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Testing FOCUS models on their effectiveness to simulate the leaching of Metribuzin herbicide under conventional cropping practices in Norway

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Abstract

This work presents a comparison of results of three pesticide leaching models applied to data generated in a Norwegian experimental site, within the Genesis EU FP7 Project. Over two experimental periods (2000/2001 and 2002/2003), soil temperature, water contents, bromide concentration and the concentrations of metribuzin herbicide were measured in the soil profile (0-80 cm). The soil is a silt loam formed from fluvial deposits. These experimental data were simulated by using three models namely, MACRO, PEARL and PRZM. Data of the water contents and the bromide concentration during the experimental period 2000/2001 were used to calibrate the hydraulic parameters for MACRO and PEARL. Parameters of the van Genuchten/Mualem retention and conductivity curves were obtained by inverse modelling of laboratory column measurements. The seasonal dynamics of the soil water contents were not simulated by any of the three models during the winter-spring period. PRZM model worked well for both bromide and metribuzin especially in surface soil layers. PEARL model simulated less efficiently than that of PRZM. Macro did not simulate at all. Freezing and thawing conditions should be considered for poor performance of these models in Norwegian sites. The thawing period is thus very important for leaching and groundwater recharge in areas with snow and soil frost in winter.

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1. Introduction

Groundwater contamination by pesticides can seriously limit water availability (Bouraoui, 2006). Directive 2000/60/EC of 22 December 2000 later called EU Water Framework Directive (WFD) provides an integrated framework for the assessment, monitoring and management of all surface and ground waters based on their ecological and chemical status. Pesticide leaching assessment is one of the issues that are studied in more detail in the FP7 EU GENESIS project due to the demand for information and knowledge about direct and indirect drivers that exert influence on the groundwater status.

The behaviour of pesticides in soils is governed by a variety of complex dynamic physical, chemical and biological processes, including sorption-desorption, volatilization, chemical and biological degradation, uptake by plants, run-off and leaching. Pesticides may also be transported rapidly to groundwater bypassing the unsaturated soil zone. These processes directly control the transport of pesticides within the soil and their transfer from the soil to water, air or food (Arias-Estevez et al. 2008).

Modelling is one of the available approaches for this assessment. In the last decades, process-based models have been developed and used for quantification or prediction of environmental contamination. These models are often used for the purpose of evaluation procedure for approval of new pesticides, and are used with site specific data for soils, agronomy and climate scenarios for the area. These pesticide fate models can be used to describe pesticide fate at field, regional and country scale and can be used for reporting chemical status according to Water Framework Directive and the Ground Water Directive.

PEARL (Tiktak et al., 2000), PRZM (Carsel et al., 1998) and MACRO (Jarvis, 1994) are one-dimensional models aimed at the prediction of pesticides dissipation and transport in soil. They are recommended by the Forum for International Co-ordination of pesticide fate models and their Use (FOCUS), to evaluate potential movement to ground water in the EU registration process. However these models are based on different concepts for the description of the main processes. In particular, PEARL and MACRO models describe the water movement in the soil according to water pressure gradients (they solve the Richards equation) while PRZM is a water capacity model and is thus not able to simulate upward movement of water in soil. Additionally, MACRO is able to simulate water preferential flow.

Through FOCUS, EU has developed model scenarios for both groundwater and surface water. These scenarios describe some of the pedoclimatic conditions prevailing in Europe. However, they do not cover special Norwegian conditions such as high precipitation, strongly sloping fields and the occurrence of snowmelt on frozen ground (Eklo et al., 2009). Typical climatic conditions for the Norwegian sites compared to other European sites are the combination of long periods in winter with low temperatures and snow covered ground, which usually lead to large water flows during snow melt (Bolli et al. 2011). These specific Nordic conditions can modify pesticide degradation as it is highly temperature dependent (Benoit et al., 2007). Melting-freezing episodes during winter are of great concern with respect to runoff of pesticides (Riise et al.,2006) and transport of pesticides in soil may be increase during soil thawing. Benoit et al. (2007) showed that during periods of low temperature, intense precipitation or snow melt, there was an increased risk of groundwater pollution by metribuzin residues in such alluvial soils. Indeed, the Norwegian site is characterized by low sorption and degradation capacities. Thus, there is a need to focus on the influence of cold climate on pesticide degradation in soil and the risk of leaching to surface and groundwater (Stenrød et al. 2008).

This work was conducted at INRA (France) in collaboration with Bioforsk (Norway) and UCSC (Italy), and is a part of the Genesis Project. We aim to realize a benchmark study in order to compare the ability of these pesticide fate models to simulate pesticide leaching in the Norwegian scenario. For this purpose, one single data set has been selected from a Norwegian site monitored by Bioforsk (Norway) after application of metribuzin herbicide during two experimental periods; i.e. period of calibration (2000/2001) and period of validation (2002/2003). The main objectives are thus to identify key variables on calibration and to validate and evaluate the performance of these models to describe the Norwegian scenario.

2. Material and methods

2.1 Field study

2.1.1 Site description

Grue experimental field is located in the northeast of Oslo (N 60°28'; E12°02) in the bottom valley of the Glomma River. The studied area (0,324 ha) is relatively flat even if slightly undulated and the slope gradient never reaches the value of 1%.

Grue is characterized by an intensive agriculture since centuries, with fertilization, and the last decade also, irrigation. Annual rotations of potatoes and barleys are performed on that site. Since 1995 several investigations on risk assessment of leaching of pesticides and nitrate to groundwater have been conducted in a research area at Grue, where more than 90 per cent of area is used for grain and potato production. The surface displays neither rock outcrop, nor surface coarse fragment, and presents only slight risks of water and wind erosion when it is bare. The soil appears to be moist, seldom saturated, and well drained. Floods occur less than once in ten years. Permeable soil types cover the major part of the area. Only a small area has soils with low permeability. These soils, however, can temporarily be completely saturated with surface water. The thickness of the unsaturated zone in observation wells has varied between 1.8 and 5.9 m. In 2000, the measured mean depth to the groundwater surface was 3.75 m. The mean groundwater recharge is estimated to be at a size of 300 mm year-1. The aquifer is characterised by groundwater flow towards the river Glomma in W, NW and N. Only during flood peaks in spring and autumn water will flow into the aquifer from the river Glomma. The hydraulic gradients and the velocity of the groundwater flow have been small (less than 40 cm day^{-1} at a hydraulic gradient of 0.2 %). The soil is a silt loam soil, which is built from fluvial deposits (Fluvic Cambisol). The field site represents a Nordic climate with freezing of soil for extended periods during winter (Stenrød et al., 2008). Average annual temperature and precipitation in this area is 3.3 degrees and 635 mm, respectively. On these areas, the vegetation zones on the river banks and a few small lakes can be characterized as groundwater dependent ecosystems.

2.1.2 Experimental site

The climate data for Grue were provided by the station of Roverud, located only 30 Km south of Grue. Mean annual soil temperature (top 10 cm layer) is approximately + 5.5 °C with a mean minimum at – 5.7 °C and maximum at 18.1 °C, as estimated from registrations over the last 5 years period (Stenrød et al., 2008). These registrations also show a mean of 133.4 days with topsoil temperatures below 0 °C, 3.2 days below -5 °C and 0.6 days below -10 °C. More specifically, the precipitation pattern in 2000 was characterized by heavy autumn rain, with a total precipitation of 800 mm (Fig.2). From June 2002 till September 2002 is observed air and top soil temperatures above 20°C and little precipitation during autumn (year total of 500 mm), and top soil temperatures during winter rarely below -3°C. There was a rapid decrease in temperature during the last week of December causing soil frost in the top soil layers, and top soil temperatures down to and below -5ºC from January until March.

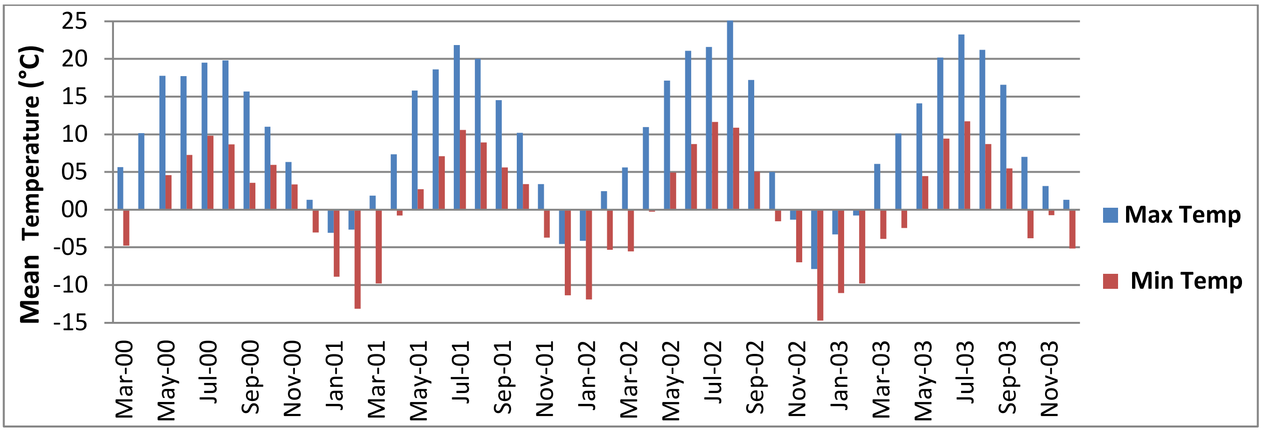


Figure 1. Mean monthly maximum and minimum temperatures

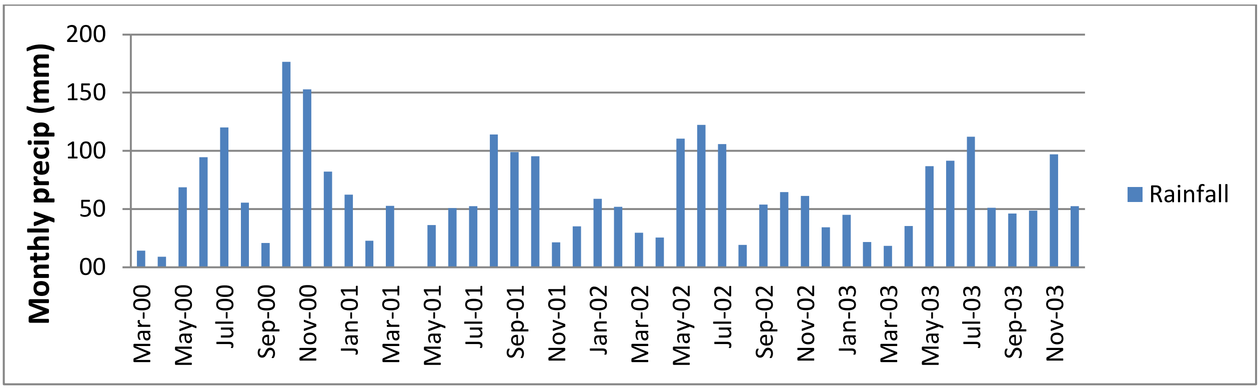


Figure 2. Monthly amount of rainfall

The soil is characterized by seven horizons. The main properties of the soil profile and the soil properties are given in Table 1.

Horizon	Depth (cm)	Organic matter (%)	pH	Soil Density (g/cm3)	Soil Texture (%)		
					Clay	Silt	Sand
Ap	0-30	0.8	5.9	1.48	5	49	46
Bw	30-56	0.4	5.5	1.37	5	82	13
Bw/Cg	56 – 69	0.4	5.8	1.29	5	89	6
Apb/C	69 – 84	0.5	5.7	1.27	3	75	22
C1	84 – 95	0.1	5.4	1.33	3	60	37
Apb2	95-110	0.8	5.4	1.20	8	87	5
C	110-140	0.7	5.5	1.25	7	93	0

Table 1.Grue physical properties

A strong textural change is observed in the soil profile at 30 cm (Table 1), changing from a sandy loam texture in the Ap horizon to a silt texture in the lower horizons. An increase in the silt fraction from 49 (Ap horizon) to 82% (Bw horizon) and a concomitant decrease in the sand fraction, passing from 47 to 13%, is observed. The trend is even more pronounced in the lower horizon (Bw/Cg). The clay proportion remains very low and nearly constant in the whole profile (4–5%).

Potatoes were grown on the field in both periods of study with rotations of barley crop between each period. Only potatoes crop years have been simulated.

Land Use		
Period	**2000/2001**	**2002/2003**
Crop	Potatoes	Potatoes
Date of Emergence	07/06/00	07/06/02
Date of Maturity	30/08/00	30/08/02
Date of Harvest	04/09/00	04/09/02

Table 2. Crop rotation description

The herbicide sprayed in the potatoes crop is metribuzin (4-Amino-6-tert-butyl-3-méthylthio-1,2,4-triazine-5(4H)-one). Potassium bromide (KBr) was applied in Grue site together with the pesticide to follow the transport of water.

Properties	Metribuzin	KBr
Molar Mass	214.3 g · mol-1	80 g · mol-1
Solubility in water	1200 mg/L (20°C)	650 g/L (20°C)
Vapor pressure	5.8 x 10-5 Pa (20°C)	100000 Pa (25 °C)
Coefficient of plant uptake	0.9	0.67

Table 3. Metribuzin and Bromide properties

Metribuzin was applied in early June 2000 and early June 2002, along with a non reactive tracer (potassium bromide). The date, the amount applied and the mode of application of metribuzin and bromide are represented in the table 4.

Substance Application		
Period	**2000/2001**	**2002/2003**
Date of application	09/06/00	07/06/02
Theoretical sprayed amount of KBr	79.4 Kg/ha	79.4 Kg/ha
Sprayed amount of Metribuzin	0,211 Kg/ha	0,141 Kg/ha
Mode of application	On bare soil	On bare soil

Table 4. Metribuzin and Bromide application in Grue site

2.2. Modelling

2.2.1. Description of the models

We present an incomplete description of the three models, as we focused mainly on the water movement, solute transport and heat transport. A complete description of the models is provided in the following references: MACRO user's manual (Stenemo & Jarvis, 2003), PRZM (Carsel et al., 2006) and PEARL (Tiktak et al., 2000).

2.2.1.1 MACRO

Jarvis et al. (1991a) developed MACRO, which is a detailed mechanistic dual-porosity model of water and solute transport in a macroporous soil. MACRO performs non-steady-state simulation of water flow and solute transport in a 1-dimensional (vertical) heterogeneous-layered field soil. A complete water balance is considered in the model, including saturated and unsaturated water flow, canopy interception and root water uptake, and seepage to drains and groundwater. It can be used to simulate non-reactive tracers (bromide, chloride), tritium, colloids, and pesticides including metabolites and colloid-facilitated pesticide transport.

One of the important features of the model is that it can be run in either 1 (micropore) or 2 flow domains (micropore+macropore) using the same soil hydraulic properties. In the 2-domain flow, the total soil porosity in each layer of the soil profile is divided into microporosity and macroporosity. The partition is defined through a boundary soil water pressure, ψ_b, and corresponding boundary water content, θ_b, and boundary hydraulic conductivity K_b. These boundary parameters describe the saturated state of the micropore domain.

The vertical water flow through the micropores in the unsaturated zone is described by the Richards equation:

$$C\frac{\partial\psi}{\partial t} = \frac{\partial}{\partial z}\left(K\left(\frac{\partial\psi}{\partial z}+1\right)\right) - \sum S_i \quad (1)$$

where $C = \partial\theta/\partial\psi$ is the differential water capacity (L^{-1}), ψ is the soil water pressure head (L), t is the time (T), z is the depth (L), K is the unsaturated hydraulic conductivity (LT^{-1}) and S_i are source/sink terms ($L^3L^{-3}T^{-1}$) for water exchange with macropores, drainage and root water uptake respectively.

In the macropore domain capillarity is assumed to be negligible in the macropores, so water flow is governed by the Darcy's equation assuming a unit hydraulic gradient (laminar flow under gravity):

$$\frac{\partial\theta_{ma}}{\partial t} = \frac{\partial K_{ma}}{\partial z} - \sum S_i \quad (2)$$

Where θ_{ma} and K_{ma} are the macropore water content and hydraulic conductivity respectively.

The interaction between the 2 regions is represented by exchange of water and solute. Water exchange is described by the source/sink term of Richards' equation along a first-order kinetic equation, neglecting the influence of gravity and assuming a rectangular-slab geometry for the agregates (van Genuchten and Dalton 1986):

$$S_w = \left(\frac{3D_w\psi_w}{d^2}\right)(\theta_b - \theta_{mi}) \quad (3)$$

WhereD_w is the effective water diffusivity, ψ_w is the scaling factor introduced to match the approximate and exact solutions to the diffusion problem (Gerke and van Genuchten 1993), d is the effective diffusion pathlength related to aggregate size and the influence of coatings on macropore and aggregate surfaces, θ_b is the boundary water content (the saturated water content in the micropores) and θ_{mi} is the water content in micropores. Because the scaling factor does not vary much with the initial water content and hydraulic properties (Gerke and van Genuchten 1993), it is set to an average value of 0.8 in the model.

The potential evapotranspiration is calculated according to the Penmann-Monteith (Monteith, 1965) using values of air temperature, solar radiation, wind speed, and air humidity.

The transport of solute in both domains is described by the convection-dispersion equation with dispersion neglected in the macroporosity.

$$\frac{\partial(\theta c)}{\partial t} = \frac{\partial}{\partial z}\left(D\theta\frac{\partial c}{\partial z} - qc\right) - \sum U_i \quad (4)$$

$$D = D_v v_{mi} + D_0 f^* \quad (5)$$

Where c is the solute concentration (ML^{-3}), D is the dispersion coefficient (L^2T^{-1}), D_v is the dispersivity (L^2T^{-1}), D_0 is the diffusion coefficient in free water (L^2T^{-1}), ν_{mi} is the pore water velocity (LT^{-1}), f* is the impedance factor (Millington and Quirk), q is the Darcy water flux density ($L^3L^{-2}T^{-1}$) and U_i is the mass exchange between flow domains, respectively. U_i include different sources/sink terms (mass exchange between flow domains, kinetic sorption, solute uptake by the crop, biodegradation and lateral leaching losses to drains and/or regional groundwater) ($ML^{-2}T^{-1}$)

The solute transport in the macropores is calculated by neglecting the dispersion and diffusion in the CDE so that convective transport is a dominant process in the macropores. The diffusive exchange of solute between the two flow domains and the convective fluxes of water and solute into the micropores are considered in the model. The exchange rate of solute between the micropores and macropores, U_i, is calculated by a combination of diffusion and convection (Jarvis and Larsson 1998).

The sorption of pesticides is described using the Freundlich isotherm. Additional kinetic sorption is considered in the model.

Finally, heat transport is modelled according to Fourier’s equation.

$$C_{\mathrm{heat}} \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(\lambda_{\mathrm{heat}} \frac{\partial T}{\partial z}\right) \qquad (6)$$

Where C_{heat} is the soil heat capacity ($ML^{-3}K^{-1}$), T is the soil temperature (°C), λ_{heat} is the thermal conductivity ($ML^{-1}K^{-1}T^{-1}$).

2.2.1.2 PEARL

The PEARL (Pesticide Emission Assessment at Regional and Local scales-model) (Tiktak et al., 2000) deals with the pesticide transformation and fate and is linked with the SWAP model (van Dam et al., 1997) for the water cycle and transport.

The water transport is described by the Richard’s equation (1) in a unique domain porosity, where Si are sink terms corresponding to the rate of root water uptake ($L^3L^{-3}T^{-1}$) and rate of lateral drainage discharge ($L^3L^{-3}T^{-1}$), respectively.

As for MACRO, PEARL can compute the potential evapotranspiration, the Penmann-Monteith (Monteith, 1965) that is used when daily values of air temperature, solar radiation, wind speed, and air humidity are available, and the Makkink (1957) approach can be used when only air temperature and solar radiation are available.

PEARL allows pesticides to be either injected into the soil or spread at the surface. When the latter option is selected, the applied pesticide is then distributed over the crop canopy using the soil cover fraction, the remainder of the dosage being applied to the soil. PEARL then simulates at the plant surface volatilisation in the air, penetration in the plant, degradation using first order kinetics, and wash-off via rainfall.

The transport of solutes into the soil is described the same way as MACRO, where the source/sink term U_i correspond to the transformation rate, the formation rate, the root uptake rate and the lateral pesticide discharge rate (all rates in $ML^{-3}T^{-1}$). Additionally to MACRO, PEARL describes the transport of pesticides in the gas phase.

The sorption in the equilibrium phase is described by Freundlich isotherm. Kinetic sorption is used in the non-equilibrium phase. For the topsoil the Freundlich coefficient is calculated as the product of the organic matter content and the sorption coefficient on organic matter. For the lower layers, the Freundlich coefficient is equal to that of the top layer adjusted by a depth effect factor. The partitioning of the pesticide between the liquid and the gaseous phases is described by Henry's law. As for MACRO, the degradation of the pesticide is described by a first order equation adjusted for the effects of temperature, soil moisture and soil depth.
The pesticide uptake by roots is directly proportional to the volumetric water uptake.

2.2.1.3 PRZM

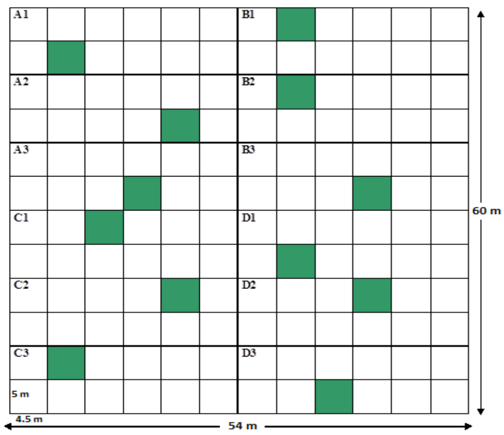
The pesticide root zone model (PRZM) is a one-dimensional, dynamic, compartmental model used to simulate the movement of chemicals in unsaturated soil systems within and immediately below the plant root zone. The model has two major components: hydrology and chemical transport. PRZM3 (Carsel et al., 1985), is a capacity type models, which means that water movement in soil are described in a simplistic way based on the resolution of water balance equations in each defined layers of the soil. Water movement is determined with a capacity approach in which water in excess of field capacity percolates to deeper soil layer. PRZM is not able to simulate neither preferential flows nor upward movement of water in soil. Evapotranspiration (evaporation from crop interception and soil, and transpiration by the crop) is estimated by pan evaporation data or by an empirical formula. Irrigation can also be taken into account. PRZM take in account soil frost by reducing the soil hydraulic conductivity under frozen conditions.
The chemical component (for a parent substance and two metabolites at most) includes adsorption (instantaneous and reversible, or time dependent), degradation (first order or biphase), volatilization, uptake by plants, leaching, runoff, erosion and foliar washoff. Solute transport is described by the advection–dispersion equation, and dispersion and diffusion in liquid and vapour phases are described by Fick's law. The transport equations can be solved using a finite-difference numerical solution or a method of characteristic algorithm (MOC) that reduces numerical dispersion.

2.3. Data sets

2.3.1. Field measurement

The experimental data for the soil water content and soil temperature have been measured at daily time step at five different depths (10 cm, 35 cm, 60 cm, 85 cm and 120 cm depth) since October 2000 to December 2003.

The field site was sampled 6 days for the period of calibration (2000-2001) and 6 days for the period of validation (2002-2003) at 4 different depths (between 0-20 cm, 20-40 cm, 40-60 cm and 60-80 cm). Field map from Grue, 60 m long and 54 m wide, consist of 4 squares (ABCD) divided each into 36 subplot, 5 m long and 4.5 m wide. Each subplot was sampled only during the duration of the experiment. Within one square three parallel samples at each depth were mixed together and analysed for metribuzin and bromide (results reported in Stenrød et al., 2008)



Date	Bromide (g/m^3)				Metribuzin (mg/m^3)			
	0-20	20-40	40-60	60-80	0-20	20-40	40-60	60-80
09/06/2000	42.39	0	0	0	98.2	0	0	0
29/06/2000	6.384	6.59	0	0	3.8	0	6.9	0
20/07/2000	4.185	9.79	0	0	12.9	13.6	13.4	8.8
24/08/2000	1.73	1.587	4.208	7.916	12.3	0	0	0
16/11/2000	0	0	0	3.736	8.5	0	0	0
28/05/2001	0	0	0	0	10.3	10.7	7.5	9.3

Table 5. Bromide and Metribuzin measured in experimental field in Grue soil in 2000-2001

Date	Bromide (g/m^3)				Metribuzin (mg/m^3)			
	0-20	20-40	40-60	60-80	0-20	20-40	40-60	60-80
07/06/2002	29.16	2.98	1.49	6.82	54.9	12	8.894	12.081
20/06/2002	15.46	0.68	4.38	6.73	14.71	7.279	4.32	0
09/07/2002	7.56	1.44	0.46	1.9	7.39	10.189	0	0
13/08/2002	0.53	1	1.72	2.11	6.6	8.463	5.27	4.87
18/09/2002	18.73	6.82	1.42	2.66	8.31	0	0	0
27/05/2003	0.71	4.53	8.33	11.31	2.62	0	2.814	0

Table 6. Bromide and Metribuzin measured in experimental field in Grue soil in 2002-2003

2.3.2. Laboratory measurements

2.3.2.1 Parameter estimation from water retention curve in soil

The description of the soil water retention curve, h=f(θ), and hydraulic conductivity curve, K=f(h), is needed for PEARL and MACRO models. Both models used the Mualem-Van Genuchten equation [Van Genuchten, M. (1980)] to describe these relations (figure 3).

Water Content

$$\theta = \theta_r + \frac{(\theta_s - \theta_r)}{[1+|\alpha\varphi|^n]^{(1-1/n)}} \quad (7)$$

Unsaturated hydraulic conductivity

$$K(H) = K_s S_e^{\lambda}\left[1 - \left(1 - S_e^{1/m}\right)^m\right]^2 \quad (8)$$

where $S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$ (9) is the relative saturation,

θ_s is the saturated volume fraction of water (L^3L^{-3}), θ_r is the residual volume fraction of water (L^3L^{-3}), Ks is the saturated hydraulic conductivity (LT^{-1}), λ,n,m are experimental parameters [m=1-1/n] and α is the reciprocal of the air entry value ($1L^{-1}$).

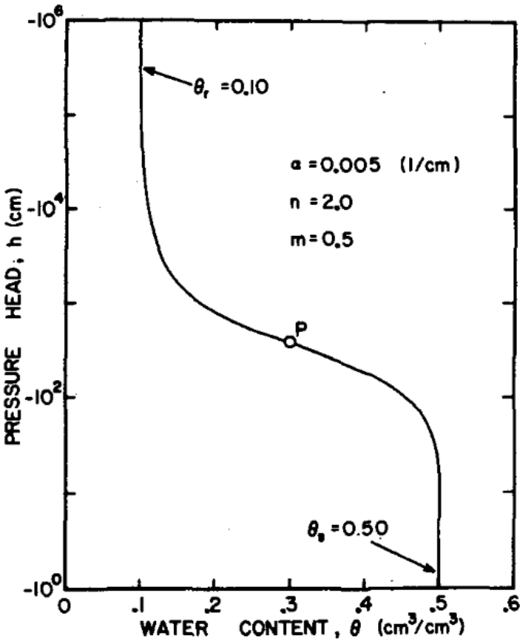


Figure 3. Retention curve (Van Genuchten, 1980)

Laboratory measurements to obtain experimental water retention curve have been performed for each horizon (Moni, 2004). The parameters θsat, n and Ksat were estimated by inversion procedure in which the Van Genuchten –Mualem model, equations (7) and (8), were fit with the measured retention points (Moni, 2004). Hysteresis is not considered, so α_{dry} and α_{wet} are the same.

Horizon	Θ_{Sat}	Θ_{Res}	α	n	Ksat	λ	Field capacity	Wilting point
	(m^3 m^{-3})	**(m^3 m^{-3})**	**(cm^{-1})**	**(-)**	**mm h-1**	**(-)**	**(m^3 m^{-3})**	**(m^3 m^{-3})**
Ap	0.412	0.002	0.013	1.47	3.6	0.5	0.301	0.034
Bw	0.463	0.0053	0.0113	1.62	65.7	0.5	0.349	0.024
Bw/Cg	0.493	0.001	0.0124	1.58	39	0.5	0.366	0.028
Apb/C	0.497	0.002	0.0117	1.59	26	0.5	0.377	0.028
C1	0.434	0.0115	0.0318	1.87	13.6	0.5	0.517	0.012
Apb2	0.537	0	0.013	1.41	116	0.5	0.419	0.041
C	0.515	0	0.009	1.49	220	0.5	0.424	0.035

Table 7. Hydraulic parameters of Grue site

To get the water retention parameters of the macroporosity that MACRO need, the inversion was performed also under several restricted conditions (reported in Moni. 2004). The hydraulic conductivity at saturation of the total pore system was chosen as the lowest value of the measured total saturated hydraulics conductivity among six replicates for each horizons [Ks min](moni,2004). Then Kb was estimated by using the Mualems' model which describes the evolution of unsaturated conductivity with the tension of water soil. To do so, the value of Kb has to be determined.
As the limit between macro- and microporosity is not known, different values of $\psi_b$were tested in Moni (2004). Jarvis (2007) concluded that the weight of empirical evidence suggests that pores of 'equivalent cylindrical diameter' larger than about 0.3 mm can be considered as macropores. Thus, the minimum water potential defining the boundary between macropores and matrix in MACRO is fixed at -10 cm. we decided to use the value of -10 cm as the boundary pressure head between micropores and macropores. θ_b was then calculated from the retention curve (eq 7) and Kb from the conductivity curve (eq 8). The values of the parameters so-estimated are displayed in table 8.

								ψb=-10 cm	
Horizon	**Θ_{Sat}**	**Θ_{Res}**	**α**	**n**	**Ksat**	**λ**	**Ksatmin**	**Θ_b**	**Kb**
	(m^3 m^{-3})	**(m^3 m^{-3})**	**(cm^{-1})**		**mm h-1**		**mm h-1**	**(m^3 m^{-3})**	**mm h-1**
Ap	0.397	0.007	0.0107	1.51	3.6	0.5	0.67	0.39	0.312
Bw	0.448	0.0116	0.0095	1.69	65.7	0.5	2.23	0.445	0.301
Bw/Cg	0.48	0.0079	0.0105	1.64	39	0.5	2.54	0.475	1.486
Apb/C	0.485	0.0081	0.0101	1.65	26	0.5	1.6	0.48	0.962
C1	0.412	0.0133	0.0277	1.95	13.6	0.5	0.61	0.4	0.308
Apb2	0.531	0	0.0119	1.42	116	0.5	0.65	0.52	0.228
C	0.509	0	0.0082	1.51	220	0.5	0.71	0.5	0.37

Table 8. Water retention parameters for tension boundary between macropores and micropores at -10cm

In that table Ks is the total saturated hydraulic conductivity measured, whereas Ks min is the lowest value measured of the total hydraulic conductivity, and Kb is the hydraulic conductivity of the microporosity domain when macropores are empty.

2.3.2.2 Metribuzin dissipation parameters

Pesticide leaching is mainly controlled by sorption and degradation processes, because both affect the availability of a pesticide in the soil solution (Benoit et al. 2007).

Sorption

Sorption plays a fundamental role in the advective-dispersive transport dynamics, persistence, transformation and bioaccumulation of pesticides (Arias-Estevez et al. 2008). Sorption characteristics for metribuzin were previously obtained through a batch equilibrium procedure (Benoit et al., 2007). Sorption characteristics for metribuzin were obtained through a batch equilibrium procedure. Sorption was characterized at 4 different soil depths (0-20, 20-40, 40-60, and 60-80 cm), and the experiment was set up in triplicate.

Sorption coefficients, Kd (L Kg^{-1}), were calculated as $K_d = \frac{X/m}{C_e}$, where x/m is the amount of metribuzin sorbed on the soil (mg kg-1 dry soil) calculated from the concentration difference between the initial metribuzin solution and Ce, the equilibrium metribuzin concentration measured after equilibrium was reached. A couple of parameter (Kf and n) was also calculated (Moni, 2004)

Soil depth (cm)	Metribuzin Kd (L Kg^{-1})	Kf (L Kg^{-1})	n
0 - 20	0.36 ± 0.05	0,278	0,906
20 - 40	0.14 ± 0.04		
40 - 60	0.18 ± 0.05		
60 - 80	0.42 ± 0.03	0,308	0,842

Table 9. Sorption parameters (Moni, 2004 ; Benoit et al., 2007)

This indicates a weak sorption capacity of this soil to sorb metribuzin. In the 60-80 cm layer, the results indicated a stronger sorption than in the upper layer, might result from an increase in the silt proportion together with a relative increase of organic C in the Apb/C horizon (Stenrød et al., 2008).

Transformation (results described in Benoit et al., 2007; Stenrød et al., 2008)

Transformation studies under controlled conditions at 20°C, were performed to describe the degradation process for metribuzin in the investigated soil. From the mean value for the transformation rate constant (estimated by linear regression of log-transformed data (µg metribuzin g-1 soil)) at 20°C (k = 0.0139 (± 0.00051) day-1, regression coefficient (r2) = 0.97), a half- life of 22 days could be calculated for these optimum conditions (Stenrød et al., 2008).

2.4 Evaluation of model performances

The agreement between observed and simulated values was carry out by a MS Excel file provided by Alessia Perego (University of Milan, Italy) to calculate the indexes proposed by Loague and Green (1991) and more recently discussed by Martorana and Bellocci (1999) and Fila et al (2003): the relative root mean squared error (RRMSE), the coefficient of residual mass (CRM), the Pearson correlation (r), slope index and modelling efficiency (EF). For all the indexes O_i is the *ith* observed value, whereas S_i is the *ith* simulated value and n in the number of pairs. $\bar{O}$ and $\bar{S}$ are the mean of observed and simulated data respectively (Perego, A. 2010).

The relative root mean square error RRMSE (Loague[2] and Green (1991) has a minimum and optimun value at 0. It is a difference-based measure of the model performance in a quadratic form divided by observed mean, being a relative measure of the fitting.

$$RRMSE = \frac{\sqrt{\frac{\sum_{i=1}^{n}(S_i - O_i)^2}{n}}}{\bar{O}} \times 100 \quad (10)$$

The coefficient of residual mass CRM, ranges between – inf and + inf, with the optimum value equal 0. If positive CRM indicates a good performance of the model, if negative indicates overestimation and when is close to zero indicates the absence of trends:

$$CRM = \frac{\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} S_i}{\sum_{i=1}^{n} O_i} \quad (11)$$

The coefficient of correlation r, has its optimum value to maximum (+1). Zero means no correlation:

$$r = \frac{\sum_{i=1}^{n}(O_i - \bar{O})(S_i - \bar{S})}{\sqrt{\sum_{i=1}^{n}(O_i - \bar{O})^2}\sqrt{\sum_{i=1}^{n}(S_i - \bar{S})^2}} \quad (12)$$

The slope quantifies the steepness of the linear regression. It equals the change in S_i for each unit change O_i. It is expressed in the units of the Si divided by the units of the O_i. Slope best value is equal to 1

$$slope = \frac{\sum_{i=1}^{n}(O_i - \bar{O})(S_i - \bar{S})}{\sum_{i=1}^{n}(O_i - \bar{O})^2} \quad (13)$$

Modelling efficiency (EF) (Nash and Sutcliffe, 1970) can get either positive or negative values, 1 being the upper limit, while negative infinity is the theoretical lower bound. EF values lower than 0 results from a worse fit than the average of measurements.

$$EF = 1 - \frac{\sum_{i=1}^{n}(S_i - O_i)^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2} \quad (14)$$

If EF is less than zero the model-predicted values are worse that simply using the observed mean. Several of the above statistics are sensitive to a few large errors especially in small data sets

Parameter	RRMSE	EF	CRM	Slope	R^2
Min	0.00	-inf.	-inf.	-inf.	-inf.
Max	+inf.	1.00	+inf.	+inf.	+inf.
Best	0.00	1.00	0.00	1.00	1.00

Table 10. Range and best value of statistical indexes

3. Results and discussion

We present here the results of the three models. However, we faced a technical problem with MACRO during the crop season as the model did not simulate the growth of the plant. We did not found the error at the moment of the report writing. Nevertheless, we decided to present the results of MACRO as the model is still valid for bare soil periods.

3.1. Period of calibration 2000-2001

The simulation has been done for each model for the period of calibration between 01/01/2000 until 31/12/2001. An equal “warming period” of 6 months was introduced for each model in order to decrease the impact of the initial conditions (initial profiles of soil water pressure and temperature) onto the results.

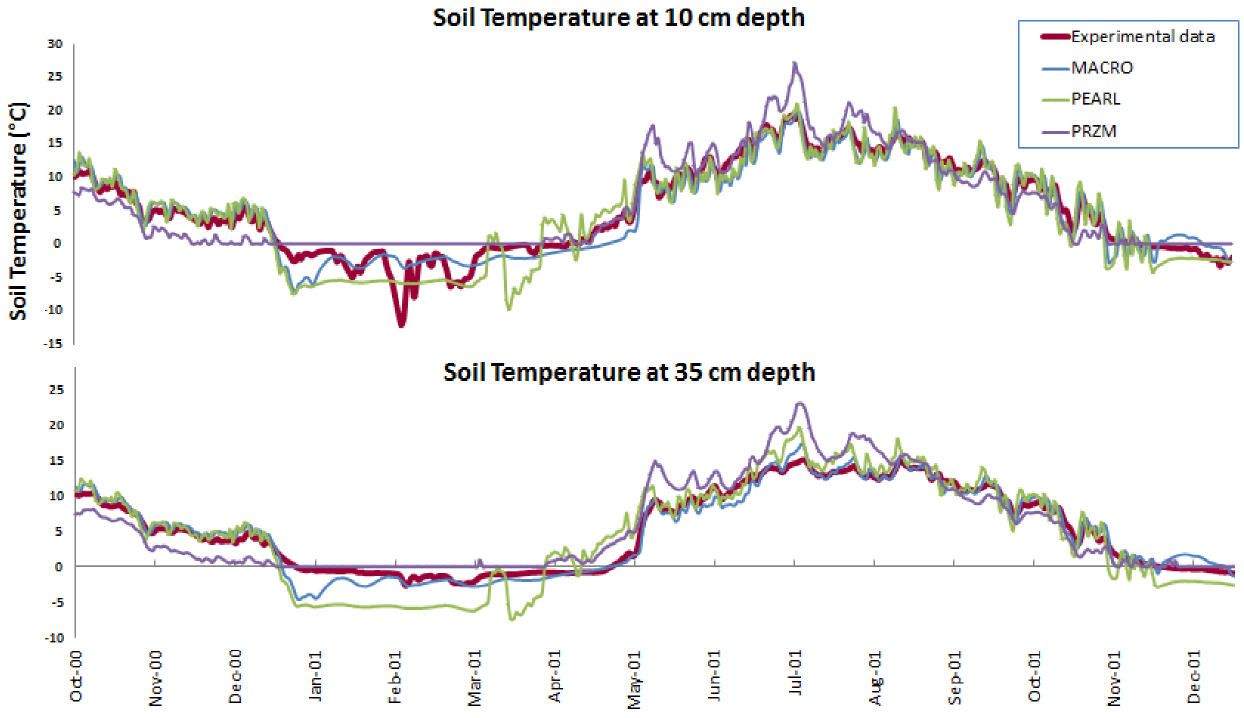
The models for the environmental behaviour of pesticides are usually calibrated in two stages (Kolupaeva et al. 2006). The first stage is the calibration of the model in terms of the water regime. The second stage is the calibration of the model for the particular pesticide.

3.1.1. Calibration for the water Regime

The simulation results are processed, which encompassed the graphical comparison of the simulation results as compared to the field measured experimental data and the calculation of the relative root mean square error (RRMSE), the slope, the model efficiency (EF), the coefficient of residual mass (CRM) and the coefficient of correlation (r).

3.1.1.1. Soil Temperature

The three models simulate well the soil temperature at different depths (Fig. 4).



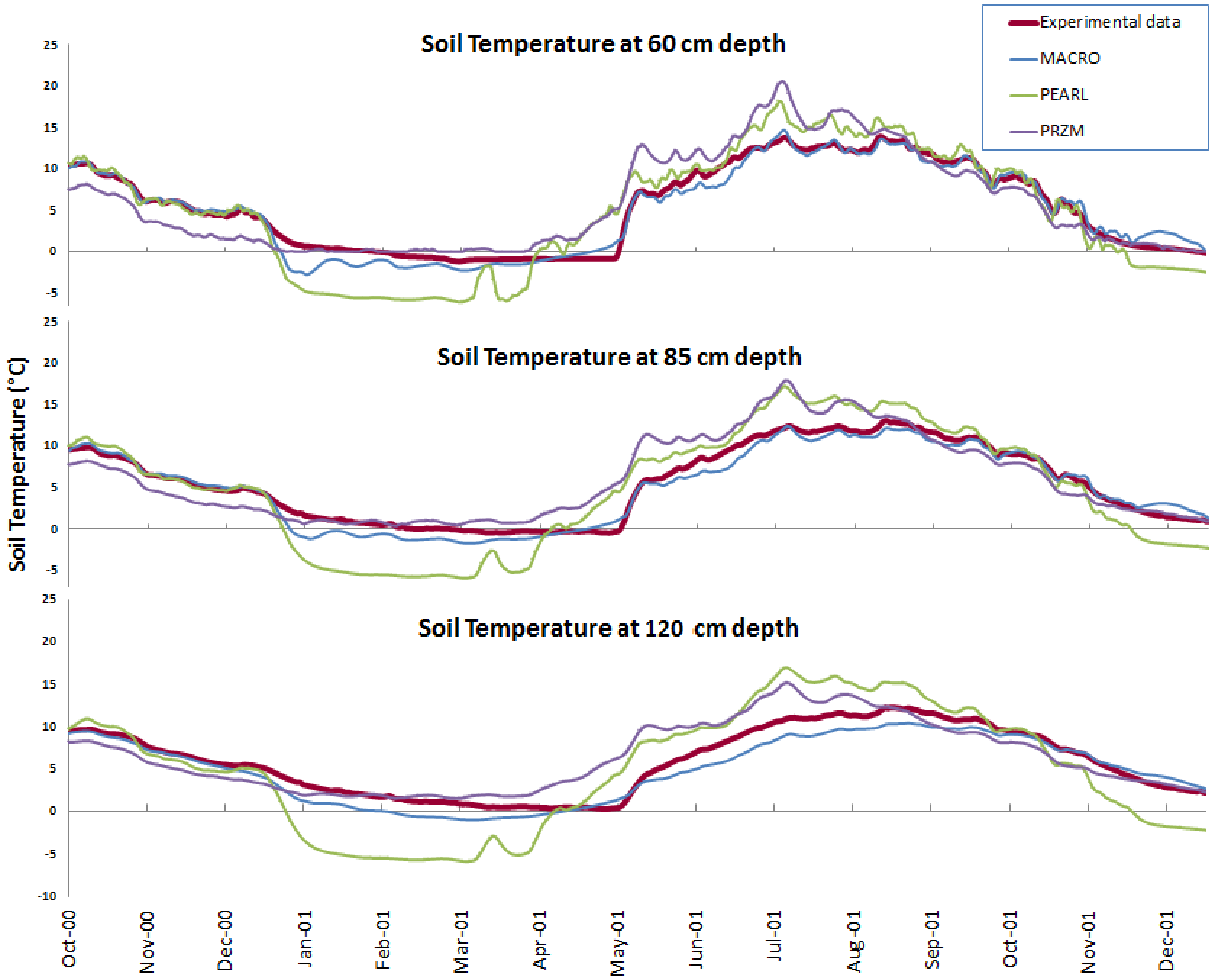


Figure 4. Soil temperature simulations profiles (2000/2001)

The statistical indices for the simulated soil temperature profiles for each model are given in Table 11. The best value for each parameter at each depth is marked in bold.

		RRMSE	EF	CRM	Slope	R2
10cm	MACRO	**35.50**	**0.93**	0.05	**0.99**	**0.93**
	PEARL	45.93	0.88	0.12	0.86	0.91
	PRZM	37.20	0.88	**0.00**	0.83	0.91
35cm	MACRO	**22.19**	**0.96**	**0.04**	**0.93**	**0.97**
	PEARL	51.35	0.78	0.10	0.73	0.91
	PRZM	43.36	0.81	-0.05	0.78	0.88
60cm	MACRO	**19.52**	**0.96**	**0.06**	**0.96**	**0.96**
	PEARL	53.78	0.69	0.11	0.68	0.90
	PRZM	46.00	0.76	-0.07	0.79	0.83
85cm	MACRO	**17.98**	**0.95**	**0.07**	**0.97**	**0.96**
	PEARL	59.02	0.51	0.10	0.61	0.90
	PRZM	42.20	0.75	-0.11	0.81	0.81
120 cm	MACRO	**21.85**	**0.90**	**0.15**	**1.00**	**0.94**
	PEARL	68.33	-0.02	0.16	0.50	0.84
	PRZM	39.06	0.67	-0.10	0.82	0.72

Table 11. Statistical parameters of soil temperature simulation at different depths (2000/2001)

MACRO provided the best simulation for the soil temperature for all depths with a modelling efficiency (EF) close to 1 in each layer.

For the surface layer, PEARL behaved equally as MACRO. For the deeper horizons, the model showed a constant and underestimated temperature value of -5ºC during the snow period and overestimated the soil temperature during summer time, particularly at 80 and 120 cm depth.

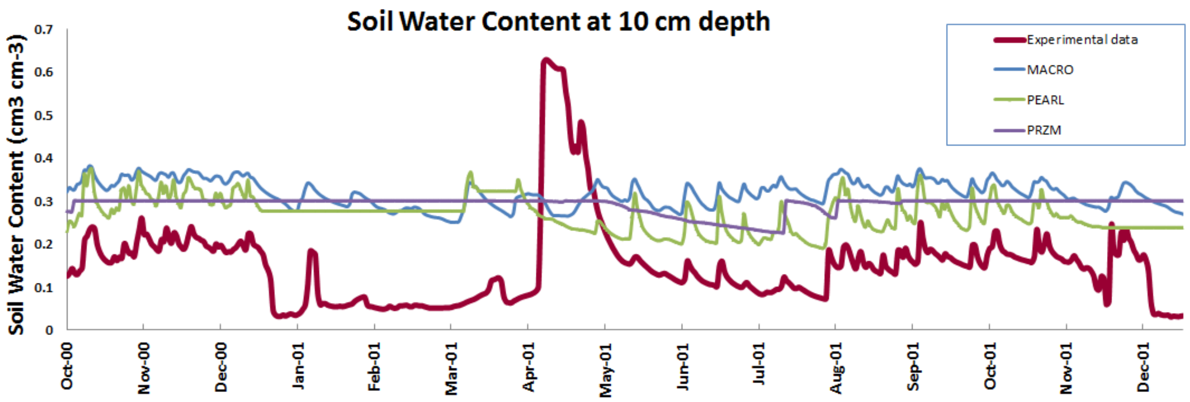
PRZM is not able to simulate negative temperatures in soil, for this reason the simulation show a constant value of 0°C during frost periods. The soil temperature is generally underestimated in the period between September to December, while it is generally overestimated the period between May and September. However, the statistical analysis for the simulations at 10, 35 and 60 cm showed rather good values (table 11)

When ice is melting due to the increase of air temperature, it absorbs the energy necessary to the change of state from solid to liquid, so that its temperature remains at 0°C. This explains why the measured soil temperature was still close to zero degree when thawing started (Figure 4). Neither of the three models take into account the absorption of energy during thawing so that the simulated soil temperature remained increasing during that period.

3.1.1.2 Soil Water content

From December to April, it is possible to observe a very strong decrease of the soil water content and a high increase (above water content at saturation measured in laboratory) during spring thawing followed by rapid transport of water down the soil profile on release of soil frost (results reported in Kværner et al., 2005). These variations can be observed until 85 cm but not anymore at 120 cm.

The dynamics of soil water content, although not the absolute values, between simulated and measured values corresponded well during the summer season for MACRO and PEARL. PEARL is the only model that simulates an increase of water content during the thawing period, although this increase is advanced in time compared to experimental data. The simulation for the PRZM is the worst and it does not follow the pattern of the real data like the other models. It is observed that a difference exists in the model performance of the Richards' type of flow models and the more simple capacity models. The capacity type models like PRZM are not able to simulate drying in the soil layers below the root zone due to their inability to simulate capillary rise (Garrant et al. 2002) and hence upward water flow may be systematically biased in cases of prolonged evaporation or groundwater intrusion in the soil profile [Vanclooster et al. 2000].



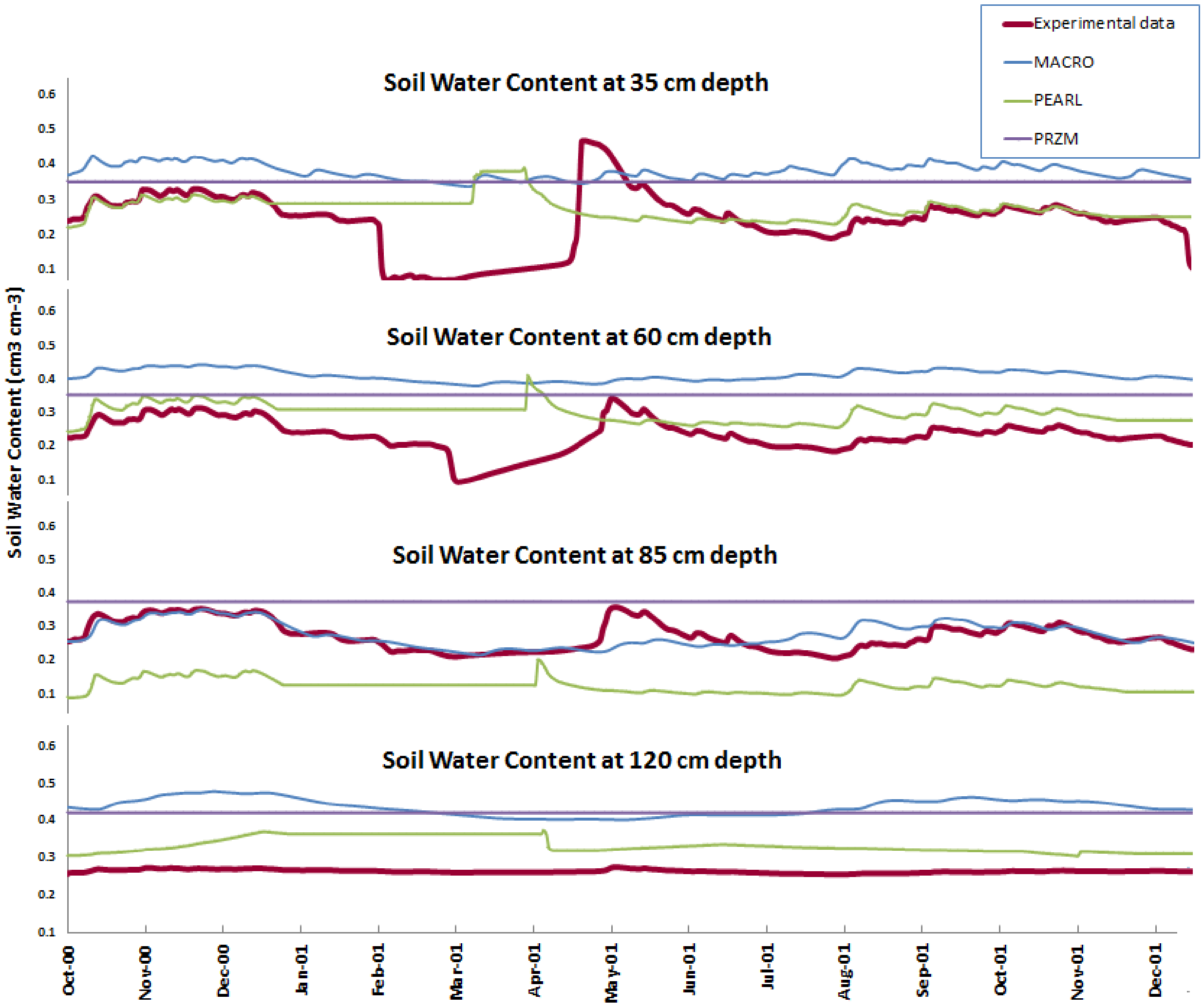


Figure 5. Soil water content simulations profiles (2000/2001)

We tried to calibrate MACRO model by adjusting the snow melt factor (SNOWMF) equal to 0.4. PEARL has also an option to activate the effect of the snow during winter season but the model does not let us to change the parameter to simulate the snow melting at the end of April. However, neither winter conditions, melting season or spring infiltration are simulated correctly by the three models (negative EF). The leaching during thawing is thus probably underestimated.

		RRMSE	EF	CRM	Slope	R2
10cm	MACRO	126.45	-2.63	-1.09	0.77	0.05
	PEARL	103.46	-1.43	-0.77	0.17	0.00
	PRZM	113.42	-1.92	-0.92	0.74	0.02
35cm	MACRO	67.09	-2.59	-0.59	2.22	0.30
	PEARL	44.51	-0.58	-0.15	-0.80	0.10
	PRZM	58.49	-1.73	-0.47	-0.01	0.00
60cm	MACRO	79.85	-13.59	-0.78	1.95	0.45
	PEARL	36.64	-2.07	-0.29	0.29	0.02
	PRZM	56.23	-6.23	-0.52	0.08	0.00
85cm	MACRO	11.98	0.44	-0.02	1.39	0.47
	PEARL	56.90	-11.71	0.55	1.07	0.23
	PRZM	41.26	-5.68	-0.38	0.05	0.00

120 cm	**MACRO**	64.65	-1648.18	-0.64	0.07	0.14
	PEARL	26.76	-281.46	-0.26	0.02	0.01
	PRZM	58.29	-1339.75	-0.58	-0.09	0.00

Table 12. Statistical criteria for the uncalibrated simulated soil moisture profiles (2000/2001)

The water transport components of the leaching models are driven by the soil hydraulic parameters such as the soil moisture retention curve, the hydraulic conductivity curve, the wilting point and the field capacity. In most cases, calibration was performed on these hydraulic parameters. Laboratory measured values of the moisture retention curve were given in the dataset report. However, given the spatio-temporal variability of the small scale hydraulic properties in the field, effective field scale hydraulic properties may be significantly different from the small scale laboratory values, which justifies the calibration of the laboratory values to simulate field behaviour. [Vanclooster et al. 2000].
The PEARL model is sensitive to changes in the moisture content under saturated conditions (θsat) and the parameter *n* in the van Genuchten equation for approximating the water retention curve (WRC) (Kolupaeva et al. 2006).

For the calibration some hydrological parameters were thus modified. The calibration was performed on PEARL and MACRO models. The calibrated parameters are represented in the following tables 13 and 14.

Horizon	Θ_{Sat} ($m^3\ m^{-3}$)	Θ_{Res} ($m^3\ m^{-3}$)	α	n	Ksat m day^{-1}	λ
Ap	0.32	0.002	0.02	1.87	0.087	0.5
Bw	0.48	0.005	0.025	1.49	2.074	0.5
Bw/Cg	0.48	0.001	0.02	1.88	0.936	0.5
Apb/C	0.49	0.002	0.02	1.89	0.624	0.5
C1	0.45	0.01	0.05	1.27	0.326	0.5
Apb2	0.45	0	0.05	1.31	2.784	0.5
C	0.4	0	0.05	1.19	5.29	0.5

Table 13. New Van Genuchten parameters used to calibrate PEARL

								ψb=-10 cm	
Horizon	Θ_{Sat}	Θ_{Res}	α	n	Ksat	λ	Ksatmin	Θ_b	Kb
	($m^3\ m^{-3}$)	($m^3\ m^{-3}$)	(cm^{-1})		mm h-1		mm h-1	($m^3\ m^{-3}$)	mm h-1
Ap	0.291	0.007	0.035	4	3.6	0.5	0.67	0.29	0.312
Bw	0.398	0.0116	0.015	2.7	65.7	0.5	2.23	0.395	0.301
Bw/Cg	0.378	0.0079	0.02	2.6	39	0.5	2.54	0.375	1.486
Apb/C	0.485	0.0081	0.01	1.65	26	0.5	1.6	0.481	0.962
C1	0.412	0.0133	0.02	1.95	13.6	0.5	0.61	0.404	0.308
Apb2	0.531	0	0.0119	1.42	116	0.5	0.65	0.524	0.228
C	0.409	0	0.01	1.8	220	0.5	0.71	0.405	0.37

Table 14. New Van Genuchten parameters used to calibrate MACRO

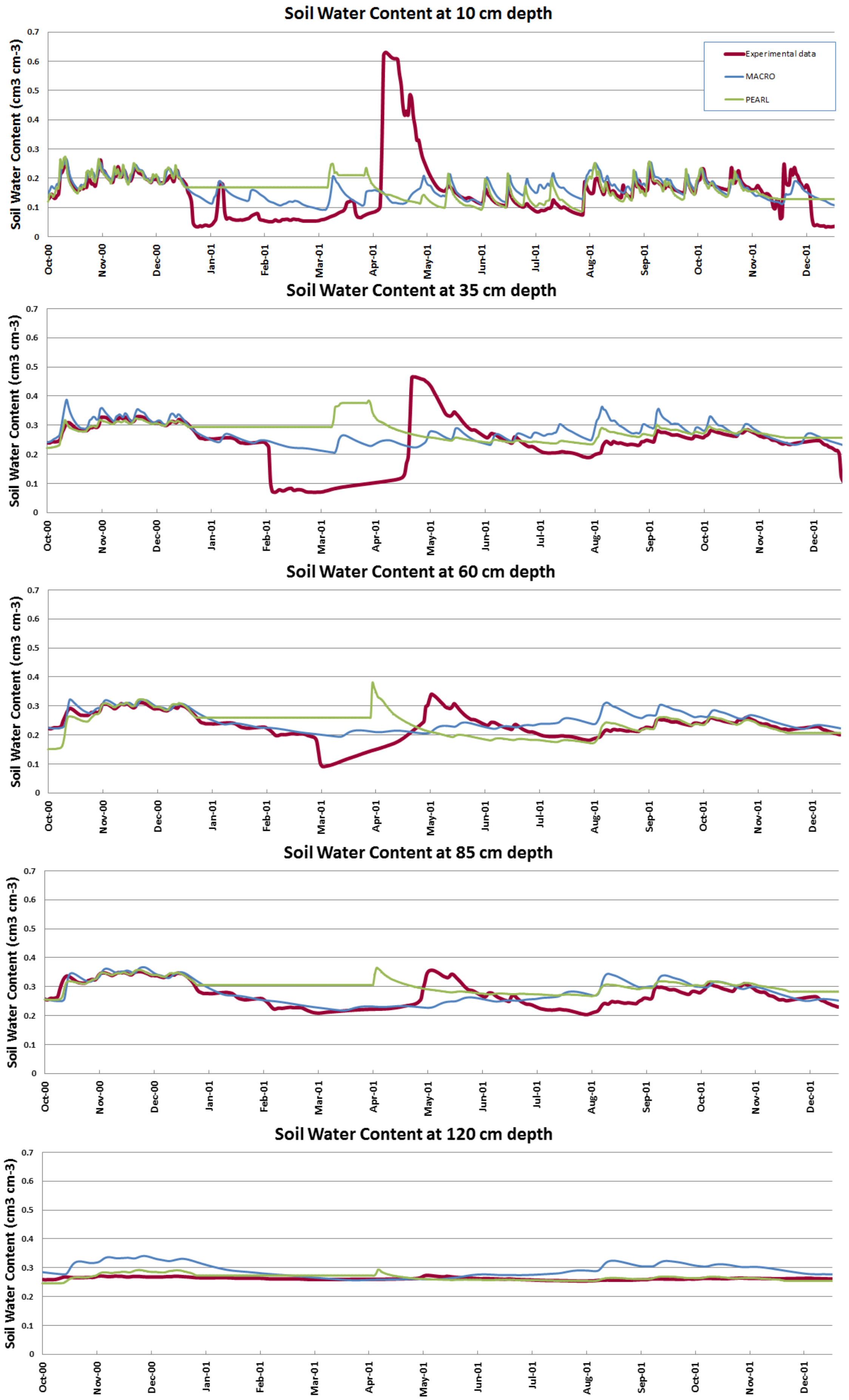


Figure 6. Soil water content simulations profiles calibrated for PEARL (2000/2001)

		RRMSE	EF	CRM	Slope	R2
10cm	MACRO	65.20	0.04	-0.17	0.82	0.11
	PEARL	70.16	-0.12	-0.06	0.13	0.00
35cm	MACRO	30.46	0.26	0.00	1.63	0.31
	PEARL	44.71	-0.60	-0.18	-0.75	0.08
60cm	MACRO	16.17	0.40	0.04	0.96	0.44
	PEARL	25.80	-0.52	-0.04	0.17	0.02
85cm	MACRO	12.80	0.36	-0.05	0.90	0.45
	PEARL	18.16	-0.29	-0.12	0.90	0.23
120 cm	MACRO	25.63	-258.17	-0.24	0.08	0.16
	PEARL	3.53	-3.91	-0.01	0.19	0.23

Table 15. Statistical criteria for the calibrated simulated soil moisture profiles for PEARL (2000/2001)

The calibration considerably increased the results (Figure 6) as can be seen from the efficiency, that although far to 1, increased considerably (Table 15). The RRMSE is lower than the models without calibration. MACRO presents the best efficiency also. The EF of PEARL was improved if the critical winter-spring period from 10/12/00 until 20/05/2001 was not considered. We thus used these calibrated parameters to perform the simulation of bromide and metribuzin leaching.

3.1.2 Solute leaching

3.1.2.1 Bromide leaching

We considered Bromide as a water tracer, with no transformation or adsorption occurring in the soil

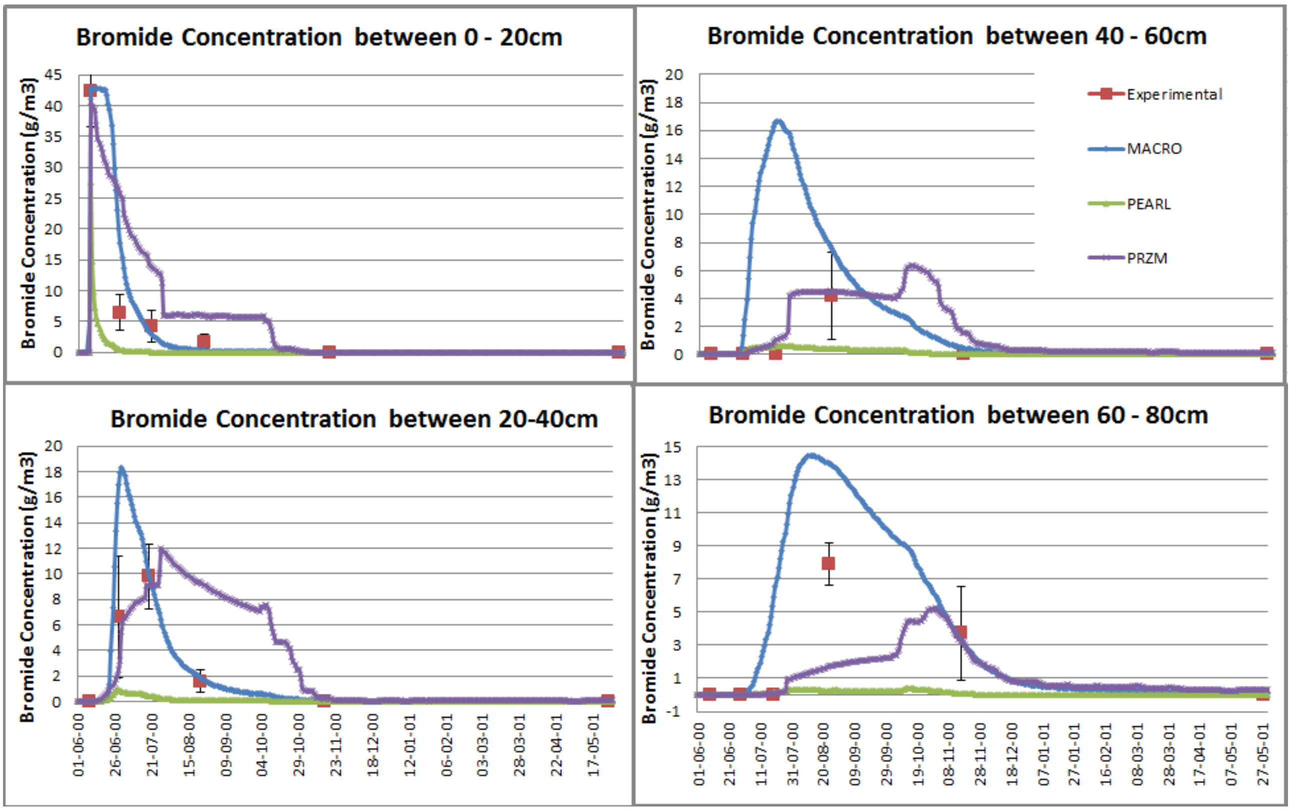


Figure 7. Bromide concentration simulations profiles (2000/2001)

The bromide concentration measured in soil samples at different depths indicated that after one year, the bromide has completely leached the 80 first cm of soil (Figure 7). In the second layer the highest concentration was measured one month before application and two months later in the deeper layers. The time appearance of the maximum of the bromide peak in the different layers indicated a mean solute velocity of 0.77 ± 0.14 cm/d.
PEARL simulation underestimated Bromide concentration at all depths. MACRO and PRZM models follow rather well the dynamic of the measured data in all layers. Results show that MACRO and PRZM overestimated the bromide mass recovery, compared to experimental measurements while PEARL underestimated it. The effect of the crop may be seen in the different results of MACRO as no solute uptake was simulated.

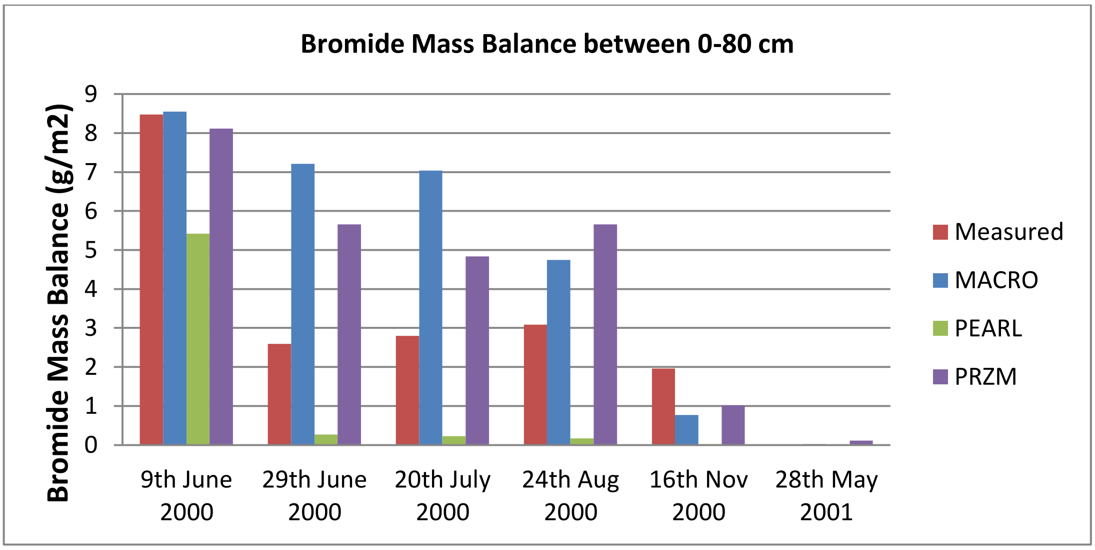


Figure 8. Measured and simulated bromide mass balance from the 0-80 cm depth (2000/2001)

3.1.2.2 Metribuzin leaching

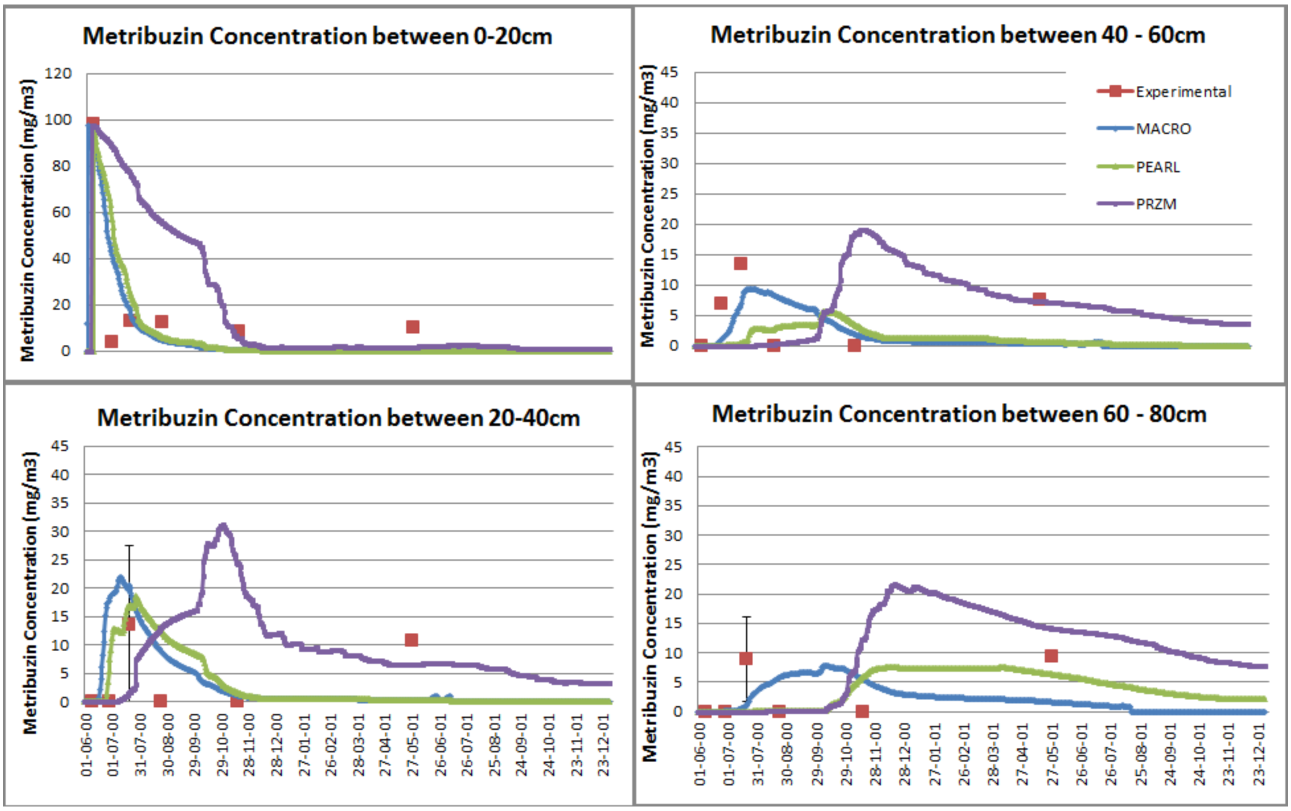


Figure 9. Metribuzin concentration simulations profiles (2000/2001)

For the upper layer (0-20 cm) there is a good match between simulated and measured values for the three models.
The experimental data are not easy to interpret, particularly in the deeper horizons. Indeed, a concomitant appearance of the metribuzin concentration peak at all depths and at roughly the same concentration value suggests that no delay due to sorption of the herbicide occurred during the transport. While no metribuzin is measured in the 20-80 cm after 20th of July, metribuzin is detected in May 2001 (27th) at the end of the winter-frost period with a similar concentration value throughout the depth (around 10mg/m^3).
In the Nordic countries, pesticide behaviour and transfer in soil may be modified by soil freeze/thaw cycles. This measured concentration maybe the consequence of a rapid leaching due to thawing which starts around 15th May 2001. The snow melt period is thus critical for the lixiviation and the recharge on groundwater. It constitutes a period with risk if the pesticides are available for the transport.
Observation of similar concentration throughout the soil profile suggests that some preferential flow would have occurred. As can be seen on Figure 8, none of the models are able to simulate correctly these rapid events. MACRO who is capable to simulate preferential flow did not succeed, as this event is a particular situation in the year, and hydraulic properties cannot be changed during the continuous simulation of one-year period. Both PEARL and MACRO succeed to simulate the peak evolution in the upper layers (0-40cm) although the models did not simulate the continuous metribuzin concentration of about 10 mg/m^3 of the upper layer. The models then describe a delayed appearance of the peaks at the higher depths as expected from the solving of the convection-dispersion equation. We observed that PEARL showed a higher delay than MACRO in the deepest horizons. Finally, PRZM generally over-predicted the metribuzin leaching (Figure 10), but is the only model that simulates the presence of metribuzin after thawing. Indeed, PRZM exhibited a long tailing elution curve at all depths.

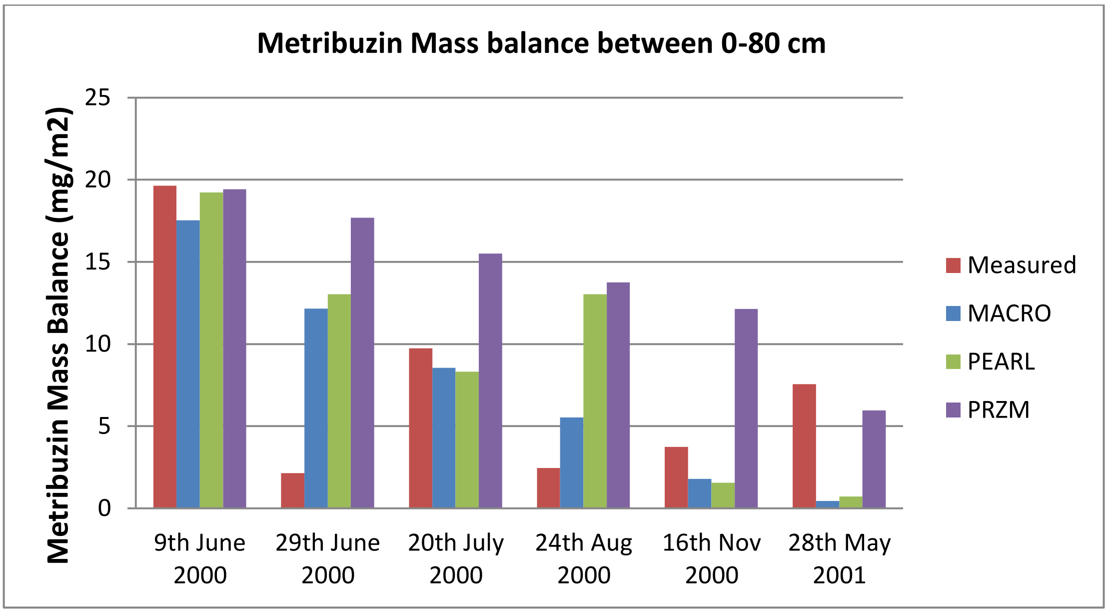


Figure 10. Measured and simulated Metribuzin mass balance from the 0-80 cm depth (2000/2001)

3.2 Period of validation

3.2.1 Soil Temperature

Similar efficiencies are found for the soil temperature (Figure 11, Table 6) that the period 2000/2001

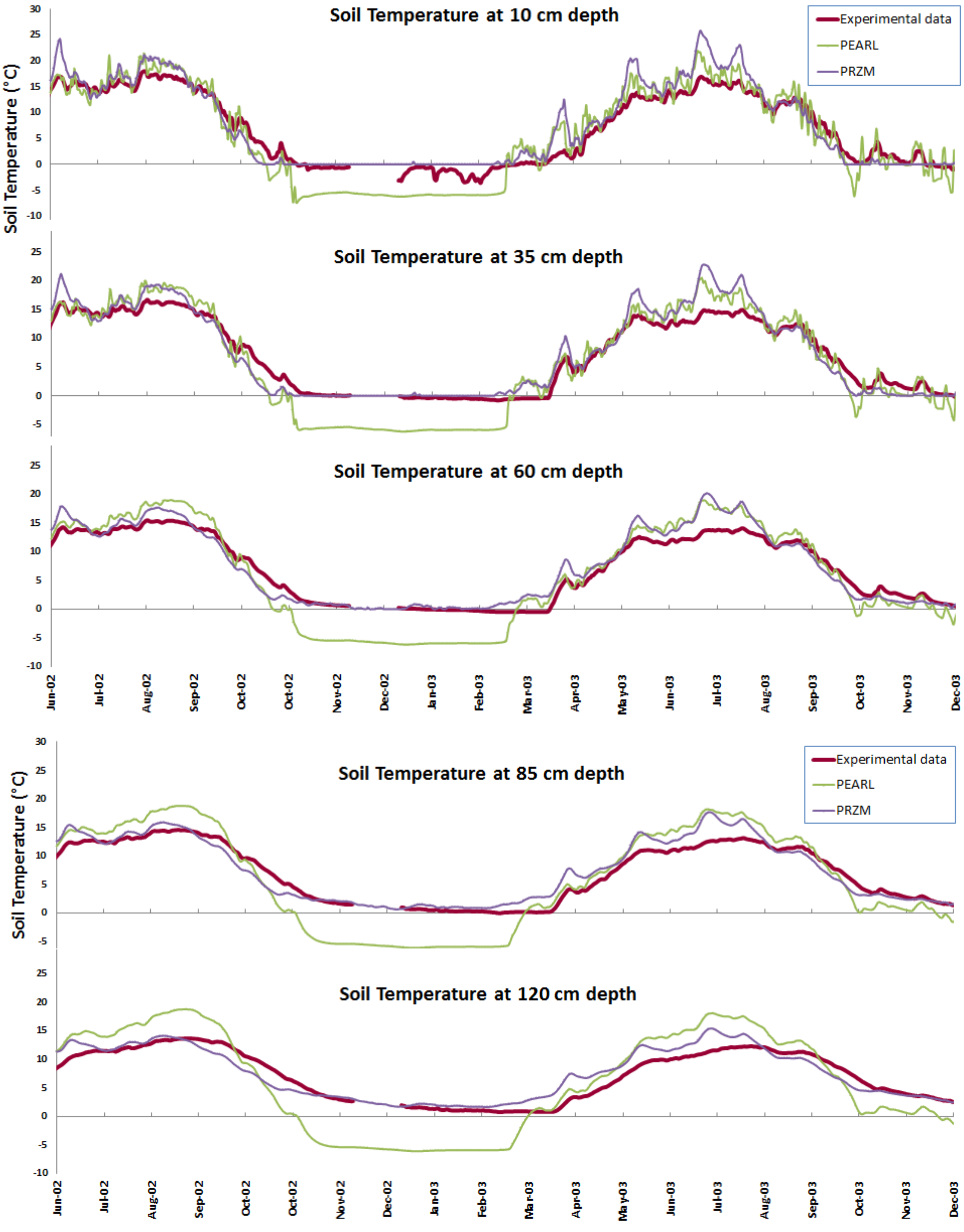


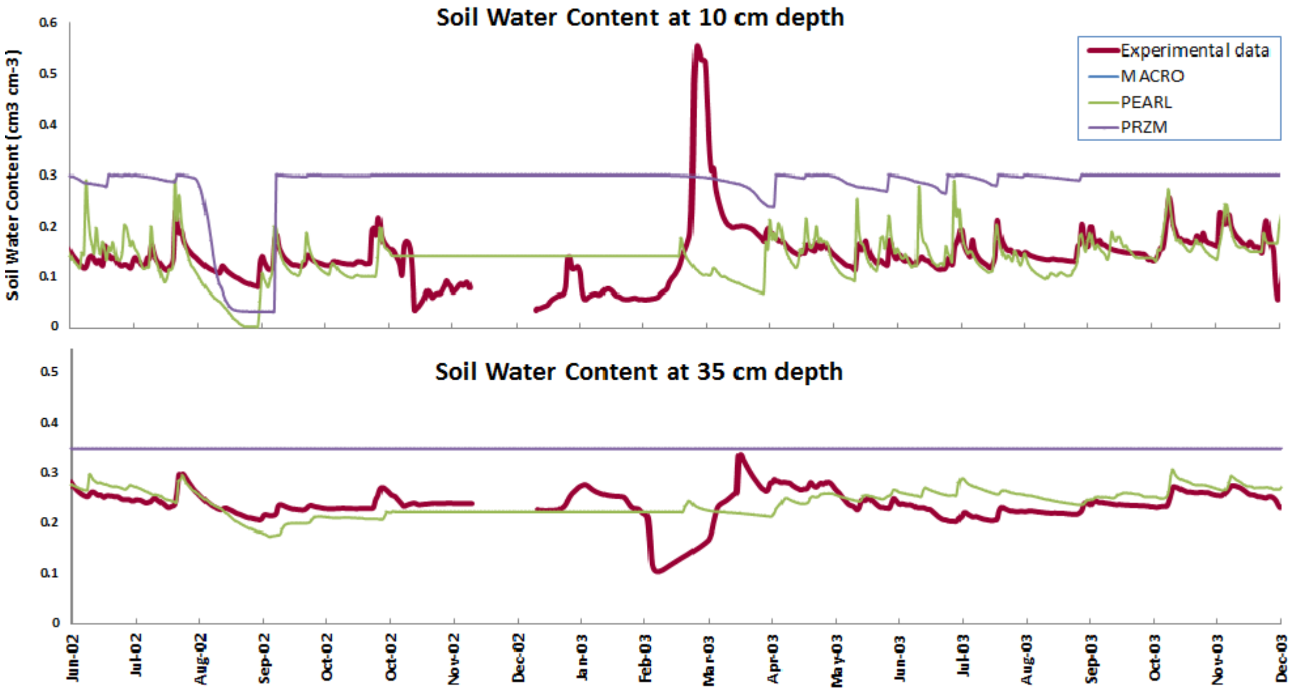
Figure 11. Soil temperature simulations profiles (2002/2003)

		RRMSE	EF	CRM	Slope	R2
10cm	PEARL	43.19	0.81	0.06	0.74	0.92
	PRZM	35.96	0.86	-0.14	0.81	0.93
35cm	PEARL	43.14	0.75	0.09	0.70	0.94
	PRZM	30.87	0.87	-0.09	0.81	0.93
60cm	PEARL	46.54	0.66	0.06	0.65	0.94
	PRZM	27.66	0.88	-0.09	0.84	0.93
85cm	PEARL	53.19	0.43	0.06	0.58	0.94
	PRZM	25.16	0.87	-0.09	0.88	0.90
120 cm	PEARL	63.48	-0.10	0.07	0.49	0.88
	PRZM	25.27	0.83	-0.07	0.92	0.84

Table 16. Statistical criteria for simulated soil temperature (2002/2003)

3.2.2 Soil Water content

Except at the depth of 60 cm, the model calibrated generally correctly the dynamics and described the mean value of the water content (Fig. 12) with comparable efficiencies than in the calibrated period (Table 17).



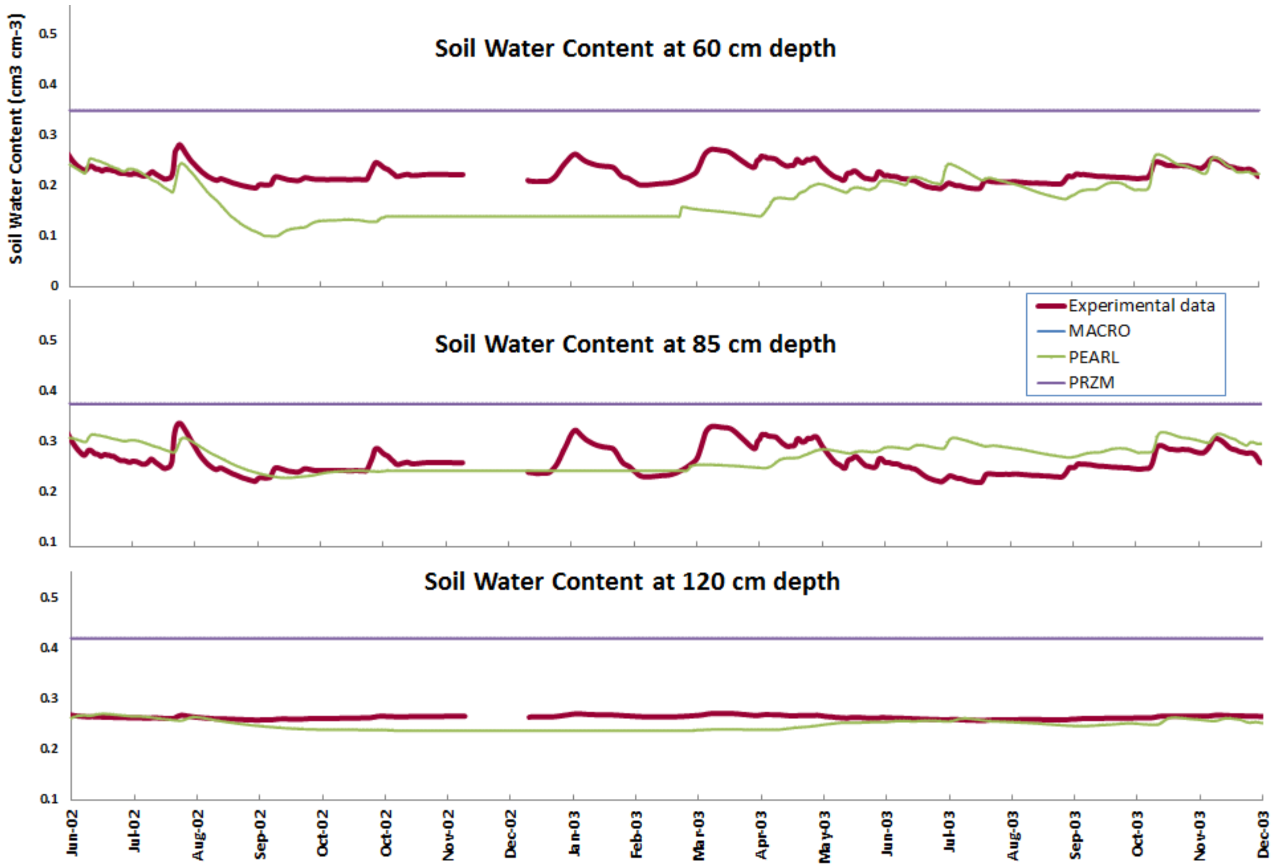


Figure 12. Soil water content simulations profiles (2002/2003)

		RRMSE	EF	CRM	Slope	R2
10cm	PEARL	48.72	-0.32	0.04	0.16	0.01
	PRZM	110.30	-5.77	-0.96	0.12	0.01
35cm	PEARL	15.57	-0.28	-0.02	0.30	0.06
	PRZM	48.70	-11.49	-0.47	0.05	0.00
60cm	PEARL	27.87	-10.77	0.20	0.07	0.03
	PRZM	55.68	-45.99	-0.55	0.04	0.00
85cm	PEARL	13.88	-0.73	-0.03	0.14	0.02
	PRZM	44.15	-16.53	-0.43	-0.02	0.00
120 cm	PEARL	7.09	-29.21	0.06	-0.12	0.11
	PRZM	59.20	-2103.32	-0.59	-0.01	0.00

Table 17. Statistical criteria for simulated soil moisture profiles (2002/2003).

3.2.3 Bromide leaching

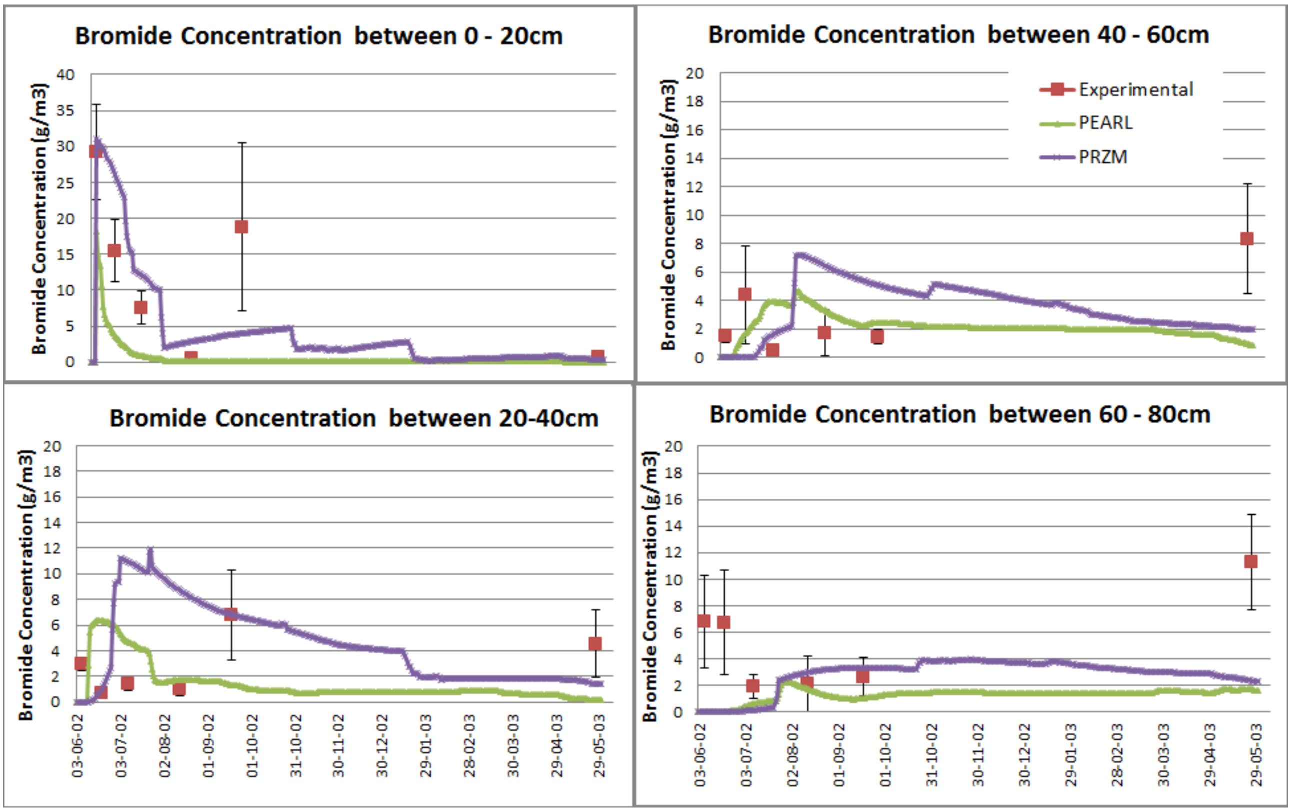


Figure 13. Bromide concentration simulations profiles (2000/2001)

Both models simulated rather well the dynamics of the experimental data in all layers (Fig. 13). Simulations in both models were almost similar although PEARL simulation was underestimated, like in the calibration period. The both models poorly simulated bromide contents during last days.

Bromide concentrations were experimentally measured in all layers at application day which was very strange and difficult to interpret.

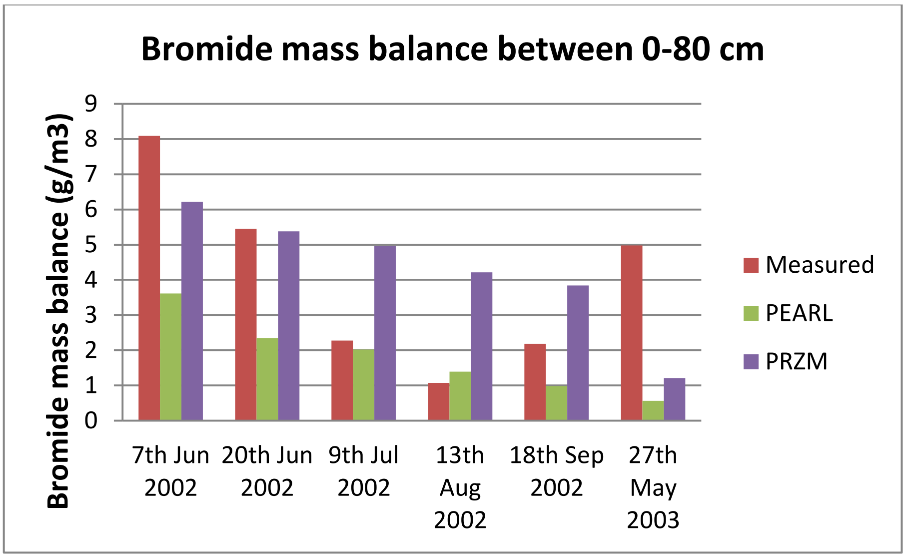


Figure 14. Measured and simulated bromide mass balance from the 0-80 cm depth (2002/2003)

3.2.4 Metribuzin leaching

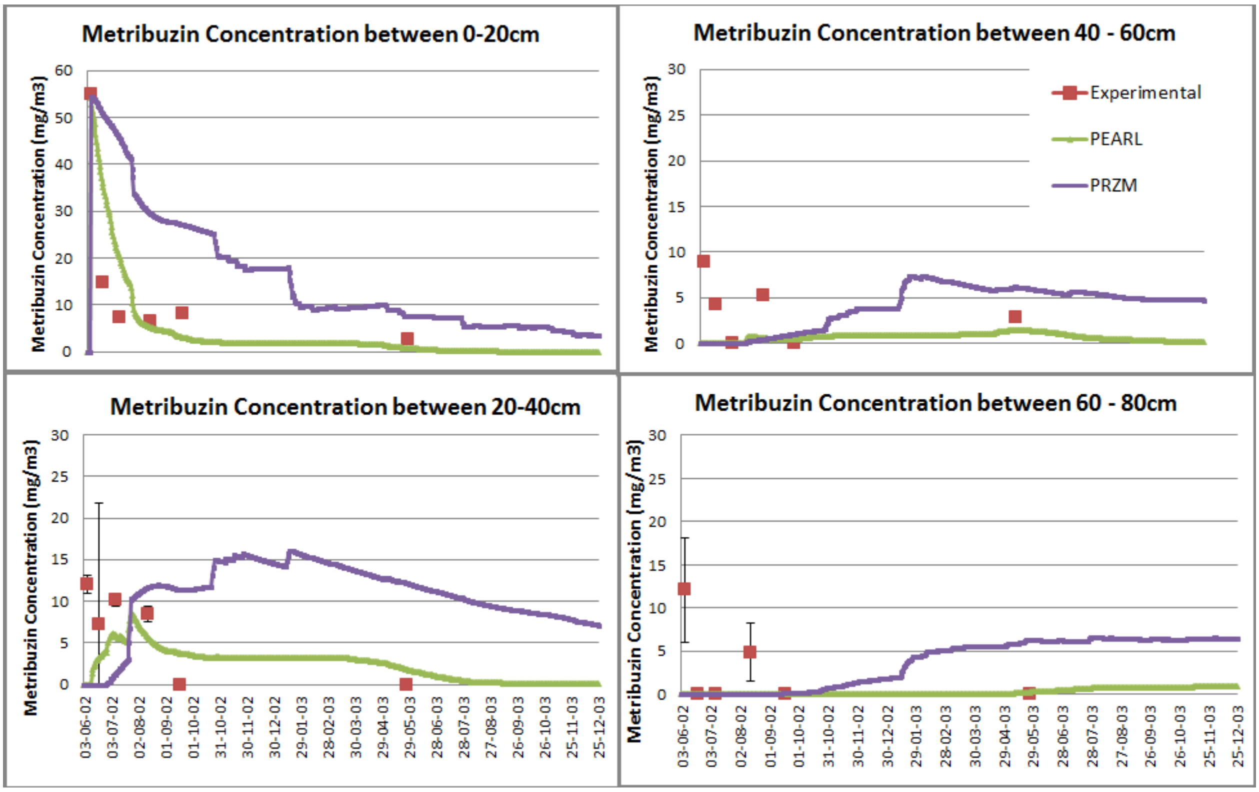


Figure 15. Metribuzin concentration simulations profiles (2002/2003)

The simulation of metribuzin with both models (Fig. 15) was rather similar than during the calibrated period, however the experimental data are not easy to interpret. For instance, there was metribuzin concentration in the deeper layers at application date. Both models did not simulate metribuzin concentrations in these layers until October 2002. Spatial heterogeneity of the metribuzin concentration can be responsible for these scattered data. Indeed, preferential flow may have occurred at different places throughout the plot. By contrast, PEARL simulated the metribuzin dissipation quite good in the top layer (0-20 cm). Simulation was also good in soil layer of 20-40 cm. At these two depths, simulation by PRZM was rather good. However, it overestimated at 20-40 cm soil depth.

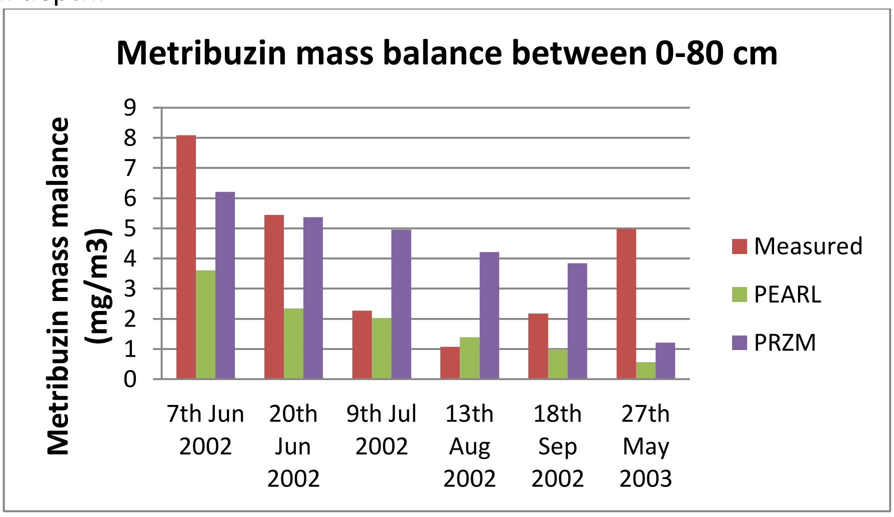


Figure 16. Measured and simulated Metribuzin mass balance from the 0-80 cm depth (2002/2003)

4. Conclusions

This work was conducted to compare and validate the performance of three major models (MAC-RO, PEARL and PRZM) using the data obtained from Norwegian experimental site. The seasonal dynamics of the soil water content were not simulated by any of three models during the winter-spring period. None of the three models took into account the absorption of energy during thawing. However, soil water dynamics were successfully calibrated with PEARL model by optimising Van Genuchten parameters. Experimental data of Bromide and Metribuzin were simulated during calibration period by all three models whereas only PEARL and PRZM were used during validation period. Simulation by Macro model was poor compared to other two models that may be due to crop parameters which MACRO did not take into account. The perspective is now to fix the problem to finish the simulation for both periods. Metribuzin was well simulated by PEARL model especially in surface soil horizon. Metribuzin simulation was good in PRZM also model but its efficiency was lesser than in PEARL model. Typical climatic conditions of Norwegian sites compared to other European sites are the combination of long winter periods having low temperature and snow covered soils, which usually lead to large water flow during snow melting. Soil frost and melting are very important processes, and lack of these processes within these models can explain the poor performance during winter and spring periods.

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