

ON DIFFUSIVE MASS-TRANSFER LIMITATIONS IN RELATION TO REMEDIATION OF POLLUTED GROUNDWATER SYSTEMS

Jasper Griffioen^{1,2} and Rolf A.A. Hetterschijt²

¹ Institute of Earth Sciences, Utrecht University, Budapestlaan 4, 3508 TA Utrecht, The Netherlands

² Netherlands Institute of Applied Geoscience TNO, P.O. Box 6012, 2600 JA Delft, The Netherlands

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SUMMARY

Limited diffusive mass transfer is one cause for stagnant groundwater remediations. We characterise the diffusive mass transfer process as a three stage cyclic process of mass transfer into and out of stagnant or immobile zones. The first stage is the contamination stage, where net inward diffusive mass transfer happens and the last stage is the remediation stage where the opposite happens. An intermittent stage may happen when the immobile zone has reached equilibrium with the mobile zone. Using an analytical solution for diffusive mass transfer into and out of an immobile zone, we show that decades may be involved to reach this stage for natural systems. If this stage does not get reached, continuous inward diffusion happens during the remediation stage. Then, the remediation period required lasts much longer than the contamination period available. Numerical simulation for a simplified two-layer mobile/immobile system further shows that excessive pumping rates do not speed up remediation, since the rate-limiting process is not significantly affected by this. Intermittent pumping or continuous pumping at low rates is equally effective from remediation point of view. Other criteria are then decisive whether continuous pumping or intermittent pumping is most interesting.

INTRODUCTION

Prolonged tailing is often encountered during in-situ remediation of groundwater contamination plumes. One cause for prolonged tailing is the limited diffusive mass flux of the contaminant from less permeable zones (stagnant or immobile zones) to more permeable zones, where advective groundwater flow dominates (mobile zones). Many remediation strategies therefore turn out to be overdimensioned. Optimization of remediation strategies is noteworthy for reasons of environmental and economic benefit.

Investigations on optimization of pump-and-treat techniques have been performed in the past few years. The investigations focus on two aspects: 1. the effect of aquifer heterogeneity (Rabideau & Miller, 1994; Berglund & Cvetkovic, 1995) and 2. the efficiency of intermittent pumping versus continuous pumping (Harvey et al., 1994). The investigations usually focus on groundwater concentrations within the mobile, advection dominated zone. We studied the diffusive mass transfer process within the stagnant, immobile zone and the related transverse mass transfer process between the mobile and the immobile zone, i.e., we have characterised the cyclic diffusive mass transfer process into and out of immobile zones for pulse-type cases. The specific objectives of this study are as follows. First, we characterise the mass-transfer process into and out of stagnant layers within the context of aquifer remediation. Second, we examine the time periods that are involved to fill stagnant zones in natural porous media, its implications for the associated time periods for remediation of these media and the related pumping strategy.

THEORY

Diffusive mass-transfer is described by Fick's second law:

$$\frac{\partial c}{\partial t} = D' \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where c is aqueous concentration, t is time, D' is diffusion coefficient and x is distance. The diffusion coefficient is equal to the effective diffusion coefficient in a porous medium when conservative transport is involved, and it is equal to the apparent diffusion coefficient when linear retardation in a porous medium happens due to sorption. When appropriate initial and boundary conditions are used, analytical solutions can be obtained for cyclic diffusion into and out of a porous medium from those for continuous diffusion into a porous medium. The analytical solution is obtained from Carslaw & Jaeger (1959) or Crank (1975), using the principle of superposition, where diffusion happens into and out of a homogeneous layer for the case of a solute in contact with the exterior of the layer for a limited time (Griffioen, 1998):

$$c^*(x^*, t^*) = 1 - A(x^*, t^*), \quad 0 < t^* \leq t_{in} \quad (2a)$$

$$c^*(x^*, t^*) = A(x^*, t^* - t_{in}) - A(x^*, t^*), \quad t^* > t_{in} \quad (2b)$$

with:

$$A(x^*, t^*) = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-(2n+1)^2 \pi^2 t^*/4} \cos\left(\frac{(2n+1)\pi x^*}{2}\right) \quad (2c)$$

and with the following initial and boundary conditions:

$$\frac{\partial c^*(0, t^*)}{\partial x^*} = 0 \quad (3a)$$

$$c^*(x^*, 0) = 0 \quad (3b)$$

$$c^*(1, t^*) = 1 \quad 0 < t^* \leq t_{in} \quad (3c)$$

$$c^*(1, t^*) = 0, \quad t^* > t_{in} \quad (3d)$$

where the following nondimensional parameters are defined:

$$c^* = c/c_{out} \quad (4a)$$

$$x^* = x/L \quad (4b)$$

$$t^* = D't/L^2 \quad (4c)$$

where c^* is relative concentration, c_{out} is the boundary concentration on the outside of the infinite layer, t^* is relative time, x^* is relative distance from the middle of the layer and L is half the thickness of the layer, and t_{in} is the period during which the exterior of the layer is in contact with a fluid containing a solute of c^* is 1.

MODELLING APPROACH

The above presented analytical solution cannot be used when no discrete concentration changes occur at the exterior of the stagnant zone. This is more likely in natural systems, where aquifer remediation using e.g. pump-and-treat is applied. We used the finite difference transport model MT3D (Zheng, 1992) to study mass transfer into and out of a stagnant clayey layer that is in contact with a permeable sand layer.

Contamination histories were simulated using a sandy layer of 10.0 meters long, 1.0 meter width and 2.0 meters thick with a hydraulic conductivity of 5.0 m/day. Adjacent to this layer is an impermeable layer of similar geometry, but with a hydraulic conductivity of $10^{-5.0}$ m/d. The discrepancy of the permeability between mobile and immobile zones was chosen this large, to assure that exchange of contaminant between the zones is only due to diffusion.

Two contamination cases were considered: a retardation factor of 1.9 and one of 9.9, respectively. This corresponds to transport of toluene and that of naphthalene with an

organic matter content of 0.16%, porosity of 0.3 and specific density of 1860 kg/m^3 . The contaminant source was modelled as cells with a constant concentration at the upstream side of the model. 'Natural' groundwater flow along the source cells caused the contamination to enter the sandy layer. The pore water velocity was 15 m/yr. The period of contamination lasted 20 years. This resulted in a situation where the stagnant zone is almost in full equilibrium for toluene, but not at all for naphthalene.

The performance of the numerical approach was evaluated by comparing results with an analytical solution of Duijn and Van der Zee (1986) for solute transport in a horizontally layered two layer system. The analytical solution describes the average concentration in the more permeable zone, accounting for transversal dispersion between the two layers and neglecting longitudinal dispersion. The concentration difference between the two approaches is at most 5 percent for naphthalene and less for toluene. This is attributed to numerical dispersion of the initial sharp concentration gradient between the permeable and the stagnant zone. The numerical approach is considered to be satisfactory at the used scale of discretisation (thickness of model cell 20 cm.).

In situ remediation by pump-and-treat was simulated by inflicting a hundred-fold increase of the groundwater velocity and reversing the direction of the flow. It should be noted that the simulated velocity field during remediation was uniform and not radial as one would expect in case of flow to a single well. Therefore, the results of this study can be applied to areas not too near to wells, where flow velocity changes much along a short distance. The period of remediation lasted 20 years as well. Two remediation strategies were compared with respect to efficiency: continuous pump-and-treat during 20 years and pulsed pump-and-treat during 20 years.

RESULTS

Figure 1 presents, for sake of convenience, the trend in concentration during continuous net inward mass transfer. The figure shows that the concentration is still 0 at $x^* = 0$ for $t^* = 0.05$ and that for larger t^* the solute diffuses up to the middle of the layer. The

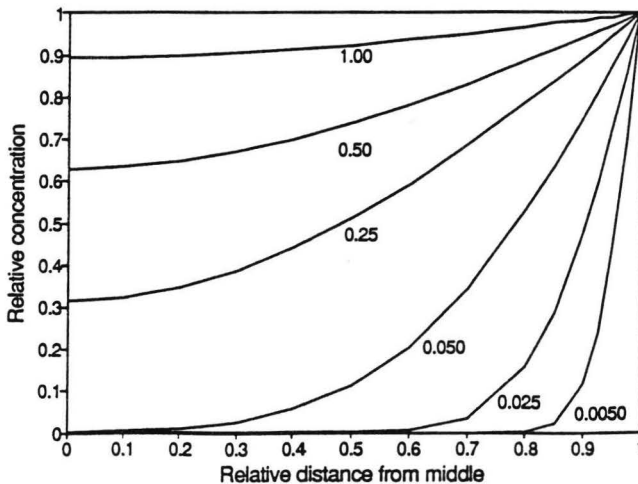


Figure 1. Concentration profiles at several relative times (as indicated) during continuous net inward mass transfer.

relative concentration in the middle of the layer is 0.9 for $t^* = 1.0$. The layer can in practice be considered as in near-equilibrium with the permeable zone for t_{in} is larger than 1.0. The period during which no further contamination happens will be called the equilibrium period. The first period where net inward transport of contaminant happens, i.e., t_{in} is smaller than 1.0, will be called the filling period.

The time span required for stagnant layers to fill can be evaluated in a general way from literature data on diffusion coefficients, using eq. [4c]. The upper limit for diffusion of aqueous solutes is approx. $1.0E-09 \text{ m}^2/\text{s}$. Experimentally determined values for the effective diffusion coefficients of solutes range from 10^{-9} to $10^{-14} \text{ m}^2/\text{s}$; here, the empirical studies considered two different types of solids: aggregates comprised of individual grains (e.g., Rowe et al., 1988; Myrand et al., 1992) and loose grains having diameters of approx. 0.01 to 1 mm (Wu & Gschwend, 1986; Grathwohl & Reinhard, 1993). The apparent diffusion coefficient can thus be as low as $10^{-16} \text{ m}^2/\text{s}$ when a retardation factor of 100 is encountered. This retardation factor can be expected, e.g. for the adsorption of trichloroethylene in a peaty solid matrix containing 10 % organic carbon.

Note that diffusion lengths equal to the radius of spherical media have always been assumed while fitting the mathematical diffusion concept to the experimental measurements. This seems realistic for aggregates, but may be erroneous for individual grains: diffusion lengths equal to the radius will mean voids up to the centre of the porous medium and this raises doubt about whether such a medium is still a firm grain or should be considered to be an aggregate. This is even more pertinent when one remembers that fitting is often based on measurements of the aqueous concentration of the bulk solution.

Figure 2 shows the characteristic time required to fill the stagnant layer for three relative time steps and two values of the diffusion coefficient (the coefficient may be apparent for reactive transport, or effective for conservative transport). Clearly, time spans in the order of years can be expected for layer thicknesses in the order of

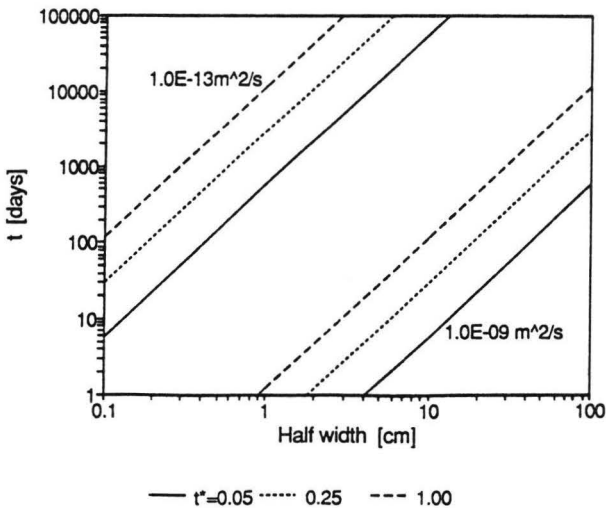


Figure 2. Relationship between real time and half width of stagnant layer for filling up to three relative time intervals (t^* is 0.05, 0.25 and 1.0) and two diffusion coefficients ($1.0E-9$ and $1.0E-13 \text{ m}^2/\text{s}$; see values indicated).

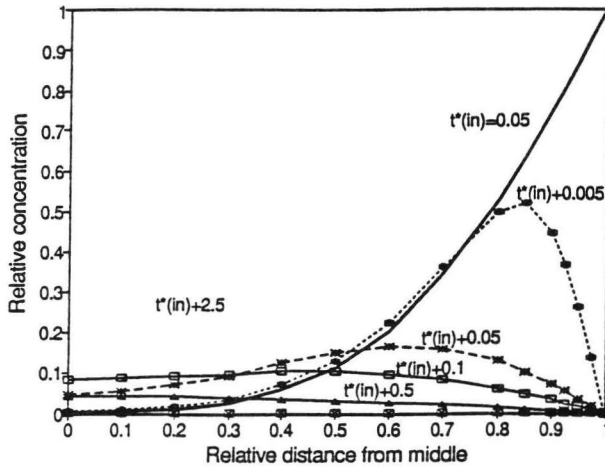


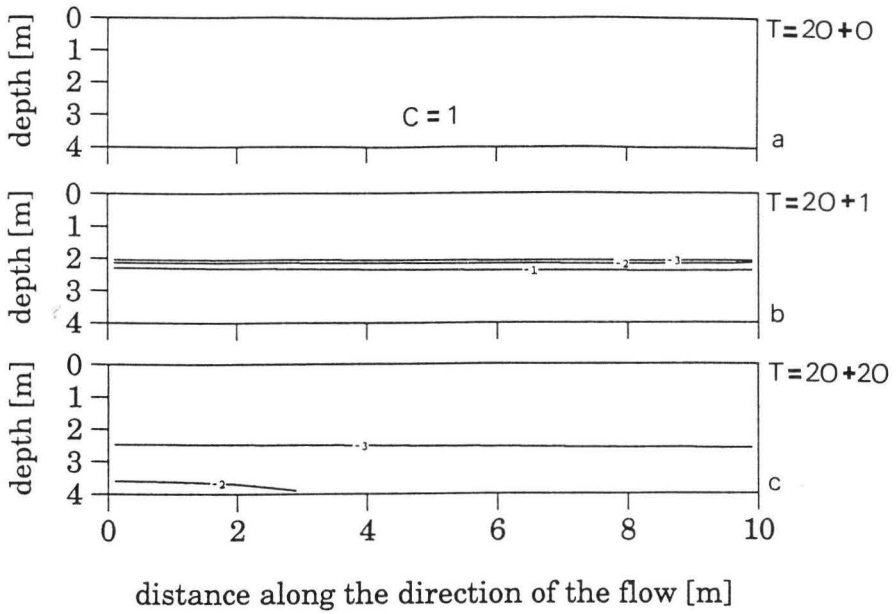
Figure 3. Concentration profiles in a stagnant layer at various relative times (as indicated) during the remediation period when the filling period t_{in} was 0.05.

centimetres to decimeters. For slowly diffusing compounds such as PAH's, (tens of) years are even involved to reach equilibrium between the mobile and the stagnant zones when the latter are less than a centimeter. The usual age of contamination cases is in the order of tens of years; gas works can be as old as one century. This illustrates that filling of stagnant zones can be incomplete for actual contamination cases.

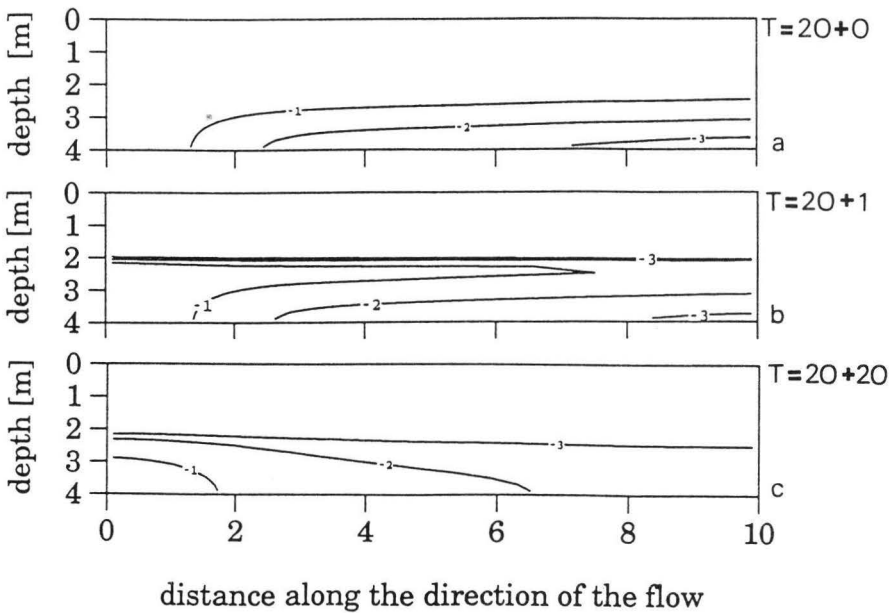
Interesting phenomena can be noticed when incomplete filling has happened (Griffioen, 1998). Figure 3 shows as an example the development of the concentration profiles within a stagnant layer during the remediation stage when t_{in} was 0.05. Two major observations can be made. First, diffusion into the stagnant layer happens during the first part of the remediation stage, because of the steep concentration gradient within the stagnant zone. The contaminant thus moves into two opposite directions during remediation in case of incomplete filling. Second, the relative time period required for the desorptive stage, i.e., for remediation, is long compared to that for the adsorptive stage, i.e., for contamination. The remediation period is easily more than ten times the contamination period, when incomplete filling has happened and the relative concentration has to decrease to 0.01.

For a contamination period, t_{in} , of 1.0, the relative concentration is less than 0.1 at any location in the layer after a relative remediation period equal to 1.0 (not shown here); the relative concentration is less than 0.01 for a relative remediation period that equals 2.0. This illustrates that remediation periods will at least be as long as the contamination period, if diffusive mass transfer controls mass transfer and low concentrations have to be attained. Prolonged periods are thus required for remediation of stagnant zones when diffusive mass transport happens within these zones. Natural subsurface systems will behave somewhat differently, because the concentration gradients at the edge of stagnant zones are not as sharp as assumed in the analytical approximation presented.

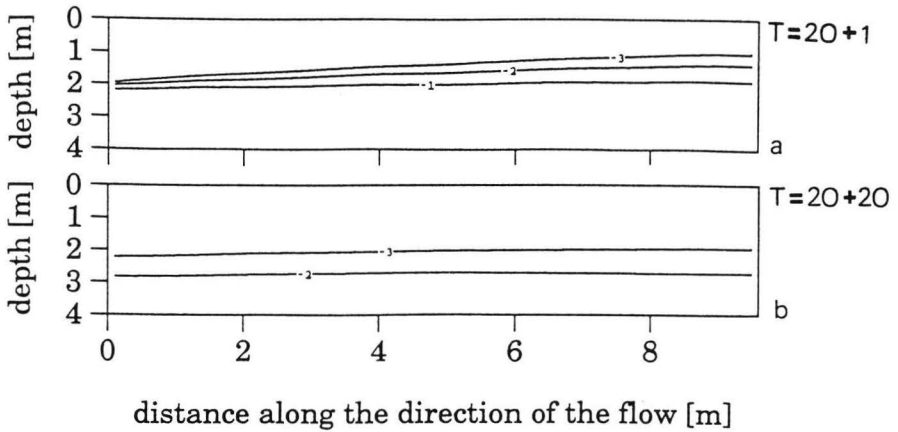
Figures 4a and 5a show concentration patterns of toluene and naphthalene as logarithmic values after a 20 year period of contamination for the contamination histories described. Both toluene and naphthalene concentration are equal to the input concentration in the entire permeable zone. The toluene concentration in the stagnant zone resembles the



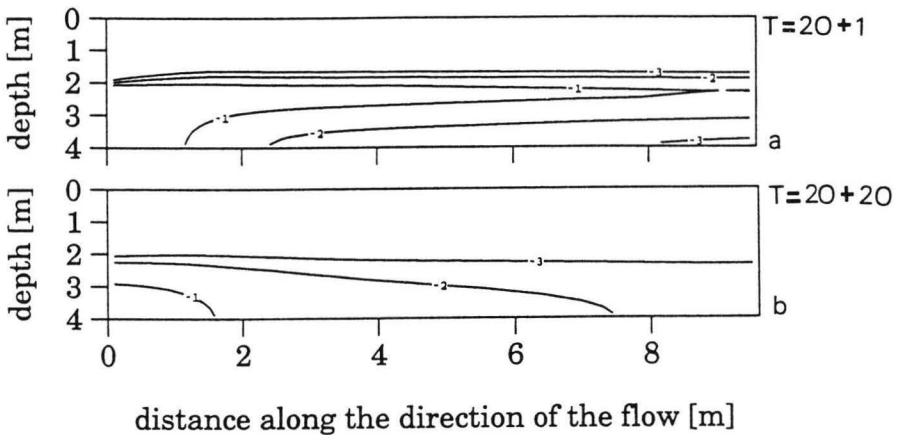
Figures 4. Plots of log value of the toluene concentration in a two layer medium (with 0.2 m permeable zone and 2.4 m stagnant zone) from a contamination period of 20 years on in case of continuous pumping.



Figures 5. Plots of the log value of the naphthalene concentration in a two layer medium (with 0.2 m permeable zone and 2.4 m stagnant zone) from a contamination period of 20 years on in case of continuous pumping.



Figures 6. Concentration plots of naphthalene in a two layer medium from a contamination period of 20 years on in case of intermittent pumping.



Figures 7. Concentration plots of naphthalene in a two layer medium from a contamination period of 20 years on in case of intermittent pumping.

concentration of the permeable zone and the equilibrium period has thus been reached for the stagnant zone. The naphthalene concentration in the lower reaches of the stagnant zone is only a few percent of the naphthalene concentration in the permeable zone. The stagnant zone is still getting contaminated after 20 years; the system is still in the filling period for the more strongly sorbing contaminant. The longer time span needed can be attributed to a combination of two effects: 1. less adsorbing contaminants like toluene move faster through the sandy layer, so diffusion into the stagnant zone starts earlier at a fixed position, and 2. the apparent diffusion coefficient of weakly adsorbing compounds as toluene is much larger than that of a strongly one as naphthalene.

The characteristic time to fill stagnant zones explains the different progress of the remediation of the toluene and naphthalene contaminated system (cf. Figures 4 and 5). Within a few days, both toluene and naphthalene are removed from the permeable zone by advective flow and a steep concentration gradient between the stagnant and the permeable zone is established. The stagnant zone is slowly remediated by a diffusive

mass flux out of the stagnant into the permeable zone. Interesting is that the non-equilibrium state of the naphthalene contaminated stagnant zone causes an inward diffusive mass flux, which is in accordance with analytical results (Figure 5b): the stagnant zone is being remediated close to the mobile zone as well as getting polluted more inward at the same time. After 20 years, the progress of the remediation of the toluene contamination is much larger than that of the naphthalene contamination, although much more toluene had to be removed at the start of the remediation period (cf. Figures 4c and 5c). This needs to be attributed to the larger apparent diffusion coefficient for toluene compared to that for naphthalene.

A comparison was made between the efficiency of continuous and pulsed pump-and-treat. Pulsed pump-and-treat is believed to be more efficient in terms of volumes of pumped groundwater for the remediation of two-zone porous media, where mass transfer between stagnant and permeable zones is rate limited. Pumping is only required to remove mass from the permeable zone and should be stopped when mass removal gets limited by diffusion of contaminant out of the stagnant zone. After pumping has ceased, concentrations in the permeable zone will rise again, and spreading of the contaminant in the permeable zone may occur due to natural groundwater flow. An unacceptable extent of spreading is the sign to resume pumping. The environmental benefit of this strategy is that less groundwater is pumped while the same amount of mass removed.

Pulsed pump-and-treat was engineered as 20 cycles of one year in which the permeable zone was flushed R times per cycle (where R is the retardation factor for toluene or naphthalene, respectively). For this particular case, one cycle consisted of 4.6 pumping days for toluene and 24 pumping days for naphthalene. Natural groundwater flow happens for the rest of the year. The total volume of extracted groundwater is 240 m^3 for toluene and 1300 m^3 for naphthalene compared to a volume of 19700 m^3 which is extracted during continuous pump-and-treat at a pore water velocity of 1500 m/day. Comparison of Figures 5c and 7b reveals that pulsed pumping results in similar naphthalene concentrations in the stagnant zone as in the case of continuous pumping, but 7% of the groundwater volume is extracted compared to continuous pump-and-treat.

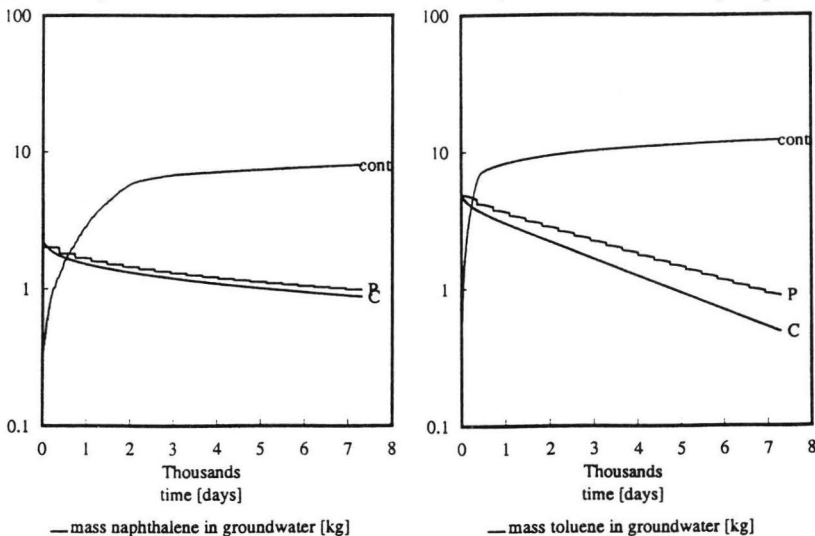


Figure 8. Amount of dissolved mass present during 20 years of contamination and 20 years of remediation for naphthalene (left) and toluene (right).

Pulsed pumping of toluene is somewhat less efficient regarding the resulting concentration in the stagnant zone (cf. Figures 4c and 6b). However, the volume of extracted groundwater is only 1% of that in the case of continuous pumping.

The amount of mass of contamination present was calculated to compare pulsed and continuous pumping: Figure 8 shows that continuous pumping is somewhat more efficient in removing mass out of stagnant zones, although the differences are small. Other criteria are then decisive whether continuous or pulsed pumping is most interesting. Pulsed pumping can be a cheaper alternative if sharing of a treatment installation between several contaminated sites is possible. A mobile treatment unit could serve several closely situated sites, if the duration of the interval between pumping is large enough compared to the number of sites. In our case, almost 50 toluene contaminated sites or 14 naphthalene contaminated sites could be treated on a yearly basis with just one ex-situ treatment unit. One should avoid that the contaminant gets transported out of the reach of the capture zone of the withdrawal pump by natural groundwater flow. The duration of the interval between pumping might have to be more reduced in order to prevent this unwanted spreading. The presence of several contaminants may complicate optimization of remediation cycles.

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