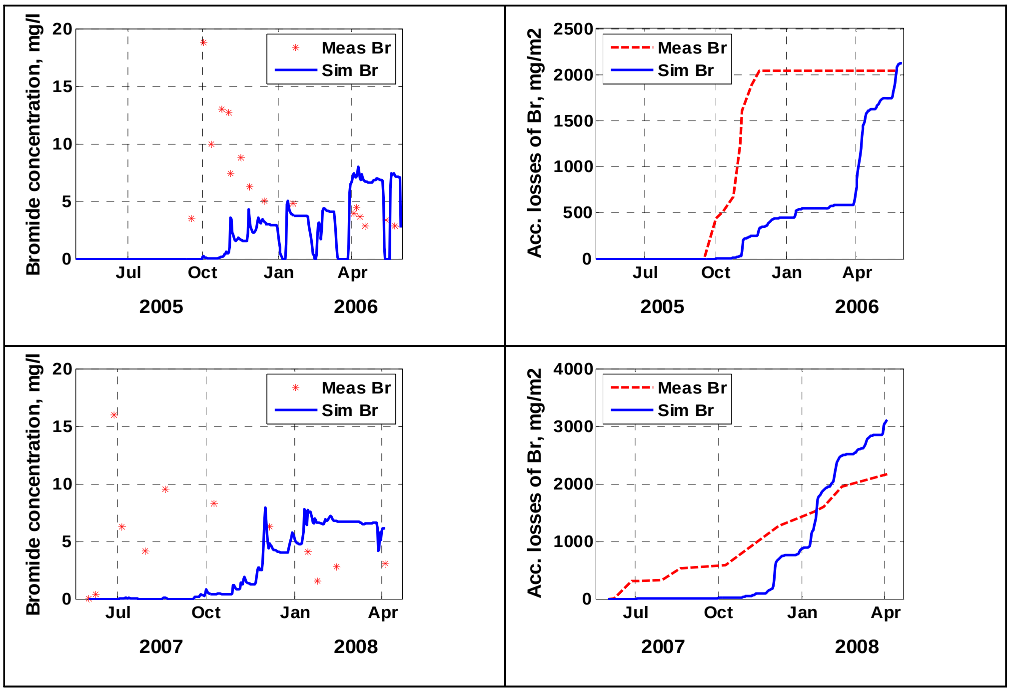


Figure 28. Measured and simulated bromide concentration and accumulated losses. The measured concentrations are in volume-weighted water samples for the periods between sampling.

5.2.3.2 Pesticides

Propiconazole, a strongly adsorbed pesticide ("immobile") and metalaksyl, a weakly adsorbed pesticide ("mobile") were sprayed in the spring 2005 and 2007. The parameter-file which gave the best fit for water flow (drainage water) was used for the pesticide simulation. Only values of adsorption and degradation rate were changed according to measured values from laboratory experiments.

Immobile pesticide

Low concentration of the pesticide was measured in the drainage water, < 0.1 ug/l. The simulated concentration and accumulated amount of propiconazole in the drainage water was ~0. The result is only shown for 2005/06. Turbidity, which was also measured in the drainage water (results not shown here) indicated that there could be a relationship between concentration of propiconazole and amount of particles in the drainage water. The disagreement between model simulations and field measurement indicate that other processes than ionic transport is important for strongly adsorbed pesticides. Model simulations, with synthetic rainfall, indicated that an ionic transport of strongly adsorbed pesticide most probably would occur in connection with heavy rainfall just after spraying.

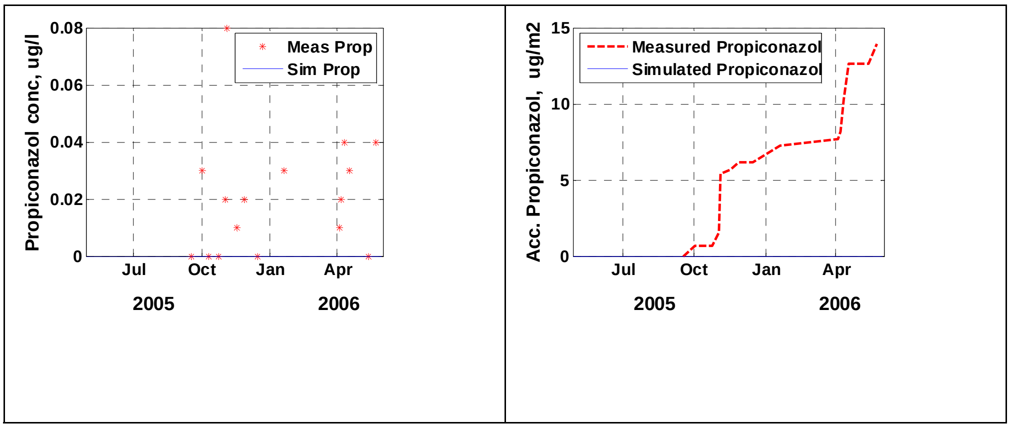


Figure 29. Measured and simulated concentration and accumulated losses of propiconazole. The measured concentrations are from volume-weighted water samples between sampling periods.

Mobile pesticide

The concentrations of metalaxyl, measured and simulated, are of the same order of magnitude in 2005/06. But as described for bromide, there is a tendency to a faster measured transport to the drainage system both years, see figure 30. For 2007/08 the measured concentrations are close to zero when metalaxyl reaches the drainage water according to the simulations. The accumulated values show that the simulated leaching of metalaxyl continues after the end of the measurement period and reaching 4-5 times higher amounts. The only way to reduce this seems to be a decrease in half-life of the pesticide, which is not investigated further here.

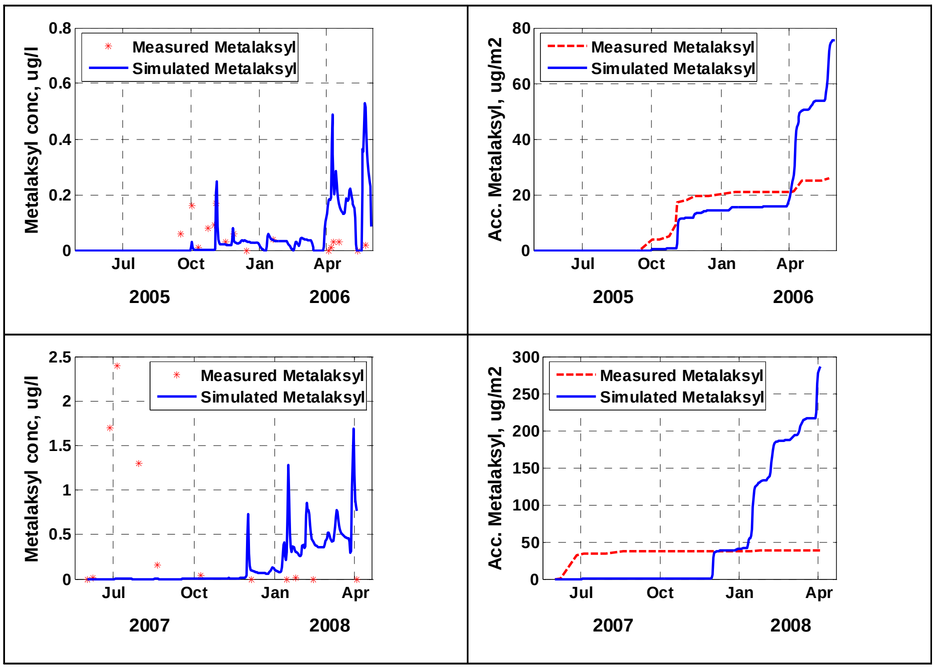


Figure 30. Measured and simulated concentration and accumulated losses of metalaxyl. The measured concentrations are for volume-weighted water samples for the periods between sampling.

6. Conclusions

Valuable knowledge is gained from controlled, small scale field experiments concerning runoff of pesticides. Loss of pesticides with different sorption capacity is to a large extent dependent on soil properties, agricultural practices and hydrological flow pattern. In the investigated period (2007/2008), special climate conditions promoted high loss of pesticides. The Syverud field has a high infiltration capacity which reduces the amount of water available for surface runoff. June and July 2007 received high amounts of precipitation, but there were no significant contribution from surface runoff until late autumn and winter. Transport of water through the drainage system contributed especially with high values in the late autumn and winter period. Special climatic conditions during the winter season, with high temperature and precipitation values, explain the high runoff during the cold season. The soil at Bjørnebekk is more susceptible to erosion and surface runoff compared to Syverud. High amounts of water are transported as surface runoff at Bjørnebekk due to low infiltration capacity. The highest amount of runoff was observed during late autumn and winter, such as for Syverud.

The largest losses of metalaxyl occurred at Bjørnebekk, at plots subject to autumn ploughing. Less transport of metalaxyl from the plot without autumn ploughing can be explained by less surface runoff, especially at the period shortly after the pesticide application. Low runoff values at the SPL plot, especially during the summer months, when the pesticide concentrations are at their highest, also explains the differences in average metalaxyl concentrations for the APL and SPL plots. Comparing the two different flow paths at Syverud, there was a larger loss of metalaxyl through the drainage than the surface runoff, as the water transport is much more extensive through the drainage system compared to the surface runoff.

Generally, there was a larger loss of propiconazole from Bjørnebekk compared to Syverud, especially at plots with autumn ploughing. There was a much higher loss of particles from the APL plot compared to the SPL plot at Bjørnebekk and for propiconazole which have a high affinity to soil surfaces, particles can facilitate the transport. At Syverud, the loss of propiconazole is rather low, as propiconazole to a large extent is retained in the soil.

Compared to a previous study (2005/2006), the present study (2007/2008) showed higher pesticide loss, due to high precipitation in the summer and high precipitation and temperatures in the winter of 2007/2008. For metalaxyl, the highest loss occurred at Bjørnebekk APL plots next to Bjørnebekk SPL plots for both the investigated periods. At Syverud, more metalaxyl were passing through the drains than the surface runoff for both the investigated periods. A larger amount of propiconazole was lost as surface runoff from both the Syverud and Bjørnebekk field in 2007/2008 compared to 2005/2006, due to higher surface runoff and transport of particles. For the present investigation period, the surface runoff of propiconazole from the SPL plots at Bjørnebekk was much higher than the transport through the drains at Syverud compared to the previous period were the loss of propiconazole was more similar.

The data obtained in the field experiments at Bjørnebekk and Syverud were used to validate the models PRZM and MACRO, and further to establish Norwegian scenarios for future risk assessment work. PRZM predicts the water flow from the experimental fields adequately. The timing of runoff events was simulated satisfactory in most cases, but there were problems in periods characterized by frozen soil, freezing and thawing cycles, and high surface runoff during snowmelt events. This is climatic conditions where Norway differs from other countries in Europe. At both catchments the model estimates too much runoff for metalaxyl and propiconazole in surface water compared to observed values. Simulated and observed concentrations in runoff follow the same pattern, but with the tendency for metalaxyl to give high concentrations at the beginning of the period. In drainage water, both pesticides are underpredicted. PRZM tends to overpredict both the water flow and pesticide runoff for low-intensity rainfalls and small runoff events, and to underpredict for high-intensity rainfalls and large runoff events. Calculations of the mean annual concentrations show that the simulations of metalaxyl are quite good from both catchments in surface runoff, with a deviation from 1 to 12 between predicted and measured values. The simulations of propiconazole are somewhat poorer with a deviation from 3 to 21 between simulated and observed values.

MACRO simulates the water flow in the period 2005/2006 as daily fluxes and accumulated values, and the comparison between simulated and measured values shows a good fit. Measured and simulated values of accumulated drainage for 2007/2008 show a good fit, but there was some deviation in early June probably due to local showers. Measured and simulated concentration of bromide in the drainage water showed larger disagreement. The measurements showed that bromide reached the drainage system faster than simulated both years. The simulated concentration and accumulated amount of propiconazole in the drainage water was almost zero. The measured concentration of propiconazole was <0.1 µg/l. The disagreement between model simulations and field measurement indicate that other processes than ionic transport is important for strongly adsorbed pesticides. Model simulations, with synthetic rainfall, indicated that an ionic transport of strongly adsorbed pesticides most probably would occur in connection with heavy rainfall just after spraying. Simulated and measured concentrations of metalaxyl are of the same order of magnitude in 2005/2006. For 2007/2008 the measured concentrations are close to zero when metalaxyl reaches the drainage water according to the simulations. The accumulated values show that the simulated leaching of metalaxyl continues after the end of the measurement period and reaching 4-5 times higher amounts.

7. References

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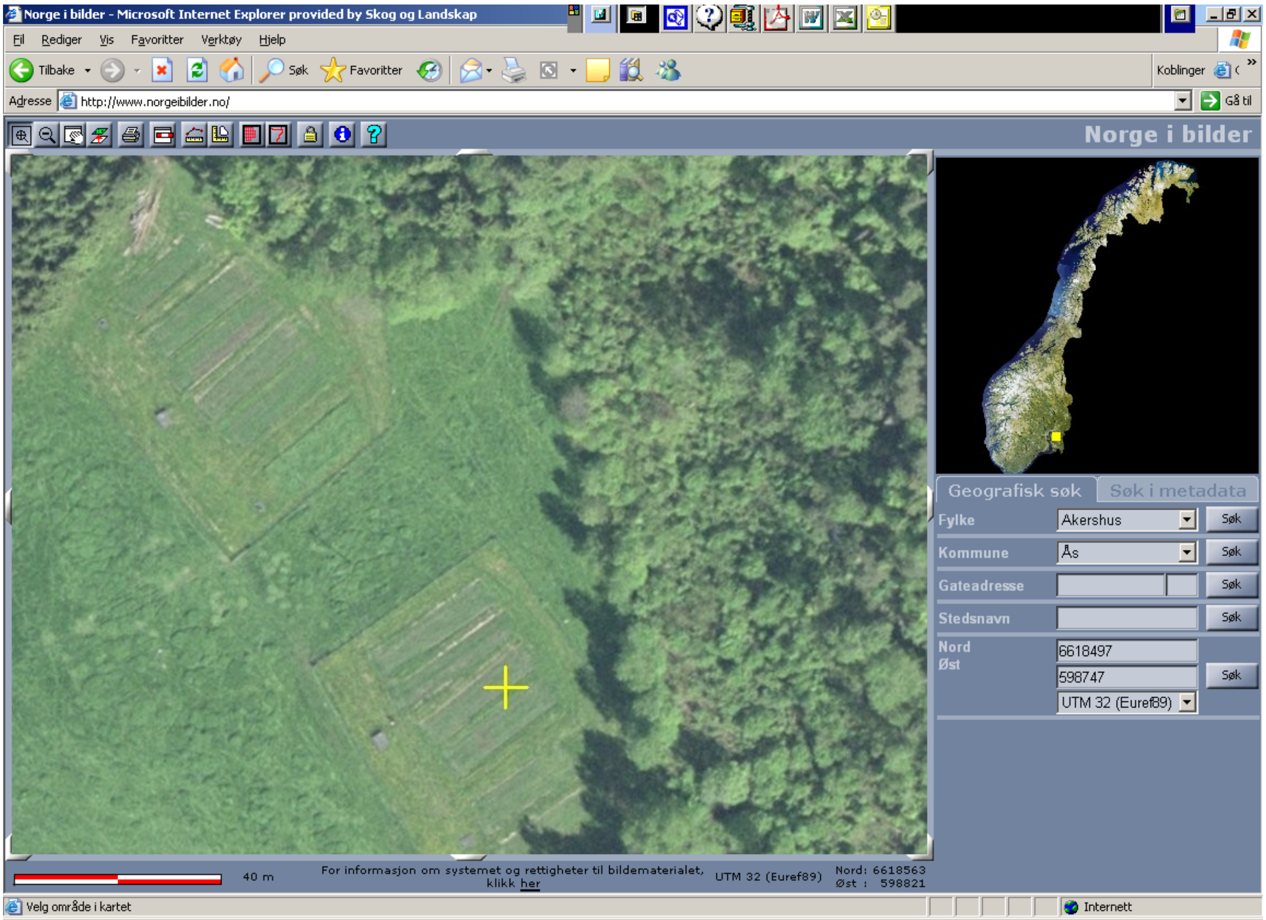
8. Appendixes

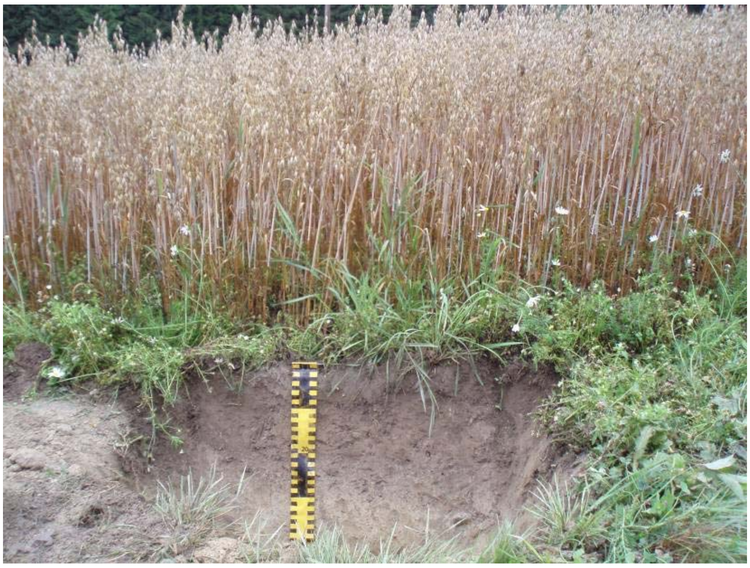
8.1 Soil characterization from Syverud and Bjørnebekk

Eivind Solbakken, the Norwegian Forest and Landscape Institute, 1431 Ås, Norway

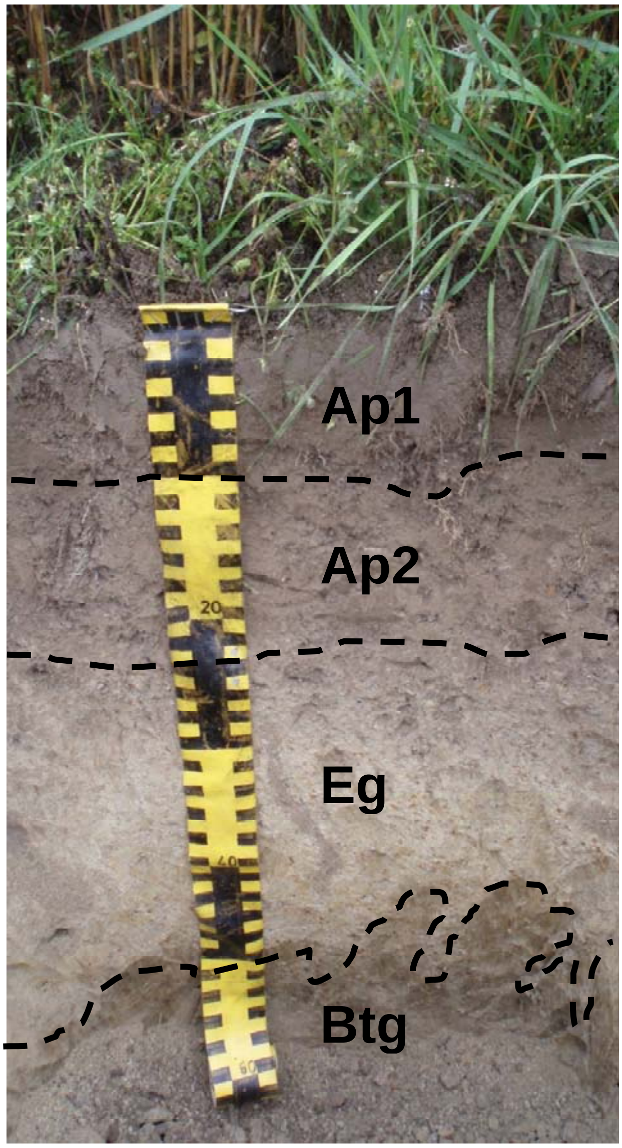
Syverud



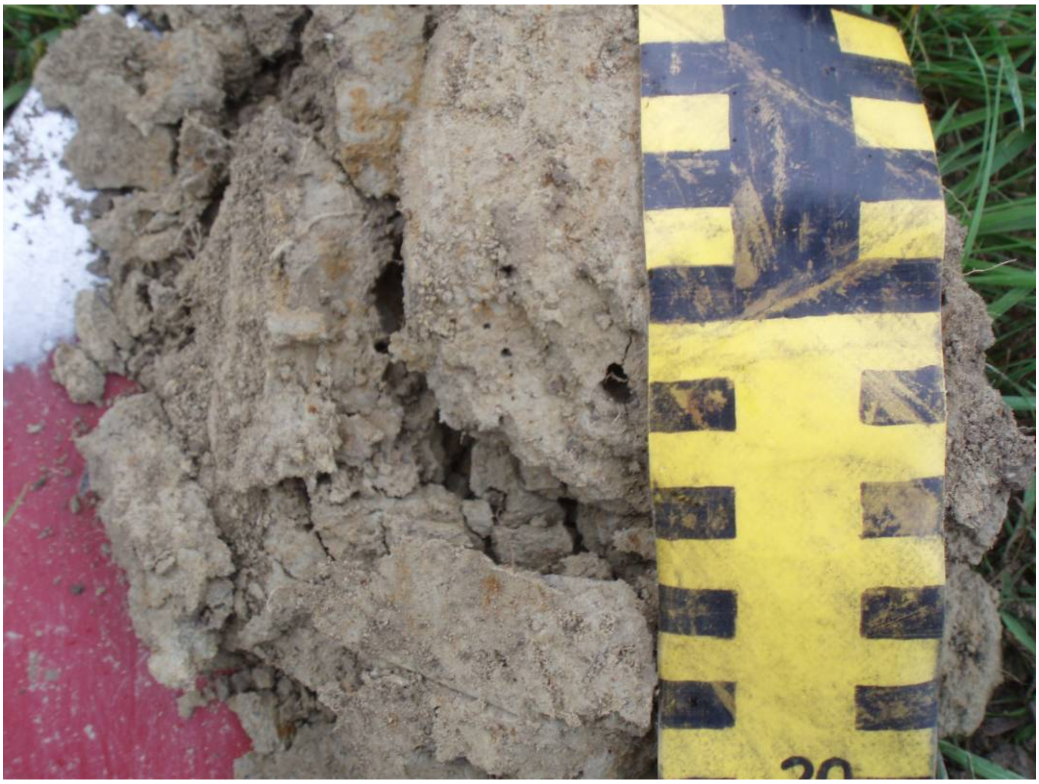
Picture 1: Location of the test site



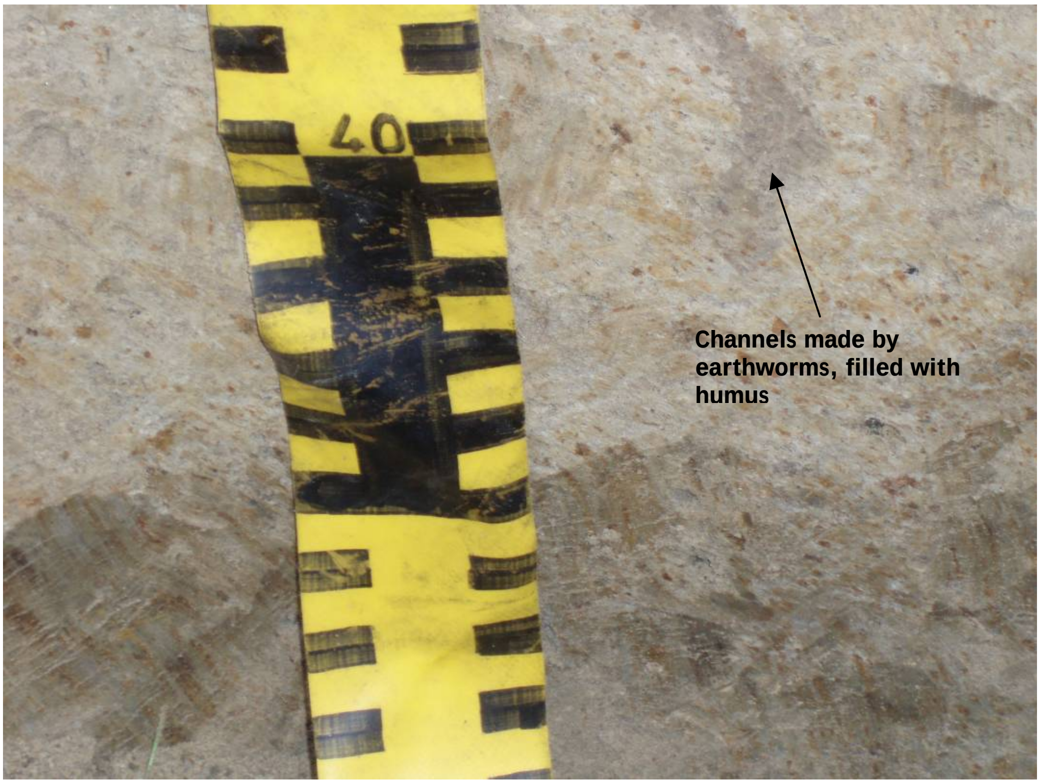
Picture 2: Profile from Syverud, represents ERk



Picture 3: All layers are sampled. Cg which starts at 70 cm was also sampled



Picture 4: A lot of macro pores through the profile. The profile was very dry, despite a lot of rain



Picture 5: The transition between Eg and Btg

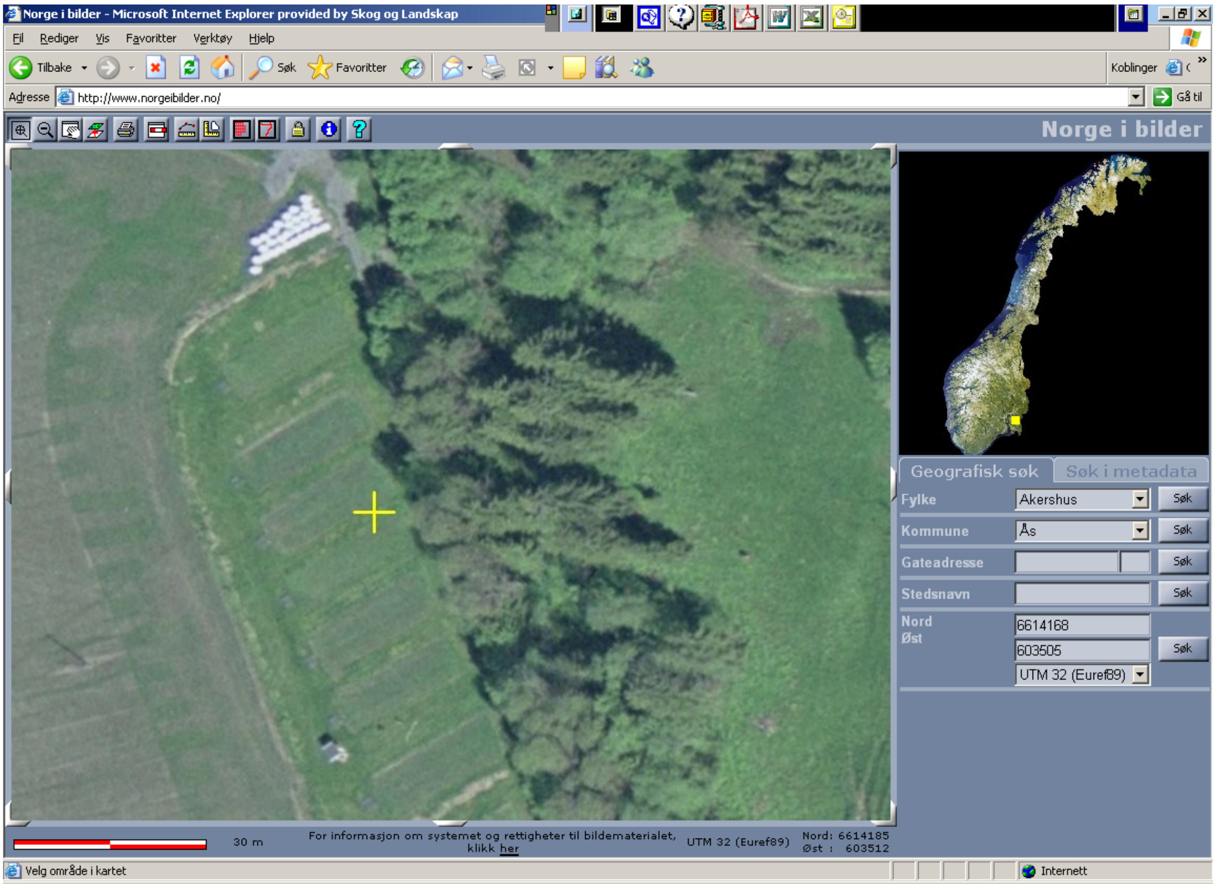
Table 1: Soil characterization, Syverud

Sjikt	Tykkelse	Frasikt	Kornstørrelsesfordeling (%)										
	cm	%	2-0,6 mm	0,6-0,2 mm	0,2-0,1 mm	0,1-0,06 mm	0,06-0,02 mm	0,02-0,006 mm	0,006-0,002 mm	<0,002 mm	Sand %	Silt %	Leir %
Ap1	0 - 10	6	7,23	8,47	5,48	4,87	14,3	17,9	14,8	27	26	47	27
Ap2	10 - 22	9	6,62	8,28	5,5	4,99	14,5	17,8	15,3	27,1	25	48	27
Eg	22 - 48	9	6,7	5,72	5,14	7,93	23,6	20,4	13	17,6	25	57	18
Btg	50 - 70	10	3,14	4,16	3,9	6,02	19,7	18,2	14,7	30,1	17	53	30
Cg	70+	13	2,43	3,53	3,3	3,88	14,2	17,4	16,7	38,6	13	48	39

Sjikt	Tykkelse	pH	Tot C	Tot N	Ombyttb. Kationer (meq/100g)					CEC	BM	Tørrst
	cm	H_2O	%	%	H	K	Na	Mg	Ca	meq/100g	%	%
Ap1	0 - 10	5,45	3,1	0,29	10,3	0,41	0,058	1,38	4,37	16,5	38	98
Ap2	10 - 22	5,47	2,9	0,28	9,5	0,37	0,057	1,46	4,69	16,1	41	98,1
Eg	22 - 48	5,59	0,4	0,05	3,9	0,13	0,039	0,74	1,93	6,7	42	99,2
Btg	50 - 70	6,00	0,3	0,05	3,4	0,22	0,076	2,28	6,33	12,3	72	98,7
Cg	70+	6,67			2,9	0,27	0,117	3,36	9,03	15,7	82	98,4

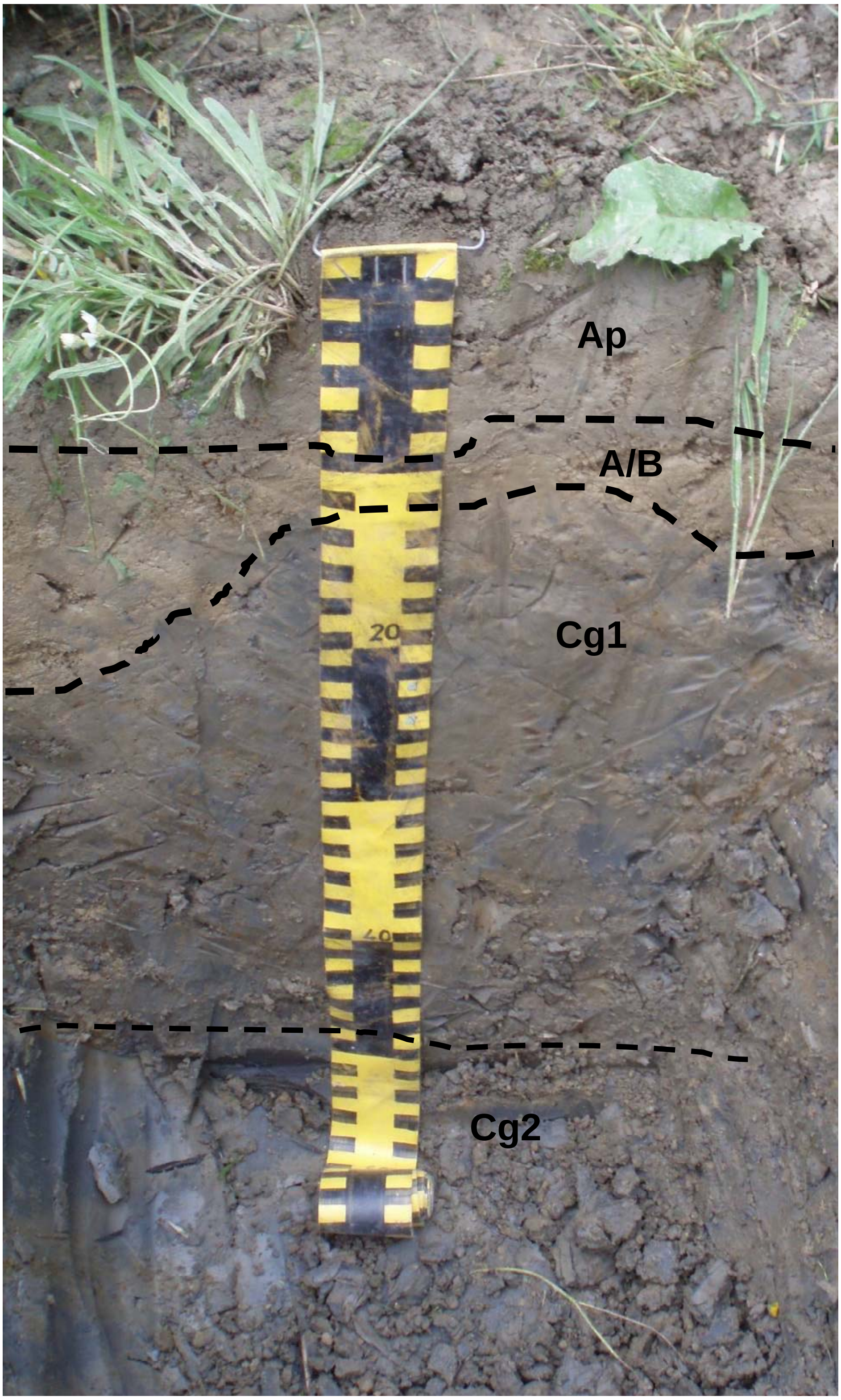
Classification (WRB 2006): Epistagnic Albeluvisol (Endoeutric, Siltic)

Bjørnebekk



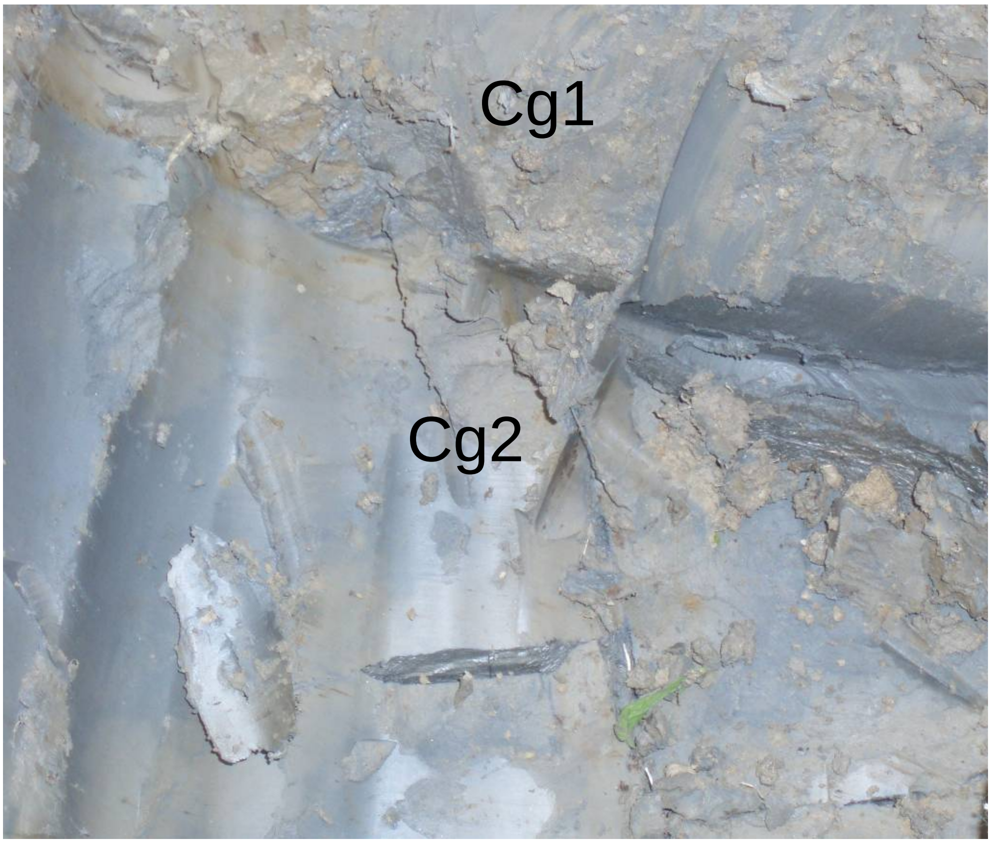
Picture 6: Location of the test site

Picture 7: Profile from Bjørnebekk. Artificially levelled silty clay loam



Picture 8: The profile was quiet wet. There were wet clay films in the pores and channels made by earthworms. There was a certain accumulation of water in the transition between A/B and Cg1. Cg1 had cracks in very coarse, heavy blocks. Cg2 was very solid and plastic. There were macro pores in the profile, but not so many as in the profile from Syverud. A sample was taken from Cg2 (88-100 cm)

Picture 9: Water transport through the channels made by earthworms. The transition between A/B and Cg1

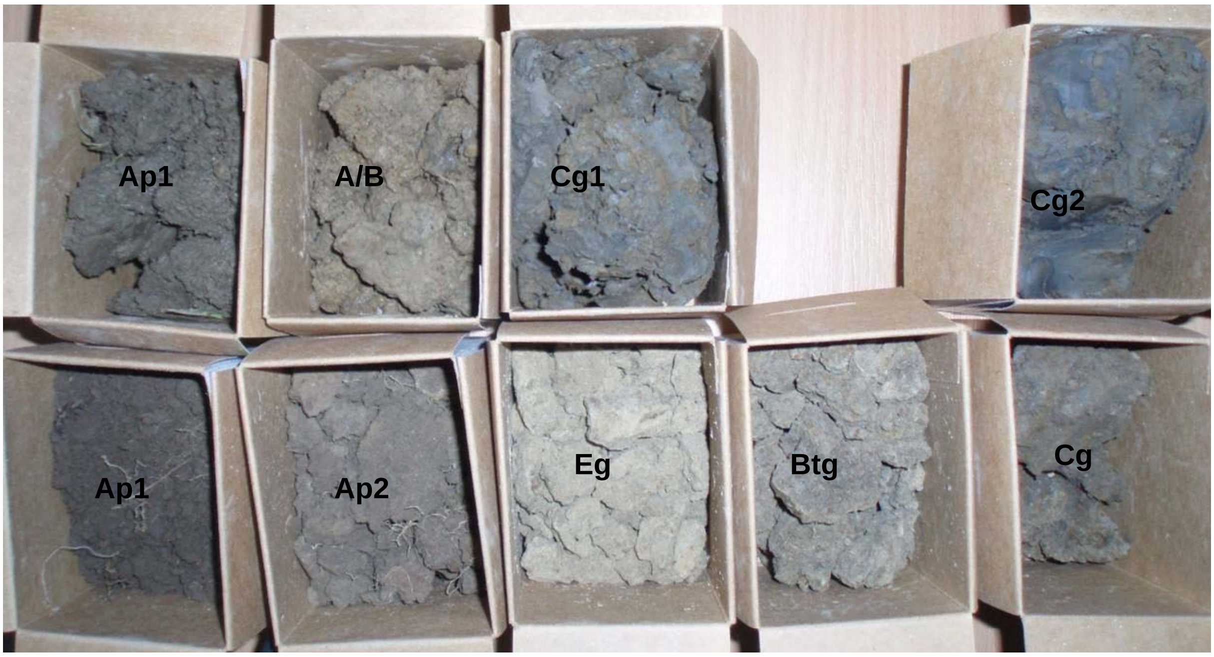


Picture 10: Cg2 seems very solid and dense

Tabell 2: Soil characterization, Bjørnebekk

Sjikt	Tykkelse cm	Frasikt %	Kornstørrelsesfordeling (%) 2-0,6 mm	0,6-0,2 mm	0,2-0,1 mm	0,1-0,06 mm	0,06-0,02 mm	0,02-0,006 mm	0,006-0,002 mm	<0,002 mm	Sand %	Silt %	Leir %
Ap	0 - 10	1	1,35	1,27	2,39	4,23	19,4	29,6	15,3	26,5	9	64	26
A/B	10 - 13	1	1,39	1,34	3,23	7,65	26,3	24,9	12,5	22,7	14	64	23
Cg1	13 - 50	0	0,05	0,26	0,39	0,72	10,1	29,5	17,4	41,6	1	57	42
Cg2	50+	0	0,07	0,12	0,19	0,41	10,7	26,7	16,5	45,4	1	54	45

Sjikt	Tykkelse cm	pH H_2O	Tot C %	Tot N %	Ombyttb. Kationer (meq/100g) H	K	Na	Mg	Ca	CEC meq/100g	BM %	Tørrst %
Ap	0 - 10	5,95	1,5	0,2	5,1	0,5	0,06	2,2	4,57	12,4	59	98,8
A/B	10 - 13	5,98	0,6	0,1	5	0,2	0,08	2	3,34	10,6	53	98,9
Cg1	13 - 50	7,08	0,3	0,1	2,3	0,5	0,09	4,4	6,91	14,2	84	98,8
Cg2	50+	7,64			2	0,6	0,13	3,5	8,52	14,7	86	98,8



Picture 11: Samples taken from the profiles at Bjørnebekk (at the top) and Syverud (at the bottom)

8.2 Plan for spraying

Sprøyting av metalaksyl og propikonazol på Syverud og Bjørnebekk

Plan nr: 02/2007

Prosjektnr.: 1110198 Norske Scenarier II

1. **Tidspunkt for sprøyting:**
   Uke 23, 7. juni 2007

2. **Personale:**
   Forsøksleder: Marit Almvik
   GLP-inspektør: Randi Bolli
   Sprøyteansvarlig: Kjell Wærnhus

3. **Feltene:**
   Syverud og Bjørnebekk i Ås Kart over feltene er vedlagt

4. **Tillaging av sprøyteløsninger:**
   Doser:
   Ridomil MZ 300 g/daa
   Tilt Top 100 ml/daa
   Væskemengde: 25 l/daa tankblanding, XR111002 dyser
   På Syverud skal det også sprøytes med lavdosemidlene Express og Gratil,
   se sprøyteplan 01/2007. De 4 pesticidene kan blandes i samme tank. Express må tilsettes/løses opp først. Express krever også at et klebemiddel tilsettes – med mindre de andre preparatene inneholder klebemiddel.

   Kaliumbromid: 10 kg/daa
   Væskemengde: 100 l/daa, XR111006 dyser

   Syverud: rute 3 og 4
   Sprøyteareal: 25 m x 3 drag (2.5 m bom) = 187.5 kvm/rute
   Væskeblanding: 15 kg
   Oppveid mengde:
   Ridomil MZ 180 g, Tilt Top 60 ml. Teoretisk forbruk: 4.7 kg/rute x2 = 9.4 kg
   Bromid: Hver rute sprøytes separat med ferdig oppløst blanding 2 kg bromid i 20 L vann. Teoretisk forbruk per rute: 18.8 liter

   Bjørnebekk rute 3 og 6:
   Sprøyteareal: 20 m x 3 drag (2.5 m bom) = 150 kvm/rute
   Væskeblanding: 12 kg
   Oppveid mengde: Ridomil MZ 144 g, Tilt Top 48 ml.
   Teoretisk forbruk: 3.75 kg/rute x 2 = 7.5 kg
   Bromid: Hver rute sprøytes separat med ferdig oppløst blanding 2 kg bromid i 20 L vann. Teoretisk forbruk per rute: 15.0 liter

5. **Prøvetaking**
   Før sprøyting:
   - ✓ Ta ut jordprøver fra rutene fra 0-60 cm sjikt, 3 stikk i hver rute.
   - ✓ Mål dekningsgraden av kornet.
   - ✓ Mål gjennomsnittlig høyde på kornet.
   - ✓ Ta bilder av feltene.
   - ✓ Hver rute deles i 4 underruter, deretter fordeles 3 petriskåler i hver underrute, totalt 12 skåler per hovedrute. Skålene merket A legges øverst, D nederst. Skålene merket ”1” legges til venstre, ”2” i midten og ”3” til høyre. Hver skål er 1.2 cm høy og fylles jevnt med overflatejord til toppen. Pass på å ikke presse jorda sammen når de overføres til skålene; tettheten av jorda skal være som den er når den ligger på overflata av feltet. Legg skålene på overflaten, oppå byggvekstene, slik at de er fritt eksponert for sprøyteväska. Tegn opp utleggingen.

Bruk bare ett sett skåler (4x12 stk.) for alle sprøytingene med lavdosemidler, propikonazol, metalaksyl og bromid (la skålene ligge til alle sprøytingene er utført).

Etter sprøyting:
- ✓ Bruk hansker og legg lokk på petriskålene og forsegl med parafilmstrimler langs skjøten.
- ✓ Før opp faktisk forbrukt væskemengde av sprøyteløsningene.
- ✓ Ta ut ca. 50 ml sprøyteløsning fra tanken av sprøyteløsningene i en plastflaske. Flaskene skal være merket med tittel, konsentrasjon, felt og dato.

6. Behandling/oppbevaring av prøver etter uttak

Emballasje

Etter prøvetaking overføres prøvene til egnet emballasje:
- ✓ Petriskålene overføres til merkede (felt, sprøytemidler og dato) plastposer.
- ✓ Jordprøvene overføres til palstposer

Transport/Lagring
- ✓ Prøvene bringes til laboratoriet samme dag.
- ✓ Ved ankomst laboratoriet registreres og lagres prøvene som angitt i prosedyre P0101.
- ✓ Jordprøvene og petriskålene fryses.

7. Registrering av data/forhold ved feltet under prøvetaking

Registrering av data gjøres i feltloggboken som inneholder skjemaet "SK34 Registrering av feltdata". I tillegg til de faste parametrene som står på skjemaet skal også alle variable faktorer som kan ha innflytelse på resultatet fra sprøytingen registreres. Dette kan være værforhold, fuktighet, topografi, vannansamlinger på feltet og plantedekke. I tillegg til registrering i feltloggboken, dokumenteres også disse forholdene ved bruk av digitalkamera.

8. Utstyrsliste

- Jordbor
- Slegge
- Tellefirkant (for å anslå dekningsgraden)
- Plastposer og merkelapper.
- Saks
- Kniv
- Skje (2)
- Linjal (2)
- Petriskåler (48 stk.)
- Parafilmstrimler (48 stk.)
- Engangshansker
- Plastflaske (6 stk., ca. 60 ml)
- Vannfast tusj
- Penn
- Feltkart (se vedlegg)
- Digitalkamera

9. Liste over dokumenter som tas med til feltet:

Feltloggbok med SK34 Registrering av feltdata
Sprøyteplan

KH07 Ekstern prøvetaking og prøvebehandling
SK01 Avviksskjema (2 stk.)

10. Vedlegg

Feltkart for Syverud og Bjørnebekk

Feltkart Syverud

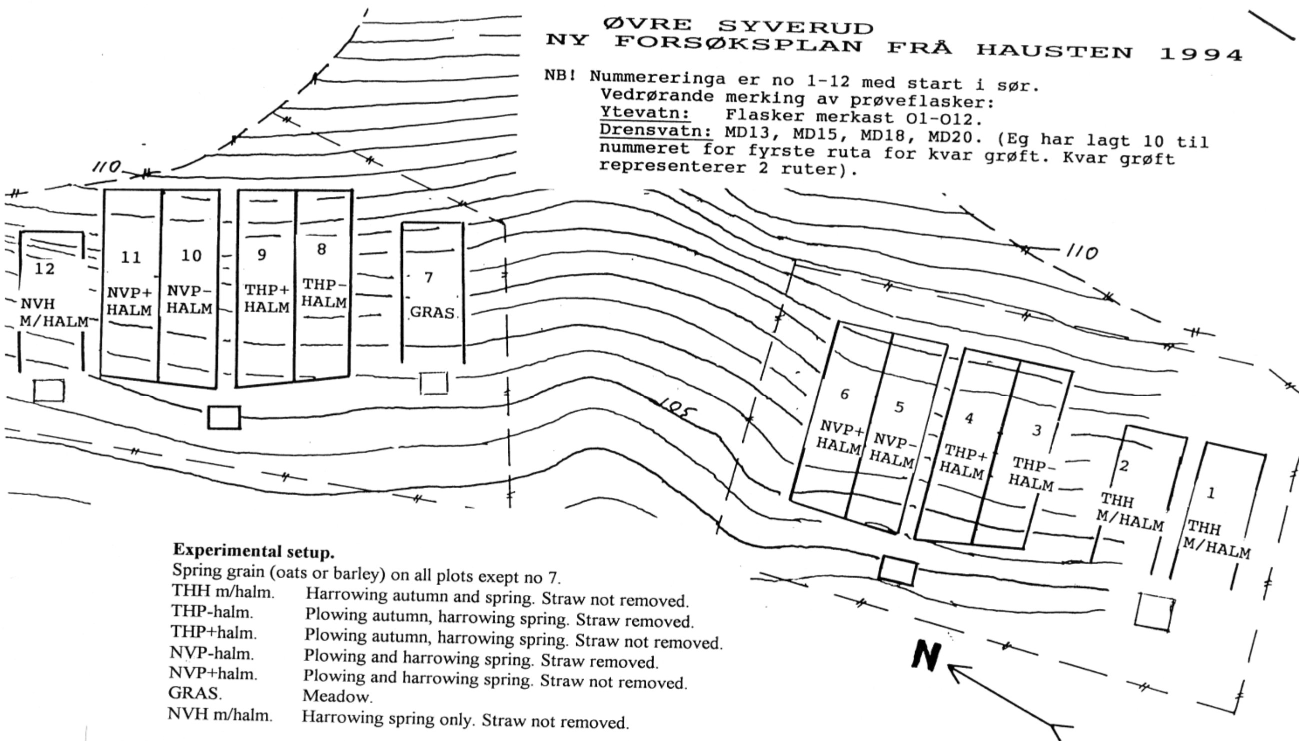


Figure 1. Layout and experimental setup.

Det er rute 3 og 4 som skal sprøytast.
Areal: Rute 3 er 199 m^2, rute 4 er 203 m^2.
Rutene er nummererte slik at den fyrste ruta ein kjem til er nummer 1.

Feltkart Bjørnebekk.

Table 1. Experimental layout.

1 Harr aut	2 Wint. Wheat Straw re- moved	3 Plow aut	4 Harr aut	5 Plow aut	6 Plow spring	7 Wint. Wheat Straw re- moved	8 Harr spring Ekstra straw added	9 Harr spring Straw re- moved	10 Harr spring Ekstra straw added	11 Plow spring

Det er rute nummer 3 og nummer 6 som skal sprøytast.
Rutene er ca 22 m lange.
Areal: nummer 3 er 178 m^2 og rute 6 er 172 m^2.
Rutene er nummererte slik at fyrste ruta ein kjem til er nummer 1.

8.3 Report from Kjell Wærnhus on the spraying with pesticides and bromide at the fields

Utført sprøyting på Syverud og Bjørnebekk 7/6 2007

Syverud
Sprøyterute: 25 x 7,5 = 187,5 kvm

Rute 3 og 4:

Preparat	Dose pr dekar	Oppveid mengde
Express	1,875 g	1,125 g
Dp-klebemiddel	0,05 % av væskemengden	7,5 ml
Gratil	8 g	4,8 g
Ridomil MZ	300 g	180 g
Tilt Top	100 ml	60 ml

Væskemengde 25 l/daa
Væskeblanding 15 l
Teoretisk forbruk for riktig dekardose = 9,4 l
Faktisk forbruk = 9,1 l

Bromidsprøyting
Væskemengde 100 l/daa
Væskeblanding 20 l
Teoretisk forbruk for riktig dekardose pr sprøyterute = 18,8 l
Faktisk forbruk rute 3 = 19,8 l
rute 4 = 18,5 l

Bjørnebekk
Sprøyterute: 20 x 7,5 = 150 kvm
Rute 3 og 6:

Preparat	Dose pr dekar	Oppveid mengde
Ridomil MZ	300 g	144 g
Tilt Top	100 ml	48 ml

Væskemengde 25 l/daa
Væskeblanding 12 l
Teoretisk forbruk for riktig dekardose = 7,5 l
Faktisk forbruk = 6,6 l

Bromidsprøyting
Væskemengde 100 l/daa
Væskeblanding 20 l
Teoretisk forbruk for riktig dekardose pr sprøyterute = 15 l
Faktisk forbruk rute 3 = 12,5 l
rute 6 = 14,8 l

12/6-2007 Kjell Wærnhus

8.4 Laboratory experiments

Degradation study

A degradation study has been carried out with the pesticides metalaxyl and propiconazole in the topsoil (0-20 cm) and subsoil (20-40 cm) from the experimental fields at Syverud and Bjørnebekk, according to an internal method (T01) based on the OECD guideline 307 (2002). The topsoil at Syverud is a loam/silt loam, while the topsoil from Bjørnebekk is a silty clay loam. The soil from the two plots at each field was mixed. The degradation study was carried out at 20 °C in the laboratory at 60 % of their water holding capacity. The soils were incubated for 12 weeks. Table 1 shows the results from the degradation study.

Table 1. Half-lifes (days) of the pesticides in the topsoil and subsoil from Syverud and Bjørnebekk

Soil	Depth	Metalaxyl ($t_{1/2}$)	Propiconazole ($t_{1/2}$)
Syverud	0-20 cm	38	281
	20-40 cm	32	389
Bjørnebekk	0-20 cm	107	144
	20-40 cm	546	172

The microbial activity in the subsoil from Syverud was significant higher than in Bjørnebekk, which was expected from measurements done of the microbial activity (henvise til forrige rapport). The topsoil from Syverud had a higher microbial activity but not significant higher than the soil from Bjørnebekk. It was therefore expected a faster degradation rate in the soil from Syverud.

<u>Metalaxyl</u>
The degradations rates for metalaxyl show a faster degradation in Syverud than in Bjørnebekk, as expected from measurements of the microbial activity. It is a slightly slower degradation in the Syverud topsoil (38 days) compared to the Syverud subsoil (32 days) which may be due to sorption to organic matter in the topsoil, making the metalaxyl molecule less available for microbial degradation.

The degradation of metalaxyl was particularly slow in the Bjørnebekk soil ($100<t_{1/2}<550$ days) probably owing to low microbial activity. Sorption processes could influence the degradation, as metalaxyl appears to be preferentially adsorbed on soil mineral surfaces (Sukop & Cogger, 1992). However, the sorption capacity of metalaxyl is usually low (K_d < 1), so the effect of sorption on degradation is regarded as low.

In the literature you find degradation rates for metalaxyl from 19 to 70 days at 20 °C. Previous studies for Norwegian soil types show degradation rates from 21 to 68 days. The degradation rate in the subsoil from Bjørnebekk is compared to this very long.

<u>Propiconazole</u>
Despite higher microbial activity in the soils from Syverud, propiconazole had a faster degradation in the Bjørnebekk soils as compared to the Syverud soils. This is probably due to a strong sorption in the Syverud soil, as organic matter plays a dominant role in the sorption of propiconazole. The soil from Syverud has almost twice as high content of organic matter as the soil from Bjørnebekk (Eklo et.al., 2008).

Faster degradation rate in the Syverud topsoil compared to the subsoil can be explained by the microbial activity which is twice as high in the topsoil.

Even if the microbial activity in the subsoil from Bjørnebekk was low, the sorption of propiconazole to the subsoil was three times lower than in the topsoil. These factors make the degradation rate not so different in the topsoil compared to the subsoil as you may expect.

A Danish degradation study with propiconazole in different topsoils (0-20 cm) gave half-lives from 106-444 days, which are in accordance with our study.

The results show that the soil from Bjørnebekk has little ability to degrade metalaxyl, but good ability to degrade propiconazole. The field has been sprayed with propiconazole the previous years, so adaption of the soils to propiconazole degradation could not be excluded. However, no lag-phase was observed in the degradation curves, indicating no effects of adaption. The degradation curves showed a strong correlation to the first order kinetic with $r^2 < 0.9$ in the Bjørnebekk soil.

Sorption study

A sorption study has been carried out with the pesticides metalaxyl and propiconazole in top- (0-20 cm) and subsoil (20-40 cm) from the experimental fields at Syverud and Bjørnebekk. The sorption study was carried out in accordance to the OECD guideline 106 (OECD, 1997).

The sorption isotherms of metalaxyl showed a good fit to both linear (r^2>0.96) and Freundlich (r^2>0.97) isotherms through the tested concentration range for both soils and soil depths. Metalaxyl is a mobile pesticide and the sorption of metalaxyl was in general low (K_d<1), but somewhat stronger in Bjørnebekk soil compared to Syverud soil. The results show a higher sorption in the topsoil compared to the subsoil at Syverud, corresponding with a higher organic carbon content. The results also indicated a slightly stronger sorption in Bjørnebekk subsoil compared to topsoil, which might indicate sorption to other compounds in soil than organic matter.

Based on the sorption study it was impossible to consider if the sorption isotherms for propiconazole were linear through the tested concentration range for both soils and soil depths. The large spread in the observed values for replicate samples may partly be explained by in-homogeneity of the test-solution added to the test tubes. Propiconazole is almost a non-mobile pesticide who generally shows a high degree of sorption to organic matter in soil. The studies indicated a connection between the sorption and the content of organic matter in soil. The strongest sorption appeared in the Syverud topsoil (K_d=25.7) followed by the Syverud subsoil (K_d=17.3) and the Bjørnebekk topsoil (K_d=20.9), and also the weakest sorption in the Bjørnebekk subsoil (K_d=5.7). Distribution coefficients adjusted for the content of organic matter in the soil, showed high values for propiconazole (K_{oc}: 791-1536).

A complementary sorption study for propiconazole at the mean concentration 2 mg/l, without the viscous solution Tilt Top Gel, confirmed the results from the sorption isotherm studies. The results from this point sorption study also showed that the presence of Ridomil MZ do not affect the sorption of propiconazole.

Microbial activity

The microbial activity in soil from the experimental fields at Syverud and Bjørnebekk was studied, because it will affect the degradation of the examined pesticides. Table 2 shows the results and the microbial activity levels are named as microbial respiration.

Table 2. Microbial activity in soil from the experimental fields at Bjørnebekk and Syverud

Site	Soil sampling depth (cm)	Microbial respiration rate (mg CO_2-C kg^{-1} dry soil $24h^{-1}$)
Syverud	0-20	9.8 (± 0.8) *
	20-40	5.1 (± 0.9) *, ‡
Bjørnebekk	0-20	8.5 (± 0.2) **
	20-40	3.3 (± 0.2) **, ‡

*, ** and ‡ indicate statistically significant differences when p<0.05.
(p=0.055 for ANOVA of soil samples from Bjørnebekk 0-20 versus Syverud 0-20.)

The observed soil microbial activity levels (table 2) show that the observed differences in degradation rates for the pesticides propiconazole and metalaxyl partly can be prescribed to differences in general activity levels. Bjørnebekk soil, in general, has a lower activity level than Syverud soil, as could be expected from the soil structure. The microbial activity decreased with increasing soil depth. This is in correspondence with the general observation in soils where soil microbial biomass and substrate availability decrease with depth.

The observed activity levels give the relative activities in the different soils and soil depths. Due to the large variability of this parameter, the results should not be extrapolated in time or in space. The observed values are within the range of results from other investigations in Norwegian sandy and silt loam soils utilizing the same technique (i.e. Stenrød, 2005; Stenrød et al., 2006).

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8.5 Manuscript from Island 2008

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Nordic Hydrological Programme NHP Report 5

INFLUENCE OF CLIMATE ON RUNOFF OF PESTICIDES

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ABSTRACT

Changes in climatic conditions affect concentrations and total losses of pesticides in runoff from agricultural fields. Measurements on runoff of pesticides with different mobility characteristics have been performed at three agricultural fields in SE-Norway. Volume proportional samples of both surface and drainage runoff have been collected at an annual bases for three years (2001-02, 2002-03 and 2005-06). At an annual scale, accumulated losses of pesticides in drainage runoff might be significant, especially for mobile pesticides. Predictions of environmental concentrations of pesticides have been performed from one of the fields, based on simulations with the MACRO model. Here, the drainage runoff of the mobile pesticide metalaxyl has been simulated for three different years with different climatic conditions. Generally, simulated values agreed well with measured values for annual losses of the pesticide, where climatic events of importance for the runoff of the pesticide were well accounted for.

INTRODUCTION

Regardless of water solubility or affinity for solid surfaces, pesticides that are applied at agricultural fields are frequently found in brooks and rivers (e.g. Ludvigsen and Lode, 2005). Concentrations and total losses of pesticides are, however, heavily dependent on climatic conditions. Especially, precipitation events shortly after application and melting-freezing episodes during winter are of great concern with respect to runoff of pesticides (Riise et al., 2006). The transport of pesticides occurs both through surface and drainage runoff, depending on soil and climate conditions. Concerning annual fluxes of pesticides, a significant part might pass through the drainage water (Riise et al., 2004).

At three agricultural fields in SE-Norway, primary data on runoff of pesticides with different mobility characteristics (bentazone, metalaxyl, propiconazole) have been collected, at a plot scale, for several years. Volume proportional samples have been taken from both surface and drainage runoff at the edge of the fields, to calculate annual fluxes. In addition, the pesticide losses to drainage from one of the sites have been simulated with MACRO, a dual permeability model (Jarvis, 1991). The aim of the study has been to improve the knowledge on factors contributing to the loss of pesticides from fields with different soil characteristics under different climatic conditions.

MATERIAL AND METHODS

Field experiments: Pesticides were applied in the beginning of June at three agricultural plots in SE-Norway (Askim, Bjørnebekk and Askim) the following years: 2001, 2002 and 2005. KBr was applied at the same time as the pesticides. Runoff measurements were performed from 1. June – 31. May.

Two of the sites - Bjørnebekk and Syverud – are located at Ås and one site at Askim, 30 km east of Ås. The soils at all sites have a clay content greater than 20 %; and are characterized as loam/silt loam to silty clay loams (Tab. 1). Two sites, Bjørnebekk and Askim, are artificially levelled. Surface runoff was measured at all sites, while drainage runoff was measured at Syverud and Askim only. Surface runoff was collected by a plastic half pipe at the end of the plots. Volume proportional samples were taken by using tilting buckets which added a small volume of water to a collecting can every second tilt. A further description of the experimental sites and setup can be found in Lundekvam (2007). In general, all plots were subject to either harrowing or ploughing both during spring and autumn. For the season 2005/2006 one plot with no tillage during autumn was also included (Fig. 3). The plots were fertilized and sown (spring barley) in spring.

Climate: Precipitation, air temperature and snow depth were measured at the agrometeorological field station (http://www.umb.no/imt/fagklim/metdata) at Ås, and soil frost depth is estimated from measurements with soil moisture resistance blocks at the Soil Water Monitoring Station at Ås (Hervé Colleuille, NVE pers.comm.).

Table 1. Soil properties of the agricultural plots at Askim, Bjørnebekk and Syverud

	Askim	Bjørnebekk	Syverud
Soil type	Silty clay loam	Silty clay loam	Loam/silt loam
Plot area (m^2)	324	178	402
Slope	13	13	13
Organic C (%)	1,1	1,0	3,0
Dry bulk density	1,40	1,52	1,22
Pore volume (%)	40,7	44,1	54,4
Drainable pores at -10 kPa (%)	5	6	16

Pesticides: Runoff of the following pesticides have been studied; bentazone (Basagran-87 % a.i.), metalaxyl (Ridomil MZ – 7,5 % a.i), and propiconazole (Tilt – 62,5% a.i). Important characteristics of the pesticides are given in Tab. 2.

Table 2. Partitioning coefficients (K_d and K_{oc}) and degradation rate ($T_{1/2}$) for selected pesticides estimated in Norwegian soils

	Bentazone	Metalaxyl	Propiconazole
K_d (cm^3/g)	0,38-0,81***	0,34-0,84*	17-26*
K_{oc}	24-60***	17-45*	791-1536*
$T_{½}$ (days)	> 84**	38-546*	144-389*

*Norske scenarier II 2005-2006, **Torstensen and Lode (2001) and ***unpublished data

RESULTS AND DISCUSSION

Climate:

Period 1 (2001-2002) had the highest annual air temperature, 6.7 °C (normal 5.3 °C), with only two months with mean temperatures below 0°C. The monthly air temperatures are usually below zero for 3-4 months at Ås (Fig. 1). The first winter 2001-02 (Period 1) had deepest average frost depth, longest period with soil frost, lowest number of days with snow cover and highest number of days with soil frost (Tab. 3 and Fig. 2). The two other winter periods (Period 2 and 3) were colder, but the longer and deeper snow cover these years reduced the soil frost depth compared to 2001-02 (Fig. 2).

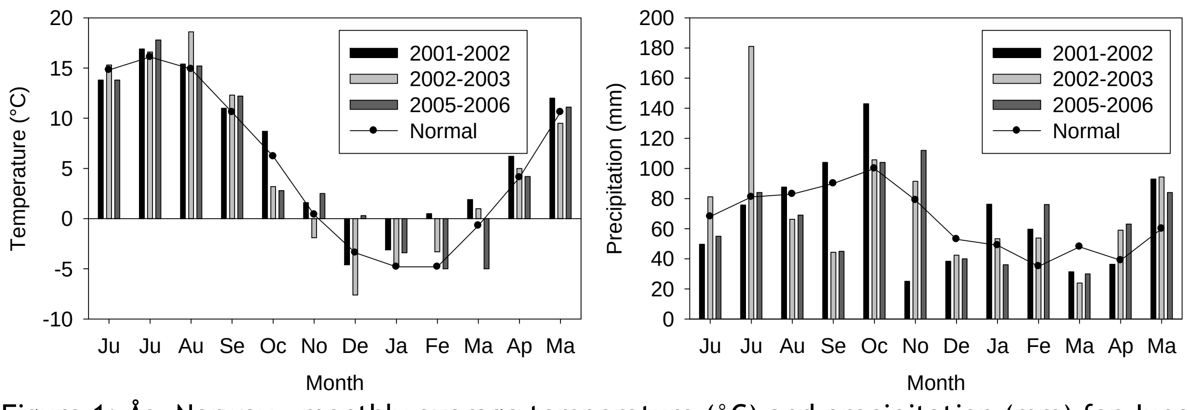

Figure 1: Ås, Norway - monthly average temperature (°C) and precipitation (mm) for June - May for Period 1 (2001-2002), Period 2 (2002-2003), Period 3 (2005-2006) and the normal period (1961-1990).

Table 3. Winter climate at Ås during Period 1, 2 and 3 (1. June - 31. May).

Year	Frost (days)	∑Temp. <0°C	Snow cover (days)	Avg. snow depth (cm)	Soil frost (days)	Avg. frost depth (cm)
2001-02	74	-286	55	5	82	-18
2002-03	105	-581	131	21	50	-8
2005-06	107	-505	123	29	66	-12

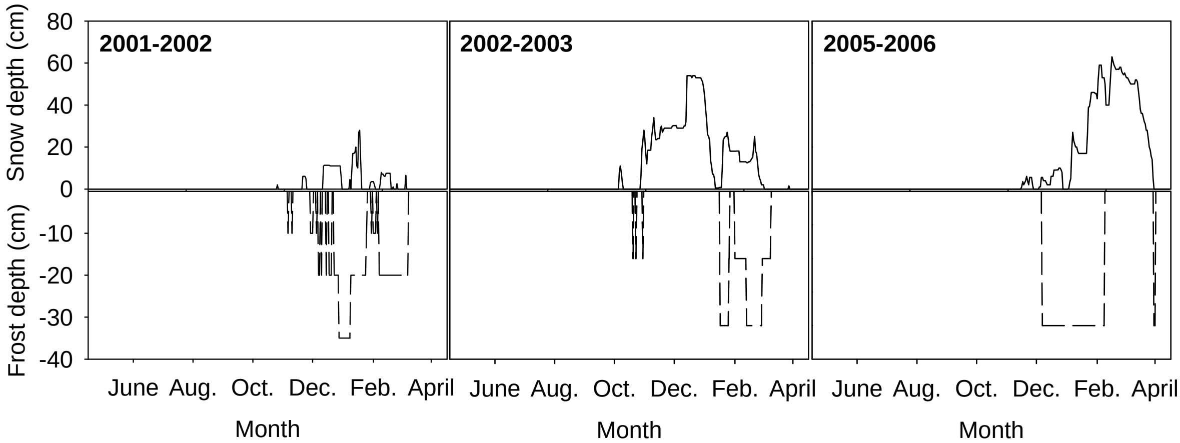

Figure 2. Snow depth (m) at the agrometeorological field station at the University of Life Sciences, Ås and soil frost depth (m) estimated from measurements with soil moisture resistance blocks at the Soil Water Monitoring Station, Ås (H. Colleuille pers.comm)

The annual precipitation was close to normal (785 mm) for all three periods; with largest deviation in total sum (+125 mm) for period 2 (2002-03). Both June and especially July 2002 (Period 2) had precipitation above the normal values Usually, the rainfall intensity for individual storms at Ås is in the range 1 to 4 mm/h, but in July 2002 (Period 2), 80 mm/h for one hour was observed (Lundekvam, 2007). Such rainfall events are rare at Ås and eventually occur in connection with thunderstorms.

Loss of pesticides different years

Generally, there were higher losses of pesticides from the more erodible soils at Askim and Bjørnebekk compared to Syverud. High content of soil organic carbon, high aggregate stability and high infiltration capacity contributed to lower losses of particles and thereby pesticides at Syverud. An exception was, however, some extreme rainfall events in the summer of 2002 which resulted in very high losses from all fields (Fig. 3). Pesticides are generally more sensitive to runoff shortly after application and the extreme events in the summer of 2002 was the main reason for the high losses. In addition measurements of snow cover and soil frost indicates that the snow melting in 2002-03 occurred on frozen soil, which contributed to high surface runoff. More than 3 % of applied bentazone was lost through runoff at Askim in Period 2, which is a very high number. Lowest runoff of pesticides occurred in 2001-02 (Period 1).

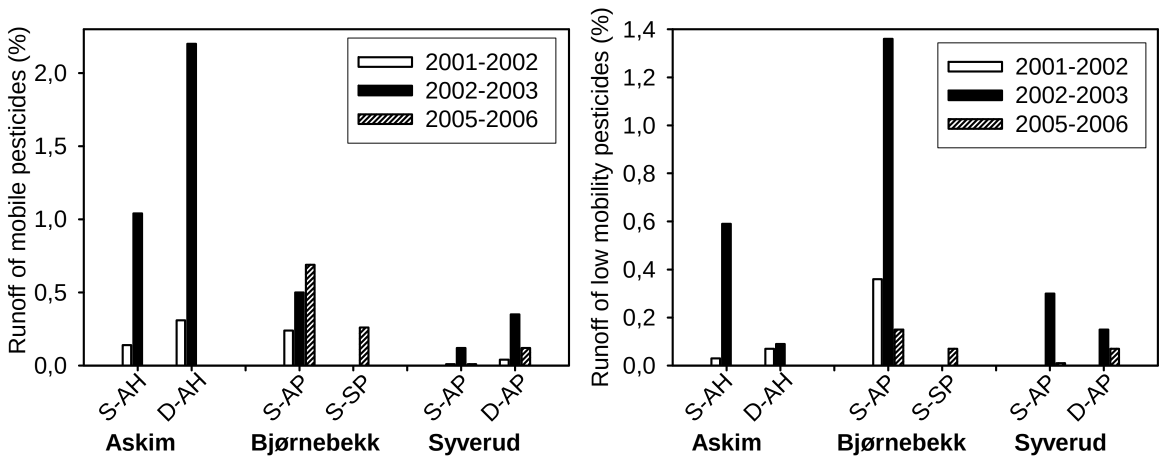

Figure 3. Loss of mobile (bentazone in 2001-03 and Metalaxyl in 2005-06) and less mobile pesticides (propiconazole all years) through surface and drainage runoff from three agricultural fields (Askim, Bjørnebekk and Syverud). S=surface runoff, D=drainage runoff, AH=autumn harrowing, AP=autumn ploughing and SP=spring ploughing.

While, the low mobility pesticide, in general, was most susceptible to surface runoff, drainage losses dominated for the mobile pesticides, which is in accordance with the mobility concept. However, significant amounts of both the mobile and less mobile pesticides were observed in the drainage water, which probably was due to bypass flows in the soil.

A more detailed runoff pattern is given for one of the sites – Askim for 2001-02 (Period 1), showing peak concentrations of pesticides in both surface and drainage runoffs early in the season, and thereafter a rapid decrease (Fig. 4). The peaks for the mobile pesticide appeared very early, prior to the peaks for both bromide and the less mobile pesticide. This transport behaviour can be attributed to a size- or anion exclusion effect, which increases the mobility of the compounds through the soil. Enhanced concentrations were also observed during freezing/thawing episodes during the winter. Although the levels are low, pesticides are measured a long time after their application, showing that their persistence is high.

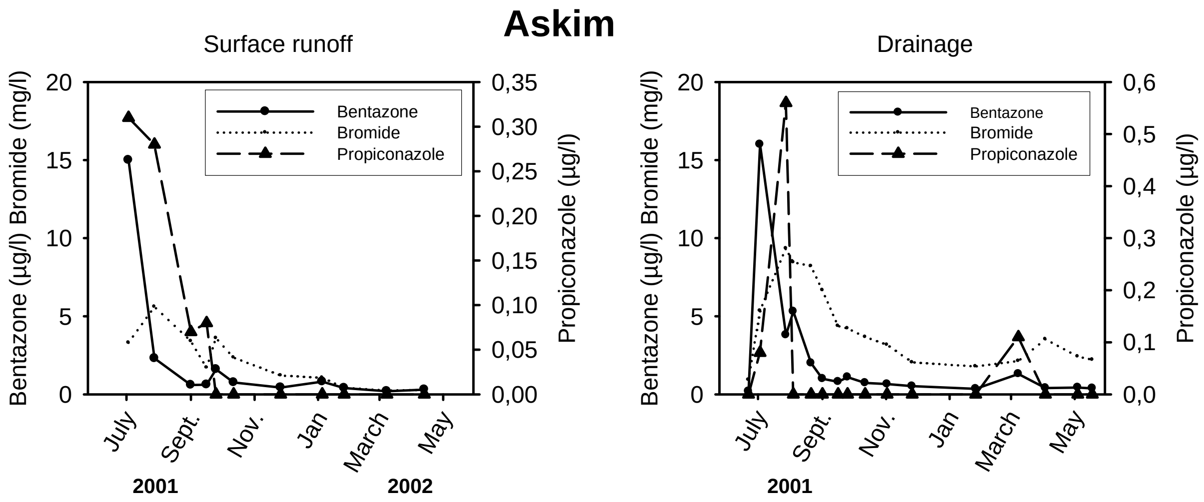

Figure 4: Runoff of mobile (bentazone) and less mobile (propiconazole) pesticides through surface and drainage water in 2001-2002 at Askim. Bromide was used as a tracer for the transport of water.

Mobile pesticide – measurements and simulations.

Major fluxes of water pass through the drainage system (Figs. 6 and 7), which also is shown to be an important transport pathway for pesticides, and especially mobile pesticides. Losses of pesticides show large differences between years. Here, the runoff of the mobile pesticide metalaxyl, is compared for different years through model simulation at the site Syverud. The MACRO-model (Jarvis 1991) was parameterized for the period April 2005 to the end of June 2006 against measurements (pesticide, bromide and runoff) at Syverud. As the site is the location for a proposed national Norwegian scenario, the FOCUS-guidelines for the parameterisation of the MACRO-model are followed. Here a short description of the parameterisation of the model is given. A more detailed description can be found in Eklo et. al (2008).

The soil water retention curves for different depth are shown in Fig. 5. The simulation was performed as a two-domain flow with the limit between domains set at -5 cm H_2O suction and with a saturated conductivity of the micro pores equal to 0.4 mm/hour. The critical potential for plant water uptake was set to -1.9 m H_2O. The half-life of Metalaxyl in the plough layer was according to laboratory measurements 38 days (T=20°C, optimum water content) and the distribution coefficient (K_d) equal to 0.56 cm^3/g. The decomposition rate was reduced according to FOCUS-guidelines (FOCUS 2000), a 50% reduction (compared to plough layer half life) for 40-60 cm depth, 70% reduction at 60 to 100 cm depth and no decomposition below 100 cm depth.

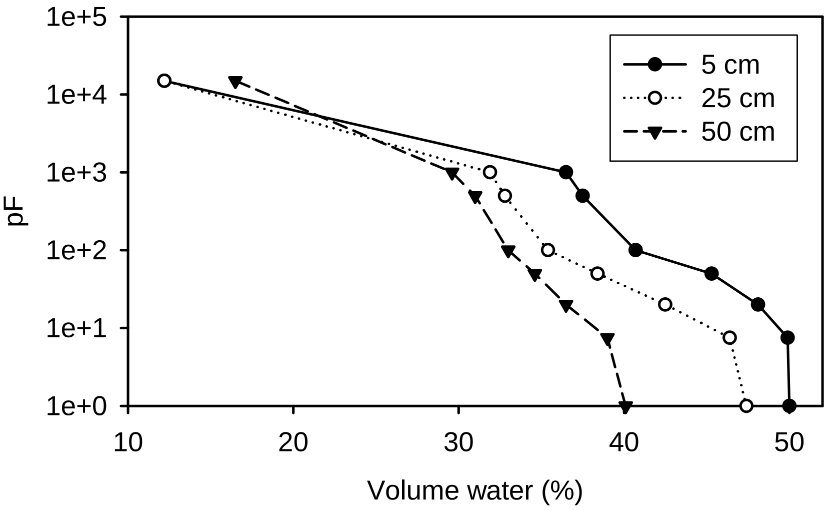

Figure 5: Soil water retention curves at different depths (cm) for Syverud.

The model was parameterized against data of drainage flow and the best fit, found by trial and error, are shown in Fig. 6. The agreement between measured and simulated drainage are quite good. The largest deviations are found around the peaks of the measured drainage fluxes. The simulated peaks correspond in time, but underestimate the drainage compared to measured values. Since daily climatic data is used in the simulation, a better time resolution in precipitation data could probably give a better fit to the measured peak values.

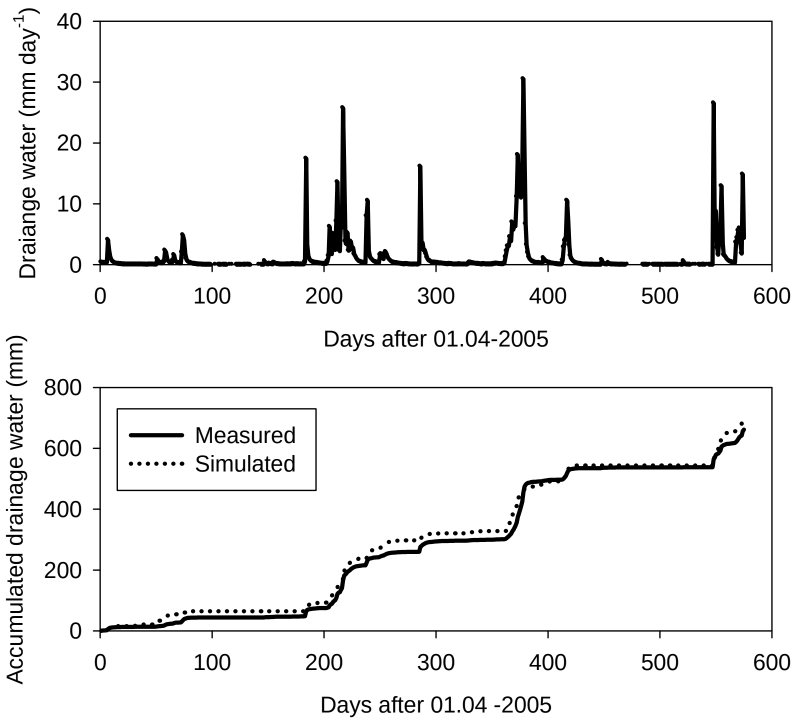

Figure 6: Measured and simulated values for runoff of drainage water (mm day^{-1}). Results are given as daily (a) and accumulated values (b).

The measurements of metalaxyl in the drainage water showed an earlier breakthrough than the simulations, the same pattern as for bromide (results not shown). At an annual scale (Fig. 7), simulated fluxes of metalaxyl, applied at an amount of 25 mg/m^2 each year, are in agreement with the results shown in Fig. 3, where total loss of pesticides clearly dominated in 2002-03 (Period 2).

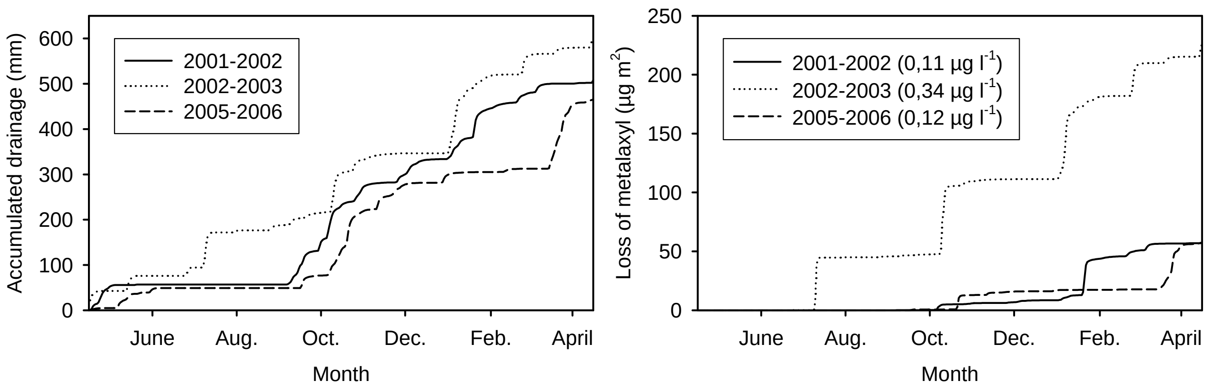

Figure 7: Simulated fluxes of drainage (mm)) and metalaksyl (µg m^{-2}) for Period 1 (2001-02), Period 2 (2002-03) and Period 3 (2005-06). Average concentration of metalaxyl is given in parentheses.

For the period with the highest loss of pesticides, 2002-03, simulated values of metalaxyl (Fig. 7) showed that half of the amount were lost before the end of October, first peak 24th – 25th July and the second peak between 23rd to 25th October. The third episode in January 2003, corresponds with the snow melting episode. Thus, climatic events that promote runoff of pesticides are very well simulated based on an annual loss of pesticides (Fig. 7). See also Fig. 8 for simulated concentration of metalaxyl related to time. From this, it can be seen that climatic conditions of special importance for runoff of pesticides are:
heavy showers or wet soil (high precipitation) in the growing season
high amounts of precipitation in the autumn that leads to high leaching
snow melting episodes during winter, where the distribution between surface and drainage runoff depends on soil frost conditions

The runoff of pesticides was far less for Period 1 and 3. In 2001-02 (Period 1) most of the losses were related to a snow melting episode in February 2003. It was a mild winter with sporadic occurrence of soil frost and little snow cover (Fig. 2), and at Syverud most of the water losses occurred through the drainage pipes.

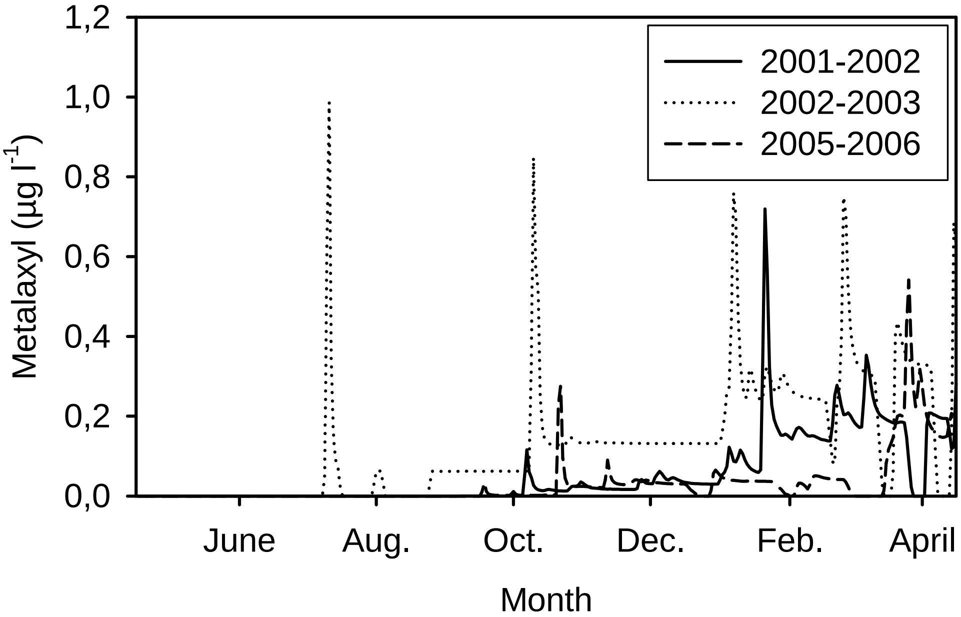

Figure 8. Simulated concentration of a mobile pesticide (Metalaxyl) in drainage water (ug l^{-1}) for three different periods (1/5 to 30/4).

For Period 3 (2005-06), accumulated runoff of metalaxyl prior to the snow melting, was, simulated very well. During the snow melting period in April 2006, however, the simulations indicated higher losses of metalaxyl than actual measured. In addition, the simulation indicated later runoff of metalaxyl than the measurements. On the other hand, simulation of the water transport through the drainage system, fitted well, even though the model failed to simulate the precise time for runoff of metalaxyl. Simulated loss of metalaxyl through the drainage runoff was, therefore, overestimated according to the actual measurements at an annual scale in 2005-06. Preliminary analysis indicates that the degradation rate of metalaxyl, which is used in the model, could be too slow, especially as a function of depth. But turned the other way around, pesticides abandoned for several years are still found in water samples from groundwater and rivers, an observation which is in agreement with the simulated values. Although at low concentration, leaching of persistent pesticides may continue for a long period of time.

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