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CONTAMINATION OF DRINKING WATER SUPPLY WELLS BY PESTICIDES FROM SURFACE WATER RESOURCES

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Summary. A reactive transport model is developed to evaluate the potential of contamination of drinking water wells by surface water pollution. The model is validated using data of a tracer experiment. The fate of MCPP, glyphosate and its degradation product AMPA is investigated. Global sensitivity analysis using the Morris method is used to identify model dominant parameters. Results show that the existence of a clay aquitard, pollutant properties and the well depth are the crucial factors when evaluating the risk of drinking water well contamination from surface water.

1 INTRODUCTION

Drinking water wells are often placed near streams because streams often overly permeable sediments and the water table is near the surface in valleys and so pumping costs are reduced. The lowering of the water table by pumping wells can reverse the natural flow from the groundwater to the stream, inducing infiltration of surface water to groundwater and consequently to the drinking water well. Many attenuation processes can take place in the riparian zone, mainly due to mixing, biodegradation and sorption[1]. However, if the water travel time from the surface water to the pumping well is too short, or if the compounds are poorly degradable, contaminants can reach the drinking water well at high concentrations, jeopardizing the drinking water quality. While the hydraulic connection between surface water and wells has been recognized for unconfined aquifers[2, 3, 4], no information is available in the literature on the risk of contamination by surface water infiltration to confined pumping wells. Here we perform a sensitivity analysis using the Morris method. Various geologic settings, fracture transport in clays, as well as sorption and degradation processes are considered to identify dominant parameters influencing the risk of well contamination. Two pesticides and a pesticide metabolite are considered:

an older pesticide MCPP which is mobile and poorly degradable, glyphosate (roundup): a newer readily degradable and strongly sorbed pesticide and aminomethylphosphonic acid (AMPA), which is a more mobile, less degradable glyphosate degradation product. All three pesticides are common in Danish streams. The aim of this work is to set up a reactive transport model of pesticide leaking from surface water into nearby pumping wells and to identify the risk of contamination of drinking water wells by surface water pollutants.

2 PESTICIDE CHARACTERISTICS

2.1 Sorption

MCPP does not significantly sorb to aquifer sediments[8, 9, 10]. However, some sorption has been observed in topsoil[11], where MCPP can bind to organic matter. Glyphosate is considered to be almost immobile in the soil matrix and its sorption is usually described by the Freundlich sorption isotherm[12]. Glyphosate sorption is higher on clay minerals and in soils with high cation-exchange capacity (CEC) and is pH-dependent with a maximum at approximately neutral pH[13]. Linear sorption coefficients were obtained by linearizing Freundlich isotherm data from the literature[14, 15, 13, 16] for concentrations smaller than 50 $\mu g/L$. Unfortunately, sorption data from low-concentration experiments are not available, which means that there is a high uncertainty associated with the glyphosate sorption parameter. The glyphosate degradation product, AMPA, is more mobile than its mother compound: studies estimated its K_d value to be 40 % of glyphosate sorption coefficient[17].

2.2 Degradation

The herbicide MCPP has been found to be persistent in anaerobic conditions[18, 19, 20], with half lives ranging from 1 to 7 years. In aerobic conditions in sandy and chalk aquifers, MCPP can be degraded[21, 22, 23]. Half lives usually increase with depth[24], from a couple of days in the upper first centimeters of soil to hundreds of days in deeper layers. The half lives of herbicide are known to be concentration dependent, with great persistency at low concentrations[9, 11]. Glyphosate has been found to be readily degradable under aerobic conditions [25, 26, 27] with half lives ranging from 1 to 20 days, while under anaerobic conditions, glyphosate seems to be more persistent, but with some degradation reported in a few cases[28]. Degradation of AMPA is not well documented in the literature, however, studies suggests that AMPA is less degradable than its mother compound Glyphosate[29].

3 MODEL DEVELOPMENT

3.1 Conceptual model

The conceptual model of the system considered is presented in Fig.1. A pumping well is placed at a distance d [m] from a stream and constantly pumps water at a pumping rate Q [m^3/d] from a depth D [m]. The geology is simplified with a 3-layers system: a hyporheic

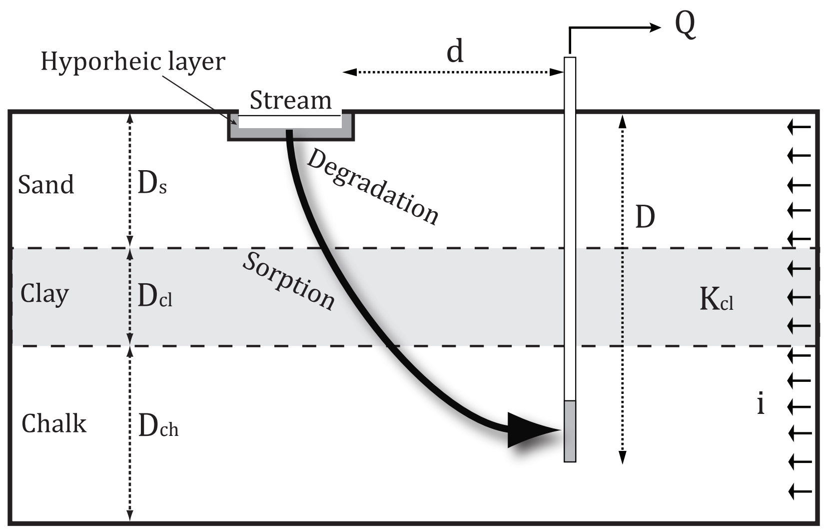

Figure 1: Conceptual model of the system considered.

layer separates the stream from an underlying sandy aquifer, below which a clay aquitard overlies a chalk aquifer; D_s, D_{cl} and D_{ch} are the thicknesses of the three layers, and K_{cl} is the hydraulic conductivity of the fractured clay till. The natural flow in the aquifer is driven by a regional groundwater gradient i $[m/m]$: to simplify the system, the hydraulic gradient is assumed to be the same in both aquifers. When pumping, the well modifies the natural water flow, lowering the water head in the aquifer, so that surface water from the stream can seep into the groundwater and reach the pumping well. Pollutants present in the stream may be retarded by sorption and degraded by microorganisms during their travel to the well. Both the sandy and chalk aquifer are strictly anaerobic, while the hyporheic zone can host aerobic conditions[5].

3.2 Model formulation

The model is set up using COMSOL Multiphysics, a finite-element modeling package for solving partial differential equations. For each simulation, the head equation is solved in steady state, and then, for each pollutant, the advection-diffusion equation is solved:

$$(1 + \frac{\rho_b}{n} K_d) \frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{v}C) - \nabla \cdot (\mathbf{D}\nabla C) = -kC \tag{1}$$

Where ρ_b is the sediments bulk density, n is the soil porosity, K_d is the sorption coefficient, $\mathbf{v}$ is the water pores velocity, $\mathbf{D}$ is the dispersion tensor and k is the degradation rate. Degradation kinetics are assumed to follow a first-order rate with different half lives for aerobic and anaerobic conditions. Despite the fact that for many pollutants sorption is often better described by non-linear isotherms, linear sorption isotherms were considered when calculating the retardation factor in the diffusion-advection equation, since low concentrations are expected and to avoid concentration shock fronts and rarefactions during the solution of the advective transport equation[6]. The transport of a conservative tracer was also implemented in the model to quantify the water travel time and dilution processes.

3.3 Validation

The model has been validated using data from a tracer experiment performed in 2002 on the river Aare, Switzerland[7]. The aim of this experiment was to investigate the vulnerability of wells located in the riparian zone to river water contamination. A 10m-thick highly permeable aquifer hosted two horizontal wells located at around 100 meters from the river shore and one vertical well located at around 50 meters from the river shore. A tracer pulse (fluorescein) was injected in the river upstream of the study area and tracer concentrations at the pumping wells were measured every 2-4 hours. A three-dimensional model of the zone has been set up: the size of the model domain was 2 by 1 km and the aquifer has a constant thickness of 10 meters. Two different isotropic hydraulic conductivities were assigned to the 2-m thick hyporheic zone and the highly permeable aquifer. The model was calibrated for 5 parameters (hydraulic conductivity of the hyporheic zone, hydraulic conductivity of the highly permeable aquifer, longitudinal and transverse dispersivity and hydraulic gradient parallel to the river at the downstream boundary) using a Levenberg-Marquardt algorithm on the breakthrough curves obtained at two pumping wells. Fig. 2 shows the calibrated breakthrough curve of fluorescein concentrations at the vertical well: both arrival time and peak concentration were simulated correctly.

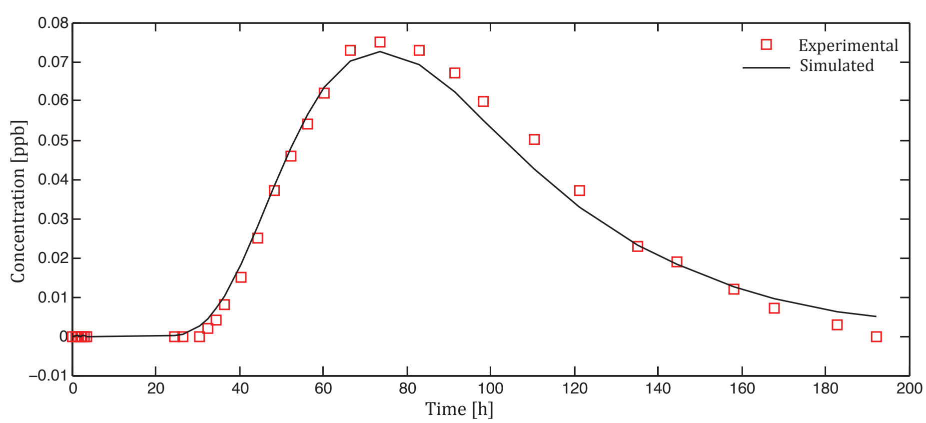

Figure 2: Breakthrough curve of measured and simulated tracer concentration at the vertical well located 50 m far from the river shore.

4 SENSITIVITY ANALYSIS

The aim of the sensitivity analysis is to determine which parameters most affect the risk of contamination of drinking water wells from pollutants in nearby streams. Moreover, the sensitivity analysis provides information on the way that parameters influence the seepage of pollutant from the stream to the pumping well.

4.1 Method

The finite-element solution is computationally expensive, and so the sensitivity analysis is performed using Morris method[30], which produces qualitative results with limited computational effort. The Morris method is a global sensitivity analysis method, determining the sensitivity over the whole parameter space. The method determines *elementary effects* for each input. Parameters are varied one at a time, and for every change the model is evaluated: the elementary effect is then defined to be the output change divided by the input change. The distribution of elementary effects is evaluated for the parameter space and the mean and the standard deviation of the elementary effects are used as sensitivity measures.

4.2 Model domain and parameter space

The three-dimensional domain used for the sensitivity analysis was composed of a 5-m wide stream surrounded by a 1-m thick hyporheic layer, placed in the middle of a 1km by 1km area; the vertical structure of the domain is described in Fig. 1. The abstraction well was modeled as a vertical well with a diameter of 150 mm and a screen length of 6 m (representative of a typical Danish drinking water well). Fixed head boundary conditions were set to on vertical boundary parallel to the stream, while no flux boundary conditions were chosen for the vertical boundaries perpendicular to the stream and for the bottom of the lower horizontal layer. We investigated the influence of the distance of boundaries on the stream seepage through different domain size simulations, and we found that a 1km by 1km area was the smallest domain that ensured results independent of boundary distance.

An optimal sensitivity analysis should investigate all model parameters, however, due to computational constraints, some parameters were kept fixed to reduce the number of model evaluations needed to obtain results. Values for sand and chalk horizontal saturated hydraulic conductivity were 8.64 and 5 $[m/d]$, while a lower value (1 $[m/d]$) was assigned the horizontal hydraulic conductivity of the hyporheic zone[31]. For each layer, the vertical hydraulic conductivity was assigned to be one tenth of the horizontal values. We choose quite high values for longitudinal and transverse dispersivities (4 m and respectively 0.4 m) since the travel distances and water velocity are both high[32], and to decrease simulation times. Sorption coefficients and first-order degradation rates were also kept constant and are listed in Table 2. The inputs which were varied are presented in table 1. The range for the well depth and the abstraction rate are representative of 99% of the drinking wells in Denmark. Values for clay hydraulic conductivity account for different level of clay till fracturing and they are among typical values for Denmark[33]. Each model run simulated the system for 30 years, which corresponds to the time to remove 99% of the least degradable compound. Model outputs are: the percentage of pollutant in the stream that reached the well at the end of the simulation (pollutant concentrations at the pumping well are independent of initial concentrations since first order degradation and linear sorption are used) and pollutant arrival times at the pumping well.

Parameter	Range	Unit
Sand aquifer thickness (D_s)	1-30	m
Clay layer thickness (D_{cl})	0-30	m
Chalk aquifer thickness (D_{ch})	1-100	m
Distance from the stream (d)	3-150	m
Well depth (D)	8 - 100	m
Aerobic hypoheric zone	yes/no	-
Abstraction rate (Q)	1 - 100	m^3/h
Natural hydraulic gradient (i)	-1% - 1%	m/m
Clay hydraulic conductivity (K_{cl})	0.026 - 8.6e-4	m/d

Table 1: Variable parameters

	MCPP	Glyphosate	AMPA
Kd_{rz} (L/kg)	3	80	32
Kd_{sa} (L/kg)	0.07	150	60
Kd_{cl} (L/kg)	0.07	300	120
Kd_{ch} (L/kg)	0.07	150	60
Half life aerob. (d)	200	5	50
Half life anaerob. (d)	1500	200	300

Table 2: sorption and degradation parameters

5 RESULTS

Glyphosate and AMPA concentrations at the pumping well were negligible in all simulations, including both those with and without a confining clay layer. In contrast, the percentage of MCPP able to travel from the stream to the pumping well was clearly influenced by the clay layer: a maximum of 7% was obtained for the unconfined aquifer case, while values 200 times lower were calculated in confined aquifer setups. Well depth was identified as most influent parameter on pollutant concentration in the wells in both confined and unconfined cases, while pumping rates seems to have the strongest effect on pollutant breakthrough times (Fig 3).

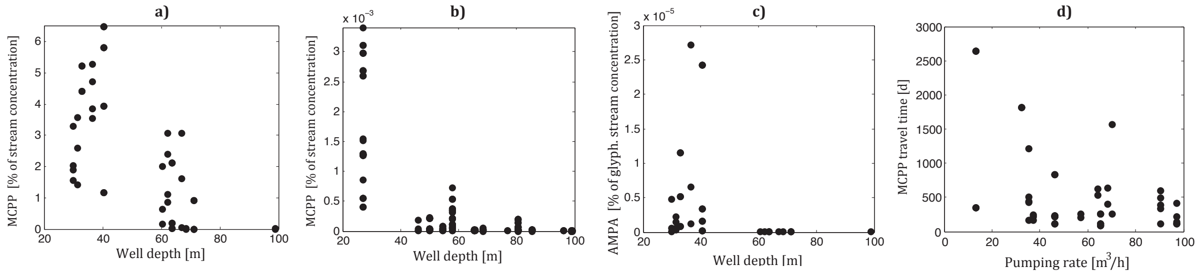

Figure 3: Results of multiple model runs. Percentages of stream pollutant concnetrations reaching the well for MCPP in unconfined (a) and confined (b) aquifers, and for AMPA in unconfined aquifers (c). Fig. d) shows the effect of the pumping rate on the MCPP breakthrough time in unconfined aquifers.

6 DISCUSSION

Results indicate clay aquitards and pollutant properties are important features controlling infiltration of pollutants from surface water to drinking water wells. Concentrations at the pumping well of highly sorbable, readily degradable pesticides are likely to be low, due to transformation and dilution processes. In contrast, persistent, mobile pesticides such as MCPP in streams may be a threat to drinking water resources when no clay layer is present. In some simulated cases 7% of the MCPP in stream reaches the drinking water well, and then the EU drinking water threshold (0.1 $\mu g/L$) will be exceeded for stream water concentrations around 1.5 $\mu g/L$, a common concentration in agricultural streams[34].

The model assumed constant concentrations in the stream during the simulation period, while usually high peaks of pollutants are recorded for short periods during or just after rain events, due to water runoff from agricultural fields. This may lead to an overestimation of concentration loads at the pumping well: future investigations with transient concentrations in surface water may provide more reliable results. Water abstraction rates seem to be more influent on pollutant travel times than on concentrations. High pumping rates increase water velocity and pollutant infiltration from the stream, but at the same time more water is drawn from the aquifer, thus increasing pollutant dilution. Even though there is a substantial difference between simulations in confined and unconfined aquifer, the sensitivity analysis suggests that the thickness of the clay layer is not an important parameter. This is because we performed only a relatively small number of simulations and did not considered very thin clay layers. Further investigation of smaller clay layer thicknesses is necessary to determine the critical thickness required to ensure safe drinking water.

7 CONCLUSION

We investigated the possibility of drinking water wells contamination by pesticides in surface water. Two pesticides and a pesticide degradation product were considered: MCPP, glyphosate and AMPA. A numerical code was used to study the influence of selected parameters on the risk of contamination of drinking water wells. Multiple model evaluations showed that is very unlikely that glyphosate in streams can pose a threat to drinking water wells, while MCPP in surface water can represent a serious risk when pumping in unconfined aquifers. Results show that pesticides properties are a crucial factor when considering transport from surface water to groundwater. Sensitivity analysis using the Morris method indicates that the pumping well depth is the most important parameter affecting pollutant concentrations in the drinking well, while breakthrough times were mostly influenced by the pumping rates.

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