Mathematical transport simulation of pharmaceutical active substances into groundwater via bank filtration

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Summary

Following the EMA (2006) "Guideline on the environmental risk assessment of medicinal products for human use" a value for the predicted environmental concentration in groundwater (PEC_{GW}) at bank filtration sites has to be calculated when potential risks of medicinal products to the environment are evaluated. In the above-mentioned guideline PEC_{GW} is calculated based on the predicted environmental concentration of surface water (PEC_{SW}) multiplied by 0.25. Due to this calculation PEC_{GW} is invariably connected to the PEC_{SW} without taking into account the groundwater flow situation or transport behavior of the compounds.

The aim of the project is to develop a program to calculate the PEC_{GW} of pharmaceutical compounds from human medical care in groundwater at bank filtration sites. The result is a Microsoft Access application in form of a query mask based on groundwater flow and transport modeling of pharmaceutical compounds.

The first step required a definition of the "bank filtration" process. We define "bank filtration" as an artificially induced process of groundwater withdrawal in the vicinity of surface water bodies with the aim of drinking water production. This water originates from surface water but it is purified along its path to the well in the subsurface. At the beginning, an intensive literature research revealed a multitude of papers (about 200 references) on this topic. In Europe, bank filtration is mainly used in Germany and the Netherlands on the rivers Rhine and Meuse, on the Danube River in Austria and further downstream in the Slovak Republic, in Hungary, and in Serbia / Montenegro.

All bank filtration sites are located in the vicinity of surface water bodies and the wells are screened in medium to highly permeable unconsolidated sediments. Therefore, geological and hydrogeological properties of the aquifer, depth of screen interval and – as far as published – also the extraction rates are comparable within certain quite narrow ranges. The distance between surface water body and the extraction wells varies between 1.5 and 1200m and screen depths reach from 4 to 70m. Extraction rates are often difficult to acquire but own results from the Berlin area show typical values between 500 and 5000 m^3 /day per extraction well. The various bank filtration sites show similar conditions. However, only little information is available on transport and mobility of pharmaceuticals from human medical care at bank filtration sites. Studies on the complete path of pharmaceutical compounds from surface water to groundwater including time series are especially rare. Some of these studies were performed at so called transects in the Berlin area at the rivers Havel and Spree, at the river Rhine (Flehe), and at the river Elbe (Torgau).

The above-mentioned characteristics that are quite comparable at the different sites do not apply for groundwater flow conditions. Especially, information on groundwater flow times is rare. However, these flow times are essential for the description of solute transport in groundwater. Numerical groundwater flow models are capable of calculating these flow times and their variability. The programs Exposit and FOCUS-Pelmo were developed to assess the concentration of pesticides and the program FOCUS-Pearl to assess the concentrations of medicinal products in the groundwater based on a diffusive input via land surface and the water unsaturated zone. This approach is not suitable for bank filtration sites because there is no unsaturated zone between surface water and groundwater water and the input can be regarded as a linear source. Therefore, it was decided to build a new application from the scratch based on a groundwater flow model.

All commonly available software packages for simulation of groundwater flow and transport were evaluated and finally the software package for groundwater flow modeling VISUAL MODFLOW was chosen to create a basic model which would enable to model the groundwater flow at all bank filtration sites. The model area has a spatial extend of 1500m from the bank of the surface water body to the extraction well, a depth of 100m – which coincides with the maximum length of the filter screen and a width of 300m. Within this strip all previously studied bank filtration sites can be adapted. The horizontal discretisation was performed using rectangles with sizes of 5 x 5m. With this model the shortest flow times for groundwater flow from the bank to the well were determined for all combinations of possible hydrogeological and water management conditions. These data pairs were obtained by variations of these variables:

- Distance from bank to groundwater well
- Depth of screen and screen interval (thickness of aquifer)
- Hydraulic conductivity
- Groundwater extraction rate at the well

Calculation of groundwater flow time was performed using defined steps within certain ranges. These steps and ranges were adjusted to values that have been reported from bank filtration sites. As a result of these calculations 1290 data pairs representing combinations of shortest flow time and groundwater drawdown at the well were obtained. The flow times varied between a few hours and 135 years. The median of these data had a value of 129 days and coincides very well with the average flow time from real bank filtration locations. All data pairs are stored in a Microsoft Access Data Base.

The occurrence and concentration of pharmaceutical compounds in groundwater well depends on the advective transport of the substance and on the reactions along the flow path. The aim of this study was to calculate a value for PEC_{GW} that does not depend on site-specific characteristics. Therefore, all aspects regarding spatial variability within the aquifer (heterogeneity, layers, etc.) have been neglected, as they only refer to specific sites. Additionally, knowledge on transport relevant characteristics of the compounds is limited to certain values that have to be delivered in the course of the environmental risk assessment. These parameters are K_{OC}, K_d (Henry isotherm) and sometimes also K_f (Freundlich isotherme) determined at different pH values and in different soil materials as well as DT_{50} values for aerobic and anaerobic conditions. Using these parameters, sorption and elimination processes can be described quite well.

Based on the residence time the concentration of pharmaceutical compounds at the extraction well was calculated by including transport parameters sorption and degradation. In case of sorption, linear sorption isotherms K_d are used to calculate the retardation. Retardation leads to increased residence times of the compounds compared to the residence time of the groundwater. The K_{OC} is used as suggested in the EMEA guideline (2006) where no entry of compounds via bank filtration is considered for a K_{OC} > 10.000 mL/g.

Furthermore, values for the Disappearance Time for 50 % (DT_{50}) of the compound are provided during the application process for medicinal products. As this is the only indication for degradation of a compound we took this data on elimination and regarded the DT_{50} to calculate a degradation factor. With this degradation factor and residence time of the compound in groundwater the final concentration of the pharmaceutical compound in groundwater is calculated analytically applying the first order decay equation. Linear sorption and first order degradation can be calculated quite easily and flow conditions are assumed steady-state. Therefore, it was preferred not to incorporate sorption and degradation into a transport model. Sorption and degradation were calculated analytically based on the previously modeled values for the residence time and based on the initial concentration as provided by the PEC_{SW}. The advantage of this approach is that sorption and degradation parameters can be entered as they are.

The final task was to define the so-called "realistic worst case" for PEC_{GW} calculation. Therefore, the groundwater flow times were analyzed statistically with a focus on fast flow times indicating early arrival and little time for elimination. We decided to choose the 20 % percentile as the "realistic worst case" which means a groundwater flow time of 5 days between the surface water and the groundwater well. For comparison the 5 % percentile (0.15 days) as "worst case" and the median (110 days) as "median case" are also reported.

The results of the groundwater model are available in a database. These data are combined with calculations on sorption and degradation and can be used via a user controlled query mask called SiMBaFi (Simulation Model Bank Filtration). This interface offers possibilities for an input of data on the pharmaceutical compounds and calculates concentrations for the above-mentioned cases. Additionally, individual calculations can be performed with flow times retrieved from the database.