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4 Risk assessment and prioritisation of contaminated

5 sites on the catchment scale

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1 **Abstract**

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3 Contaminated sites pose a significant threat to groundwater resources worldwide. Due to limited
4 available resources a risk-based prioritisation of the remediation efforts is essential. Existing risk
5 assessment tools are unsuitable for this purpose, because they consider each contaminated site
6 separately and on a local scale, which makes it difficult to compare the impact from different sites.
7 Hence a modelling tool for risk assessment of contaminated sites on the catchment scale has been
8 developed. The CatchRisk screening tool evaluates the risk associated with each site in terms of its
9 ability to contaminate abstracted groundwater in the catchment. The tool considers both the local
10 scale and the catchment scale. At the local scale, a flexible, site specific leaching model that can be
11 adjusted to the actual data availability is used to estimate the mass flux over time from identified
12 sites. At the catchment scale, a transport model that utilises the source flux and a groundwater
13 model covering the catchment is used to estimate the transient impact on the supply well. The
14 CatchRisk model was tested on a groundwater catchment for a waterworks north of Copenhagen,
15 Denmark. Even though data scarcity limited the application of the model, the sites that most likely
16 caused the observed contamination at the waterworks were identified. The method was found to be
17 valuable as a basis for prioritising point sources according to their impact on groundwater quality.
18 The tool can also be used as a framework for testing hypotheses on the origin of contamination in
19 the catchment and for identification of unknown contaminant sources.

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23 *Keywords:* Flux; Mass discharge; CatchRisk; Groundwater contamination; Catchment scale; Leaching models;

24 Prioritisation; Risk assessment

1 **1. Introduction**

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3 Releases of organic chemicals to the subsurface are a significant threat to groundwater resources
4 worldwide. To date 300 000 sites across the EU have been identified as definitely or potentially
5 contaminated, but the European Environment Agency estimates that there may be as many as 1.5
6 million contaminated sites (European Environment Agency, 2007). The costs for investigation and
7 clean-up of these sites are very high. In Denmark 24 000 contaminated sites were registered in 2005
8 and an additional 55 000 sites are estimated to follow within the next 40 years. The total expected
9 cost of managing and remediating these contaminated sites is estimated to be 14.3 billion DKK (~ 2
10 billion euros) (Danish EPA, 2006; Kiilerich, 2006). The available resources for site investigation
11 and clean-up are limited compared to the large number of contaminated sites. To meet the future
12 demand for site clean-up, regulators therefore face the challenge of prioritising remediation efforts
13 in order to ensure that the sites that pose the greatest risk to groundwater are remediated first. In this
14 context, risk assessment is an important tool (Cushman et al., 2001).

15 Various methods and models exist for assessing the risk of groundwater contamination (Aziz et
16 al., 2000; Davison and Hall, 2003; Newell et al., 1996; Spence, 2001). Most of these methods are
17 based on generic standards, meaning that a contaminated site is considered to pose a risk if the
18 resulting plume concentrations at some predefined point downstream of the source are above the
19 water quality limit. Hence, the risk is assessed at a *local scale*. This approach makes it easy to
20 evaluate whether a given contaminated site is a threat to groundwater and has for the last decade
21 been the common practice in many countries including Denmark (Bardos et al., 2002).

22 Traditional risk assessment tools are unsuitable for prioritisation purposes because they consider
23 the contaminated sites separately, and focus only on calculating plume concentrations at the local
24 scale. This focus on local assessment allows for an identification of sites posing a risk to
25 groundwater, but does not quantify the risk to water resources at a catchment scale. The risk of
26 different sites can therefore not be compared, which is essential in performing a prioritisation.
27 Additionally, these tools do not consider if, and to what extent, downstream receptors (drinking
28 water supply wells, lakes, streams etc.) are affected by releases from contaminated sites. However,
29 the motivation for carrying out remediation at specific sites is often governed by the measured
30 impact or concern about future impact on water supply wells. Thus, it has been proposed to shift the
31 focus from the local scale to a *catchment scale* and to assess the risk by evaluating the impact on the
32 supply wells in the catchment (Einarson and Mackay, 2001; Frind et al., 2006).

1 Einarson and MacKay (2001) present a conceptual framework for risk assessment and
2 prioritisation of contaminated sites in a groundwater catchment, and focus on the estimation of
3 worst-case concentration in the abstracted water at a supply well. They propose the use of mass flux
4 or mass discharge ($M T^{-1}$) estimates from the point sources within the catchment to do this. Only a
5 few catchment-scale risk assessment models have been published (Table 1). Arey and Gschwend
6 (2005) use a mass flux approach to predict the impact of different gasoline constituents on water
7 supply wells based on average contaminated site conditions in the United States. Frind et al. (2006)
8 developed a well vulnerability concept for quantifying the impact of contaminated sites within the
9 capture zone of a well, where forward and backward transport modelling is used for generating
10 intrinsic well vulnerability maps displaying different information (e.g. expected times of arrival of a
11 contaminant, dispersion-related reduction in concentration and exposure time). Tait et al. (2004)
12 present the Borehole Optimisation System (BOS) for identifying the optimum locations for new
13 supply wells in urban areas, which is based on an estimation of the cumulative impact of a chosen
14 contaminant from all identified sources relevant to the supply well in a given year. None of these
15 screening models are designed for prioritisation purposes and they can not be used for determining
16 which of the identified sources pose the greatest threat to a water supply.

17 Since contaminated sites vary greatly in complexity, in the amount of available data and type of
18 contamination, there is a need for flexible source models that can be adjusted to suit any given
19 contaminated site and its data availability. Frind et al. (2006) do not include a source model, but
20 focus only on the protective characteristics of the pathway medium. For describing the ability of the
21 pathway medium to dilute a potential contamination and reduce the impact on a supply well, a unit
22 pulse is released at the pumping well within an inverted flow field. A backward-in-time advective-
23 dispersive transport simulation then provides the impact on the well of a unit pulse released
24 anywhere within the capture zone. BOS assumes that the contaminant source is only present in the
25 vadose zone (Chisala et al., 2007; Tait et al., 2004), and in the model of Arey and Gschwend
26 (2005), the source is conceptualised as a LNAPL pool present on the groundwater table. These
27 source models are specific and thus are not sufficient, on their own, for describing the many
28 different types of contaminated sites that may exist within the catchment. At the catchment scale
29 BOS is the only model that considers the impact from multiple contaminated sites on a water supply
30 in the catchment, but BOS focuses only on calculating the cumulative impact from these sites and
31 not on estimating the relative impact from the different sites.

1 Table 1. Comparison of screening models/methodologies for estimating contaminant impact on water supply wells

	Frind et al. (2006)	Tait et al. (2004)	Arey & Gschwend (2005)	CatchRisk
Local scale (source model)				
Modular and flexible design				X
Built-in database		X		
Source	Unit pulse *	Constant	Pulse	Constant; Decaying
Multiple types of contaminant		X	X (LNAPLs)	X
Source history		X		X
Degradation				First-order; Sequential
Sorption				X
Residual Phase			X	X
Catchment scale				
Catchment delineation	Backward transport modelling	Particle tracking		Particle tracking
Advection	X	X	X	X
Dispersion	X		X	Not needed
Degradation		First-order		First-order; Sequential; 2 degradation zones
Sorption		X	X	X
Dilution in supply well	X	X	X	X
Multiple contaminated sites	X	X		X
Hydrogeology	Complex multi-layer, multi-zone 3D groundwater model	Single-layer, multi-zone 3D groundwater model	Uniform flow field	Complex multi-layer, multi-zone 3D groundwater model
Impact on supply well	Time-dependent	Time-dependent; Cumulative	Static	Time-dependent; Cumulative; Relative contribution from different sources
Built-in uncertainty analysis	X (through dispersion)	X		

2 * By applying convolution, the unit pulse can be extended in space and time

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We aim to develop a screening method for risk assessment and prioritisation of contaminated sites that describes the risk associated with the sites in terms of their ability to contaminate abstracted groundwater in a catchment. The CatchRisk model combines site specific transient mass flux estimates from all known point sources at the local scale with catchment scale transport and fate simulations in a complex three-dimensional groundwater system. The modelling approach is designed to be simple and modular so that the method can be tailored to suit data availability. CatchRisk is tested on the catchment area of a municipal water works located in the northern part of Copenhagen, Denmark and the results are presented in a GIS framework. The model provides an integrated overview of the contaminant sites that have been identified in a given catchment, and can

1 also be used to help identify new contaminated sites, thereby allowing a more optimal prioritisation
2 of contaminant site remediation.

3 When examining the risk assessment approach presented here, it is important to understand the
4 context in which it will be used. In Denmark, the management strategy consists of a desktop
5 *mapping phase*, where potential contaminated sites are identified based on former or current
6 activities at the sites; a *field investigation phase* that aims at documenting the presence and the
7 degree of contamination at the site, and is followed by a risk assessment to clarify the need for
8 further site investigation and/or if clean-up should be initiated; a *clean-up phase*, where the
9 contamination is removed; and a *monitoring phase* to evaluate the effect of the remediation (Danish
10 EPA, 2002). The CatchRisk model is mainly applicable for sites where contamination has been
11 documented, i.e. sites that have passed into the *field investigation phase*, where suitable data already
12 exist.

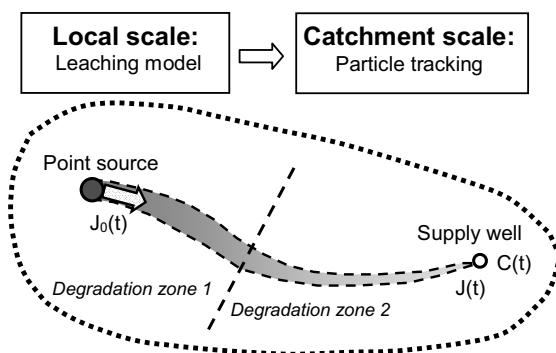
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14 2. Model development

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16 2.1. Model concept

17 CatchRisk aims at quantifying the transient contaminant impact from a point source to the water
18 supply in a catchment (Table 1). As illustrated in Fig. 1 the model focuses on two scales, a local
19 scale and a catchment scale. Each scale is represented by a separate model: an analytical leaching
20 model set up in a Microsoft Excel spreadsheet and developed to calculate the contaminant mass flux
21 from the point source at the local scale; and a catchment-scale transport model (CSTM) that utilises
22 the source flux and a MODFLOW (McDonald and Harbaugh, 1988) groundwater model covering
23 the catchment to estimate the resulting concentration in the abstracted water at the supply well.
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26 Fig. 1. The CatchRisk conceptual model.

1 *2.2. Analytical leaching model*

2 The analytical leaching model is developed to determine the transient mass flux from a point
3 source to the first significant (i.e. regional) groundwater aquifer at the local scale by employing
4 basic site data. To cope with the many different types of contaminated sites that exist, the leaching
5 model is designed to be simple and modular so that it can be adapted to suit each site and its data
6 availability. This is achieved by basing the leaching model on a series of reactor models, each
7 representing different compartments of the contaminated site (e.g. the vadose zone, aquitards and
8 aquifers) as illustrated in Fig. 2. The size of each reactor is determined through an assessment of the
9 geology and extent of contamination at the given site. To assure wide applicability, the leaching
10 model is designed to handle residual (non-moving) NAPL phase in the source zone and to describe
11 sequential first-order decay of compounds like tetrachloroethylene (PCE) and trichloroethylene
12 (TCE) undergoing anaerobic dechlorination.

13 The configuration of the leaching model is based on the following assumptions: (I) the mass flux
14 from the different reactors is governed solely by advection of water; (II) the influence of dispersion,
15 diffusion and evaporation can be neglected; (III) soil-water-air equilibrium is linear, reversible and
16 instantaneous; (IV) the geological and hydrogeological properties of each reactor are homogenous;
17 (V) all water flows (local groundwater flow and recharge) are constant with time; (VI) the
18 dimensions of the contamination (i.e. the size of the reactors) do not change with time; (VII)
19 degradation only proceeds in the water phase and follows first-order kinetics; (VIII) the multi-
20 component systems are handled as single components without interaction. Because the model only
21 handles single components it can, in its current state, only act as an initial screening tool for multi-
22 component mixtures (e.g. creosote sources), where the different components can have different
23 mole-fractions that change over time.

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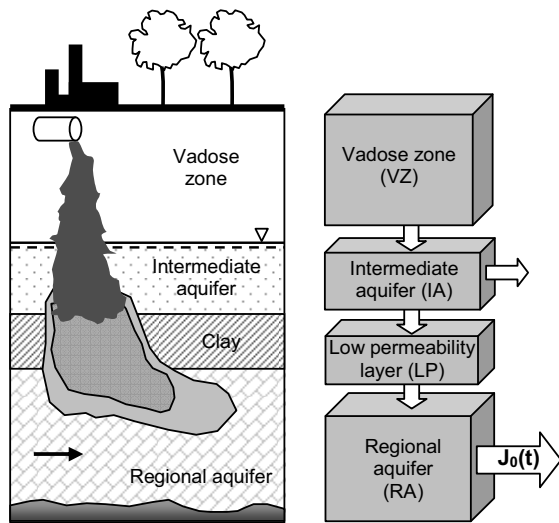


Fig. 2. Conceptualisation of leaching model. Note that the structure is modular and that the reactors are assembled to represent a given source as well as possible.

As depicted in Fig. 2, the leaching model describes the movement of contaminants from the source to regional groundwater aquifers using one or more coupled reactor models. Each reactor represents different compartments of the source: a vadose zone (VZ), a non-regional intermediate aquifer (IA), a low-permeability layer (LP) and a regional aquifer (RA).

The contamination in the VZ, the IA and the RA is represented by a Completely Mixed Flow Reactor (CMFR) (Nazaroff and Alvarez-Cohen, 2001), meaning that the spatial concentration within these reactors is assumed uniform in space, but not constant in time. The concentration within the VZ and the IA is determined from a computation of the mass in each of these reactors. The LP is represented by a Plug Flow Reactor (PFR) (Nazaroff and Alvarez-Cohen, 2001) to allow for potentially significant travel times through the aquitard.

The reactors can be coupled to each other so that the mass outflow from one reactor acts as positive input to another. The reactors are assembled to represent the source as well as possible, depending on the specific site and the data availability. When more data are available, a more detailed model can be justified, and more reliable mass flux estimates can be obtained. The mass flux out of the RA is the output of the leaching model.

The mass flux J ($M T^{-1}$) leaving a reactor is defined as (Basu et al., 2006; Feenstra et al., 1996):

$$J(t) = C(t) \cdot q \cdot A \quad (1)$$

1 where C ($M L^{-3}$) is the solute contaminant concentration within the reactor, q ($L T^{-1}$) is the specific
 2 discharge and A (L^2) is the surface area of the reactor perpendicular to water flow.

3 At many sites the available data will be inadequate for an estimation of the initial mass within
 4 the reactors. In these cases, the source is represented by a single reactor and the mass flux is
 5 considered constant with time, and is calculated from Eq. (1) using a (constant) representative
 6 measured groundwater concentration. It is assumed that the flux will be constant from the time
 7 where the potential contaminating activities were initiated at the site.

8 However, if the available data allow for an estimation of the total (initial) contaminant mass at
 9 the site, then a more detailed form of the leaching model can be used. The mass within each reactor
 10 will gradually be reduced due to both leaching and degradation, which results in a decreasing mass
 11 flux leaving the source. In this case, the mass flux estimated to be leaving the source will depend on
 12 the mass fluxes released from each reactor that has been included in the leaching model to represent
 13 the source. The following presents how each reactor is mathematically modelled.

15 2.2.1. Vadose zone compartment (VZ)

16 The advective mass flux leaving the VZ, $J_{vz}(t)$ ($M T^{-1}$), is given by:

$$18 J_{vz}(t) = N \cdot A_h \cdot C_{vz}(t) \quad (2)$$

19
 20 where N ($L T^{-1}$) is the infiltration rate, A_h (L^2) is the horizontal source area, and $C_{vz}(t)$ ($M L^{-3}$) is the
 21 time-dependent source concentration in the VZ. The mass in the VZ, M_{vz} (M), is reduced due to
 22 dissolution in infiltrating water and degradation. A mass balance for the VZ is therefore:

$$24 \frac{dM_{vz}}{dt} = V_{vz} (\theta_w + K_d \rho_b + \theta_a K_H) \frac{dC_{vz}}{dt} = -N \cdot A_h \cdot C_{vz} + V_{vz} \theta_w r_{vz} \quad (3)$$

25
 26 where V_{vz} (L^3) is the volume of the VZ, θ_w is the water filled porosity, K_d ($L^3 M^{-1}$) is the water-soil
 27 partition coefficient, ρ_b ($M L^{-3}$) is the bulk density, θ_a is the air filled porosity, K_H is the
 28 dimensionless Henry's constant, and r_{vz} ($M L^{-3} T^{-1}$) is the reaction rate in the VZ. Assuming that
 29 degradation follows first-order kinetics ($r_{vz} = -\lambda_{vz} C_{vz}$) Eq. (3) has the following solution:

$$C_{vz}(t) = C_{0,vz} \exp(-k_{vz}t)$$

$$\text{where } k_{vz} = f_w \cdot \left(\frac{N}{\theta_w d_{vz}} + \lambda_{vz} \right) = \left(\frac{\theta_w}{\theta_w + K_d \rho_b + \theta_a K_H} \right) \left(\frac{N}{\theta_w d_{vz}} + \lambda_{vz} \right) \quad (4)$$

where f_w is the fraction of contaminant in the vadose zone water phase (Schwarzenbach et al., 1993), λ_{vz} (T^{-1}) is the first-order decay rate, and d_{vz} (L) is the depth of the VZ. From Eq. (4) it can be seen that the concentration (and thus the mass flux) in the VZ decreases exponentially.

2.2.2. Intermediate aquifer compartment (IA)

The mass flux infiltrating from the IA into an underlying low-permeability layer compartment (LP), $J_{ia}(t)$, is given by:

$$J_{ia}(t) = I \cdot A_h \cdot C_{ia}(t) = K_z \cdot i_z \cdot A_h \cdot C_{ia}(t) \quad (5)$$

where I ($L T^{-1}$) is the infiltration rate through the LP, $C_{ia}(t)$ is the time-dependent source concentration in the IA, K_z ($L T^{-1}$) is the vertical hydraulic conductivity of the LP, and i_z (dimensionless) is the vertical hydraulic gradient across the LP.

The mass inside the IA, M_{ia} (M), is reduced due to degradation and by dissolution and transport out of the IA by the lateral groundwater flow and/or by downward flow from the IA to the LP. A mass balance for the IA results in the following ordinary differential equation:

$$\frac{dM_{ia}}{dt} = V_{ia} n R \frac{dC_{ia}}{dt} = -I \cdot A_h \cdot C_{ia} - q_{ia} A_{ia} C_{ia} + n V_{ia} r_{ia} + J_{vz}(t) \quad (6)$$

where V_{ia} (L^3) is the volume of the IA, R (dimensionless) is the retardation factor, n (dimensionless) is the porosity, A_{ia} (L^2) is vertical area of the IA perpendicular to the horizontal groundwater flow, q_{ia} ($L T^{-1}$) is the horizontal Darcy flux out of the IA, and r_{ia} ($M L^{-3} T^{-1}$) is the reaction rate in the IA. Assuming first-order degradation ($r_{ia} = -\lambda_{ia} C_{ia}$), the general solution to Eq. (6) is given by:

$$C_{ia}(t) = \frac{\exp(-pt)}{V_{ia}nR} \int \exp(pt) J_{vz}(t) dt + \alpha \exp(-pt) \quad (7)$$

$$\text{where } p = \frac{I \cdot A_h + q_{ia} A_{ia} + \lambda_{ia} V_{ia} n}{V_{ia} n R}$$

where λ_{ia} (T^{-1}) is the first-order decay rate in the IA. The coefficient α can be determined by applying the initial condition $C_{ia}(0) = C_{0,ia}$, where $C_{0,ia}$ ($M L^{-3}$) is the initial source concentration in the IA. The solution to Eq. (7) depends on the flux from the VZ, which can be either exponentially decaying or constant (if residual phase is present, see section 2.2.6.). It should be noted that we here assume that the contaminant mass leaving the IA with the horizontal groundwater flow does not infiltrate through the LP. However, if horizontal groundwater flow occurs in the IA, the resulting horizontal mass flux should be evaluated separately.

2.2.3. Low-permeability layer compartment (LP)

The breakthrough of a mass flux entering the LP to an underlying aquifer depends on the residence time through the LP. The residence time $t_{R,lp}$ (T) depends on the infiltration rate and the thickness of the LP d_{lp} (L), effective porosity n_{ef} , and retardation factor:

$$t_{R,lp} = t_{w,lp} R = \frac{d_{lp} n_{ef} R}{I} \quad (8)$$

where $t_{w,lp}$ is the unretarded travel time through the LP. In the calculation of the residence time it is assumed that diffusion and dispersion can be neglected. The transport through the LP is described as a plug flow and is governed by the following equation that incorporates advection, first-order degradation ($r = -\lambda C$) and sorption:

$$R \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial s} = -\lambda C \quad (9)$$

where v ($L T^{-1}$) is the pore water velocity, s (L) represents the flow direction and λ (T^{-1}) is a first-order degradation constant. Inserting the mass flux definition from Eq. (1) into (9) and assuming Aq to be constant in space and time leads to:

$$R \frac{\partial J}{\partial t} + v \frac{\partial J}{\partial s} = -\lambda J \quad (10)$$

2

3 Eq. (10) is valid under steady-state conditions. From a Lagrangian point of view Eq. (10) can be
4 written:

5

$$\frac{DJ}{Dt} = -\frac{\lambda}{R} J \quad (11)$$

6

$$\text{where } \frac{D}{Dt} = \frac{\partial}{\partial t} + \frac{v}{R} \frac{\partial}{\partial s}$$

7

8 From Eq. (11) it can be seen that the effects of degradation are separated from the effects of
9 transport. The reduction in mass flux due to degradation during transport therefore can be expressed
10 solely as a function of the residence time. By solving Eq. (11) the mass flux leaving the LP, J_{lp} (M
11 T^{-1}), is (Bockelmann et al., 2003; Kao and Wang, 2001):

12

$$J_{lp}(t) = J_{ia}(t - t_{R,lp}) \exp\left(-\frac{\lambda_{lp} t_{R,lp}}{R}\right) = J_{ia}(t - t_{R,lp}) \exp\left(-\frac{\lambda_{lp} d_{lp} n_{ef}}{I}\right) \quad (12)$$

14

15 where λ_{lp} (T^{-1}) is the first-order degradation rate in the LP.

16

17 2.2.4. Regional aquifer compartment (RA)

18 The mass fluxes entering and leaving the RA, $J_0(t)$ ($M T^{-1}$) are assumed equal to each other and
19 these fluxes are the output of the leaching model. It is this flux that is employed in the catchment-
20 scale transport model (section 2.3).

21 In some cases it is important to assess local contaminant concentrations based on output from the
22 leaching model. In these instances, the resulting concentration in the RA can be calculated by
23 assuming complete mixing within the RA:

24

$$C_{ra}(t) = \frac{J_0(t)}{IA_h + q_{ra} A_{ra}} \quad (13)$$

26

1 where q_{ra} ($L T^{-1}$) is the horizontal Darcy flux through the RA, and A_{ra} (L^2) is the vertical area of the
 2 RA perpendicular to the horizontal groundwater flow. This concentration can be compared with
 3 measured average concentrations in the RA (e.g. from a fully screened well or an integrated value
 4 from multiple point measurements) to check how well the model agrees with measured data.

6 2.2.5. Sequential first-order degradation

7 Many xenobiotics (e.g. chlorinated solvents) are known to degrade sequentially, where
 8 degradation products further react to produce new species. In many cases, these by-products also
 9 have adverse effects on the environment and this behaviour should therefore be taken into account in a
 10 risk assessment. In the literature, sequential degradation is often simulated based on a set of coupled
 11 partial differential equations assuming first-order kinetics (Clement et al., 2000; Sun et al., 1999). This
 12 approach has, for example, been used for simulating anaerobic dechlorination of tetrachloroethylene
 13 (PCE) to trichloroethylene (TCE), to dichloroethylenes (cis-1,2-DCE, trans-1,2-DCE, and 1,1-
 14 DCE), and vinyl chloride (VC) (Aziz et al., 2000; Clement et al., 2000; Falta et al., 2005).

15 The leaching model can be used to describe sequential first-order degradation of up to four
 16 components ($C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$). The reaction rate equations are (Sun et al., 1999):

$$\begin{aligned}
 r_1 &= -\lambda_1 C_1 \\
 r_2 &= y_1 \lambda_1 C_1 - \lambda_2 C_2 \\
 r_3 &= y_2 \lambda_2 C_2 - \lambda_3 C_3 \\
 r_4 &= y_3 \lambda_3 C_3 - \lambda_4 C_4
 \end{aligned}
 \tag{14}$$

19
 20 where r_i ($M L^{-3} T^{-1}$) are the reaction rates, λ_i (T^{-1}) are the first-order degradation rate constants, y_i
 21 (dimensionless) are yield coefficients specifying the relationship between the molar weight of the
 22 daughter and mother product, and C_i ($M L^{-3}$) are the solute concentrations for component i . These
 23 reaction rates replace the degradation term in Eq. (3), (6) and (10).

24 It should be noted that sequential first-order kinetics can often only be considered to be an
 25 approximate description of the degradation process. For example, it has been shown that
 26 competitive Monod kinetics is a more precise description of anaerobic dechlorination of chlorinated
 27 ethenes (Friis et al., 2007; Garant and Lynd, 1998; Yu et al., 2005). However, Monod kinetic
 28 models are more data demanding and are not easily implemented in an analytical solution. The first-
 29 order kinetic formulation is simpler and can easily be incorporated into an analytical model and is
 30 thus considered more applicable for risk assessment purposes. In general, first-order kinetics are

1 considered valid only when substrate concentrations are much less than the half-saturation constant
2 (Bekins et al., 1998).

3 4 2.2.6. *Separate phase*

5 The leaching model can also be used when there is a residual NAPL phase present in the source
6 zone. If water has passed through an area containing residual phase, it is assumed to reach solubility
7 concentration, which leads to a constant mass flux output. The mass flux from a reactor containing a
8 free single-component NAPL phase is therefore calculated as:

$$9 \quad J = q_0 AS \quad (15)$$

10
11 where S ($M L^{-3}$) is the aqueous solubility. This mass flux is, for the current purpose, assumed to
12 remain constant for as long as free phase is present. This is a simple approach for relating mass flux
13 to the remaining mass in the source and corresponds to a power function exponent value of zero
14 (Falta, 2008). It is assumed that the free phase is depleted when the remaining mass is reduced to:

$$15 \quad m_{equilibrium} = V_{reactor} (\theta_w + K_d \rho_b + \theta_a K_H) S \quad (16)$$

16
17
18 If the mass inside a reactor is higher than $m_{equilibrium}$, separate phase is present and the mass flux
19 leaving the reactor is constant given by (15). However, if the mass is less than $m_{equilibrium}$, residual
20 phase is not present and the mass flux leaving the reactor decreases with time e.g. as given by (2)
21 and (5) for the VZ and the IA, respectively. This method of describing the leaching from an area
22 with free NAPL phase is similar to that in the widely used risk assessment tool RISC4 (Spence,
23 2001).
24

25 At many sites the source concentration will be spatially varying, and in this case it might be
26 desirable to divide the source area into zones. In this way it is possible to simulate the mass flux
27 from a site where, for instance, residual NAPL phase is present in a hot spot surrounded by a less
28 contaminated area. Each zone can be represented with a reactor as illustrated in Fig. 3. The total
29 mass flux from the source can then be calculated as the sum of mass fluxes leaving each zone (J_{total}
30 $= J_{0,hotspot} + J_{0,I}$).

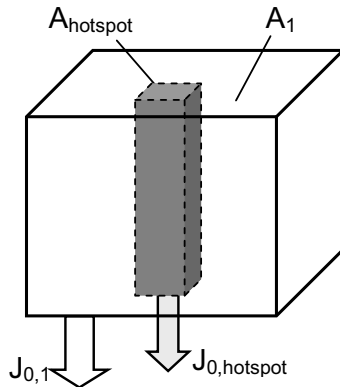


Fig. 3. Leaching from a contaminated area containing a hotspot.

2.3 Catchment-scale transport model

The catchment-scale transport model (CSTM) uses the local-scale mass flux estimated with the leaching model to simulate contaminant fate during transport from the source through the catchment to the supply well. The output consists of an estimate of the mass flux received by the supply well over time, together with a calculation of the resulting concentration in the abstracted water.

The basis of the CSTM is a stationary MODFLOW-based three-dimensional finite-difference groundwater flow model covering the area of interest. The groundwater model is used for delineating the capture zone to identify which contaminated sites are situated within the catchment and thus constitute a potential threat to the abstracted groundwater at the supply well. This requires that the output from the groundwater model is integrated into a GIS framework displaying all known contaminated sites.

To calculate the mass flux abstracted by the supply well, the CSTM uses a simplified solute transport model that incorporates advection, degradation and sorption. Longitudinal dispersion is conservatively neglected in the transport model to ensure that a maximum impact is calculated. This assumption is valid in cases where leaching from the point sources is assumed constant and continuous relative to breakthrough times and where the focus is on the long-term well impact. Although the contaminant plume is dispersed transverse to the flow, contaminant flow to the well is convergent and so transverse dispersion can be neglected and the quantity that must be estimated is the total flux, not the dispersed concentrations in groundwater (Chisala et al., 2007; Kennedy and Lennox, 1999). Since the main purpose of the model is as a screening tool to support prioritization and not to predict the exact concentration levels in the well over time, neglecting dispersion is

1 considered reasonable. Solute transport through the catchment is therefore described as a plug flow
2 similar to that through the low-permeability layer in the leaching model, i.e. Eq. (10).

3 Advective transport is simulated using the groundwater flow model, and the unretarded travel
4 time t_w (T) through the catchment is determined by use of particle tracking in MODPATH (Pollock,
5 1994). This travel time is multiplied by the retardation factor R to account for sorption of the
6 contaminants ($t_R = t_w R$). If no degradation takes place during the transport, the mass flux captured
7 by the supply well J_{well} is identical to that calculated by the leaching model J_0 , but with a time-
8 displacement corresponding to the retarded travel time t_R :

$$9 \quad J_{well}(t) = J_0(t - t_R) \quad (17)$$

11
12 Eq. (17) is a conservative estimate of the mass flux captured by the well and does not account for
13 mass losses due to diffusion into low conductivity layers or due to dispersion of contaminants
14 outside of the catchment (which might occur for sources located close to the catchment boundary).

15 During transport through the catchment, the mass flux released from the source can be reduced
16 due to degradation. As illustrated in Fig. 1 two degradation zones have been included in the CSTM
17 to account for changing degradation rates in the catchment (e.g. due to changes in redox
18 conditions). The degradation can be described either as regular first-order degradation without
19 formation of degradation products, or as sequential first-order degradation to include formation of
20 undesired by-products.

21 The reduction in mass flux due to regular first-order degradation is determined by using an
22 equation similar to (12), where the travel time in the degradation zone is determined by particle
23 tracking in MODPATH. If two degradation zones are included, the mass flux abstracted by the
24 supply well is given by:

$$25 \quad J_{well}(t) = J_0(t - t_{R,1} - t_{R,2}) \exp(-\lambda_1 t_{w,1}) \exp(-\lambda_2 t_{w,2}) \quad (18)$$

27
28 where J_0 is the mass flux leaving the source, $t_{w,1}$ and $t_{R,1}$ are the unretarded and retarded travel time
29 in degradation zone 1, respectively, and $t_{w,2}$ and $t_{R,2}$ are the unretarded and retarded travel time in
30 degradation zone 2, respectively.

31 The sequential first-order degradation during transport through a degradation zone is based on
32 the coupled 4-component reaction rates from Eq. (14). Because the effects of transport and

1 degradation can be separated, the description of the sequential degradation during transport is
 2 similar to Eq. (11). The coupled reaction rate equations in Eq. (14) are solved analytically by
 3 applying the transformation techniques presented in Sun (1999) and assuming that all four
 4 components have the same retardation factor.

6 2.3.1. Dilution in well

7 The mass flux into the supply well, J_{well} , constitutes the CSTM output. This mass flux will be
 8 mixed with the clean groundwater abstracted at the supply well, which results in concentrations in
 9 the well that are often significantly lower than the concentrations in the aquifer. Therefore if the
 10 resulting concentration in the supply well C_{well} ($M L^{-3}$) is to be estimated, dilution is an important
 11 process to include. The resulting concentration can be calculated as (Einarson and Mackay, 2001)

$$13 \quad C_{well} = \frac{J_{well}}{Q_{well}} \quad (19)$$

14
 15 where Q_{well} ($L^3 T^{-1}$) is the supply well pumping rate. By applying CatchRisk to every known
 16 contaminated site within the catchment it is possible to estimate the total impact on the supply well
 17 over time. This is done by adding the mass flux into the well from each site $J_{well,i}(t)$:

$$19 \quad C_{well}(t) = \sum_{i=1}^{N_{sites}} C_{well,i}(t) = \sum_{i=1}^{N_{sites}} \frac{J_{well,i}(t)}{Q_{well}} \quad (20)$$

20
 21 where N_{sites} is the total number of identified contaminated sites.

23 3. Case study: The catchment for Nærum Waterworks

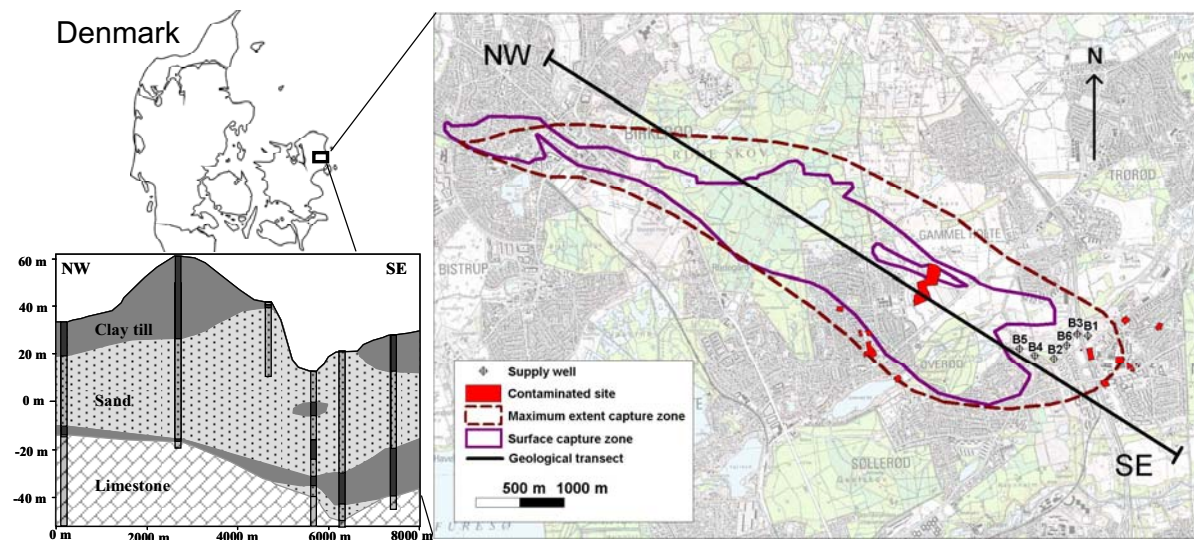
24
 25 The CatchRisk model has been evaluated on a case study located in northern Copenhagen (Fig.
 26 4). The study area covers the capture zone for the municipal waterworks of Nærum and an
 27 industrial estate just east of the supply wells. Since 1987 TCE has been observed in some of the
 28 supply wells, which has resulted in a partial closure of the facility. In 2004 five supply wells (B2-
 29 B6) were operating at Nærum Waterworks which pump a total of 880 000 m^3 water annually
 30 (Tuxen et al., 2006).

1 Several contaminated sites have been identified in the study area. The authorities wanted to
2 prioritise remedial actions for the sites and to identify which sites caused the contamination at the
3 waterworks.

5 3.1 Geology and hydrogeology

6 The geology is characterised using data from more than 150 boreholes in the area. A geological
7 transect is shown in Fig. 4. The top 50 meters consists of quaternary glacial deposits characterised
8 by alternating layers of sand and clay till. The quaternary sediments are dominated by a sand layer
9 up to 40 metres thick. This layer constitutes a generally unconfined upper aquifer in the focus area.
10 Beneath the quaternary sediments a limestone formation is encountered at around 30 metres below
11 sea level. The limestone formation is the primary groundwater resource in the area.

12



13
14 Fig. 4. Overview of the focus area with the location of contaminated sites, a geological profile and the catchment of
15 Nærum Waterworks.

16
17 Groundwater flow in the upper (sand) aquifer is predominantly directed towards the east with a
18 hydraulic gradient between 0.003 and 0.01. Hydraulic conductivities between $5 \cdot 10^{-6}$ and $7 \cdot 10^{-4}$ m/s
19 have been reported for the upper aquifer based on several investigations in the area. The upper
20 aquifer is generally characterised as aerobic based on measurements of redox parameters.

21 The lower aquifer is confined and the general flow direction is south-eastern with a hydraulic
22 gradient of 0.003 to 0.007. The hydraulic conductivity of the upper 10 meters of the limestone

1 aquifer has been estimated to $1 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ m/s. Measurements of redox parameters in the
2 abstracted groundwater at the supply wells indicate that anaerobic conditions prevail in the lower
3 (limestone) aquifer.

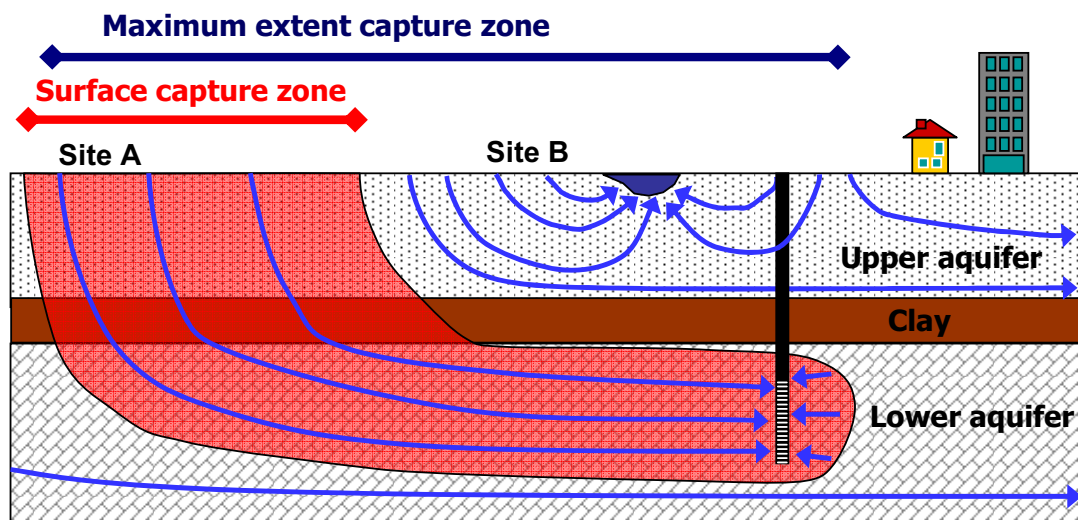
4 The two aquifers are in most cases separated by a clay layer and an overall downward vertical
5 gradient from the upper to the lower aquifer is observed based on hydraulic head differences of 1 to
6 10 meters between the aquifers. However, sporadic windows in the separating clay layer have been
7 identified. Thus local hydraulic contact between the aquifers exists, creating a complex groundwater
8 flow system (Tuxen et al., 2006).

10 *3.2 Catchment delineation*

11 A key component of the model concept is a steady-state groundwater flow model. A primary
12 objective of this groundwater model is to delineate the catchment of Nærum Waterworks and
13 identify which contaminant sources potentially can affect the waterworks. An existing steady-state
14 MODFLOW groundwater model developed by a Danish consulting agency (Watertech, 2005)
15 covering the study area was used as basis for the risk assessment. The actual geology described in
16 section 3.1 was represented by seven multi-zone layers of varying thickness, where the five topmost
17 layers comprise the quaternary sediments and the two lowermost layers represent the pre-quaternary
18 limestone formation. The groundwater model has been calibrated and has been declared valid for
19 simulating average flow conditions in the saturated zone based on performance criteria presented by
20 the Geological Survey of Denmark and Greenland (Sonnenborg and Henriksen, 2005; Watertech,
21 2005). The groundwater model was originally set up with a horizontal grid spacing of 250 m, but
22 has here been refined to a grid spacing of 50 m.

23 The catchment of Nærum Waterworks was delineated by use of reverse particle tracking in
24 MODPATH, and the results are displayed in Fig. 4 together with the identified contaminated sites.
25 The delineation was based on the maximum recorded annual abstraction rate to ensure that the
26 largest possible catchment was realized. Because of the complex hydrogeology, both a maximum
27 extent capture zone and a surface capture zone have been delineated following the definitions of
28 Frind et al. (2002). The maximum extent capture zone shows where groundwater is abstracted from
29 the lower limestone aquifer, while the surface capture zone indicates areas where a particle released
30 at the water table of the upper aquifer will be transported to the lower aquifer and end up at the
31 waterworks (Fig. 5). It is important to consider both of these zones in a risk assessment on the
32 catchment scale. While all contaminated sites located within the surface capture zone (site A in Fig.

1 5) pose a potential risk to the supply well, a site located inside the maximum extent capture zone
2 does not necessarily affect the supply well. If a spill occurring at site B (Fig. 5) consists only of
3 aqueous phase contaminants it will not affect the supply well. However, if the contaminant of
4 concern is a spill of DNAPL, the contamination can potentially penetrate directly to the underlying
5 lower aquifer by free phase transport and thereby affect the water supply (Frind et al., 2002;
6 Kinzelbach et al., 1992).
7



8
9 Fig. 5. Conceptual definition of the maximum extent capture zone and the surface capture zone. Note that
10 communication between the upper and lower aquifer exists in the case study, which affect how these zones look in the
11 actual case.
12

13 3.3 Contaminated sites

14 Several contaminated sites have been identified in the study area. Most of the identified sites are
15 situated in the industrial zone and many are dry cleaning facilities. Chlorinated solvents and oil and
16 gasoline components are the main contaminants in the area. However, only TCE has been observed
17 above the Danish groundwater standards at the waterworks (Danish EPA, 2002).

18 The surface capture zone and the maximum extent capture zone are used as the basis for an
19 initial screening of those contaminated sites which can potentially affect the waterworks. All
20 identified sites located within either of these zones were selected. Because the groundwater model
21 has inherent uncertainties, contaminated sites situated just outside the catchment border have also
22 been included in this first phase screening.

1 The travel times from the selected contaminated sites to the water supply wells are determined
 2 by particle tracking. At DNAPL contaminated sites, particles were released in both the upper and
 3 lower aquifer to account for the possibility that vertical free phase transport may have occurred. The
 4 travel time from sites located outside, but very close to the border of, the surface capture zone or the
 5 maximum extent capture zone (if the given site is DNAPL contaminated), was estimated by
 6 releasing particles just inside the respective zones.

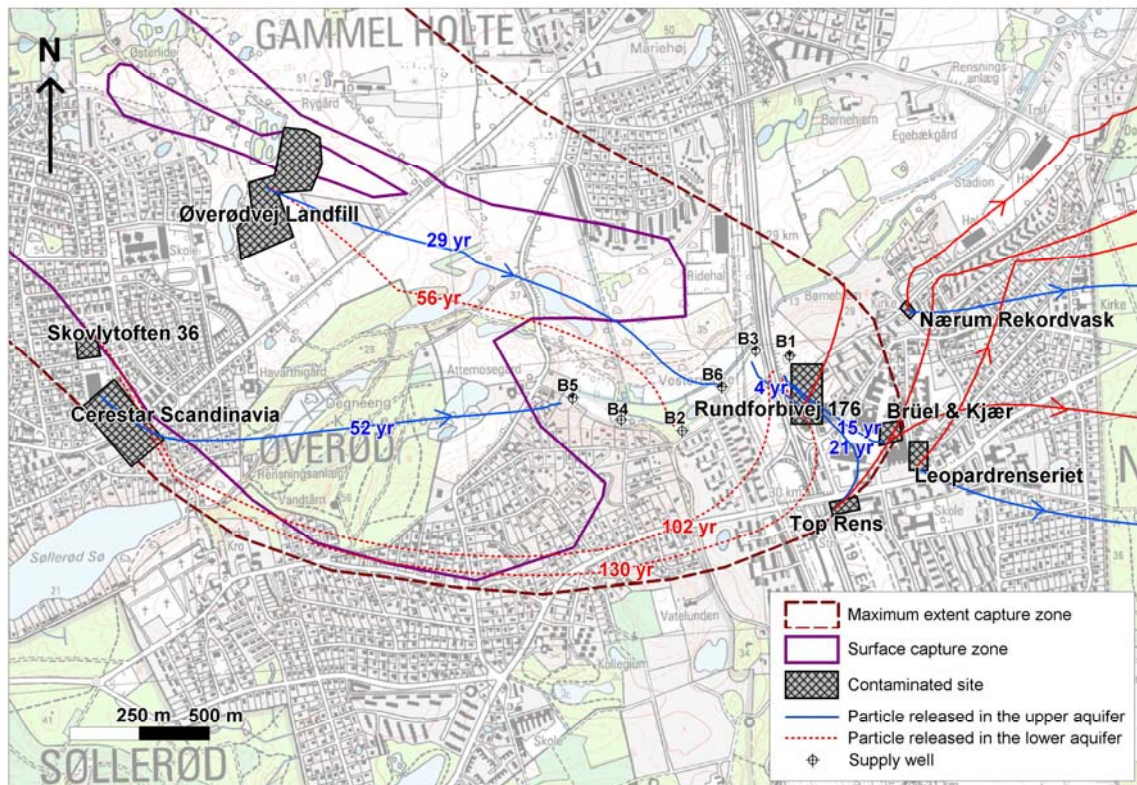
7 The initial screening has resulted in a selection of 8 contaminated sites that are potential threats
 8 to groundwater abstraction at the Nærum Waterworks (Table 2). The location of the selected sites
 9 and the particle pathways are shown in Fig. 6. All the contaminated sites in the industrial area east
 10 of the supply wells are located far outside the surface capture zone. Contamination solely in the
 11 upper aquifer at these sites will therefore not contribute to the observed contamination at Nærum
 12 Waterworks. However, these sites have still been selected because all are contaminated with
 13 DNAPL's (PCE and TCE). Cerestar Scandinavia and Skovlytoften 36 are located outside the
 14 surface capture zone, and thus according to the groundwater model, will not pose a threat to Nærum
 15 Waterworks. However, because both sites are located very close to the surface capture zone border
 16 and Cerestar Scandinavia is also polluted with DNAPL, they were also included.

17

18 Table 2. Overview of contaminated sites in the study area that are potential threats to Nærum Waterworks.

Name	Type	Contaminant	Potential contamination period	Unretarded travel time (yr)	Estimated total mass (kg)	Mass flux to groundwater (g/yr)	Reliability of estimated mass and mass flux
Brüel & Kjær	Industrial site	PCE, TCE	1951 - ?	15 *	?	?	Uncertain
Øverødvej Landfill	Landfill	Waste	? - 1956	56	?	0 g TCE/yr	Uncertain
Cerestar Scandinavia A/S	Industrial site	TCE, PCE, oil	1962 - 1968	130	35	500 g TCE/yr	Reliable
Top Rens	Dry cleaning service	PCE	1958 - 1987	21 *	3	80 g PCE/yr	Uncertain
Leopard renseriet	Dry cleaning service	PCE	1961 - 1983	-	20	250 g PCE/yr	Reasonable certainty
Nærum Rekordvask	Dry cleaning service	PCE	1961 - 1969	-	0,2	50 g PCE/yr	Uncertain
Skovlytoften 36	Haulage firm	Gas oil	1960 - ?	102	10000	200 g/yr	Uncertain
Rundforbivej 176	Industry, tank system	TCE, oil and pesticides	1952 - 1976	4 *	20	1150 g TCE/yr	Reliable

19 * This travel time requires that the contamination has reached the lower aquifer locally i.e. a free phase is or has been present at the site.



1
 2 Fig. 6. Particle traces from the selected contaminated sites. At sites contaminated with DNAPL, particles were released
 3 in both the upper (red traces) and the lower aquifer (blue traces).

4
 5 The mass flux from the different contaminated sites to the first significant aquifer (i.e. the upper
 6 aquifer) was calculated with the leaching model by employing available data gathered from site
 7 investigations. The results are presented in Table 2. Since local intermediate aquifers and aquitards
 8 were not observed at any of the sites, the leaching models used to represent the different sites
 9 consisted at the most of two reactors: one for the vadose zone (VZ) and one for the contaminated
 10 part of the upper aquifer (RA). The data availability at each site differed greatly and different forms
 11 of the leaching model were therefore used to estimate the contaminant flux from each of the sites.
 12 This is illustrated in Fig. 7, where the mass fluxes from two different sites have been calculated.

13

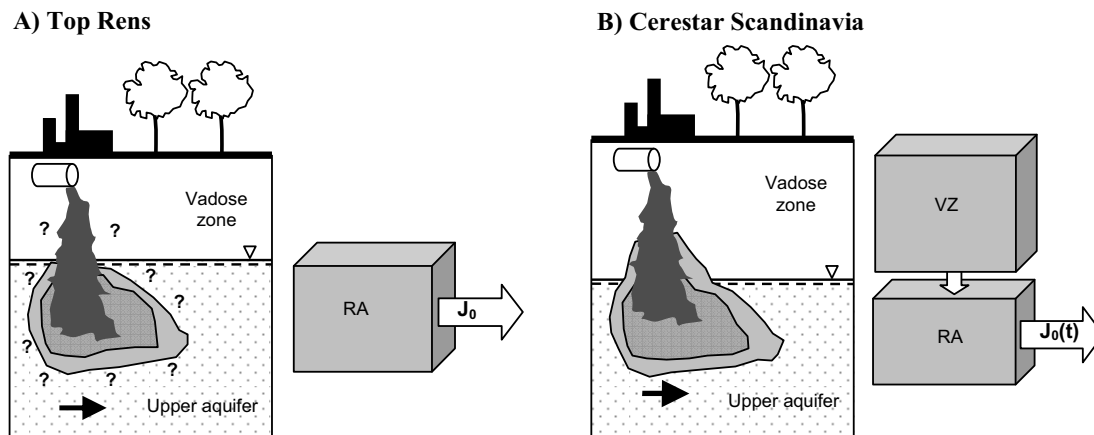


Fig. 7. Leaching model applied at the contaminated sites A) Top Rens and B) Cerestar Scandinavia.

At Top Rens, PCE contamination has been observed in the vadose zone and the upper aquifer. Former site investigations provided 22 near-surface pore gas samples together with groundwater samples from 6 wells screened in the top of the upper aquifer. From these data the contamination was poorly delineated. Furthermore, there were no data available on hydraulic properties of the porous media. Therefore the simplest form of the leaching model was chosen meaning that the mass flux was assumed to be constant with time. According to Eq.(1) a representative concentration, a contaminated area perpendicular to water flow, and a specific discharge (Darcy) is needed in order to calculate the flux leaving the site. Because the highest concentrations were measured in groundwater, the mass flux calculation was conservatively based on these measurements. The width of the contaminant plume was roughly estimated from the measurements, while the depth of the plume was set to the length of the longest well screen from which the concentration measurements were obtained. The specific groundwater flow (Darcy flux) was calculated based on a measured hydraulic gradient and an assumed hydraulic conductivity considered appropriate for a fine sand aquifer. A mass flux from the site of 80 g PCE/yr was estimated using the leaching model (Tuxen et al., 2006). This mass flux is considered uncertain since the local hydraulic properties are unknown and because of the poor delineation of the contamination.

At Cerestar Scandinavia detailed investigations have demonstrated widespread TCE contamination in the vadose zone and upper aquifer. The contamination in the vadose zone and the upper aquifer have been well delineated based on 31 pore gas samples and water samples extracted at several depths from more than 30 wells (screened wells and Geoprobe sampling points). The data enabled an assessment of the contaminated volume and the average concentrations from which the

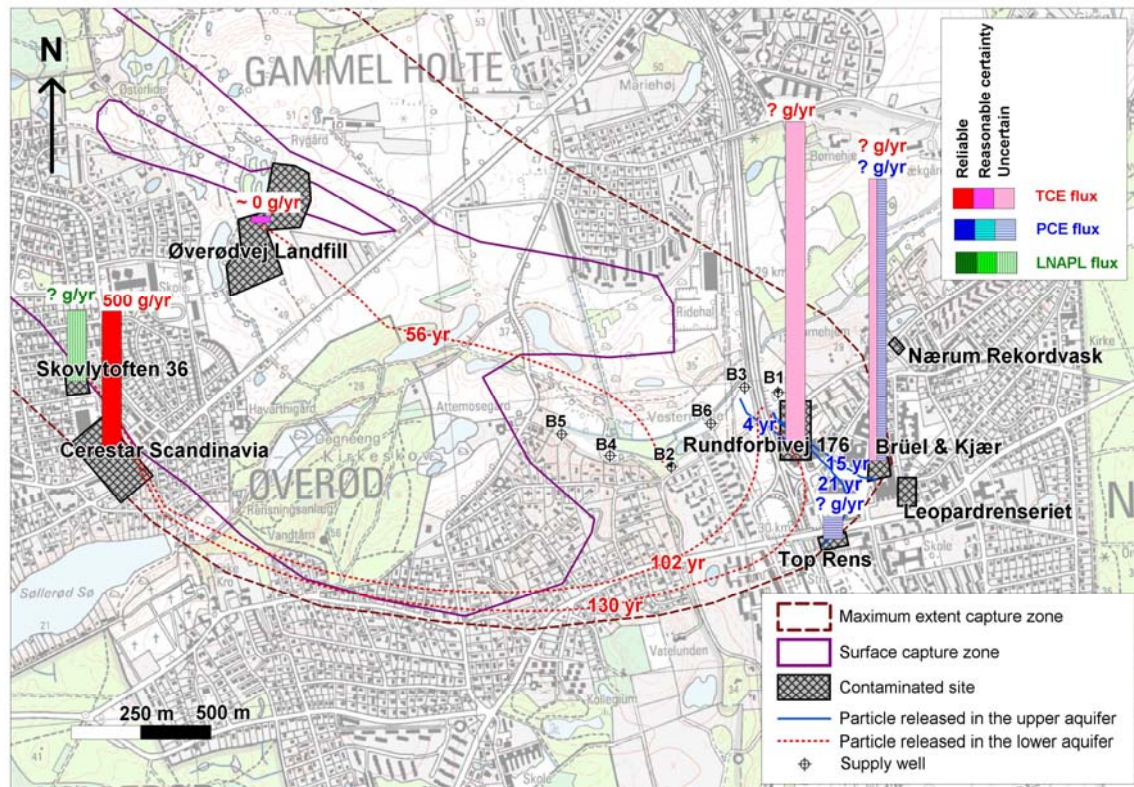
1 residual contaminant mass at the site was estimated. The mass estimate did not account for presence
2 of free phase since this was not indicated from the measured concentrations at the site. Furthermore,
3 the hydraulic properties of the aquifer have been evaluated based on pumping tests, slug tests and
4 flowlogs. Both a simple leaching model (similar to Top Rens) and a two-reactor leaching model
5 have therefore been used to estimate the mass flux over time. The detailed investigations made it
6 easier to decide the size of the reactors, representative concentrations and specific discharges. With
7 the simple leaching model a constant mass flux of 500 g TCE/yr was estimated, while a decreasing
8 mass flux with time was estimated with the two-reactor model. Because of the amount and quality
9 of the available data the calculated mass flux is considered to be reliable (Tuxen et al., 2006).

10 Due to the huge variation in the data quantity for each site, the quality of the mass flux estimates
11 varied accordingly. At most sites the simple one-reactor leaching model has been applied and at
12 some sites it was not even possible to calculate the mass flux because of lack of data. In Table 2 an
13 evaluation of reliability has therefore been assigned to each mass flux.

14 It should be noted that the mass fluxes estimated for the DNAPL contaminated sites in the
15 industrial area (Table 2) are worst-case estimates of the impact on the waterworks. These sites are
16 within the maximum extent capture zone, but not the surface capture zone. In order for these sites to
17 have an impact on the water supply, the contamination must therefore penetrate directly to the lower
18 aquifer by free phase transport. The extent of DNAPL penetration is not known at these sites and so
19 worst-case estimates of the mass flux to the lower aquifer are used as a precautionary measure of
20 the impact.

21 22 *3.3 Risk assessment and prioritisation on the catchment scale*

23 A final risk assessment of the selected contaminated sites is shown in Fig. 8, where the estimated
24 mass fluxes (indicated with bars) and likely particle pathways from the sites that potentially affect
25 the waterworks are displayed. The evaluated reliability has also been assigned to each flux estimate.
26



1
 2 Fig. 8. Risk assessment of contaminated sites in the catchment of Nærum Waterworks. Estimated mass fluxes
 3 (displayed with bars) and likely particle traces are shown.
 4

5 A risk-based prioritisation is performed to identify which sites are most likely responsible for the
 6 contamination at the waterworks. Factors that determine site risk include: i) the distinction between
 7 maximum extent and surface capture zone in relation to the contaminated site location and type of
 8 spill (presence or absence of free DNAPL phase), ii) the size of the estimated mass fluxes from the
 9 different sites; iii) the type of contamination, because different contaminants have different physical
 10 and chemical properties, and therefore behave and react differently in the subsurface. The type of
 11 contamination is also important because of the direct coupling between observed contamination at
 12 the different sites and at the receptor point (i.e. supply well); iv) and the calculated travel times
 13 from the different sites to the supply wells in relation to site history. A contaminated site cannot be
 14 responsible for the currently observed contamination if the travel time is much longer than the time
 15 since contamination occurred at that site. It can, however, be of concern in the future.

16 The above considerations result in the prioritisation shown in Table 3. In general, TCE
 17 contaminated sites have been given most attention, since only TCE has been observed at the
 18 waterworks. In principle TCE contamination could originate from a PCE spill that has been

1 undergoing anaerobic dechlorination. However, the potential for anaerobic dechlorination seems
 2 low, because of lack of degradation products and oxidised redox conditions, especially in the upper
 3 aquifer.

4 Two sites (Rundforbivej 176 and Brüel & Kjær) are likely suspects for contamination of the
 5 waterworks. The primary suspect is Rundforbivej 176, where recent investigations have shown a
 6 TCE contamination deep into the upper aquifer, indicating that free phase transport may have
 7 occurred at some stage. It has not been possible to estimate a mass flux to the lower aquifer from
 8 Rundforbivej 176 with the leaching model using the available data, and thus the true impact is not
 9 known for this site. Brüel & Kjær is located at the border of the maximum extent capture zone and
 10 is the secondary suspect. Investigations have shown very high concentrations of both TCE and PCE
 11 in the soil above the groundwater table of the upper aquifer indicating potential presence of free
 12 phase. Remediation was carried out in the upper part of the upper aquifer in 1997, but the
 13 contamination in deeper parts has never been evaluated and a residual contamination is most likely
 14 still present. Lack of data has made it impossible to use the leaching model for calculating the mass
 15 flux originating from Brüel & Kjær. The other sites are either cleared or most likely cleared of
 16 suspicion for reasons presented in Table 3.

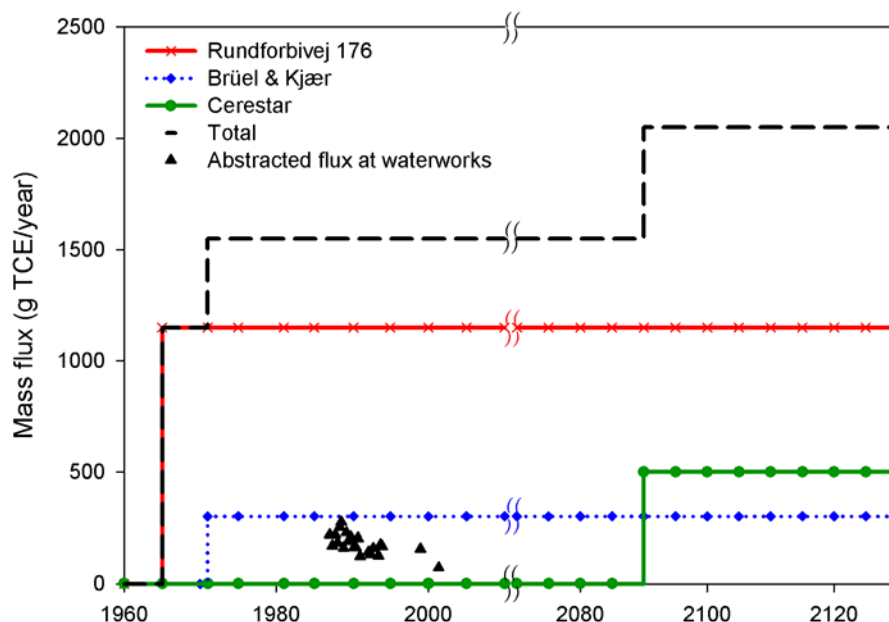
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 18

Table 3. Prioritisation of contaminated sites in the catchment of Nærum Waterworks.

	Site	Status	Explanation
1	Rundforbivej 176	Suspect	TCE contaminated. Indications of presence of free phase
2	Brüel & Kjær	Suspect.	TCE and PCE contaminated. Indications of presence of free phase. Unknown residual mass.
3	Cerestar Scandinavia	Might be of concern in the future	TCE contaminated. Long travel time provided that the site is located inside surface capture zone.
4	Top Rens	Most likely cleared	Is located at the capture zone border. No indications of free phase. PCE has not been measured at Nærum Waterworks
5	Skovlytoften 36	Cleared	Heavy, immobile gas oil. Long travel time if site is located inside surface capture zone.
6	Øverødvej Landfill	Cleared	Mass flux is approximately 0 g TCE/yr.
7	Leopardrenseriet	Cleared	Is located outside maximum extent capture zone. No indications of free phase. PCE has not been measured at Nærum Waterworks
8	Nærum Rekordvask	Cleared	Is located outside maximum extent capture zone. No indications of free phase. PCE has not been measured at Nærum Waterworks

1 The total contaminant impact on Nærum Waterworks can be assessed based on the results above.
 2 Degradation was not included in the transport through the catchment. Based on the groundwater
 3 modelling and particle tracking, this reduces the number of relevant sites causing the problems at
 4 the waterworks to four TCE-contaminated sites. However, the estimated TCE flux at Øverød
 5 Landfill is so low that this site is not considered a threat to the waterworks. The estimated impact of
 6 TCE on Nærum Waterworks from the remaining three sites is shown in Fig. 9. It should be noted
 7 that the TCE fluxes from each of these sites represent worst-case estimates and has been calculated
 8 in the upper aquifer. Furthermore, the mass flux from each site is assumed to be constant from the
 9 time contamination was first possible at the respective sites.

10 From Eq. (20) the time-dependent accumulated impact on the waterworks can be calculated. This
 11 can be compared to the actual measured mass flux at the waterworks, which is shown in Fig. 9. The
 12 abstracted TCE flux at the waterworks is the sum of the recorded TCE fluxes to each active supply
 13 well, and has been calculated based on concentration measurements in the supply wells and the
 14 recorded annual abstraction rate distributed equally over the active supply wells. A relatively
 15 constant annual abstracted TCE flux of around 150 g/yr has hereby been calculated. Note that there
 16 is doubt about which supply wells have been active at the waterworks and that the measured TCE
 17 fluxes therefore are considered uncertain.



18
 19 Fig. 9. Estimated and measured TCE flux at Nærum Waterworks as a function of time. Note the discontinuous
 20 timescale.

1 An accumulated TCE flux at the waterworks of about 1500 g/yr has been estimated for the three
2 sites. This flux is about an order of magnitude higher than the measured flux. The disagreement
3 between the measured and calculated mass flux results from the combination of the complex
4 hydrogeology and the uncertainties related to the mass flux estimates from the different sites. It
5 should be emphasised that CatchRisk is developed for risk assessment and not to match the
6 measured data perfectly. Hence, the mass fluxes from each site have been calculated using
7 parameter values that ensure conservative results. An overestimation of the total impact is therefore
8 not surprising.

11 **4. Discussion**

13 *4.1. Model applications*

14 CatchRisk is intended for decision support and has several features that may be beneficial to
15 regulators and other stakeholders. The main feature is a risk-based prioritisation of known
16 contaminated sites in the catchment to a water supply. In the catchment of Nærum Waterworks, and
17 according to traditional risk assessment at the local scale, eight sites are considered a threat to the
18 groundwater resources in the area. However, traditional risk assessment tools provide no
19 information on the relative significance of threats posed by the different sites, and cannot determine
20 which sites are responsible for the observed contamination at the waterworks. Thus, it is not clear
21 which sites should receive priority by the regional authorities for securing the abstracted
22 groundwater at the waterworks. The use of CatchRisk provides an integrated overview of the
23 impact from the identified sites at the Nærum Waterworks and provides a more reasonable
24 foundation on which to base a prioritisation. Five out of eight potential sites have been disregarded,
25 and the primary focus of further assessment is now on two sites. The CatchRisk output on which the
26 prioritisation is based consists of a time-dependent estimate of the mass flux from each site to the
27 water supply. This output can also be used to indicate how long the supply well will be
28 contaminated or whether it may become contaminated in the future.

29 CatchRisk can also be used for identifying whether unknown contaminated sites are present in
30 the catchment, because the model directly relates known contaminated sites to the observations at
31 the water supply. Thus, if the calculated mass flux is much lower than the measured mass flux at the
32 supply well then it is possible that unknown sites exist in the catchment. In the case of Nærum

1 Waterworks it is uncertain whether all sites have been identified in the area. This is because the true
2 impact on the waterworks from the two sites considered to be the main suspects is basically
3 unknown. Additionally, Brüel & Kjør is situated close to the maximum extent capture zone border,
4 and it must be regarded as uncertain whether this site is even within this capture zone. Finally,
5 CatchRisk can be used to identify the sites where more information is needed to improve the
6 analysis, and the framework might therefore be helpful in allocating resources on a larger scale.

8 *4.2. Model complexity and data needs*

9 CatchRisk combines mass flux estimates at the local scale with transport and fate simulations on
10 the catchment scale. This overall conceptual structure is similar to existing catchment-scale risk
11 assessment tools. However, a risk-based prioritisation requires an assessment of many different sites
12 and an evaluation of huge volumes of data. Often the available data at these sites are flawed. It is
13 therefore important that a model for prioritisation is simple enough so that it can be applied to any
14 given site, even when only limited data are available. The model should, however, still allow for an
15 inclusion of important site characteristics such as the presence of residual phase, local aquitards,
16 degradation etc. In this context the modular form of the leaching model in CatchRisk is an advance
17 on existing catchment-scale risk assessment tools that rely only on a single conceptual model to
18 represent the contaminant source (Table 1). The flexible leaching model can be adjusted to suit any
19 given site and its data availability; the more data available, the better the model will reflect reality
20 and the more reliable the calculated mass fluxes are. The simulations presented for the catchment of
21 Nærum Waterworks are entirely based on existing data, obtained from regional authorities. Even
22 though these data were scarce it was still possible to achieve a prioritisation of the sites, where
23 contamination has been documented.

24 However, CatchRisk does have limitations. The leaching model is based on a set of simplifying
25 assumptions described in section 2.2. Most of these assumptions result in an overestimation of the
26 mass flux to groundwater (e.g. neglecting diffusion and evaporation in the vadose zone and the
27 assumption of instantaneous dissolution equilibrium), and can therefore be considered conservative.
28 CSTM assumes steady-state conditions and requires a groundwater model of the catchment area
29 that simulates the flow patterns satisfactorily. If such a model is not available it needs to be
30 constructed and calibrated, which is very time-consuming. However, in Denmark the regional
31 authorities are very often able to provide groundwater models that cover the area of interest and can
32 therefore be used as basis for the application. Overall the assumptions are considered acceptable in

1 relation to the aim of the model, namely to support the prioritisation of the contaminated sites in a
2 catchment.

3 4 *4.3. Uncertainty, validation and prioritisation*

5 CatchRisk, as all modelling tools, has inherent uncertainties, which are related to both the
6 leaching model and the CSTM. In general, the uncertainties originate from the limited data, which
7 may lead to poor conceptual understanding and makes the choice of model parameters uncertain.
8 The uncertainties in the leaching model affect the calculated mass fluxes at the local scale, while the
9 uncertainties in the groundwater model influence the catchment delineation. The catchment
10 determines which sites are potential threats to the water supply, and a reliable delineation of the
11 catchment boundary is therefore crucial for the final risk assessment and prioritisation. The exact
12 location of the catchment border could be particularly important in the case of Nærum Waterworks,
13 where several sites were located close to the simulated catchment boundary. To account for the
14 uncertainties in the catchment delineation the macrodispersion approach presented by Frind et al.
15 (2002) could be applied, where backward advective-dispersive modelling is used to determine
16 probability-of-capture plumes. A probabilistic approach similar to the one employed in BOS (Tait et
17 al., 2004), which is based on the use of Monte Carlo and/or Generalised Likelihood Uncertainty
18 Estimation (GLUE) (Beven and Binley, 1992), could also be used. However, in both these
19 approaches, only the influence of uncertainties in hydrogeological parameters is considered. In the
20 catchment for Nærum Waterworks the hydrogeology is rather complex, because of geologic
21 windows in the clay layer separating the upper and lower aquifer. The location and the extent of
22 these aquitard windows are not well known and the uncertainties related to this are not captured by
23 Monte Carlo simulations. In this case the conceptual model uncertainty related to geology,
24 hydrogeology and contaminant sources might be much more important, and this kind of uncertainty
25 is only rarely considered in environmental modelling (Refsgaard et al., 2006).

26 27 **5. Conclusions**

28
29 The CatchRisk model has been developed for integrated risk assessment and prioritisation of
30 contaminated sites on the catchment scale. The model describes the risk associated with
31 contaminated sites in terms of their ability to contaminate the abstracted groundwater in the
32 catchment. CatchRisk combines site specific mass flux estimates from identified sites at the local

1 scale with transport and fate simulations on catchment scale. CatchRisk was tested on the catchment
2 for Nærum Waterworks, north of Copenhagen, where several contaminated sites have been
3 identified. One site is considered the most likely cause of the observed TCE contamination at
4 Nærum waterworks, while another site is a suspected source. Conclusions of more general
5 relevance are as follows:

- 6
- 7 1. A simple and flexible leaching model for estimating mass fluxes at the local scale is required to
8 handle the many different types of contaminated sites and their data availability.
- 9 2. Both the surface capture zone and the maximum extent capture zone should be regarded in a
10 risk assessment on the catchment scale. All contaminated sites located in the surface capture
11 zone pose a threat to the water supply, while a site in the maximum extent capture zone is only
12 a concern in case of contamination by DNAPL penetrating into deeper layers.
- 13 3. An integration of mass flux estimates, catchment delineation considerations and information
14 regarding contaminant, type of spill, travel time, source history and location provide an
15 effective risk assessment on the catchment scale.
- 16 4. CatchRisk is an effective tool for supporting the prioritisation of contaminant sites and for
17 detection of unknown contaminant sources in a catchment. Unknown sources can be identified
18 by comparing measured contaminant loads with the contributions from known sources in the
19 catchment.
- 20 5. Uncertainty and its role in risk assessment and site prioritisation should be investigated.

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24

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