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Modelling the factors impacting pesticide concentrations in groundwater wells

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Abstract

This study examines the effect of pumping, hydrogeology and pesticide characteristics on pesticide concentrations in production wells using a reactive transport model in two conceptual hydrogeologic systems; a layered aquifer with and without a stream present. The pumping rate can significantly affect the pesticide breakthrough time and maximum concentration at the well. The effect of the pumping rate on the pesticide concentration depends on the hydrogeology of the aquifer; in a layered aquifer a high pumping rate resulted in a considerably different breakthrough than a low pumping rate, while in an aquifer with a stream the effect of the pumping rate was insignificant. Pesticide application history and properties also have a great impact on the effect of the pumping rate on the concentration at the well. The findings of the study show that variable pumping rates can generate temporal variability in the concentration at the well, which helps understanding the results of groundwater monitoring programs. The results are used to provide guidance on the design of pumping and regulatory changes for the long-term supply of safe groundwater. The fate of selected pesticides is examined, for example, if the application of bentazone in a region with a layered aquifer stops today, the concentration at the well can continue to increase for 20 years if a low pumping rate is applied. This study concludes that because of the rapid response of the pesticide concentration at the drinking well due to changes in pumping, well head management is important for managing pesticide concentrations.

Keywords

Pumping, pesticides, groundwater, production wells, bentazone, MCPP

Introduction

Many countries depend on groundwater as a source of safe drinking water. In Europe, 70% of drinking water is based on groundwater resources, and in Austria and Denmark drinking water is almost entirely sourced from groundwater (Navarrete et al. 2008). Such groundwater must be of high quality and meet the standards of the Groundwater Directive and the Water Framework Directive (EU 2006). Diffuse source pollution of groundwater has been recognized as a major threat to global water quality (United Nations World Water Assessment Program (UN/WWAP), 2009). This paper focusses on pesticides which are one of the most important diffuse source pollutants, and are frequently found in groundwater, (e.g., the Netherlands (Schipper et al. 2008), United States (Gilliom et al. 2007), UK (Reid et al. 2003), Denmark (GEUS 2009)).

Management and control of agricultural pollutants have been the subject of considerable research (e.g., Pavlis et al. 2010; Kourakos et al. 2012), and requires in depth understanding of the linkage between pollutant sources and groundwater discharge to users. Foster et al. (1991) discuss the mechanisms leading to pesticide pollution of groundwater and how pesticides move from the land surface into aquifers. The pesticide concentration reaching a well field is known to be a function of many factors including: physio-chemical properties (Barbash et al. 2014); sorption and degradation processes in aquifers (Buss et al. 2006; Foster et al. 1991); pesticide sources and application methods (e.g., Zhang and Hiscock 2011); the spatial extent of the catchment area and recharge area (e.g., Kinzelbach et al. 1992; Paradis et al. 2007); contact between groundwater and surface water bodies (e.g., Hunt et al. 2005; Malaguerra et al. 2010); heterogeneity of the subsurface (e.g., Jørgensen et al. 2004); and intraborehole flow (Reilly and Gibbs 1993; Martin-Hayden 2000; Zinn and Konikow 2007).

Groundwater monitoring programs often report large spatio-temporal variability of contaminant concentrations. For example, Figure 1 shows data over a period of 20 years for a phenoxy acid and bentazone in drinking and monitoring wells at Nybølle Øst, an abstraction field in Denmark (Levi et al. 2014). Temporal variability of observed concentrations has been attributed to various factors, such as the hydrogeology of the aquifer, the pesticide application history, the chemical-physical properties and fate of pesticides. Beltman et al. (1996) analyzed systems that were difficult to protect with a protection zone and found that the strongest fluctuations in the pesticide concentrations in the well were for the lowest frequency of application, shortest travel time in the saturated zone, and shortest half-life in the saturated zone. Kourakos et al. (2012) showed that the timing of nitrate breakthrough in wells is significantly controlled by aquifer recharge and pumping rates in non point source areas and by the effective porosity of the aquifer system. However, we still do not have a complete understanding of the importance of the pumping rate and groundwater hydrogeology for variability of pesticide concentrations at the drinking and monitoring wells. Such an understanding is crucial when designing management strategies to prevent pesticide contamination of abstraction wells.

Mathematical models can be used to simulate contaminant transport in groundwater. Some simple mathematical formulations such as the zero-order mixing model (Lee 2007), the one-dimensional plug flow model (Refsgaard et al. 1999), and the advective travel time method (Darracq et al. 2010) have been used, but these cannot capture the spatio-temporal variability of contaminants or the effect of non-steady contaminant loading. Detailed spatio-temporal assessment of the impact of diffuse sources requires flow and transport models in three dimensions. Such models are available for diffuse source prediction, but they use relatively coarse grids (e.g., Jiang and Somers 2009; Zhang and Hiscock 2011), and such grids are not suitable for the detailed examination of processes at production wells.

Typical diffuse source pollution occurs across entire groundwater basins as part of recharge (UN/WWAP, 2006). This presents a challenge for models because catchments are often very large, while a high-spatial resolution is required to properly capture individual elements, such as streams and wells. High-spatial resolution is also necessary to resolve dispersive mixing and to investigate the effects of spatial variability in hydraulic conductivity (Sanford 2010; Kourakos et al. 2012). Hence, the implementation of a fully three-dimensional flow and transport model to simulate diffuse source pollution in a catchment is often limited by computational resources.

Alternative methods have been proposed to reduce the computational load. Lin et al. (2010) developed a simplified numerical model where the 3-D equations for groundwater flow and contaminant transport are replaced by a 2-D finite element approximation in the x-y direction and 1-D finite difference approximation in the vertical direction. An alternative technique is the streamline simulation model, where the three-dimensional problem is decoupled into many one-dimensional problems (Martin and Wegner 1979). Kourakos et al. (2012) used the streamline model to investigate the effect of spatio-temporal variability in nitrate application and the effect of aquifer heterogeneity on nitrate concentration in domestic and large production wells. McMahon (2008) used the streamline model and applied it to investigate nitrate transport for four aquifer systems in the United States. The computational efficiency of the streamline model results from focusing on specific flow paths and neglecting the transverse dispersion. However in many scenarios it is important to simulate transverse dispersion, for example when there are significant concentration contrasts in the aquifer because of heterogeneity or streams.

Analytical models can also be used to study pesticide transport both through the unsaturated (e.g., Roulier et al. 2008) and saturated zone. Beltman et al. (1995; 1996; 2008) present a series of papers in which they developed an analytical model to study the pesticide transport from the coupled unsaturated-saturated homogeneous, soil surface to a drinking water well. Although the

model provides a good estimate of the pesticide concentration reaching a well, it does not consider the effect of different application scenarios, hydrogeologic systems or pumping rates; and only a steady state scenario where the drinking well pumps all the water in the catchment is studied.

Groundwater abstraction has a major impact on groundwater flow and pumping rates in abstraction fields vary due to changing socioeconomic factors (e.g., urbanisation, increased value of water) and maintenance procedures at the abstraction field. Although the effect of pumping on the capture zone (Kinzelbach et al. 1992) and the transport in the vicinity of the well (Reilly and Gibbs 1993) has been recognized, little work has been done on the direct influence of different pumping strategies on the transport and degradation of pesticides. One study examining the impact of pumping on pesticide concentrations is that of Stuart et al. (2006), who measured concentrations in three abstraction wells pumping in a UK sandstone aquifer. They observed sharp variations in concentrations at the wells, but could not identify successfully the source of pesticide problem and variation at the well.

When studying pesticide transport, it is relevant to consider groundwater age and transport times. Zinn and Konikow (2007) used numerical tools to analyse the effect of pumping on the groundwater age distribution at a drinking well in different conceptual hydrogeologic systems and showed that different pumping rates can significantly affect the simulated groundwater ages. Groundwater age indicators from public supply wells have been used to interpret the water quality and verify rapid recharge hazards in chalk aquifers (Morris et al. 2005 and Darling et al. 2005, Lapworth and Gooddy 2006). However since groundwater-mixing processes under pumping conditions are complex, especially in chalk aquifers, an understanding of the local hydrogeological setting was necessary to use groundwater age indicators.

The literature reviewed shows that there is a lack of understanding of the impact of pumping on the breakthrough of pesticides at wells. A set of generally applicable conceptual models is

needed to obtain an understanding of the processes occurring. The development of such models is the subject of this paper.

The aim of this paper was to investigate the effect of pumping rates (both constant and variable), aquifer hydrogeology and pesticide characteristics (degradation rate, sorption and application history) on the pesticide concentration reaching a groundwater production well through the use of numerical models. The effect of each parameter on the breakthrough time at the well and the maximum concentration at the well was systematically investigated. Such an understanding provides insight to the cause of variability reported in groundwater monitoring programs (Figure 1) and enables the development of pesticide remediation strategies for well head protection. Finally this paper aimed to discuss the effectiveness of age tracers and simulated groundwater age distribution in providing useful information on the vulnerability of wells to pesticide contamination.

Methodology

Conceptual hydrogeologic models

Two conceptual hydrogeologic models were investigated to represent typical well fields; a layered aquifer and an aquifer with a stream (Figure 2 a and b). In each case, a 2D geometry was used like that of Molson and Frind (2012). The well field studied included a series of wells that pump equal amounts of water, placed in a line perpendicular to the regional hydraulic gradient and therefore to the flow direction, and parallel to the stream. Such a configuration of well fields are quite common (e.g., Larsen et al. 2003; Bekesi et al. 2012), because the water level is close to the land surface and pumping costs are low. Figure 2 shows the model set up; water recharge flows from the water divide (on the left hand side) to the production wells and to the outflow boundary on the right. The 2-D cross section is 10 km long and represents a groundwater catchment. The 2-D numerical simplification enabled the efficient solution of the problem with a high spatial resolution.

Fine grid solutions were necessary to properly capture the well and stream, to demonstrate the effects of spatial variability in hydraulic conductivity, and to incorporate realistic longitudinal and transverse dispersivity values. Such large scale simulations were not possible in 3-D.

The models represent two typical hydrogeologic settings in Denmark (Zealand, (Jupiter 2012)), see Figure 2. In both models a no-flow condition was imposed on the left boundary and a constant-head boundary condition, h=20 m at the right boundary. The bottom boundary was a no-flow boundary since it was assumed that the aquifer was underlain by impermeable layer. A uniformly distributed recharge of 0.15 m/year was assigned at the top boundary, which represents the water table. The unsaturated zone is not considered in this work, which focusses exclusively on changes to pesticide concentrations in the saturated zone.

The first hydrogeology considered a layered aquifer system, where a 10 m sand layer overlies a 30 m chalk aquifer, above a low hydraulic conductivity, 50 m deep zone (Figure 2a). The production wells were placed 6 km away from the water divide (left boundary) and its 15 m long well screen was located in the chalk, between 20-35 mbs (meters below surface).

The second hydrogeology considered a scenario where the production wells were placed in parallel to a stream (Figure 2b). The conceptual model was designed to describe the hydrogeology at Nybølle Øst, an abstraction field in Denmark where significant water quality data has been gathered during the last 20 years and pesticides have been detected (Figure 1; Levi et al. 2014). A constant-head boundary condition, h=20 m was imposed at the stream, which is located at 200 m upstream from the well and has dimensions of 0.5 m in depth and 1 m in width. This led to a steady state regional flow field with a groundwater divide and downward infiltration at the left boundary, mainly horizontal flow towards the stream, and predominantly upward flow near the stream. The geology of the cross section and the precipitation are the same as those for the layered aquifer geology.

Typical values for the hydraulic conductivity and porosity for the sand, chalk and clay layers were chosen and are summarized in Table 1. An equivalent porous media model is used (Chambon et al. 2011; Worthington et al. 2012), which does not explicitly include fractures, and instead employs effective parameters such as the bulk conductivity and effective porosity. The porosity for the chalk was 0.1, which is the effective porosity and considers the fractures in the chalk. This value is an approximation, since a hypothetical case is simulated, but is similar to the value suggested by Worthington et al. (2012).

Table 1. Hydrogeological parameter values used in the model simulations.

Geological units	**Horizontal hydraulic conductivity m/s**	**Vertical hydraulic conductivity m/s**	**Storativity 1/m**	**Porosity**
Sand	10^{-4}	10^{-5}	10^{-6}	0.25
Chalk aquifer	10^{-4}	10^{-5}	10^{-6}	0.1
Lower confining unit	10^{-8}	10^{-9}	10^{-6}	0.35

Pesticides simulated

Two pesticides with different application histories, chemical structure and compound properties were considered: MCPP (Mecoprop) and bentazone (Table 2). The pesticides selected were motivated by findings in Nybølle Øst (Figure 1) and the national Danish monitoring program (GRUMO 2012). MCPP was one of the most commonly used herbicides (Donaldson et al. 2002) and has been banned or restricted in some countries because of frequent findings (e.g. banned in 1997 in Denmark, and in 2006 in Canada and restricted in many cities in North America (Wargo et

al. 2010)). Bentazone was introduced later and is still in use worldwide, although its use is currently being re-assessed and a registration review decision in the US is pending (USEPA 2012).

The chemical structure and compound properties for MCPP and bentazone are different (Table 2) which is reflected in different sorption and degradation characteristics (see Table 3)). Bentazone is low-sorbing pesticide and persistent under aerobic and anaerobic aquifer conditions (Broholm et al. 2001; Levi, 2013). MCPP was chosen as a representative for MCPP, 2,4-D, dichlorprop and MCPA belonging to the group of phenoxy acids. Phenoxy acids are weakly sorbing, degradable under aerobic conditions and are expected to be persistent under anaerobic aquifer conditions, but anaerobic degradation has been reported in few cases (Buss et al. 2006; Reitzel et al., 2004). Their degradation rate coefficients depend on many parameters such as the specific compound, flow field and the biogeochemical conditions in the aquifer, and their range can vary up to three orders of magnitude. Therefore three degradation rates were tested for MCPP; 0.05 day^{-1}, 0.005 day^{-1} and 0.0005 day^{-1}. The two larger degradation rates caused complete removal at the well in the aquifer systems studied, so the smaller degradation rate was used. Linear sorption and first order degradation under aerobic conditions were assumed for a 10 m thick layer below the ground surface.

The pesticides chosen have also different application histories in Denmark, and so the effect of application history on the breakthrough at the well was also considered. MCPP was in use from 1955 to 1997, while bentazone was introduced in 1973 and still in use (Table 3). A hypothetical scenario where bentazone application was stopped today (2013) was also investigated. A constant application rate at the upper model boundary (representing pesticide concentrations entering the upper groundwater) was assumed for the application period of each pesticide. A unit concentration at the upper boundary was used for simulations in order to make comparisons between model simulations easier. Since the equations used are linear (linear sorption and first order degradation

were assumed) the model output concentrations can easily be scaled by a constant factor according to whichever input concentration is applied at the top boundary. Since the unsaturated zone is not considered in this work, the input concentration at the top boundary is the concentration reaching the water table. To assist in the interpretation of results, simulations are also presented for a conservative tracer subject to no sorption or degradation.

The future scenarios investigated are hypothetical and assumptions about degradation rates or future application rates for the next century cannot be supported by data. However, the effects of pesticide parameters and application rates are useful information for management of pesticides and well fields.

Table 2. Information on selected herbicides in this study (modified from Tomlin, 1997; Levi, 2013).

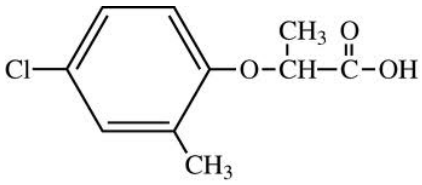
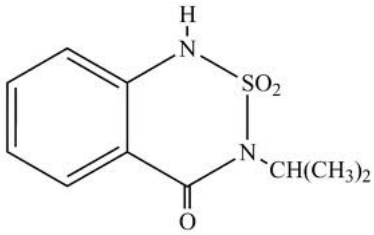
	Mecoprop	**Bentazone**
IUPAC name	(RS)-2-(4-chloro-2-methylphenoxy) propanoic acid	3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one-2,2-dioxide
Formula	$C_{10}H_{11}ClO_3$	$C_{10}H_{12}N_2O_3S$
Structure		
Molecular weight (g/mol)	214.6	240.3
Water solubility (mg/L)	880	570
Log K_{ow}	3.2	0.46
pK_a	3.78	3.3
Application	Post-emergence control of broad-leaved weeds in e.g. wheat and barley	Post-emergence selective herbicide used for weed control in agricultural lands, orchards and in soybeans
Application period	1955-1997	1973, Still permitted

Table 3. Sorption and degradation parameters and application dates of bentazone and MCPP. Degradation rates apply for aerobic conditions, described as a 10m thick layer below the ground surface.

	Bentazone	Mecoprop
Sorption coefficient, K_d		
[L/kg]Sand	0.045 [a]	0.07 [c]
Clay Chalk	0.045 [a]	0.07 [c]
	0.045 [g]	0.07 [c]
Degradation rates *k* [day^{-1}]		
Aerobic conditions	0 [b]	0.0005[d]
Anaerobic conditions	0	0[e]
Application period	1974-present	1955-1997

[a](Tuxen et al, 2000), [b](van der Pas et al. 1998) [c](Madsen et al. 2000), [d](Rodriguez-Cruz et al. 2006) [e] (de Lipthay et al. 2007)

Pumping strategies

A steady state flow field with no pumping was first computed. A well field was then introduced in 1920 when the Nybølle Øst abstraction field was constructed, and the effect of different pumping regimes was investigated: i) a constant low rate pumping of 6,000 m^3/week, ii) a constant high rate pumping of 21,000 m^3/week, and iii) a varying pumping rate. The rates used are representative rates of a productive abstraction field. For a well field composed of multiple wells placed in a line over a 1 km distance (Figure 2), the per unit width constant pumping rates are 6 m^2/week and 21 m^2/week respectively. These rates correspond to about 20% and 70% of the total recharge to the 2-D cross section. The trend of the variable pumping rate consisted of a gradual increase in pumping during

the first 30 years, due to urbanisation, a period with constant pumping followed by gradual decay during the last period because of public awareness and increased price of water.

The varying pumping rate was based on historical pumping data for the Nybølle Øst abstraction field, and the development in rates is typical for many abstraction fields. The model included a simplifying assumption of a constant catchment area. In the real catchment, the size of a catchment area is time dependent and is a function of the pumping rate. While a varying catchment size does affect results, it does not change the trends reported in this paper.

The pesticide concentration for natural conditions with a zero pumping rate was also estimated for comparison with the pumped scenarios. In all cases, the concentration reported is the concentration averaged over the whole length of the 15 m long well. Such averaging simulates the concentration of pumped water where spatially variable concentrations at the well screen are fully mixed at the well head.

Numerical Modelling

The 2-D model simulated groundwater flow, transport and degradation of the pesticides. The groundwater flow equation was used to describe the flow in the aquifer:

$$\mathrm{S_s}\frac{\partial \mathrm{h}}{\partial \mathrm{t}} = \nabla \cdot \mathbf{K} \cdot \nabla h - R \tag{1}$$

where Ss is the specific storage (1/m), **K** is the hydraulic conductivity (m/s) and R is a fluid sink, simulating the pumping occurring along the well screen. Transport and degradation of chlorine was described by the advection-diffusion-reaction equation:

$$\left(1 + \frac{\rho_b}{n} K_d\right)\frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{v}C) - \nabla[\boldsymbol{D}\nabla C] = -kC \tag{2}$$

where $(1 + \rho_b K_d/n)$ is the retardation factor, ρ_b (kg/m^3) is the bulk density of the sediment, n is the soil porosity, K_d(kg/m^3) is the sorption coefficient, and k (1/s) is the degradation rate. It is assumed that degradation occurs in both the solid and water phases. $\boldsymbol{D}$ is the dispersion tensor (m^2/s) and is dependent on the average linear flow velocity **v** (m/s), the longitudinal and transverse dispersivities, α_L (m) and α_T (m) and the effective molecular diffusion coefficient D_o (m^2/s):

$$\boldsymbol{D_{ij}} = (\alpha_L - \alpha_T)\frac{v_i v_j}{|\mathrm{v}|} + \alpha_T|\mathbf{v}|\boldsymbol{\delta_{ij}} + D_o\,\boldsymbol{\delta_{ij}} \tag{3}$$

Equations (1) and (2) were solved using COMSOL Multiphysics 4.3, a finite-element modelling package for solving partial differential equations (COMSOL 2010). The longitudinal and transverse dispersivity values assigned to all layers were constant throughout the system and were 1 m and 0.01 m respectively. These values are typical for the type and scale of the aquifer (Schulze-Makuch 2005; Zinn and Konikow 2007). The finite element model employed a triangular mesh with elements having a maximum size of 5 m in the x- direction and 1 m in the z-direction. Discretization was varied as a function of the geology and element sizes of 0.01 m were specified around the well and the stream in order to enable the use of sufficiently small values of dispersivities; these prevented excessive smoothing of concentration gradients due to numerical dispersion. Sensitivity tests conducted with smaller dispersivity values (0.1 m and 0.001 m) and a finer mesh (2.5 m and 0.5 m in the x- and z-direction respectively), yielded results similar to the ones presented in this paper. In the layered aquifer with a stream, the fine spatial resolution (0.01 m) used around the stream was necessary in order to describe the sharp gradient generated by the clean water flowing upwards towards the stream and the contaminated water from the top. Additional simulations using grid sizes around the stream of only 2 times larger caused excessive dispersion and the loss of detail in the pesticide distribution in the system.

Results and discussion

No pumping conditions: Effect of hydrogeology on tracer breakthrough at the well.

Figure 3 shows the breakthrough curves at a production well placed in the layered aquifer (Figure 2a) and the aquifer with the stream (Figure 2b) for bentazone and MCPP respectively. In the no pumping case, natural hydraulic gradients drive water flow from the location of recharge at the upper surface to the outflow boundary at the right (see streamlines and tracer in Figure 4a). Tracer breakthrough at the location of the (unpumped) well was 11 years after the start of application at the surface in the homogeneous layered aquifer (Figure 3a). The application period affected the maximum concentration at the well, with a longer application period resulting in a higher concentration at the well; a 42 year application period resulted in a maximum normalised concentration C/Co at the well of 0.8, while a 100 year application period resulted in a uniform distribution of pesticide in the aquifer with the tracer input concentration (Figure 3a).

The stream significantly affected the streamlines in the aquifer by pulling some very old and clean water from the bottom layers of the aquifer towards the top layers (Figure 4d). In the stream geology, the water reaching the well travelled a shorter distance but experienced a longer travel time than in the no-stream geology if the well was not pumped (see capture zone in Figure 4a and d). The smaller velocity resulted in a delayed breakthrough and less dispersion of the pesticide in the direction of the flow. Therefore a sharper pulse of contaminant with a higher concentration is observed for the stream geology; Figure 3a shows that the breakthrough was 7 years later and the maximum concentration was 15% higher than in the no-stream geology.

Effect of hydrogeology and pumping rate on the tracer concentration at well

Figure 3a and d show the effect of the pumping rate on the conservative tracer breakthrough at the well for the two conceptual hydrogeologic models. The effect of the pumping rate on the

concentration at the well is a function of the hydrogeology. In the layered aquifer, the pumping rate significantly affected the tracer breakthrough curve, while in the aquifer with the stream the rate of pumping had no effect on the results. The different behavior can be explained by examining the effect of the pumping rate on the streamlines in the two aquifers (Figure 4). In the layered aquifer, a low pumping rate had little effect on the streamlines and thus on the pesticide transport to the production well (Figure 4b); and so the breakthrough is similar to that resulting from the no-pumping scenario (Figure 3a). Low rate pumping accelerated the breakthrough by only 2 years and did not affect the maximum concentration at the well. In contrast, a high pumping rate significantly affected the capture zone of the well and the travel time of the pesticides to the well (Figure 4c), drawing contaminated water to the top of the well screen and resulting in a 10 year faster breakthrough (Figure 3a). The concentration of the conservative tracer and bentazone (Figure 3b) observed at the well was not affected by the change in residence time associated with the pumping rate, because of their non-degrading characteristics. However, a lower maximum concentration resulted from the high pumping rate due to dilution with clean water drawn from the bottom layers of the aquifer (Figure 4c); for the high pumping, the maximum normalised concentration C/Co was 7% lower than that for the low pumping rate (Figure 3a).

In the aquifer with the stream similar results were obtained for all pumping rates, although they were significantly different from the no-pumping case (Figure 3d). As shown in Figure 4d, the stream affected the streamlines in the aquifer and the capture zone of the well by pulling some very old and clean water from the bottom layers of the aquifer towards the top layers. During pumping, this clean water coming from the bottom of the aquifer was drawn to the well (Figure 4e), resulting in a lower concentration than the no-stream geology (Figure 3a). A faster breakthrough at the well was observed for the stream geology because the capture zone during pumping was right above the well and so travel time from the surface were reduced (Figure 4e). In contrast to the no-stream

geology, when a stream is present the pumping rate did not affect the breakthrough curve at the well (Figure 3d). The pumping rate affected the size and shape of the capture zone and the hydraulic equilibrium between water drawn to the stream and water drawn to the well (Figure 4d-f). However, these effects did not change the resultant concentration at the well screen.

Model results show that at a low pumping rate, contaminated water from the top of the aquifer with a small residence time reached the top ½ of the well screen, while the bottom 1/2 of the well screen drew clean water. At a high pumping rate, contaminated water supplied from the top layers of the aquifer had a very small residence time but satisfied only a small proportion of the pumping needs and was therefore drawn only to the top 1/5 of the well screen; the rest of the well drew clean water. Therefore the average pesticide concentration at the well was not sensitive to the pumping rate.

Effect of pesticide properties on the pesticide concentration at production well

The effect of the pumping rate and the hydrogeology on the breakthrough at the well was more pronounced when sorption and degradation were taken into consideration. Figure 3b, c, e and f show the breakthrough curves for bentazone (low-sorbing, non-degradable) and MCPP (sorbing and degrading under aerobic conditions).

Bentazone (Figure 3b and 3e) had an increased residence time and responded slower than the tracer (Figure 3a and 3d)to the changes in concentration applied at the surface in both aquifer systems). For example, in the layered aquifer, bentazone's breakthrough was 6 years later than that of the tracer with the same application history (compare Figure 3a and b). For the hypothetical scenario where bentazone application stopped today, the concentration at the well did not start decreasing before 2040 (13 years later than for the tracer) and it took 200 years for it to be flushed out of the aquifer (50 years more than the tracer). Sorption resulted in an attenuation of the

concentration breakthrough at the well with a lower maximum normalised concentration; the maximum C/Co was 27% lower than that observed for the tracer. Because of its non-degrading characteristics, the change in residence time associated with the different pumping rates had no effect on the concentration at the well (Figure 3b and e).

For a sorbing and degrading pesticide such as MCPP, the increased residence time due to sorption and due to a low pumping rate had a large impact on the breakthrough time and the available time for degradation, and hence the maximum concentration at the well (Figure 3c and f). For example, for the no pumping scenario, the long residence time combined with the high degradation resulted in a maximum C/Co at the well in both aquifer systems, of 0.04, 95% lower than that resulting from the tracer application in the same conditions. High pumping decreased the residence time leading to a 67% increase in C/Co at the well.

The concentration of MCPP at the well depended greatly on the pumping rate. However the sensitivity of the MCPP concentration at the well due to the pumping rate depended on the hydrogeology. In the aquifer with the stream the pesticide concentration at the well was not sensitive to the pumping rate over a range between 6.6 m^2/week and 21 m^2/week (Figure 3f). In contrast, the same range of pumping rates generated markedly different results for the scenario without the stream (Figure 3c). Hence, a stream near a well field can significantly impact the effect of the pumping rate on the pesticide concentration at the wells.

Effect of varying pumping rate on pesticide concentration at production well

Figure 5 shows the effect of the variable (time dependent) pumping rate on the breakthrough at the well located in the layered aquifer without and with a stream. The results are shown for bentazone and MCPP, when sorption and degradation are and are not considered. Sorption resulted in a delay and attenuation of the breakthrough curve while degradation resulted in a lower

concentration (Figure 5c). The variable pumping rate generated significant temporal fluctuations in the concentration at the well, similar to the ones observed in the data obtained from pesticide monitoring programs (Figure 1). Figure 6 shows the MCPP breakthrough curve in the aquifer with the stream (the scenario in Figure 5d) subject to both a variable and constant pumping rate. It can be seen that the variable pump rate solution rapidly converges to the steady rate solutions each time the rate is changed (Figure 6). Hence the breakthrough curve resulting from the time dependent pumping rates can be derived from the steady state simulations.

These results show that a variable pumping rate could be one of the factors responsible for the temporal variability observed in the field data (e.g., Figure 1). Figure 3c and f also present the analytical solution proposed by Beltman et al. (1995) for MCPP reaching a fully penetrating water well in a homogeneous aquifer, when 100% of the recharge in the catchment reaches the water well. This analytical solution does not consider different geologies, pump rates or application histories; it considers only continuous pesticide input and input of Dirac-pulses with different frequency. Beltman et al. (1996) showed that the unsaturated zone is responsible for most of the fluctuations and that ignoring it may decrease the fluctuations at the well by one half. The unsaturated zone is not considered in this work.

Well field management

Current regulations for the prevention of contamination of production wells by pesticides from agriculture focus on pesticide approval procedures, controlling the source of contamination, i.e. control of the application frequency, and application methods, definition of protection areas around wells, and definition of buffer zones along watercourses and lakes for the protection of surface water resources. Our numerical simulations show that it is also important to consider the design of pumping strategies in order to control the transport of pesticides in groundwater.

Depending on the local conditions, such as land use changes, contaminant application and the hydrogeology, a different pumping strategy could be beneficial. By controlling the pumping rate strategies can be devised to maintain low pesticide concentrations at production wells. Moreover, these aspects should be considered when sampling from monitoring wells where a very low concentration might not be of interest. Simulations show that pesticide concentrations can rapidly respond to changes in pumping regime. In contrast it has been shown that time scales of the order of several decades to centuries may be necessary to achieve changes in aquifer concentrations of agricultural pollutants in response to land-use changes (Zhang and Hiscock 2011).

Pumping rates and hydrogeology must also be considered when assessing restrictions in application. For example, if bentazone was banned today (2013) its decrease in concentration at the production well would depend on the hydrogeology and the pumping rate (Figure 3c and g). In the layered aquifer, the concentration at the well would decrease immediately after the banning of the pesticide if a high pumping rate was applied, while it would continue to increase in concentration for 20 more years for a low pumping rate. In the aquifer with the stream, the decrease would be immediate and irrespective of the pumping rate applied. In both cases it would take more than 50 years for the pesticide to be flushed out of the aquifer.

Our numerical simulations can also be used to investigate the influence of pesticide characteristics on groundwater impact. Bentazone is a pesticide that has been in use for the last 30 years and has not been banned by governmental agencies. Since it is not very degradable and only sparingly sorbed (Table 3), the concentration resulting from a diffuse source application at a production well in 2013 is simulated to be approximately 60% of the concentration input to groundwater (Figure 3b and e). Considering a typical bentazone concentration leaching to a Danish groundwater table of 0.05 µg/L (Kjær et al. 2011), this corresponds to a concentration of 0.03 µg/L at the well. This simulated concentration is much higher than the values reported in groundwater

monitoring programs (Jupiter 2012) implying that although degradation is not observed in anaerobic conditions in the laboratory (van der Pas et al. 1998), bentazone degradation may be occuring in groundwater.

The transport of pesticides to production wells is affected by degradation processes, which strongly depended on the pathways between the surface and the wells, and the aquifer redox conditions (Tuxen et al. 2002; Prommer et al. 2006). In this work, degradation rates were assumed to be constant in the aquifer and transition zones with different redox conditions were not taken under consideration. However, groundwater pumping could affect the flowlines (Figure 4) and drive pesticides through layers that would not be crossed under low- or no-pumping conditions, such as the aerobic transition zone around the production well. Pumping could also lower the water table and generate larger aerobic transition zones and affect mixing processes of pesticides during their travel to the well and consequently their degradation. Hence the effects of the pumping rate on the breakthrough curves at the production wells could be even more significant that those presented in this paper.

Comparison between pesticide breakthrough and groundwater age simulations

Measurements of environmental tracer concentrations are commonly used to deduce information on the travel time of water in aquifers and hence the available time for degradation (e.g., Sanford 1997; Weissmann et al. 2002). Consequently the average groundwater age at a production well is also used as an indicator of the water quality at the well (e.g., Tesoriero et al. 2007; Molson and Frind 2012). More recently interest has been growing for the simulated groundwater age distributions at water drinking wells, since the average groundwater age measured by chemical analyses represents a mixture of ages entering the well from different depths and the range of ages contributing to the well are necessary for a correct assessment (e.g., Ginn 1999; Zinn

and Konikow 2007). In general, young ground water is expected to be more contaminated by diffuse sources such as pesticides since these contaminants have mainly been applied over the last 50 years (Weissmann et al. 2002, Tesoriero et al. 2007). Pumping can greatly affect the age distribution of water flowing to a well, increasing both the capture of young water from the top of aquifers and old water from deeper groundwater. Groundwater age measurements based on environmental tracers typically only determine the average (fully mixed) groundwater age in a production well and this can be misleading. In fact in most hydrogeological settings very young water will be drawn at the top of the well screen after pumping is initiated making the well susceptible to contamination. Average age data will typically not reveal this portion of younger water since it is mixed with older water from deeper groundwater.

Figure 7a shows the groundwater age in the layered aquifer system after 33 years of constant high rate pumping (21 m^2/week) and Figure 7b shows the age distribution along the production well at that time. Groundwater age was simulated by the transport equation for groundwater age (Goode 1996). Figure 7c shows the breakthrough curve of a tracer and MCPP, both applied in 1955, i.e. 33 years after the initiation of pumping, at the production well placed in the same aquifer. It can be observed that even the youngest of the age components simulated along the well (i.e. 17 years, Figure 7a and b) is significantly older than the observed breakthrough time of the tracer or the MCPP in the production well (3 years, Figure 7c). Similar breakthrough times of diffuse source contaminants in drinking water wells have been observed (e.g., Hinsby et al. 2007) or estimated (Beltman et al. 1995) in the literature; the travel time of these is typically only a few years (3-10 years) depending on sorption and degradation characteristics.

The reason for this discrepancy is that the direct groundwater age simulations describe mean ages that consider diffusion and dispersion along each flowpath rather than the actual advective travel times. Figure 7a also shows the stream lines determined by particle tracking,

ending at t=3 years and confirms that 3 years is the advective travel time for the contaminant to reach the well. The groundwater age of the water reaching the top of the well screen is larger due to mixing with high groundwater ages from the surrounding water. Similarly any environmental tracer concentration estimated at a particular location represents a mixture derived from multiple flow paths carrying water of different ages and travel times (Zinn and Konikow 2007).

This discrepancy between age and contaminant travel times has been noted in the literature for systems at steady state with no pumping, where the groundwater ages in fast flow regions were larger than the ones estimated from advective velocity, due to mixing with adjacent low-velocity regions (Sanford 1997; Becker and Shapiro 2000; Bethke and Johnson 2002). Our study shows that pumping can further increase the mixing of different ages, and thereby the discrepancy between ages and contaminant travel times.

This discussion shows that although the groundwater age data can provide important information on the complex interactions between the wells and the flow systems and is related to the processes affecting contaminant fate and transport through the aquifer, it must be used with caution when determining the breakthrough times of contaminants to assess the vulnerability of production wells.

Conclusions

This study investigated the influence of pumping strategies, the hydrogeology of the aquifer and the pesticide characteristics (sorption, degradation and application histories) on pesticide concentrations reaching a production well used for water supply. The pumping rate can significantly affect the pesticide concentration at the production well, including both its breakthrough time and maximum concentration. Variable pumping rates can generate variability in the concentration at the well, similar to those observed in field data. The pesticide concentration at the well responds rapidly to

changes in pumping rate and the breakthrough curve resulting from the time dependent pumping rates can be derived from the steady state simulations.

The presence of a stream near a well field can significantly impact the concentration of tracers and pesticides at the production well. In the simulated aquifer with a stream, the pumping rate had little effect on simulated concentrations of pesticides at the well. This is because the pumping rate affects both the hydraulic balance between water drawn from the stream and water drawn to the well, and the size and shape of the capture zone. In contrast, in a layered aquifer without a stream, the pumping rate affects the capture zone and travel time to the well and is crucial to the pesticide breakthrough at the well.

Pesticide characteristics must be considered when assessing the effect of the pumping rate on the breakthrough at the well. For a sorbing and non-degrading pesticide (e.g. bentazone), the pumping rate does not affect concentrations at the well. In contrast, for a sorbing and degrading pesticide (e.g. MCPP), the pumping rate can significantly affect the maximum concentration and the breakthrough time at the well.

Our numerical simulations can be used in combination with field data to improve understanding of the fate of pesticides in groundwater. Bentazone is currently thought to be non-degradable in groundwater. However, the high concentration of bentazone computed at the well in 2013 contrasts with the results of field observations, suggesting that bentazone degradation actually does occur in groundwater.

Observations of groundwater age can also provide useful information on the complex interactions between wells and aquifer flow and are related to processes affecting contaminant fate and transport through the aquifer. However, age data must be used with caution and can give misleading results on the breakthrough times of contaminants, since they describe the mixed age of the water along its travel path.

Current regulations to prevent contamination of production wells from agricultural use of pesticides focus on controlling the source of contamination. Our numerical simulations show that by controlling the pumping rate and acknowledging the rapid response of the pesticide concentration at the production well, pumping strategies can be devised to maintain low concentrations of the pesticide concentrations at the well. For example, the MCPP concentration in a layered aquifer can be controlled by the pumping rate; a low pumping rate will result in low (possibly undetectable) concentration at the well for a long period of time, while a high pumping rate will result in a high concentration and faster responses to the input changes at the surface.

Pumping rates and hydrogeology must be considered when assessing regulatory changes. If application of bentazone in a layered aquifer stops today, the concentration at the well may continue to grow for 20 years if a low pumping rate is applied, while an immediate decay will be observed for a high pumping rate. In contrast, in the simulated aquifer with a stream, the pumping rate did not affect the start of bentazone decay at the well.

Acknowledgments

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List of the figure captions

Figure 1 - Concentration of dichlorprop and bentazone in Nybølle Øst, a drinking water well field in Denmark. Observations in abstraction and monitoring wells are shown; well numbers are from Jupiter database (Jupiter 2012).

Figure 2 - Two conceptual hydrogeologic systems studied and boundary conditions used. The line of symmetry A-A' is used to develop 2-D model.

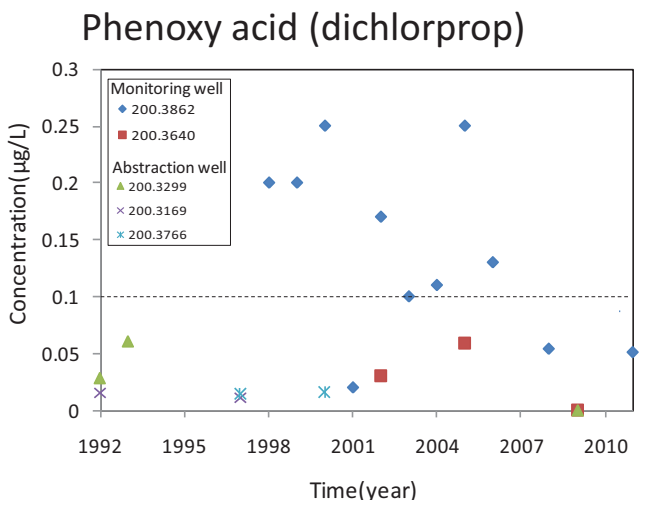
Figure 3 – Effect of constant pumping rates on the normalised pesticide concentration reaching a well placed in a layered aquifer (left figures), and in a layered aquifer with a stream (right figures). Solutions are shown for: i) a tracer with the application history of bentazone (a and d), ii) bentazone (b and e) and iii) MCPP (c and f). Solution of an analytical model for a continuous input concentration is also shown for MCPP (c and f). A hypothetical scenario where bentazone application stops in 2013 is also shown with red lines in a, b, d and e.

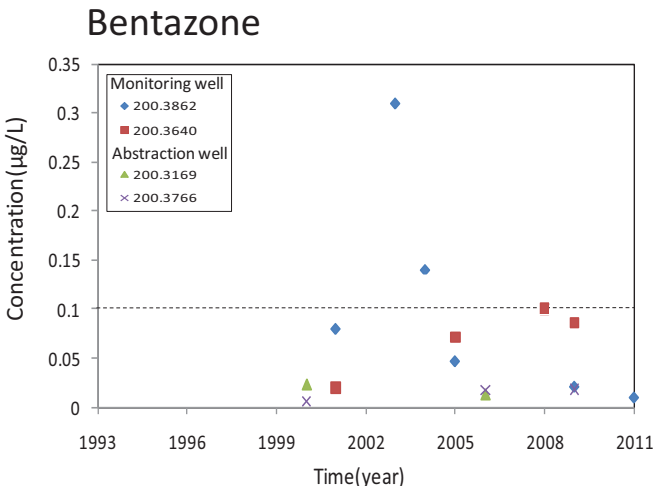
Figure 4 – Effect of different constant pumping rates (no pumping – a and d, low pumping – b and e and high pumping rate – c and f) on streamlines and tracer concentration in a layered aquifer (a, b and c) and a layered aquifer with a stream (d, e and f). Theoretical tracer was applied in 1955, pumping started in 1922 and snapshots are shown in the year 1965. Note that except for the no-pumping case where the whole catchment is shown, only a small area around the well is shown with a 1:1 scale.

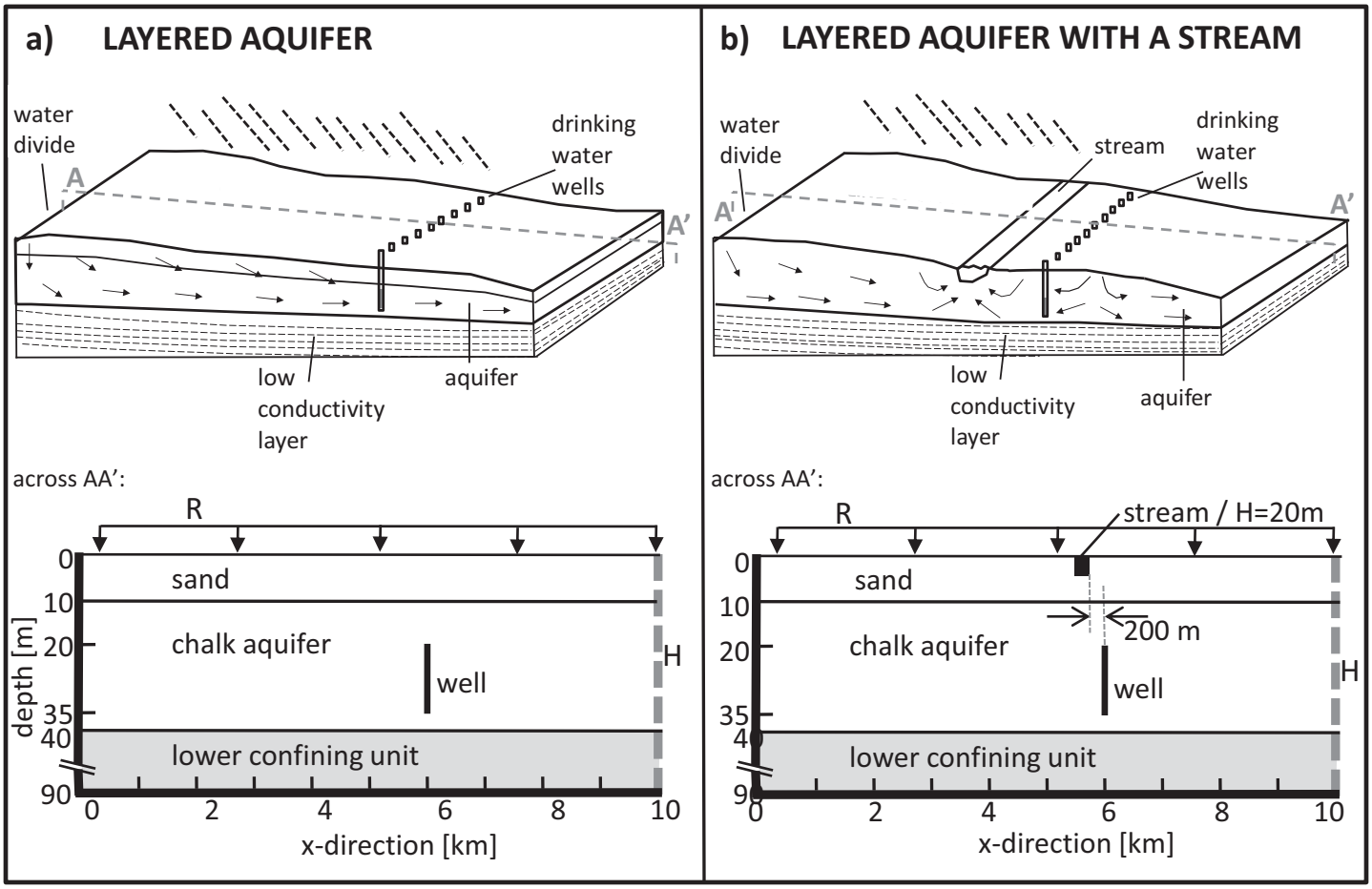
Figure 5 - Effect of variable pumping rate on normalised bentazone (a,b) and MCPP (c,d) concentration reaching a well placed in a layered aquifer (column 1) and in a layered aquifer with a stream (column 2). The cases when sorption and degradation are and are not considered are shown. The hypothetical scenario where bentazone application stops in 2013 is also shown with red lines.

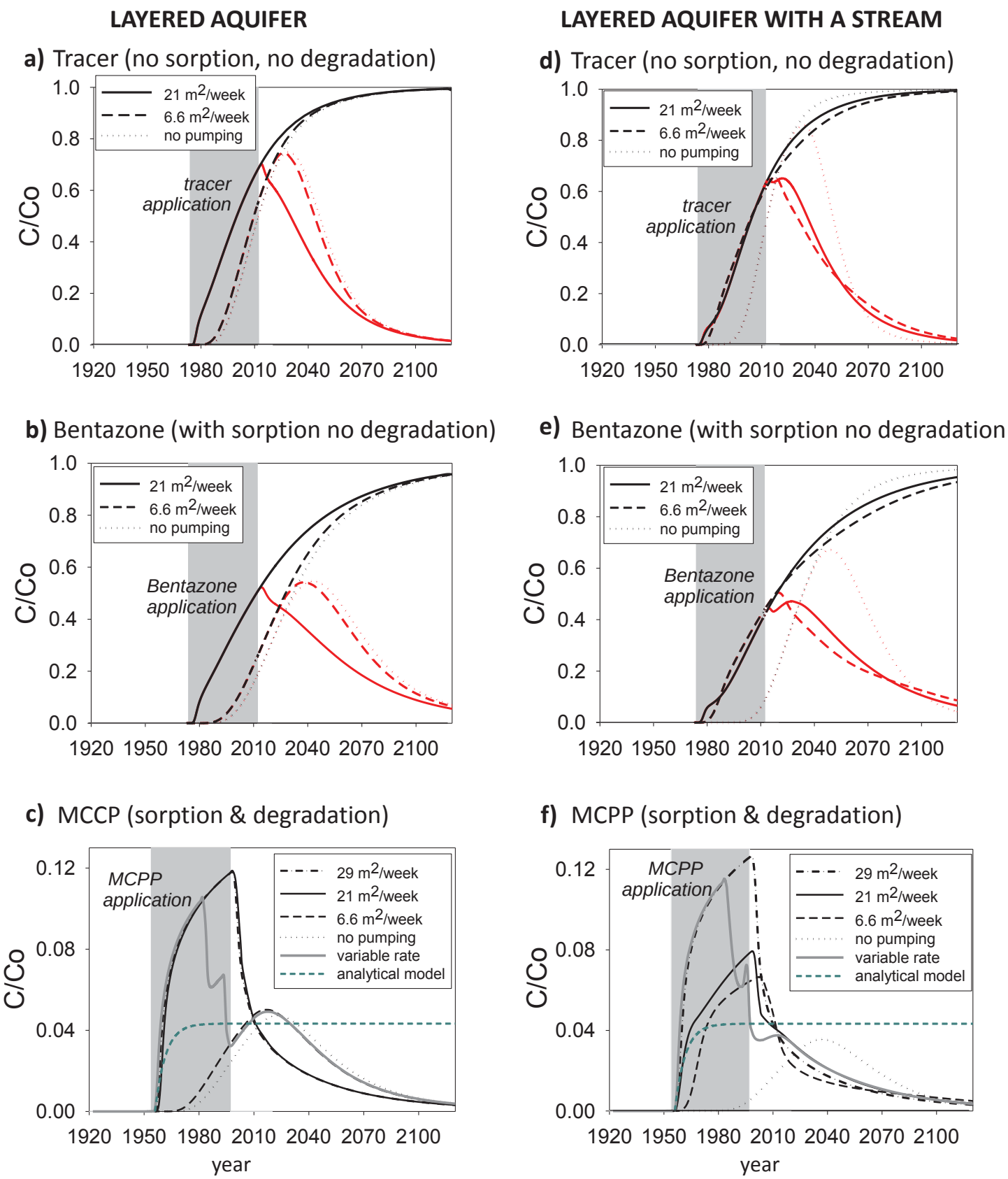
Figure 6 – Effect of variable pumping rate and different constant pumping rates on the normalised MCPP concentration (with sorption and degradation) reaching a well placed in a layered aquifer with a stream. All pumping scenarios started in 1922.

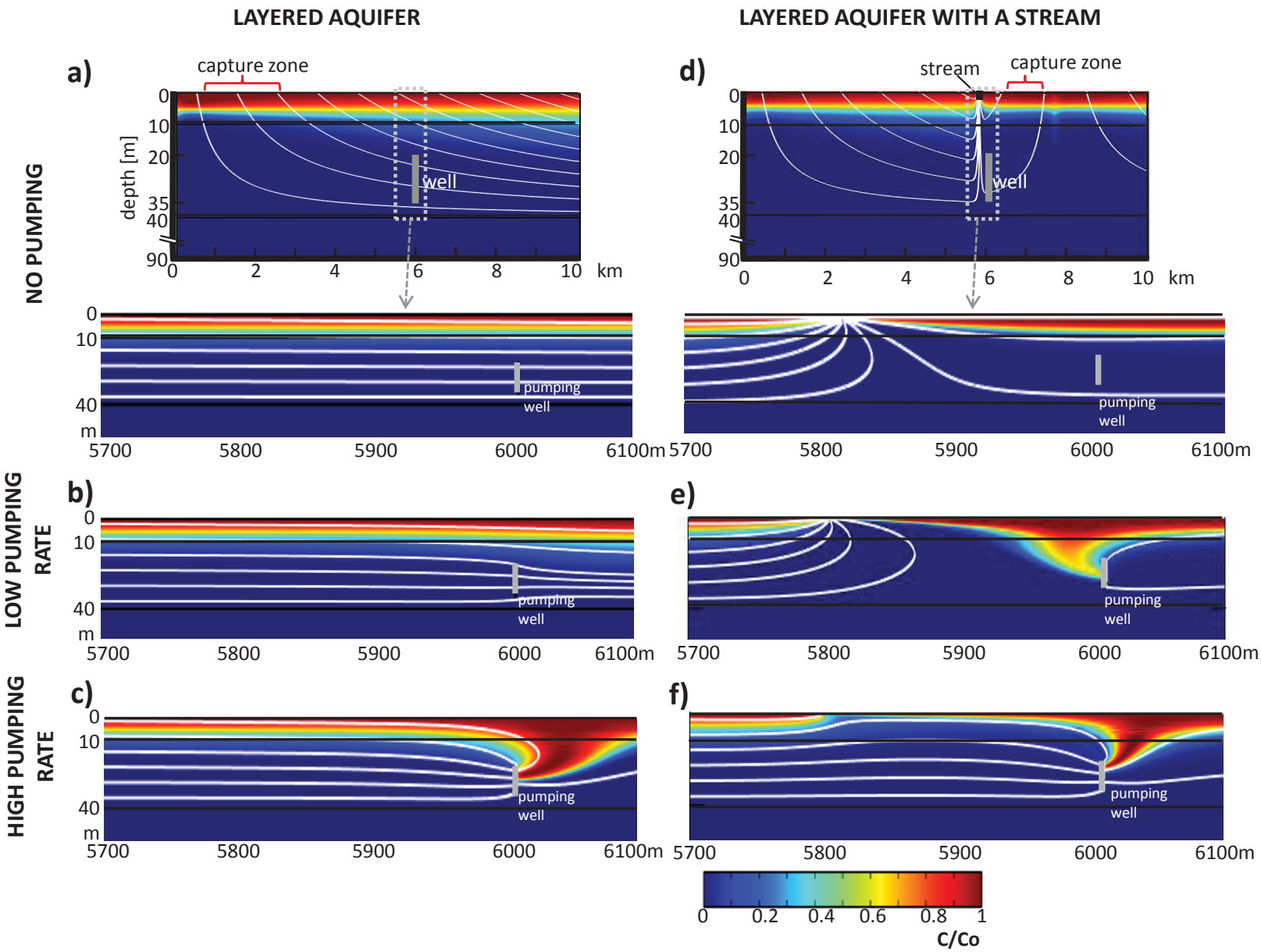
Figure 7 - For a well placed in a layered aquifer with constant pumping rate equal to 21 m^2/week: a) simulated groundwater age in the aquifer after 33 years of pumping and particle tracking ending at t=2 years, b) Simulated groundwater age distribution at the production well after 33 years of pumping, c) simulated tracer and MCPP breakthrough in well.

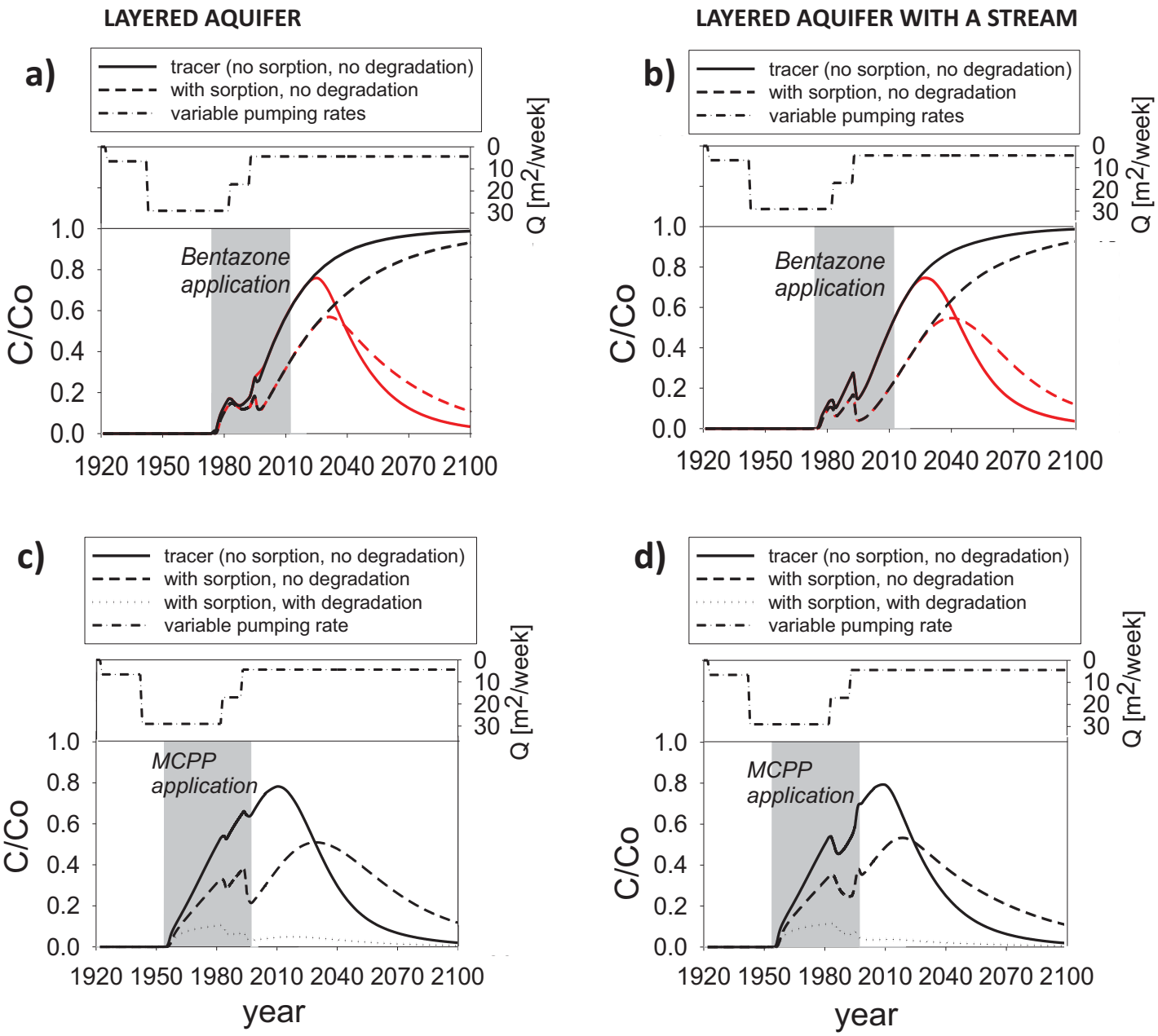

Phenoxy acid (dichlorprop)
Monitoring well
200.3862
200.3640
Abstraction well
200.3299
200.3169
200.3766
Concentration(µg/L)
0.3
0.25
0.2
0.15
0.1
0.05
0
1992
1995
1998
2001
2004
2007
2010
Time(year)

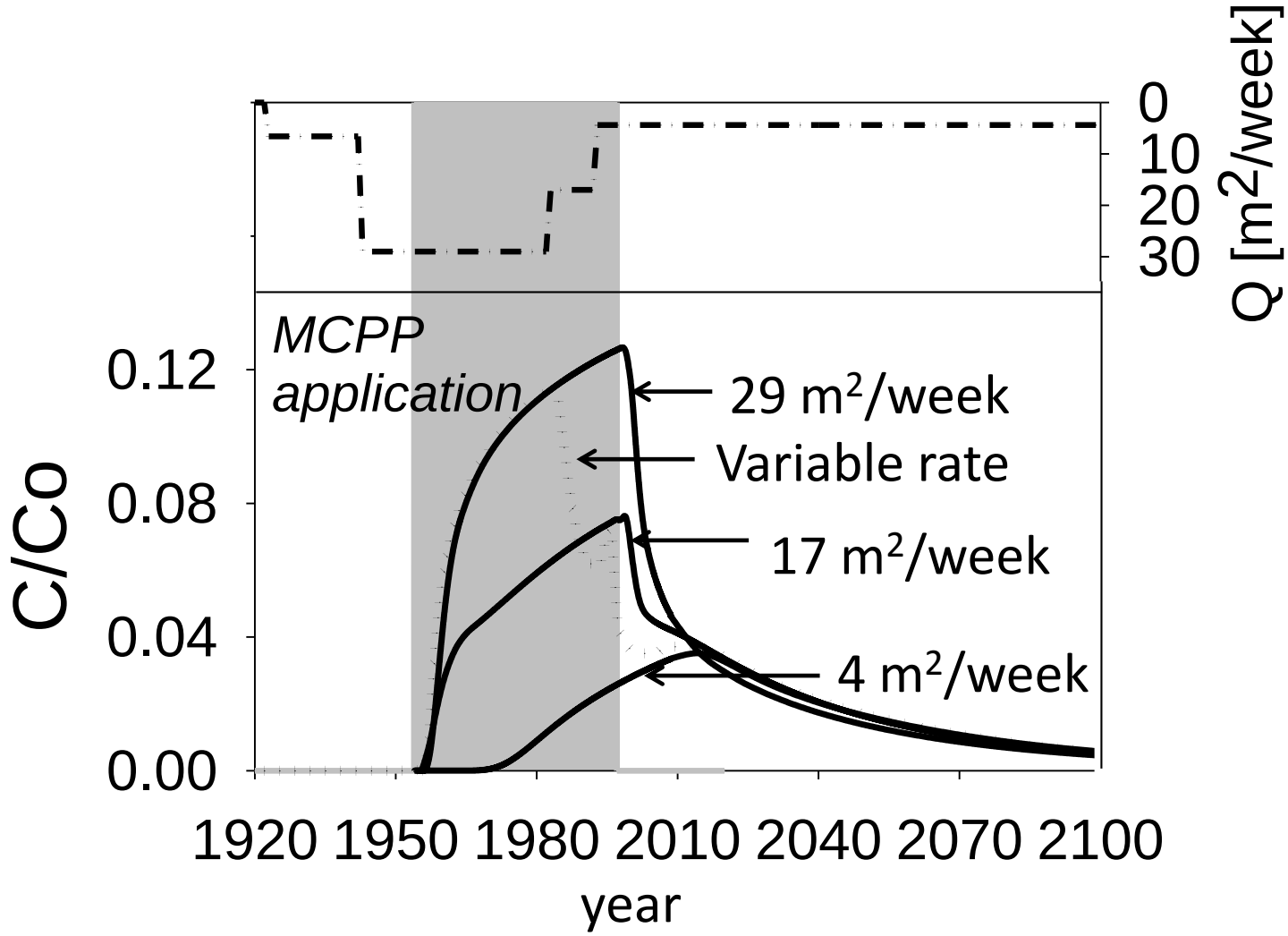

Bentazone
Monitoring well
200.3862
200.3640
Abstraction well
200.3169
200.3766
Concentration(µg/L)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
1993
1996
1999
2002
2005
2008
2011
Time(year)

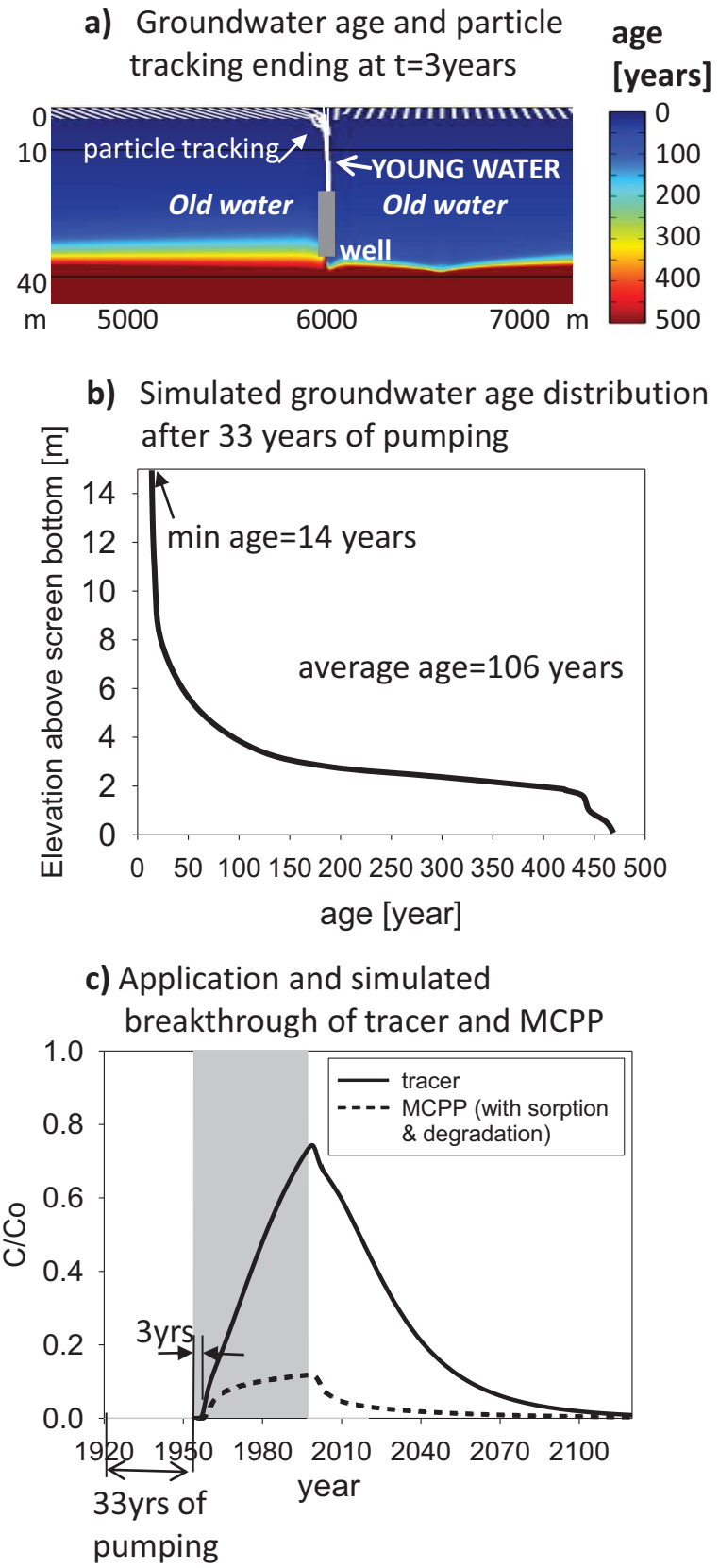

a) LAYERED AQUIFER
water divide
A
A'
drinking water wells
low conductivity layer
aquifer
across AA':
R
sand
chalk aquifer
well
H
lower confining unit
depth [m]
0
10
20
35
40
90
0
2
4
6
8
10
x-direction [km]
b) LAYERED AQUIFER WITH A STREAM
water divide
stream
drinking water wells
A'
A'
low conductivity layer
aquifer
across AA':
R
stream / H=20m
sand
200 m
chalk aquifer
well
H
lower confining unit
0
10
20
35
40
90
0
2
4
6
8
10
x-direction [km]


LAYERED AQUIFER
LAYERED AQUIFER WITH A STREAM
a) Tracer (no sorption, no degradation)
d) Tracer (no sorption, no degradation)
b) Bentazone (with sorption no degradation)
e) Bentazone (with sorption no degradation
c) MCCP (sorption & degradation)
f) MCPP (sorption & degradation)
21 m2/week
6.6 m2/week
no pumping
29 m2/week
variable rate
analytical model
tracer application
Bentazone application
MCPP application
C/Co
year
1920 1950 1980 2010 2040 2070 2100


LAYERED AQUIFER
LAYERED AQUIFER WITH A STREAM
NO PUMPING
LOW PUMPING RATE
HIGH PUMPING RATE
a)
b)
c)
d)
e)
f)
capture zone
stream
well
pumping well
depth [m]
km
m
C/Co


LAYERED AQUIFER
LAYERED AQUIFER WITH A STREAM
a)
b)
c)
d)
tracer (no sorption, no degradation)
with sorption, no degradation
with sorption, with degradation
variable pumping rate
variable pumping rates
Bentazone application
MCPP application
C/Co
Q [m2/week]
year
0
10
20
30
0.0
0.2
0.4
0.6
0.8
1.0
1920 1950 1980 2010 2040 2070 2100


0
10
20
30
Q [m2/week]
MCPP
application
0.12
0.08
0.04
0.00
C/Co
29 m2/week
Variable rate
17 m2/week
4 m2/week
1920 1950 1980 2010 2040 2070 2100
year


a) Groundwater age and particle tracking ending at t=3years
age [years]
0
100
200
300
400
500
0
10
40
m
5000
6000
7000
m
particle tracking
YOUNG WATER
Old water
Old water
well
b) Simulated groundwater age distribution after 33 years of pumping
Elevation above screen bottom [m]
14
12
10
8
6
4
2
0
min age=14 years
average age=106 years
0
50
100
150
200
250
300
350
400
450
500
age [year]
c) Application and simulated breakthrough of tracer and MCPP
C/Co
1.0
0.8
0.6
0.4
0.2
0.0
tracer
MCPP (with sorption & degradation)
3yrs
1920
1950
1980
2010
2040
2070
2100
year
33yrs of pumping