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Propagation of water pollution uncertainty and risk from the subsurface to the surface water system of a catchment

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SUMMARY

This paper investigates the propagation of quantifiable probability and quantification uncertainty of water pollution from local pollutant sources at and below the land surface, through the groundwater system, to downstream surface water recipients. Methodologically, the study shows how the risk and uncertainty of surface water pollution within a catchment may be assessed by a combined methodology of a Lagrangian stochastic advective-reactive modelling approach, which accounts for the quantifiable pollutant transport randomness, and a scenario analysis approach, which accounts for different quantification uncertainties. The results show that, in general, unambiguous risk assessment requires at least a reliable order-of-magnitude quantification of the prevailing relation between the average rate of physical pollutant transport from source to recipient and the average rate of pollutant attenuation. If this average relation can be reliably estimated to fall within two identified, relatively wide open value ranges, the assessment of pollution risk to surface waters from localised sources at or below the soil surface may be unambiguous even under otherwise large quantification uncertainty. For a relatively narrow, closed value range of this average rate relation, however, risk assessment must either rely on conservative assumptions, or else be based on a more detailed and resource demanding quantification of pollutant transport.

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Introduction

Various contaminated land sites and groundwater pollutant plumes may be located within the catchment areas of sensitive water recipients, such as drinking water supplies, lakes, streams and coastal waters. The pollutant releases from such sites and plumes, and from possible future releases in the catchments (for instance from planned or present industrial and transportation activities and pollution accidents), pose pollution risks to the downstream surface water environments. These risks need to be assessed, for instance according to the EU Water Framework Directive (WFD; [European Commission, 2000](#)), which requires catchment-scale water management for achieving and maintaining good physico-chemical and ecological status in all the waters of the EU member states.

To assess the water pollution risks posed by present and potential future pollutant releases within a catchment area, we need to model the pollutant transport and mass exchange that take place along the transport pathways from the sources to the water recipients

within and downstream of the considered catchment area. However, model predictions are associated with uncertainty that needs to be accounted for in this catchment-scale risk assessment. Most model parameters cannot be precisely determined due to large and irregular variability in time and space combined with measurement errors, a general lack of data and site-specific information, and uncertainty about whether the model itself constitutes an adequate mathematical representation of the real-world pollutant transport process (e.g. [Kavanaugh et al., 2003](#); [O'Hagan and Oakley, 2004](#); [Beven, 2006](#); [Baresel and Destouni, 2007](#)).

Numerous studies have in the past decades developed stochastic modelling approaches to account for the physical spreading effect of random spatial aquifer heterogeneity on subsurface solute transport (see for instance [Dagan, 1989](#) and [Rubin, 2003](#) for reviews of different approaches to stochastic solute transport modelling in randomly heterogeneous formations). Some of these approaches use probability density functions (pdfs) of advective solute travel times as a basis for deriving the statistics of solute concentrations and mass flows. Such travel time-based, Lagrangian stochastic approaches have been applied to solute transport through subsurface water systems (soil water, groundwater; e.g. [Shapiro and Cvetkovic, 1988](#); [Destouni, 1992](#); [Cvetkovic and Dagan, 1994](#); [Destouni and Graham, 1995](#); [Simmons et al., 1995](#); [Yabusaki et al., 1998](#); [Foussereau et al., 2001](#); [Tompson et al.,](#)

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2002; Malmström et al., 2004) and catchments (Simic and Destouni, 1999; Lindgren et al., 2004; Lindgren and Destouni, 2004; Botter et al., 2005). The travel time pdfs that must be quantified in these approaches are commonly unknown and approximated by assuming some common pdf type (e.g. lognormal, inverse Gaussian) based only on knowledge about the travel time mean and variance (e.g. Cvetkovic et al., 1998; Destouni et al., 2001). The physical solute travel time statistics can further be coupled with relevant pollutant reaction models. This coupled Lagrangian stochastic advective-reactive (LaSAR) modelling approach can be used for quantifying the transport of reactive pollutants in terms of both expected transport (e.g. Destouni and Graham, 1995; Lindgren et al., 2004; Lindgren and Destouni, 2004; Malmström et al., 2004) and transport variance (e.g. Destouni, 1992; Andricevic and Cvetkovic, 1996; Destouni and Graham, 1997; Andersson and Destouni, 2001; Baresel and Destouni, 2007). The expected transport accounts then for the physical solute spreading effect of aquifer heterogeneity in a statistically quantifiable population of random heterogeneity outcomes, and the transport variance is a measure of the uncertainty implied by this randomness with regard to the actual field outcome from the whole statistical population.

However, pollutant transport uncertainty does not only result from the statistically quantifiable randomness of aquifer heterogeneity. Even if the mean and variance of solute travel time can be quantified from some, relatively readily obtainable field statistics of measurable groundwater hydraulics (e.g. Destouni and Graham, 1997; Simic and Destouni, 1999; Destouni et al., 2001), the further derivation of solute concentration and mass flux statistics requires more field knowledge, for example about the spatial correlation structure of groundwater hydraulics, which is more difficult and resource demanding to assess than independent population statistics. Furthermore, also other essential factors, such as pollutant release from the source zone and biogeochemical reaction rates, may be quite difficult and resource demanding to measure in the field. Our uncertainty about all these factors leads to additional pollutant transport uncertainty to that from the statistically quantifiable randomness in aquifer heterogeneity.

In this paper, we develop a combined methodology for quantifying the propagation of both the statistically quantifiable probability and the quantification uncertainty of water pollution through the groundwater system to downstream surface water recipients. The methodology combines a LaSAR modelling approach, which accounts for statistically quantifiable randomness in aquifer heterogeneity, with a scenario analysis approach, which accounts for quantification uncertainty about: (1) the spatial correlation structure of aquifer heterogeneity, (2) the pollutant release from the source zone, and (3) the biogeochemical pollutant attenuation rate. This combined approach is used for investigating the main effects of these different types of quantification uncertainties and statistically quantifiable randomness on the probability of exceeding a given, environmental or health-based, pollutant concentration limit at a surface water recipient boundary downstream of a short-term accidental (e.g. resulting from accidents involving dangerous goods), or a long-term continuous (e.g. resulting from contaminated land sites) pollutant release. Furthermore, the practical usefulness of this approach is finally also demonstrated for assessments of surface water pollution risk posed by existing or possible future local source releases within a catchment area.

General problem and methodology description

Fig. 1 illustrates schematically the general water pollution problem considered in this study: in a catchment area there may be

Fig. 1. Illustration of a hypothetical case for pollution risk assessment at catchment-scale. In a catchment area, like the coastal catchment area in Forsmark, Sweden, which is here used as our illustration example, there may be various present or potential future sources of pollutants (e.g. the hypothetical sources that are here marked as black dots and fields in the Forsmark catchment area example) from which contaminants may be transported by the groundwater towards the nearest downstream groundwater–surface water interaction boundary, which in the figure and in the main text is referred to as the ‘compliance boundary’.

various present or potential future sources of pollutants of various spatial extents and locations (a number of hypothetical pollutant sources are marked as black dots and fields with red circles around them on the map). Some of the pollutants released from these sources may dissolve quickly in the water, whereas others may leak during a long period of time. Even after abatement measures have been taken, some pollutant fraction may reach the groundwater table below or within a pollutant source zone of arbitrary extent x_s along the mean groundwater flow direction. This pollutant fraction may then be transported by the groundwater towards a groundwater–surface water interaction boundary at distance x_1 downstream of the source zone along the mean groundwater flow direction. At that boundary, which may for instance be associated with a stream or a lake, as exemplified in Fig. 1, an environmental or health-based pollutant concentration limit C_T may be given from an independent assessment of the ecosystem and the toxicological risks that are associated with different pollutant exposure levels in the surface water system. In the following, we refer to the groundwater–surface water interaction boundary as the compliance boundary for meeting the given concentration limit C_T .

The probability P_R that the concentration limit C_T will, at any time t , be exceeded by any local concentration value C in the groundwater that flows through the nearest compliance boundary downstream from the source zone may then be estimated from the concentration pdf $f(C(t, x_1))$ as

$$P_R(t, x_1) = P(C > C_T) = 1 - \int_0^{C_T} f(C(t, x_1)) dC \quad (1)$$

The pdf $f(C(t, x_1))$ may be of any realistic type or form but will, for simplicity, in the following calculations be exemplified as log-

normal, following similar assumption examples in previous stochastic contaminant spreading and abatement management studies (Andricevic and Cvetkovic, 1996; Batchelor et al., 1998; Andersson and Destouni, 2001; Gren et al., 2002). Thereby, $f(C(t, x_1))$ is fully determined by the two most readily quantifiable statistics of concentration C : the expected value $E[C(t, x_1)]$ and variance $V[C(t, x_1)]$. We consider here C to be the local concentration, sampled at any point for comparison with the given concentration limit C_T . Destouni and Graham (1997) showed that the sampling size and method will affect the statistics of locally measured concentration C . For simplicity, we quantify here C only as a point concentration, neglecting the sampling size-method effect to generally decrease the variance $V[C(t, x_1)]$ relative to a corresponding point concentration variance.

Two different cases of contaminant release from the source zone are considered in the assessment of the exceedence probability P_R : (i) a short-pulse release scenario, which may for instance represent the first, fast release phase of easily soluble contaminant fraction after a pollution accident at the soil surface, and (ii) a continuous release scenario, which may for instance represent a long-term industrial leakage, or the second, slow leakage phase after a pollution accident, when some hydrophobic pollutant fraction that has been retained in the accidental source zone slowly leaks out during a long period of time. For both release cases, we quantify the local concentration statistics $E[C]$ and $V[C]$, which fully determine the example lognormal pdf $f(C)$ in (1).

In the continuous release case, $E[C]$ and $V[C]$ will be constant in time after the continuously fed pollutant plume has reached its steady-state condition, and the associated concentration pdf $f(C)$ and exceedence probability P_R will then also remain constant. In the short-pulse release case, $E[C(t, x_1)]$ and $V[C(t, x_1)]$, and through them also $f(C(t, x_1))$ and P_R , will vary in time at the compliance boundary at x_1 as the finite pollutant plume that is bounded by the short-pulse input passes through the boundary. In all the transport-attenuation scenarios considered here for the short-pulse release case, the peak values of the concentration statistics $E[C(t, x_1)]$ and $V[C(t, x_1)]$ coincide in time, in accordance with the model results reported by Andersson and Destouni (2001). The timing of the peak values of $E[C(t, x_1)]$ and $V[C(t, x_1)]$ is then also the timing of the maximum exceedence probability P_R . However, for strongly asymmetrical expected BTCs (occurring, for instance, if the pollutant undergoes slow reversible non-equilibrium sorption–desorption), the peak $E[C]$ and $V[C]$ values may not coincide in time and the timing of the maximum exceedence probability must be found by calculating P_R from Eq. (1) as a function of time (Andersson and Destouni, 2001). In the following, the notation P_R will generally refer to the maximum probability of concentration C exceeding the given concentration limit C_T , which for the short-pulse release case occurs at the time of the peak $E[C]$ and $V[C]$ values at the compliance boundary location x_1 .

To account for the effect of the statistically quantifiable randomness in aquifer heterogeneity, we quantify P_R in Eq. (1) based on the LaSAR approach to solute transport modelling. The groundwater velocity field is then assumed to be essentially stationary or unidirectional, implying that transport pathways coincide with groundwater streamlines or streamtubes. The mixing that may occur between different streamtubes due to pore-scale dispersion and molecular diffusion is often neglected for simplicity; previous results imply that this neglect should not affect the expected concentration much, but may lead to overestimation of the concentration variance (Dagan and Fiori, 1997; Fiori and Dagan, 2000; Fiori et al., 2002; Janssen et al., 2006). For non-reactive solute in the short-pulse release case, the expected value $E[C(t, x_1)]$ and the variance $V[C(t, x_1)]$ of the point concentration may then be expressed as (adapted from Destouni and Graham, 1997 for explicit expression of the source input concentration C_0)

$$E[C(t, x_1)] = \int_0^\infty \left(\frac{M_0}{A_0 n v_0} \right) \delta(t - T) g(T; x_1) dT \\ = C_0 x_s \int_0^\infty \left(\frac{1}{v_0} \right) \delta(t - T) g(T; x_1) dT \quad (2)$$

$$V[C(t, x_1)] = E[C(t, x_1)](C_0 - E[C(t, x_1)]) \quad (3)$$

where A_0 is the cross-sectional area normal to the mean groundwater flow through the source zone, $M_0 \delta(T)/A_0$ is the assumed instantaneous release of pollutant mass M_0 per unit of cross-sectional area at running time $t = 0$, δ is the Dirac delta function, $C_0 \equiv M_0/(A_0 n x_s)$ is the average pollutant concentration within the source zone pore water, n is the assumed constant porosity, $g(T; x_1)$ is the pdf of the spatially variable advective solute travel time T from the source zone boundary at x_s to the compliance boundary at x_1 , and v_0 is the groundwater velocity along the mean groundwater flow direction at x_s .

For the continuous release case, the corresponding statistics of C are obtained as

$$E[C(t, x_1)] = C_0 \int_0^\infty H(t - T) g(T; x_1) dT \quad (4)$$

$$V[C(t, x_1)] = C_0^2 \int_0^\infty H(t - T) g(T; x_1) dT - E[C(t, x_1)]^2 \quad (5)$$

where H is the Heaviside step function and C_0 is in this case the temporally constant input concentration from the source zone at x_s . In the following, we will for simplicity also for the continuous release case refer to the average pollutant concentration within the source zone pore water, $C_0 \equiv M_0/(A_0 n x_s)$, as the input concentration, but note that the local input concentration values vary (because v_0 varies) and the $C_0 \equiv M_0/(A_0 n x_s)$ definition is only an approximation of the average input concentration in that case.

The expressions (3) and (5) quantify the variance of C in the bounding case of zero pore-scale dispersion and concentration measurement at a true point, i.e., for measurement volume approaching zero (Dagan, 1989). In such a case, the concentration of non-reactive solute in an individual streamtube is either $C = 0$ or $C = C_0$, i.e., the true point concentration is bi-modally distributed. Real local concentrations, however, are always measured in finite sampling volumes, wherein the solute mass is mixed, destroying the bi-modality of hypothetical point concentration values. This mixing does not much affect the expected concentration value, but it decreases the local concentration variance relative to the point variance expressed in (3) and (5). In applications with specific sampling information, the variance expressions (3) and (5) can be exchanged to corresponding ones that account for the mixing effect of finite sampling volume on the concentration variance, for example as suggested by Destouni and Graham (1997). In generic pollution risk studies like the present one, however, one may conservatively choose to overestimate the local concentration variance by use of the upper limit point variance expressions (3) and (5), even though the local concentration pdf $f(C)$ in (1) is not assumed to be bi-modal.

For reactive pollutant transport, relevant reaction functions (here accounting for irreversible first-order attenuation and reversible linear equilibrium sorption–desorption) extend the basic non-reactive δ and H transport functions in the above $E[C]$ and $V[C]$ expressions, as outlined in the Appendix 1. For simplicity, the results illustrated in the following include only the effects of irreversible first-order attenuation, but a reversible sorption–desorption process may also readily be accounted for by the use of the full $E[C]$ and $V[C]$ expressions given in the Appendix 1.

To account for the effect of the statistically quantifiable randomness in aquifer heterogeneity, we quantify the exceedence probability P_R (1) for lognormally distributed hydraulic conductivity K with different variance, $V[\ln K]$, but the same mean value of

In K . The effect of $V[\ln K]$ translates then differently into the solute travel time and C statistics depending on which spatial correlation structure of aquifer heterogeneity that prevails in the field.

To investigate the effect of quantification uncertainty about the spatial correlation structure of aquifer heterogeneity (i.e., quantification uncertainty 1 in the Introduction) on P_R , we will in the following consider two extreme correlation structure scenarios. The first scenario is a perfectly stratified aquifer (in the following referred to as a 1D aquifer), where the advective velocity of groundwater transport is constant in the mean flow direction along any individual streamline, or streamtube, between the source zone and the compliance boundary at x_1 , but varies randomly due to random variation of hydraulic conductivity among the different streamlines. The second scenario is a three-dimensional isotropic aquifer (in the following referred to as a 3D aquifer), where hydraulic conductivity and advective groundwater transport velocity vary randomly with equal spatial correlation lengths in all three spatial directions.

Appendix 1 outlines the expressions for the mean and variance of solute travel time T and concentration C in the 1D and 3D aquifer scenarios. For lognormal hydraulic conductivity, the resulting travel time pdf $g(T; x_1)$ is lognormal in the 1D aquifer scenario. For simplicity, we assume here that $g(T; x_1)$ is lognormal also in the 3D aquifer scenario (see e.g. Destouni et al., 2001 for justification of this assumption). Fig. 2 further shows the very different normalised lognormal solute travel time pdfs $g_1(T)(nx_1)/(K_g J)$ resulting for the two different correlation structure scenarios, even for the same $V[\ln K]$ value. The normalising term $(nx_1)/(K_g J)$ corresponds to the geometric mean travel time T_g from the source zone to x_1 in the 1D aquifer scenario, and to the expected travel time $E[T]$ from the source zone to x_1 in the 3D aquifer scenario. Moreover, K_g is the geometric mean hydraulic conductivity, and J is the constant hydraulic gradient in the 1D aquifer scenario and the mean hydraulic gradient (denoted $\bar{J}$ in the Appendix 1) in the 3D aquifer scenario.

In general, the variability of physical solute travel times is a result of various processes that are difficult or impossible to quantify with accuracy and precision in real field situations. Examples of such processes are pore-scale dispersion and molecular diffusion

(Dagan and Fiori, 1997), as well as diffusive mass transfer between mobile and immobile groundwater zones (Lindgren et al., 2004). The travel time pdfs illustrated in Fig. 2, which correspond to the 1D and 3D aquifer scenarios considered in the following calculations, are so different that they are likely to bound a quite wide range of possible travel time pdfs for more complex field-process situations. The present aquifer scenario analysis may therefore implicitly give a good indication of the practical importance of different quantification uncertainties associated with the physical solute travel time pdf.

To investigate the effect of the often large quantification uncertainty (e.g. Kavanaugh et al., 2003) about the input concentration from the source zone (i.e., quantification uncertainty 2 in the Introduction), we will in the following quantify the exceedence probability P_R for a range of different scenarios of relative input concentration, C_0/C_T . To investigate finally the effect of quantification uncertainty about the prevailing biogeochemical attenuation rate (i.e., quantification uncertainty 3 in the Introduction) we will also consider different scenarios for such attenuation rate. These will be represented by the relation between average characteristic attenuation and transport rates (or time scales), quantified as $\lambda(nx_s)/(K_g J)$, where λ is the rate of attenuation and the term $(nx_s)/(K_g J)$ corresponds to the arithmetic and the geometric mean advective solute travel time through the source zone extent x_s in the 3D aquifer and the 1D aquifer scenario, respectively. The constant source zone extent x_s is included here instead of the variable transport distance x_1 in order for the normalising term to be constant.

Results and discussion

The short-pulse release case

Fig. 3 shows the resulting probability P_R to exceed the concentration limit C_T downstream of a short-pulse contaminant release for different scenarios of aquifer correlation structure (1D or 3D aquifer), relative source input concentration ($C_0/C_T = 100$ and 1000), and relation between average characteristic attenuation and transport rates ($\lambda(nx_s)/(K_g J) = 0, 0.01, 0.1$ and 1).

For illustrative clarity, Fig. 3 shows P_R results only for one value of the hydraulic conductivity variance, $V[\ln K] = 1$. Lower hydraulic conductivity variance reduces the difference between the 1D and 3D aquifer structure cases (see Fig. A-1 in Appendix 2, which shows P_R results for both $V[\ln K] = 0.3$ and $V[\ln K] = 1$). The results in Fig. 3 and in all the following figures and tables are further based on the example relative correlation length of hydraulic conductivity $l/x_s = 0.1$ for the 3D aquifer. The travel time pdfs in Fig. 2 that underlie the P_R results for the 3D aquifer at the relative distances $x_1/x_s = 10$ and $x_1/x_s = 100$ are thus the curves for $V[\ln K] = 1$ and $l/x_1 = 0.01$ $l/x_1 = 0.001$, respectively. For the 1D aquifer, the shape of the travel time pdf does not depend on x_1 and the travel time pdf that underlies the P_R results for this aquifer scenario is that for $V[\ln K] = 1$ in Fig. 2.

As one possible example of a water pollution risk level that might be considered acceptable by environmental managers and other stakeholders, Fig. 3 emphasises the 1% P_R level (dashed line). Table 1 shows the relative distance x_1/x_s at which the exceedence probability P_R falls below the 1% level in different analysed scenarios. Table 1 shows more results than Fig. 3, including both $V[\ln K] = 0.3$ and $V[\ln K] = 1$ and a wider range of source input concentration scenarios of $C_0 = 10$ –1000 C_T .

The obtained P_R results for the very differently shaped travel time pdfs resulting from the two extreme 1D (infinite correlation length in x_1) and 3D isotropic (equal correlation length in all directions) aquifer scenarios are likely to bound corresponding results for intermediate, more realistic anisotropic aquifer scenarios,

Fig. 2. Effects of uncertainty in the correlation structure of aquifer heterogeneity (perfectly stratified aquifer scenario, denoted 1D aquifer, or three-dimensional isotropic aquifer scenario, denoted 3D aquifer), the relative hydraulic conductivity correlation length l/x_1 (in the 3D aquifer), and the log-conductivity variance $V[\ln K]$, on the probability density function (pdf) of the advective solute travel time $g(T)$. Both $g(T)$ and T are normalised with characteristic mean travel time $(nx_1)/(K_g J)$ (see further notation explanations in the main text).

Fig. 3. Effects of uncertainty in the correlation structure of aquifer heterogeneity (perfectly stratified aquifer, denoted 1D aquifer, or three-dimensional isotropic aquifer, denoted 3D aquifer), relative solute input concentration C_0/C_T and attenuation-transport rate relation $\lambda(nx_s)/(K_gJ)$ on the probability P_R to exceed the concentration limit C_T at different relative distances x_1/x_s from the source zone in a short-pulse pollutant release case. The log-conductivity variance is $V[\ln K] = 1$ and the relative conductivity correlation length in the 3D aquifer is $l/x_s = 0.1$.

Table 1

The relative transport distance x_1/x_s at which the probability P_R to exceed the concentration limit C_T falls below 1% for different scenarios of aquifer heterogeneity, relative input concentration C_0/C_T , and attenuation-transport rate relation $\lambda(nx_s)/(K_gJ)$ in a short-pulse pollutant release case.

C_0/C_T	Aquifer scenario	$\lambda(nx_s)/(K_gJ)$		
		≤ 0.01	0.1	≥ 1
10	1D aquifer	$>40^a$	$\approx 20^{a,b}$	$<10^{a,b}$
	3D aquifer	$>60^b$	$\approx 40^{a,b}$	
100	1D aquifer	$>180^a$	$\approx 60^a$	$<10^{a,b}$
	3D aquifer	$>200^b$	$\approx 50^b$	
1000	1D aquifer	$>200^{a,b}$	$\approx 120^a$	$<30^a$
	3D aquifer		$\approx 80^b$	$<10^b$
			$\approx 80^{a,b}$	$<10^{a,b}$

^a $V[\ln K] = 1$.

^b $V[\ln K] = 0.3$.

where correlation lengths in the essentially horizontal x_1 direction are commonly greater than in the vertical direction. The present aquifer scenario analysis may therefore indicate the practical importance of the greatest possible quantification uncertainty about the correlation structure of aquifer heterogeneity, i.e., of essentially not knowing anything about the prevailing correlation

structure. Such large uncertainty may be relevant for instance in pollution accidents with very limited available site-specific information and with fast abatement measure decisions that must be made in spite of these limitations.

As we have seen in Fig. 2, the resulting variance of advective solute travel time is, for any given $V[\ln K]$ value, much higher for the 1D than the 3D aquifer. Large travel time variability implies that the travel time along many streamlines deviates significantly from the mean travel time. Attenuation along the fastest streamlines will then be much lower than along streamlines that are closer to the mean, whereas the transport along streamlines with much longer than average travel times will not affect the total pollutant mass delivery much, since the mean travel time is there already large enough for most of the pollutant mass to be attenuated. On the one hand, the large travel time variability in the 1D aquifer scenario thus implies less pollutant mass attenuation than in the 3D aquifer scenario, which has smaller travel time variability for the same conductivity variance $V[\ln K]$. On the other hand, however, the larger travel time variability in the 1D aquifer scenario also implies greater spreading of the migrating pollutant plume, so that the pollutant becomes more diluted in the short-pulse release case. These two counteracting effects of the larger travel time variance in a 1D than in a 3D aquifer explain the results shown in Fig. 3, where the 1D aquifer scenario generally implies high P_R for the relatively large attenuation-transport rate relation $\lambda(nx_s)/(K_gJ) = 1$ (for

which the reducing effect of larger travel time variability on mass attenuation dominates the result), whereas the 3D aquifer scenario generally implies high P_R for the scenarios of non-reactive solute and solute with the relatively small attenuation-transport rate relation $\lambda(nx_s)/(K_gJ) \leq 0.01$ (i.e., for relatively non-reactive solute, for which the dilutive effect of larger travel time variability dominates the result). For the intermediate attenuation-transport rate relation $\lambda(nx_s)/(K_gJ) = 0.1$, the 3D aquifer implies high P_R close to the source zone, while the 1D aquifer implies high P_R further downstream, where the pollutant attenuation has had sufficient time to yield significant effects.

We see then in Fig. 3 and Table 1 (and in Fig. A-1, Appendix 2) that in many cases, neither the quantifiable aquifer heterogeneity degree nor the quantification uncertainty about its correlation structure may be very important with regard to whether or not the risk of water pollution exceeds some given or agreed upon acceptable risk level. Generally, the quantification uncertainty about the average attenuation-transport rate relation $\lambda(nx_s)/(K_gJ)$ seems to be the key for this type of risk level acceptability assessment.

For a high attenuation-transport rate relation of $\lambda(nx_s)/(K_gJ) \geq 1$, the C_T exceedance probability P_R declines below 1% at distances closer than $x_1/x_s = 30$ (i.e., 30 times the source zone extent) for any input concentration $C_0 \leq 1000C_T$. This applies regardless of the aquifer heterogeneity details, as long as the log-conductivity variance is, as often assumed, about 1 or less (Dagan, 1989; Rubin, 2003), which indicates a possibility to give remediation and prevention needs relatively lower priority if one can know with some certainty that $\lambda(nx_s)/(K_gJ) \geq 1$, even though there might be large quantification uncertainty about the precise λ and advection parameter values.

For an attenuation-transport rate relation of $\lambda(nx_s)/(K_gJ) \leq 0.01$, the C_T exceedance probability P_R is highly likely to remain above 1% at distances up to 200 times the source zone extent for any input concentration $C_0 \geq 100C_T$ and aquifer heterogeneity assumption. This indicates a need to prioritise prevention measures and remediation efforts if such conditions of $\lambda(nx_s)/(K_gJ) \leq 0.01$ can be expected, even in the face of otherwise large uncertainty. Only for a small relative input concentration, $C_0/C_T = 10$ in the extreme 1D aquifer scenario, does P_R decline below 1% at a relatively short distance x_1/x_s if $\lambda(nx_s)/(K_gJ) \leq 0.01$.

For the intermediate attenuation-transport rate relation of $\lambda(nx_s)/(K_gJ) \approx 0.1$, the distance at which P_R declines below 1%

ranges between 20 and 120 times the source zone extent, mostly depending on the magnitude of relative input concentration C_0/C_T . For a given C_0/C_T , the distance x_1/x_s of $P_R < 1\%$ is relatively insensitive to the assumed aquifer heterogeneity scenario (within the limit $V[\ln K] \leq 1$).

The continuous release case

Fig. 4 shows the probability P_R to exceed the concentration limit C_T downstream of a continuous contaminant release for the example hydraulic conductivity variance $V[\ln K] = 1$. As in the short-pulse release case, lower hydraulic conductivity variance reduces the difference between the 1D and 3D aquifer structure cases (see Fig. A-2 in Appendix 2, which shows P_R results for both $V[\ln K] = 0.3$ and $V[\ln K] = 1$). Table 2 further shows the relative distance x_1/x_s at which P_R falls below the example 1% risk acceptance level. In the continuous release case, the travel time variability does not affect the contaminant plume dilution after steady-state is reached, but larger travel time variability may still imply smaller overall pollutant mass attenuation (see discussion above in “The short-pulse release case”). The latter effect explains why P_R generally declines below the 1% level at greater relative distance x_1/x_s from the source zone in the 1D than in the 3D aquifer scenario.

Table 2

The relative transport distance x_1/x_s at which the probability P_R to exceed the concentration limit C_T falls below 1% for different scenarios of aquifer heterogeneity, relative input concentration C_0/C_T , and attenuation-transport rate relation $\lambda(nx_s)/(K_gJ)$ in a continuous pollutant release case.

C_0/C_T	Aquifer scenario	$\lambda(nx_s)/(K_gJ)$		
		≤ 0.01	0.1	≥ 1
10	1D aquifer	>200 ^{a,b}	$\approx 170^a$ $\approx 70^b$	<20 ^a <10 ^b
	3D aquifer	>200 ^{a,b}	$\approx 30^{a,b}$	<20 ^a <10 ^b
100	1D aquifer	>200 ^{a,b}	$\approx 150^b$	<50 ^a <20 ^b
	3D aquifer	>200 ^{a,b}	$\approx 50^{a,b}$	<10 ^{a,b}
1000	1D aquifer	>200 ^{a,b}	>200 ^{a,b}	<90 ^a <20 ^b
	3D aquifer	>200 ^{a,b}	$\approx 80^{a,b}$	<10 ^{a,b}

^a $V[\ln K] = 1$.

^b $V[\ln K] = 0.3$.

Fig. 4. Effects of uncertainty in the correlation structure of aquifer heterogeneity (perfectly stratified aquifer, denoted 1D aquifer, or three-dimensional isotropic aquifer, denoted 3D aquifer), relative solute input concentration C_0/C_T , and attenuation-transport rate relation $\lambda(nx_s)/(K_gJ)$ on the probability P_R to exceed the concentration limit C_T at different relative distances x_1/x_s from the source zone in a continuous pollutant release case. The log-conductivity variance is $V[\ln K] = 1$ and the relative conductivity correlation length in the 3D aquifer is $l/x_s = 0.1$.

In general, uncertainty about the correlation structure of aquifer heterogeneity affects the P_R propagation more in the continuous than in the short-pulse release case. However, also in the continuous release case, the aquifer heterogeneity details may be important for whether or not the risk of water pollution exceeds an acceptable risk level only for a relatively narrow value range of the average attenuation-transport rate relation $\lambda(nx_s)/(K_gJ)$.

Specifically, for $\lambda(nx_s)/(K_gJ)$ values around 0.1, the distance at which P_R declines below the example of 1% risk acceptance level varies greatly depending on the prevailing correlation structure and also on the degree of heterogeneity (Fig. A-2, Appendix 2) in the 1D aquifer scenario. For $\lambda(nx_s)/(K_gJ)$ outside of this range, however, the water pollution risk may in many cases be judged unambiguously as acceptable or unacceptable (below or above the example 1% risk level) regardless of actual input concentration ($C_0 = 10\text{--}1000C_T$) or correlation structure and magnitude of aquifer heterogeneity. For $\lambda(nx_s)/(K_gJ) \leq 0.01$, the probability P_R to exceed the limit C_T is highly likely to remain above 1% even at greater distances from the source zone than $x_1/x_s = 200$. As in the short-pulse release case, this may serve as a clear indication to prioritise prevention measures and remediation efforts if one has reason to expect $\lambda(nx_s)/(K_gJ) \leq 0.01$, even under otherwise large uncertainty. For $\lambda(nx_s)/(K_gJ) \geq 1$, P_R is instead highly likely to decline below 1% at shorter distances than $x_1/x_s = 50$ for all input concentrations $C_0 \leq 100C_T$ and independently of aquifer heterogeneity details. Similarly to the short-pulse release case, this indicates a possibility to give remediation and prevention relatively low priority in expected conditions of $\lambda(nx_s)/(K_gJ) \geq 1$.

The risk of surface water pollution in a catchment area

We use the relatively well investigated (e.g. Johansson et al., 2005; Lindborg, 2005; Jarsjö et al., 2008) 29.5 m² Swedish coastal catchment area of Forsmark, north of Stockholm (Figs. 1 and 5) as an example of how scenario analysis results like those presented

in the above sections may be used for assessing the risk of surface water pollution, for instance for the nearest lake or stream, downstream of different groundwater pollution sources within a catchment area. We relate here such an analysis to the risk assessment requirements of the WFD (European Commission, 2000) and exemplify its use for continuous pollutant releases (using the results in Table 2). We consider local source zone extents of $x_s = 10$ m, which correspond to the finest pixel resolution of reported hydrological modelling of the Forsmark catchment area (e.g. Jarsjö et al., 2008). Smaller sources can anyhow not be spatially resolved beyond the finest available model resolution, and analogous risk assessment analysis can be readily extended to larger source extents.

The basic WFD demand is for good ecological status to be achieved or maintained in all the waters of the EU member states. In order to meet this demand, the WFD requires the member states to characterise the present status of their waters and assess the future risk of declining water status. In this context, the concentration limit C_T may represent a regulatory pollutant concentration limit, which is set for maintaining or achieving good ecological water status and must not be exceeded at any compliance boundary of a surface or coastal water body. However, the present scenario analysis shows that the probability P_R of the concentration limit C_T to be exceeded at some point in time, somewhere on a compliance boundary, may always be greater than zero (Figs. 3 and 4). There must therefore exist some non-zero probability of pollutant concentrations to exceed C_T sometime and somewhere in a catchment, which is tacitly or openly acceptable to environmental managers and other stakeholders. If this acceptable probability level is not explicitly stated and agreed upon, it may differ considerably among different stakeholders and constitute an important, unresolved cause of stakeholder conflict and ineffective environmental management.

In this study, we consider the example of an acceptable P_R level of 1%, corresponding to an expectation that the water status will

Fig. 5. Pollution risk at the nearest surface water system downstream of some hypothetical groundwater pollution sources (marked as black dots) for an average attenuation-transport rate relation of: (a) $\lambda(nx_s)/(K_gJ) \leq 0.01$; (b) $\lambda(nx_s)/(K_gJ) \geq 1$; and (c) $\lambda(nx_s)/(K_gJ) \approx 0.1$. The corresponding risk categories are indicated by: red colour = at risk; yellow colour = probably at risk; green colour = probably not at risk; blue colour = not at risk.

remain acceptably good even if about 1% of the groundwater that flows through a surface water compliance boundary at different points in space and time has greater pollutant concentration than the regulatory concentration limit C_T . In general, the results in Table 2 for continuous pollutant releases (as well as in Table 1 for short-pulse releases) indicate that quantification uncertainty about the average attenuation-transport rate relation $\lambda(nx_s)/(K_gJ)$ is the key to whether and where P_R declines to 1% (or some other possible acceptable P_R level) within a catchment. To evaluate how this uncertainty affects the pollution risk at the nearest surface water compliance boundaries of the different hypothetical pollutant source locations that are illustrated in Fig. 5, we can then use the scenario results for each value range of $\lambda(nx_s)/(K_gJ)$ in Table 2, along with the following definitions of four different risk categories: (1) *at risk* – if $P_R > 1\%$ in all or nearly all the investigated source input concentration and aquifer heterogeneity scenarios for each $\lambda(nx_s)/(K_gJ)$ value range; (2) *probably at risk* – if $P_R > 1\%$ in most or in the most probable investigated scenarios; (3) *probably not at risk* – if $P_R < 1\%$ in most or in the most probable investigated scenarios; (4) *not at risk* – if $P_R < 1\%$ in all or nearly all the investigated scenarios. The flow paths from each source to the nearest surface water compliance boundary are determined from a high-resolution (10 m) digital elevation model of the area, as explained in more detail by Jarsjö et al. (2008). The lengths of the flow paths from the different hypothetical sources in Fig. 5 to their nearest surface water recipient range between 100 and 1300 m.

Fig. 5a shows that if there is sufficient site-specific information to at least estimate the average attenuation-transport rate relation to be in the range $\lambda(nx_s)/(K_gJ) \leq 0.01$, the nearest surface water bodies to all of the six source locations are unambiguously *at risk*, across a wide value range of all other scenario parameters, which determine the pollutant input concentration and the physical transport through the heterogeneous groundwater system. For a possible reliable quantification of $\lambda(nx_s)/(K_gJ) \geq 1$, Fig. 5b shows that the nearest surface waters are unambiguously *not at risk* for three of the sources and *probably not at risk* for the other three sources; if the 1D aquifer scenario can further be reliably estimated as unlikely, based on the available site information, all surface water bodies can be unambiguously judged as *not at risk*. For $\lambda(nx_s)/(K_gJ) \approx 0.1$, Fig. 5c finally shows that the risk may vary widely among the different sources and their nearest surface water bodies, implying that the result is here sensitive to the details of pollutant input and/or aquifer heterogeneity scenario parameters and their quantification uncertainty. Decisions about whether any and which pollutant abatement measures that are necessary for the different sources then rely heavily on the accuracy of the quite specific estimate of $\lambda(nx_s)/(K_gJ) \approx 0.1$ and require in addition reliable judgement and quantifications of the actual probability of different possible pollutant input and/or aquifer heterogeneity scenarios.

In general, all risk assessments depend on the chosen definitions of the different risk categories. In practice, such as in real WFD implementation situations, the risk category definitions will commonly be decided by the competent water management authorities, after consultations with different stakeholders and the interested public. In this study, we have exemplified how the risk definitions can be directly related to a scenario analysis, which accounts for quantifiable variability and randomness as well as quantification uncertainty in essential risk-determining parameters. If sufficient and accurate information is not available about the key average attenuation-transport rate relation, or about the other pollutant input and groundwater transport parameters for some specific $\lambda(nx_s)/(K_gJ)$ conditions, the results in Fig. 5 demonstrate that the risk of surface water pollution may be assigned any possible category value, depending on which subjective assumptions are made about these parameters.

Conclusions

This paper has investigated the propagation of quantifiable probability and quantification uncertainty of water pollution from local sources at and below the land surface, through the groundwater system, to downstream surface water recipients. Methodologically, the study has shown how the risk and uncertainty of surface water pollution within a catchment may be assessed by a combined methodology, including a LaSAR modelling approach, which accounts for quantifiable pollutant transport randomness, and a scenario analysis approach, which accounts for quantification uncertainty. The investigated latter uncertainty regards the correlation structure of aquifer heterogeneity, the released pollutant concentration from the source zone, and the pollutant attenuation rate along the transport from the source to the surface water compliance boundary.

The application results of this methodology have shown that, in general, unambiguous risk assessment for any pollutant source requires at least a reliable order-of-magnitude quantification of the prevailing average attenuation-transport rate relation, quantified here as $\lambda(nx_s)/(K_gJ)$. If this average parameter value can reliably be estimated to fall within any of the open ranges of $\lambda(nx_s)/(K_gJ) < 0.01$ or $\lambda(nx_s)/(K_gJ) > 1$, the assessment of pollution risk to surface waters may be unambiguous even under otherwise large quantification uncertainty. If even such range estimates are uncertain, so that the prevailing average $\lambda(nx_s)/(K_gJ)$ value can possibly be of the order of 0.1, additional investigations may be necessary for reducing the quantification uncertainty about the additional investigated factors of pollutant input concentration and transport through the heterogeneous groundwater system. If such investigations are not possible within the time and resources available for the pollution abatement effort, or if their costs are greater than the possible pollution abatement measures, one should conservatively assume and plan abatement measures for the relatively non-reactive scenario of $\lambda(nx_s)/(K_gJ) < 0.01$.

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Appendix

Statistics of travel times and local concentrations

In the short-pulse release case, the local solute concentration at time t and location x_1 along the mean flow direction in an individual streamtube can be expressed as $C(t, x_1) = C_0 x_s \delta(t - T(x_1)) / v_0$. If the solute along its transport through the individual streamtube undergoes first-order irreversible attenuation from the aqueous phase at the rate λ and linear equilibrium sorption-desorption with the resulting retardation factor R , the local concentration becomes instead $C(t, x_1) = C_0 x_s \exp(-\lambda T) \delta(t - RT(x_1)) / (v_0)$ (adapted from Destouni and Graham, 1997; Destouni and Cvetkovic, 1991 for explicit expression of both C_0 and R). In the 1D aquifer scenario, the advective velocity along a streamtube is constant so that $v_0 = x_1 / T$ and the expected concentration $E[C(t, x_1)]$ in the ensemble of streamtubes in the aquifer becomes (adapted from Destouni and Graham, 1997 (Eq. (9)) and Destouni and Cvetkovic, 1991 (Eq. (6)) for explicit expression of both C_0 and R)

$$\begin{aligned} E[C(t, x_1)] &= \int_0^\infty \frac{C_0 x_s}{v_0} \exp[-\lambda T] \delta(t - RT) g_1(T; x_1) dT \\ &= \frac{C_0 x_s t}{x_1 R^2} \exp[-\lambda t / R] g_1\left(\frac{t}{R}; x_1\right) \end{aligned} \quad (A1)$$

The statistics of T in the 1D aquifer scenario can further be derived from the statistics of the lognormally distributed K as

$$T_g = \frac{nx_1}{K_g J} \quad (A2)$$

$$V[\ln T] = V[\ln K]$$

where J , in this aquifer scenario, is the constant hydraulic gradient in the mean flow direction x_1 , $T_g \equiv \exp(E[\ln T])$ is the geometric mean travel time, $K_g \equiv \exp(E[\ln K])$ is the geometric mean hydraulic conductivity, $V[\ln T]$ is the variance of $\ln T$, and $V[\ln K]$ is the variance of $\ln K$.

In the 3D aquifer scenario, with equal correlation length of hydraulic conductivity in all three directions, $E[C(t, x_1)]$ becomes instead (adapted from Destouni and Graham, 1997 (Eqs. (15) and (16)) and Destouni and Cvetkovic, 1991 (Eq. (6)) for explicit expression of both C_0 and R)

$$E[C(t, x_1)] = \frac{C_0 x_s}{R} \frac{n(1 + 11V[\ln K]/30)}{K_g \bar{J}} \exp[-\lambda t/R] g_1\left(\frac{t}{R}; x_1\right) \quad (A3)$$

The mean travel time $E[T]$ and variance $V[T]$ can in this aquifer scenario be derived from the statistics of the lognormally distributed K for far-field transport, $x_1 \gg l$, as

$$E[T] = \frac{nx_1}{K_g \bar{J}} \quad x_1 \rightarrow \infty$$

$$V[T] = \frac{2l}{x_1} V[\ln K] \left(\frac{nx_1}{K_g \bar{J}}\right)^2 \quad x_1 \rightarrow \infty \quad (A4)$$

where $\bar{J}$ is the mean hydraulic gradient in the mean flow direction, x_1 , and l is the correlation length of the hydraulic conductivity. As explained in the appendix of Destouni and Graham (1997), the expression of $E[T]$ in Eq. (A4) is a consistent (with the following first-order expression of $V[T]$) first-order approximation of mean arrival time, as discussed by Cvetkovic et al. (1992). The expression for $V[T]$ is identical to Eq. (23) of Shapiro and Cvetkovic (1988).

Note that if contaminant attenuation takes place in both the aqueous phase and at the sorption sites, the local concentration along an individual streamtube is $C = C_0 x_s \exp(-\lambda RT) \delta(t - RT)/(v_0)$ instead of $C = C_0 x_s \exp(-\lambda T) \delta(t - RT)/(v_0)$ because the solute is attenuated all the time RT that it travels and stays sorbed along the streamtube and not only during the travel time T . The expected concentration expressions (A1) and (A3) must also then be modified accordingly.

For the continuous release case, the local concentration in an individual streamtube can be expressed as $C = C_0 \exp(-\lambda T) H(t - RT)$, where $H(t)$ is the Heaviside step function. The statistics of C are then for both the 1D and the 3D aquifer scenarios obtained as

Fig. A-1. Effects of uncertainty in the aquifer heterogeneity magnitude (log-conductivity variance, $V[\ln K]$), correlation structure (perfectly stratified aquifer, denoted 1D aquifer, or three-dimensional isotropic aquifer, denoted 3D aquifer), and attenuation-transport rate relation $\lambda(nx_s)/(K_g J)$ on the probability P_R to exceed the concentration limit C_T at different relative distances x_1/x_s from the source zone in a short-pulse pollutant release case. The relative source input concentration is $C_0/C_T = 1000$ and the relative conductivity correlation length in the 3D aquifer is $l/x_s = 0.1$.

Fig. A-2. Effects of uncertainty in the aquifer heterogeneity magnitude (log-conductivity variance, $V[\ln K]$), correlation structure (perfectly stratified aquifer, denoted 1D aquifer, or three-dimensional isotropic aquifer, denoted 3D aquifer), and attenuation-transport rate relation $\lambda(nx_s)/(K_g J)$ on the probability P_R to exceed the concentration limit C_T at different relative distances x_1/x_s from the source zone in a continuous pollutant release case. The relative source input concentration is $C_0/C_T = 1000$ and the relative conductivity correlation length in the 3D aquifer is $l/x_s = 0.1$.

$$E[C(t, x_1)] = C_0 \int_0^\infty \exp(-\lambda T) H(t - RT) g(T; x_1) dT$$

$$V[C(t, x_1)] = C_0^2 \int_0^\infty \exp(-2\lambda T) H(t - RT) g(T; x_1) dT - E[C(t, x_1)]^2 \quad (\text{A5})$$

with the travel time statistics also given here by Eq. (A2) for the 1D aquifer scenario and by Eq. (A4) for the 3D aquifer scenario. If attenuation takes place in both the aqueous phase and at the sorption sites, the local concentration would further in this scenario be $C = C_0 \exp(-\lambda RT) H(t - RT)$ instead of $C = C_0 \exp(-\lambda T) H(t - RT)$ and the concentration statistics in Eq. (A5) would be modified accordingly.

The effects of the reversible sorption–desorption process are for simplicity not included in any of the results presented in the main paper, i.e., $R = 1$ in the equations above.

Propagation of exceedence probability for different magnitude of heterogeneity

As complements to Figs. 3 and 4 in the main paper, Figs. A-1 and A-2 show P_R results for both $V[\ln K] = 0.3$ and $V[\ln K] = 1$ in a short-pulse and continuous pollutant release case, respectively.

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