© *Acta hydrotechnica* **22/37 (2004)** Ljubljana
ISSN 1581-0267

UDK/*UDC*: 519.61/.64:504.4:556.38
Kratki znanstveni prispevek – *Preliminary scientific paper*

Prejeto/*Received*: 18. 6. 2005
Sprejeto/*Accepted*: 25. 11. 2005

UPORABA MODELA PEARL ZA SIMULACIJO EMISIJE PESTICIDOV V PODTALNICO LJUBLJANSKEGA POLJA
USAGE OF MODEL PEARL FOR SIMULATION OF PESTICIDE EMISSION INTO THE LJUBLJANSKO POLJE GROUNDWATER

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Podtalnica Ljubljanskega polja je eno najpomembnejših vodnih teles v Sloveniji in predstavlja vir pitne vode za okoli 300.000 ljudi. Tla, ki prekrivajo vodonosnik, so večinoma plitva in dobro prepustna, zaradi tega podtalnico ogrožajo pesticidi, ki pronicajo iz kmetijskih površin na Ljubljanskem polju. Velike količine v preteklosti uporabljenega atrazina na Ljubljanskem polju so privedle do tega, da sta atrazin in njegov razgradni produkt desetil atrazin presegla mejne vrednosti in sta še vedno prisotna v podtalnici. Zaradi manjše porabe po letu 1995 in prepovedi uporabe atrazina leta 2003 se njuna vrednost počasi zmanjšuje. Da bi se v prihodnosti takšna stanja preprečilo, smo skušali ugotoviti uporabnost modela PEARL za ocenjevanje bilance atrazina in mobilnosti pesticidov, ki se danes uporabljajo.

Ključne besede: *podtalnica, atrazin, metolaklor, PEARL, Ljubljansko polje*

Groundwater of the plain of Ljubljansko polje is one of the most important water bodies in Slovenia and represents the source of drinking water for around 300,000 people. Soil covering the aquifer is mostly shallow and permeable. Because of that the percolation of pesticides from the Ljubljansko polje fields represents a considerable threat to the groundwater. In the past atrazine was used in large amounts at the Ljubljansko polje, which was the reason that atrazine and its metabolite desethyl atrazine have exceeded the limit value and are still present in the groundwater. After 1995, the use of atrazine started to decrease, and in 2003 the use of atrazine was prohibited. Because of that the quantity of atrazine and desethyl atrazine in groundwater is slowly reducing. In order to prevent such scenarios in the future, we tried to establish the suitability of the PEARL model for the Ljubljansko polje. With the model one can evaluate the pesticide mobility, before they are registered and deployed to fields.

Key words: *groundwater, atrazine, metolaclor, PEARL, Ljubljansko polje*

1. UVOD

Uporaba različnih kemičnih sredstev za zaščito rastlin, ki se jih uporablja v kmetijstvu, onesnažuje okolje. Ker gre za strupene snovi, je njihova prisotnost v okolju in še posebej v pitni vodi nevarna. Ko pesticidi z dolgo razpolovno dobo pridejo do podtalnice, se dolgo časa zadržijo v njej, pri tem počasi razpadajo in prehajajo v druge, tudi strupene snovi. Lahko samo počakamo, da se odstranijo po naravni poti, kar pa traja dolgo časa, ogroža zdravje ljudi ter povečuje stroške oskrbe s pitno vodo. Ker je treba takšne primere preprečiti, smo preverjali uporabnost modela

1. INTRODUCTION

The usage of different chemical agents for plant protection used in farming has been the cause of environmental pollution. Because of toxicity of chemical agents their presence in the environment, especially in drinking water, is hazardous. Once pesticides with long half lives enter the groundwater, they stay there for a long time, slowly breaking down and transforming themselves into other also toxic substances. We have no other choice but to wait for the pesticides to break down by themselves. However, that takes a long time, represents health risks to people and increases the costs of water supply. Such situations need to be prevented. Because of that we examined the PEARL model (Pesticide Emission

PEARL (Pesticide Emission Assessment at Regional and Local Scales) za ugotavljanje mobilnosti pesticidov pri pogojih, kakršni obstajajo na Ljubljanskem polju. Uporabnost je bilo treba preveriti, ker je bil model razvit na Nizozemskem in je prilagojen njihovim razmeram. Z uporabo takih modelov bi se lahko pred registracijo pesticidov simuliralo njihovo obnašanje v okolju in bi se tako preprečilo kontaminiranje podtalnice.

Vodonosnik Ljubljanskega polja je eden največjih in tudi najpomembnejših vodnih teles v Sloveniji. Tla, ki ga prekrivajo, so plitva in dobro prepustna, zato je tudi eden izmed najbolj ogroženih vodonosnikov v Sloveniji. Njegove dinamične zaloge so ocenjene na 3 do 4 m^3/s (Andjelov *et al.*, 2005). Njegove statične zaloge ob povprečnem vodostaju podtalnice pa po oceni znašajo 1,801 x 10^{12} m^3 . Kljub tako velikim količinam vode so bile v nekaterih vodnjakih presežene mejne vrednosti za atrazin – v vodarni Hrastje pa so še vedno. To je vodilo k temu, da se je uporaba atrazina začela po letu 1995 zmanjševati, leta 2003 pa je bila sprejeta prepoved uporabe atrazina.

2. MATERIAL IN METODE

Pesticidi, ki se uporabljajo v kmetijstvu, se lahko izcejajo v podtalnico ali izhlapevajo v ozračje. Za ocenjevanje nevarnosti emisij pesticidov iz rastlin in tal ter njihovo obnašanje v okolju se vse bolj uporabljajo računski modeli. Izbrali smo model PEARL in preverili njegovo uporabnost za vodonosnik Ljubljanskega polja (Leistra *et al.,* 2001).

PEARL (slika 1) je enodimenzionalni numerični model, ki simulira obnašanje pesticidov v sistemu zemljina–rastlina. Razvit je bil na Nizozemskem. Tok vode po zemljini je opisan z Richardovo enačbo, upoštevajoč vrsto možnih spodnjih robnih pogojev. Evaporacija zemljine in transpiracija rastlin sta izračunana z množenjem referenčne evapotranspiracije s faktorji rastlin in zemljine. Tok toplote po zemljini je opisan s Fourierjevim zakonom. Toplotne lastnosti so funkcija poroznosti in vodne vsebnosti in so zato funkcija časa in globine zemljine.

Assessment at Regional and Local Scales) for simulating pesticide mobility in conditions present in the plain of Ljubljansko polje. Since the model has been developed in the Netherlands and adapted to their conditions, we had to check the applicability of the model in Slovenia. Namely, prior to the actual registration and application of pesticides to cropland, we could, with the help of these types of models, simulate the pesticide behaviour in the environment. In this way the contamination of groundwater could be prevented.

The aquifer of the Ljubljansko polje is one of the biggest and most important water bodies in Slovenia. The soil covering the Ljubljansko polje aquifer is shallow and permeable, which is why this is one of the most vulnerable aquifers in Slovenia. Its dynamic reserves were estimated at 3–4 m^3/s (Andjelov *et al.*, 2005), whereas its static reserves at the average water level of groundwater were estimated at 1.801 x 10^{12} m^3. Despite such enormous quantity of water in some wells, the concentrations of atrazine were over the boundary value. In the Hrastje water plant, the concentrations are still over the boundary value. Because of high concentrations of atrazine in groundwater its usage has begun to decrease after 1995; since 2003 the usage of atrazine has been prohibited.

2. MATERIAL AND METHODS

Pesticides used for farming can leach into underground waters or evaporate into the atmosphere. For evaluating the danger of pesticide emission from plants and soil, numerical models are used. We chose the PEARL model and examined its applicability for the Ljubljansko polje aquifer (Leistra *et al.,* 2001).

PEARL (Fig. 1) is a one-dimensional numerical model, which simulates pesticide behaviour in the soil–plant system. It was developed in the Netherlands. The water flow in soil is described by Richard’s equation including a range of possible lower boundary conditions. Evaporation from the soil and transpiration from plants are calculated so that the reference evapotranspiration is multiplied by soil and plant factors. Soil heat flow is described by Fourier’s law. The thermal properties are a function of porosity and water content and are therefore a function of time and soil depth.

Model PEARL temelji na:

- konvekcijsko/disperzijski enačbi, vključujoč difuzijo v plinasti fazi s temperaturno odvisnim Henryjevim koeficientom,
- modelu Freundlichove absorpcije,
- hitrosti transformacije, ki je odvisna od vsebnosti vode, temperature in globine zemljine,
- pasivnem rastlinskem dvigovanje vode.

Model računa tudi tvorbo in obnašanje produktov transformacije in opisuje tudi stranski izpust pesticidov v drenaže. Model ne simulira preferenčnega toka. Izhlapevanje iz površja zemljine je izračunano tako, da se privzame laminarno zračno plast na površini zemljine (Leistra *et al*., 2001).

PEARL sam ne računa toka vode in temperatur zemljine, ampak uporabi izračune iz modela SWAP (Soil Water Atmosphere Plant). Programski paket za simulacijo je torej sestavljen iz dveh modelov: SWAP in PEARL (slika 2) (Leistra *et al*., 2001).

Simulirali smo nanašanje atrazina na Ljubljansko polje, in sicer v realnih količinah, ki so jih ocenili na Inštitutu za hmeljarstvo in pivovarstvo Žalec (Simončič *et al*., 2004). Privzeli smo, da so atrazin nanašali vsako leto na isto polje, porašceno s koruzo. Takega stanja v realnosti zaradi kolobarjenja ni. Količine in datumi nanosov, uporabljeni v modelu, so prikazani v preglednici 1.

The PEARL model is based on:

- the convection/dispersion equation including diffusion in the gas phase with the temperature dependent on the Henry coefficient,
- the Freundlich sorption model,
- the transformation rate that depends on water content, temperature and depth in soil,
- the passive plant uptake rate.

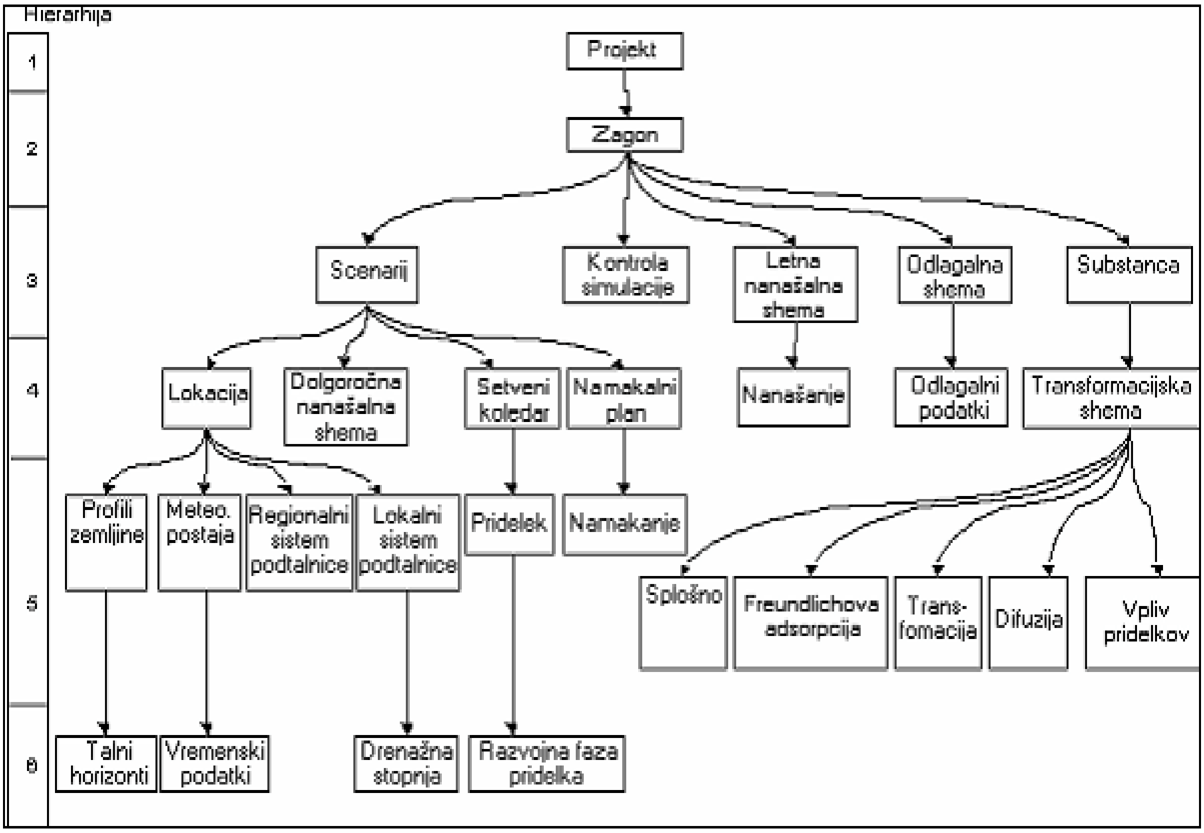
PEARL also calculates the formation and behaviour of transformation products and describes the lateral discharge of pesticides into drains. The volatilisation from the soil surface is calculated with the assumption that there is a laminar air layer on the soil surface (Leistra *et al.*, 2001).

The PEARL model does not calculate water flow and soil temperatures but uses calculated values from the SWAP model (Soil Water Atmosphere Plant). The program package for the simulation consists of two models: SWAP and PEARL (Fig. 2) (Leistra *et al.*, 2001).

We simulated the application of atrazine to the Ljubljansko polje and took real quantities that were estimated by the Slovenian Institute of Hop Research and Brewing (Simončič *et al*., 2004). We assumed that the atrazine was applied to the same cornfield every year. In reality such a condition does not exist because of the rotation of crops. Quantities and dates of application used in the model are represented in Table 1.

Preglednica 1. Nanašanje atrazina na polje v simulaciji.
Table 1. Application of atrazine to the field in simulation.

Datum / ***Date***	**Nanos /** ***Application*** **(kg/ha)**	**Datum /** ***Date***	**Nanos /** ***Application*** **(kg/ha)**
13.05.1989	1.500	06.05.1997	0.833
11.05.1990	1.500	13.05.1998	0.500
14.05.1991	1.500	08.05.1999	0.300
11.05.1992	1.500	07.05.2000	0.233
07.05.1993	1.500	15.05.2001	0.167
10.05.1994	1.500	08.05.2002	0.067
10.05.1995	1.500	2003	0.000
07.05.1996	1.330	2004	0.000



Slika 1. Pregled podatkovne baze modela PEARL (Tiktak *et al.*, 2000).

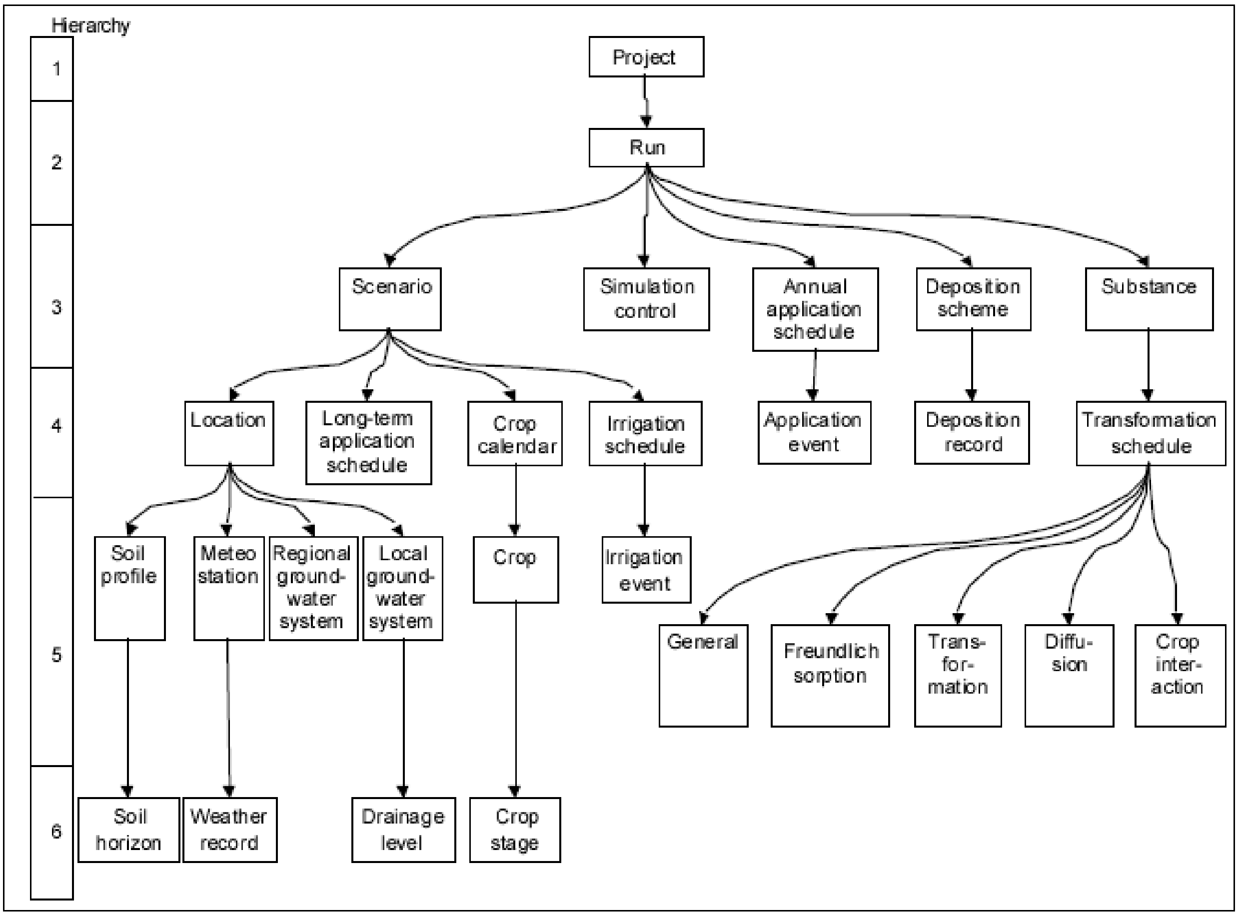
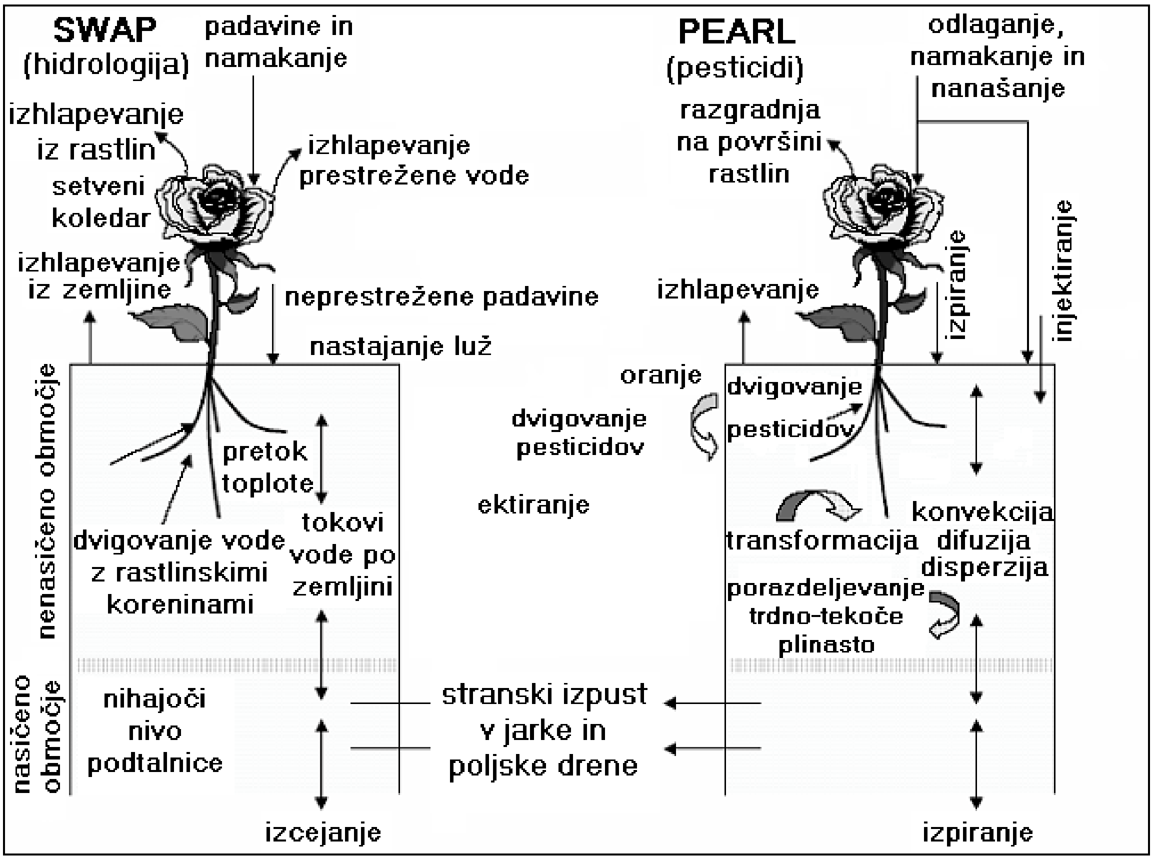


Figure 1. Overview of the PEARL database (Tiktak et al., 2000).



Slika 2: Pregled procesov, vključenih v model PEARL (Tiktak *et al.*, 2000).

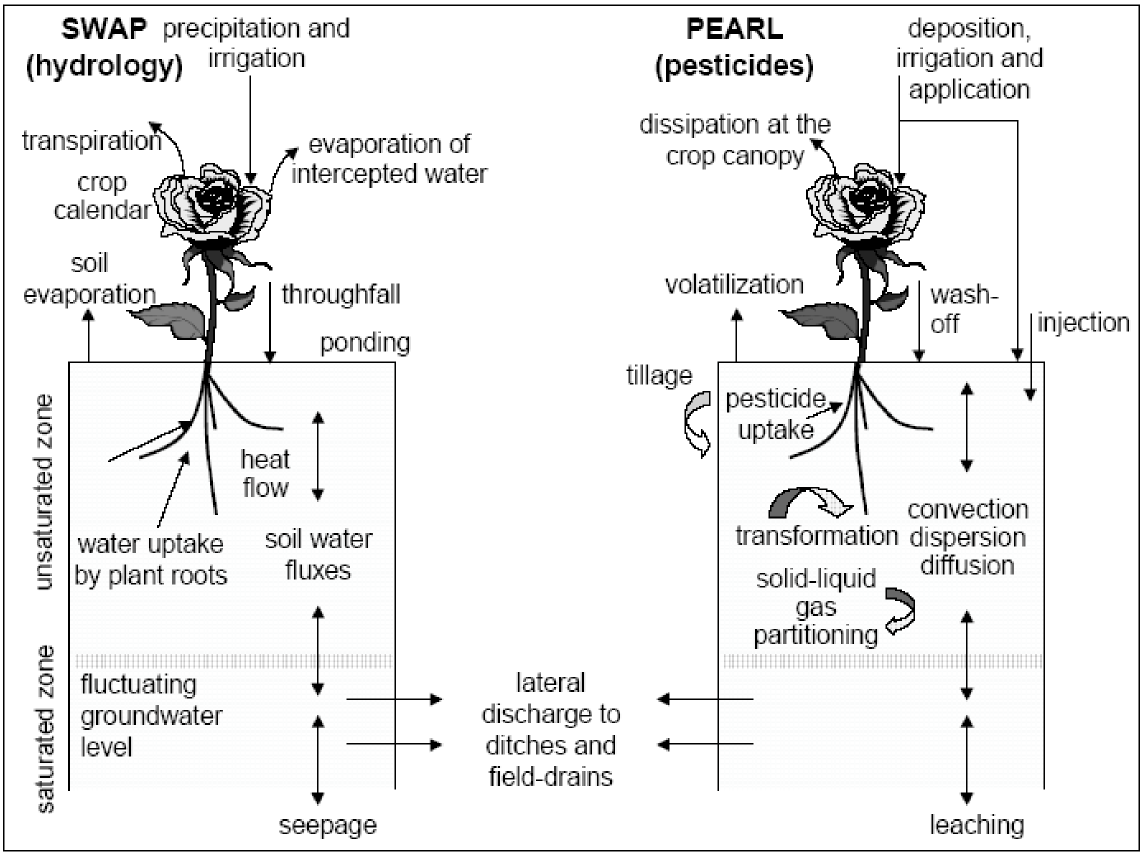


Figure 2. Overview of processes included in the PEARL model (Tiktak et al., 2000).

Uporabljeni so bili realni meteorološki podatki, kot so: sončno sevanje, maksimalna dnevna temperatura, minimalna dnevna temperatura, povprečni parni tlak, hitrost vetra in padavine od 1. 1. 1989 do 30. 9. 2004 (ARSO). V simulaciji smo uporabili troje različnih tal: lahka tla, lahka in srednje težka tla in srednje težka tla. Lahka tla ležijo ob reki Savi in predstavljajo področje, kjer je ogroženost podtalnice zaradi uporabe fitofarmacevtskih sredstev največja. Večji del teh tal prekrivajo gozdovi, grmičevje in travniki. Največji del prispevnega področja, iz katerega se napajajo vodnjaki v vodarnah, je prekritega z lahkimi in srednje težkimi tlemi. Srednje težka tla so prisotna le na zelo majhnem delu prispevnega območja. Podatki o lastnostih tal so podani v preglednicah 2–9. Simulirali smo tudi nanašanje atrazina na železniške nasipe (podatki o nanašanju so isti kot pri poljedelstvu).

Za primerjavo smo simulirali tudi distribucijo metolaklora po zemljini. Metolaklor smo izbrali, ker se je uporabljal približno v istih količinah kot atrazin, vendar pa mejnih vrednosti v vodnjakih vodarn ni nikoli presegel (Andjelov *et al.*, 2005). Lastnosti pesticidov atrazina in metolaklora, uporabljene v izračunu, so navedene v preglednicah 10 in 11.

The applied meteorological data were real; they were obtained from the Environmental Agency of the Republic of Slovenia (ARSO). We entered the following data: daily global sun radiation, maximum daily temperature, minimum daily temperature, average vapour pressure, average wind speed and daily precipitation, dating from 01/01/1989 to 30/09/2004. In the simulation we used three types of soil: light soil, light and moderate soil, and moderate soil. Light soil is to be found near the river Sava and represents the area where the groundwater is most vulnerable to the use of pesticides. The major part of light soil is covered with woods, bushes and meadows. The largest part of the drainage basin is covered with light and moderate soil. Moderate soil is present only in a small part of the drainage basin. Data about soil properties are given in Tables 2 to 9. We also simulated the application of atrazine to railway dikes (application data are the same as for farming).

For comparison we also simulated soil distribution of metolaclor. Metolaclor was chosen because it was used in almost the same quantities as the atrazine, however, the concentrations of metolaclor in the wells of water plants were never exceeded (Andjelov *et al.*, 2005). Properties used in the model for atrazine and metolaclor are given in Tables 10 and 11.

Preglednica 10. Razpolovni čas atrazina v dneh v odvisnosti od vrste tal in globine.
Table 10. Half life of atrazine in days, as a function of soil type and depth.

Horizont *Horizon*	1	2	3	4	5	6
Lahka tla *Light soil*	40	146	300	1000	1000	–
Lahka in srednje težka tla *Light and moderate soil*	40	146	300	1000	1000	–
Srednje težka tla *moderate soil*	40	146	146	300	1000	1000
Železniški nasipi *Railway dikes*	146	1000	1000	–	–	–

Preglednica 2. Parametri, uporabljeni v modelu PEARL, za lahka tla.
Table 2. Parameters used in PEARL for light soil.

	Debelina plasti *Layer thickness* [cm]	Teksturni razred *Texture class*	pH	Organska snov *Organic matter* [%]	Pesek *Sand* [%]	Glina *Clay* [%]	Suha pros. gostota zem. *Dry bulk density* [kg/m^3]
1. horizont/*horizon 1*	15	PI – peščena ilovica *SaL – Sandy Loam*	8	5	46	6	1260
2. horizont/*horizon 2*	14	MI – meljasta ilovica *SiL – Silty Loam*	8	3.25	33	15	1260
3. horizont/*horizon 3*	50	prod in pesek *Gravel and Sand*	8	1	90	6	1860
4. horizont/*horizon 4*	200	prod in pesek *Gravel and Sand*	7	0	95	2.5	2000
5. horizont/*horizon 5*	721	prod in pesek *Gravel and Sand*	7	0	95	2.5	2000

Preglednica 3. Uporabljeni Van Genuchtenovi parametri za lahka tla
(Tiktak *et al.* , 2000: K_{sat} iz SWCHPC, 2004).
Table 3. Van Genuchten parameters used for light soil
(Tiktak et al., 2000: K_{sat} from SWCHPC, 2004).

	θ_s (m^3/m^3)	θ_s (m^3/m^3)	α_d (1/cm)	α_w (1/cm)	n (–)	K_{sat} (m/d)	λ (–)
1. horizont (TOP Soils – B4)	0.524	0.01	0.016	0.016	1.56	10	0.18
2. horizont (SUB Soils – O14)	0.523	0.00	0.0025	0.0025	1.686	3.0912	0.057
3. horizont (SUB Soils – O1)	0.379	0.01	0.022	0.022	2.17	8	0
4. horizont (SUB Soils – O1)	0.323	0.01	0.022	0.022	2.17	10	0
5. horizont (SUB Soils – O1)	0.323	0.01	0.022	0.022	2.17	10	0

Preglednica 4. Parametri, uporabljeni v modelu PEARL, za lahka in srednje težka tla (iz Simončič *et al.*, 2004).
Table 4. Parameters used in PEARL for light and moderate soil (from Simončič et al., 2004).

	Debelina plasti *Layer thickness* [cm]	Teksturni razred *Texture class*	pH	Organska snov *Organic matter* [%]	Pesek *Sand* [%]	Glina *Clay* [%]	Suha pros. gostota *Dry bulk density* [kg/m^3]
1. horizont/*horizon 1*	20	MI – meljasta ilovica *SiL – Silty Loam*	6	7	16	23	1100
2. horizont/*horizon 2*	16	MI – meljasta ilovica *SiL – Silty Loam*	6	5	18	25	1100
3. horizont/*horizon 3*	50	prod in pesek *Gravel and Sand*	7	1	90	6	1860
4. horizont/*horizon 4*	200	prod in pesek *Gravel and Sand*	7	0	95	2.5	2000
5. horizont/*horizon 5*	724	prod in pesek *Gravel and Sand*	7	0	95	2.5	2000

Preglednica 5. Uporabljeni Van Genuchtenovi parametri za lahka in srednje težka tla
(Tiktak *et al.*, 2000: K_{sat} iz SWCHPC, 2004).
Table 5. Van Genuchten parameters for light and moderate soil (Tiktak et al., 2000: K_{sat} *from SWCHPC, 2004).*

	θ_s (m^3/m^3)	θ_s (m^3/m^3)	α_d (1/cm)	α_w (1/cm)	n (–)	K_{sat} (m/d)	λ (–)
1. horizont (TOP Soils – B09)	0.584	0	0.0065	0.0065	1.325	6.0648	–2.161
2. horizont (SUB Soils – O14)	0.586	0.00	0.0025	0.0025	1.686	4.8504	0.057
3. horizont (SUB Soils – O1)	0.379	0.01	0.0224	0.0224	2.167	8	0
4. horizont (SUB Soils – O1)	0.323	0.01	0.0224	0.0224	2.167	10	0
5. horizont (SUB Soils – O1)	0.323	0.01	0.0224	0.0224	2.167	10	0

Preglednica 6. Parametri, uporabljeni v modelu PEARL, za srednje težka tla.
Table 6. Parameters used in the PEARL model for moderate soil.

	Debelina plasti *Layer thickness* [cm]	Teksturni razred *Texture class*	pH	Organska snov *Organic matter* [%]	Pesek *Sand* [%]	Glina *Clay* [%]	Suha pros. gostota zem. *Dry bulk density* [kg/m^3]
1. horizont/*horizon 1*	20	MI – meljasta ilovica *SiL – Silty Loam*	6	7	16	23	1100
2. horizont/*horizon 2*	16	MI – meljasta ilovica *SiL – Silty Loam*	6	5	18	25	1100
3. horizont/*horizon 3*	29	MI – meljasta ilovica *SiL – Silty Loam*	6	3	22	22	1210
4. horizont/*horizon 4*	15	MG – meljasta glina *SiC – Silty Clay*	6	0	19	40	1310
5. horizont/*horizon 5*	200	prod in pesek *Gravel and Sand*	6.5	0	95	2.5	2000
6. horizont/*horizon 6*	720	prod in pesek *Gravel and Sand*	7	0	95	2.5	2000

Preglednica 7. Uporabljeni Van Genuchtenovi parametri za srednje težka tla
(Tiktak et al., 2000: K_{sat} iz SWCHPC, 2004).
Table 7. Van Genuchten parameters used for moderate soil
(Tiktak et al., 2000: K_{sat} from SWCHPC, 2004).

	θ_s (m^3/m^3)	θ_s (m^3/m^3)	α_d (1/cm)	α_w (1/cm)	n (–)	K_{sat} (m/d)	λ (–)
1. horizont (TOP Soils – B09)	0,584	0	0.0065	0.0065	1.325	6.0648	–2.161
2. horizont (SUB Soils – O14)	0.586	0.00	0.0025	0.0025	1.686	4.8504	0.057
3. horizont (SUB Soils – O14)	0.542	0	0.0025	0.0025	1.686	1.6848	0.057
4. horizont (SUB Soils – O12)	0.508	0	0.0095	0.0095	1.159	0.0312	–4.171
5. horizont (SUB Soils – O1)	0.323	0.01	0.0224	0.0224	2.167	10	0
6. horizont (SUB Soils – O1)	0.323	0.01	0.0224	0.0224	2.167	10	0

Preglednica 8. Parametri, uporabljeni v modelu PEARL, za železniški nasip.
Table 8. Parameters used in model PEARL for railway dike.

	Debelina plasti *Layer thickness* [cm]	Teksturni razred Texture class	pH	Organska snov *Organic matter* [%]	Pesek *Sand* [%]	Glina *Clay* [%]	Suha pros. gostota zem. *Dry bulk density* [kg/m^3]
1. horizont/*horizon 1*	10	prod in pesek / *Gravel and Sand*	8	2	90	6	1860
2. horizont/*horizon 2*	90	prod in pesek / *Gravel and Sand*	7	0	95	2.5	2000
3. horizont/*horizon 3*	200	prod in pesek / *Gravel and Sand*	7	0	95	2.5	2000
4. horizont/*horizon 4*	700	prod in pesek / *Gravel and Sand*	7	0	95	2.5	2000

Preglednica 9. Uporabljeni Van Genuchtenovi parametri za železniški nasip (Tiktak *et al.*, 2000: K_{sat} iz SWCHPC, 2004).
Table 9. Van Genuchten parameters for railway dike (Tiktak et al., 2000: K_{sat} from SWCHPC, 2004).

	θ_s (m^3/m^3)	θ_s (m^3/m^3)	α_d (1/cm)	α_w (1/cm)	n (–)	K_{sat} (m/d)	λ (–)
1. horizont (SUB Soils – O1)	0.379	0.01	0.0224	0.0224	2.167	8	0
2. horizont (SUB Soils – O1)	0.353	0.01	0.0224	0.0224	2.167	10	0
3. horizont (SUB Soils – O1)	0.353	0.01	0.0224	0.0224	2.167	10	0
4. horizont (SUB Soils – O1)	0.353	0.01	0.0224	0.0224	2.167	10	0

Preglednica 11. Absorpcija atrazina v odvisnosti od zemljine – K_{oc} iz (ARS PPD, 2005).
Table 11. Sorption of atrazine in dependence of soil – K_{oc} *from (ARS PPD, 2005).*

	K_{oc}	K_{om}
peščena ilovica (PI) / *Sandy Loam (SaL)*	57	33
meljasta ilovica (MI) / *Silty Loam (SiL)*	120	70
glina (G) / *Clay (C)*	87	50
pesek (P) / *Sand (Sa)*	90	52

Simulirali smo precedek atrazina in metolaklora na globini 10 m (največja globina, ki jo podpira model PEARL), kar pa ni dovolj globoko, saj podtalnica Ljubljanskega polja ponekod leži tudi 30 m pod površjem. Vendar so izračuni pokazali, da se atrazin v globljih plasteh, kjer ni veliko organskih snovi in mikroorganizmov, skoraj ne razkraja, zato izračunani rezultati dajejo dober približek dejanskim procesom.

3. REZULTATI IN RAZPRAVA

Dobljeni rezultati (slika 3) so pokazali, da so tla na Ljubljanskem polju zaradi svoje plitvosti zelo slaba zaščita podtalnice, saj zadržijo večjo koncentracijo atrazina samo v zgornji plasti tal (lahka tla do 29 cm, lahka in srednje težka tla do 36 cm in srednje težka tla do 65 cm). Ko pa atrazin doseže globino 1 m, se veže na tla samo v zelo majhnih količinah, ostalo pa pronica proti podtalnici.

Rezultati so pokazali tudi (slika 4), kako z globino pada koncentracija atrazina v precedku. Največji padec koncentracije je v plasteh nekaj centimetrov pod površjem. Naslednji padec se zgodi, ko atrazin preide iz zemljine v prod in pesek. Potem pa koncentracije v precedku z globino zelo počasi upadajo. To pomeni, da do podtalnice, ki je ponekod v globini 30 m, pridejo koncentracije, ki niso veliko manjše od koncentracij, ki so bile izračunane za precedek na globini 10 metrov.

Izračunali smo tudi precedke na globini 10 m (sliki 5 in 6) za atrazin (za vse podlage) in metolaklor (za lahka tla).

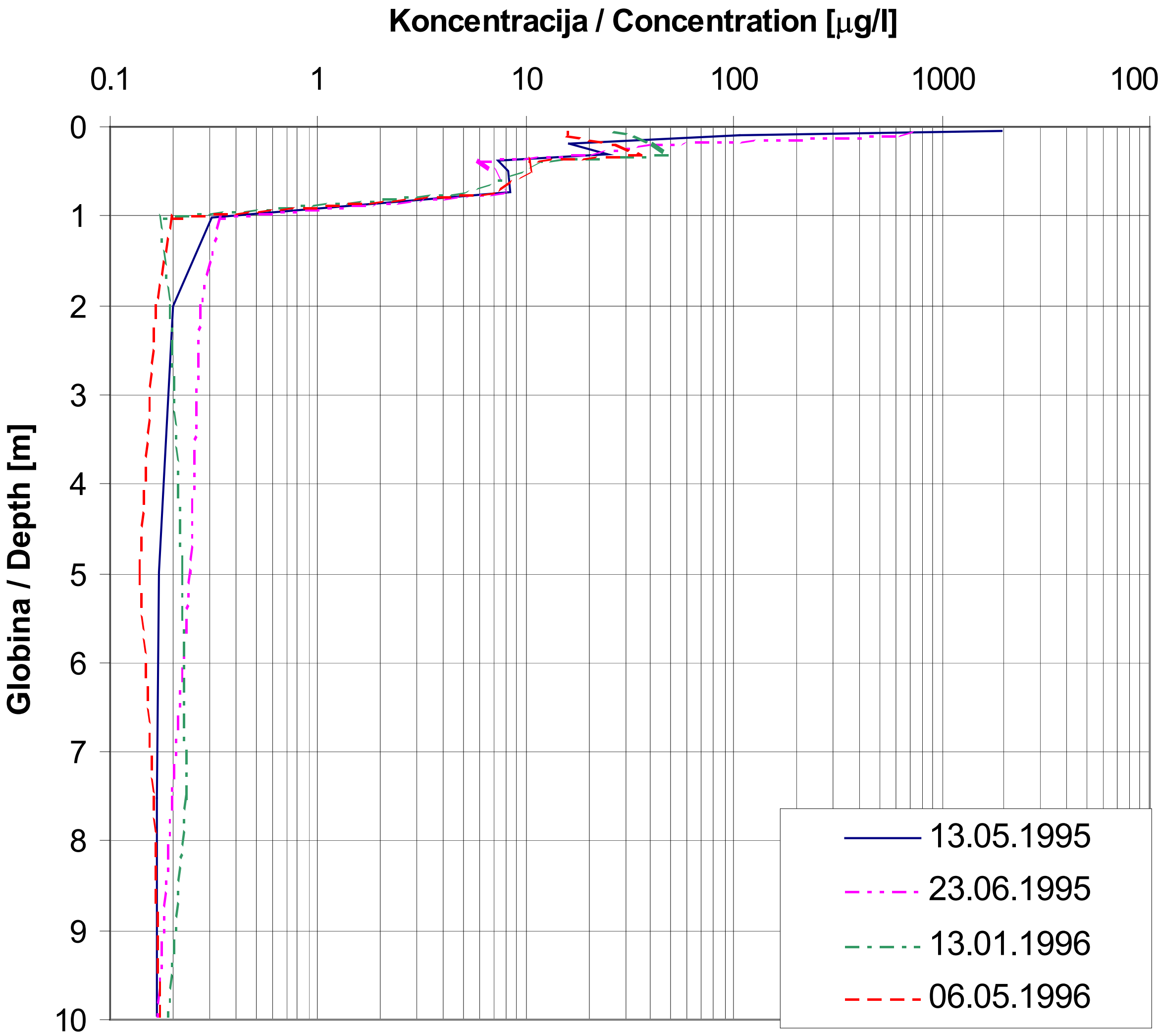
We simulated the atrazine and metolaclor percolate at a depth of 10 m (this is the maximum depth supported by the model), which is not deep enough, because the groundwater of the Ljubljansko polje in some places lies as much as 30 m deep. However, calculations have shown that the atrazine decomposes very slowly in deeper layers of soil where there is almost no organic matter or microorganisms. Thus the calculated results give a good approximation for the actual processes.

3. RESULTS AND DISCUSSION

The results given on Figure 3 have shown that the shallowness of the soil of the Ljubljansko polje represents poor protection to its groundwater. A considerable amount of atrazine is retained in the top layer of soil: light soil up to 29 cm, light and moderate soil up to 36 cm, and moderate soil up to 65 cm. When the atrazine reaches the depth of 1 m, only small amounts of atrazine bind to the soil and the rest leaches into the groundwater.

The results given on Figure 4 show how the concentration of the atrazine in the percolate decreases with depth. The most significant fall of the concentration happens in the layers just a few centimetres under the surface. The next fall happens when the atrazine passes from the soil into sand and gravel. After that the concentration in the percolate reduces slowly. It can be assumed that the concentrations in the percolate at 30 m depth are not much lower than the concentration at a depth of 10 m.

We also calculated the percolates at 10 m depth (Figures 5 and 6) for atrazine (for all soils) and metolaclor (for light soil).



Slika 3. Koncentracija atrazina v lahki in srednje težki zemljini
na različnih globinah ob različnih časih.

Figure 3. Concentration of atrazine in light and moderate soil at different depths and at different dates.

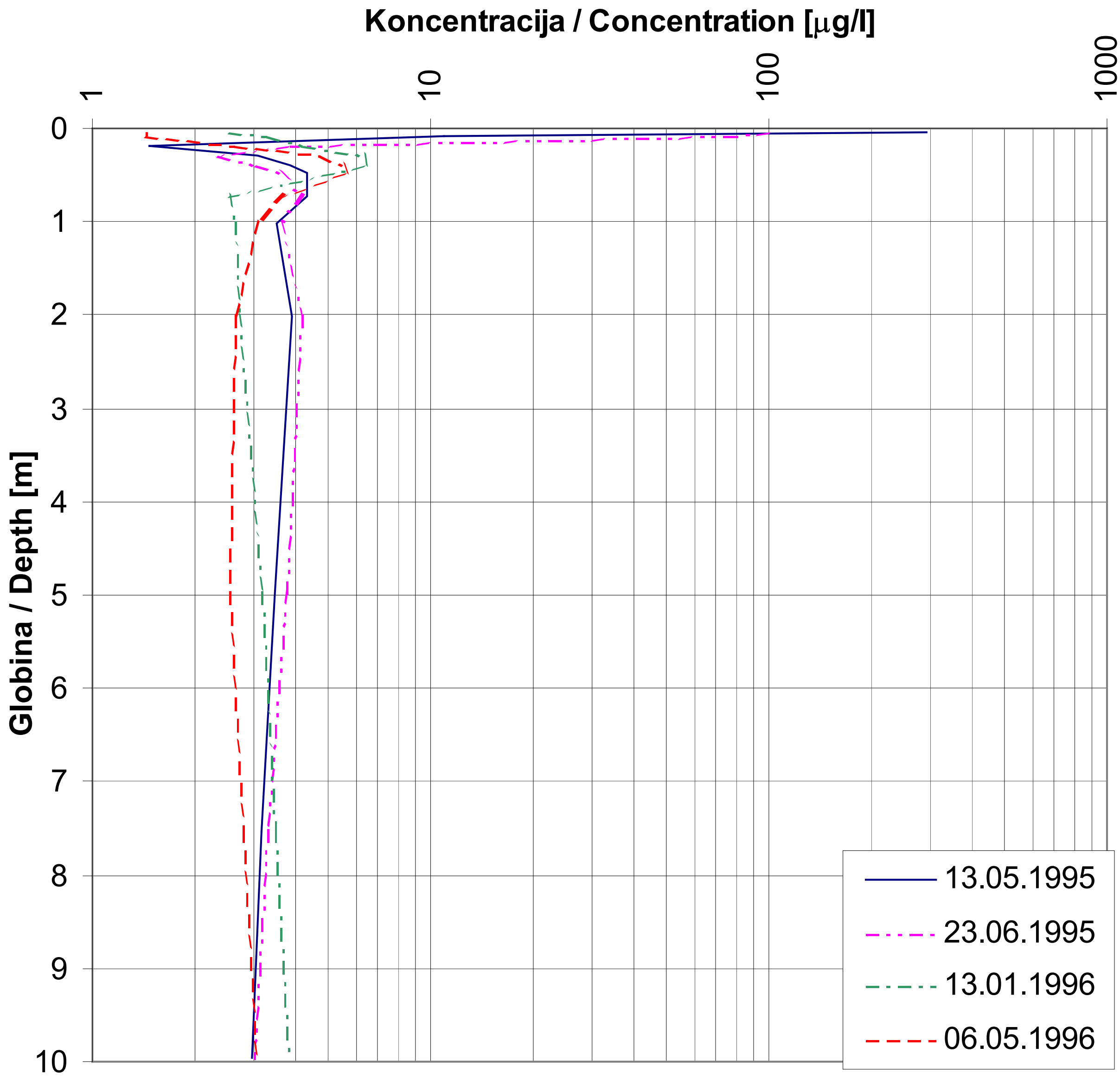
V preglednici 12 so prikazane maksimalne koncentracije v precedku na globini 10 m. Prikazana je tudi frakcija atrazina, ki je dosegla podtalnico.

Primerjali smo izračunane vrednosti za različne tipe tal z izmerjenimi vrednostmi na merilnih mestih. Pokazalo se je, da obstaja neka korelacija. Težava je v tem, da so izmerjene vrednosti podane od 1992 naprej, na nekaterih mestih celo od leta 1995 naprej. Prva merjenja so bila izvedena s predolgimi presledki, zato je podatke težje primerjati. Pri simulaciji pa je največja napaka na njenem začetku zaradi privzetega začetnega pogoja, da je koncentracija atrazina v tleh in podtalnici enaka nič. Podatki se razlikujejo tudi po tem,

In Table 12 maximum concentrations in the percolate at a depth of 10 m are shown. Fractions of atrazine that leached into the groundwater are also shown.

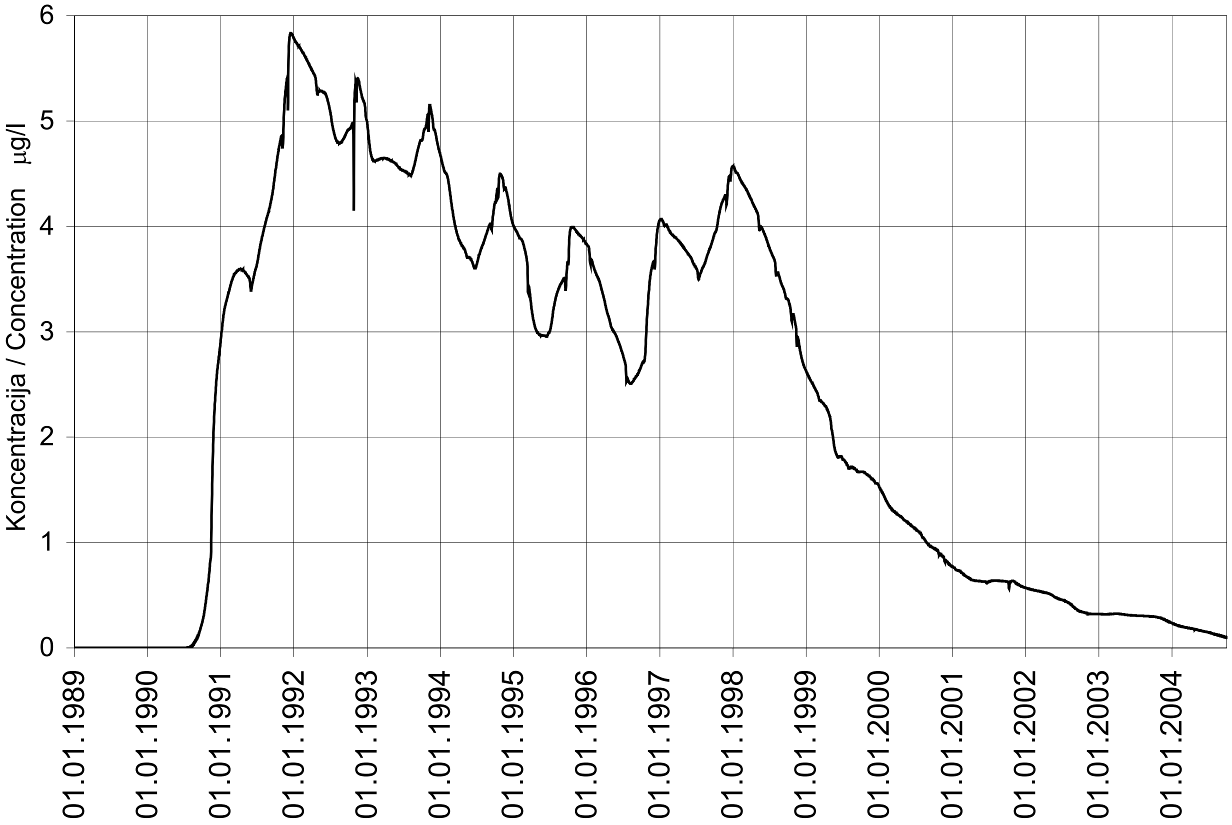
We compared the calculated results for different types of soil with values measured in the wells. The comparison showed some correlation between the measured and calculated data. The problem was that measured data were available only from 1992 onwards, and at some sampling sites even only from 1995 onwards. These first measurements were taken in long intervals, consequently it was hard to compare the data. In a simulation, however, the greatest mistake occurs at the beginning because of the assumed initial condition that the concentration of atrazine in soil and in the groundwater is zero. The da začnejo računane vrednosti po zmanjšanju porabe atrazina močno padati, medtem ko merjene vrednosti le počasi padajo. Razlog temu je, da se pri računanju upošteva samo plast na globini 10 m pod računano površino, na merjene vrednosti pa vpliva širše prispevno območje, s katerega se atrazin izceja v podtalnico. Kot primer bi lahko podal vodarno Hrastje, ki ima najbolj raztegnjeno prispevno območje; to se pozna tudi pri izmerjenih vrednostih, saj so koncentracije atrazina v tej vodarni še vedno nad dovoljeno vrednostjo.

difference is also that after a decreased application of atrazine the calculated values in the percolate start decreasing quickly, whereas the measured values decrease slowly. The reason for that is that in the calculated values only the layer at 10 m is considered, whereas the measured values are affected by a wide drainage basin from which the atrazine leaches into the groundwater. A good example of this is the Hrastje water pumping station, which has the most extended drainage basin. That is probably why concentrations in the water pumping station are still above the permitted values.

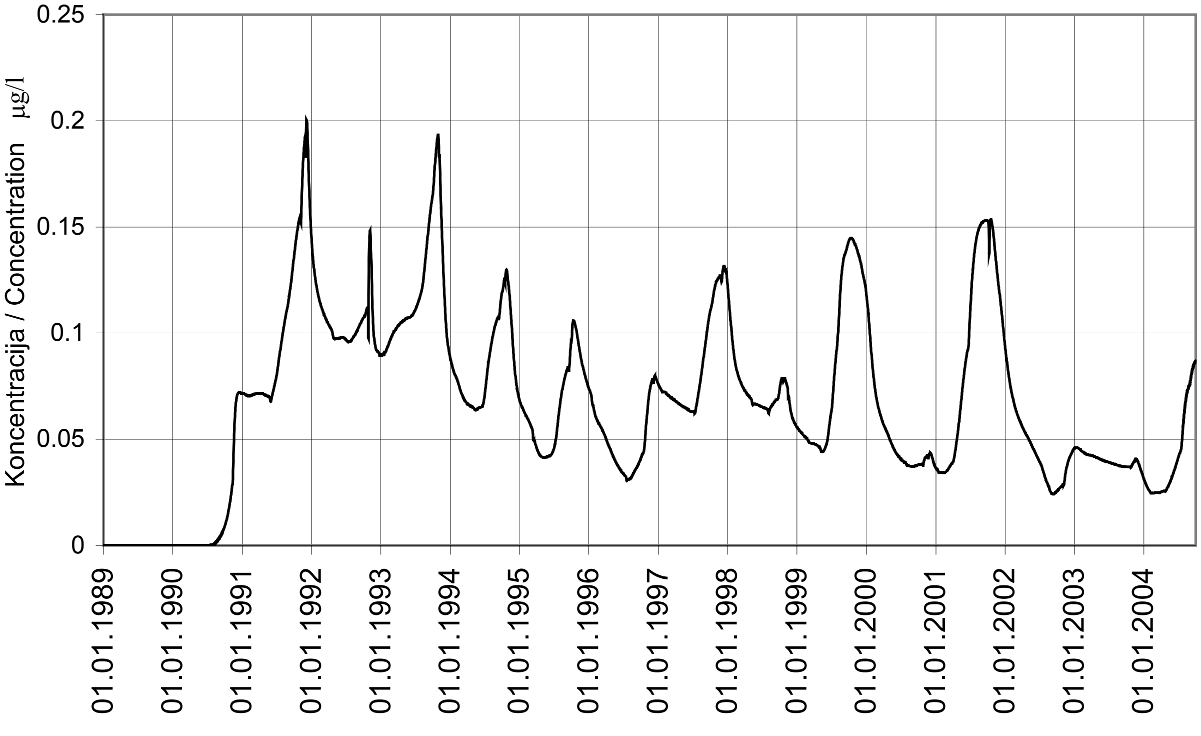


Slika 4. Koncentracija atrazina v precedku v lahki in srednje težki zemljini
na različnih globinah ob različnih časih.

*Figure 4. Concentration of atrazine in the percolate of light and moderate soil
at different depths and at different dates.*



Slika 5. Koncentracija atrazina v precedku v lahkih in srednje težkih tleh na globini 10 m.
Figure 5. Concentration of atrazine in percolate in light and moderate soil at a depth of 10 m.



Slika 6. Koncentracija metolaklora v precedku v lahkih in srednje težkih tleh na globini 10 m.
Figure 6. Concentration of metolaclor in percolate in light and moderate soil at a depth of 10 m.

Preglednica 12. Maksimalne koncentracije atrazina v precedku na globini 10 m.
Table 12. Maximum concentrations of atrazine in the percolate at 10 m depth.

	Maksimalna koncentracija *Maximum concentration*	Datum maksimalne koncentracije *Date of maximum concentration*	Frakcija atrazina, ki je pronicala v podtalnico *Fraction of atrazine leached in groundwater*
	[μg/l]		[%]
Lahka tla *Light soil*	18.51	18.11.1991	8.9
Lahka in srednje težka tla *Light and moderate soil*	5.83	16.12.1991	3.2
Srednje težka tla *Moderate soil*	1.98	06.11.1993	1.1
Železniški nasip *Railway dike*	96.75	12.08.1991	67.8

Da bi se prepričali o uporabnosti modela, smo simulirali tudi distribucijo metolaklora po zemljini. Metolaklor smo izbrali, ker se je uporabljal v približno istih količinah kot atrazin, vendar pa ga v podtalnici niso zaznali. Rezultati so potrdili, da je metolaklor veliko manj mobilen kot atrazin, saj je model za lahka tla izračunal do stokrat manjše vrednosti (slika 6) kot za atrazin. Vendar se te vrednosti zelo hitro spremenijo (povečajo ali zmanjšajo) ob spremembi koeficientov, ki najbolj vplivajo na mobilnost pesticidov. Ti koeficienti so absorpcija na organsko snov (K_{om}), razpolovni čas in topnost v vodi. V literaturi smo za atrazin našli koeficiente K_{om} v različnih zemljinah, ki so se med seboj razlikovali tudi za faktor 3. Pri atrazinu so izračunane koncentracije atrazina v lahkih tleh tako visoke zaradi tega, ker je za zemljino, ki se nahaja na lahkih tleh Ljubljanskega polja, koeficient K_{om} najmanjši, kar pomeni, da se pesticid na tako zemljino ne veže, ampak pronica v podtalje. Za metolaklor pa takih podatkov nismo našli. Morda je tudi to razlog za tolikšno razliko med koncentracijama.

4. ZAKLJUČKI

Slabost modela je ta, da računa samo do globine 10 m. Vseeno menimo, da je model uporaben tudi za globlje podtalnice, saj se izračunana koncentracija atrazina v precedku

To check the applicability of the model we then simulated the distribution of metolaclor in the soil. Metolaclor was chosen because it was used in the same amounts as atrazine, but it was not found in the wells of the water pumping stations. Results confirmed that metolaclor is less mobile than atrazine. The calculated values (Figure 6) of metolaclor in percolate were up to a hundred times smaller than those of atrazine. But these values can change quickly (increase or decrease) by changing the coefficients that mostly influence the pesticide mobility. These coefficients include sorption on organic matter (K_{om}), half life, and solubility in water. In the literature, we found coefficients K_{om} for atrazine in different soils; they vary up to a factor of 3. The calculated atrazine concentrations in light soil were found so high because coefficient K_{om} for such soil is the lowest, meaning that the pesticides do not bound to the soil, but percolate into the groundwater. For metolaclor, no such data were found. Maybe that is the reason for such a discrepancy in percolate concentrations of atrazine and metolaclor.

4. CONCLUSIONS

The weakness of the model is that the maximum depth of the calculation is 10 m. Nevertheless, we believe that the model is suitable for deeper groundwater, because the concentration in the percolate at a depth of 7.5

na globini 7,5 m skoraj ne razlikuje od koncentracije na 10 m (glej sliko 4). Nastane samo časoven zamik zaradi potovanja pesticida po zemljini navzdol. Model se lahko uporabi za prvo oceno obnašanja pesticidov v tleh, preden se jih registrira in začne uporabljati. Kvaliteta simulacije modela je odvisna od kvalitete vhodnih podatkov, ki jih je treba določiti z laboratorijskimi preiskavami in terenskimi meritvemi.

Na Ljubljansko polje je bilo po ocenah od leta 1991 do 1995 letno nanešeno 450 kg atrazina. Dinamične zaloge podtalnice se po ocenah gibljejo med 3 in 4 m^3/s, to je 126.144.000 m^3/leto. Da se z atrazinom do mejne vrednosti 0,1 µg/l onesnaži 126.144.000 m^3 vode, je dovolj že 12,6 kg atrazina, kar je 2,8 % od 450 kg.

Z modelom PEARL smo izračunali, da do podtalnice skozi lahka tla pride 8,9 % atrazina, skozi lahka in srednje težka tla 3,2 %, skozi srednje težka tla 1,1 % atrazina in skozi železniški nasip 67,8 % atrazina. V podtalju ni intenzivnega mešanja vode, zato so bile vrednosti atrazina v vodarnah višje, kot pa bi bile v primeru popolnega premešanja. Iz tega lahko sklepamo, da je model kar dobro izračunal odstotek izcejanja atrazina v podtalnico.

Model PEARL omogoča ocenjevanje posledic uporabe različnih vrst pesticidov na onesnaženje podtalnice in je kot tak dobro orodje za oceno različnih ukrepov.

ZAHVALA

Avtor se zahvaljuje prof. dr. Mitji Brillyju in prof. dr. Branetu Matičiču za strokovno pomoč. Za podatke, ki jih je uporabil pri pripravi članka, se zahvaljuje Kmetijskemu inštitutu Slovenije in Agenciji RS za okolje.

m is almost identical to the concentration at 10 m (see Figure 4). The difference is only in terms of time when the concentration reaches the maximum. The reason for that is the travel of a pesticide through soil. The model can be used for a first evaluation of pesticide mobility before they are registered and used. Quality of simulation is depended upon the quality of input data, which must be defined with laboratory analysis and field measurements.

It has been evaluated that from 1991 to 1995, 450 kg of atrazine was applied yearly to the fields of the Ljubljansko polje. According to evaluations, dynamic groundwater storages are in a range of 3–4 m^3/s, which amounts to 126,144,000 m^3/year. For contamination of 126,144,000 m^3 of groundwater with atrazine up to the boundary value, which is 0.1 µg/l, 12.6 kg of atrazine is enough, this being just 2.8 % of 450 kg.

With the PEARL model we calculated the amounts of atrazine, which leach into the groundwater. Through light soil, 8.9 % of the whole application percolates into the groundwater, through light and moderate soil 3.2 %, through moderate soil 1.1 %, and through the railway dike 67.8 % of atrazine. In the aquifer, intensive mixing of water is not present, and because of that values of atrazine in water plants were higher than they would be in the case of absolute mixing. Therefore we can assume that the model yielded quite a good estimation of the atrazine leaching into the groundwater.

ACKNOWLEDGMENTS

The author would like to thank Prof. Mitja Brilly and Prof. Brane Matičič for their professional support. For the data used for the preparation of the article the author would like to thank the Agricultural Institute of Slovenia and the Environmental Agency of the Republic of Slovenia.

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